

5th Edition

White's Handbook of
Chlorination
and **Alternative**
Disinfectants

Black & Veatch

 **WILEY**

WHITE'S HANDBOOK OF CHLORINATION AND ALTERNATIVE DISINFECTANTS

FIFTH EDITION

Black & Veatch Corporation

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A JOHN WILEY & SONS, INC., PUBLICATION

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey

Published simultaneously in Canada

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Library of Congress Cataloging-in-Publication Data:

White's handbook of chlorination and alternative disinfectants. – 5th ed. / Black & Veatch Corporation.

p. cm.

Rev. ed. of: Handbook of chlorination and alternative disinfectants / Geo. Clifford White. 4th ed. 1999.

Includes bibliographical references and index.

ISBN 978-0-470-18098-3 (cloth)

1. Water–Purification–Chlorination. 2. Sewage–Purification–Chlorination.
3. Water–Purification–Disinfection. I. White, George Clifford. Handbook of chlorination and alternative disinfectants. II. Black & Veatch. III. Title. IV. Title: Handbook of chlorination and alternative disinfectants.

TD462.W47 2010

628.1'662–dc22

2009022484

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

This Fifth Edition of the Handbook of Chlorination and Alternative Disinfectants is dedicated to George Clifford White for his lifetime commitment to the disinfection industry.

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PREFACE

Over the years, the science and practice of disinfection has provided innumerable health benefits, although the general public is unaware of many of them. With the recognition of infectious organisms such as *Cryptosporidium* in our raw water supplies, along with the detrimental chronic health effects associated with disinfection by-products, it is critical to balance the extent of their inactivation with the concentrations of disinfection by-products. Many water and wastewater utilities are implementing the use of multiple disinfectants in order to optimize the results while minimizing unwanted side effects.

The four previous editions of this handbook have proven to be a valuable resource to countless utilities, regulators, engineers, and operators for information on disinfection of potable water, wastewater, industrial water, and swimming pools. George Clifford White's efforts in compiling these editions are invaluable; and much of the information he has gathered is included in this current edition; some of it is retained solely to provide a historical perspective.

Since the publication of the fourth edition, the water industry has gained a substantial amount of experience with chlorine, hypochlorite, and alternative disinfectants through research, development, and regulation. Consequently, this handbook has been extensively revised and updated to reflect the most current understanding and practices. The reader will find substantial and important information not only on chlorination but also on alternative disinfectants such as ozone, chlorine dioxide, bromine-related products, and ultra-violet light. In addition, the global focus on reuse to address the issue of water scarcity has elevated the use of advanced oxidation practices, and that chapter has therefore been updated to reflect today's environment.

Each chapter has been prepared by experts and reviewed by their peers in an effort to impart accurate, complete, and current knowledge on the subject being discussed. Black & Veatch considers it a privilege to present this updated resource on chlorination and alternative disinfectants for the water and wastewater industries.

It is our intention that this handbook continue to be the disinfection reference of choice for designers, operator, engineers, students, and regulators.

CINDY WALLIS-LAGE
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LIST OF ABBREVIATIONS

AC	alternating current
ACC	American Chemical Council; automatic control center
ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
ANSI	American National Standards Institute
AOB	ammonia oxidizing bacteria
AOC	assimilable organic carbon
AOP	advanced oxidation process
AOXP	advanced oxidation process
AS	analog subsystem
ATEX	explosive atmosphere directive (UK)
AWT	advanced wastewater treatment
AWWA	American Water Works Association
AwwaRF	American Water Works Association Research Foundation
BAC	biological activated carbon
BDOC	biodegradable dissolved organic carbon
BF	baffling factor
BOCA	Building Officials and Code Administrators, International
BOD	biochemical oxygen demand
B-P	breakpoint
CA	cellulose acetate
CAA	chloroacetic acid
CAC	combined available control system
CANUTEC	Canadian Transport Emergency Centre
CCCS	central computer control system
CFD	computational fluid dynamics
CHEMTREC	Chemical Transportation Emergency Center
CI	Chlorine Institute
COD	chemical oxygen demand
COMAH	control of major accident hazard (U.K.)
CP	chloropicrin
CPRV	chlorine pressure-reducing valve
CRC	combined residual chlorine
CS	control system

CSB	Chemical Safety and Hazard Investigation Board (U.S.)
CSO	combined sewer overflow
CT	chlorine residual $\times$ contact time
CTC	central terminal control
D/DBPR	Disinfectants/Disinfection Byproducts Rule
DBP	disinfection byproduct
DC	direct current
DE	diatomaceous earth
DIW	deionized water
DNA	deoxyribonucleic acid
DO	dissolved oxygen
DOC	dissolved organic carbon
DOT	Department of Transportation
DPD	diethyl-p-phenylenediamine
DPH	Department of Public Health
DPP	differential pulse polarography
DSA	dimensionally stable anodes
DXAAs	dihaloacetic acids
EBCT	empty bed contact time
ED	electrodialysis
EDC	endocrine disrupting compound
EDP	ethyl dibromide
EES	emergency service specialist
EFV	excess flow valve
EPA	Environmental Protection Agency (also USEPA)
EPDM	ethylene propylene diene monomer
EPS	extracellular polymer substances
ERPG	Emergency Response Planning Guidelines
FAC	free available chlorine
FACTS	free available chlorine test – syringaldazine
FAS	ferrous ammonium sulfate
FC	fecal coliform
FIA	flow injection analysis
FPA	flavor profile analysis
FRC	free residual chlorine
FRP	fiberglass-reinforced plastic
GAC	granular activated carbon
GOX	gaseous oxygen
GUDI	groundwater under the direct influence
GWR	Groundwater Rule
HAA	haloacetic acid
HAA5	five regulated HAAs
HAN	halo acetonitrile
HFF	hollow fine fiber
HPC	heterotrophic plate count

HRT	hydraulic retention time
HSE	Health and Safety Executive (U.K.)
IC	ion chromatography
ICR	Information Collection Rule
IDLH	immediate danger to life and health
IESWTR	Interim Enhanced Surface Water Treatment Rule
IFCI	International Fire Code Institute
IX	ion exchange
LCR	Lead and Copper Rule
LOX	liquid oxygen
LSL	lower sensitivity limit
LT1ESWTR	Long-term 1 Enhanced Surface Water Treatment Rule
LT2ESWTR	Long term 2 Enhanced Surface Water Treatment Rule
MCA	Manufacturing Chemists Association
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
MDL	method detection limit
MF	microfiltration
MFI	modified fouling index
MIB	2-methylisoborneol
MLVSS	mixed liquor volatile suspended solids
MPN	most probable number
MRDLG	maximum residual disinfectant level goal
MSDS	material safety data sheets
MWC	minimum water column
MWD	maximum water depth; Metropolitan Water District; minimum water depth
NDMA	N-nitrosodimethylamine
NF	nanofiltration
NFPA	National Fire Protection Association
NMW	nominal molecular weight
NOB	nitrite-oxidizing bacteria
NOM	natural organic matter
NPDES	National Pollutant Discharge Elimination System
NSF	National Sanitation Foundation
NTSB	National Transportation Safety Board
ORP	oxidation-reduction potential
OSHA	Occupational Safety and Health Administration
OT	orthotolidine
OTA	orthotolidine-arsenite
PAC	powdered activated carbon
PAO	phenylarsine oxide
PC	programmable controller
PCB	polychlorinated biphenyl
PCS	process control software

PDWF	peak dry weather flow
PFU	plaque-forming unit
PICS	process instrument control system
PLC	programmable logic controller
PPCP	pharmaceutical and personal care product
PSA	pressure swing adsorption
PSM	process safety management
PSS	point summation source
PSU	power supply unit
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
RAA	running annual average
RAS	return activated sludge
RCP	reinforced concrete pipe
RMP	risk management program
RMPP	risk management protection plan
RO	reverse osmosis
RSI	Railway Supply Institute
RTK	right-to-know
RTU	remote terminal unit
SCF	short circuiting factor
SDH	succinic dehydrogenase
SDI	silt density index
SDWA	Safe Drinking Water Act
SETIQ	Sistema de Emergencias en Transporte para la Industria Quimica
SFPC	Standard Fire Prevention Association
SHMP	sodium hexametaphosphate
SLS	sodium lauryl sulfate
SMCL	secondary maximum contaminant levels
SOC	synthetic organic compound
SPC	standard plate count
SS	suspended solids
STEL	short-term exposure limit
SW	spiral wound
SWTR	Surface Water Treatment Rule
TC	total coliform
TCA	trichloroacetic acid
TCE	trichloroethylene
TCEP	tris (2-chloroethyl) phosphate
TDD	triple distilled deionized
TDH	total dehydrogenase; total dynamic head
TDS	total dissolved solids
TFC	thin-film composite
THM	trihalomethanes

THMFP	trihalomethane formation potential
TLV	threshold limit value
TOC	total organic carbon
TON	threshold odor number
TOX	total organic halides
TRANSSCAER	Transportation Community Awareness and Emergency Response
TRC	total residual chlorine
TSS	total suspended solids
TTCE	tetrachloroethylene
TTHM	total trihalomethane
TWA	time weighted average
UBC	Uniform Building Code
UF	ultrafiltration
UFC	Uniform Fire Code
UP	Union Pacific
USEPA	United States Environmental Protection Agency (also EPA)
USGS	United States Geological Service
UV	ultraviolet
UVA	ultraviolet absorbance at 254 nm
VOC	volatile organic carbon/compound
VSA	vacuum swing adsorption
WEF	Water Environment Federation
WPCF	Water Pollution Control Federation
WTP	water treatment plant
WWTP	wastewater treatment plant

ACKNOWLEDGMENTS

We give special thanks to Alan Ingham and Dan Wright for assistance with graphic arts. We are also grateful for the assistance and compilation efforts of Rhonda Hoyt.

1 Chlorine: History, Manufacture, Properties, Hazards, and Uses

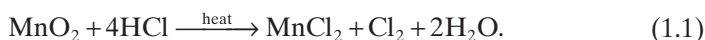
HISTORICAL BACKGROUND

Elemental Chlorine

Chlorine is an element of the halogen family, but it is never found uncombined in nature. It is estimated to account for 0.15% of the earth's crust in the form of soluble chlorides, such as common salt (NaCl), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), and sylvite (KCl). In nature, it exists only as the negative chloride ion with a valence of -1 . Because its properties in the gaseous, liquid, and aqueous states differ widely, each phase will be discussed separately.

Chlorine Gas

Medieval Arab chemist Geber must have known this element (ca. 720–810). Chlorine was discovered, in its gaseous state, in 1774 by Karl W. Scheele, a Swedish chemist, when he heated manganese dioxide with hydrochloric acid.¹



Scheele called the gas he discovered “dephlogisticated muriatic acid” on the theory that manganese had displaced “phlogiston” (as hydrogen was then called) from the muriatic acid (HCl). Scheele also observed that the gas was soluble in water, that it had a permanent bleaching effect on paper, vegetables, and flowers, and that it acted on metals and oxides of metals.

During the decade following Scheele's discovery, Lavoisier attacked and, after a memorable struggle, completely upset the phlogiston theory of Scheele. Lavoisier was of the opinion that all acids contained oxygen. Berthollet found that a solution of Scheele's gas in water, when exposed to sunlight,

White's Handbook of Chlorination and Alternative Disinfectants, 5th edition,
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gives off oxygen and leaves behind muriatic acid. Considering this residue proof of Lavoisier's theory, Berthollet called it oxygenated muriatic acid.² However, Humphry Davy was unable to decompose Scheele's gas. On July 12, 1810, before the Royal Society of London, he declared the gas to be an element, in which muriatic acid is combined with hydrogen. Therefore, Lavoisier's theory that all acids contain oxygen had to be discarded. Davy proposed to name the gas "chlorine" from the Greek *chloros*, variously translated "green," "greenish yellow," or "yellowish green," in allusion to its color.

Pelletier in 1785 and Karsten in 1786 succeeded in producing yellow crystals of chlorine hydrate by cooling Scheele's gas in the presence of moisture. From this, they inferred that it was not an element. In 1810, Davy proved that the crystals could not be formed by cooling the gas even to -40°F in the absence of moisture. It is now known that these crystals are in fact chlorine hydrate ($\text{Cl}_2 \cdot 8\text{H}_2\text{O}$) and will form under standard conditions with chlorine gas in the presence of moisture and at a temperature of at least 49.3°F .

Chlorine Liquid

In 1805, Thomas Northmore noted that Scheele's gas became a yellowish amber liquid under pressure, and upon release of the pressure it volatilized rapidly and violently into a green gas. He further noted that it had a pungent odor and caused severe damage to machinery.

Michael Faraday (1791–1867) also observed liquid chlorine. On March 5, 1823, he was visited in his laboratory by J.A. Paris while he was working with chlorine hydrate in a sealed tube. Paris noted a yellowish, oily-appearing substance in the tube and chided Faraday for working with dirty apparatus. When Faraday tried to open the tube, it shattered and the oily substance vanished. After studying the accident, Faraday concluded the oil in the sealed tube was liquid chlorine.¹

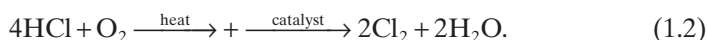
MANUFACTURE OF CHLORINE

History

From 1805 to 1888, Scheele's gas remained a laboratory curiosity—and a dangerous one—until it began to be produced on a commercial scale. This occurred when Kneitsch discovered in 1888 that dry chlorine did not attack iron or steel, which made it possible to package chlorine as a liquid under pressure.

Until then, chlorine had been used as a bleaching agent in the form of a solution. In 1785, Berthollet prepared this solution by dissolving Scheele's gas in water and adding it to a solution of caustic potash. This was done at a chemical plant in Javel, then a small French town now a part of Paris.

Hence, the solution was known as Javelle water. James Watt, the inventor, obtained a license for the manufacture of Javelle water and brought it to Scotland for Charles Tennant. In 1789, Tennant produced another liquid bleaching compound, a chlorinated milk of lime. A year later, he improved it by making it into a dry compound, known as bleaching powder. The chlorine for producing it was obtained by Berthollet's method of heating sodium chloride, manganese, and sulfuric acid in lead stills. At the same time, chlorine was also being made on a limited scale by the Weldon process, which employed the reaction discovered by Scheele, who reacted hydrochloric acid with manganese dioxide. This method was given considerable impetus when Gossage invented coke towers in 1836 for the absorption of waste hydrochloric acid.¹ The cheap hydrochloric acid produced from these towers was used in the Weldon process. However, the Weldon process became nearly obsolete in 1868 after Henry Deacon and Ferdinand Hurter patented a process for producing chlorine by decomposing hydrochloric acid with atmospheric oxygen in the presence of a catalyst.² In this process, a mixture of hydrochloric acid and air is heated. About 70% of the hydrogen chloride is converted to chlorine as it mixes with the air and steam. The gas is then condensed, and the steam absorbs the hydrogen chloride, forming a very strong muriatic acid mixed with hydrogen chloride gas. This mixture is passed first through a superheater at a temperature about 430°C, then through a decomposer consisting of a brick- or pumice-lined chamber impregnated with cupric chloride catalyst, and is finally washed first with water and then with sulfuric acid. The remaining mixture of nitrogen and oxygen contains 10% of chlorine gas, which can be used in manufacturing liquid or powdered bleach. The remaining HCl is recycled back through the process. Considering the amount of chlorine produced, the plant is extremely bulky. The reaction is



This reaction is reversible and incomplete. The rate of reaction is made satisfactory by the addition of heat and the catalyst.

The hydrogen chloride used in the Deacon process was a by-product of the LeBlanc soda process. With the advent of the Solvay sodium ammonia process in 1870, the LeBlanc process fell into a sharp decline, causing the abandonment of the Deacon process in favor of the emerging electrolytic methods.

Electrolytic Processes

History. In 1883, Faraday postulated the laws that govern the action produced by passing electric current through an aqueous salt solution. He coined the word "electrolysis" to describe the resulting phenomenon. These fundamental laws are among the most exact in chemistry and are as follows:

- The weight of a given element liberated at an electrode is directly proportional to the quantity of electricity passed through the solution. (The unit of electrical quantity is the coulomb.)
- The weights of different elements liberated by the same quantity of electricity are proportional to the equivalent weights of the elements.

Charles Watt obtained an English patent for manufacturing chlorine by the electrolyte process in 1851. However, at that time electric current generators of sufficient size were not available. When they became available, interest in electrochemistry was greatly stimulated. In 1890, the first commercial production of chlorine by the electrolytic method, the chlor-alkali process, was introduced by the Elektron Company in Griesheim, Germany.¹ The first manufacturer to use an electrolytic plant in America was the Oxford Paper Company at Rumford Falls, Maine, in 1892. In 1894, Mathieson Chemical Company acquired the rights to the Castner mercury cell and began to produce bleaching powder at a demonstration plant in Saltville, Virginia. In 1897, this operation was moved to Niagara Falls, New York. The original Castner rocking cells were operated successfully until they were shut down in 1960.^{3,4}

At first, the electrolytic process was used primarily for making caustic. Chlorine was an unwanted by-product. At the Niagara Falls plant, a small amount of chlorine was used for making bleach and hydrochloric acid; the remainder was discharged into the Niagara River. Not until 1909 was liquid chlorine manufactured commercially. It was first packaged in 100-lb steel cylinders. The demand for it grew slowly but steadily, mostly for bleaching textiles, pulp, and paper. The first American tank car, with a capacity of 15 tons, was manufactured in 1909. The next year, 150-lb cylinders came into use, and in 1917 ton containers were made for use in chemical warfare.¹

Current Practice. Today, chlorine is manufactured primarily by using three types of electrolytic cells: membrane, diaphragm, and mercury. Other methods, which are designed to fit the raw material containing the chlorine ion, include electrolysis of hydrochloric acid, salt process, and hydrochloric acid oxidation processes. Chlorine is also a by-product of heavy metal recovery, such as the tungsten sponge process, or extraction of magnesium from magnesium chloride ore.

ELECTROLYTIC CELL DEVELOPMENT

The Ideal Electrochemical Cell

An electrochemical cell is composed of an anode, a cathode, and a separator forming an anode chamber and a cathode chamber. The function of the separator is to isolate the two chambers while allowing selected ions in the liquid to migrate from the anode chamber into the cathode chamber. A brine of

sodium chloride and water is introduced into the anode chamber, where oxidation of the chloride ion takes place. Chlorine gas is released at the anode. The sodium ions are attracted to the negatively charged cathode and are transported through the separator. If the separator is doing a perfect job, all of the chloride will be contained on the anode side of the cell.

Water is reduced at the cathode and hydrogen gas is evolved. The remaining hydroxide ion combines with the sodium ion to form sodium hydroxide solution (caustic), which exits the cathode chamber. The ideal separator will keep all the hydroxide ions on the cathode side of the cell.

Process Developments

In practice, electrolytic cells are plagued with a variety of problems such as corrosion, erosion of electrodes, and plugging of the separator. All of these problems contribute to maintenance costs. There is also great concern over the cost of electrical energy required to drive the oxidation reaction. In recent years, industry has made important advances on all of these fronts. Energy consumption has been significantly reduced by improvements to cell design and improvements to the electrical equipment used to convert alternating current (AC) to direct current (DC).

Major advances that have revolutionized electrolytic cell design include the use of new materials of cell construction and diaphragms, as well as the use of cladding processes that eliminate or retard the corrosion of cell components. The chlor-alkali industry has long sought a stable metal anode for chlorine production. In 1968, Diamond Shamrock Corporation announced the development and commercialization of new types of metallic anodes, which it named dimensionally stable anodes (DSA).⁵ These anodes have been instrumental in reducing both capital and operating costs. As their name implies, they retain their size and shape during use and have a life longer than 10 years in diaphragm cells, compared with about 180 days for the older graphite anode. Moreover, they eliminate hydrocarbon contamination of chlorine caused by the graphite, which poses a health problem in potable water chlorination (see the section “Impurities in the Manufacture of Chlorine” in this chapter).

The anodes can be reactivated by redeposition of the metal coating. In addition to reducing the downtime and labor for anode replacement, the savings in the cost of graphite consumed per ton of chlorine produced is substantial.

Membrane Cell

Description. A schematic of a membrane cell is shown in Figure 1.1⁶. An ion exchange membrane separates the cell into two compartments. This membrane allows sodium ions, and a very small quantity of water, to move into the cathode compartment but prevents the migration of chloride ions and chlorine gas across this barrier. The membrane also prevents the movement

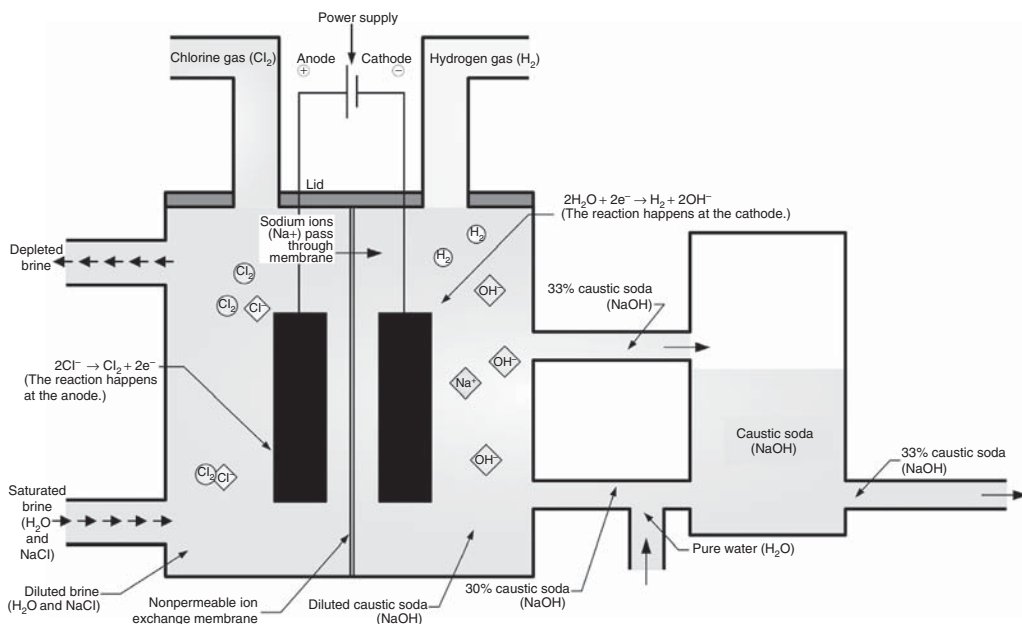


Figure 1.1. Schematic of a membrane cell.

of hydroxyl ions from the cathode compartment to the anode compartment. Chlorine gas is formed at the anode and hydrogen gas is formed at the cathode.

A saturated brine solution enters the anode compartment, provides the chloride and sodium ions used in the process, and then flows out of the compartment to be dechlorinated, resaturated with sodium chloride, and recycled. The caustic formed by the sodium ions passing through the membrane is recycled through the cathode compartment. Pure water is added to this recycle stream. The excess caustic solution is stored prior to evaporation to increase the concentration of this product. The chlorine produced in the cell is hot and wet, and it contains trace concentrations of air, oxygen, and carbon dioxide. These contaminants are removed by cooling, drying, and liquefying the chlorine.

History. Hooker Chemicals and Plastics (now Occidental Chemical Corporation) and Diamond Shamrock Corporation began membrane cell development programs in the 1950s.⁷ The largest producer of chlorine in the United Kingdom, the ICI Corporation, began to develop membrane cells 20 years later.⁸ The concept was made feasible by the development of selective ion exchange membranes that could withstand the very harsh environment inside an electrolytic cell.

Approximately 23% of the chlorine manufactured in the United States and 20% of the chlorine manufactured in Canada during 2006 were produced using membrane cells. These percentages will increase in the future as mercury and diaphragm cells are phased out of service. None of the chlorine producers in Mexico used membrane cells in 2006.⁹

Theory of Operation. The membrane cell is a very good simulation of the ideal cell. The operation of any electrolytic cell is limited by the ability of its individual components to perform as required. To overcome these limitations, it is necessary to find the proper materials for the electrodes and the separator (membrane) that result in the greatest yield and purity of product with the least expenditure for energy and maintenance.

Salt, water, and electric current are the raw materials. Solid salt is dissolved in a saturator with fresh water and depleted brine. The saturated brine is chemically treated to precipitate impurities, which are removed by clarification and filtration. The filtered brine is then passed through an ion exchange process to lower the final concentration of calcium ion to less than 0.05 mg/l. The cell membranes are highly sensitive to calcium deposits, and if this limit is not achieved, process performance will suffer and maintenance costs will escalate.

Hydrochloric acid is added to the brine to neutralize part of the back migration of hydroxide ions. These ions reduce the formation of objectionable by-products before the purified brine is fed to the anode compartments of the cells. The salt is electrically decomposed to produce the chlorine gas generated at the anode. The sodium ions remain in solution and are transported through the membrane to the cathode, where they combine with hydroxide ions formed in the cathode chamber. The depleted brine leaving the anode chamber is treated to separate any remaining chlorine, and recycled to the brine saturator. The caustic solution formed in the cathode compartment flows to a caustic surge tank, where most of it is cooled and recycled to control the concentration and temperature of the caustic in the membrane cells. Softened water is added to the caustic solution to maintain the desired product concentration. The hydrogen produced in the cathode chambers may be vented or recovered. The feed brine contains about 320 g/l of sodium chloride and not more than 30 g/l of chlorate ion. Depleted brine has a pH range of 2–5 and contains about 170 g/l sodium chloride. The chlorine produced is 97%–99.5% pure, and contains 3.0%–0.5% oxygen. This oxygen is removed by liquefaction and evaporation downstream from the cell. The caustic product, which is approximately 30% by weight sodium hydroxide, contains 40–50 ppm sodium chloride and 5–15 ppm chlorate ion. The hydrogen is 99.9% pure.

Advantages and Disadvantages of Membrane Cells. One of the most important advantages of the membrane cell is that the overall plant process requires less energy than either the mercury cell or the diaphragm cell. However, the membranes are relatively expensive and have a short service life.

Membrane cells require the use of very pure solid salt to make the influent brine. The brine prepared from this salt must also be purified to a greater degree than the brine used with other types of electrolysis cells.

Membrane cells produce a very pure grade of caustic directly from the cell. However, the highest concentration of caustic that can be produced by these cells is about 33%–35%. Higher concentrations of caustic are desirable for many uses of this product. Additional caustic concentration steps are, therefore, provided at most of the chlor-alkali plants that use membrane cells. The chlorine gas produced by membrane cells contains some oxygen that must be removed by liquefaction and evaporation. The hydrogen gas is very pure. Membrane cells do not utilize either mercury or asbestos, which minimizes adverse impacts on workers at the plants and on the environment.

Diaphragm Cells

Description. A schematic of a diaphragm cell is shown in Figure 1.2.⁶ A permeable diaphragm separates the cell into two compartments. Brine enters

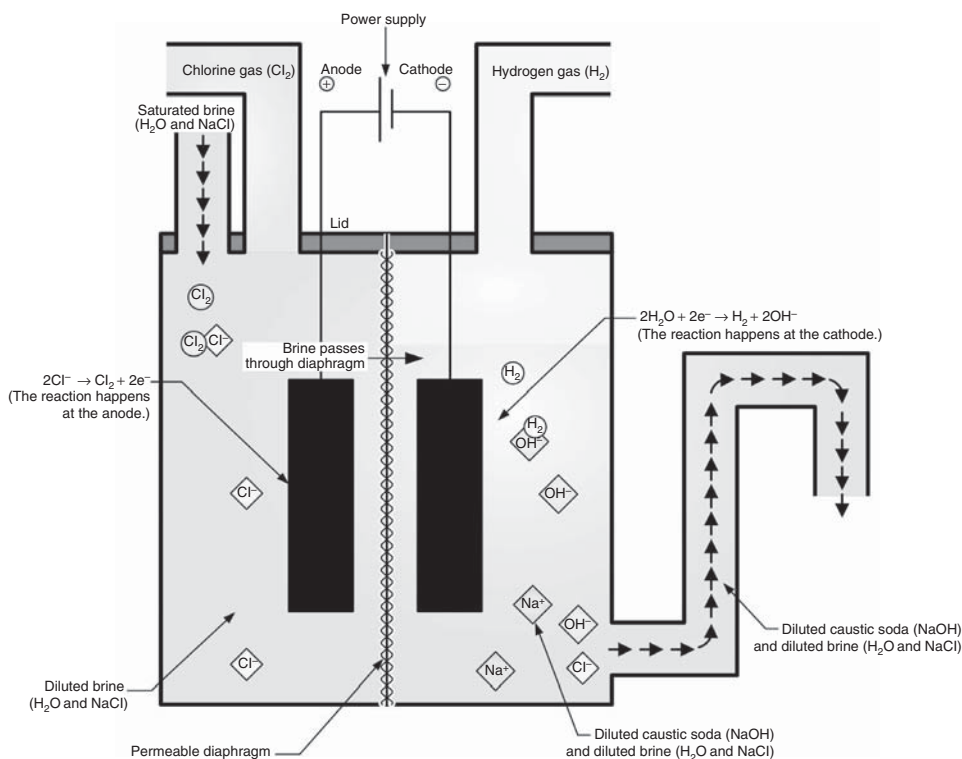


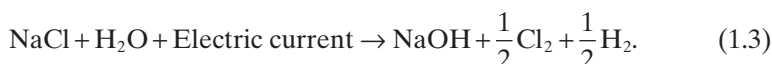
Figure 1.2. Schematic of a diaphragm cell.

the cell in the anode compartment, flows through the diaphragm, and exits the cell from the cathode compartment. Chlorine gas is formed at the anode, and hydrogen gas is formed at the anode. Both of these gases are vented from the cell and processed elsewhere in the plant. The liquid discharged from the cathode compartment is a mixture of diluted brine and dilute sodium hydroxide. This mixture is concentrated, and the brine is removed from the caustic, by additional treatment steps downstream from the cell. The salt removed from the caustic solution is recycled to prepare additional brine. The chlorine leaving the cell contains the contaminants previously identified in the description of the gas discharged from membrane cells.

History. Diaphragm cells were initially designed in the 1880s. Several hundred configurations of these cells have been developed since that time. These modifications have focused on improvements to the anodes and the diaphragms. Details about designs currently in use can be obtained from equipment manufacturers and from the technical literature.

Diaphragm cells were used to make approximately 66% of the chlorine produced in the United States and 76% of the chlorine produced in Canada during 2006.⁹ Use of these cells will gradually decline as new facilities are constructed using membrane cells. Two of the chlorine plants in Mexico used diaphragm cells in 2006.⁹

Theory of Operation. The overall chemical reaction in a diaphragm cell is



The principal anode reaction is



Chlorine formed at the anode saturates the anolyte, and an equilibrium is established as follows:



The principal cathode reaction is



$$\frac{107.880}{0.00111801} = 96,493 \text{ C}. \quad (1.8)$$

Therefore, from Faraday's law we know that 96,493 coulomb (1 f) will liberate 1.0080 g of hydrogen and 35.457 g of chlorine in the electrolysis of salt. Converting this to amperes per pound of chlorine per day, we get

$$\frac{A \times 86,400 \text{ s/day}}{96,493 \text{ C}} \times \frac{35.457 \text{ gCl}_2}{454 \text{ g/lb}} = 0.07 \quad (1.9)$$

$$A \times 0.07 = \text{lb/day Cl}_2$$

A diaphragm cell using 135,000 A of electricity, with a current efficiency of 95.8% will produce 9053 lb of chlorine per day.

Since chlorine gas evolves at the anode and hydrogen gas evolves at the cathode, the sodium ion in the influent brine is free to associate with the excess hydroxyl ion formed in the cathode compartment when the depleted brine flows into the second chamber.

The flow through the porous diaphragm produces a differential hydraulic head between the two chambers. This difference in water level prevents migration of hydrogen gas into the influent chamber.

Flow through the porous diaphragm also inhibits migration of hydroxyl ions from the cathode to the anode compartment. This is desirable because the presence of hydroxyl ion in this compartment will result in the formation of hypochlorite ion instead of elemental chlorine.

Purified brine is added at the cell inlet at a temperature of 60–70°C. By maintaining the pH of this solution between 3 and 4 and by maintaining a differential head between the solution levels in the two chambers, the diaphragm cell can be kept in chemical equilibrium to produce hydrogen gas at the cathode and 11%–14% sodium hydroxide in the effluent from the cathode compartment. The spent brine discharged from this compartment contains approximately 322 g/l of sodium chloride. Facilities are needed downstream from the cell to remove this salt and to increase the concentration of the sodium hydroxide.¹⁰

The most common material used to make diaphragms has been asbestos. Fluorinated polymer resins have been used since the early 1980s to strengthen the asbestos membranes. However, special steps are required in the manufacturing and disposal of all products containing asbestos because of the environmental hazards associated with this material. New fluoropolymer-based diaphragms entered the marketplace in 1997. These diaphragms are more expensive than asbestos but they have a longer life and provide more stable operation in the cells.

Advantages and Disadvantages of Diaphragm Cells. Diaphragm cells require lower purity brines than membrane cells. They also use lower voltage and less electric power than mercury cells. However, the sodium hydroxide produced in diaphragm cells is both dilute and contaminated with chloride ion. Evaporative concentration of this solution is required to increase the concentration of the sodium hydroxide and remove the chloride contamination. The chlorine gas produced by diaphragm cells contains some oxygen that must be removed by liquefaction and evaporation. The hydrogen gas is very pure. There are high costs associated with handling and disposal of asbestos membranes.

These costs can be avoided by using the newer membranes that are now available.

Mercury Cells

Description. A schematic of a mercury cell is shown in Figure 1.3.⁶ The cell has two parts: (a) the electrolyzer and (b) the amalgam decomposer. The electrolyzer is a covered tray with a sloped metal bottom that functions as a conducting base plate in the electrolysis process. Titanium metal anodes are located a short distance above the bottom of the tray. Concentrated salt brine and a supply of mercury enter the shallow end of the tray and flow toward the deep end. The mercury spreads out on the bottom of the tray and is the cathode for electrolysis of the brine. Chlorine gas is liberated at the anodes and bubbles out of the brine to exit at the top of the tray. Sodium is deposited at the surface of the flowing mercury cathode where it dissolves to form a very dilute sodium/mercury amalgam. The hydrogen formed at the cathode is entrapped in this amalgam and leaves the electrolyzer in this mixture. The depleted brine flows out of the electrolyzer, is resaturated with sodium chloride, and is then recycled back to the inlet of this process.

The sodium/mercury amalgam and the entrapped hydrogen flow to the amalgam decomposer. This consists of a closed vessel that contains a graphite catalyst. Pure water flows into the bottom of the catalyst bed and reacts with the amalgam to free the sodium ions and hydrogen. The clean mercury flows out the bottom of the decomposer and is pumped back to the inlet of the electrolyzer. The caustic solution and the hydrogen gas are processed elsewhere in the plant.

History. Two men on different continents simultaneously discovered the mercury cell process for producing chlorine and caustic. Each discoverer was unaware of the other's efforts. One was an American, Hamilton Y. Castner; the other an Austrian, Karl Kellner. Both applied for patents in 1892.^{3,4}

The first Castner cell installation was a 550-A demonstration plant designed in 1897 for the Mathieson Chemical Company at Saltville, Virginia. The plant was later moved to Niagara Falls, New York, where it was operated successfully until 1960, when it was replaced with a 100,000-A installation using an upgraded version of the original mercury cells. These mercury cells are no longer in use.^{3,4}

In the 1970s, mercury cell facilities in North America were found to be discharging excessive amounts of mercury in their effluent. Additional monitoring also showed significant quantities of mercury being volatilized and discharged into the air. Despite steps taken by chlorine manufacturers to reduce these emissions, public and regulatory pressure to discontinue the use of mercury cells has continued. By 2005, more than 100 mercury cell facilities had been converted to using membrane or diaphragm cells, and by 2007 only five mercury cell installations remained in operation in the United States.

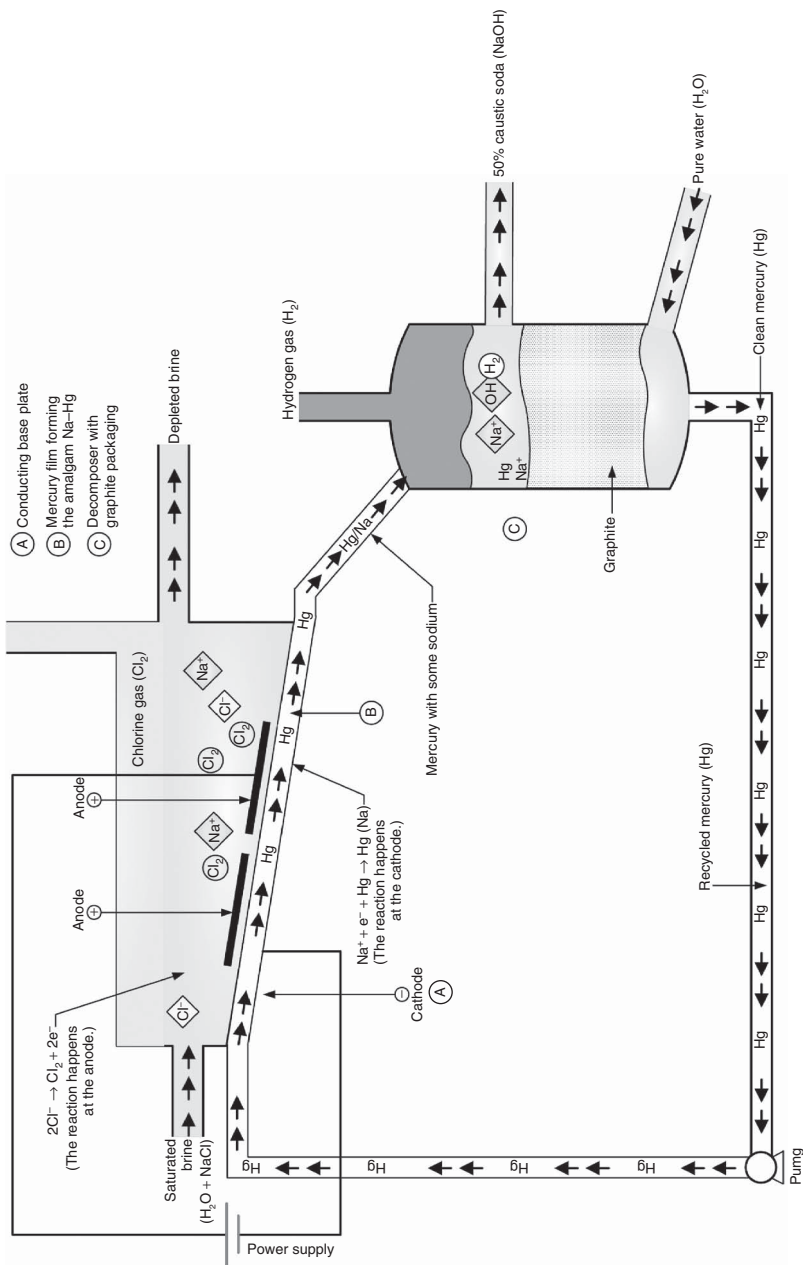


Figure 1.3. Schematic of a mercury cell.

Plans have been announced to convert several of these plants to membrane or diaphragm cell facilities by mid- to late 2009.

In Europe, there were 48 mercury-based chlorine plants in 2005, which accounted for almost 50% of European chlorine production capacity. The industry has agreed to voluntarily phase out these plants or to convert them to nonmercury technology by 2020. Public pressure is being applied to accelerate this schedule. The World Bank does not finance construction of chlorine production facilities that use mercury cell technology.

Mercury cells were used to produce about 9% of the chlorine manufactured in the United States and 4% of the chlorine manufactured in Canada during 2006. There were four mercury cell plants operating in Mexico in 2006, and new construction was underway at all of these plants. It is not known whether any mercury cells will be retired when this work is completed.⁹

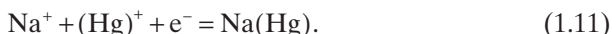
Theory of Operation. The principal chemical reactions in a mercury cell are as follows:

1. Electrolyzer

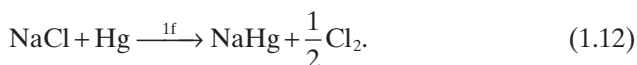
At the anode:



At the cathode:

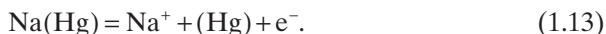


Overall reaction:

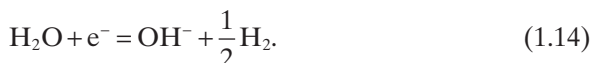


2. Decomposer

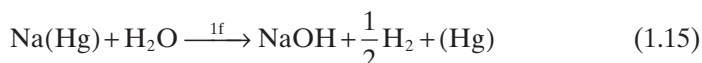
At the anode:



At the cathode



Overall reaction:



The main differences between the mercury cell and the diaphragm cell are as follows: The spent brine is withdrawn separately from the mercury amalgam. The caustic is produced in the decomposer as a by-product from preparation of the amalgam to be returned as the mercury cathode. Both processes use about 1.7 tons of salt per ton of chlorine produced. The net result is essentially the same as produced by diaphragm cells. The ingredients are the same, except for the inventory of mercury.

Electrolyzer. The purified, saturated (305 g/l) alkaline brine solution is fed to the electrolyzer portion of the cells where the pH is adjusted with HCl to a range of 2.5–5. The pH is somewhat dependent on the amount of calcium sulfate that can be tolerated in the brine. The pressure on the anode side is atmospheric (± 15 mmHg). DC in the amount specified for the cell rating is applied at 4–4.5 V between the metal anode and the mercury cathode, with the chlorine being liberated at the anode. The spent brine is monitored as it leaves the cell to keep its sodium chloride concentration at 260–280 g/l and its temperature no higher than 85 °C. This is done by regulating the quantity of brine fed to the cells. The spent brine is dechlorinated by air stripping, regenerated by contacting it with solid salt, the pH is adjusted to 10 with sodium hydroxide, and the solution is settled and filtered. The regenerated brine is recycled to the cells. The chlorine gas produced in the electrolyzer is treated in the same way as the chlorine produced in diaphragm cells.

Decomposer. The decomposer is a tower packed with lumps of graphite. A distributor plate spreads the amalgam over the top of this packing. Purified and softened water enters the bottom of the packing and flows out the top of the packing as 50% sodium hydroxide. Sodium amalgam in contact with the graphite packing and water is decomposed into sodium hydroxide and hydrogen. The hydrogen, which is collected from the top of the decomposer, is wet and contains some mercury vapor and entrained caustic spray. These contaminants are removed by cooling the hydrogen in a scrubber or a condenser. The mercury flows out of the bottom of the decomposer and is pumped back to the electrolyzer.

This method produces a 50% caustic solution (diaphragm cells produce 11%–12% caustic, and membrane cells 30%–35% caustic). The caustic solution is filtered to remove the graphite particles picked up in the decomposer, which contains some of the mercury recovered from the sludge during filtering. The mercury recovered from the chlorine, hydrogen, caustic, and sludge is recycled back to the electrolyzer.

Occupational Health. All industries that produce or use hazardous chemicals must comply with rules promulgated by the federal Occupational Safety and Health Administration (OSHA) under 29CFR 1910 or with rules established and enforced by state OSHA agencies. These rules are addressed later in this chapter.

The Chlorine Institute (CI) recommends medical surveillance of all personnel working in chlorine production, use, or handling facilities who are potentially exposed to chlorine gas above the American Conference of Governmental Industrial Hygienists (ACGIH) guideline of 0.5 ppm time-weighted average (TWA) or the 1 ppm short-term exposure limit (STEL).¹¹ It is especially important for workers in the cell area of mercury cell plants to undergo regular health checks because they are potentially exposed to two hazardous chemicals.¹²

The U.S. Environmental Protection Agency (USEPA) promulgated the Final Rule for mercury emissions from mercury cell chlor-alkali plants on December 19, 2003.¹³ This rule limits the allowable quantities of mercury in emissions from by-product hydrogen streams, end box ventilation system vents, mercury thermal recovery unit vents, and the storage areas for mercury-containing wastes. In addition, the rule establishes comprehensive standards for work practice that must be met in mercury cell rooms. These standards include specific design, operation, and maintenance requirements; inspection, monitoring, and reporting requirements; and specify the actions for responding to liquid mercury spills and the collection of liquid mercury.

The USEPA rule does not regulate atmospheric emissions of chlorine and hydrochloric acid from mercury cell, diaphragm cell, or membrane cell plants.

Advantages and Disadvantages of Mercury Cells. Mercury cells produce a pure 50% concentration solution of sodium hydroxide. There is no need for evaporative concentration of the caustic produced in a mercury cell plant. However, trace concentrations of mercury will occasionally contaminate the caustic. Some purchasers will not buy caustic from these plants because of this potential hazard. Mercury cells produce a pure chlorine gas with virtually no oxygen contamination. But a higher voltage is required in this cell than in the other two types of cells. The electrical power requirements of mercury cells are 10%–15% higher than the power requirements of the other two cell types. The costs of brine purification in mercury cell plants are higher than those in the other two types of cells. The major disadvantage of mercury cells is the mercury itself. The chlor-alkali industry has made large financial investments to minimize exposure of workers to mercury in these plants and to ensure that mercury does not contaminate the environment. However, strong pressure to eliminate the continued use of this technology will continue to be exerted.

Process Diagram for a Typical Chlor-Alkali Plant

Figure 1.4 is a process diagram of a typical chlor-alkali plant producing chlorine and sodium hydroxide by electrolysis.¹⁴ Most of the unit processes shown in this figure are required in the plant regardless of the type of cell used, that is, membrane, diaphragm, or mercury; however, the scope of the individual processes will vary depending on the needs of the cell and the characteristics

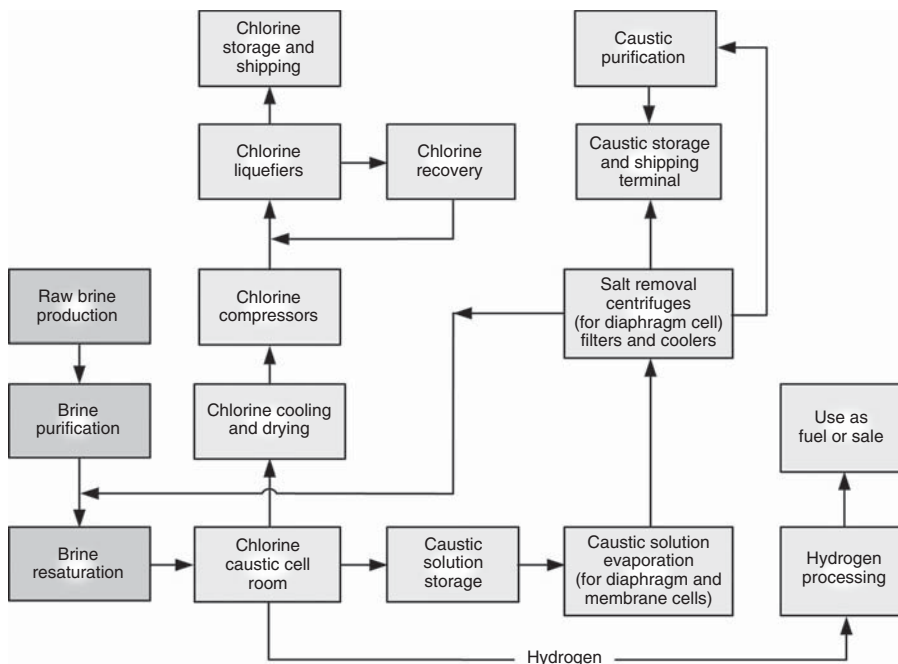


Figure 1.4. Process diagram of a chlor-alkali plant.

of the chlorine and sodium hydroxide produced. These differences will be discussed below.

The ingredients required for all of the cells are brine, water, and electric power. Brine is obtained in one of two ways: (a) from rock salt delivered to the plant and dissolved in water or (b) locating the plant adjacent to underground deposits of salt, from which brine is produced by injecting water into a well. Impurities such as calcium, magnesium, and iron must be removed from the brine by adding sodium carbonate and sodium hydroxide, followed by sedimentation and filtration. The brine used in membrane cells must be further treated by ion exchange to remove trace impurities that could plug the membrane. The water used to prepare the brine must also be free of ammonia and all chemical compounds containing nitrogen. This is necessary to prevent the formation of nitrogen trichloride during electrolysis.

The salt content of the purified brine is increased to approximately 27% by heating to evaporate some of the water. Salt removed from the sodium hydroxide produced in diaphragm cells is also recycled to the inlet of the electrolysis cell. This recycle stream is not present when membrane or mercury cells are used.

The electrical power required for electrolysis is usually obtained from a high-voltage AC source that has been stepped down and rectified to 3–5V of DC. Depending on the type, size, and design of the cell, power consumption

is usually about 2200–2900 kWh per ton of chlorine produced in a diaphragm cell plant. Electrical power consumption in the membrane cell process is about 2000–2400 kWh per ton of chlorine. Approximately 3600–3900 kWh are required to produce a ton of chlorine in a mercury cell.

The gas leaving the cathode of the electrolysis cell is about 99.8% pure hydrogen. It is scrubbed with water to cool it and to remove traces of caustic or other impurities (salt in diaphragm cells and mercury vapor in mercury cells). The purified hydrogen is then compressed for use in various processes or as fuel.

The gas leaving the anode is about 97.5% pure chlorine. The contaminants usually consist of a mixture of water vapor, oxygen, nitrogen, and carbon dioxide. This gas is hot (approximately 210 °F or 100 °C), moist, and extremely corrosive. It is usually cooled with water in a packed tower, dried by scrubbing with sulfuric acid, and then compressed to about 60 psi, before being fed into a fractionating tower to remove impurities such as chloroform and chlorinated hydrocarbons. These impurities are removed at the bottom of the tower in a solution containing little or no chlorine.

After leaving the fractionating tower, the chlorine gas is liquefied by refrigeration and pumped to storage tanks, from which it is repumped into tank cars and ton containers. Manufacturers generally prefer to ship liquid chlorine in rail tank cars to packagers who transfer it into tanker trucks, ton containers, and 150-lb cylinders. Trucks are used to transport the ton containers and 150-lb cylinders to the consumer.

The packagers have liquid bleach manufacturing operations to utilize the “snift gas” that would otherwise be discharged to the atmosphere when the containers are being filled. Some packagers also prepare bulk shipments of commercial-strength bleach for delivery to customers.

Manufacturing plants usually recover the snift, or “blow gas,” as well as the chlorine lost in the water used for cooling the gas. One process used to recover this chlorine is the Hooker process, which uses water to absorb the chlorine in the gas. This water is then used in the cooler, and upon leaving the cooler, is heated with steam and then acidified to strip it of chlorine, which is returned to the packaging cycle. Another process, the Diamond–Alkali process uses carbon tetrachloride to absorb the chlorine. The carbon tetrachloride is then heated and stripped from the chlorine.¹⁰

The sodium hydroxide formed in the electrolysis cell is sent to storage tanks pending the additional treatment required to produce a marketable product. Very high-quality sodium hydroxide is produced in membrane cells, so the only additional treatment required is evaporation to increase the concentration of the solution to the level desired by customers. The concentration of the sodium hydroxide produced by mercury cells is high enough for direct commercial use, but this product should be monitored to make certain that trace amounts of mercury are not present. The spent liquor discharged from diaphragm cells usually contains about 11.5% sodium hydroxide and 16% sodium chloride. Before it can be marketed, the salt must be removed, and

the concentration of caustic must be raised to 35%–50%. This is done by first evaporating the liquid. The salt is then separated from the caustic solution by centrifugation and filtration. This salt is washed to remove residual caustic, dissolved, and recycled back into the brine system. The caustic is cooled and settled to remove additional salt prior to pumping the purified solution into storage tanks.

OTHER CHLORINE MANUFACTURING PROCESSES

The following processes are available but are not in widespread use. They are useful in using excess hydrochloric acid.

Salt Process

The salt process for producing chlorine is based on the reaction between sodium chloride and nitric acid. This process was initially developed to manufacture sodium nitrate for the fertilizer industry. Allied Chemical Company implemented this process, on a commercial basis, at Hopewell, Virginia, in 1936. The overall reaction is



In this process, dilute nitric acid (55% or less) is first concentrated by evaporation to 63%–66%, mixed with sodium chloride, and heated with steam to cause the reaction that produces nitrosyl chloride, chlorine, and sodium nitrate in equal molar quantities. The solution is stripped of nitrosyl chloride and chlorine, which are scrubbed, dried, and liquefied with refrigerated brine. The nitrosyl chloride–chlorine mixture is then passed through a separating column; the chlorine leaves as a gas from the top of the column and is reliquefied and sent to storage. The nitrosyl chloride leaves the column at the bottom as a liquid and is sent to a recovery operation. Additional oxidation of this nitrosyl chloride can be used to recover additional chlorine.

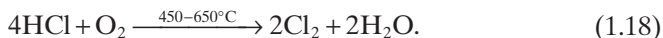


The nitrogen tetroxide gas produced in this reaction can be separated from solution and marketed separately, or the solution can be recycled to manufacture sodium nitrate.¹⁰

HCl Oxidation Processes

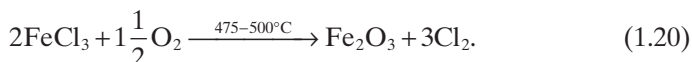
The market for chlorine has expanded rapidly, while the market for hydrochloric acid has declined. This situation has created a demand for the production of chlorine from the hydrochloric acid produced as a by-product from

other chemical processes. This demand has revived the Deacon process, which is attractive because of its simplicity. It involves a mildly exothermic reaction, with low electric power and thermal energy use. The reaction—HCl oxidation—takes place in the vapor phase over a copper base catalyst as follows:



There are no side reactions or competing reactions: The principal problem is the development of operating conditions that best balance the higher rate of reaction achieved at higher temperatures against higher yields obtained at lower temperatures. The Air Reduction Company improved the Deacon process to make it practical to produce chlorine at a ton-per-day rate from by-product HCl at about 27% chlorine by volume with air, and about 90% chlorine with 95% oxygen.³

The Grosvenor Miller process, with a fixed-bed system, utilizes the following reactions:¹⁰



A final-product gas containing a maximum of 70% chlorine can be obtained with this process by using a three- to five-bed continuous reactor system. The process is as follows: Reactor I is laden with dry ferric chloride at 250–300°C and is fed oxygen. The ferric chloride is converted to chlorine and ferric oxide. The gas formed in reactor I (which contains approximately 30% chlorine gas, 70% unreacted oxygen, hydrochloric acid vapor, and some air), passes into reactor II, which is a mixed bed of ferric oxide and ferric chloride maintained at 500°C to serve as both chlorinator and oxidizer. Some of the hydrochloric acid vapor in the gas entering reactor II reacts with ferric oxide to produce ferric chloride. This ferric chloride produced in this reaction, plus the ferric chloride in the bed of this chamber, react with the excess oxygen in the gas to produce additional chlorine. The chlorine gas does not react, so it and the remaining hydrochloric acid vapor and oxygen pass into reactor III, which is maintained at 250–400°C. This reactor was previously reactor I, and thus is oxygen laden. Reactor III strips the remaining hydrochloric acid vapor from the gas. The chlorine gas does not react, and it passes through reactor III, carrying with it steam and excess oxygen until this reactor becomes saturated with chlorides. At this point, the functions of reactor III are transposed to those of reactor I, and gas flow is III to II to I. There are other variations of this process, such as the Dow moving bed process and others using molten metallic chlorides as catalysts.

The Kel-Chlor process, developed by the M.W. Kellogg Company of Houston,¹⁵ is a modification of the Deacon process. This modification was

developed to correct chemical equilibrium problems in the original process that produced low yields of chlorine. The Kel-Chlor process solved these problems by combining a very active catalyst (nitrogenous compound) with a powerful dehydrating agent (sulfuric acid). This reduces the activity of the steam to a negligible value and allows the reaction to proceed to completion.

Electrolysis of Hydrochloric Acid Solutions

Bayer MaterialScience Process. Bayer Corporation intends to finish construction of the world's largest hydrochloric acid recycling plant in 2008. This plant will be located in Shanghai, China, and will use a new oxygen-depolarized cathode technology in the production of chlorine. A smaller plant used to develop this technology was run in Brunsbüttel, Germany in 2003.¹⁶

The Hoechst-Uhde Process.¹⁷ Considerable quantities of aqueous hydrochloric acid and hydrogen chloride gas are produced each year as by-products from a number of chemical manufacturing activities. These materials are difficult to dispose of; so a process that utilizes them is of special interest. The I.G. Farben Industrie began to develop a process in 1938 at its plant in Bitterfeld, Germany, using bipolar diaphragm cells, which had a limited production capacity, usually less than 50 tons of chlorine per day, and were subject to many fabrication and operating problems. A joint effort by Farbwerke Hoechst AG and Friedrich Uhde GmbH resulted in a successful design, which was placed into operation in 1963.

The first electrolysis unit in the United States was built in 1971–1972 at the Mobay Chemical Corporation in Baytown, Texas, by the Hoechst-Uhde Corporation. This plant had the capacity to produce 198 short tons of chlorine per day, and used waste hydrogen chloride gas from the manufacture of isocyanate. This plant is now owned by Bayer MaterialScience, and the plant capacity has been expanded.

IMPURITIES IN THE MANUFACTURE OF CHLORINE

Historical Background

Special attention has to be given to the production of chlorine when it is used for treatment of potable water, wastewater, and reclaimed water. The total amount of chlorine used for this purpose is only about 5% of all the chlorine produced in the United States. Industry thinks in terms of using thousands of pounds of chlorine per hour, whereas treatment plant users think in terms of hundreds of pounds per day.

In the early days of chlorination (1920s), metering equipment was continually plagued by fouling. The material causing this fouling was commonly called “gunk” or “taffy.” Its source was difficult to identify until Wallace and Tiernan

developed the bell-jar chlorinator (1922), which incorporated a self-cleaning pressure-reducing valve (visible through a glass dome) that operated under a vacuum. When this valve became plugged with enough “gunk” to stop the flow of chlorine, it would automatically shift from the throttled position to a wide-open position by raising the water level in the bell jar. In most cases, the wide-open valve would purge itself of the gunk and spew it all over the inside of the bell jar. This would allow the water level to decline, and the chlorinator would automatically resume operation. The material collected from the inside walls of the bell jars allowed customers to back up their complaints with samples of gunk. After receiving many such complaints, chlorine manufacturers added a fractionating tower¹⁸ to their manufacturing process to eliminate the gunk (ca. 1935).

In July 1977, high concentrations of carbon tetrachloride were found in finished water from the Belmont and Queen Lane water treatment plants (WTPs) in Philadelphia.¹⁹ The source of this material was traced to the chlorine used in the plants. When the chlorine supplier was changed, the problem disappeared. It was revealed that the manufacturer of the tainted chlorine was using a carbon tetrachloride scrubbing system to recover traces of chlorine from the off-gases produced during the manufacturing process. The problem was solved by separating the chlorine that was to be used for treatment of potable water from the chlorine that contained the gas recovered from the scrubbing system. This problem was investigated by the CI and several chlorine manufacturers. The outcome of this investigation led to the establishment of an interim maximum level for carbon tetrachloride in the chlorine used for potable water treatment. The USEPA set this level at 100mg/l, which was agreed to by the manufacturers’ association pending an assessment of what the chlorine industry was capable of producing.

The standard for the purity of chlorine used in potable water treatment is given in American National Standards Institute (ANSI)/American Water Works Association (AWWA) B301-04 which became effective September 1, 2004.²⁰ This standard limits the maximum concentration of carbon tetrachloride to not more than 100ppm (0.010%). However, testing for carbon tetrachloride is not required unless a carbon tetrachloride tail-gas scrubbing system is used to produce the chlorine. Chlorine supplied under this standard shall not contain more than 50ppm (0.005%) nonvolatile residue when loaded by the manufacturer into railroad tank cars or chlorine tank trucks. Up to 150ppm (0.015%) nonvolatile residue is allowed in the liquid chlorine later packaged in cylinders or ton containers. Other limitations are as follows: moisture not to exceed 150ppm (0.015%) by weight; heavy metals not to exceed 30ppm (0.003%) expressed as lead; mercury not to exceed 1ppm (0.0001%) reported as mercury; arsenic not to exceed 3ppm (0.0003%); and the sum of all heavy metals not to exceed 30ppm (0.003%) by weight expressed as lead.

AWWA has also issued standards for anhydrous ammonia (ANSI/AWWA B305-06) and aqua ammonia (ANSI/AWWA B306-07) used to form chloramines in potable water.^{21,22}

All of the AWWA standards are revised periodically. The reader should contact this organization to determine which standards are in effect.

The following are the major sources of impurities found in chlorine:

- 1. moisture entrapment during packaging;
- 2. organic impurities in the salt;
- 3. hydrocarbons from valve lubricants, pump seals, and various packing materials used in the manufacturing process; and
- 4. recovery systems used to separate the chlorine product from entrained hydrogen and air.

The impurities produced from these sources are summarized in Table 1.1.

Consequences of Impurities

Of the impurities listed in Table 1.1, moisture is the worst offender because it makes the chlorine highly corrosive, leading to the formation of ferric chloride, which causes fouling of the metering equipment (chlorinators). The next most offensive impurities are hexachloroethane and hexachlorobenzene, which form a taffylike substance commonly called “gunk” that can cause serious equipment fouling. These impurities can originate from valve-lubricating compounds, valve and pump packing, and gaskets used in the piping system. Most of these impurities are soluble in liquid chlorine. Ferric chloride plates out on metal piping, most notably in areas of chronic flashing, usually at restrictions or locations of turbulent flow. Ferric chloride appears to spread from the liquid to the vapor phase, so this contamination carries through the chlorination equipment. The largest deposits occur at points of pressure reduction and areas of reliquefaction. Both hexachlorethane and hexachlorobenzene tend to sublime at room temperature, and are usually deposited at points of pressure reduction in metering and control equipment.

TABLE 1.1. Impurities in Commercially Available Chlorine^{20,23}

Gases	Volatile Liquids	Volatile Solids	Nonvolatile Solids
CO ₂	Bromine	Hexachlorbenzene	FeCl ₃ ·6H ₂ O
H ₂	Carbon tetrachloride	Hexachlorethane	—
O ₂	Carbonyl chloride (phosgene)	—	Fe ₂ (SO ₄) ₃ ·6H ₂ O
N ₂	Chloroform	—	Nitrosyl chloride
NCl ₃	HCl, methylene chloride, moisture	—	Nitrogen tetroxide, H ₂ SO ₄

Nitrogen Trichloride in Liquid Chlorine

Occurrence, Formation, and Significance. Nitrogen trichloride (NCl_3) was first observed in 1811 from the action of chlorine on a solution of ammonium chloride. When generated in the laboratory, this compound is a yellow oil with a pungent chlorinelike odor. It is practically insoluble in water but easily soluble in most organic solvents. It has been reported that a drop of the oil explodes violently when touched with a feather dipped in turpentine.²⁴

Nitrogen trichloride is not listed as an impurity in chlorine produced in the United States or Canada, where its occurrence has been virtually nil since about 1930. It is occasionally found in chlorine produced elsewhere in the world.

Nitrogen trichloride is formed during the production of chlorine when ammonia nitrogen is present in the brine fed to the electrolytic cells. It is soluble to the extent of 7.3 mg/l in liquid chlorine, but it is not soluble in water or in the concentrated sulfuric acid that is used in the production of chlorine to remove moisture. Once NCl_3 forms in the electrolytic cells, it will pass with the chlorine gas through the coolers, scrubbers, and acid-sealed pumps, and will be condensed with the liquid chlorine. The danger of explosion is greatest when the liquid chlorine in the container is depleted and only chlorine vapor remains. The NCl_3 concentrates itself in the layer of liquid chlorine next to the vapor phase. As the liquid chlorine is used up, the concentration of NCl_3 keeps increasing at the vapor-liquid interface.

Explosions Caused by Nitrogen Trichloride. The last reported chlorine explosions from NCl_3 in liquid chlorine in the United States and Canada occurred 1929. However, many chlorine producers outside the United States, Canada, and the European Union are unaware of the dangers of NCl_3 . An evaporator explosion was reported in India in 1965, and in 1981 White investigated several explosions in South America, all of which were the result of ammonia N in the water entering the chlorine cell at concentrations between 50 and 300 mg/l.

Prevention of Nitrogen Trichloride Formation in Liquid Chlorine. The most effective method of dealing with NCl_3 is to remove all ammonia nitrogen from the water used to prepare the brine solution. This can be done by using breakpoint chlorination followed by aeration of the water.

A second method is to decompose the NCl_3 formed during electrolysis by irradiating the chlorine gas exiting the cells with ultraviolet (UV) light in the spectrum of 3600–4400 before the chlorine enters the scrubbers. As it is difficult to monitor the effectiveness of removing the NCl_3 by UV, it is more practical and reliable to use breakpoint chlorination, followed by aeration. However, the UV method has been used successfully to remove the small quantities of NCl_3 formed when the raw water contains trace concentrations of ammonia.

Silica Contamination

Contamination of chlorine by silica produces the formation of white silicon dioxide crystals (SiO_2) when the chlorine gas enters the injector assembly of a chlorinator. The injector inlet port plugs up rapidly, which makes the chlorinator inoperable. The source of silica may be contaminated brine water or silicone grease used in valves by the chlorine packager. Silica contamination of brine water is most likely to occur when the chlorine is a by-product from a metal refining process such as the extraction of magnesium from magnesium chloride ore.

If the brine contains silica, electrolysis will convert the silica to silicon tetrachloride (SiCl_4), which becomes a contaminant in the chlorine. When the liquid chlorine is vaporized, the chlorine vapor carries the SiCl_4 through the chlorinator and into the injector. When chlorine comes into contact with the water in the injector, the SiCl_4 is immediately transformed into SiO_2 crystals, which eventually plug the injector inlet.

PHYSICAL AND CHEMICAL PROPERTIES OF CHLORINE

General

Chlorine has an atomic number of 17 and an atomic weight of 35.457. Molecular chlorine, Cl_2 , has a weight of 70.914. Two isotopes of chlorine, Cl^{35} and Cl^{37} , occur naturally, and at least five other isotopes have been artificially produced.²⁵ Ordinary atomic chlorine consists of a mixture of about 75.4% Cl^{35} and 24.6% Cl^{37} . Chlorine usually forms univalent compounds, but it can also combine with a valence of 3, 4, 5, or 7 (Chapter 2).

In its elemental form, chlorine is a greenish yellow gas that can be readily compressed into a clear, amber-colored liquid that solidifies at atmospheric pressure at about minus 150°F. Chlorine gas forms into a soft ice upon contact with moisture at 49.3°F and at atmospheric pressure. (This is chlorine hydrate, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$.)

In commerce, chlorine is always packaged as a liquefied gas under pressure in steel containers. The liquid is about 1½ times as heavy as water, and the gas is about 2½ times as heavy as air. The liquid vaporizes readily at normal atmospheric temperature and pressure. It has an unmistakable irritating, penetrating, and pungent odor. The properties of chlorine gas and liquid are listed in Tables 1.2 and 1.3, and on Figures A1 through A8.

Some of the properties of chlorine merit comment.

Critical Properties

The *critical temperature*, above which chlorine exists only as a gas, despite the pressure is 291.2°F (144°C). The *critical pressure* is the vapor pressure of liquid chlorine at this critical temperature. The *critical density* is the mass of a unit volume of chlorine at the critical pressure and temperature.

TABLE 1.2. Properties of Chlorine Gas

Symbol: Cl ₂
Atomic weight: 35.457
Atomic number: 17
Isotopes: 33, 34, 35, 36, 37, 38, 39
Density (see Appendix) at 34 °F (1.1 °C) and 1 atm: 0.2006 lb/ft ³
Specific gravity at 32 °F (0 °C) and 1 atm: 2.482 (air = 1)
Liquefying point at 1 atm: -30.1 °F (-34.5 °C)
Viscosity (see Appendix) at 68 °F (20 °C): 0.01325 cP (approximately the same as saturated steam between 1 and 10 atm)
Specific heat at constant pressure of 1 atm and 59 °F (15 °C): 0.115 Btu/lb/°F
Specific heat at constant volume at 1 atm pressure and 59 °F (15 °C): 0.085 Btu/lb/°F
Thermal conductivity at 32 °F (0 °C): 0.0042 Btu/h/ft ² /ft
Heat of reaction with NaOH: 626 Btu/lb Cl ₂ gas
Solubility in water at 68 °F (20 °C) and 1 atm: 7.29 g/l.

Combining quantities:

1-lb chlorine gas combines with

- 1.10-lb commercial hydrated lime (95% Ca(OH)₂)
- 2Ca(OH)₂ + 2Cl₂ = Ca(OCl)₂ + CaCl₂ + 2H₂O 0.83-lb commercial quicklime (95% CaO)
- 2CaO + 2H₂O + 2Cl₂ Ca(OCl)₂ + CaCl₂ + 2H₂O 1.13-lb caustic soda (100% NaOH)
- 2NaOH + Cl₂ = NaOCl + NaCl + 2H₂O 2.99-lb soda ash
- 2Na₂CO₃ + Cl₂ + 2H₂O = NaOCl + NaCl + 2NaHCO₃

TABLE 1.3. Properties of Liquid Chlorine

Critical temperature	144 °C; 291.2 °F
Critical pressure	1118.36 psia
Critical density	573 g/l; 35.77 lb/ft ³
Compressibility	0.0118% per unit vol per atm increase at 68 °F (20 °C)
Density (see Appendix) at 32 °F	91.67 lb/ft ³
Specific gravity at 68 °F	1.41 (water = 1)
Boiling point (liquefaction point) at 1 atm	-34.5 °C; -30.1 °F
Freezing point	-100.98 °C; -149.76 °F
Viscosity (see Appendix) at 68 °F	0.345 cP [approximately 0.35 times water at 68 °F (20 °C)]
1-vol liquid at 32 °F and 1 atm	457.6-vol gas
1-lb liquid at 32 °F and 1 atm	4.98-ft ³ gas
Specific heat	0.226 Btu/lb/°F
Latent heat of vaporization	123.8 Btu/lb at -29.3 °F
Heat of fusion	41.2 Btu/lb at -150.7 °F

Compressibility Coefficient

The compressibility coefficient of liquid chlorine is greater than that of any other liquid element. The compressibility coefficient represents the percentage decrease in volume corresponding to a unit increase in pressure when the liquid is held at constant temperature. This physical characteristic is the reason

why the volume–temperature relationship of chlorine is very important, as described below.

Volume–Temperature Relationship

The volume of liquid chlorine increases rapidly as its temperature rises. Because of this characteristic, coupled with noncompressibility, extreme care must be taken to prevent hydrostatic rupture of containers or pipelines by the expansion of liquid chlorine produced by a rise in temperature. All containers are filled to their prescribed weight of chlorine at 60 °F (15.6 °C) so that 15% of the container volume is vapor space.

The vapor space provided in a container when it is initially filled with liquid chlorine is intended to accommodate a temperature rise sufficient to melt the fusible plugs installed in these containers. A 150-lb cylinder is equipped with one fusible plug. A 1-ton container is equipped with six fusible plugs (three on each end). The metal in these plugs is designed to yield or melt between 158 and 165 °F (70–74 °C), thus relieving pressure in the container and preventing rupture in case of fire or other exposure to high temperature.

Figure A7 illustrates the volume–temperature relationship in a container filled to the authorized limit. From this curve, the container will be “skin-full” when the liquid chlorine temperature reaches 153.64 °F (65.58 °C). At this temperature (see Fig. A6), the vapor pressure is 290 psi. At the lowest melting temperature of the fusible metal plug (158 °F, 70 °C), the vapor pressure would be about 310 psi. This indicates that the criteria for filling a chlorine container does not provide enough volume to match the fusible plug melting temperature of 158–165 °F (70–74 °C). However, an elastic volumetric expansion of the metal in chlorine cylinders and ton containers occurs when the pressure increases. When these containers are hydrostatically tested at 500 psig, it is not uncommon for a 3% volumetric expansion to be observed. This increase in volume would easily permit a temperature higher than 160 °F (71 °C) without fear of rupture. Ton containers have an added expansion factor in the dished heads at both ends of the container. These heads can reverse from the concave configuration installed when containers are manufactured to a convex position before the vessels rupture. This reversal in configuration has been observed several times when ton containers were overpressured by nitrogen trichloride explosions.

Railroad tank cars and stationary chlorine storage tanks used for WTP or wastewater treatment plant (WWTP) services are usually fitted with a spring-loaded CI safety valve combined with a breaking pin assembly that breaks at 225 psig. On cars used in pulp and paper chlorination, the safety valve relieves at 375 psig because the chlorine is air-padded at a higher pressure.

Automatic shutoff valves and protective hoods for manway covers are available to protect operators of tank cars and storage tanks from exposure to chlorine when a leak occurs.

Density of Chlorine Vapor

The density of chlorine vapor varies widely with change in pressure and moderately with change in temperature. This is a most important variable in calculating the pressure drop for gas flow in both vacuum and pressure systems. The relationships of vapor density at various pressures and temperatures are shown on Figures A1 and A2.

Density of Liquid Chlorine

The density of liquid chlorine varies only slightly with temperature. At 40°F (4.4°C) it is 90.85 lb/ft³, and at 140°F (60°C) it is 79.65 lb/ft³ (see Fig. A4).

Viscosity of Chlorine

Viscosity is the measure of internal molecular friction when a substance is in motion. It is necessary to know this property for both liquid and gaseous chlorine because it is a variable in the calculation of the Reynolds number used to measure friction losses in pipelines. The temperature-viscosity relationship for both chlorine liquid and the gas is shown on Figure A3.

Latent Heat of Vaporization

Latent heat is the heat required to change one mass of liquid to vapor without a change in temperature. If the temperature of liquid chlorine is at 70°F (21.1°C), it requires about 100 Btu to vaporize 1 lb of liquid chlorine (see Fig. A5).

Vapor Pressure

Vapor pressure is the pressure of chlorine gas above liquid chlorine when the vapor and the liquid are in equilibrium. This relationship varies widely with temperature (see Fig. A6). It is necessary to know the range of vapor pressure that can occur when liquid chlorine is being transferred from tank cars to vaporizing equipment. Lowering the pressure in the transfer lines below the vapor pressure will produce gas bubbles in the liquid chlorine.

Specific Heat

Specific heat is the amount of heat required to raise the temperature of a unit weight of chlorine vapor by 1°F. At atmospheric pressure and a temperature of 59°F (15°C), the specific heat requirement is 0.085 Btu/lb of chlorine.

Solubility of Chlorine Gas in Water

Chlorine gas has limited solubility in water. At atmospheric pressure and 68°F (20°C), its solubility in water is 7.29 g/l. However, the equipment to produce

the chlorine solutions used in water and wastewater treatment facilities is operated at partial pressure (vacuum). At the vacuum levels used in this equipment, the maximum solubility of chlorine is about 5000 mg/l. The upper limit of solubility recommended by chlorinator manufacturers is 3500 mg/l. This arbitrary value has been used successfully to protect chlorine solution discharge systems from developing gas pockets in the solution piping and off-gassing at the point of application.

Solubility of Liquid Chlorine in Water

The solubility of liquid chlorine in water is a controversial subject. Many people say that as soon as liquid chlorine is discharged into water, it flashes off into vapor, and during this flash-off the water temperature in the immediate vicinity of the chlorine discharge drops to 49 °F (9.4 °C) or lower. At this temperature, the chlorine vapor and the water combine to form a solid hydrate, $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$, known as “chlorine ice.” However, the interesting part of this phenomenon is that this chlorine ice is highly soluble in water.

The solubility of chlorine vapor at various water temperatures and pressures is illustrated on Figure A8, and is discussed further below.

In 1940, the Standard Oil Company in Richmond, California, was using liquid chlorine to treat a cooling water system for its wax plant. The cooling water was seawater obtained from San Francisco Bay at a temperature of 50 °F (10 °C). The chlorine was applied to the suction of a 50,000 gpm pump. The chlorination system consisted of six inverted 150-lb cylinders manifolded to a common control valve in the pipeline leading to the pump suction. The liquid chlorine feed point was about 15 ft below the water surface adjacent to the pump suction. According to Figure A8, the solubility of liquid chlorine under these conditions would be approximately 12 lb of chlorine per 100 gal of cooling water (approximately 14,400 mg/l). Chlorine was applied intermittently at a rate sufficient to produce a 4–5 mg/l residual at the condensers in the wax plant, which were about 5 min downstream from the point of chlorination.

The 5-min chlorine demand of seawater is usually about 1.5 mg/l. Therefore, the chlorine dosage at the pump intake was approximately 6.5 mg/l, which means that the liquid chlorine feed rate was slightly less than 3 lb/min. The chlorine was applied for a total of about 60 min/day.

The remarkable thing about this installation was the absence of any operating problems. There were no incidences of flash-off, off-gassing, or pump corrosion, which proves that under proper conditions liquid chlorine actually is soluble in water.

Many years later, White and Tracy discharged liquid chlorine into the San Francisco Water Department’s Crystal Springs Reservoir to determine the feasibility of using an open reservoir for disposal of a leaking container in case of an emergency. This test consisted of releasing liquid chlorine from a 150-lb cylinder approximately 10 ft below the water surface at a

deep portion of the reservoir, where the water temperature was about 55 °F (12.8 °C).

The results were quite interesting: The liquid that rose from the end of the discharge pipe without flash-off, or any indication of turbulence, had the shape of an inverted ice cream cone. This cone had the color of pale amber. Within not more than about 6 in. from the surface, the water in the reservoir turned a pale green, indicating the formation of chlorine vapor, but there was no indication of chlorine hydrate formation. Some ammonia solution was squirted onto the water surface where off-gassing was considered likely. Surprisingly, only a small white puff of ammonium chloride vapor appeared just above the area where the water turned pale green. A slight chlorine odor was detected within a radius of 10–12 ft from the chlorine cone, but it disappeared quickly after the cylinder was shut down.

It should be noted that regulatory authorities do not recommend disposing of a leaking chlorine cylinder in a body of water. The hole in the container will rapidly increase because of the concentrated hydrochloric acid formed at the water–chlorine interface. The container will also float to the surface of the water after enough chlorine has escaped for it to become buoyant. Chlorine gas will then continue to escape to the atmosphere until the container is completely empty.

A chlorination facility formerly used by the Sanitation Districts of Los Angeles County in Carson, California, was somewhat unique in the water and wastewater treatment industry. The facility was shut down after the events of September 11, 2001 to avoid presenting 90-ton railcars of chlorine as targets for terrorists (S. Krai, pers. comm.). The installation manufactured a 15,000 mg/l calcium hypochlorite solution from liquid chlorine, lime slurry, and plant effluent. Over a period of 16 years, the capacity of this system was increased from 30,000 lb/day to 100,000 lb/day without changing any of the structures housing the equipment. Approximately 90,000 lb/day of liquid chlorine was dissolved into a mixture of lime slurry and 350 gpm of plant effluent using a water pressure at the chlorine injection point of about 30 psi. According to Figure A8, the solubility of liquid chlorine is about 10.5 lb/100 gal of effluent plus the slurry. This is approximately 53,000 lb/day of chlorine. However, the system was capable of using 100,000 lb/day of chlorine without experiencing any problems due to “flashing” or off-gassing at the point of injection.

Chemical Reactions

In the absence of moisture, liquid chlorine will not attack ferrous metals, which makes it possible to store it in steel containers. However, absolutely “dry” liquid chlorine cannot be produced by the commercial processes currently available. The steel containers are therefore provided with extra wall thickness to offset the small amount of corrosion that will occur inside these containers.

Liquid chlorine will attack and very quickly destroy polyvinyl chloride (PVC) and rubber, hard or soft. Dry chlorine gas will not attack copper, ferrous metals, or ferrous alloys. It will support combustion of carbon steel at 483°F (250°C). Above a temperature of 291.2°F (144°C), chlorine exists only as a gas regardless of pressure.

Moist chlorine gas will attack copper and all ferrous metals, including stainless steel and ferrous alloys. Gold, platinum, and tantalum are the only metals that are totally inert to attack by moist chlorine gas. Because of the very high cost of these metals, silver is widely used in instruments that could come into contact with moist chlorine gas. The silver chloride formed on the surface of the silver when it comes into contact with moist chlorine gas is inert to further attack.

Aqueous solutions of chlorine are extremely corrosive. For this reason, PVC, fiberglass, Kynar, polyethylene, certain types of rubber, Saran, Kel-F, Viton, and Teflon are commonly used where exposure to both moist chlorine gas and chlorine solutions are likely.

Chlorine reacts with ethyl alcohol and ether in trace amounts to form solid, waxy hexachloroethane. It also reacts with grease and oils to form a voluminous frothy substance. Solid complex hydrocarbons are formed by the reaction of chlorine and various petroleum distillates. At normal temperatures, there are no reactions between chlorine gas and chloroform, wood alcohol, or carbon tetrachloride.

The chemical reactions of chlorine gas and chlorine solutions in potable water and wastewater treatment are discussed in other chapters.

HAZARDS FROM CHLORINE VAPOR AND LIQUID

Toxic Effects

Liquid chlorine is a skin and eye irritant that can cause severe damage resembling a burn or frostbite. The gas in low concentrations is an irritant to the mucous membranes, the respiratory system, and the eyes. The amount of gas exposure determines the severity of impairment.

There are two types of gassing by chlorine. The type usually referred to in the literature is the damage caused by inhaling dry chlorine gas. The second type, which is the more dangerous of the two, occurs when chlorine fumes are released from an aqueous solution. This occurs when a pipe carrying a concentrated chlorine solution is ruptured in a confined area. If the concentration of the solution exceeds approximately 750ppm of titrable chlorine, gas will be rapidly released. Because these chlorine fumes are laden with moisture, they seem more tolerable to the respiratory tract, and the victim will unwittingly inhale large amounts of molecular chlorine. This can produce pulmonary edema that could cause death by “drowning” during sleep. A victim of moist chlorine inhalation should be immediately placed under the care of a physician.

Gassing from dry chlorine gas is more common and much more disagreeable. The victim will immediately sense a sudden stricture to the upper respiratory tract. This is nature's way of preventing passage of the gas into the lungs. The victim must attempt to get out of the area of the leak by immediately moving upwind, and take only very short breaths through the mouth while they are in the chlorine cloud. Normal breathing will cause coughing, which must be prevented because it draws chlorine further into the lungs. Exposure to dry chlorine gas will also cause irritation of the eyes.

First Aid²⁶⁻²⁸

Prompt action is essential in severe cases of inhalation. The local emergency medical response team or fire department should be contacted immediately. Individuals responding to the crisis should don appropriate self-contained breathing apparatus before entering the area affected by the chlorine leak. The patient should be moved outdoors because the victim's clothing will have absorbed a considerable amount of chlorine. This chlorine will be further inhaled if the victim is moved indoors. If blankets are available, the clothing should be removed and the patient kept warm and quiet. If an emergency shower is available, the patient should be rinsed before being wrapped in blankets. The eyes should be flushed immediately with tepid water for at least 15 min. Artificial respiration should be started immediately if the victim stops breathing or starts to turn blue (cyanosis).

The emergency response team will immediately further decontaminate the victim by flushing the skin and hair with plain water for 3-5 min followed by additional washing with warm water and mild soap and a thorough rinse. Additional flushing will also be provided to the eyes. Moist oxygen or moist air will be administered as required. Cardiac monitoring will be initiated and steps taken to stabilize erratic heart rhythm. Bronchodilators may be administered if the victim is wheezing.

A physician should perform the procedures needed to reduce the formation of pulmonary edema, arrest declining blood pressure, and administer longer-term oxygen therapy.

After recovering from anoxemia or pulmonary edema, a severely gassed victim must be closely nursed for an extended period of time to prevent the development of pneumonia.

In treatment of mild cases of gassing, the first step is to leave the area of the fumes, breathe lightly, move slowly without exertion, remain quiet, keep warm, and resist the impulse to cough.

The victim will be at first seized with fear and may become panicky because they feel symptoms of suffocation. Assuring the victim these symptoms will subside with the passage of time can allay the fears. Sedatives should be given only under the supervision of qualified medical personnel.

For most patients, there are no residual symptoms attributable to severe gassing by chlorine. However, some anxiety reactions may linger for months. Victims with a history of asthma have had lingering effects of distress. Exposure

to chlorine can also lead to reactive airways dysfunction syndrome (RADS), a chemical irritant-induced type of asthma.

Physiological Response

The USEPA Technology Transfer Network Air Toxics Web Site describes the following physiological responses to various concentrations of chlorine gas (see Table 1.4).

Death occurs very rapidly for most animals when the chlorine concentration in the air approaches 1000 ppm.

The data summarized in Table 1.4 indicate that physiological responses start to occur at very low chlorine concentrations. These levels are much lower than the concentrations cited in material safety data sheets (MSDS) to produce the same physiological reactions. The reason for this apparent discrepancy is the target audience for this information. The information in Table 1.4 applies to the general population, which includes children and the elderly. The MSDS prepared by chlorine manufactures, packagers, and users are for the use of healthy adults who chose to work in industries that use this chemical. Individuals continuously exposed to low levels of airborne chlorine gradually lose their sensitivity to it and usually do not start to experience stress until the concentration approaches 1 ppm. Everyone exposed to more than 30 ppm of chlorine will be adversely affected.

Intentional Release

Unfortunately, in recent years, the intentional release of chlorine gas to cause physical harm and damage has become a distinct possibility. Chlorine cylinders have been used in terror attacks in Iraq, and attempts, some successful,

TABLE 1.4. Concentrations of Chlorine Gas Required to Produce Physiological Responses²⁹

Effect	Parts of Chlorine per Million Parts of Air by Volume
Tickling of the nose	0.014–0.054
Tickling of the throat	0.04–0.097
Itching of the nose and cough, stinging, or dryness of the nose and throat	0.06–0.3
Burning of the eyes and pain after 15 min	0.35–0.72
Discomfort ranging from eye and respiratory irritation, coughing, shortness of breath, and headaches	Above 1.0
Chest pain, vomiting, labored breathing, and coughing	30
Toxic pneumonitis and pulmonary edema	40–60

have been made to obtain chlorine cylinders from packagers and water treatment facilities in the United States. Utilities need to become proactive in monitoring their in-plant supplies of chemicals and securing them to the maximum extent possible.

Concern over theft of chlorine containers, coupled with the hazards of transporting chlorine through populated areas in railcars, has led the U.S. Congress along with the Department of Homeland Security to evaluate the feasibility of discontinuing the use of chlorine gas for disinfecting drinking water and wastewater. Congress enacted a temporary chemical security legislation in October 2006. This law required the Department of Homeland Security to promulgate chemical plant security regulations by April 4, 2007. However, it exempted WTPs and WWTPs from these rules and did not address security concerns associated with the transportation of hazardous gases. Additional congressional hearings were conducted on chemical security during 2007 and more legislation is pending. The preliminary drafts of the bills being considered do not exempt WTPs and WWTPs from the new regulations. Final action on this legislation will probably be delayed until after the 2008 presidential election.

A secondary disinfectant must be carried throughout potable water distribution systems, and chlorine will be required to provide this secondary residual either as free chlorine or chloramine. If the use of chlorine gas is discontinued in WTPs, either the purchase of bleach from chlorine vendors or the installation of on-site chlorine generation facilities will be required.

Discontinuing the use of chlorine gas at WWTPs will require conversion to liquid bleach or installation of the alternative wastewater disinfection technologies discussed elsewhere in this book.

CHLORINE LEAKS

Definitions

Chlorine leaks, usually referred to as emissions or releases, are simply discharges of chlorine liquid or vapor (gas) into the atmosphere. Leaks are characterized as minor, major, or catastrophic.

Minor leaks usually occur at the start-up of a new installation or immediately after completion of maintenance or inspection procedures in an operating facility. These leaks usually are the result of gasket failures, valve packing that needs to be adjusted, or equipment malfunction.

Major leaks include “guillotine breaks” in a pipeline under pressure, broken flexible connections, fusible plug failures, and/or leaks produced by accidents associated with repair work done while a system is under chlorine supply pressure. Major leaks can also occur when the temperature of chlorine reaches 483°F (250°C) and spontaneous combustion takes place between chlorine and steel.

A catastrophic leak at a WTP or WWTP is a “one-in-a-million event” produced by rupturing a chlorine container or “blowout” of a fusible plug.

In potable water and wastewater chlorination systems that meter chlorine under a vacuum of 18–20 in. of mercury, the leaks are usually minor.

Fire and Building Codes

In the United States, there are three major organizations that produce model fire codes. The International Fire Code Institute (IFCI), with headquarters in Austin, Texas, publishes the Uniform Fire Code (UFC), which is used predominantly in the western United States. The Building Officials and Code Administrators, International (BOCA), headquartered in Country Club Hills, Illinois, publishes a code used in the Midwest and in the northeastern United States. The Southern Building Code Congress International in Birmingham, Alabama, publishes the Standard Fire Prevention Code (SFPC), or Standard Building Code. This code covers the south-central and southeastern states. An additional organization, the National Fire Protection Association (NFPA) in Quincy, Massachusetts, does not produce a model code, but it does develop and publish numerous standards and technical documents. NFPA materials cover a number of subjects related to fire and building code issues, including hazardous materials and emergency response. NFPA standards are frequently referenced as code documents by governmental groups. In addition, the Uniform Building Code (UBC), published by the International Conference of Building Officials in Whittier, California, contains provisions that impact facilities that use chlorine.

These codes contain requirements establishing minimum distances between classes of chemicals, secondary containment systems, design of piping systems, need for gas detectors, installation of fire sprinkling systems, and requirements for emergency response teams.

These model codes are modified annually. Completely new editions of the codes are published every three years. To properly address these codes in the design, construction, and operation of facilities using chlorine, the local government should be contacted to determine which specific codes have been adopted and the applicable year for each code.

The requirements of these codes are discussed in more detail in Chapter 8.

Characteristics of a Major Liquid Chlorine Release

Brian Shera's Bucket. The following demonstration of a catastrophic chlorine leak was conducted by Brian Shera of Pennwalt Corporation.

All observers were wearing an air pack breathing apparatus and were positioned upwind from the test site. The ambient temperature was about 60°F (15°C). Shera dug a hole about 6 in. in diameter and 10–12 in. deep in an open area of sandy soil using a posthole digger. Next, he withdrew liquid chlorine from an adjacent storage system into a bucket, walked a few steps, and poured

it into the hole. There had been an immediate flash-off of chlorine vapor when the bucket was being filled, so Shera calculated that the amount poured into the hole was close to 28 lb. There was a thin film of ice at the surface of the bucket after the flash-off and immediately before chlorine was poured into the hole. When he poured the chlorine into the hole, there was another brief flash-off, followed by another coating of the ice film. If 25% of the chlorine flashed off when it was poured into the hole (7 lb), then approximately 20 lb still remained to be vaporized by the ambient air, whose temperature was about 65°F (18°C). The exposed area of the hole was about 0.2 ft². The observers continued to watch the intermittent flash-off phenomenon for over an hour, and when they left, there was a substantial amount of liquid chlorine remaining in the hole.

The most significant characteristics of a major leak demonstrated by this performance were the long drawn-out vaporization cycle and the rapidity of the freezing cycle. It also verified that the flash-off phenomenon would occur only when chlorine liquid is spilled into the atmosphere. In other words, a chlorine container of any kind cannot undergo flash-off unless a rupture occurs that exposes the liquid surface to the atmosphere—such as a dished head being blown off. However, the liquid that spills will flash off, and the remainder will vaporize at a rate of approximately 7 lb/h/ft² of the liquid chlorine.

CALCULATING CHLORINE LEAK RATES

Liquid Release

$$Q = 77A\sqrt{(P_1 - P_2)(p)} = \text{lb/s}, \quad (1.21)$$

where

A = area of opening to atmosphere (ft²);

P_1 = upstream pressure (psi);

P_2 = downstream pressure (psi); and

p = density of liquid chlorine upstream from the opening to atmosphere (lb/ft³).

Vapor Release

$$Q = 36.64A\sqrt{P/V} = \text{lb/s}, \quad (1.22)$$

where

A = area of opening to the atmosphere (ft²);

P = upstream pressure (psi);

V = 1/density of chlorine vapor at opening (lb/ft³).

Tanker Truck Leak during Unloading

The following is a method for estimating the leak rate from a road tanker while transferring its contents to the consumer's storage tank. The cause of the leak is assumed to be a separation of the loading lines.

The usual capacity of a tanker is 17 tons. It can empty its contents in 2.75 h with a 30 psi pressure differential. Therefore, this flow rate is $34,000 \text{ lb}/165 \text{ min} = 206 \text{ lb/min} = 3.43 \text{ lb/s}$. Then, using the equation $Q = 77A\sqrt{(P_1 - P_2) \times p}$ and substituting 3.43 lb/s for Q and 30 psi for $P_1 - P_2$ and 88 lb/ft^3 for p , A is calculated as follows:

$$3.43 = 77A\sqrt{(30 \times 88)}$$

$$A = 3.43/77(51.38) = 0.00087$$

Use $77A = 0.0667$ for convenience.

The tanker truck leak rate can be calculated for any differential pressure. The value of P_1 would be based upon the pressure in the road tanker at the time of the leak. Assuming that the tanker pressure is 90 psi, the leak rate would be

$$Q = 0.0667\sqrt{(90 \times 88)}$$

$$Q = 0.0667 \times 88.99 = 5.94 \text{ lb/s}$$

$$Q = 356.44 \text{ lb/min.}$$

This is the worst-case scenario because the excess flow check valves would not only limit this flow rate but would more than likely stop the spill entirely, as has been the case in many railcar accidents when the valves on the dome of a derailed car are completely destroyed. The road tankers are fitted with $14,000 \text{ lb/h}$ (233 lb/min) excess flow valves (EFVs) in order to shorten the transfer time.

Guillotine Break in a Pipeline: Ton Container Supply

If the installation involves liquid withdrawal from ton containers, then evaporators will be an integral part of the chlorine supply system. Therefore, the worst-case scenario would be a rupture in the liquid header between the containers and the evaporators. To simplify the concept, the calculations should be confined to one container, one evaporator, and 100 ft of 1-in. header pipe.

The liquid discharged from the container must pass through a $\frac{3}{8}$ -in.-diameter tubing in the dished head, then through the container shutoff valve,

then through the auxiliary shutoff valve, and finally through the header valve. All these components are flow restrictors compared with a 1-in. pipe. It is important that these restrictions be accounted for in calculating the chlorine leakage rate.

Circa 1950, operating personnel needed to know the maximum possible liquid withdrawal rate from a single ton container at the East Bay Municipal Utility District WWTP in Oakland, California. The chlorinator capacity was 18,000 lb/day. The test, which was performed several times, indicated that the maximum liquid chlorine flow rate into this chlorinator was only about 10,200 lb/day. The pressure drop between the ton container and the pipe entering the chlorinator ranged from 85 to 40 psi and averaged about 45 psi because there was a pressure-reducing valve between the evaporator and the chlorinator. The flow at this pressure drop has to be recalculated to reflect zero pressure at the leak. To apply a worst-case situation, let us assume a container pressure of 120 psi.

Using the liquid release formula,

$$Q = 77A\sqrt{[(P_1 - P_2) \times p]} = \text{lb/s}, \quad (1.21)$$

where

$$Q = 10,200 \text{ lb/day} = 0.1181 \text{ lb/s}$$

$$p = 88 \text{ lb/ft}^3.$$

Substituting in the above formula, the value of the unknown, $77A$, can be found:

$$Q = 77A\sqrt{(45 \times 88)}$$

$$Q = 0.1181 \text{ lb/s}$$

$$0.1181 = 77A \times 62.93$$

$$77A = 0.1181/62.93 = 0.00188.$$

Assuming a container pressure of 120 psi, chlorine density at 88 lb/ft³, and substituting $77A = 0.00188$ in Equation (1.21), the liquid leak rate Q will be

$$Q = 0.00188\sqrt{(120 \times 88)}$$

$$Q = 0.1899 \text{ lb/s} \times 60 = 11.4 \text{ lb/min}.$$

This then is the worst-case leak rate from a single ton container “on line” when there is a guillotine break in the liquid chlorine header piping. When ton containers are being used for liquid withdrawal, an evaporator is also part

of the system, so when there is a guillotine break in the liquid header, the contents of the evaporator become part of the leak.

All chlorine evaporators are designed to vaporize chlorine at a temperature between 160 and 180°F (71 and 82°C), regardless of the feed rate. This means that the level of liquid chlorine in the evaporator remains fairly constant. It is safe to assume that the evaporator content is never more than 100lb. At 20lb/min, the evaporator will empty in about 5 min because of the chlorine header rupture. Therefore, the probable maximum chlorine release rate in the chlorinator room for each container “on line” and each evaporator will be 11.4 + 20lb/min for the first 5 min and then 11.4lb/min after that interval. If the guillotine break occurs in the container storage room, the probable maximum release rate in this room will be 11.4lb/min. Leak rates of this magnitude will rapidly reduce the air temperature in the chlorine room, or the chlorine storage room, and reduce the rate of chlorine vaporization.

A Major Leak from PVC Header Failure

When a small WWTP in Alaska was being upgraded, the chief operator requested the plumbing contractor to replace the rusty steel chlorine header piping between the cylinder room and the chlorinator room with PVC piping to eliminate the rusting “problem.” This was done without anyone questioning this change.

When PVC piping is used to convey pressurized chlorine gas, the pressure must not exceed 2–3psi. If the pressure is increased above these limits, the PVC reacts with the chlorine. This reaction produces heat, and at about 150°F (65°C) the PVC begins to melt. This happened at the plant in Alaska. The plant operator was on duty from 7:30 a.m. to 4:00 p.m. on the day before the leak. On the following day, the fire department received a 911 call about a strong chlorine odor, and a large cloud was reported above the WWTP. The fire department called the plant operator, who arrived with an assistant and turned off the gas flow from the chlorine cylinder. The room temperature at the time was estimated to be about 100°F (37.7°C). The leak lasted about 2½h. Because there were no gauges and no scales in the cylinder room, the total quantity of chlorine leaked from the cylinder could not be determined.

One of the most interesting aspects of this leak was the formation and travel of the plume of chlorine vapor. Immediately after the cylinder was shut down, the firefighters opened two large doors, allowing 2200 cu ft of 100°F (37.7°C) air containing the chlorine to form a plume in the atmosphere, which was at 5°F (–15°C) and 90% humidity. The total amount of chlorine in this plume was estimated to be about 500lb.

Because of the weather conditions and the extreme heat of the chlorine-laden air discharged from the cylinder room, the plume rose quickly, affecting only the residents within 600–700 ft from the plant. This illustrates the importance of heat at the site of a leak. In this case, the chlorine plume rose quickly

(chimney effect) and drifted away from the site without causing significant damage at ground level.

Ton Container Flexible Connection Failure

Severing the flexible connection tubing at the auxiliary container valve is a worst-case chlorine leak from a ton container. Without the flow restrictions produced by the header valve and 4 ft of $\frac{3}{8}$ -in.-diameter flexible connector, the rate of chlorine release will exceed the rate from the typical rupture of a header pipe. Based on the calculations discussed earlier in this chapter, at 120 psi pressure in the container, a reasonable estimate would be a 20% increase in flow: $(11.4 \times 0.2 = 2.28) + 11.4 = 13.68 \text{ lb/min}$.

Fusible Plug Failure from Corrosion

Corrosion is the most common cause of fusible plug failure. A $\frac{3}{4}$ -in. plug consists of a $\frac{3}{16}$ -in.-diameter lead core in a brass body. The small quantity of moisture contained in “dry” chlorine begins an immediate attack on the vulnerable brass body, eventually producing a cone-shaped hole with its base on the inside of the cylinder. The end result of this corrosive attack is a pinpoint hole between the brass body and the threaded steel of the dished cylinder head. Routine replacement of all fusible plugs is the best way to prevent leaks from occurring through these holes. Packagers should install new plugs at 5-year intervals to minimize this hazard.

When leaks do occur, field observations by White indicate that the diameter of the hole in the fusible plug is never larger than 0.1 in. before the problem is discovered.

Liquid Release. To assume a worst-case situation, the hole diameter is assumed to be 0.15 in., with the fusible plug located below the liquid level in the ton container. The pressure inside the container is assumed to be 120 psi. Therefore,

$$Q = 77 A \sqrt{(120 - 0) \times p} = \text{lb/s}, p = 81 \text{ lb/ft}^3$$

$$A = \pi D^2 / 4 = \pi (0.15)^2 / 4 = 0.018 \text{ in}^2$$

$$A = 0.000125 \text{ ft}^2$$

$$Q = 77 \times 0.000125 \sqrt{(120 \times 81)} = \text{lb/s}$$

$$Q = 0.949 \text{ lb/s} = 56.94 \text{ lb/min.}$$

Vapor Release. This is an important comparison because there is a huge difference in the chlorine release rate. When a fusible plug fails as a result of corrosion, the safety crew should attempt to rotate the container to move the leaking plug into the area filled with chlorine vapor. If this is done, the escaping vapor will cool the liquid chlorine to 40°F (4.4°C) in 3–4 min. This drop

in temperature should be taken into account when using the vapor release formula:

$$Q = 36.64 A \sqrt{(P/V)} = \text{lb/s.} \quad (1.22)$$

The pressure of the chlorine gas in the container is reduced enormously because the escaping gas is at zero gauge pressure. Under these conditions, pressure in the container will be as low as 40 psi. The density of chlorine vapor at 40°F (4.4°C) is 0.77 lb/ft³. Therefore,

$$\begin{aligned} V &= 1/0.77 = 1.3 \text{ ft}^3/\text{lb} \\ Q &= 36.64 \times 0.000125 \sqrt{(40/1.3)} = 0.0254 \text{ lb/s} \\ Q &= 1.52 \text{ lb/min.} \end{aligned}$$

Fusible Plug Blowout. Fusible plug blowouts rarely occur, but it is frequently used as an example of a catastrophic failure that would be almost equivalent to completely rupturing the walls of a container. If a blowout were to occur, the worst-case situation would be for the total discharge to consist of liquid chlorine. There would be no “flash-off” unless ambient air reached the inside surface of the liquid chlorine in the container. Assuming pressure in the container pressure drops to 30 psi, which would be equivalent to a liquid temperature of 20°F (−6.7°C), the density of the liquid chlorine would be 93 lb/ft³.

The leak rate is calculated as follows:

$$\begin{aligned} Q &= 77 A \sqrt{(P_1 - P_2)} p = \text{lb/s} \\ p &= \text{Density at } 20^\circ\text{F} = 93 \text{ lb/ft}^3 \\ A &= [\pi \times (0.75 \text{ in.})^2] / 4 = 0.44 \text{ in.}^2 = 0.003 \text{ ft}^2 \\ Q &= 77 \times 0.003 \sqrt{[(30 - 0) \times 93]} = 12.2 \text{ lb/s} \\ Q &= 732.09 \text{ lb/min.} \end{aligned} \quad (1.21)$$

Obviously, this calculation is based on an incorrect assumption. The contents of the container could never be discharged at that rate; otherwise, the container would be empty in less than 30 min. The scenario that is closer to what would actually happen is as follows. The rapid drop in pressure inside the container would produce sudden cooling of the liquid chlorine. This cooling would lower the pressure inside the container to atmospheric pressure. Then the liquid chlorine would go into a freeze-and-thaw cycle that would cause the escape of chlorine to extend over several hours (as described in the section “Brian Shera’s Bucket”). A fusible plug blowout is considered a one-in-a-million occurrence.

SUMMARY

1. Whenever there is a major leak, the flash-off phenomenon will always prevent positive pressure from developing in a containment structure. The sudden vaporization caused by the flash-off cools the atmosphere in the enclosed space so fast that a negative pressure develops.
2. There will always be a significant amount of liquid chlorine that must be dealt with as soon as possible. Because liquid chlorine is much more soluble in water than chlorine vapor, it can be removed using a water-operated eductor or by pumping.
3. The only way liquid chlorine can be cooled by a leak is to withdraw vapor from it. Liquid flowing out of a container as a result of a major leak will not cool the cylinder or reduce the vapor pressure unless the source of the leak is a large hole in the container such as caused by a fusible plug blowout. When this type of leak occurs, the flash-off phenomenon begins as soon as the liquid chlorine is exposed to the room atmosphere, which will cool the room so quickly that it will usually produce negative atmospheric pressure in the room.
4. High temperatures inside chlorine storage or feeding rooms occasionally cause major chlorine leaks. If the temperature of the chlorine-laden air trapped inside these rooms is much higher than the temperature of the outside air, the plumes of chlorine vapor produced in this type of accident will move upward in the atmosphere and cause little ground-level damage. However, only trained professionals should authorize the intentional release of chlorine vapor into the environment.

USEPA RISK MANAGEMENT PROGRAMS (RMPs)

The USEPA regulates the release of hazardous chemicals into the atmosphere under the authority granted to it by the Clean Air Act. A large number of toxic chemicals are included in these regulations. However, this discussion will focus on the accidental release of chlorine, anhydrous ammonia, and aqueous ammonia.^{30,31}

The quantities of chemicals stored on-site determine whether a facility is required to develop and implement an RMP. The thresholds for chlorine, anhydrous ammonia, and aqueous ammonia are listed in Table 1.5.

The aqueous ammonia threshold in Table 1.5 is based on the weight of ammonia in solution and is applicable only when the concentration of the ammonia solution is 20% or higher.

A few states have adopted RMPs with lower chemical thresholds and more stringent rules than the USEPA RMP requirements. Organizations that develop an RMP should consult their state's current regulations before following the USEPA rules.

**TABLE 1.5. USEPA RMP Chemical Thresholds
Applicable to Water and Wastewater Treatment Plants**

Chemical	EPA RMP Threshold (lb)
Chlorine	2,500
Anhydrous ammonia	10,000
Aqueous ammonia	20,000

The USEPA thresholds are based on the quantities of chemicals stored at a specific location. For example, when a maximum of 16 150-lb chlorine cylinders are stored in one building and additional 150-lb chlorine cylinders are in use in other buildings, all of these buildings can be considered separate processes if they are located far enough apart, so an accident (e.g., a fire or an explosion) in the chlorine storage building would not affect the cylinders in the other buildings.

Treatment plants using 1-ton containers, bulk storage tanks, or railroad tank cars will exceed the USEPA threshold for chlorine and are required to implement an RMP. Chlorine manufacturers and packagers are also required to comply with this program.

The scope of the RMP required for a specific facility depends on the magnitude of risk associated with that facility. The USEPA has established three programs that must be met as the level of risk to the public or the environment increases. A decision tree for determining which program level is applicable to a specific facility is shown on Figure 1.5. Facilities are regulated under Standard Industrial Classification (SIC) codes. WTPs are classified under SIC 4941, and WWTPs are classified under SIC 4933. Neither of these types of plants is automatically required to meet the requirements of program 3. Chlor-alkali plants are subject to SIC 2812 and are required to comply with program 3.

The requirements of the three RMPs are summarized in Table 1.6. Prevention program 2 elements that were given different names by the USEPA from similar program 3 elements are listed in square brackets in this table.

The objectives of the management systems required in programs 2 and 3 are to identify the individual responsible for the development and implementation of the program and to establish formal procedures for the delegation of specific program responsibilities to other individuals in the organization. An organization chart defining the lines of authority between these individuals must be part of the management system.

A hazards assessment is required for all three programs; however, the assessment required under program 1 is not as extensive as those required under programs 2 and 3. All three programs require compilation of a 5-year accident history for the facility, which must include all incidents from RMP-related processes that resulted in on-site or off-site death or injury, evacuation from the site, sheltering in place, property damage, or environmental damage. In addition, the assessments for all three programs must include a worst-case

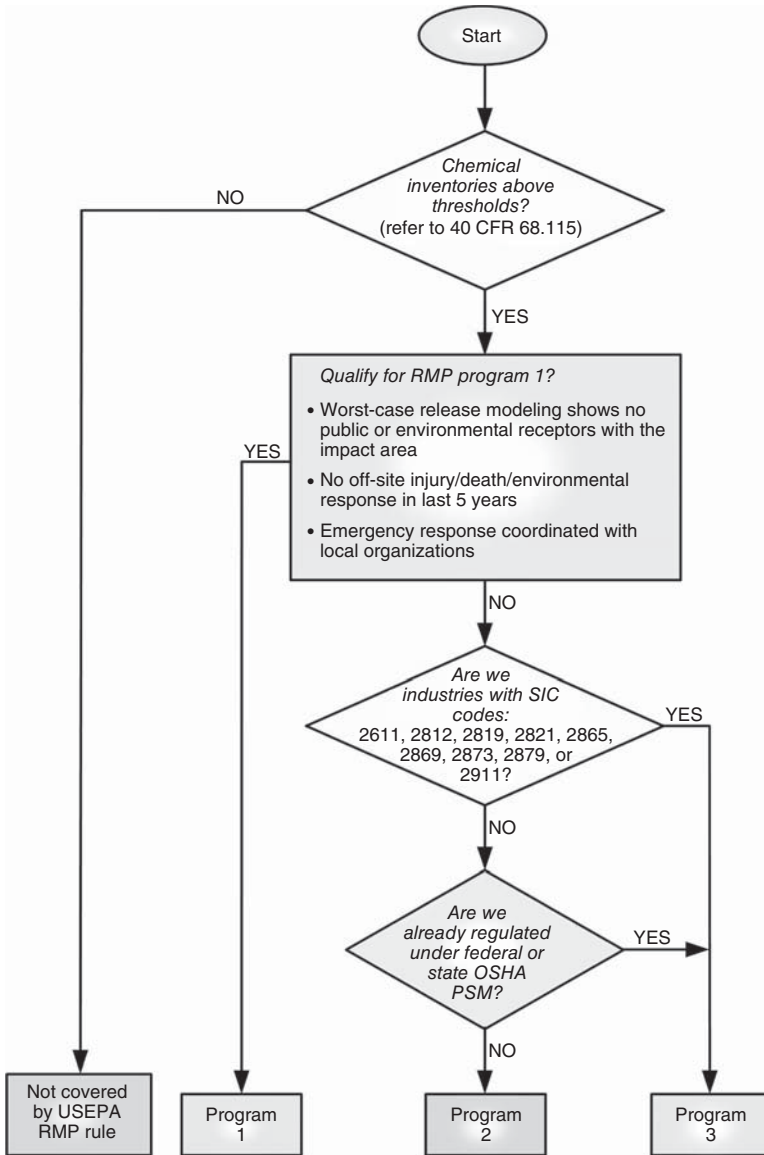


Figure 1.5. Decision tree for risk management programs (RMPs).

analysis to estimate the potential off-site area affected by the release of chlorine or ammonia. Programs 2 and 3 must also consider the impacts produced by an alternative release of these gases. A more detailed discussion of worst-case and alternative releases is included later in this chapter.

The topics that must be addressed in the accident prevention programs required by the USEPA RMP are identified in Table 1.6. Specific details

TABLE 1.6. USEPA Risk Management Programs 1, 2, and 3 Requirements*

RMP Element	Program 1	Program 2	Program 3
Management system	—	x	x
Hazard assessment			
Worst-case analysis	x	x	x
Alternative release analysis	—	x	x
5-year accident history	x	x	x
Prevention program			
Process safety information [Safety information]	—	x	x
Process hazard analysis [Hazard review]	—	x	x
Operating procedures	—	x	x
Training	—	x	x
Mechanical integrity [Maintenance]	—	x	x
Management of change	—	—	x
Pre-start-up review	—	—	x
Compliance audits	—	x	x
Incident investigation	—	x	x
Employee participation plan	—	—	x
Hot work permit	—	—	x
Contractors	—	—	x
Emergency response program	—	x	x

* x indicates the element is included as one of the program requirements.

about each of these topics are provided in the Federal Register (40 CFR Part 68) dated June 20, 1996. Documents and manuals developed by the USEPA and others to assist in completing a comprehensive RMP can be obtained by contacting the National Service Center for Environmental Publications* (phone: 1-800-490-9198), the AWWA,[†] the Water Environment Federation (WEF),[‡] or the USEPA's Risk Management Hotline (phone: 1-800-824-9346).

The USEPA RMP requires the development and implementation of an emergency response program that shall include the following elements:

- procedures for informing the public and local emergency response agencies about accidental releases;
- documentation of proper first-aid and emergency medical procedures necessary to treat accidental human exposures;
- procedures for emergency response after an accidental release;

*National Service Center for Environmental Publications, PO Box 42419, Cincinnati, OH 45242-0419.

[†]AWWA, 6666 W. Quincy Ave., Denver, CO 80235.

[‡]Water Environment Federation, 601 Wythe St., Alexandria, VA 22314-1994.

- procedures for inspection, testing, and maintenance of emergency response equipment;
- training for all employees in relevant procedures; and
- procedures to regularly review and update this program and to ensure that employees and local emergency response agencies are informed of any changes.

Prevention program 2 elements that were given names different from similar program 3 elements are listed in square brackets. Requirements for prevention program 2 elements may differ from prevention program 3 requirements, even when the name of the program element is the same. The reader should consult the American Water Works Association Research Foundation (AwwaRF) and WEF manuals for details about these elements.

The implementation date for the USEPA RMP was June 21, 1999. Plans for individual facilities are reviewed and updated at 5-year intervals.

OSHA Process Safety Management (PSM) Regulations

The OSHA PSM rules are codified in the Federal Register (29 CFR 1910.119) and have been in effect since 1992. These rules require comprehensive management systems for handling highly hazardous chemicals by industry- and privately operated WTPs and WWTPs. Government-operated WTPs and WWTPs are also bound by PSM rules in OSHA plan states, which have their own state rules and enforcement programs approved by the federal OSHA. Organizations contemplating the development of a PSM plan should check with the state where their facility is located to determine which rules apply.

The threshold quantities of hazardous chemicals that trigger the development of an OSHA PSM plan are different from the thresholds established by the USEPA's RMP. The OSHA thresholds for chemicals used in WTPs and WWTPs are listed in Table 1.7.

The aqueous ammonia PSM threshold shown in Table 1.7 is based on the total weight of the solution and is only applicable when the ammonia concentration is higher than 44%.

The OSHA PSM program does not include the Management System and the Hazard Assessment elements required in the USEPA RMP. However, the Prevention Program and the Emergency Response Program elements are

**TABLE 1.7. OSHA PSM Chemical Thresholds
Applicable to Water and Wastewater Treatment Plants**

Chemical	OSHA PSM Threshold (lb)
Chlorine	1,500
Ammonia (anhydrous)	10,000
Aqueous ammonia	15,000

essentially identical in both. This commonality is by design. The USEPA did not want to require facilities that were already included in the OSHA PSM to develop new safety programs. Eliminating the confusion associated with complying with two programs also makes it possible for OSHA inspectors to conduct site inspections, so that the USEPA does not have to employ personnel to perform this function.

The net effect of the USEPA and OSHA rules is that all public- and privately owned facilities producing, handling, or using significant quantities of hazardous chemicals are required to conduct proactive safety programs for the personnel employed in these facilities. The USEPA RMP expands the scope of this responsibility by requiring these facilities to also evaluate the potential impacts produced by the release of hazardous gases into the environment outside the boundaries of these facilities.

Worst-Case and Alternative Release Analyses

The most controversial requirement of the USEPA RMP is preparation of a worst-case analysis for off-site release of hazardous gases and conveying this information to the general public. Most of this controversy stems from the USEPA definition of "worst case." For chlorine and ammonia, this is the release, as a gas, of all of the contents of the largest vessel on-site over a 10-min period. A very large area is impacted by a worst-case release. This could have a significant effect on public perception and emergency planning. The USEPA recognizes that a worst-case scenario may be highly improbable, that it may require active communication efforts to explain it to the public, and that it may not be the most appropriate basis for emergency planning. Careful selection of more credible alternative release scenarios that provide a better basis for emergency planning is very important.

The alternative release scenarios selected for analysis should be more likely to occur than the worst case, and must reach an end point off-site. They may be based on the accident history for the facility or on accidents known to have occurred at similar facilities. While not explicitly stated in the regulation, the intent is to select credible scenarios that would serve as realistic bases for developing on-site and off-site emergency response plans.

The procedure used to estimate the area affected by worst-case and alternative release scenarios is straightforward:

- determine the quantities of gas released and the time intervals over which these releases will occur;
- select a mathematical model to calculate the maximum distances at which toxic concentrations of gas are expected to occur;
- obtain a detailed map of the area surrounding the source(s) of the potential release(s);
- draw circles on this map showing the maximum distances at which potentially hazardous concentrations of gas are predicted to occur;

the location where the gas will be released is the centerpoint of these circles;

- determine the estimated population and the protected environmental receptors located inside these circles; and
- present this information to the USEPA by submitting one copy of the USEPA developed RMP Submittal Data Elements form for each release scenario.

The USEPA recommends that dispersion modeling to support RMP plans be done using the “RMP*Comp” model available on the USEPA Emergency Management Web site.³² This model is free, and the USEPA updates it. However, it is a planning model. Its only output is an estimate of the distance required to dilute the concentration of a hazardous gas to nontoxic levels.

More sophisticated models can be used to prepare RMP plans if an applicant desires to do so. However, much more documentation is required when this course is chosen. The USEPA recommends the use of more sophisticated models to track the plume produced when an accident actually occurs. A number of very good commercial models, and modeling firms, are available to perform this function.

The end point concentrations for hazardous gas plumes in 2007 were 3 ppm for chlorine and 150 ppm for ammonia. These are ERPG-2 values, set by the American Industrial Hygiene Association (AIHA) and revised when warranted by additional data. ERPG-2 is the maximum airborne concentration, below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects that could impair their ability to take protective action.

Maps suitable for RMP planning can be obtained from the U.S. Geological Survey (USGS). Population estimates can be obtained from the U.S. Census Bureau or from electronic databases such as LANDVIEW III. This is a public domain computer model that can be accessed from the Right-to-Know (RTK) Network at <http://www.rtk.net>.

CHLORINE TRANSPORT ACCIDENTS

Railroad Transportation

Railroads handle more than 1.7 million shipments of hazardous materials annually. These shipments consist of millions of tons of explosive, poisonous, corrosive, flammable, and radioactive materials. Rail transportation is a safe method for moving large quantities of hazardous materials. In 2004, there were only 29 accidents that involved the release of a hazardous material. In these accidents, a total of 47 hazardous materials cars released some amount of product (the capacity of a tank car is 34,500 gal). The Department of

Transportation (DOT) Hazardous Materials Information System's 10-year incident data for 1997 through 2007 identify a total of 17 fatalities resulting from hazardous material incidents occurring at railroad facilities.

On June 28, 2004, two trains collided in Macdona, Texas, breaching a loaded tank car containing chlorine. This car instantaneously released approximately 9400 gal of chlorine that formed a toxic vapor plume that engulfed the accident site to a radius of at least 700 ft before drifting away from the site. Four locomotives and 36 cars belonging to the two trains were derailed. This accident killed three people and seriously injured 30 others. The National Transportation Safety Board (NTSB) determined that the probable cause of the accident was train crew fatigue that resulted in the failure of the engineer and the conductor on one of the trains to appropriately respond to wayside signals governing the movement of their train. Damages to rolling stock, track, and signal equipment were estimated to be \$6.3 million. As of July 20, 2006, \$150,000 had been spent to clean up the environmental consequences. Other significant costs, including evacuation of the accident site, rerouting, and associated out-of-service expenses to the railroad, disruption to nonrailroad businesses, and settlement of damage claims arising from the accident had not yet been resolved by early 2008.³³

On January 6, 2005, a freight train was improperly switched from a main line track onto an industry line track in Graniteville, South Carolina. This train struck an unoccupied parked train located on a rail spur leading to a textile manufacturing facility. The collision resulted in the derailment of three locomotives and 17 cars belonging to the two trains. One tank car was punctured in the shell by the coupler of another car and instantaneously released approximately 9220 gal of chlorine, creating a toxic vapor plume that engulfed the surrounding area. Approximately 5400 people located within a 1-mile radius of the derailment site were evacuated for several days. Nine persons were fatally injured and 554 sustained other injuries (75 requiring hospitalization). The NTSB concluded that the probable cause of the accident was the failure of a train crew to return a main line switch to its normal position after this crew had completed work on the industrial track owned by Avondale Mills. Property damage to the rolling stock and track owned by the railroad exceeded \$9.6 million. The railroad also reported spending \$41 million in 2005 for expenses related to the accident. The total direct costs of the accident were estimated to be approximately \$138 million, excluding chlorine cleanup costs. This estimate probably greatly underestimates the actual costs incurred by those affected by the accident. For example, according to the South Carolina Emergency Center and the USEPA Situation Reports, schools were closed for several days and mail service for the evacuated areas had to be forwarded to a neighboring post office. Preliminary estimates of costs to Aiken County, South Carolina, were in the millions of dollars as a result of potential damage to electrical systems and equipment in homes and businesses, cost of the first response and recovery operations, damage to fire and emergency response vehicles, and the treatment of the victims.

The fate of the textile manufacturing company, Avondale Mills, illustrates the significant long-term economic impacts of catastrophic hazardous materials transportation accidents. In May 2006, the company reached a \$215 million settlement with its primary property and casualty insurer for all claims related to the derailment. However, this was not enough to make the company whole. In July 2006, after spending \$140 million in unsuccessful efforts to clean and repair the facilities damaged by chlorine, the company declared it would be unable to recover financially from this accident and the subsequent disruption to its business plan. It was forced to close its 10 mills in South Carolina and Georgia and to lay off approximately 4000 employees.

A federal judge approved a class action settlement in excess of \$10.5 million between the railroad and almost 500 individuals who claimed to have suffered serious injuries after the derailment. In May 2005, a settlement was reached between the railroad and Graniteville residents and businesses who were evacuated but did not seek medical attention. Under the terms of this settlement, the railroad paid \$2000 to each person who was evacuated plus \$200 per person per day for the time they were away from their homes. These amounts were in addition to any property damage claims. The railroad settled separately with the families of the nine people killed in the action.³³

The deaths, injuries, and economic costs caused by these accidents were large. However, in all three cases, NTSB investigators commented on the unique circumstances that made these losses much smaller than they could have been. All three accidents occurred during the early morning hours when few people were outside their homes. Each accident occurred in a rural area where the population density was relatively low. The meteorological conditions prevailing at the time of each accident limited the speed of expansion and the final size of the toxic plumes. All of these plumes also moved away from the accident sites in directions that minimized the number of people exposed to the toxic gases. Thus, impacts of these accidents could have been much worse than they actually were.

Numerous agencies of the federal government, academic researchers, private railroad companies, and committees from the Association of American Railroads had been working together to develop safer ways to ship hazardous chemicals before the three accidents discussed above. Their efforts were significantly accelerated by these events. Many approaches are being explored, among them design of a completely new type of railcar for transporting poison inhalation hazard (PIH) or toxic inhalation hazard (TIH) materials, development of recommended operating practices for trains hauling hazardous cargos, and establishment of performance standards for construction of chlorine and ammonia tank cars that would reduce the probability of a release in a given accident by 65%.

To provide additional focus in this area, The DOT proposed a rule on April 1, 2008 to "Improve the Safety of Railroad Tank Car Transportation of Hazardous Materials" (49 CFR Parts 171, 173, 174 and 179). This proposed rule would include the following requirements:³³

- All tank cars built 2 years after the effective date of the final rule are to have tank head puncture-resistance systems conforming to the requirements of this rule.
- Each owner must bring 50% of its tank car fleet used to transport PIH materials into compliance with the tank head puncture-resistance requirements specified in the rules within 5 years of the effective date of the final rule.
- Five years after the effective date of the final rule, tank cars manufactured using nonnormalized steel for head or shell construction may not be used for transportation of PIH materials (these are primarily tank cars fabricated before 1989).
- Tank cars manufactured 8 years after the effective date of the final rule must meet both the tank head and the shell puncture-resistance system requirements specified in the rule.
- Tank cars that do not meet both the tank head and the shell puncture-resistance requirements specified in the rule cannot be used to transport PIH materials 8 years after the effective date of the rule.
- The insulation installed on tank cars used to ship chlorine must be improved to meet requirements specified in the rule.
- Tank cars used to transport bromine, ethylene oxide, and hydrogen chloride refrigerated liquid must meet both the tank head and the shell puncture-resistance requirements specified in the rule 8 years after the effective date of the rule.

The proposed rule also states that trains transporting tank cars containing PIH materials will have a maximum allowable speed of 50mph. However, if a tank car does not meet the tank head and shell puncture-resistance requirements specified in the rule, the maximum allowable speed will be reduced to 30mph when the train is moving over nonsignaled territory. (Nonsignaled territory means a rail line not equipped with a traffic control system or automatic block control system that conforms to the requirements of the proposed rule.)

The proposed rule is open for review and comment. Based upon the input received during the three public meetings held during the development of the proposed rule, many comments will be submitted to the DOT. After the issues raised in these comments have been resolved, a Final Rule will be promulgated.

None of the organizations that contributed to development of the proposed rule believe improved tank cars and slower train speeds will completely eliminate accidental releases of chlorine and ammonia into the atmosphere. Parallel efforts are also being pursued to reduce the numbers of tank cars containing PIH materials and to shorten the length of travel for tank cars conveying these materials.

One of the more effective nongovernmental programs developed to date to achieve these goals is the “Safety Initiative” started in October 2005 between Dow Chemical Company and Union Pacific Railroad (UP), Dow’s largest rail service provider.³³

Specific goals in the Dow/UP agreement include the following:

- reducing idle times for hazmat shipments by 50% in high-threat urban areas;
- redesigning Dow’s customer supply chains to cut in half the amount of “highly hazardous chemicals” shipped by 2015;
- eliminating all nonaccidental leaks of certain hazardous chemicals by 2008;
- monitoring shipments of hazardous materials by satellite tracking tags and other sensors;
- improving the routing for hazardous material shipments;
- strengthen the Dow/UP commitment to Transportation Community Awareness and Emergency Response (TRANSSCAER); this is a voluntary national outreach effort that focuses on assisting communities to prepare for and respond to a possible hazardous materials transportation incident; its members are volunteer representatives from the chemical manufacturing, transportation, distribution, and emergency response industries, as well as the government; and
- redesigning Dow’s interdivision supply chains to reduce the number and distance of shipments involving high-hazard materials; this includes evaluating the potential for colocation of production and consuming facilities; the use of pipelines instead of rail in some instances; and conversion of highly hazardous products to less hazardous derivatives before shipping.

Dow reduced the amount of chlorine it ships by rail in the United States by 80% between 1999 and 2006.

The decrease in rail car shipments of chlorine to WTPs and WWTPs has not been so rapid. Only six WTPs and 19 WWTPs eliminated rail shipments of chlorine between 1999 and 2007. All six of the WTPs and 16 of the WWTPs changed to using rail delivery of liquid bleach. Three WWTPs converted to UV for disinfection.³⁴

Twenty-four WTPs and 13 WWTPs still shipped chlorine by rail in 2007. Six of these utilities (four WTPs and two WWTPs) had firm plans to convert from chlorine gas to another disinfectant by 2009.³⁴

Highway Transportation

Statistics developed by the Railway Supply Institute (RSI) indicate that it is 16 times safer to move hazardous materials by rail than shipping the same

quantity of material over highways. However, it is very difficult to obtain specific information on the releases of chlorine or ammonia gas during highway accidents. One of the reasons for underreporting these accidents is that the amounts of gas released are usually small enough to not make them “news-worthy” unless there is a gas-related fatality involved. Another reason is the training received by the truck drivers employed by chlorine distributors in North America and Europe. These individuals and local hazmat teams know what to do when a leak occurs.

Occasionally, a “newsworthy” accident is reported. One example was reported in Austin, Texas, in May 2006.³⁵ A leak occurred in a 12,000-gal tractor-trailer filled with commercial-grade sodium hypochlorite solution. The driver parked the truck alongside a major highway while repairs were attempted. Attempts to stop the leak were not successful so the tractor-trailer was hauled to a nearby WWTP. A private hazmat contractor disposed of the hypochlorite solution over a period of several days. Residents of homes adjacent to the highway and the students in several nearby schools were evacuated until the chlorine fumes released by the spilled hypochlorite dissipated. The truck driver was treated in a hospital for breathing problems and later released. The only property damage was the grass killed in the drainage ditch adjacent to the highway.

China. A chlorine tanker burst a tire and ran head-on into another truck on a highway between Shanghai and Beijing in March 2005.³⁶ Both trucks turned over and the chlorine tank ruptured. At least 29 people were killed and 350 hospitalized. Approximately 10,000 people were temporarily evacuated from nearby villages.

Egypt. A major accident involving a chlorine tank truck occurred in Alexandria, Egypt, in December 1965. Five people died, including the truck driver and two would-be rescuers.

A chlorine tank truck, loaded with 7 tons of liquid chlorine, swerved to avoid hitting a passenger car, overturned, and sheared off a gas valve. The truck did not have a protective cover over the exterior valves or EFVs installed inside the tank. The most seriously exposed individuals were those who tried to rescue the injured and unconscious truck driver. Approximately 2 tons of chlorine leaked out before the opening for the gas valve was sealed. By this time, some 500 people were exposed to chlorine fumes.

NOTABLE CONSUMER ACCIDENTS

General

There have been a variety of accidents involving chlorine gas leaks at WTPs, WWTPs, and industrial plants. One of these accidents was discussed earlier

in this chapter (see the section “A Major Leak from PVC Header Failure”). Additional consumer accidents are discussed below.

A Fatal 1-Ton Container Leak

One of the more serious chlorine accidents in North America at the consumer level occurred at a WTP. It caused the deaths of two people who lived close to the plant. A team of newspaper reporters who made a comprehensive investigation of this accident arrived at the following conclusions:

- The accident probably would not have occurred if there had not been a power failure during a brief rainstorm.
- If working gas masks had been conveniently available, the leak could have been halted immediately, and no injuries would have resulted.
- Residents adjacent to the plant would not have been affected if the chlorine container room had been farther than 65 ft away from their homes.

An analysis of this accident leads to the following observations.

The power failure plunged the chlorine container room into practically total darkness (a rain squall shut out most of the exterior light). This caused a delay in the response of the operator who was on duty at the plant. He reported smelling a strong chlorine odor, indicating a severe leak, but he was unable to find a gas mask in the dark and immediately left the contaminated area.

Without power, the operator was unable to relieve the liquid pressure in the chlorine piping system. During a power failure, all of the liquid chlorine in the piping system between the containers and the metering equipment can discharge through any leaking joint unless the system is equipped with isolating valves. When power is available, the metering equipment can be used to withdraw liquid chlorine from the supply piping system, and thus avert a large leak.

Auxiliary lighting to illuminate the chlorine facilities and auxiliary power to operate the chlorine withdrawal system are essential safety features in chlorine handling facilities.

Readily accessible chlorine gas masks are of top priority. As soon as the fire department arrived with gas masks and emergency lights, the operator was able to locate the leaking connection. By this time power had been restored, and the operator was able to relieve the system of pressure and repair the leak.

Isolating valves are used to reduce the length of pressurized piping adjacent to a leak. This is why every container should be connected with an auxiliary valve attached to the container outlet valve. The outlet of the auxiliary valve is then connected to the inlet of the flexible connection and the outlet to the stationary header valve. Some operators prefer an auxiliary header valve at the outlet of the flexible connection, so that for liquid withdrawal the flexible

connection can be shut off at each end and removed during each container change without discharging liquid chlorine.

The deaths caused by this accident could have been avoided had the residents of the house been promptly evacuated when the operator became aware of the leak. The children of the victims did leave the house, which undoubtedly saved their lives.

A Leak from Four 1-Ton Containers

This leak resulted in the discharge of the contents of four 1-ton chlorine containers that were “on line” at the time of the leak. Fortunately, there was no loss of life, but many nearby residents were treated for various degrees of chlorine inhalation.

This massive leak was the result of the following factors:

- The operator attempted to stop a leak at the stem of a chlorine header valve while the system was under full pressure from the four 1-ton containers.
- The leak was caused by structural failure of a bushing located in the 1-in. chlorine header into which the leaking header valve was threaded.
- The failure of the bushing was brought about by corrosion that occurred over a long period.

The lessons to be learned from this accident are as follows:

- Operators should never attempt to repair a chlorine leak while the system is under supply pressure.
- The first step in repairing a leak is to relieve the system of the pressure from the chlorine containers. Pressure gauges must be included in chlorine delivery piping systems to provide the operator with this vital information.
- Duplicate header systems can be constructed to allow replacement of the piping systems on an as-needed basis or on a regular schedule (i.e., every 5 years for systems passing 2 tons or more of chlorine per day, and every 10 years for those passing less than 2 tons per day).

A Leak from a Buried Chlorine Pipe

This leak resulted from a freak accident and was compounded by mistakes made by persons untrained in accident response procedures.

A workman for a natural gas utility company was using a cutting torch in an industrial area. He was cutting into sections of empty, unused natural gas pipelines. By mistake he cut into a 6-in. underground buried pipeline about 7000-ft long that was used to convey chlorine gas from a chemical plant to a nearby plastics plant and was under tank pressure of about 85 psi.

About 1600lb of chlorine gas escaped into the atmosphere. Fortunately, the line was equipped with automatic shutoff valves at both ends. When the pressure dropped as a result of the hole made by the cutter's torch, these valves automatically closed.

A short distance from the site of the leak, 300–400 workers employed at a nearby refinery were waiting to be admitted to their work site. The morning air was cool, the humidity was about 70%, and the wind was blowing in their direction at 10–15 mph. Even though this was a massive leak, only 30 to 40 of these people were taken to the hospital for observation. It is probable that the high humidity, coupled with the strong wind, was responsible for the rapid dilution and dispersal of the chlorine into the atmosphere.

However, the high humidity and the body moisture on these workers caused the chlorine to be adsorbed into their clothing. The people who were taken to the hospital were herded into a small room where they were immediately exposed to the chlorine escaping from their clothing. A hospital attendant realized what was happening, and they were ushered outdoors and then brought in one at a time to have their clothing removed and to be given a wash-down shower. These workers remained in the hospital long enough for a thorough observation and time to get a change of clothes. None stayed in the hospital longer than one night.

The lessons to be learned from this accident are as follows:

- Pipelines carrying chlorine liquid or gas should never be buried. The preferred method is to place them in a grate-covered concrete channel at grade level or in overhead support systems.
- Persons exposed to chlorine should have their clothing removed as soon as possible and be given a warm shower to avoid further shock.
- Persons exposed to chlorine should not remain in a confined space, particularly in a room with rugs, carpets, drapes, or upholstered furniture, but should be moved into the open air as soon as possible.
- It is important to remember the difference between inhaling chlorine gas and the effects of inhaling “off-gassing” from a strong chlorine solution. The effects on the human pulmonary system are totally different: Chlorine gas produces a sharp throttling effect that simulates strangling. The off-gas from chlorine solution does not “throttle” the throat muscles but creates a mild-to-strong irritation in breathing that allows the chlorine to reach the lungs, where it generates watery mucus. Some cases of “off-gassing” are so severe that the victim dies while asleep after being exposed to moist chlorine.

A 14,000-lb Liquid Leak

The largest known leak in a raw water pumping station occurred in an unattended facility that withdrew water from a lake and discharged it into an open channel to be conveyed to a WTP located at some distance from the lake. The

pumping station was controlled by operators at the WTP. There were no personnel on-site.

The chlorination facilities installed at the pumping station were used on an intermittent basis to keep the conveyance channel free from biological growths, which was part of the problem, because the chlorination equipment was not included in the routine maintenance program.

The chlorination system consisted of two chlorinators and two evaporators equipped with electrically heated water baths, installed with protective devices for both low and high temperatures, plus an automatic switch that was to shut down the evaporators if the water bath temperature exceeded 200°F (93°C). Because of the lack of routine maintenance, the electrical supply switch became fouled with debris from dead insects and became stuck with the heaters energized, so the water bath temperature rose high enough to produce a reaction between the chlorine and the steel tubing in the bath, which destroyed the tubing and allowed liquid chlorine to flow into the water. As the chlorine was stored in a 25-ton tank, there was an ample supply of chlorine available for volatilization. The leak continued until it was discovered by a WTP operator inspecting the raw water pumps.

Fortunately, the facility was located in a sparsely populated area, 3000–4000 ft from the nearest residences. A major WWTP was located about 6000 ft from the pumping station. The chlorine plume was hot enough to rise almost straight up, so no one at these locations was aware of the danger. This is another example of the chimney effect produced by hot chlorine vapor discharged into the cooler outdoor air (see the section “A Major Leak from a PVC Header Failure” earlier in this chapter).

The lessons to be learned from this accident are as follows:

- Chlorination facilities should be included in routine maintenance programs. This is especially important for unattended facilities at remote locations.
- Chlorine gas detectors should be installed at all chlorination facilities and should transmit an alarm to a location attended by a WTP operator. If an operator is not on duty 24/7, the alarm should roll over to a continuously attended police or fire station.

In addition to the problems discussed above, the design of the chlorination facilities at this pumping station had the following shortcomings:

- The chlorine diffusers were installed in the raw water pumps' discharge piping. This approach required the use of booster pumps to mix the chlorine solution into the raw water. Repairing a leak in a piping system containing a concentrated chlorine solution and being operated under substantial pressure is very difficult. Additional valves in the chlorine solution piping would remedy this problem.

- The piping and accessories between the storage tank and the evaporators were not correct. The only pipe from the tank to the evaporators was a liquid chlorine delivery line, with no pressure gauge on top of the tank. This prevented the operator from withdrawing chlorine gas from the tank or from evaluating conditions inside the tank. An operator should be able to feed either chlorine gas or liquid chlorine.

Comment. When shutting down an evaporator system, the first action should be to shut off the evaporator and then the discharge valve if it has not automatically shut off. If heat is a problem, liquid chlorine may boil back into the storage tank. If the pressure in the storage tank reaches its upper limit, the safety relief valve on the tank cover will release gas to the atmosphere. This would be a comparatively small leak that would tell the operator that the temperature in the evaporator water bath was too high.

A Tank Car Leak at a Chlorine Packager

On August 14, 2002, approximately 48,000 lb of chlorine was released from a tank car parked in a rail siding owned by DPC Enterprises (DPC) near Festus, Missouri.³⁷ DPC receives liquefied chlorine in 90-ton tank cars and packages it into 150-lb cylinders and 1-ton containers for commercial, industrial, and municipal use in the St. Louis metropolitan area.

The accident occurred when a chlorine transfer hose ruptured. DPC had an emergency shutdown system to stop chlorine releases from tank cars, but it failed to operate and the cloud of chlorine gas made it impossible to reach the self-contained emergency breathing apparatus stored at the plant. An emergency response team manually closed the shutdown valves on top of the tank car approximately 3 h after the leak started.

The plume of chlorine from the leak tended to hug the ground and was only a few feet high. It slowly drifted away from the accident site. The wind was “calm” with short intervals of 3- to 5-mph speeds. Mathematical modeling after the accident calculated the ground-level, centerline concentration of chlorine in the plume to exceed 3 ppm at 3.7 miles from the release point.

The emergency evacuation plan for the area was inadequate. However, by using shelter-in-place at a high school and an assisted living facility, combined with door-to-door notification of residents of a trailer park and a housing development, it was possible to avoid serious injuries. The accident caused 63 people to seek medical evaluations for respiratory distress, three of whom were admitted into the hospital for overnight observation. No estimates of economic damage are available. However, the losses were probably small.

An investigation by the U.S. Chemical Safety and Hazard Investigation Board (CSB) determined that the hose ruptured because the metal braid in it was stainless steel rather than the Hastelloy C specified for this use. Neither

the manufacturer nor DPC confirmed that the hose was constructed of the proper material before it was put into service.³⁸

The investigation also found that the EFVs installed in tank cars will not function when a hose rupture occurs. These valves are designed to close when chlorine flow rate exceeds 7000–32,000 pph, depending on the application. Chlorine flow rates never exceed 7000 pph when a hose fails because the friction losses in the valves, couplings, and the hose itself preclude flows of this magnitude. A survey of 30 municipal WTPs and WWTPs conducted by CSB after the DPC accident found that approximately 30% of these plants were relying on EFVs to stop chlorine flow if a transfer hose failed. Unfortunately, the USEPA and OSHA regulations discussed earlier in this chapter do not include specific requirements for chlorine tank car unloading systems. These systems also do not fall under DOT rules because the tank cars are the responsibility of the consignee once they are delivered. The NTSB has requested the DOT to issue new rules to remedy this regulatory gap. DOT regulations require tank trucks to be equipped with chlorine transfer systems because the truck's owner retains ownership of the chlorine until it has been transferred into the buyer's tank.

The CI has taken a very strong stand regarding the installation of chlorine transfer systems. All of its members must agree to install these systems at their facilities and to ensure that their customers are in compliance with the "Chlorine Customers Generic Safety and Security Checklist" published in CI Pamphlet 85.³⁹ Bulk chlorine customers (those who receive chlorine by railcars, barges, or tank trucks) were required to be in compliance with the checklist by December 31, 2007. Packaged chlorine customers (those who receive chlorine in ton containers or 150-lb cylinders) must be in compliance by December 31, 2008.

A chlorine transfer system consists of motor-operated valves on both ends of the chlorine transfer hose and a chlorine gas detector. The valves close automatically when the detector senses the presence of chlorine in the atmosphere. Operators can also press an emergency shutdown button if the detector fails to close the valves. This system failed to operate at the DPC facility because it had not been regularly maintained to prevent corrosion inside the electrical switches that operated the valves.

The rupture of a chlorine transfer hose at Honeywell International's Baton Rouge chemical plant on August 11, 2005 had a very different outcome. When chlorine began to escape from the tank car, the detector alerted control room operators, who stopped the release by remotely closing the emergency shutdown valves on the chlorine transfer hose. The chlorine release lasted less than 1 min. Several contractors working near the tank car inhaled some chlorine and were taken to a hospital where they were treated and released. All returned to work the next day. Tests conducted immediately after this accident showed that no chlorine gas had passed beyond the Honeywell property line.

Brush Fire

A brush fire accompanied by “Santa Anna” winds produced failures in four 1-ton chlorine containers in use at a small WTP plant in Southern California. The fusible plugs on all four containers melted. One container was also breached. Apparently, the intense heat from the fire caused the pressure in this container to rise very rapidly while the atmosphere near the fusible plugs was not yet hot enough to melt the plugs. The intense fire raging outside the building dispersed the chlorine into the atmosphere without further adverse consequences.

The chlorine building was constructed of concrete block, with a brick facing and metal roof. The building was “scorched,” but structurally intact, after the fire but the chlorinators and chlorine piping were completely destroyed.

This incident illustrates the importance of locating structures that contain chlorine containers well away from flammable vegetation.

Frequency and Magnitude of Chlorine Leaks

The causes of chlorine leaks at customer facilities are listed below. These causes are ranked in the order of severity of the leak and the hazard posed by its occurrence.

1. Fire
2. Flexible connection failure
3. Fusible plug corrosion
4. Accidents caused by carelessness and ignorance
5. Valve packing failure
6. Gasket failure
7. Piping failure
8. Equipment failure
9. Physical damage of containers in collision accidents
10. Container failure
11. Chlorine pressure gauge failure

These causes are discussed below.

1. Fire in WTPs or WWTPs chlorine storage or chlorinator rooms is not a serious hazard because there is very little flammable material in these rooms. The two case studies presented in this chapter illustrate that intense heat can be produced by reactions between chlorine and PVC and between chlorine and steel. However, neither of these accidents produced fires at the plants.

Fire is a very serious hazard at facilities where swimming pool chemicals are stored. The buildings housing these facilities often incur serious damage when stored granular hypochlorite spontaneously explodes. If 150-lb cylinders of chlorine are stored near the hypochlorite, they will either explode or their fusible plug will melt, releasing chlorine gas into the atmosphere. Fire officials should inspect the premises of swimming pool chemical companies often to ensure that such hazards are minimized.

In the early years, ton container explosions were caused by the spontaneous combustion of nitrogen trichloride. When chlorine is made from water containing ammonia nitrogen, the product will contain NCl_3 , which is soluble in liquid chlorine. When the liquid is withdrawn, the NCl_3 evolves as a vapor that will explode. This problem has been corrected in the United States. However, Americans have not done a very good job of exporting this information. In 1981, White investigated such explosions in Bogota, Colombia. During his investigation of the local chlor-alkali plant, he counted more than a dozen U.S.-made ton containers with their dished heads still intact although they had been blown from a concave to a convex position.

2. Probably the most frequent cause of chlorine emissions that expose operating personnel to risk is failure of the lines that connects the chlorine containers to metering and control equipment. These connecting lines are made of cadmium-plated annealed copper, 2000 psi in strength. Copper is used because it is flexible and has sufficient structural strength to withstand the pressure inside the chlorine container. However, each time an empty container is removed from a connector, the chlorine remaining in the tubing reacts with moisture in the room to form a tiny quantity of hydrochloric acid, which is corrosive to copper. Therefore, the flexible connectors have finite service lives. To check the condition of a flexible connector, it should be bent carefully; if it screeches slightly, it is due for replacement as the sound indicates that sufficient corrosion has occurred to cause failure of the connector.
3. Fusible plug failure without any evidence of elevated temperature caused by fire or direct sunlight is next in the order of hazard magnitude. A fusible plug may leak from corrosion between the lead alloy and the plug retainer. There is only one fusible plug on a 150-lb cylinder. It is located at the base of the outlet valve. There are three in each of the dished heads of a ton container.
4. Carelessness is another cause of chlorine accidents. One such accident involved a 6-in. buried chlorine gas line that was originally located entirely within the property of two chemical plants.⁴⁰ The property was subdivided 20 years after installation, and the ground above the piping was paved over. The chlorine gas line was mistakenly cut into by a

welder who was inactivating abandoned natural gas lines. The heat from the torch burned a small hole into the pipe, and the chlorine supported combustion of the carbon steel pipe. Within seconds, the hole was approximately 8 in. in diameter and allowed almost immediate discharge of the contents of 7000 feet of the 6-in. pipe. A few months later, the chlorine line was cut again on successive days by a backhoe excavating underground lines. After these experiences, the pipe was lowered from the original 2 ft to approximately 5 ft below the ground surface.

5. Valve packing failures are not known to have caused any serious problems. If the leak is minor, it can often be corrected by tightening the packing nut. The appropriate chlorine safety kit must be used to enclose serious leaks. The chlorine container can then be returned to the packager for final disposal.
6. Gasket failures are serious only when they occur on the seal between the dome and the tank of a chlorine tank car. Other gaskets are so located that the chlorine supply can be secured, the system emptied of gas, and the gasket replaced. Gasket failures on tank cars are rare. An appropriately trained hazmat team should be notified immediately when a gasket on a railcar is observed to be leaking.
7. Piping failures are rare, but are sometimes caused by unsuitable materials. Lines carrying liquid chlorine are a potential hazard. The correct materials for use in chlorine pipelines are discussed in Chapter 8.
8. Most equipment failures occur in the chlorine vaporizers between the storage containers and the metering and control equipment, primarily as a result of corrosion of the heat exchange pipes in the water bath. Failure is a function of the pipe wall thickness and the amount of chlorine passing through the vaporizer. This type of accident occurs rarely; however, regular inspection of the interior of the heat exchange pipes should be part of the preventive maintenance program.
9. Accidents producing chlorine or ammonia emissions from railroad tank cars are rare considering the quantities of these chemicals shipped. However, as indicated by the three examples earlier in this chapter, the impacts of such accidents are huge. It is to be hoped that the new tank cars and the changes in train speeds called for in the Federal Rule proposed in 2008 will further reduce such hazards. The voluntary actions by several chlorine manufacturers and users to reduce the number of chlorine shipments by railcars will also reduce the frequency of accidents.
10. Container failures, except those caused by fire, are extremely rare. The chlorine packagers throughout North America and Europe are keenly aware of the hazards associated with handling chlorine containers. This awareness has led to the development of strict programs for monitoring the physical condition of these containers and replacing them when

needed. Failures of chlorine tank cars are practically unheard of for a very good reason: Their owners inspect the interiors of these tanks frequently.

PRODUCTION AND USES OF CHLORINE

Annual Production

The CI publishes annual reports⁹ summarizing the quantities of chlorine manufactured in North America. Chlorine production in the United States is subdivided into two categories: gas production (the total quantity of chlorine produced) and liquid production (the quantity of gas that is liquefied so it can be sent off-site). Between 1990 and 2006, 80%–87% of the gas produced in the United States was liquefied, and 17%–20% of the total was produced by industries that immediately used it to manufacture other products. Combining the chlorine production facilities and the manufacturing processes that use the chlorine at adjacent locations is one of the goals of the Dow/UP “Safety Initiative” discussed earlier in this chapter.

Total chlorine gas production in the United States during 2006 was approximately 11.3 million short tons. Total gas production in Canada during the same year was about 1.0 million metric tons. Mexico produced about 391,000 metric tons in 2006. The CI report does not include a breakdown between gaseous and liquid chlorine production for Canada and Mexico.

Annual chlorine gas production in the United States peaked in 2004 at 13.6 million short tons; Canada’s peak production was at 1.5 million metric tons in 1990. Mexico’s years of highest production were 1996 and 1997 at about 415,000 metric tons each. Chlorine is a basic building block in many products, so the demand for it fluctuates with the overall manufacturing economy.

The installed capacity of chlorine manufacturing facilities is also closely tied to the manufacturing base in specific geographic regions, as indicated in Table 1.8.

The information summarized in Table 1.8 was developed for the World Chlorine Council. It vividly illustrates the very rapid increase in total manufacturing capacity of the Pacific Rim countries during the past decade. Chlorine manufacturing capacity in China is growing very rapidly and is projected to overtake the manufacturing capacity of North America by 2010.

End Uses of Chlorine

Chlorine is used in more than 50% of all industrial chemical processes. More than 90% of all pharmaceutical manufacturing processes use chlorine in one or more steps. Chlorine is used to make approximately 96% of all chemicals used in producing agricultural crops. The list goes on and on because chlorine

TABLE 1.8. Distribution of Total Global Chlorine Manufacturing Capacity by Geographic Region⁴¹ (Based on Total Capacity in 2005)

Geographic Region	Percentage of Total World Capacity
North America	22
Western Europe	21
China	20
Other Asia	12
Japan	9
Central and Eastern Europe	5
Middle East and Africa	5
South America	3
Other	3
Total	100

TABLE 1.9. World Chlorine Consumption by Different Sectors of the Economy⁴¹

Economic Sector	Percentage of Total World Consumption
Vinyl	36
Phosgene	9
Hydrochloric acid	8
Propylene oxide	7
Chloromethane and chloroethane solvents	6
Water and wastewater treatment	5
Allylics	4
Pulp and paper	4
Other organics	7
Other inorganics	14
Total	100

is a truly versatile chemical. To illustrate this, the American Chemical Society published a visual aid many years ago for use in schools. This poster was titled “The Chlorine Tree.” It now exists in many configurations that have been developed for specific purposes.

Uses of chlorine in different sectors of the world economy are summarized in Table 1.9. The information summarized in this table was developed for the World Chlorine Council and is based on 2002 consumption data.

Estimates of chlorine consumption by different sectors of the economy are also available for specific geographic areas (the United States, Western Europe, and so forth). However, the percentage distribution for chlorine consumption in these smaller geographic areas is remarkably similar to the data summarized in Table 1.9, which reflects globalization of the industrial economy. The great strides in worldwide transportation networks have made this possible. In 2002, the United States exported \$81.1 billion worth of

chemicals and allied products, and imported \$86 billion worth of chemicals. Liquid chlorine was not part of this international flow of materials because it is a basic building block for other chemicals. Most liquid chlorine shipments travel less than 300 miles from their point of manufacture. However, the higher-value chemicals that are derived from chlorine can travel many hundreds of miles to their final destination.

Only 5% of the total annual chlorine consumption is used in water and wastewater treatment. This percentage has not changed very much in the past several decades. Municipalities use about 2% of the chlorine, and the remaining 3% is used for industrial water treatment.

Help in Chlorine Emergencies

Chemical Transportation Emergency Center (CHEMTREC)⁴² was established in 1971 by the Manufacturing Chemists Association (MCA) as a public service hotline for firefighters, law enforcers, and other emergency responders. MCA has since changed its name to the American Chemical Council (ACC), but CHEMTREC has continued to grow and prosper because it is a very valuable source of assistance during emergency incidents involving chemicals and hazardous materials.

CHEMTREC's Emergency Communications Center is located in Arlington, Virginia. It is open 24h a day, 7 days a week.

When an emergency service specialist (EES) on duty at the center receives a telephone call about an emergency situation, he or she will immediately request the following information:

- caller's name and phone number;
- location of the emergency and description of the area;
- products and equipment involved;
- injuries;
- whether there was a fire; and
- the carrier's and the shipper's names and the name of the consignee.

The EES will provide immediate technical information to the accident scene from an extensive technical library. This can be done by telephone, fax, or electronically. The EES will also relay information to the shipper's or manufacturer's 24-h emergency contact expert and will link that expert to the emergency response team at the scene of the accident. If necessary, the EES will use CHEMTREC's telephone conferencing capabilities to link the local emergency response team to all of the individuals who have expertise in solving the problem. The EES can also link local medical personnel to experts who are experienced in treating injuries caused by the accident.

After the initial response to the emergency has been completed, CHEMTREC will prepare a written report of the incident based on the information collected. This report is immediately sent by fax or e-mail to the

shipper or shipper-designated compliance organization. In certain situations, CHEMTREC can relay written instructions provided by the registrant to the scene of the accident for disposing of small releases of the product. It also maintains a network of chemical industry and for-hire contract emergency response teams to assist in product containment, spill mitigation, and product removal.

PHONE—TOLL FREE—DAY OR NIGHT
CHEMTREC
1-800-262-8200

This number may be used for emergencies or to obtain information.

There are emergency response centers in Canada and Mexico that are similar to CHEMTREC. The center in Canada is named CANUTEC and is operated by the Canadian government. CANUTEC can be reached by telephone by calling collect to the following number:

CANUTEC
613-996-6666 (Call Collect)
Cellular: *666 (Canada Only)

Non-emergency information may be obtained at 613-992-4624 (Call Collect).

The emergency response center in Mexico is named Sistema de Emergencias en Transporte para la Industria Quimica (SETIQ). SETIQ can be reached by telephone by calling collect to the following number:

SETIQ
5255-5559-1588

Both of these emergency response centers have been extremely successful in assisting with incidents involving shipments either into or from these countries.

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2 Chemistry of Aqueous Chlorine

This chapter describes the chlorine species formed when chlorine is dissolved in water; the reactions of these species with nitrogenous compounds, especially ammonia and organic nitrogen; their reactions with selected constituents that may be present in water and wastewater; and their germicidal significance. A good understanding of this information, and the fundamental reactions involved, will facilitate understanding of the discussion in subsequent chapters of the use of chlorine for water and wastewater treatment.

DISSOLUTION AND HYDROLYSIS OF CHLORINE

Using conventional gas feed chlorination equipment, chlorine gas can be dissolved into a sidestream of water, forming a concentrated chlorine solution that can then be piped to the point of application, or it can be directly dissolved into the process stream using a direct gas feed chlorinator. Chlorine can also be dissolved into a caustic solution, in a specially controlled process, to produce a concentrated solution of sodium hypochlorite (NaOCl) that can then be dosed into the process stream; and it can also be used to produce solid forms of chlorine—calcium hypochlorite and chlorinated lime.

Chlorine gas is both hazardous and highly corrosive, so it is important that it be completely dissolved in the water and that it not be allowed to escape back into the atmosphere in concentrations that pose a threat to human health and the environment or to equipment and materials used in the treatment facility. The equilibrium relationship between dissolved and gaseous chlorine can be described, using Henry's law, as follows:

$$p_{\text{Cl}_2} = K_{\text{H}} [\text{Cl}_2 (\text{aq})], \quad (2.1)$$

where

- p_{Cl_2} = partial pressure of Cl_2 in atmospheres (atm),
- K_{H} = Henry's constant (atm-l/mol), and
- $[\text{Cl}_2(\text{aq})]$ = aqueous concentration of Cl_2 in moles per liter.

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The value of K_H varies with the temperature and ionic strength of the water and can also be influenced by the presence of other constituents in the water such as acids or salts. Aieta and Roberts¹ evaluated K_H over the temperature range of 10–30 °C and found the value of K_H at 20 °C and zero ionic strength to be 13.57 atm-l/mol. They also found that K_H was strongly influenced by temperature (roughly doubling from 10 to 30 °C); that K_H increased (solubility decreased) with an increasing salt (NaCl) concentration, consistent with the “salting-out” effect commonly observed for dissolution of gases in water; and that K_H decreased (solubility increased) with an increasing concentration of hydrochloric acid (HCl) and with an increasing concentration of chlorine. The following equation, derived using their data and the van’t Hoff relationship, can be used to estimate K_H at zero ionic strength as a function of temperature:

$$K_H = (6.554 \times 10^5)(e^{-3163.7/T}), \quad (2.2)$$

where e is the base of the natural logarithm (2.71828 ...) and T is absolute temperature in degrees Kelvin ($273.15 + ^\circ\text{C}$).

Example. Estimate the aqueous concentration of molecular chlorine, in moles per liter (M) and milligrams per liter (mg/l), in pure water at 30 °C in equilibrium with chlorine gas at a partial pressure of 1 atm.

$$K_H = (6.554 \times 10^5)(e^{-3163.7/303.15}) = 19.2 \text{ atm-l/mol}$$

$$[\text{Cl}_2(\text{aq})] = (1 \text{ atm})/(19.2 \text{ atm-l/mol}) = 0.0521 \text{ M}$$

$$[\text{Cl}_2(\text{aq})] = (0.0521 \text{ M})(70,906 \text{ mg/mol}) = 3694 \text{ mg/l.}$$

Note that Henry’s law applies only to molecular chlorine (Cl_2). Significant concentrations of other chlorine species may be present in a chlorine solution, so the total concentration of chlorine (and its total solubility) may be substantially higher than that predicted from Henry’s law. One reason for this is that chlorine hydrolyzes rapidly in water to form hypochlorous acid (HOCl), which is also an active form of chlorine:



Based on the data of Shilov and Solodushenkov,^{2,3} Morris⁴ proposed that HOCl might be produced by the reaction of Cl_2 with hydroxyl (or hydroxide) ion (OH^-); but after collecting more accurate data, Shilov and Solodushenkov⁵⁻⁷ showed that this could not be the case when preparing concentrated chlorine solutions because in one experiment the rate of hydrolysis increased as the OH^- concentration decreased. This was later confirmed by Lifshitz and Perlmutter-Hayman,⁸ who showed that OH^- ions cannot form rapidly enough (by dissociation of water) to significantly contribute to the observed hydrolysis rate. Thus, Equation (2.3) best describes chlorine hydrolysis in concentrated

(and very acidic) chlorine solutions, although the reaction of chlorine with OH^- ions may be important under other circumstances.^{9,10}

Chlorine hydrolysis (Eq. 2.3) is also referred to as a disproportionation reaction since the two chlorine atoms, which initially have the same oxidation state (0) and share two electrons, end up in different oxidation states. One chlorine atom is oxidized, becoming Cl^{+1} , while the other is reduced, to Cl^{-1} , and ends up with both of the electrons. For low ionic-strength solutions (for which the activity of a dissolved substance is approximately equal to its molar concentration), the equilibrium constant for chlorine disproportionation can be expressed as follows:

$$K_d = \frac{[\text{HOCl}][\text{H}^+][\text{Cl}^-]}{[\text{Cl}_2]}, \quad (2.4)$$

where K_d is the disproportionation constant (mol^2/l^2) and the square brackets indicate concentration expressed in moles per liter (M).

Connick and Chia¹¹ evaluated K_d over the temperature range of 0–45°C and found the value of K_d at 25°C to be 3.94×10^{-4} . The following equation, based on their data, can be used to estimate values of K_d at temperatures from 0 to 45°C:

$$\log K_d = -982,798/T^2 + 5485.7/T - 10.7484, \quad (2.5)$$

where T is absolute temperature in degrees Kelvin ($273.15 + ^\circ\text{C}$).

Equations for estimating the values of K_d , K_H , and the acid ionization constant for hypochlorous acid (discussed below) can also be derived from thermodynamic data if it is assumed that there is no change in the enthalpy (heat) of the reaction with temperature.^{12,13} In the absence of data, such equations can be very useful for estimating purposes; but they generally provide less accurate estimates than equations based on accurate measurements. There are two reasons for this. First, the enthalpy change may vary significantly with temperature, which is known to be the case for K_d .¹¹ Second, many thermodynamic constants are known only to two or three significant figures and the relationships involved are logarithmic, so the values of equilibrium constants estimated from thermodynamic data are only approximate and are generally less accurate than values based on careful measurements.

If chlorine is dissolved into pure water, and if the concentration is sufficient for hydrolysis to lower the pH to a value of 5 or less, then the concentrations of HOCl , H^+ , and Cl^- will be approximately equal. In this case, Equation (2.4) can be revised and rearranged to give the following equation:

$$[\text{HOCl}] = (K_d [\text{Cl}_2])^{1/3}. \quad (2.6)$$

Assuming that the concentrations of other chlorine species (hypochlorite ion and trichloride ion) are negligible, and also assuming that ionic strength

effects can be ignored, Equation (2.6) can be used together with Henry's law (Eq. 2.1) to estimate the total solubility of chlorine in water.

Example. Estimate the total concentration of chlorine, in milligrams per liter, in pure water at 30°C in equilibrium with chlorine gas at a partial pressure of 1 atm. Ignore ionic strength effects and chlorine species present in trace amounts.

$$\log K_d = -982,798/(273.15 + 30)^2 + 5485.7/(273.15 + 30) - 10.7484 = -3.347$$

$$K_d = 10^{-3.347} = 4.498 \times 10^{-4}.$$

$$[\text{Cl}_2(\text{aq})] = 0.0521 \text{ M (from the previous example)}$$

$$[\text{HOCl}] = \{(4.498 \times 10^{-4})(0.0521)\}^{1/3} = 0.0286 \text{ M}$$

$$\text{Total chlorine} = 0.0521 + 0.0286 = 0.807 \text{ M}$$

$$\text{Total chlorine} = (0.807 \text{ M})(70,906 \text{ mg/mol}) = 5722 \text{ mg/l}$$

$$\text{Also, since } [\text{H}^+] \approx [\text{HOCl}] = 0.0286 \text{ M, pH} = -\log[\text{H}^+] \approx 1.54.$$

Chlorine solubility data for water temperatures of 0–40°C (the range typically encountered in water and wastewater treatment) and for selected pressures up to about 2 atm (1 atm = 760 mmHg) are listed in Table 2.1. Data for broader ranges of temperatures and pressures were reported by Adams and Edmonds,¹⁴ and their full data set is included in *Perry's Chemical Engineers' Handbook*.¹⁵ Chlorine solubility data for a total pressure of 760 mmHg (including the partial pressure of water vapor, which varies with temperature) are included in *Lange's Handbook of Chemistry*.¹⁶

The chlorine solubility calculated in the example (5722 mg/l) compares reasonably well with the value for 30°C shown in Table 2.1 (5.8 g/l, or 5800

TABLE 2.1. Solubility of Chlorine in Water (g/l) as a Function of Temperature and Pressure

Pressure (mmHg)	Temperature (°C)				
	0	10	20	30	40
100	2.79	2.08	1.77	1.57	1.42
250	5.71	3.95	3.19	2.69	2.34
500	#	6.85	5.29	4.30	3.61
750	#	9.65	7.29	5.80	4.77
1000	#	#	9.27	7.27	5.89
1500	#	#	13.23	10.14	8.05

Values are as reported by Adams and Edmonds¹⁴ and represent total chlorine (the sum of molecular chlorine, hypochlorous acid, trichloride ion, and traces of hypochlorite ion).

Chlorine ice ($\text{Cl}_2 \cdot 8\text{H}_2\text{O}$) forms;¹⁴ but it is a clathrate having no definite chlorine to water ratio.¹⁷

mg/l). The difference between the two values is attributable to the slight difference in pressure (760 vs. 750 mmHg), to the fact that traces of hypochlorite and trichloride were ignored in the calculation, and to the precision and accuracy of the measurements on which both the measured values and the estimated constants were based.

The trichloride ion is a complex formed by molecular chlorine and the chloride ion:



For low ionic-strength solutions (for which the activity of a dissolved substance is approximately equal to its molar concentration), the equilibrium constant for this reaction, K_3 , can be defined as follows:

$$K_3 = \frac{[\text{Cl}_3^-]}{[\text{Cl}_2][\text{Cl}^-]} \quad (2.8)$$

Zimmerman and Strong¹⁸ found the value of K_3 to be 0.191 at 25°C, a value similar to those reported by other investigators,^{11,19} and one that is thought to vary little with temperature.¹ Morris²⁰ indicated that H_2OCl^+ and Cl^+ may also be present as transient species under some circumstances, but that they are likely to be of little significance in dilute solution, although H_2OCl^+ may play a role in acid catalysis of reactions involving HOCl. Swain and Crist²¹ concluded that it is “extremely improbable that Cl^+ is significantly involved in any thermal reaction ever studied in solution.” Only the trichloride ion will be further considered herein.

The trichloride ion contains “active” or “available” chlorine, but its concentration in a chlorine solution, relative to $\text{Cl}_2(\text{aq})$ and HOCl, is expected to be quite small unless a high concentration of chloride is present, as might be the case if the dilution water contains hydrochloric acid (HCl), sodium chloride (NaCl), or seawater. Dissolution of chlorine in pure water can form only a limited amount of trichloride ion since it must hydrolyze to produce chloride ions, but this in turn, reduces the concentration of molecular chlorine. In the example immediately above, the concentration of chloride is approximately 0.0286 M. Multiplying this by the concentration of molecular chlorine present (0.0521 M) and the value of K_3 (0.191), the trichloride ion concentration is found to be only 2.85×10^{-4} M, or 0.035% of the total chlorine concentration.

At low chlorine concentrations, such as those typically employed to disinfect drinking water, hydrolysis of chlorine is extremely rapid² and is virtually complete in less than 1 s even at 1°C.^{4,22} Furthermore, if the chlorine concentration is low relative to the alkalinity present in the water being treated (i.e., if the pH remains neutral), virtually no molecular chlorine will remain. Because absorption of chlorine gas into water is so rapid and complete at low chlorine concentrations, it is possible to chlorinate water by

directly feeding gaseous chlorine into the process stream, provided that the combination of immersion depth and bubble size is adequate to ensure that no chlorine escapes into the air to pose a hazard to the operators or the public. However, since chlorine gas is extremely hazardous and since unsafe conditions could develop due to unforeseen circumstances (such as a flow stoppage, a change in water level, or a break in the diffuser), direct gas feed chlorination may be prohibited by regulatory authorities. Even if direct feeding is permitted, the regulatory authority may require the gas feed line to be operated under vacuum, limiting the types of equipment that may be employed, or the designer or owner may choose to avoid direct feeding as a safety precaution. For these reasons, the practice of direct gas feed chlorination may be limited to emergency applications, especially in situations where more time and equipment would be required to implement other application methods.

At high chlorine concentrations and at low pH (when the acidity produced by chlorine hydrolysis exceeds the alkalinity of the water being treated), chlorine hydrolysis (Eq. 2.3) is not complete and a significant fraction of the chlorine remains in the form of molecular chlorine (Cl_2). Under these conditions, it is important to avoid supersaturation, which could cause chlorine gas bubbles to form and escape into the atmosphere.

Injector systems are usually designed to maintain a pressure of at least 2 psig at the injector discharge. At this pressure and at a temperature of 20°C , the solubility of chlorine in water exceeds 7500 mg/l .¹⁴ However, the chlorine concentration in the chlorinator discharge is limited, by design, to 3500 mg/l to avoid supersaturation (especially during the warmer months, when chlorine is less soluble in water) and to avoid the formation of chlorine ice during the winter months, when many utilities experience water temperatures approaching 0°C . Limiting the chlorine concentration to 3500 mg/l also helps avoid the release of chlorine gas into the piping. This can occur if a negative pressure develops in the piping (which normally should not occur in a properly designed system), and it has been known to adversely affect the hydraulic gradient between the injector and the point of application.

It is also important to avoid exposing concentrated chlorine solutions to the atmosphere, especially in an enclosed space, since molecular chlorine can be released into the air up to the limit described by Henry's law.

Example. Determine the atmospheric concentration of chlorine that could result if a chlorine solution containing 2062 mg/l of molecular chlorine (which would be the case for a 3500 mg/l chlorine solution prepared using pure water at 15°C) were dripped into the water being treated as it passed through an enclosed chemical feed room. Assume water and air temperatures of 15°C .

$$K_H = (6.554 \times 10^5) (e^{-3163.7/288.15}) = 11.17 \text{ atm-l/mol}$$

$$[\text{Cl}_2 (\text{aq})] = (2062 \text{ mg/l}) / (70906 \text{ mg/mol}) = 0.0291 \text{ M}$$

$$p_{\text{Cl}_2} = (11.17 \text{ atm-l/mol}) (0.0291 \text{ M}) = 0.325 \text{ atm.}$$

A pressure of 0.325 atm corresponds to 325,000 ppm. Even if the room were ventilated, so that only a small fraction of this concentration were realized, the maximum (ceiling) exposure level recommended by the National Institute for Occupational Safety and Health²³ (0.5 ppm), could readily be exceeded, and the equipment in the room, such as pumps, motors, and control systems, could be strongly corroded. This example illustrates the importance of properly diffusing concentrated chlorine solutions into the water being treated. If this same solution were diffused into the water to produce a relatively high dosage of 20 mg/l at the relatively low pH of 6, the resulting maximum atmospheric concentration in equilibrium with the treated water would be only 0.003 ppm.

It is also worth noting that the pH of concentrated chlorine solutions is low enough to convert all of the alkalinity in the dilution water to carbon dioxide (CO₂). In most cases, this will result in supersaturation of the dilution water with CO₂ and the potential to form gas bubbles that can facilitate the release of Cl₂(g) into the air and that have also been known to interfere with rotameter readings and the hydraulics of solution lines. Maintaining a positive pressure and properly diffusing the chlorine solution below the surface of the water being treated helps minimize such problems.

DISSOCIATION OF HYPOCHLOROUS ACID

Effect of pH and Temperature

Another very important reaction is the dissociation of hypochlorous acid (HOCl) to produce hypochlorite ions (OCl⁻) and hydrogen ions (H⁺) as follows:



Hypochlorous acid is a “weak” acid, which means that it tends to undergo only partial dissociation in dilute solutions. In typical water and wastewater treatment applications, both species are present to some degree, but their relative concentrations can strongly influence both disinfection and oxidation reactions. Hypochlorous acid is generally much more effective as a disinfectant than hypochlorite ion for reasons discussed later in this chapter; and some chemical reactions may involve one species but not the other.

The extent to which hypochlorous acid dissociates depends primarily on the pH and temperature of the water. For solutions of low ionic strength (those for which the activity of a substance is approximately equal to its molar concentration), the extent of dissociation can be calculated using the following equation:

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}, \quad (2.10)$$

TABLE 2.2. Values of the Henry's, Disproportionation, and Acid Ionization Constants for Chlorine as a Function of Temperature

Temperature (°C)	0	5	10	15	20	25	30	35
K_H (atm-l/ mol)	(6.11)	(7.53)	9.17	(11.17)	13.57	(16.15)	19.16	(22.79)
$K_d \times 10^4$ (mol ² /l ²)	1.458	(1.865)	(2.329)	2.809	(3.375)	3.944	(4.498)	5.104
$K_a \times 10^8$ (mol/l)	1.496	1.761	2.041	2.329	2.620	2.906	3.183	3.443
pK_a	7.825	7.754	7.690	7.633	7.582	7.537	7.497	7.463

Values shown are for zero ionic strength (infinite dilution). Values of K_H are as reported by Aieta and Roberts¹ or, if shown in parentheses, calculated from their data (Eq. 2.2); values of K_d are as reported by Connick and Chia¹¹ or, if shown in parentheses, calculated from their data (Eq. 2.5); and the values of K_a and pK_a were calculated using Morris's²⁴ equation (Eq. 2.11).

where K_a is the dissociation (acid ionization) constant, which varies with temperature, and the square brackets are used to indicate molar concentrations.

The values of K_a and pK_a shown in Table 2.2 were computed using Morris's²⁴ best-fit formula:

$$pK_a = \frac{3000.0}{T} - 10.0686 + 0.0253 T, \quad (2.11)$$

where $pK_a = -\log (K_a)$ and T is the absolute temperature in degrees Kelvin ($273.15 + ^\circ\text{C}$). For convenience, values of the Henry's and disproportionation constants are also included in Table 2.2.

Table 2.3 shows the percentage of chlorine in the form of HOCl in dilute solution in water at various temperatures and at pH values from 5 to 11. In this range, which includes the pH values typically encountered in water and wastewater treatment, the concentrations of molecular chlorine (Cl_2) and trichloride ion (Cl_3^-) can be considered negligible. The percentage of chlorine present in the form of hypochlorite ion (OCl^-) is the difference between the tabulated numbers and 100. As illustrated in Figure 2.1, the percentage of chlorine in the form of HOCl increases with decreasing pH and declining temperature.

The fraction of chlorine present as HOCl can be calculated at any pH value, in water having low ionic strength, as follows:

$$\frac{[\text{HOCl}]}{[\text{HOCl}] + [\text{OCl}^-]} = \frac{1}{1 + \frac{[\text{OCl}^-]}{[\text{HOCl}]}} = \frac{1}{1 + \frac{K_a}{[\text{H}^+]}}. \quad (2.12)$$

TABLE 2.3. Percent HOCl as a Function of pH and Temperature

pH	Percent HOCl						
	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C
5.0	99.85	99.82	99.80	99.77	99.74	99.71	99.68
5.5	99.53	99.45	99.36	99.27	99.18	99.09	99.00
6.0	98.53	98.27	98.00	97.72	97.45	97.18	96.92
6.1	98.15	97.83	97.50	97.15	96.81	96.47	96.15
6.2	97.68	97.28	96.87	96.44	96.01	95.60	95.20
6.3	97.10	96.60	96.09	95.56	95.03	94.52	94.03
6.4	96.38	95.76	95.12	94.47	93.83	93.20	92.60
6.5	95.48	94.72	93.94	93.14	92.35	91.58	90.86
6.6	94.38	93.45	92.49	91.51	90.56	89.63	88.75
6.7	93.03	91.89	90.72	89.55	88.39	87.29	86.24
6.8	91.38	90.00	88.59	87.19	85.82	84.50	83.28
6.9	89.38	87.73	86.05	84.39	82.78	81.24	79.82
7.0	86.99	85.02	83.05	81.11	79.24	77.48	75.86
7.1	84.15	81.85	79.56	77.33	75.20	73.21	71.39
7.2	80.83	78.18	75.56	73.04	70.66	68.47	66.47
7.3	77.01	73.99	71.06	68.27	65.67	63.30	61.16
7.4	72.69	69.33	66.11	63.09	60.31	57.80	55.57
7.5	67.89	64.23	60.78	57.59	54.69	52.11	49.84
7.6	62.67	58.78	55.17	51.89	48.95	46.36	44.11
7.7	57.15	53.11	49.44	46.14	43.24	40.71	38.53
7.8	51.44	47.36	43.71	40.49	37.70	35.29	33.24
7.9	45.70	41.68	38.15	35.09	32.46	30.22	28.34
8.0	40.06	36.21	32.89	30.04	27.63	25.60	23.91
8.1	34.68	31.08	28.02	25.43	23.27	21.46	19.97
8.2	29.66	26.37	23.62	21.32	19.41	17.84	16.54
8.3	25.09	22.15	19.72	17.71	16.06	14.71	13.60
8.4	21.02	18.44	16.32	14.60	13.19	12.05	11.12
8.5	17.45	15.22	13.42	11.95	10.77	9.81	9.04
8.6	14.38	12.48	10.96	9.74	8.75	7.96	7.31
8.7	11.77	10.18	8.91	7.89	7.08	6.42	5.90
8.8	9.58	8.26	7.21	6.37	5.70	5.17	4.74
8.9	7.76	6.67	5.81	5.13	4.59	4.15	3.80
9.0	6.27	5.37	4.67	4.12	3.68	3.33	3.05
9.5	2.07	1.76	1.53	1.34	1.19	1.08	0.98
10.0	0.66	0.56	0.49	0.43	0.38	0.34	0.31
10.5	0.21	0.18	0.15	0.14	0.12	0.11	0.10
11.0	0.07	0.06	0.05	0.04	0.04	0.03	0.03

Without ionic strength corrections (assuming activities equal to molar concentrations). Values were calculated using values of K_a estimated by Morris's equation (Eq. 2.11); see Table 2.2. The concentrations of molecular chlorine (Cl_2) and trichloride ion (Cl_3^-) were assumed to be negligible.

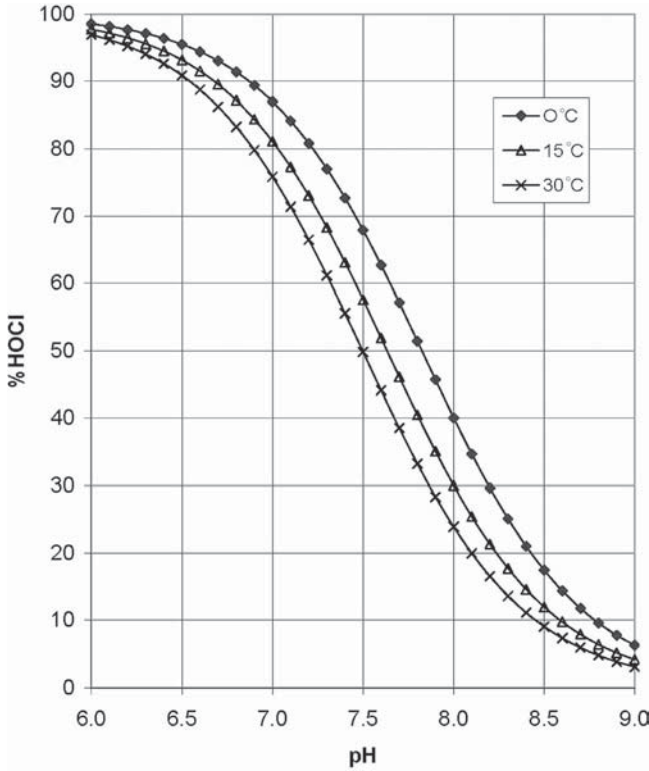


Figure 2.1. Percentage of chlorine present as HOCl as a function of pH and temperature (assuming zero ionic strength and considering HOCl and OCl^- as the only chlorine species present).

Example. At 20°C and pH 8, the percentage of chlorine present as HOCl is

$$100 \times \left[1 + \frac{2.62 \times 10^{-8}}{1 \times 10^{-8}} \right]^{-1} = \frac{100}{3.62} = 27.6\%$$

Ionic Strength Effects

The ionic strength (I) of a solution is defined as follows:^{25,26}

$$I = \frac{1}{2} \sum_{i=1}^i [i] Z_i^2, \quad (2.13)$$

where $[i]$ is the molar concentration of the i th ionic species and Z_i is the ionic charge of the i th ionic species. If the major ionic composition of a water is not

known, its ionic strength can be estimated from the total dissolved solids (TDS) concentration:^{26,27}

$$I \approx \text{TDS}/40,000. \quad (2.14)$$

If only the conductivity of the water is known:

$$I \approx 1.6 \times 10^{-5} \times C, \quad (2.15)$$

where C is the conductivity of the water in $\mu\text{mhos}/\text{cm}$.²⁶

As the ionic strength of a solution increases, ions begin to interact more strongly with one another (electrostatically), such that their activity (the concentration that is “effectively seen” by other ions) is reduced. In chemical notation,

$$\{i\} = \gamma_i [i], \quad (2.16)$$

where $\{i\}$ is the activity of species, γ_i is the activity coefficient of species i , and $[i]$ is the molar concentration of species i . At infinite dilution (zero ionic strength), the value of the activity coefficient is 1.0 and the activity of each ion is equal to its molar concentration. As ionic strength begins to increase, the value of the activity coefficient decreases, much more so for divalent ions than for monovalent ions. At very high ionic strengths not typically encountered in water and wastewater treatment, the activity coefficients of different ions follow different patterns, with some beginning to increase again and others continuing to decrease.

The mean activity coefficients of pairs of ions can be determined experimentally, and values for commonly encountered ions at various ionic strengths have been tabulated in handbooks.^{15,28} However, it is often convenient to estimate the values of activity coefficients using one of several well-known equations. One that is popular among those involved in water and wastewater treatment is the modified Davies equation:^{26,27,29}

$$-\log \gamma_i = AZ_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right], \quad (2.17)$$

where

$$A = 1.82 \times 10^6 (DT)^{-1.5}, \quad (2.18)$$

$$D = \frac{60,954}{T + 116} - 68.937, \quad (2.19)$$

and T = absolute temperature ($273.15 + ^\circ\text{C}$). This equation is valid for $I < 0.5\text{M}$.

When using this equation, small differences among ions of the same valence are ignored, and all ions of the same valence are assumed to have the same activity coefficient. Thus, the activity coefficient for monovalent ions, γ_m , is applied to all monovalent ions, and γ_d is applied to all divalent ions. Other equations, and additional information regarding ionic strength, can be found in most basic textbooks on water chemistry, including Butler's.³⁰

Uncharged molecules also behave nonideally in highly concentrated solutions. However, since uncharged molecules interact with other molecules much less strongly than ions do, such effects are generally ignored unless a solution is highly concentrated and accurate calculations are required. Nevertheless, as noted earlier, salts can significantly reduce the solubility of gases, including chlorine, in water.

For calculations involving thermodynamic equilibrium constants to be accurate, activities must be used (rather than molar concentrations) when ionic strength effects are significant. This is typically done by "correcting" the value of the equilibrium constant for ionic strength, such that molar concentrations can then be used in subsequent calculations. For example, for the dissociation of HOCl,

$$K_a = \frac{\{H^+\}\{OCl^-\}}{\{HOCl\}} = \frac{(\gamma_m[H^+])(\gamma_m[OCl^-])}{[HOCl]} \quad (2.20)$$

$${}^cK_a = \frac{K_a}{\gamma_m^2} = \frac{[H^+][OCl^-]}{[HOCl]}, \quad (2.21)$$

where ${}^cK_a$ is the molar concentration-based (corrected) equilibrium constant that can now be used in the same manner as a thermodynamic equilibrium constant, but with molar concentrations rather than activities. In making such calculations, it is important to note that pH is defined as the negative log of the hydrogen ion *activity*; thus

$$[H^+] = \frac{10^{-pH}}{\gamma_m}. \quad (2.22)$$

Example. Determine the percentage of chlorine in the form of HOCl in water having a pH of 7.5, a temperature of 15°C, and 0.1 M ionic strength.

$$D = \frac{60,954}{(273.15 + 15) + 116} - 68.937 = 81.88$$

$$A = 1.82 \times 10^6 (81.88 \times (273.15 + 15))^{-1.5} = 0.502$$

$$-\log \gamma_m = (0.502)(1)^2 \left[\frac{\sqrt{0.1}}{1 + \sqrt{0.1}} - 0.3(0.1) \right] = 0.1055$$

$$\gamma_m = 10^{-0.1055} = 0.784$$

$${}^c K_a = \frac{K_a}{\gamma_m^2} = \frac{2.329 \times 10^{-8}}{0.784^2} = 3.789 \times 10^{-8}$$

$$[H^+] = \frac{10^{-7.5}}{0.784} = 4.034 \times 10^{-8}$$

$$\%HOCl = 100 \times \left[1 + \frac{3.789 \times 10^{-8}}{4.034 \times 10^{-8}} \right]^{-1} = \frac{100}{1.939} = 51.6\%.$$

In comparison, in a water having a very low ionic strength under the same conditions, 57.6% of the chlorine would be present in the form of HOCl (Table 2.3)—a difference of 6%. As this example illustrates, an increase in ionic strength increases the dissociation of HOCl to OCl^- . Figure 2.2 illustrates HOCl dissociation at 25 °C for four ionic strengths.

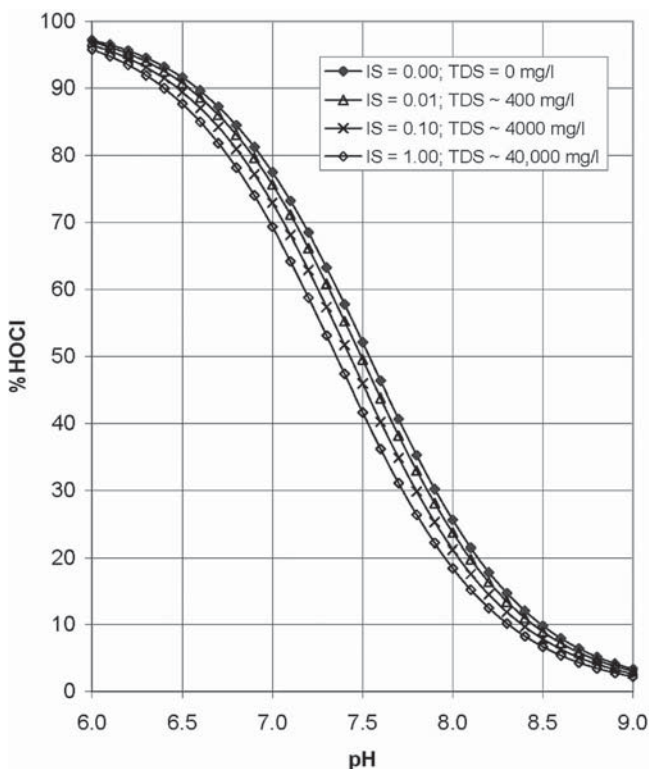


Figure 2.2. Percentage of chlorine present as HOCl as a function of pH and ionic strength at 25 °C (considering HOCl and OCl^- as the only chlorine species present).

CHLORINE SPECIATION IN CONCENTRATED SOLUTIONS

In a concentrated chlorine solution (in the absence of ammonia, which can combine with chlorine as described later in this chapter), the total concentration of chlorine (T) is as follows:

$$T = [\text{Cl}_2] + [\text{HOCl}] + [\text{OCl}^-] + [\text{Cl}_3^-]. \quad (2.23)$$

(T also equals “free” chlorine, which is defined later in this chapter.) Combining this expression with the equilibrium expressions for hydrolysis of chlorine (Eq. 2.4), dissociation of HOCl (Eq. 2.10), and trichloride ion formation (Eq. 2.8), only one additional equation is required to define the system if the pH of the solution is known or fixed. For solutions prepared in pure water, with only NaOH or a monoprotic acid other than HCl used to adjust pH, a chloride balance equation can be developed by recognizing that a chloride ion is released for each molecule of HOCl or OCl^- produced by chlorine hydrolysis, so the sum of HOCl or OCl^- must equal the sum of the chloride and trichloride ions. Solving for $[\text{HOCl}]$ as a function of $[\text{H}^+]$ yields the following cubic equation:

$$\begin{aligned} & \left[-\left(\frac{1}{K_d}\right)^2 [\text{H}^+]^3 - K_a \left(\frac{1}{K_d}\right)^2 [\text{H}^+]^2 + 4\left(\frac{1}{K_d}\right) K_3 ([\text{H}^+] + K_a)^2 \right] [\text{HOCl}]^3 \\ & + \left[-4\left(\frac{1}{K_d}\right) K_3 T [\text{H}^+] ([\text{H}^+] + K_a) \right] [\text{HOCl}]^2 \\ & + \left[\left(\frac{1}{K_d}\right) T [\text{H}^+]^2 + K_a + [\text{H}^+] + \left(\frac{1}{K_d}\right) K_3 T^2 [\text{H}^+]^2 \right] [\text{HOCl}] - T [\text{H}^+] = 0. \end{aligned} \quad (2.24)$$

This equation can be solved by trial and error or by using a root solver, but caution must be exercised since there may be more than one positive root that yields results that appear at first glance to be reasonable. (Negative roots have no physical meaning.) The effects of ionic strength can be taken into consideration by modifying the equilibrium constants as described in the preceding section of this chapter. (In the calculations below, it was assumed that the activity coefficients of HOCl and Cl_2 are approximately equal and therefore offset one another in the equilibrium expression for K_d .) If the pH of the solution is not fixed (but is instead allowed to vary with the concentration of chlorine), a charge balance can be added and an iterative approach used to find both the HOCl concentration and a pH value consistent with the resulting charge balance. If HCl is added to adjust the pH (to a value lower than would occur through chlorine addition alone), the chloride balance described above must be replaced with a charge balance, and a different cubic equation is obtained.

Table 2.4 illustrates the changes in chlorine speciation that occur with changes in pH and total chlorine concentration at 15°C, with and without activity corrections. For these conditions, Cl_2 is the dominant species at pH 1; HOCl dominates at pH values of 2–6; and OCl^- is less than 1% of total chlorine at a pH of 5 or lower. The trichloride ion accounts for less than 1% of total chlorine under all conditions except when HCl is used to lower the pH to 1. Lowering the pH to 1 with HCl also had the effect of converting most of the chlorine to Cl_2 . When the effects of ionic strength are considered, there is a slight increase in chlorine hydrolysis and in the dissociation of HOCl.

Table 2.5 illustrates the changes in chlorine speciation that occur as a function of temperature and chlorine concentration in solutions prepared in pure water without acid or base addition. Solutions having a chlorine concentration of 1000 mg/l or greater were found to have a pH of about 1.5–2.1. As temperature rose, there was a small increase in chlorine hydrolysis and in the dissociation of HOCl. Adding alkalinity (500 mg/l as CaCO_3) to the dilution water or increasing its ionic strength (to 0.03) caused a slight increase in chlorine hydrolysis; thus, ignoring the alkalinity or TDS present in the dilution water will result in a conservative estimate of the percentage of chlorine present in the form of Cl_2 .

The information provided in Tables 2.4 and 2.5 has three important practical implications. First, it can be seen that a high percentage of the chlorine in a chlorine solution can be present in the form of Cl_2 , which is both volatile and very hazardous. Thus, when generating and using chlorine solutions, proper precautions must be taken to protect human health and the environment, as well as treatment facilities. Second, it can be seen that acid addition can greatly increase the percentage of chlorine present in the form of Cl_2 . If this occurs accidentally, for example when an acidic chemical such as alum is added to a solution of sodium hypochlorite or when chlorine is combined with an acidic cleaning solution, a very hazardous situation can arise. Special precautions to prevent the release of chlorine must also be taken when chlorine solutions are intentionally acidified, as is done in generating chlorine dioxide by certain methods (Chapter 14) and in some well-cleaning procedures. Third, increasing the pH of a chlorine solution substantially reduces the concentration of molecular chlorine (Cl_2), so it is a very effective way to reduce one of the hazards associated with the use of chlorine. For this reason, many utilities have switched, or considered switching, to using sodium hypochlorite, which contains a negligible concentration of molecular chlorine. It is also the principle on which most chlorine scrubber systems are based.

HYPOCHLORITE SOLUTIONS

Sodium hypochlorite solutions, commercially available in 12%–16% strength, may be fed directly or diluted prior to feeding. Calcium hypochlorite solution may be prepared by dissolving calcium hypochlorite or chlorinated lime in

TABLE 2.4. Chlorine Species as a Percentage of Total Chlorine in Chlorine Solutions Adjusted to pH 1–6 at 15 °C

pH	Total Chlorine Concentration in Solution (mg/L as Cl ₂)									
	1000			3500			7000			
	Cl ₂	HOCl	OCl ⁻	Cl ₃ ⁻	Cl ₂	HOCl	OCl ⁻	Cl ₃ ⁻	Cl ₂	OCl ⁻
Without activity corrections and using NaOH or an acid other than HCl for pH adjustment										
1	64.16	35.78	0.000	0.062	78.61	21.23	0.000	0.156	84.16	0.000
2	26.83	73.12	0.000	0.053	47.60	52.16	0.000	0.233	58.52	0.000
3	4.57	95.42	0.002	0.012	13.19	86.70	0.002	0.108	21.43	0.002
4	0.497	99.48	0.023	0.001	1.70	98.26	0.023	0.016	3.28	0.023
5	0.050	99.72	0.232	0.001	0.175	99.59	0.232	0.002	0.348	0.232
6	0.005	97.72	2.28	0.000	0.017	97.71	2.28	0.000	0.034	2.28
With activity corrections and using NaOH or an acid other than HCl for pH adjustment										
1	60.38	39.55	0.000	0.064	76.04	23.79	0.000	0.169	82.17	0.000
2	25.20	74.75	0.000	0.051	45.00	54.77	0.000	0.231	55.68	0.000
3	4.11	95.88	0.003	0.011	11.42	88.48	0.003	0.095	18.43	0.002
4	0.442	99.53	0.026	0.001	1.41	98.55	0.028	0.013	2.62	0.029
5	0.045	99.69	0.261	0.000	0.144	99.57	0.281	0.001	0.274	0.295
6	0.004	97.44	2.55	0.000	0.014	97.24	2.75	0.000	0.027	2.88
With activity corrections and using HCl for pH adjustment										
1	94.98	2.68	0.000	2.35	94.97	2.69	0.000	2.33	94.97	0.000
2										
3										
4										
5										
6										

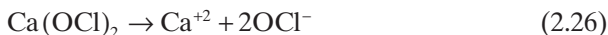
Total chlorine is the sum of the species shown. Totals may not add to exactly 100.00% due to rounding. Values were calculated assuming the following: values of K_a and K_b as reported in Table 2.2; $K_3 = 0.191$; $I = [H^+] + [Na^+]$; activity coefficients calculated using the modified Davies equation; and solutions containing only pure water, chlorine, and a sufficient amount of NaOH or acid to reach the stated pH. Acid was needed to reach pH 1 in each case and to reach pH 2 when the total chlorine concentration was 1000 mg/l as Cl₂.

TABLE 2.5. Chlorine Speciation in Chlorine Solutions as a Function of Temperature and Total Chlorine Concentration

Temperature (°C)	Total Cl ₂ (mg/l)	Resulting pH	Percentage of Total Chlorine			
			Cl ₂	HOCl	OCl ⁻	Cl ₃ ⁻
Without activity corrections						
15	250	2.47	3.924	96.073	0.001	0.003
15	1000	1.99	27.219	72.728	0.000	0.053
15	3500	1.70	58.901	40.873	0.000	0.226
15	7000	1.56	72.023	27.607	0.000	0.370
With activity corrections						
0	250	2.51	6.230	93.766	0.001	0.004
0	1000	2.07	33.276	66.664	0.000	0.060
0	3500	1.80	63.165	36.619	0.000	0.217
0	7000	1.67	74.899	24.756	0.000	0.345
15	250	2.50	3.508	96.489	0.001	0.002
15	1000	2.02	24.584	75.366	0.000	0.050
15	3500	1.72	55.699	44.071	0.000	0.230
15	7000	1.59	69.290	30.319	0.000	0.391
25	250	2.49	2.566	97.432	0.001	0.002
25	1000	2.00	20.412	79.544	0.000	0.044
25	3500	1.69	51.458	48.309	0.000	0.233
25	7000	1.55	65.983	33.604	0.000	0.413
35	250	2.49	2.011	97.987	0.001	0.001
35	1000	1.98	17.464	82.497	0.000	0.039
35	3500	1.66	48.070	51.696	0.000	0.233
35	7000	1.52	63.270	36.305	0.000	0.428
With activity corrections and with a dilution water alkalinity of 500mg/l as CaCO ₃						
15	3500	1.89	49.302	50.465	0.000	0.234
With activity corrections and with a dilution water <i>I</i> of 0.03 (TDS ≈ 1200mg/l; no Cl ⁻)						
15	3500	1.74	54.382	45.386	0.000	0.232

Total chlorine is the sum of the species shown. Totals may not add to exactly 100.000% due to rounding. Values were calculated assuming the following: values of K_d and K_a as shown in Table 2.2; $K_3 = 0.191$; $I = [H^+]$ (except for the last two entries, in which case I was increased by 0.01 and 0.03, respectively, to reflect the composition of the dilution water); activity coefficients calculated using the modified Davies equation; and solutions containing only pure water and chlorine unless otherwise indicated.

water. When used to chlorinate water or wastewater, sodium and calcium hypochlorite release hypochlorite ions as follows:



In each case, the OCl^- ions released into the water are able to associate with protons (H^+ ion), forming HOCl . The result is a mixture of HOCl and OCl^- in equilibrium as described in Equations (2.9) and (2.10) and illustrated in Table 2.3 and Figures 2.1 and 2.2. If a hypochlorite solution is acidified, as may happen if it is inadvertently added to a storage tank containing an acidic chemical such as alum, ferric sulfate, or sulfuric acid, the chlorine may be at least partially converted to Cl_2 , creating a very hazardous situation.

When disinfecting water or wastewater, the most significant difference between gaseous chlorine (Cl_2) and hypochlorite solutions, in terms of finished water quality, is that gaseous chlorine will consume alkalinity and make the water slightly more acidic due to hydrolysis of Cl_2 and dissociation of HOCl , whereas hypochlorite solutions are basic and will slightly increase the alkalinity and pH of the water being treated. The reactions of chlorine and hypochlorite solutions with alkalinity are described later in this chapter (see “Reactions of Chlorine with Selected Constituents”). The pH changes associated with chlorination can be large enough to significantly influence disinfection, the rates of many chemical reactions, and the corrosivity or scaling potential of the finished water, especially for waters that are only weakly buffered (relatively low in alkalinity); but the pH changes associated with chlorination can be readily offset by feeding a supplemental dose of an acid or base.

Concentrated hypochlorite solutions are unstable and gradually decompose, with chlorate and oxygen being the primary end products. The chemical reactions involved, factors influencing the rate of decomposition, and practical ways to limit decomposition are described in detail in Chapter 9. Concentrated chlorine solutions prepared from chlorine gas are relatively stable due to their low pH but will gradually decompose to chlorate if their acidity is neutralized.³¹ Decomposition of concentrated chlorine solutions is not an issue at full-scale treatment facilities, which neither store nor neutralize them; but stock solutions of chlorine prepared for use in the laboratory will gradually decompose if stored.

OXIDATION STATES OF CHLORINE

To properly understand the chemistry of chlorine in aqueous solutions, it is helpful to understand the oxidation states of the chlorine atom. Chlorine has

an atomic number of 17, indicating that there are 17 positively charged protons in the nucleus of the chlorine atom. For chlorine in its elemental (or reference) state, $\text{Cl}_2(\text{g})$, the charge of these protons is neutralized by 17 negatively charged electrons arranged in a series of shells. There are two electrons in the innermost shell and eight in the next, but these shells are “full” and the electrons in them are not available to participate in chemical reactions. The outer shell contains seven electrons, but has room for eight. This means that there are seven electrons available for reaction. If the chlorine atom were to lose all seven electrons in a chemical reaction, the atom would then have an excess of seven positive protons, giving the chlorine atoms a valence of +7. If the chlorine atom gains one more electron, thereby filling its outer shell, the number of electrons would exceed the number of protons by one, giving the chlorine atom a valence of -1 . An atom with a full outer shell, as is the case for the noble gases, is relatively stable and unreactive, as is the case for the chloride ion.

In chemical terms, the loss of electrons is referred to as oxidation and the gain of electrons as reduction. The chlorine atom can have different oxidation states, ranging from -1 to $+7$, depending on the number of electrons lost or gained. Examples of the chlorine atom in different oxidation states in compounds relevant to water are shown in Table 2.6.

When Cl_2 is reduced to two Cl^{-1} ions, each with a valence of -1 , or when a Cl^{+1} atom in a chlorine compound such as HOCl is reduced to Cl^{-1} , chlorine gains two electrons and is reduced. The substance from which the electrons are obtained loses two electrons and is oxidized. Therefore, chlorine is referred

TABLE 2.6. Oxidation States of Selected Chlorine Compounds

Compound	Formula	Atomic Oxidation States ^a		
Sodium perchlorate	NaClO_4	Na^{+1}	Cl^{+7}	$4(\text{O}^{-2})$
Sodium chlorate	NaClO_3	Na^{+1}	Cl^{+5}	$3(\text{O}^{-2})$
Chlorine dioxide	ClO_2	—	Cl^{+4}	$2(\text{O}^{-2})$
Sodium chlorite	NaClO_2	Na^{+1}	Cl^{+3}	$2(\text{O}^{-2})$
Hypochlorous acid	HOCl	H^{+1}	Cl^{+1}	O^{-2}
Sodium hypochlorite	NaOCl	Na^{+1}	Cl^{+1}	O^{-2}
Calcium hypochlorite	$\text{Ca}(\text{OCl})_2$	Ca^{+2}	$2(\text{Cl}^{+1})$	$2(\text{O}^{-2})$
Monochloramine	NH_2Cl	$2(\text{H}^{+1})$	Cl^{+1}	N^{-3}
Dichloramine	NHCl_2	H^{+1}	$2(\text{Cl}^{+1})$	N^{-3}
Nitrogen trichloride	NCl_3	—	$3(\text{Cl}^{+1})$	N^{-3}
Chlorinated lime	CaClOCl	Ca^{+2}	Cl^{+1} and Cl^{-1}	O^{-2}
Chlorine	Cl_2	—	$2(\text{Cl}^0)$	—
Trichloride ion	Cl_3^-	—	$2(\text{Cl}^0)$	Cl^{-1}
Hydrochloric acid	HCl	H^{+1}	Cl^{-1}	—
Sodium chloride	NaCl	Na^{+1}	Cl^{-1}	—

^aNote that the charges of the atoms must add up to the overall charge of the molecule or compound, which is zero for each of the compounds listed here except the trichloride ion.

to as an oxidant (or oxidizing agent), as are all other substances that are able to accept electrons from another substance.

When Cl_2 reacts with water, a special type of oxidation–reduction reaction, known as disproportionation, takes place (Eq. 2.3. One chlorine atom accepts an electron from the other, so one is reduced and the other is oxidized. However, there is no net loss or gain of electrons. The chlorine atom that loses an electron becomes oxidized to Cl^{+1} . This chlorine atom, now present in the HOCl molecule, is able to accept two electrons and is therefore an oxidant. The other chlorine atom accepts an electron and becomes a chloride ion, which is not able to accept another electron (since its outer shell is now full) and is therefore not an oxidant. Since the Cl_2 and HOCl molecules are both able to accept two electrons, hydrolysis of Cl_2 to HOCl results in no loss of oxidizing capacity; but this does not mean that Cl_2 and HOCl react with other species at the same rate.

FREE, COMBINED, AND AVAILABLE CHLORINE

Free chlorine is the sum of the species containing a chlorine atom in the 0 or +1 oxidation state that are not combined with ammonia or organic nitrogen. Expressed in units of moles per liter:

$$\text{Free chlorine} = [\text{Cl}_2] + [\text{HOCl}] + [\text{OCl}^-] + [\text{Cl}_3^-]. \quad (2.28)$$

In concentrated chlorine solutions prepared by dissolving Cl_2 in water, free chlorine will consist almost entirely of Cl_2 and HOCl , with perhaps a trace of Cl_3^- and virtually no OCl^- at all, as discussed earlier in this chapter. In water and wastewater treated with chlorine, the residual concentration of free chlorine will be relatively low and the pH of the water will be much less acidic, so the residual free chlorine will consist almost entirely of HOCl and OCl^- . Therefore, in textbooks and manuals describing the chlorination process and monitoring of chlorine residuals, free chlorine is typically defined as the sum of HOCl and OCl^- , the assumption (stated or unstated) being that the concentrations of Cl_2 and Cl_3^- are negligible. In hypochlorite solutions, only OCl^- is present (including any complexes and ion pairs it may form), so the free chlorine concentration is equal to the concentration of hypochlorite ion present.

Combined chlorine refers to chlorine that is combined with ammonia to form chloramines: monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramine (NCl_3), with the latter also (and more properly) referred to as nitrogen trichloride. The formation, properties, and reactions of chloramines are described in detail below. As shown in Table 2.6, the chlorine atoms in the combined chlorine species are all in the +1 oxidation state, so each is able to accept two electrons, the same number as Cl_2 . However, dichloramine has two chlorine atoms in the +1 state and trichloramine has

three; thus, compared with Cl_2 on a molar basis, dichloramine and trichloramine are able to transfer, respectively, two and three times as many electrons as Cl_2 does.

Since the species that make up free and combined chlorine have different molecular weights, their concentrations cannot simply be added together on a weight basis. Free chlorine can be expressed in moles per liter (Eq. 2.28), and both free and combined chlorine can be expressed in equivalents per liter. Although such units are preferred by chemists, they are generally avoided by practitioners, who prefer the units of milligrams per liter. A related problem is that the chemicals used for chlorination contain different amounts of chlorine and also vary in purity, as do solutions prepared with the same weights of different chemicals. To address these issues, water and wastewater treatment professionals adopted the practice of reporting concentrations of free and combined chlorine in “milligrams per liter as Cl_2 ” and comparing chlorine compounds and concentrated solutions on the basis of “available chlorine” (both of which merely disguise the use of chemical equivalents by using expressions that are more palatable to nonchemists).

In simple terms, available chlorine is a measure of the oxidizing capacity of a chemical or solution relative to that of pure Cl_2 , expressed as a weight percentage. In technical terms, available chlorine is defined as the quantity of iodine (I_2) liberated from a potassium iodide (KI) solution by a given weight of a compound or solution relative to the quantity of I_2 liberated by the same weight of Cl_2 . The technical definition is based on the liberation of iodine because all of the species making up free and combined chlorine can readily oxidize iodide to iodine (under the acidic conditions used in the assay) and, at the time this terminology was developed, the iodometric method (Chapter 3) was the only quantitative method in commercial use. For chlorine compounds (but not solutions), available chlorine can also be defined as the weight percentage of Cl in the compound times the number of electrons transferred per chlorine atom. Fundamentally, available chlorine is simply a measure of the number of electrons transferred by a given weight of chemical or volume of solution. Thus, the strength of any oxidant can be expressed in terms of available chlorine, but the use of this term is normally limited to chlorine compounds.

When chlorine is added to a KI solution, it reacts quantitatively with iodide to liberate iodine as follows:

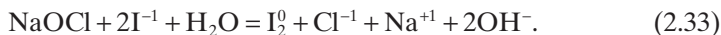


Thus, each molecule of Cl_2 gains two electrons, forming two Cl^- ions; simultaneously, two I^- ions each lose an electron and form I_2 . Other chlorine species react in similar fashion:

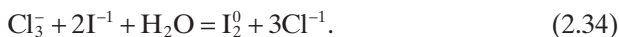
Hypochlorous acid:



Sodium hypochlorite:



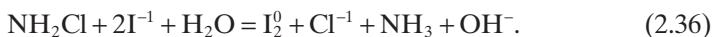
Trichloride ion:



Calcium hypochlorite:



Monochloramine:



Dichloramine:



Thus, each mole of chlorine atoms in the +1 oxidation state will liberate 1 mol of I_2 on a quantitative basis, so 1 mol of HOCl, OCl^{-} , Cl_3^{-} , NaOCl, or NH_2Cl can be said to contain 1 mol of available chlorine. Since calcium hypochlorite and dichloramine each contain two chlorine atoms in the +1 oxidation state, 1 mol of these compounds will liberate 2 mol of I_2 ; and 1 mol of these compounds contains 2 mol of available chlorine. Likewise, 1 mol of trichloramine (not shown) will liberate 3 mol of I_2 , and therefore contains 3 mol of available chlorine.

When a sample is analyzed for free chlorine, whether using iodide or another appropriate reagent (Chapter 3), all of the species involved are considered chemically equivalent (since each is able to transfer 2 equivalents of electrons per mole). Thus, the free chlorine concentration can be expressed in moles per liter as Cl_2 , equivalents per liter as Cl_2 , or milligrams per liter as Cl_2 ; and these units can be readily interconverted using the molecular weight (70.906) or equivalent weight (35.453) of chlorine. In the late 1940s, a committee of the American Water Works Association³² adopted the use of the terms “free available chlorine residual” and “combined available chlorine residual,” but since both free chlorine and combined chlorine consist only of species containing available chlorine, the term “available” was eventually recognized to be redundant and was dropped from the standard terminology.³³

Since the chloramine species are not chemically equivalent, it would be meaningless to add their molar concentrations together. However, whether they are determined individually or collectively, their combined oxidizing capacity can be determined using an appropriate method (Chapter 3) and expressed in equivalents per liter, which can then be converted into the units of milligrams per liter as Cl_2 . Very often, this conversion is made by using a simple formula or by electronic means (in an analyzer or computer). If the species making up combined chlorine are not determined individually, their overall molar concentration will not be known, but in practice only their oxidizing capacity, relative to that of Cl_2 , is important.

For bulk chemicals and solutions, a practitioner generally needs to know how much available chlorine they contain so the proper dosage can be added to the water being treated. In the case of 100% pure calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, the percentage of available chlorine is determined as follows:

$$\text{Molecular weight of } \text{Ca}(\text{OCl})_2 = 40.08 + 2(16.00 + 35.453) = 142.986$$

$$\text{Available chlorine} = 2 \text{ mol } \text{Cl}_2 \text{ per mole of } \text{Ca}(\text{OCl})_2$$

$$\text{Molecular weight of } \text{Cl}_2 = 2 \times 35.453 = 70.906$$

$$\text{Percent available chlorine} = 100 \times (2 \times 70.906) / (142.986) = 99.2\%.$$

Thus, adding 1 lb of 100% pure $\text{Ca}(\text{OCl})_2$ to a water supply or to a tank used to prepare a chlorine solution would be the same as adding 0.992 lb pound of pure chlorine. Similar calculations were made to determine the available chlorine for the other chlorine compounds included in Table 2.7. Some find it disconcerting that a compound not containing pure chlorine can have an available chlorine content greater than 100%, but available chlorine is simply a measure of oxidizing capacity and some chemicals have greater oxidizing

TABLE 2.7. Available Chlorine Content of Selected Chlorine Compounds

Compound	Molecular Weight	Available Chlorine	
		mol/mol	%
Cl_2	70.91	1	100.0
HOCl	52.46	1	135.2
NaOCl	74.44	1	95.3
$\text{Ca}(\text{OCl})_2$	142.99	2	99.2
CaClOCl	126.98	1	55.8
NH_2Cl	51.48	1	137.7
NHCl_2	85.92	2	165.1
NCl_3	120.37	3	176.7

capacity than chlorine. Even though chlorine contains two chlorine atoms, they are in the 0 oxidation state and have only half the oxidizing capacity of a chlorine atom in the +1 oxidation state, as is the case for the chlorine atoms in HOCl, OCl⁻, and NH₂Cl.

Multiplying the dosage of chlorine chemical added, in milligrams per liter, by percent available chlorine yields the dosage of chlorine in milligrams per liter as Cl₂, the customary units. This is particularly useful when the purity of the chemical varies, as is the case for commercial-grade Ca(OCl)₂, which typically contains only 65 available chlorine, and for NaOCl, which is typically shipped at a strength of 12%–16% *by volume* and may be diluted to 5%–10% strength upon receipt.

Example. What dosage of Ca(OCl)₂ having 65% available chlorine must be added to a water supply if the desired chlorine dosage is 4.0 mg/l as Cl₂?

$$(4.0 \text{ mg/l as Cl}_2)/(0.65 \text{ mg Cl}_2/\text{mg Ca(OCl)}_2) = 6.15 \text{ mg/l of Ca(OCl)}_2.$$

Example. How many gallons of 10% NaOCl solution must be added to 1 million gallons (MG) of water to provide a chlorine dosage of 3.0 mg/l as Cl₂? (Note that for NaOCl solution, available chlorine is expressed as a “trade percentage” on a weight per volume basis, with a trade percentage of 10% equal to 100 g/L available chlorine. Also note that 1 mg/l = 1 ppm = 1 gal/MG.)

$$(8.34 \text{ lb/gal})(10\%) = 0.834 \text{ lb Cl}_2 \text{ per gallon of NaOCl solution}$$

$$\text{Cl}_2 \text{ required} = (3.0 \text{ ppm})(8.34 \text{ lb/gal})(1 \text{ MG}) = 25 \text{ lb}$$

$$(25 \text{ lb Cl}_2)/(0.834 \text{ lb Cl}_2/\text{gal}) = 30.0 \text{ gal of 10\% NaOCl.}$$

CHLORINE AND NITROGENOUS COMPOUNDS

Chlorine reacts with many organic and inorganic substances in water, both natural and man made, but its reactions with nitrogenous substances are particularly important, especially those with ammonia and organic nitrogen, which are also very complex. Chlorine reacts with ammonia to form chloramines, which offer certain advantages when used in water distribution systems (Chapter 4); but reactions between chlorine and nitrogenous compounds can reduce the ability of chlorine to kill pathogens and to oxidize chemical contaminants, and can increase chlorine demand, interfere with the determination of residuals (Chapter 3), complicate control of the disinfection process, cause taste and odor problems, and produce chemical by-products that may be harmful to human health or to the environment. Therefore, the reactions of chlorine with nitrogenous compounds merit detailed discussion.

Nitrogenous Compounds in Water and Wastewater

The dominant nitrogen species in natural waters, on a concentration basis, is diatomic nitrogen (N_2), which has a solubility of about 14 mg/l at 25 °C in water in equilibrium with ambient air at 1 atm. However, N_2 does not react with chlorine and, aside from its conversion to other forms by nitrogen-fixing bacteria, it is inert in water and need not be further considered herein.

Both organic and inorganic forms of nitrogen are found in water in wastewater. Important examples of each are as follows:

<u>Inorganic Nitrogen</u>	<u>Organic Nitrogen</u>
Ammonia	Amino acids
Nitrate	Proteins
Nitrite	Amines

In natural waters, the concentrations of these compounds are typically well below 1 mg/l, but there are notable exceptions. For example, ammonia is often found in alluvial aquifers at concentrations of about 1 mg/l as N, and it has been found in some deeper aquifers at much higher concentrations. Only small concentrations of organic nitrogen are typically present in water supplies. A recent study^{34,35} of 28 water treatment plants found an average organic nitrogen concentration of only 0.15 mg/l as N. (The concentrations of nitrogen compounds in water are normally reported in milligrams per liter as N, in much the same way that chlorine species are reported in milligrams per liter as Cl_2 , so that different species can be added together and to facilitate nitrogen balance calculations.)

Domestic wastewaters generally contain relatively high concentrations of ammonia nitrogen (15–40 mg/l) and organic nitrogen (5–15 mg/l). During treatment, most of the organic nitrogen (and especially the portion attributable to proteins, polypeptides, amino acids, and urea) is either settled out (if particulate) or converted to ammonia nitrogen, so domestic wastewater effluents typically contain only a few milligrams per liter of organic nitrogen. The ammonia may be partially or fully converted to nitrate if treatment includes nitrification, and nitrate may in turn be reduced to nitrogen (N_2) in treatment plants that practice biological nutrient removal. Despite the treatment provided, a typical secondary effluent still contains enough ammonia and organic nitrogen to interfere with the disinfection process and, if there is not sufficient dilution water in the receiving stream, perhaps with downstream disinfection processes as well. Some tertiary treatment processes can greatly improve effluent quality in this regard.

Industrial wastewater effluents vary greatly in composition. Some are similar in composition to domestic wastewater, some contain little or no organic or inorganic nitrogen, and some contain nitrogenous compounds not typically found in domestic wastewater, for example, various heterocyclic compounds, amines, and azides, as well as nitro and nitroso compounds containing partially oxidized forms of nitrogen. It should be noted that the term

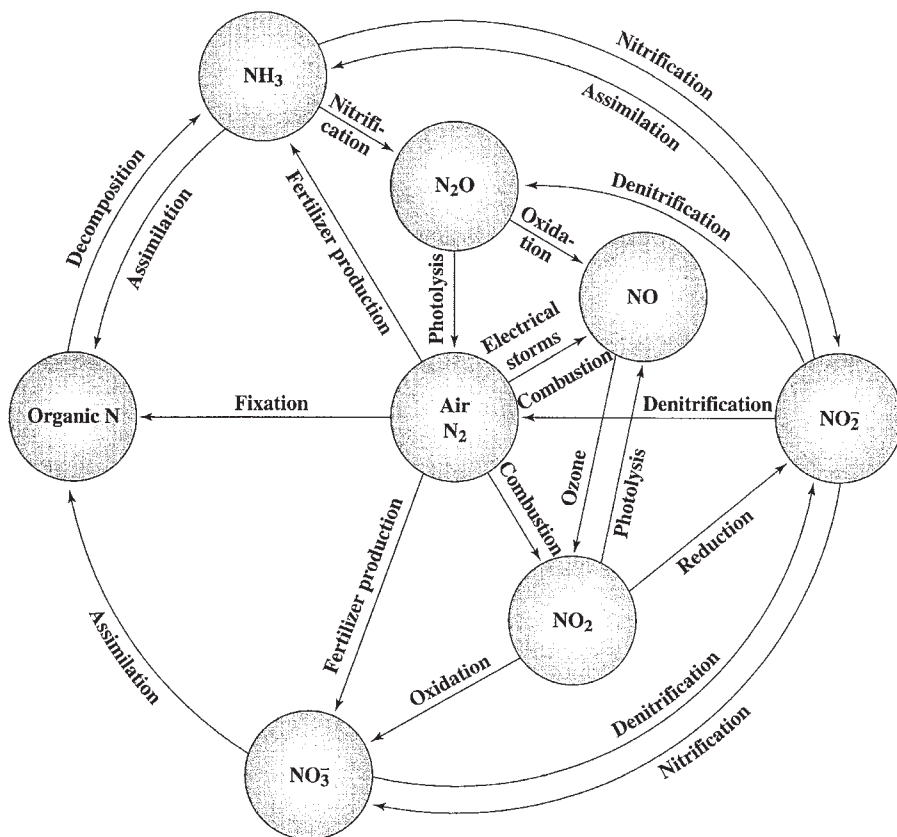


Figure 2.3. The nitrogen cycle (from Sawyer et al.,³⁶ reproduced with permission of The McGraw-Hill Companies).

“organic nitrogen,” as used in the field of water and wastewater treatment,³³ is defined as “organically bound nitrogen in the trinegative state,” which includes most of the organic nitrogen present in domestic wastewater but excludes a number of organic nitrogen compounds that may be present in certain industrial effluents.

An important characteristic of nitrogenous compounds in water is that they can readily undergo transformation from one form to another, primarily as the result of biological activity. As illustrated in Figure 2.3, key transformations in water include nitrification (conversion of ammonia to nitrite and then nitrate); denitrification (the conversion of nitrate to N_2); the decomposition of organic nitrogen (to ammonia); and biological assimilation of ammonia and nitrate by plants, algae, and bacteria to produce protein, nucleic acids, and other forms of organic nitrogen.³⁶

Nitrogen transformations can be readily observed by collecting and analyzing water quality samples downstream from a wastewater discharge during the

warmer months (or by keeping a wastewater sample aerobic and analyzing it over time). The major nitrogen species follow a predictable pattern, with the levels of ammonia and organic nitrogen decreasing and the level of nitrate increasing,³⁶ provided that an excess of nitrogen is available for the growth of plants and microorganisms. By observing these transformations, one can obtain a general indication of the “freshness” of a wastewater discharge, which can be of help in tracking a pollution source, but there are generally too many variables involved for this to be of much use in assessing risks to public health.³⁶ Nitrite is generally observed only under transient condition, that is, at the onset of nitrification, since conversion of nitrite to nitrate is much more rapid than conversion of ammonia to nitrite once the proper microbial population is established.³⁶

Nitrogenous compounds can undergo similar transformations in water treatment plants and water distribution systems if the residual chlorine concentration is not sufficient to inhibit biological activity. This is most likely to occur in remote parts of the distribution system where the residual chlorine has decayed. In fact, an increase in the concentration of nitrite or nitrate provides a good indication that biofilm growth is occurring, which may eventually lead to an increase in corrosion and taste and odor problems.

The reactions of chlorine with ammonia and organic nitrogen are of particular importance and are described in detail later in this chapter. Oxidation of nitrite with chlorine is briefly discussed in the section of this chapter on the reactions of chlorine with selected contaminants. Nitrate is already fully oxidized and therefore does not react with chlorine.

Chlorination of Ammonia to Form Chloramines

Chloramines are formed when chlorine reacts with ammonia nitrogen naturally present in the water or added for the purpose of forming chloramines. Chlorination of ammonia in dilute aqueous solutions can involve as many as 14 different chemical reactions and an unknown intermediate species,³⁷ as shown in Figure 2.4; but formation of the three chloramine species can be described in simplified fashion by the following three reactions in sequence:



When chloramines are intentionally formed to produce a combined chlorine residual, the process is commonly referred to as chloramination. In water treatment practice, it is desirable to form primarily monochloramine (Eq. 2.38) and to avoid forming dichloramine and trichloramine (Eqs. 2.39 and 2.40), which can impart chlorinous taste and odor to the water. Trichloramine is especially troublesome because it is highly volatile. Chloramine formation is also an integral part of the breakpoint reaction, in which chlorine reacts

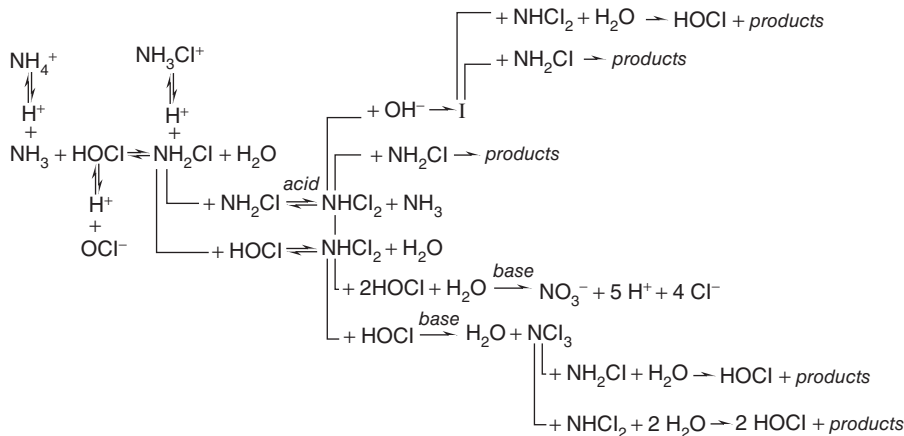


Figure 2.4. Diagram of the chlorine–ammonia reaction scheme described by Jafvert and Valentine.³⁷ (Products include N_2 , H_2O , Cl^- , H^+ , NO_3^- , and unidentified compounds, and I represents an unidentified intermediate compound.)

with ammonia nitrogen to form diatomic nitrogen, as described in detail below.

Monochloramine. Monochloramine formation (Eq. 2.38) is a second-order reaction that can be explained by either the reaction of HOCl with NH_3 or the reaction of OCl^- with NH_4^+ . Weil and Morris³⁸ favored the former mechanism, and a number of later investigators^{39,40} agreed with them. If these investigators are correct, monochloramine formation is a bimolecular reaction in which a molecule of HOCl (not Cl_2 or OCl^-) reacts with a molecule of unionized ammonia (NH_3 , and not the ammonium ion NH_4^+) to exchange a chlorine atom (Cl^+) for a hydrogen atom (H^+), thereby forming monochloramine and water.

The rate of monochloramine formation (Eq. 2.38) depends very strongly on pH and the relative concentrations of the reactants, and it is also strongly influenced by temperature.¹⁰ Its strong dependence on pH is not surprising since HOCl is a weak acid and NH_3 is a weak base. At 25°C , HOCl has a pK_a value of about 7.54 (see Eq. 2.10 and Table 2.2) and NH_4^+ has a pK_a value of 9.25.²⁸ Thus, HOCl predominates at pH values below 7.54, while NH_3 predominates at pH values above 9.25, so there is no pH value at which both species are dominant. The reaction of HOCl with NH_3 is first order with respect to each reactant (second order overall),^{38,41} so the maximum rate of reaction occurs when the product of $[\text{HOCl}]$ and $[\text{NH}_3]$ is maximized. Using basic calculus, it can be shown that this occurs (for this and similar reactions) at a pH value equal to $(pK_a + pK_b)/2$, which in this case equals 8.40 at 25°C .

The forward second-order rate constant, k_1 , for monochloramine formation by reaction of the un-ionized species HOCl and NH_3 (Eq. 2.38) was found by Weil and Morris³⁸ to have a value of $6.17 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C . They also

determined that the temperature-dependence of k_1 could be accounted for using the following equation:

$$k_1 = 4.17 \times 10^8 \times e^{-2500/RT}, \quad (2.41)$$

where k_1 has units of $M^{-1}s^{-1}$, $R = 1.987 \text{ cal/mol-K}$ (universal gas constant), and T is the absolute temperature ($273.15 + ^\circ\text{C}$). Morris and Isaac³⁹ evaluated several studies of monochloramine formation and found that a value of k_1 of $4.2 \times 10^6 M^{-1}s^{-1}$ at 25°C and a value of $k_1 = 6.6 \times 10^8 \times e^{-1510/T} M^{-1}s^{-1}$ for other temperatures “best represent the totality of the data”; but the combined data set was quite scattered relative to the data of Weil and Morris³⁸ and included data from studies not specifically designed to examine temperature effects over the same range of temperatures. Recently, using more accurate methods, Qiang and Adams,⁴⁰ found the value of k_1 to be $3.07 \times 10^6 M^{-1}s^{-1}$ at 25°C , about half the rate estimated by Weil and Morris; and they also found the rate to be slightly more dependent on temperature, with the dependence given by the following equation:

$$k_1 = 5.4 \times 10^9 \times e^{-2237/T}. \quad (2.42)$$

The reaction times shown in Table 2.8 for 99% conversion of chlorine to monochloramine in 25°C water were determined using Equation 2.42 to estimate k_1 , ignoring competing reactions and taking into consideration the fraction of chlorine present as HOCl and the fraction of ammonia nitrogen (defined as the sum of NH_3 and NH_4^+) present as NH_3 . As these calculations illustrate, the reaction proceeds very rapidly at pH values typically encountered in water and wastewater treatment. It slows appreciably at lower temperatures but at 0°C and pH 7, with conditions otherwise the same as stated in Table 2.8, the reaction time is 5.02s, slower by an order of magnitude than at 25°C , but still quite rapid. Ionic strength effects were ignored in calculating these reaction times but are expected to be minimal under typical water and wastewater treatment conditions.³⁸

The rate of monochloramine formation is also strongly influenced by the $\text{Cl}_2:\text{N}$ ratio. The reaction times listed in Table 2.8 were determined for a high concentration of chlorine (14.2mg/l as Cl_2) reacting with a large excess of ammonia nitrogen, as might occur when disinfecting a nonnitrified wastewater discharge. The reaction slows considerably at lower chlorine concentrations and at higher ratios of chlorine to nitrogen, which are typical of drinking water disinfection. For example, with an initial chlorine concentration of 1 mg/l as Cl_2 and an initial ammonia nitrogen concentration of 0.2mg/l as N, it would take 99s for 99% of the chlorine to react at pH 8.4 and 25°C , assuming that monochloramine is the only product being formed; and the reaction time would increase to 438min at pH 5 and to 74min at pH 11. However, at pH 5, dichloramine formation (Eq. 2.39) would also be expected to occur, as discussed below.

TABLE 2.8. Reaction Times for 99% Conversion of Free Chlorine to Monochloramine at 25°C

pH	Reaction Time (s)
4	321
5	32.2
6	3.31
7	0.42
8	0.13
8.4	0.12
9	0.15
10	0.63
11	5.44
12	53.6

Assuming an initial free chlorine concentration of 0.2×10^{-3} M, an initial ammonia nitrogen concentration of 0.8×10^{-3} M, and absence of other reaction products, and ignoring ionic strength effects.

Monochloramine exists in equilibrium with HOCl and NH_3 , as shown in Equation 2.38. Margerum et al.⁴² estimated the value of the equilibrium constant for this reaction to be 3.8×10^{10} . Since the equilibrium lies so strongly to the right, this reaction is often assumed to go to completion, which is a reasonable assumption for some purposes, such as calculating chemical requirements. However, when monochloramine is present there will also be a small amount of free chlorine (HOCl) present. This may be important analytically, for example, in causing the breakthrough of combined chlorine into the free chlorine fraction when measuring chlorine residuals (Chapter 3); and it may also play a role in the mode of action of monochloramine in killing or inactivating microorganisms, as discussed below.

Stoichiometrically, monochloramine formation (Eq. 2.38) involves the reaction of 1 mol of HOCl with 1 mol of ammonia nitrogen. On a weight basis, this translates to a chlorine-to-nitrogen ($\text{Cl}_2\text{:N}$) ratio of $70.906/14 = 5.06$, or about 5:1. In water treatment practice, a weight ratio between 3:1 and 5:1 is typically employed to avoid forming dichloramine and trichloramine (Eqs. 2.39 and 2.40), which impart an objectionable chlorinous taste and odor to the water, while minimizing the amount of free ammonia present in the water, which can promote the growth of nitrifying bacteria. Much lower ratios can be encountered when chlorine is used to disinfect nonnitrified secondary effluents containing high concentrations of ammonia nitrogen. To prepare relatively pure solutions of NH_2Cl in the laboratory, a chlorine solution can be added dropwise, with rapid stirring, to a solution containing excess ammonia and buffered to a pH of 8–9.

Dichloramine and Trichloramine. Once monochloramine begins to form, dichloramine and trichloramine also begin to form (Eqs. 2.39 and 2.40), but

at this point there are numerous competing reactions occurring (Fig. 2.4), each at a different rate that may be strongly influenced by pH, temperature, and the initial and relative concentrations of the reactants. Tracking the progress of each reaction and the species formed and lost requires a sophisticated computer model, such as that described by Jafvert and Valentine;³⁷ but a good qualitative understanding of the chemistry involved, coupled with basic stoichiometry, is sufficient to effectively design and operate a disinfection process involving either chloramines or the production of a free chlorine residual in a water initially containing ammonia nitrogen.

Dichloramine and trichloramine can be formed as shown in Equations 2.39 and 2.40, but these reactions do not proceed to completion under the conditions associated with water and wastewater treatment. Dichloramine formation requires a molar $\text{Cl}_2\text{:N}$ ratio of 2:1, and trichloramine formation requires a 3:1 ratio. However, at molar ratios of 1.5:1 and higher, ammonia nitrogen is destroyed (converted to diatomic nitrogen, N_2) in what is known as the “breakpoint reaction” (described in detail below). Therefore, the amounts of dichloramine and trichloramine that can be formed in practical applications are limited.

Dichloramine formation (Eq. 2.39) depends strongly on pH and the $\text{Cl}_2\text{:N}$ ratio, and to a lesser extent on temperature. At neutral pH values (7–8), dichloramine forms much more slowly than monochloramine (in minutes to hours, rather than seconds, depending on the conditions). At $\text{Cl}_2\text{:N}$ weight ratios less than 5:1 at neutral pH, very little dichloramine will form because both the kinetics and equilibria involved strongly favor monochloramine. Dichloramine formation will occur at $\text{Cl}_2\text{:N}$ weight ratios higher than 5:1 at neutral pH, but this leads to rapid loss of nitrogen in the breakpoint reaction described below.

Dichloramine can be formed by the direct reaction of HOCl with NH_2Cl , as shown in Equation 2.18. In the presence of NH_3 , HOCl can be obtained from hydrolysis of NH_2Cl to HOCl (the reverse of Eq. 2.38), but equilibrium strongly favors NH_2Cl . Morris⁴¹ estimated that at pH 7 and 25 °C, only 0.58% of the chlorine in a 2 mg/l solution of pure NH_2Cl would hydrolyze to HOCl ; and even less would be formed in the presence of excess NH_3 . Thus, dichloramine formation by this mechanism is expected to be limited; but dichloramine can also be formed by disproportionation of monochloramine, that is, the reaction of two molecules of monochloramine to form dichloramine and ammonia:



This reaction is acid catalyzed,^{41,43,44} and dichloramine formation is therefore favored at lower pH values.

Fair et al.,⁴³ based on spectrophotometric measurements, estimated the value of the equilibrium constant for Equation 2.43, K_{md} , to be 6.7×10^5 where, assuming that molar concentration equals activity,

$$K_{md} = \frac{[\text{NH}_4^+][\text{NHCl}_2]}{[\text{H}^+][\text{NH}_2\text{Cl}]^2}. \quad (2.44)$$

Morris and Isaac³⁹ noted that the value of K_{md} reported by Fair et al.⁴³ should be regarded as a first approximation and that the more well-defined experiments of Gray et al.^{45,46} yield a value of 4×10^6 at zero ionic strength. They also noted that it can take a day or so for NH_2Cl and NHCl_2 to reach equilibrium (since NHCl_2 forms very slowly), so measurements at shorter contact times may greatly underestimate the amount of NHCl_2 that will eventually be present at equilibrium.

Because the species involved in the equilibrium relationship between monochloramine and dichloramine (Eq. 2.43) are interrelated by chlorine and nitrogen balances, the ratio of dichloramine to monochloramine depends not only on pH but also on the $\text{Cl}_2:\text{N}$ ratio. McKee et al.,⁴⁷ building on the work of Fair et al.⁴³ presented in a second-hand source, derived equations to express the amounts of NH_4^+ , NH_2Cl , and NHCl_2 present at equilibrium as fractions of the total concentration of ammonia nitrogen initially present and as a function of pH and the $\text{Cl}_2:\text{N}$ ratio. In deriving these equations, they assumed that trichloramine formation is negligible, that all of the ammonia nitrogen is present in the form of NH_4^+ or chloramines, and that the water is pure, such that added chlorine is completely converted to chloramines.

Using the equations of McKee et al.⁴⁷ to solve for the molar ratio of NHCl_2 to NH_2Cl , the following expression was obtained:

$$\frac{[\text{NHCl}_2]}{[\text{NH}_2\text{Cl}]} = \frac{1}{2} \left[\frac{BZ}{1 - \sqrt{1 - BZ(2 - Z)}} - 1 \right], \quad (2.45)$$

where Z is the molar $\text{Cl}_2:\text{N}$ ratio and B is defined as follows:

$$B = 1 - 4K_{md} [\text{H}^+]. \quad (2.46)$$

Since NHCl_2 contains twice as much available chlorine as NH_2Cl does on a molar basis, the ratio of NHCl_2 to NH_2Cl is twice the molar ratio calculated using Equation (2.45) when both species are expressed in moles per liter as Cl_2 or milligrams per liter as Cl_2 . At pH values of 8 or higher, a significant fraction of the ammonia nitrogen is present in the form of NH_3 rather than NH_4^+ . To account for the presence of NH_3 , the expression for B can be modified as follows:

$$B = 1 - 4K_{md} [\text{H}^+] (1 + 5.62 \times 10^{-10} / [\text{H}^+]), \quad (2.47)$$

where 5.62×10^{-10} is the acid ionization constant of NH_4^+ at 25 °C.

Using Equations (2.45) and (2.47) and assuming $K_{md} = 4 \times 10^6$, the percentage of combined chlorine present as NHCl_2 was calculated for pH values of 5–11 and $\text{Cl}_2:\text{N}$ weight ratios of 1:1, 3:1, and 5:1. The results, shown in

TABLE 2.9. Percentage of Combined Chlorine Present as Dichloramine at 25 °C as a Function of pH and Cl₂:N Ratio

pH	Percentage of Combined Chlorine Present in the Form of NHCl ₂ for a Cl ₂ :N Weight Ratio of the Following:		
	1:1	3:1	5:1
5	79	89	93
6	49	70	80
7	14	37	55
8	2.0	9.4	28
9	0.31	1.7	13
10	0.13	0.75	8.2
11	0.11	0.65	7.6

Estimated using Equations 2.45 and 2.47 assuming that $K_{md} = 4 \times 10^6$, NCl_3 is negligible, and equilibrium is attained. Since NHCl_2 contains twice as much available chlorine as NH_2Cl , these percentages would be lower if expressed on a molar basis rather than as a percentage of the combined chlorine residual.

Table 2.9, clearly illustrate the increased formation of dichloramine at lower pH values and higher Cl₂:N ratios. These results are in reasonably good agreement with the estimates and experimental observations summarized in Figure 2.5,^{43,48–51} as well as the data of Williams,^{52,53} if it is recognized that much less dichloramine is initially formed and that it may take a day or so for equilibrium to be attained. Initial and equilibrium distributions of monochloramine and dichloramine are depicted in Figure 2.6.

In actual water and wastewater treatment applications, conditions vary (including pH, temperature, and Cl₂:N ratio); equilibrium is often not reached within the confines of the treatment plant; chlorine-consuming substances may be present; and the methods used to determine residual chlorine will be limited in their precision and accuracy and possibly subject to interferences. Therefore, it is generally not possible or practical to accurately predict the concentrations of monochloramine and dichloramine that will be present in a particular water having a combined chlorine residual. However, analytical methods are available (Chapter 3) that, in the absence of interferences, can provide reasonably good estimates of the concentrations of monochloramine and dichloramine actually present. Should it be necessary or desirable to reduce the fraction of combined chlorine present in the form of dichloramine, this can be readily accomplished by increasing the pH or reducing the Cl₂:N ratio.

Trichloramine, more properly known as nitrogen trichloride, can be formed as shown in Equation (2.40). At neutral pH values, it forms slowly relative to

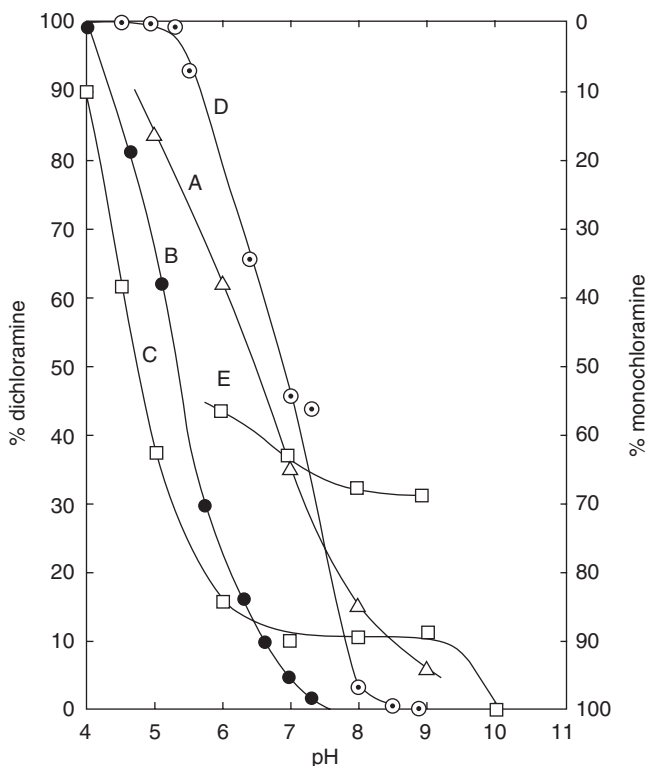


Figure 2.5. Distribution of monochloramine and dichloramine, as a percentage of combined chlorine, with pH. Curve A = Fair et al.⁴³ (calculated assuming $K_{md} = 6.7 \times 10^5$), $\text{Cl}_2:\text{N} = 5:1$ (wt); curve B = Palin,⁴⁸ $\text{Cl}_2:\text{N} = 5:1$ (wt), 2-h contact; curve C = Baker,⁴⁹ $\text{Cl}_2:\text{N} = 4:1$ (wt), 2-h contact; curve D = Chapin⁵⁰ (excess NH_3); curve E = Kelly and Sanderson,⁵¹ $\text{Cl}_2:\text{N} = 2:1$ (wt).

monochloramine and dichloramine,^{39,54} and its hydrolysis is base catalyzed. Its formation is favored by low pH values (1–4), especially those low enough to favor the formation of $\text{Cl}_2(\text{aq})$, since NHCl_2 reacts about 10^4 times more rapidly with $\text{Cl}_2(\text{aq})$ than with HOCl .⁵⁴ Therefore, strongly acidic conditions are typically employed to intentionally form trichloramine in the laboratory.^{39,54–56} At pH values below 3, trichloramine is the only stable chloramine.³¹ Trichloramine is stable in the presence of free chlorine; but it is unstable when free chlorine is absent, and at neutral pH values it is unstable in the presence of other chloramine species or ammonia.^{48,54}

It was once thought that trichloramine would not form at pH values above 4.4;⁵⁷ but it has been reported to form during water treatment at pH values as high as 9 when a high $\text{Cl}_2:\text{N}$ ratio is employed (D.B. Williams, pers. comm.), especially in the presence of organic nitrogen. Trichloramine

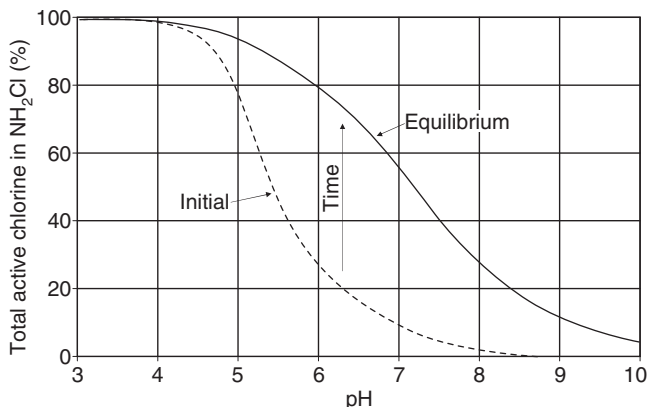


Figure 2.6. Initial and equilibrium distributions of NHCl_2 and NH_2Cl for a $\text{Cl}_2:\text{N}$ ratio of 1:1 at 25°C .³⁹ Adapted from Isaac, R.A. Transfer of Active Chlorine from NH_2Cl to Organic Nitrogenous Compounds. PhD Thesis, Harvard University, Cambridge, MA, 1981 (with the permission of the author).

formation nominally requires a $\text{Cl}_2:\text{N}$ molar ratio of 3:1 (weight ratio of ~15:1) and is known to be favored by higher $\text{Cl}_2:\text{N}$ ratios; but at pH values of 5 or less, it can form even at $\text{Cl}_2:\text{N}$ molar ratios as low as 1:1. Trichloramine formation can be minimized by maintaining a neutral pH and by avoiding excessive $\text{Cl}_2:\text{N}$ ratios when practicing breakpoint chlorination. Trichloramine can be removed by air stripping, activated carbon filtration, and dechlorination.⁵⁷

When present in potable water, trichloramine imparts a highly objectionable taste and a foul, pungent, chlorinous odor. It is highly volatile, making it easy to detect and also easy to remove. It is so volatile that it is difficult to collect for analysis, but it is never necessary to determine its concentration. The operator needs only to know whether it is there; and this is easily determined either by its odor or by the eyes tearing. It is the only chlorine species that causes tearing of the eyes, which is especially noticeable when it is formed in indoor swimming pools. It is unstable in sunlight, so it is less noticeable in outdoor pools during the day, especially if a gentle breeze is facilitating its dispersal.

Nitrogen trichloride cannot exist without the presence of HOCl . It has been known to form in the distribution system long after the water has left the treatment plant. This situation can be corrected by converting the free chlorine residual to combined chlorine by postammoniation. However, if NCl_3 has already begun to form, the preferred method is complete dechlorination of the finished water (to completely remove the NCl_3 , with the nitrogen reverting to ammonia) followed by rechlorination. This method was often used in the 1930s when superchlorination was common practice. Superchlorination was employed in an effort to adequately treat water containing relatively high concentrations of ammonia and organic nitrogen originating from upstream

discharges of raw or partially treated sewage, or to treat water polluted with phenolic wastes. Today, superchlorination is rarely, if ever, practiced in developed countries. Raw water supplies are generally protected from receiving such wastes, and modern drinking water treatment practices are designed to minimize the formation of disinfection by-products (DBPs), which makes superchlorination unacceptable.

The Breakpoint Reaction

Early Work. The practice of disinfecting drinking water with chlorine grew rapidly during the 1920s and 1930s and was heavily studied by chemists, microbiologists, treatment plant superintendents and operators, and others. A number of early investigators, including Rideal,⁵⁸ Race,⁵⁹ Holwerda,⁶⁰ Chapin,^{50,55} Gerstein,⁶¹ Enslow,⁶² and Griffin (A.E. Griffin, pers. comm.), recognized that chlorine reacts with ammonia and began to study such things as chloramine formation, reactions of chlorine with other nitrogenous compounds, the disinfecting properties of different chlorine species, and taste and odor control. Unfortunately, the analytical method then in use to control the process (the orthotolidine method; see Chapter 3) did not distinguish between free and combined chlorine. Investigators noted the existence of an initial chlorine demand in natural waters, and some, such as Faber,⁶³ noted that as the dosage of chlorine increased the chlorine residual would initially rise but would then fall before rising again. Ammonia was found to “stabilize” the chlorine residual and to also reduce chlorinous tastes and odors, so some water utilities began to intentionally add ammonia to the water.⁶⁴

During this time, many water utilities that practiced chlorination were experiencing significant taste and odor problems—some of them attributable to the chlorination process and some to other causes such as algae, natural organic matter, or upstream discharges of industrial wastes. Some utilities began to practice “superchlorination,” using very high chlorine dosages in an attempt to eliminate (to “burn out”) the taste and odor problems associated with chlorination.⁶³ This was effective in some cases, for example, where dichloramine was being formed at lower chlorine dosages or where the taste and odor were evidently associated with chemicals such as chlorophenols, which are formed when chlorine is added to water polluted with phenol, but which are broken down by higher chlorine dosages. Other utilities found that superchlorination followed by dechlorination and rechlorination produced better-tasting water. These utilities were employing very high $\text{Cl}_2\text{:N}$ ratios, which most likely resulted in the formation of large amounts of dichloramine and trichloramine. Although their understanding had advanced to the point where they had begun to recognize the nature of the problem, their knowledge was not sufficient to enable them to reliably avoid the problem.

It is clear that earlier investigators^{55,60} observed and understood from a chemical perspective what later came to be called the “breakpoint reaction”; but, as noted by Wei and Morris,⁶⁵ Griffin^{66–68} and Calvert⁶⁹ are generally

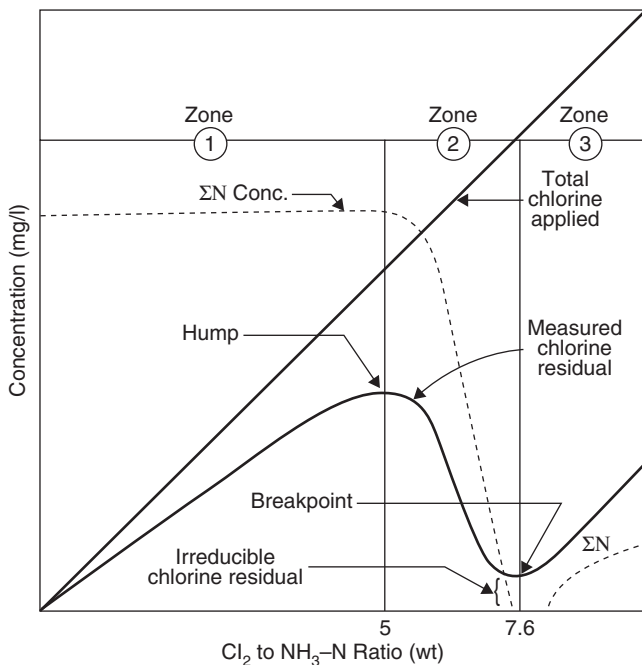


Figure 2.7. The classic breakpoint curve (ΣN is the sum of nitrogen species, including both $\text{NH}_3\text{-N}$ and chloramines).

credited with clearly elucidating the breakpoint curve (Fig. 2.7), in the terminology still in use today, and with clearly recognizing and conveying the importance of its role in disinfection and taste and odor control. Calvert⁶⁹ recognized that the breakpoint was directly related to the concentration of ammonia in the water.

Griffin was attempting to explain the sudden loss of residual chlorine and the simultaneous disappearance of ammonia nitrogen at treatment plants experimenting with higher-than-usual chlorine residuals (2–15 mg/l) in an attempt to destroy the obnoxious tastes and odors. He was startled to find that increasing the chlorine dose in certain waters not only did not increase the residual but reduced it significantly (A.E. Griffin, pers. comm.). He called the point of maximum reduction of residual the “breakpoint.” Griffin and Chamberlin⁷⁰ drew “breakpoint curves” similar to the classic curve included today in basic textbooks on water supply and treatment (Fig. 2.7). They found that the shape of the breakpoint curve varied with the source of the water, its pH, and the reaction time; that the magnitude of the peak of the curve and the chlorine dosage needed to reach the breakpoint depended to a large extent on the amount of free ammonia in the water; that both chlorine and nitrogen are lost at the breakpoint; that the optimum pH for the breakpoint reaction

is between 6.5 and 8.5; and that chloramines are more stable to the “left of the hump” than to the right of it.

Discovery of the breakpoint reaction led to numerous scientific studies. Morris and his coworkers at Harvard University thoroughly examined the reactions of chlorine with ammonia and nitrogenous organic compounds.^{38,39,41,43,54,56,57,71–77} Palin’s concurrent work^{48,78} in England is also noteworthy. Williams’s work^{57,79–81} substantiated the findings of both Palin and the Harvard group and is important because it was conducted at plant scale over a period of 20 years and demonstrated the practical value of the knowledge being gained at that time. It is of historical interest to note that all of these investigations substantiated the findings of Holwerda almost 20 years earlier.⁶⁰ New analytical methods were developed to differentiate between free and combined chlorine, with the work of Marks and coworkers and Palin being especially noteworthy (Chapter 3). To resolve conflicting reports on the relative germicidal effectiveness of chlorine and chloramines, investigations were undertaken to examine the effectiveness of the various chlorine species as disinfectants, as described in a subsequent section of this chapter. Griffin^{82,83} summarized the rapid progress in understanding and controlling the chlorination process in the years after the breakpoint reaction became widely recognized.

The Breakpoint Curve. The breakpoint curve (Fig. 2.7) is a plot of residual chlorine concentration versus the dose of chlorine added to a water containing ammonia nitrogen. The chlorine dose is typically shown in units of milligrams per liter as Cl_2 or as a $\text{Cl}_2\text{:N}$ weight or molar ratio. In Figure 2.7, the total concentration of ammonia nitrogen, including the fraction converted to chloramines, is also shown, along with the three distinct zones in which different reactions are occurring.

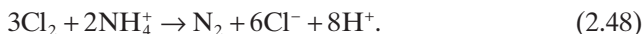
In zone 1, chlorine reacts with ammonia to form chloramines, primarily monochloramine at neutral pH values and shorter contact times. At lower pH values, longer contact times, and higher $\text{Cl}_2\text{:N}$ ratios, dichloramine formation increases; and dichloramine may represent a significant fraction of the residual chlorine in zone 1, or even a majority if the pH drops to about 5 or lower. Chlorinous tastes and odors are rarely encountered in zone 1, provided that dichloramine formation is controlled and the chemicals are added in a manner that does not cause localized trichloramine formation (due to areas of the flow that receive chemicals at an excessive $\text{Cl}_2\text{:N}$ ratio). Zone 1 encompasses the desired operating range for maintaining a combined chlorine residual in water distribution systems (a $\text{Cl}_2\text{:N}$ weight ratio of 3:1 to 5:1) and is also applicable to chlorination of nonnitrified wastewater effluents.

At the end of zone 1, at a $\text{Cl}_2\text{:N}$ weight ratio of about 5:1, the combined chlorine concentration reaches a maximum commonly referred to as the “hump.” In pure water and with ideal mixing, the hump may lie on or very close to the 45° line, so that the combined chlorine residual equals the applied chlorine dosage. In practical applications, the hump generally lies below the

45° line, as shown in Figure 2.7, because a fraction of the chlorine reacts with other constituents in the water, such as organic matter, or is lost when the breakpoint reactions occur in incompletely mixed parcels of water.

In zone 2, chlorine reacts with ammonia and monochloramine to form dichloramine, but dichloramine undergoes a series of reactions (described below) that result in the loss of both chlorine and nitrogen. Although dichloramine has about twice the germicidal power of monochloramine, a dichloramine residual has a disagreeable taste and odor; therefore, zone 2 should be avoided in drinking water treatment. Furthermore, it is difficult to maintain a combined chlorine residual in zone 2 since an increase in the chlorine dosage will result in a lower residual.

At the breakpoint, ammonia is oxidized to nitrogen (N₂) and chlorine is reduced to chloride in a complex set of reactions (Fig. 2.4). The stoichiometry of the overall reaction, under typical water and wastewater treatment conditions, is approximately as follows:



Based on Equation (2.48), both chlorine and ammonia nitrogen should disappear completely at a Cl₂:N molar ratio of 3:2 (weight ratio of 7.6:1). However, Equation (2.48) does not fully capture the complexity of the reactions involved, including their equilibria and kinetics. Ammonia nitrogen may disappear completely at the breakpoint, or be reduced to only a trace, especially at neutral pH values; but in practice an “irreducible minimum” chlorine residual (also referred to as a “nuisance residual”) remains, typically a few tenths of a milligram per liter as Cl₂. The composition of this irreducible minimum is still somewhat mysterious, even though it has been extensively studied. When titrated, it appears to be predominantly dichloramine, with traces of monochloramine and free chlorine, but it may also include organic chloramines, which generally titrate as dichloramine but have much less disinfecting power. Because of the uncertainty as to its composition and disinfecting power, the residual at the breakpoint should not be relied on as a disinfectant. Accordingly, some regulatory authorities require a chlorine residual of 0.2 mg/l or higher for disinfection credit.

In zone 3, to the right of the breakpoint, free chlorine increases in direct proportion to the chlorine dosage applied, so the curve rises at a 45° angle. This transition to a free chlorine residual can be of critical importance because free chlorine is a much stronger disinfectant than combined chlorine. As shown in Figure 2.7, and as observed by Griffin and Chamberlin,⁷⁰ ammonia nitrogen (in the form of trichloramine) may return in zone 3; and at pH values of 6 or lower, measurable amounts may persist even at the breakpoint.

Taste and odor are typically minimized at a chlorine dosage yielding a free chlorine residual of about 1 mg/l, which evidently oxidizes some of the trace compounds present in the irreducible minimum. Very high Cl₂:N ratios should be avoided because they can cause trichloramine formation, even at pH values

as high as 9. If a relatively high free chlorine residual is desired for special purposes, the breakpoint reaction should be allowed to proceed to completion before adding more chlorine. Water treatment plants operating in zone 3 are said to be practicing free residual chlorination, while wastewater treatment plants (WWTPs) operating in this zone are said to be practicing breakpoint chlorination.

It should be emphasized that the shape of the breakpoint curve is affected by contact time, temperature, the concentrations of chlorine and ammonia, pH, and organic matter. At pH values outside the range of 7–9 and at lower temperatures, the breakpoint reaction is retarded; and if measurements are made after only a short contact time, both the “hump” and the breakpoint may appear as inflection points in a continually rising curve,⁸⁴ as illustrated in Figure 2.8 and in earlier data presented by Tuepker.⁸⁵ This can also be the case for waters containing high concentrations of organic matter, especially organic nitrogen, and relatively low concentrations of ammonia nitrogen. Furthermore, when operating in zones 2 and 3, samples taken before the chloramine decomposes will include both free and combined chlorine, so control will need to be based on total chlorine or on gradual adjustments based on the analysis of samples collected further downstream.

Applied $\text{Cl}_2\text{:N}$ weight ratios significantly higher than 7.6:1 are typically needed to reach the breakpoint. Ratios between 8.5 and 10 are commonly required for drinking water treatment, and even higher ratios are commonly encountered in wastewater treatment. Other constituents in the water, such as organic matter, sulfide, and reduced forms of iron and manganese, may consume chlorine, which may also result in a “lag” or “threshold” in the

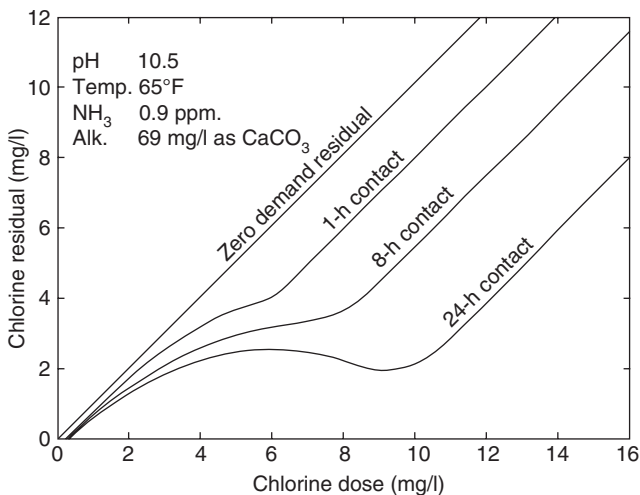


Figure 2.8. Breakpoint curves as a function of contact time in lime-softened and coagulated Missouri River water.⁸⁴

breakpoint curve, that is, the absence of a residual below the dosage of chlorine required to satisfy the immediate chlorine demand associated with these substances. Furthermore, depending on pH, temperature, and mixing conditions, other end products besides nitrogen, such as nitrate and nitrogen trichloride, may be produced, and this may affect both the shape of the breakpoint curve and the $\text{Cl}_2:\text{N}$ ratio required to reach the breakpoint.

It is important not to confuse the $\text{Cl}_2:\text{N}$ ratio applied during treatment with the ratio associated with the residual or with guidelines based on the “ideal” breakthrough curve or Equation (2.48). Chlorine added to satisfy the immediate chlorine demand of the water will not contribute to residual chlorine, and the ammonia nitrogen in the raw water may be removed by prechlorination or may still remain when the water is chloraminated.

Example. A groundwater having an $\text{NH}_3\text{-N}$ concentration of 0.3 mg/l is to be chloraminated. The treatment objective is to maintain a combined chlorine residual of 3 mg/l as Cl_2 and a $\text{Cl}_2:\text{N}$ ratio of 4:1 in the finished water. The water has a combined chlorine demand of 0.5 mg/l. What dosages of chlorine and ammonia nitrogen are needed to treat this water?

$$\text{Applied } \text{Cl}_2 \text{ dosage} = 3 + 0.5 = 3.5 \text{ mg/l}$$

$$\text{NH}_3\text{-N needed} = (3 \text{ mg/l as } \text{Cl}_2) / (4 \text{ mg } \text{Cl}_2 / \text{mg } \text{NH}_3\text{-N}) = 0.75 \text{ mg/l}$$

$$\text{Applied } \text{NH}_3\text{-N dosage} = 0.75 - 0.3 = 0.45 \text{ mg/l.}$$

Thus, an applied $\text{Cl}_2:\text{N}$ ratio of $3.5/0.45 = 7.8$ is needed to maintain a ratio of 4:1 in the finished water. The ammonia would have to be added either before, or simultaneously with, the chlorine; otherwise, the added chlorine would destroy the ammonia nitrogen in the raw water by converting it to nitrogen in the breakpoint reaction. At the moment the chemicals are added, the instantaneous $\text{Cl}_2:\text{N}$ ratio will be $3.5/0.75 = 4.7$, so there should be little or no formation of dichloramine or trichloramine if mixing is adequate. If the instantaneous $\text{Cl}_2:\text{N}$ ratio exceeds 5:1, this may result in loss of chlorine or formation of unacceptable concentrations of dichloramine or trichloramine. If so, one solution is to first breakpoint chlorinate the raw water and to delay chloramination until after the chlorine demand has been satisfied. Another solution is to increase the ammonia nitrogen dose, but this would lower the $\text{Cl}_2:\text{N}$ ratio in the finished water, encouraging the growth of nitrifying bacteria.

A common error is to assume that there is no $\text{NH}_3\text{-N}$ in the raw water. Groundwater can contain a significant concentration of $\text{NH}_3\text{-N}$, especially if it is drawn from an alluvial aquifer, as can surface water, especially if it is drawn from a lake or from a stream and river that receives an upstream discharge of domestic or industrial wastewater. Had the raw water $\text{NH}_3\text{-N}$ been ignored in the above example, 0.75 mg/l of $\text{NH}_3\text{-N}$ would have been added, resulting in a total $\text{NH}_3\text{-N}$ concentration of 1.05 mg/l and a $\text{Cl}_2:\text{N}$ ratio in the finished water of only 2.86. After 50% decay of the combined chlorine residual, which would typically take only a few days, the $\text{Cl}_2:\text{N}$ ratio would drop

to 1.43, leaving a considerable amount of free $\text{NH}_3\text{-N}$ available to stimulate the growth of nitrifying bacteria.

Example. A surface water having an influent $\text{NH}_3\text{-N}$ concentration of 0.4 mg/l and a chlorine demand of 5 mg/l is to be prechlorinated, leaving a free chlorine residual of 1 mg/l. At the end of the disinfection contact time, a free chlorine concentration of 0.5 mg/l remains. Before leaving the plant, the water is to be chloraminated at a $\text{Cl}_2\text{:N}$ ratio of 4:1, leaving a combined chlorine residual of 2 mg/l in the finished water. What dosages of chlorine and ammonia nitrogen are needed to treat this water?

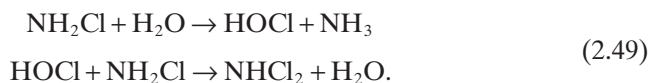
$$\text{Initial Cl}_2 \text{ dosage} = 5 + 1 = 6 \text{ mg/l}$$

$$\text{Cl}_2 \text{ required for chloramination} = 2 - 0.5 = 1.5 \text{ mg/l}$$

$$\text{NH}_3\text{-N needed} = (2 \text{ mg/l as Cl}_2) / (4 \text{ mg Cl}_2 / \text{mg NH}_3\text{-N}) = 0.5 \text{ mg/l.}$$

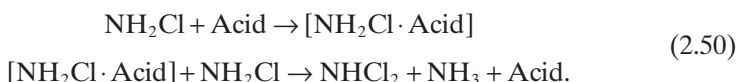
In calculating the initial chlorine dosage, it was assumed that the chlorine demand includes the demand associated with breakpointing the $\text{NH}_3\text{-N}$ present in the raw water. This $\text{NH}_3\text{-N}$ is not available for chloramination because it is removed in the initial free residual chlorination step.

Chemistry and Kinetics of the Breakpoint Reaction. Morris et al.⁷¹ suggested that the key to the final breakpoint reaction was the formation and decomposition of dichloramine, inspiring subsequent investigations of the disproportionation of monochloramine,⁷⁵ the chlorine–ammonia system,³⁹ and the dynamics of breakpoint chlorination.⁶⁵ As the $\text{Cl}_2\text{:N}$ weight ratio increases above 5:1, dichloramine formation increases but so does dichloramine decomposition. Dichloramine formation is believed to occur in two ways.³⁹ The first involves hydrolysis of monochloramine (the reverse of reaction 2.38) to form HOCl , which then reacts with monochloramine to form dichloramine (Eq. 2.39). These reactions can be shown in sequence as follows:



This reaction is limited by the rate of monochloramine hydrolysis and is thus a first-order reaction. It does not appear to be affected by pH or the buffering of the solution.

Dichloramine can also be formed from monochloramine by a second reaction that proceeds in parallel with the first. This second reaction is believed to be catalyzed by an acid complex as follows:^{39,41,43,44}



This reaction is pH and buffer dependent and has been found to be a second-order reaction.

Although these two reactions occur by different mechanisms, they both yield the same overall result described earlier, that is, disproportionation of monochloramine to form dichloramine and ammonia (Eq. 2.43). Since ammonia suppresses the disproportionation of monochloramine, there must be an excess of HOCl present for Equations (2.49) and (2.50) to proceed.

Wei and Morris⁶⁵ examined the kinetics of the breakpoint reaction and changes in the chlorine species during the course of the reaction. Results from one of their experiments are shown in Figure 2.9, which clearly illustrates the formation and decay of NHCl_2 . Under these conditions (pH 6.7 and 20°C), the reaction took about 30 min to go to completion, although the reaction of $\text{NH}_3\text{-N}$ with chlorine was virtually instantaneous. They found that the breakpoint reaction is significantly slower at lower temperatures and is also influenced by pH, the initial concentrations of the reactants, and the buffer used (phosphate vs. carbonate). In very cold water and at very high and low pH values, the breakpoint reaction can take several hours or longer to go to completion.

Saunier and Selleck^{86,87} studied the breakpoint reaction in both potable water and wastewater. Based on more than 80 experimental runs with variations in pH (6–9), $\text{NH}_3\text{-N}$ (1–20 mg/l), $\text{Cl}_2\text{:N}$ molar ratio (1.6–3.5), and temperature (12 and 21°C), they proposed a reaction scheme including hydroxylamine (NH_2OH) as an intermediate reaction product, leading to the formation of NOH as proposed by Morris and Wei,^{65,77} and they developed a computer model to predict chlorine speciation during the course of the

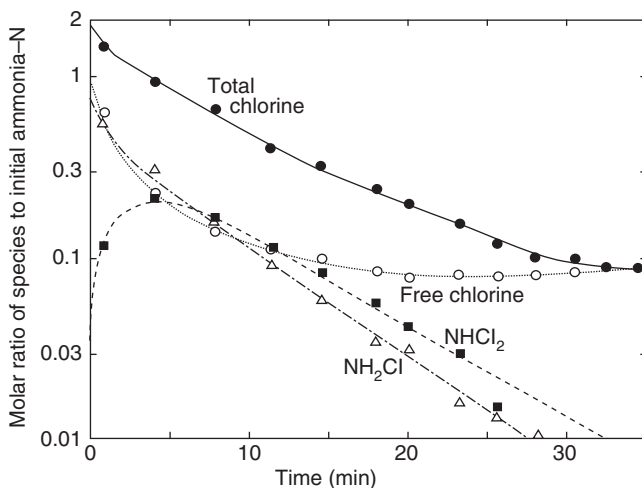


Figure 2.9. Chlorine speciation data of Wei and Morris⁶⁷ for chlorination of ammonia at pH 6.7 and 20°C ($\text{Cl}_2\text{:N}$ molar ratio = 1.8; initial $\text{NH}_3\text{-N}$ = 1 mg/l). Adapted from Wei, I.W. Chlorine-Ammonia Breakpoint Reactions: Kinetics and Mechanism. PhD Thesis, Harvard University, Cambridge, MA, 1972 (with the permission of the author).

reaction. They found that the reaction was most rapid at a pH of about 7.5 and that it took only minutes to go to completion at this pH when the initial $\text{NH}_3\text{-N}$ concentration was high (20 mg/l). They also found, in agreement with Wei and Morris⁶⁵ and others, that the reaction was much slower at higher and lower pH values, at low initial $\text{NH}_3\text{-N}$ concentrations, and at lower temperatures. They noted that it could take hours or even days to oxidize the intermediate products to nitrogen (N_2) and nitrate under nonideal conditions.^{86,87}

Figures 2.10 and 2.11 illustrate the distribution of the chlorine residual species, as predicted by Saunier's model,⁸⁶ at 2.5 and 20 min, respectively, for a relatively low initial $\text{NH}_3\text{-N}$ concentration of 0.5 mg/l and a temperature of 25 °C. These data underscore the importance of choosing a suitable sampling point and control parameter when designing a control system. Both free and

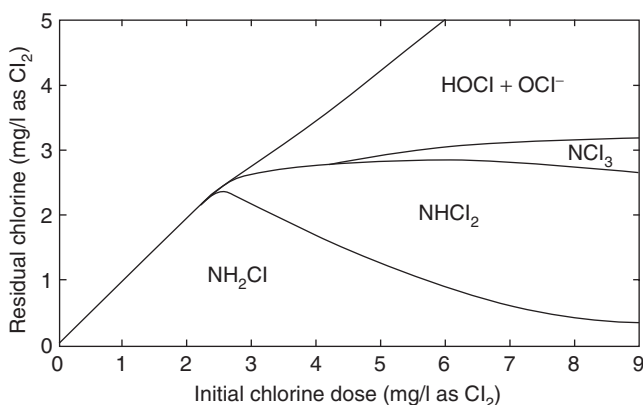


Figure 2.10. Chlorine speciation after 2.5 min⁸⁶ (pH = 7.4, $\text{NH}_3\text{-N}$ = 0.5 mg/l, 15 °C).

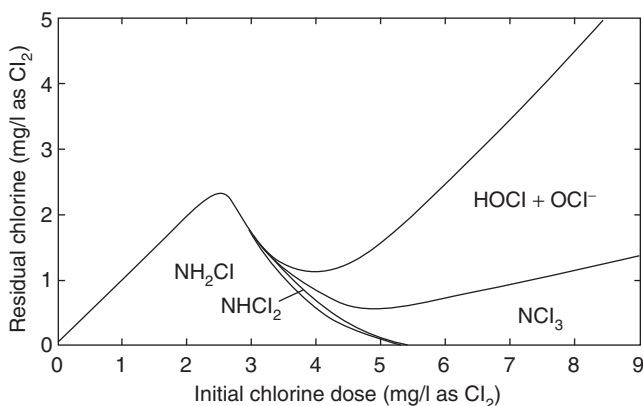


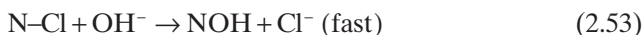
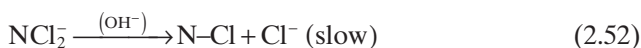
Figure 2.11. Chlorine speciation after 20 min⁸⁶ (pH = 7.4, $\text{NH}_3\text{-N}$ = 0.5 mg/l, 15 °C).

combined chlorine would be present in a sample collected 2.5 min downstream from the application point. Wet chemical tests would give very erratic results, and online instruments might also give unstable readings, especially if they were set up to distinguish between free and combined chlorine. Furthermore, if removal of $\text{NH}_3\text{-N}$ by breakpoint chlorination were among the desired outcomes, this objective would not be fully met if a dechlorinating agent was added before completion of the reaction, as any remaining chloramines would revert to $\text{NH}_3\text{-N}$.

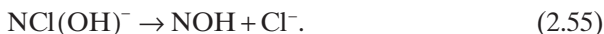
Following dichloramine formation, the next step in the breakpoint reaction is dichloramine decomposition, which is base catalyzed. Morris et al.⁷¹ proposed the following mechanism for the decomposition of dichloramine. First, dichloramine ionizes as a weak acid:



The NCl_2^- ion then proceeds to react with hydroxyl ion (OH^-), in two possible ways, to form nitroxyl (NOH):



or



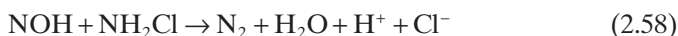
Dichloramine decomposition to NOH can also be written as a hydrolysis reaction:⁷⁷



NOH, once formed, can decompose into end products along three pathways.⁷¹ Each is conceivable since various end products are known to be formed and their formation can potentially be influenced by many variables, including the $\text{Cl}_2\text{:N}$ ratio, the initial concentrations of chlorine and ammonia, pH, temperature, and unknown side reactions of chlorine with organic matter. The first pathway leads to the formation of nitrous oxide, N_2O , as a by-product, as first postulated by Chapin.⁵⁰ It involves the dimerization of NOH to form hyponitrous acid, which slowly decomposes to N_2O :



In the second pathway, NOH reacts with NH_2Cl , NHCl_2 , and HOCl to form nitrogen (N_2) and nitrate (NO_3^-) in three parallel and competing reactions:



Equation (2.59) is consistent with the observation of Wei and Morris⁶⁵ of a slight but noticeable increase in free residual chlorine in the latter stages of the breakpoint reaction.

In the third pathway, NOH first dimerizes to hyponitrous acid (Eq. 2.57), which then reacts with a large excess of free chlorine as follows:



The second pathway, decomposition of NOH to N_2 and NO_3^- , is consistent with the general consensus that N_2 is the predominant end product in most applications and that a significant amount of NO_3^- can also be formed under suitable conditions. Formation of N_2 requires a $\text{Cl}_2:\text{N}$ molar ratio of about 1.5:1 (or 3:2), whereas the other possible end products mentioned above all require a molar ratio of 2:1 or greater: 2:1 for N_2O , 2.5:1 for NO , 4:1 for NO_3^- , and 3:1 for NCl_3 . Thus, a molar ratio of about 1.5:1 indicates that N_2 is the predominant end product, molar ratios between 1.5:1 and 2:1 indicate the formation of secondary end products, and molar ratios greater than 2:1 indicate the formation of substantial amounts of other end products besides N_2 .

At neutral pH and in pure solutions, or in relatively clean water supplies, the breakpoint reaction is generally found to require a $\text{Cl}_2:\text{N}$ molar ratio of less than 2:1 (calculated as the ratio of chlorine reduced to nitrogen oxidized). For example, Wei and Morris⁶⁵ reported ratios of 1.53 to 1.73, and Palin⁴⁸ reported ratios of 1.54 to 1.88. These observations are consistent with N_2 being the predominant end product, accompanied by lesser amounts of secondary end products, most likely NO_3^- and NCl_3 . Wei and Morris also noted that lower ratios were required as the initial concentration of ammonia increased, that this was consistent with the earlier observations of Chapin⁵⁵ that the ratio tended toward a value of 1.5 at higher ammonia concentrations, and that nitrate formation may be favored by low reactant concentrations.

Nitrate and NCl_3 are known to be produced as secondary by-products, especially at high $\text{Cl}_2:\text{N}$ ratios. Pressley et al.⁸⁸ found much more NO_3^- at pH 8 than at pH 5–6 (10% of the initial $\text{NH}_3\text{-N}$ at pH 8 vs. 1.5% at pH 5–6). Saunier and Selleck⁸⁷ found that about 10% of the $\text{NH}_3\text{-N}$, on average, was converted to NO_3^- and that NO_3^- formation increased as the $\text{Cl}_2:\text{N}$ ratio increased but was apparently independent of pH. Diyamanoglu and Selleck⁸⁹

found that NO_3^- was produced at neutral and moderately alkaline pH values and could conceivably be the primary end product under conditions approaching those encountered in drinking water treatment. Nitrite has been suggested as a possible decomposition by-product, and has been observed by Leung and Valentine;^{90,91} but it can be only an intermediate product rather than an end product since it is rapidly oxidized to nitrate in the presence of free chlorine.^{92,93}

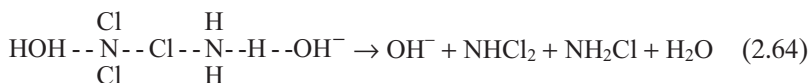
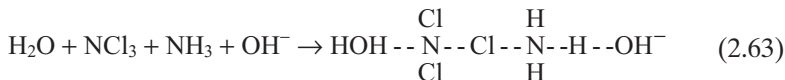
It would not be surprising if other by-products, in addition to those mentioned above, are found by future investigators. There is at least one intermediate reaction product (not NOH or NCl_3) yet to be identified, as discussed later in this chapter.

For many years, investigators have speculated about the mechanisms involved in chlorine decomposition and N_2 formation in the breakpoint reaction, but they have not yet been completely defined and verified. The NHCl_2 decomposition pathways described above, based on NOH as an intermediate,⁷¹ have not been verified, nor have other proposed pathways involving hydroxylamine and hydrazine. The lack of progress in this area is not surprising, given the many competing reactions that can occur,³⁷ the rapid rate of many of the reactions involved, and the highly reactive nature of chlorine species. Furthermore, most early investigators focused their attention primarily on NHCl_2 since NHCl_2 decomposition coincides with N_2 formation and the two processes appear to be intimately related; and they largely ignored NCl_3 , considering it both an insignificant by-product and an unnecessary analytical burden. However, later investigators^{94,95} proposed and then demonstrated that NCl_3 plays a central role in the breakpoint reaction.

Hand and Margerum⁹⁴ found that NCl_3 reacts with NHCl_2 and that this reaction generates HOCl , which can then react with NHCl_2 to produce more NCl_3 , thereby accelerating NHCl_2 decomposition. They also found that even traces of NH_3 strongly inhibited this process since NH_3 reacts very rapidly with HOCl , thereby interfering with NCl_3 formation. This is consistent with the findings of earlier investigators that free chlorine is present as the breakpoint reaction proceeds and that NCl_3 is stable only in the presence of free chlorine. It is also consistent with the observation of Saunier and Selleck⁸⁷ that back-mixing significantly slows the breakpoint reaction. Hand and Margerum postulated the following overall reaction to explain their observations:

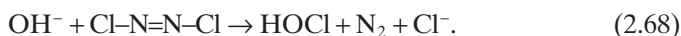
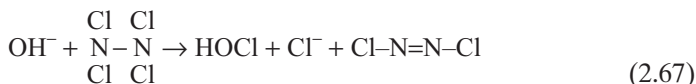
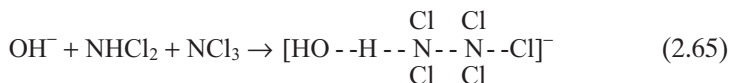


Yiin and Margerum,⁹⁵ using stopped-flow methods and computer simulations to examine the reactions of NCl_3 with NH_3 and NHCl_2 , confirmed that NCl_3 plays a key role in both dichloramine formation and its decomposition to N_2 . Their results support a base-assisted reaction scheme in which NCl_3 reacts with NH_3 to form NHCl_2 and NH_2Cl , with the base (represented herein by OH^-) helping remove a proton from the NH_3 molecule as follows:



Thus, NCl_3 not only forms NHCl_2 but also helps limit the availability of NH_3 .

NCl_3 also participates in a second base-assisted reaction that results in the destruction of NHCl_2 and the formation of N_2 in a reaction scheme that can be described as follows, with OH^- representing the base:⁹⁵



The base first helps remove the proton from NHCl_2 as it reacts with NCl_3 to displace Cl^- and form tetrachlorohydrazine (N_2Cl_4). It then helps to convert N_2Cl_4 to N_2Cl_2 and ultimately to N_2 , forming additional HOCl in the process. This scheme nicely explains the overall reaction proposed by Hand and Margerum⁹⁴ (Eq. 2.62) as well as the regeneration of HOCl observed by earlier investigators, such as Wei and Morris.⁶⁵ Moreover, taking into consideration the HOCl produced in the reaction, it is also consistent with occurrence of the breakpoint reaction at a $\text{Cl}_2:\text{N}$ molar ratio of 3:2. As noted by Yiin and Margerum,⁹⁵ there does not seem to be any information available regarding the proposed N_2Cl_4 and N_2Cl_2 intermediates, but the driving force for them to form N_2 should be very favorable, and they would be expected to be short-lived intermediates in base-assisted reactions.

The chemistry of breakpoint chlorination is clearly very complex and not yet completely understood. It will be interesting to see what future investigators discover as they strive to unlock its mysteries. Progress is expected to continue to be slow, for many of the same reasons it took so long to demonstrate the important role of NCl_3 in the decomposition of NHCl_2 and formation of N_2 . As described below, at least one decomposition product has still not been identified despite many years of intensive study.

Unidentified Decomposition Products. Saunier and Selleck⁸⁷ concluded that an intermediary nitrogen compound must be present in the early stages of the breakpoint reaction to explain the stoichiometry they observed, and

speculated that it might be hydroxylamine. Leao⁹⁶ and Hand and Margerum⁹⁴ noted the presence of a chloramine decomposition product they were not able to identify. Other investigators have observed a significant discrepancy between the results of the diethyl-*p*-phenylenediamine–ferrous ammonium sulfate (DPD–FAS) titrimetric method and the UV spectrophotometric procedure.^{97,98} At the start of the reaction, the two methods agree, but as the reaction proceeds, the results diverge, with the UV spectrophotometric method always indicating a higher total oxidant (NH_2Cl plus NHCl_2) concentration than the DPD–FAS method. There is evidently an interference in the UV spectrophotometric method caused by one or more unknown compounds.

Despite intensive study of one decomposition product by Valentine et al.,^{90,91,97,98} its identity, significance, and practical consequences are unknown at this time. It is not hydroxylamine or hydrazine, it contains both nitrogen and chlorine, and it is clearly very polar or ionic because it cannot be extracted into several common organic solvents. Its ion chromatographic behavior is consistent with that of an anion, but this is not conclusive since it may have been adsorbed by the resin or reacted with it to form an anionic product that appears as an unidentified peak. Hand and Margerum⁹⁴ thought it was probably not ionized at pH 7. Presumably, it can act as both an oxidant and a reductant since it reacts with both sulfite and chlorine. Its very slow reaction kinetics with free chlorine above pH 6 and rapid kinetics near pH 3 suggest that it is much more reactive with a chlorine species that dominates at low pH, such as $\text{Cl}_2(\text{aq})$, than with either OCl^- or HOCl . Its reactivity with activated carbon and two common amine-based resins indicates that it may be reactive toward organic compounds in drinking water.

Diyamanoglu and Selleck⁸⁹ found that about 45% of the residual chlorine was tied up in unrecognized reaction products during the early stages of the breakpoint reaction at neutral pH, but not at pH 9.3–9.6. Comparing their results with those of Valentine et al., they concluded that there may be more than one unidentified by-product. Whether there is one or more than one, this matter merits further investigation since the germicidal and human health effects of such compounds cannot be adequately evaluated until they are identified and fully characterized.

The Organic Nitrogen Problem

The wording of the heading of this section is taken from an article by Williams,⁸¹ who did not discover the problem but promoted awareness of it among water treatment professionals and explored practical ways to deal with it. The “problem” is that organic nitrogen interferes with chlorination and disinfection in several important ways. It reacts with chlorine to form compounds that are only weakly germicidal or nongermicidal, consumes chlorine, alters the shape of the breakthrough curve, renders chlorine residuals less stable, can potentially contribute to taste and odor problems, and interferes with the

determination of chlorine residuals. These various facets of the problem are discussed in more detail below.

Organic Nitrogen. Organic nitrogen is defined as “organically bound nitrogen in the tri-negative state.”³³ This includes nearly all of the organically bound nitrogen in urine and feces, the major sources of organic nitrogen in domestic wastewater,⁹⁹ and wastes produced in animal feeding. It also includes most of the organically bound nitrogen in all living (and dead) organisms, including algae, bacteria, and zooplankton, which can be present in water and wastewater in very large numbers. Chemical compounds that contain organic nitrogen and are found in wastewater and organisms include urea, uric acid, creatinine, proteins, polypeptides, amino acids, nucleic acids, amino sugars, amides, creatine, biotin, folic acid, nicotinic acid, riboflavin, thiamine, and pantothenic acid.⁹⁹ Industrial wastewaters can contain these compounds as well as others, such as aliphatic amines, arylamines, heterocyclic amines, cyanides, cyanates, thiourea, and quaternary ammonium compounds. Industrial wastewaters may also contain partially oxidized forms of nitrogen, such as nitro compounds, that are not detected by the standard methods used to determine organic nitrogen.³³

Fortunately, much of the organic nitrogen in wastewater is readily biodegradable. This is especially true of urea and proteins, the major nitrogen-containing components in domestic wastewater. Urea is rapidly broken down to ammonia with the help of urease enzymes, and proteins are rapidly broken down with the help of protease enzymes to polypeptides and amino acids, with the latter then breaking down to ammonia and organic acids. Many of the other compounds listed above are also readily degradable. Furthermore, organic nitrogen present in particulate form in water and wastewater can be readily removed by coagulation, sedimentation, and filtration. As a result, organic nitrogen concentrations are greatly reduced by wastewater treatment, typically dropping from about 5–15 mg/l in raw sewage to 1–2 mg/l in secondary and tertiary effluents; and only trace amounts are typically found in water supplies.^{34,35} The situation was much different during the early part of the 20th century, when the use of chlorine to disinfect water supplies was growing exponentially. Many wastewaters were discharged with little or no treatment and many water supplies received only minimal treatment, with some being heavily contaminated by upstream discharges of raw sewage. Today the organic nitrogen problem is much less acute in developed countries, as few water supplies are subject to upstream discharges of raw wastewater and most wastewaters receive at least secondary treatment before chlorination.

Many wastewater effluents and most water supplies are not routinely analyzed for organic nitrogen, but methods are available to aid the identification or investigation of problems associated with organic nitrogen. The standard method³³ involves acid digestion to convert the organic nitrogen to ammonia and to determine its concentration. If the ammonia is not first removed by predistillation, the result will be total Kjeldahl nitrogen (TKN), the sum of

ammonia nitrogen and organic nitrogen. Instrumental methods of analysis are also available, but these typically measure total nitrogen and thus require separate determination of inorganic forms of nitrogen or a pretreatment step to remove them.^{34,35} The term “albuminoid” nitrogen frequently appears in the older literature. Albumin refers to heat-coagulable, water-soluble proteins. A method for estimating albuminoid nitrogen, using alkaline permanganate digestion to convert proteinaceous amine groups to ammonia, was included in the 13th and earlier editions of *Standard Methods*.³³

Reactions of Organic Nitrogen with Chlorine. Organic nitrogen is made up of numerous compounds that can form countless reaction products with chlorine. Much of the organic nitrogen in water supplies and domestic wastewater is present in amine or amide form. The amines are mostly primary or secondary amines, $R-NH_2$ or R_2-NH , where R represents the organic group to which the amine group is attached. The initial reactions of amines with chlorine are in some ways similar to those of ammonia with chlorine, with organic monochloramines and dichloramines being formed as a function of pH and the $Cl_2:N$ ratio. However, organic chloramines are generally formed much faster than NH_2Cl and $NHCl_2$,¹⁰⁰ so organic nitrogen exerts an initial chlorine demand that must be satisfied before a residual consisting primarily of free chlorine or inorganic chloramines can be formed.

Free amino acids contain available amine groups that can be readily chlorinated, but most amino acids in water and wastewater are bound together by amide links (peptide bonds) in proteins and peptides. Amide nitrogen is much less readily chlorinated than amino nitrogen.¹⁰¹ Other nitrogenous functional groups also react slowly with chlorine, as does the organic matter associated with organic nitrogen. Thus, organic nitrogen is typically associated with a gradual consumption of chlorine for an extended period after the initial chlorine demand has been satisfied.^{81,102}

Morris et al.,¹⁰³ in a review of the reactions of chlorine with amines, amides, amino acids, proteins, and heterocyclic compounds, reported that the reaction is often rapid, especially for compounds having more basic nitrogen atoms, as is the case for primary and secondary amines. They also noted that amino acids and other nitrogenous compounds, after first forming *N*-chloro derivatives, can undergo oxidative deamination to yield NH_2Cl or $NHCl_2$ and keto acids. Deamination results in a loss of organic nitrogen, which is consistent with the experimental results of several studies that involved very high dosages of chlorine. Taras,^{102,104} using chlorine dosages of 500–1000 mg/l, observed a nitrogen loss of about 50 % for a number of amino acids and about 10%–20% for proteins after 24 h. Randtke et al.⁹⁹ saw no significant loss of organic nitrogen from secondary effluent at chlorine dosages up to 100 mg/l (below the breakpoint); but they observed 27%–39% loss of organic nitrogen at $Cl_2:N$ ratios of 10.4 and 15.6, respectively. Taras¹⁰⁴ found that organic nitrogen consumption after chlorine addition follows a well-defined general pattern. The ammonia nitrogen is lost almost completely within 1 h; the simple, unsubstituted amino nitrogen in many common amino acids is consumed much more

slowly, over many hours; and protein nitrogen shows only a negligible loss, even after many days. Saunier and Selleck⁸⁷ found that lower pH values favored oxidation of organic nitrogen, whereas persistent organic chloramines were formed at higher pH values.

Human and animal urine contains high concentrations of urea, a product of protein metabolism. Hydrolysis of urea to ammonia, catalyzed by the urease enzyme, takes only a few hours under normal conditions, so there is typically little urea present in a well-treated sewage effluent. However, if urease is lacking or inhibited during treatment, or if water being chlorinated contains raw or partially treated sewage, a significant concentration of urea may be present. Although urea can be chlorinated in aqueous solution,¹⁰⁰ urea chloramines do not form at low concentrations due to urea's very weak basicity (S.L. Chang, pers. comm.); and Lomas,¹⁰⁵ searching for an explanation for high dichloramine readings in swimming pool water, found that dichlorurea is unstable in the presence of free chlorine at pH 8. However, if a significant quantity of urea is present and hydrolyzes at a slow rate, an unstable residual can result since the urea serves as a reservoir for the gradual production of ammonia, which will react with any free chlorine present. Lomas also found that creatinine, another component of urine, reacts with chlorine to form chlorcreatinine, which is stable in the presence of free chlorine and exhibits characteristics of dichloramine during quantitative analysis.

Numerous other reactions between chlorine and organic nitrogen, involving both chloro-substitution and oxidation are possible. Tertiary amines can form either unstable quaternary ammonium compounds¹⁰⁰ or nitrogen oxides. The nitrogen in ring compounds (cyclic and heterocyclic) can undergo both substitutive and oxidative reactions, in some cases with ring-breakage, yielding a variety of chlorinated and unchlorinated by-products.

Some organic nitrogen compounds can react with chlorine to form *N*-chloro organic compounds that have relatively high hydrolysis constants and are therefore capable of slowly releasing free chlorine into solution. Examples include chlorinated cyanurates,¹⁰⁶⁻¹⁰⁸ chlorinated hydantoins,¹⁰⁹ and chloramine T. Such chemicals are manufactured and sold as sanitizing agents, algicides, or "stabilizers" to reduce photolysis of chlorine in swimming pools, and some are used as reagents for chemical synthesis; but these compounds and their organic precursors are not normally present in drinking water or wastewater effluents.

Not all organic nitrogen compounds react readily with free chlorine. For example, Morris et al.¹⁰³ observed little or no reaction between relatively high concentrations of chlorine and caffeine. In a study of the El Dorado, Arkansas, municipal water system, White¹¹⁰ discovered that an organic nitrogen concentration of 0.5 mg/l had no effect on the breakpoint curve. This water supply was drawn from an area having a lot of oil well activity, but the nature of the organic matter associated with the organic nitrogen was not characterized.

Organic Nitrogen and Chlorine Residuals. When a chlorine atom is substituted for hydrogen on a nitrogen atom, it does not lose its oxidizing

capacity.^{103,111} In fact, organic chloramines exist in equilibrium with free chlorine, just as monochloramine does, but equilibrium strongly favors organic chloramine formation in most cases. Since they contain “active” chlorine, organic chloramines titrate as residual chlorine,^{103,110–112} and therefore interfere in the determination of chlorine residuals (as discussed in greater detail in Chapter 3) and alter the shape of the breakthrough curve. Most organic chloramines formed during water and wastewater chlorination titrate as dichloramine when using the forward amperometric and DPD titrimetric methods,¹¹⁰ but they can intrude into both the monochloramine reading¹¹⁰ and the free chlorine reading.^{103,111,112} Organic chloramines can interfere with all methods used to determine free chlorine residuals,¹¹¹ but when only amino acids and ammonia are present, the syringaldazine and DPD methods seem to be the most specific for free chlorine.¹¹¹

White et al.¹¹³ found that organic nitrogen, in the presence of monochloramine, causes a definite shift of the monochloramine fraction to the dichloramine (organic chloramine) fraction over time. This can be attributed to hydrolysis of NH_2Cl to HOCl (the reverse of Eq. 2.38), with the HOCl reacting to form more organic chloramine. This reaction can continue over many hours, causing a gradual decline in germicidal efficiency.¹¹⁰ One way to counteract this effect is to increase the ammonia concentration, which not only inhibits both chloramine hydrolysis and organic chloramine formation but also reduces chlorine demand.^{113,114}

Although organic chloramines react rapidly enough with reducing agents to interfere with the measurement of chlorine residuals, they are expected to react less rapidly than free or combined chlorine, and some *N*-chloro compounds are expected to react even more slowly. Jensen and Helz¹¹⁵ reported that *N*-chloropeptides are dechlorinated one or two orders of magnitude more slowly than monochloramine and may therefore persist in dechlorinated wastewater effluents.

Organic Nitrogen and the Breakpoint Curve. Griffin and Chamberlin⁷⁰ and Williams (D.B. Williams, pers. comm.) found that waters containing a mixture of ammonia and organic nitrogen do not display the classic dip of the breakpoint reaction but instead exhibit a plateau effect. Figure 2.12 illustrates what may be expected with water containing 0.3 mg/l of $\text{NH}_3\text{-N}$ and 0.3 mg/l of organic nitrogen, with about half the latter associated with simple amino acids and the remainder with proteinaceous matter. The hypothetical results shown are based largely on observations by White,¹¹⁰ Williams,⁵⁷ D.B. Williams (pers. comm.), and Palin.⁴⁸

Figure 2.12 shows only a small drop in residual chlorine beyond the hump. This signifies two things: (a) continuing and competing reactions between monochloramine and dichloramine; and (b) little loss of nitrogen relative to that which would occur in the absence of organic nitrogen, hence the plateau effect. Beyond the plateau, free residual begins to appear, but the irreducible minimum residual is considerably higher than when only $\text{NH}_3\text{-N}$ is present

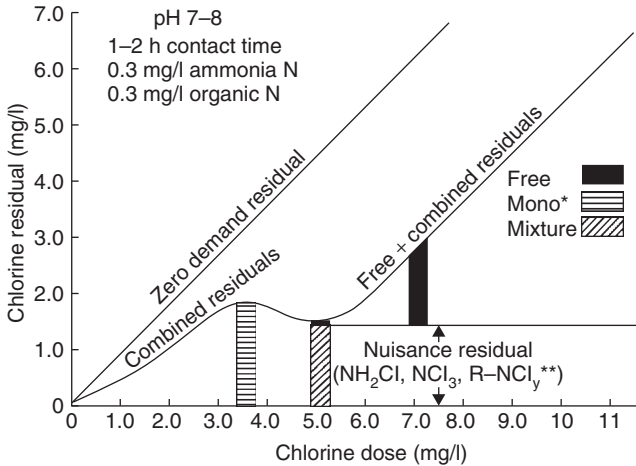


Figure 2.12. Breakthrough curve for a water containing a mixture of ammonia and organic nitrogen. *Predominantly monochloramine at first, with dichloramine increasing over time. **R-NCl_y represents organic chloramines.

(Fig. 2.7). As the Cl₂:N weight ratio increases to about 14:1, significant quantities of NCl₃ begin to form. Organic nitrogen results not only in an increase in the chlorine dosage required to reach the breakpoint but also in the production of significantly greater nuisance residuals, more NCl₃, and a higher ratio of dichloramine to monochloramine (to as much as 2 or 3:1 in the presence of free chlorine). Thus, organic nitrogen significantly increases taste and odor problems. Moreover, it makes the chlorine residual less stable since it continues to react with both organic nitrogen and the organic matter associated with it, and since any free chlorine will continue to react to decompose the monochloramine and dichloramine being formed from the continued decomposition of organic nitrogen.

At the breakpoint, there are competing reactions producing free chlorine, monochloramine, dichloramine, trichloramine, and organic chloramines, and it is difficult to identify these species individually in a mixture, especially in one that is not particularly stable. However, pure dichloramine is unstable in the presence of free chlorine, trichloramine can not form without free chlorine, and monochloramine is almost always present when trichloramine is formed. Therefore, it is reasonable to assume that nuisance residuals formed just beyond the breakpoint in the absence of organic nitrogen consist primarily of trichloramine and monochloramine. When organic nitrogen is present, the nuisance residual titrates as if it were composed of dichloramine, but it is probably made up mostly (about 90%) of organic chloramines, with much lesser amounts of monochloramine and trichloramine.

Organic nitrogen concentrations can be much higher than assumed in Figure 2.12, especially in raw sewage, partially treated wastewater effluents,

industrial wastes, and heavily used swimming pools. In such cases, the break-point curve is expected to follow the general pattern illustrated in Figure 2.12, but much higher nuisance residuals and unusually stable dichloramine residuals may be observed. For example, Lusher¹¹⁶ reported in 1959 that water in a heavily used swimming pool had been found to have a total chlorine residual of approximately 6 mg/l, a free chlorine residual of approximately 3 mg/l, and a dichloramine fraction as high as 2.4 mg/l. This condition persisted for several days, and increasing the free chlorine residual to 16 mg/l not only failed to reduce the dichloramine fraction but also increased it to between 3.0 and 4.0 mg/l. Lomas¹⁰⁵ later demonstrated that such results could be explained by the formation of chlorcreatinine.

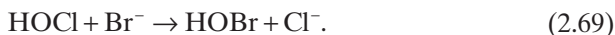
Experiences at the San Jose/Santa Clara, California, WWTP serve as an excellent example of the potential impacts of ammonia and organic nitrogen on wastewater disinfection.^{113,114} When nitrification was added to the treatment train, the plant found itself in violation of California's coliform discharge limits despite having increased the chlorine dosage. Since the plant's nitrification process was achieving virtually complete oxidation of $\text{NH}_3\text{-N}$ to nitrate, there should have been a high concentration of free chlorine in the effluent. It was first thought that perhaps nitrite was consuming additional chlorine, but this was subsequently ruled out. When the plant's chief chemist (Virginia Alford) identified the residual chlorine species using forward amperometric titration, she discovered that nearly half of the total chlorine residual of 9 mg/l was made up of organic chloramines, which titrated in the dichloramine fraction. Organic nitrogen in the effluent, at concentrations up to 3.5 mg/l, was greatly depleting the disinfecting power of the chlorine residual. Adding to the effluent 1.5–2.5 mg/l of $\text{NH}_3\text{-N}$, in the form of digester supernatant, not only reduced the chlorine demand but also improved disinfection efficiency. The lesson to be learned from this experience is that operating personnel should determine the chlorine species included in measurements of total residual chlorine and should also be aware of the ammonia nitrogen and organic nitrogen concentrations in the water and their potential impacts on disinfection by chlorine.

THE CHEMISTRY OF CHLORINE IN SEAWATER

Seawater is often chlorinated when it is used as a source water for desalination or as cooling water for power plants. The chlorine serves as a biocide, preventing or minimizing the growth of bacteria, mussels, and other organisms that can foul intakes, conduits, membranes, and the surfaces of condensers and other heat exchangers. The chemistry of chlorine in seawater is strongly influenced not only by seawater's high ionic strength but also by its high bromide concentrations. Bromide reacts with chlorine to form hypobromous acid, which in turn can dissociate to hypobromite ion. Bromine species, like chlorine species, can react with ammonia, forming bromamines, which resemble chloramines, but with some significant differences.

Effect of Bromide

When chlorine is added to seawater, it reacts with bromide ions to form hypobromous acid (HOBr):^{117, 118}



Seawater typically contains about 50–70 mg/l of bromide, so at the chlorine dosages typically employed to chlorinate seawater, there will be a large excess of bromide and virtually all of the chlorine will react to form HOBr. Thus, residuals reported in milligrams per liter as Cl_2 will actually consist of “residual bromine.” Seawater also contains traces of iodide, which will be oxidized to iodine (by chlorine or bromine species) when the water is chlorinated; but the concentration of iodide in seawater is miniscule (about 0.06 mg/l²⁸) relative to the concentration of bromide.

Oxidation of bromide to HOBr by chlorine is very rapid. The reaction has a second-order rate constant of $2.95 \times 10^3 \text{ l/mol-s}$ at 25 °C.¹¹⁷ Selleck et al.¹¹⁹ calculated the time required to convert 99% of the residual chlorine to HOBr at 25 °C and a pH of 8.3, a typical pH for seawater. Figure 2.13 illustrates the calculations by Selleck et al. for low dosages of chlorine in various percentages of seawater.¹¹⁹ For 100% seawater, it takes only about 10s for 99% of the residual chlorine to be converted to HOBr, but the reaction is considerably slower if the seawater is diluted.

HOBr dissociates to hypobromite ion (OBr^-) in much the same way that HOCl dissociates to OCl^- :



As in the case of HOCl, the extent of dissociation depends primarily on pH. Assuming that concentration equals activity, the equilibrium expression is

$$K_a = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]}, \quad (2.71)$$

where K_a is the dissociation constant for HOBr. The value of K_a listed by a recent authoritative source is 2.82×10^{-9} at 25 °C,²⁸ although many older sources cite a value of 2×10^{-9} based on the work of Farkas and Lewin.¹²¹ Assuming a value of 2.82×10^{-9} , pK_a ($-\log K_a$) for HOBr is 8.55 at 25 °C, which is close to the typical pH of seawater (~8.3), and closer yet when the ionic strength of seawater (about 0.67) is taken into consideration. Therefore, significant percentages of both HOBr and OBr^- are expected to be present chlorinated seawater, with the actual fraction of each depending not only on pH but also on temperature and ionic strength. Tribromide ion, Br_3^- , can be formed in chlorinated seawater, but to a negligible extent.³¹

The fact that HOBr predominates at pH values up to about one unit higher than HOCl does is a salient factor in the chlorination of seawater. Seawater

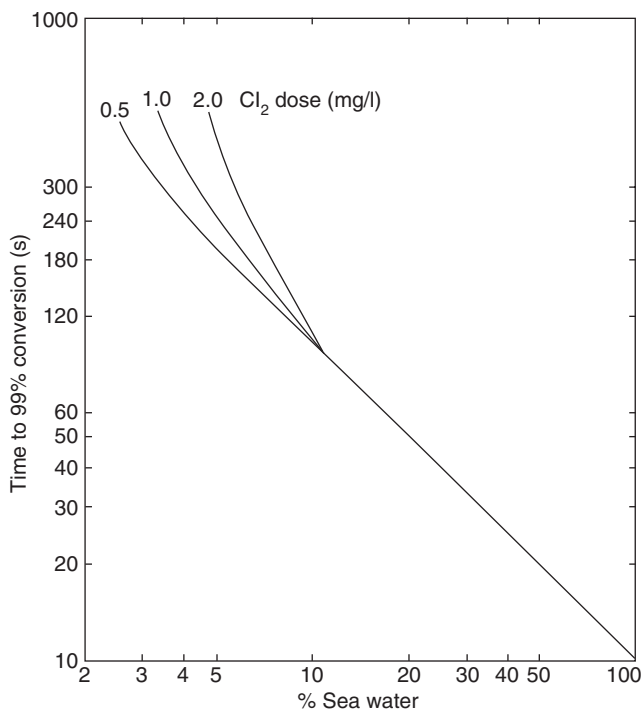


Figure 2.13. Time required for 99% conversion of free residual chlorine to HOBr at 25°C and pH 8.3¹²⁰ (courtesy of the *Journal—World Pollution Control Federation*).

chlorination has been successfully practiced by the electric power industry for nearly a century, so it is reasonable to conclude that the bromine species produced by the addition of chlorine are effective biocides. However, nearly all studies of the biocidal effectiveness of seawater chlorination have reported the residuals as chlorine when in reality they were most likely a mixture of bromine species. Thus, at typical seawater pH values, biocidal activity attributed to OCl^- might very well have been associated with HOBr, and perhaps to some extent, with OBr^- as well.

Some experiments on coliform destruction have compared chlorine generated from seawater with chlorine solutions prepared from freshwater using conventional chlorination equipment. These experiments have tended to show a better coliform kill with hypochlorite generated on-site from seawater. This may be attributable to the presence of HOBr and to its reduced dissociation in comparison with HOCl at any given pH.

HOBr exists in equilibrium with Br_2 , and the equilibrium relationship is analogous to the disproportionation reaction for Cl_2 :



The equilibrium constant (K_d) for this reaction is $5.8 \times 10^{-9} \text{ mol}^2/\text{l}^2$ at 25°C .^{31,121,122} Thus, for low ionic-strength water having a Br^- concentration of 65 mg/l and a temperature of 25°C , the concentrations of Br_2 and HOBr would be equal at a pH of 5.15. This pH is considerably higher than the pH at which equal concentrations of Cl_2 and HOCl exist under similar conditions. In seawater, the pH at which equal amounts of Br_2 and HOBr exist will be slightly lower than 5.15 due to ionic strength effects. Bromine (Br_2) was at one time extracted from seawater and from the Dead Sea by chlorination:



A pH of 3.5 was used to drive this reaction to completion. Other processes, described in Chapter 16, are used today.

Br_2 reacts with Br^- to form tribromide ion as follows:



The equilibrium constant for this reaction is 15.9 at 25°C . Significant amounts of Br_3^- are found only in highly concentrated bromine solutions, not in chlorinated seawater.

Since chlorination of seawater produces a residual consisting almost entirely of bromine, and since bromine reacts more rapidly and to a greater extent than chlorine with natural organic matter,¹²⁴ the halogenated DBPs produced when seawater is chlorinated are expected to contain mostly bromine rather than chlorine. Although seawater is not suitable for direct human consumption, the intrusion of even a small amount of seawater into a public water supply can dramatically alter the distribution of halogenated DBPs, as was nicely demonstrated by Lange and Kawczynski.¹²⁵ A public water supply located near a seacoast or estuary, or drawing water from an aquifer in contact with brackish water, such as connate water or oil-field brines, may be vulnerable to elevated concentrations of brominated DBPs.

Some halogenated DBPs, such as the trihalomethanes, are volatile or are able to pass through a reverse osmosis membrane, so chlorination of seawater prior to thermal or membrane desalination can cause these DBPs to be present in the finished water. Most seawater contains relatively little organic matter, with total organic carbon (TOC) concentrations of 0.5–1.0 mg/l commonly reported for samples collected in the open ocean. However, much higher TOC concentrations (5–10 mg/l) can occur in coastal areas, especially those subject to runoff carrying nutrients and organic matter, so desalination plants drawing water from coastal intakes may experience elevated finished water concentrations of brominated DBPs when practicing prechlorination. In such cases, an alternative oxidant, such as chlorine dioxide (see Chapter 14), may be helpful in meeting finished water quality standards. Additional information regarding DBPs is presented in Chapter 4.

Bromine, like chlorine, is photoreactive, but much less so than chlorine. Since bromine is more stable in sunlight, its use is favored when it is desirable to maintain a residual, but this can be a significant disadvantage when a treated stream is discharged into the natural environment. On the other hand, bromamines decompose much more rapidly than chloramines (chemically, not photochemically),¹²⁶ so at concentrations below the breakpoint, bromine produces a less stable residual than chlorine when ammonia is present.

More detailed information on the use of bromine, bromine chloride, and iodine for water and wastewater disinfection is presented in Chapter 16.

Ionic Strength Effects

The ionic strength of typical seawater is about 0.7M, which exceeds the limit (<0.5) associated with the modified Davies equation (Eq. 2.17). Thus, for seawater, brines, and other highly saline waters, such as those of the Salton Sea and the Dead Sea, activity corrections must be made using equations such as those developed by Pitzer and Mayorga,^{127–130} Bromley,¹³¹ or Meissner et al.^{132–134} Alternatively, conditional stability constants (based on concentrations measured in standard seawater), other empirical correlations, or tabulated values of activity can be used when appropriate.

The value of K_a for HOCl is also strongly influenced by the ionic strength of seawater. The following expression was developed by Sugam and Helz¹³⁵ to estimate the value of $p^c K_a$ for HOCl as a function of temperature and chlorinity in artificial seawater:

$$p^c K_a = 937.7/T - 0.149\text{Cl}^{1/3} + 4.433, \quad (2.75)$$

where

- $p^c K_a$ = $-\log$ (concentration-based acid dissociation constant),
- T = absolute temperature in degrees Kelvin ($273.15 + ^\circ\text{C}$), and
- Cl = chlorinity (g/kg).

However, since real seawater contains bromide, chlorine applied in the dosages typically used for seawater chlorination will be converted to bromine species, as described above. Therefore, Equation (2.75) is useful only when chlorine is applied to brines free of bromide or when it is applied in excess of the available bromide, so that a free chlorine residual actually exists.

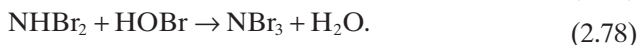
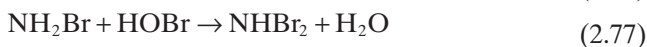
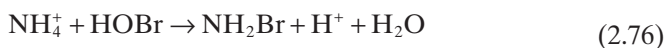
The ionic strength of seawater will influence the dissociation of HOBr but will have little effect on the activity of uncharged HOBr molecules. Disinfection data for seawater chlorination should be viewed with caution since it is not always clear which species are actually present. Both chlorine and bromine species may be present; the extent to which HOBr and HOCl have dissociated may not be accurately known; and both chloramine and bromamines (dis-

cussed below) will form if ammonia is present. Moreover, OBr^- and OCl^- may form ion pairs with sodium or other cations present in seawater;^{136–139} and the susceptibility of the organisms or microorganisms to inactivation by the disinfectant species actually present may be influenced by ionic strength or by the effects of specific ions on transport of disinfecting species through cell membranes.

Bromamine Formation and Decay

When ammonia nitrogen is present in seawater, it greatly complicates the chemical reactions between chlorine species and bromide. Initially, there are two competing reactions occurring simultaneously: (a) the reaction of chlorine with bromide to produce HOBr , which is very rapid; and (b) the reaction of chlorine with ammonia to produce chloramines, which is practically instantaneous at pH 8.3. These reactions occur at similar speeds, but the concentration of bromide in seawater (50–70 mg/l) is usually far higher than the ammonia concentration, so HOBr formation is expected to outpace chloramine formation under conditions typical of seawater chlorination, although both will be formed.

Once HOBr forms, it too will react with ammonia to form monobromamine (NH_2Br , also known as bromamide), dibromamine (NHBr_2 , also known as bromimide), and tribromamine (NBr_3 , also known as nitrogen tribromide). Mixed *N*-bromo-*N*-chloramines such as NHBrCl can also form,^{31,140} and Haag¹⁴⁰ has identified possible pathways for their formation. Bromamine formation reactions parallel those describing chloramine formation (Eqs. 2.38–2.40):

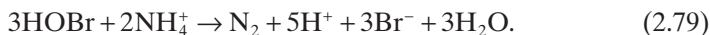


NBr_3 formation, like NCl_3 formation, is favored by lower pH values and higher $\text{Br}_2:\text{N}$ ratios.¹²⁶ Bromine reacts with organic amines in much the same manner as chlorine does, forming organic bromamines, with the rate of reaction depending on the basicity of the nitrogen group, and in many cases greatly exceeding the rate of reaction with ammonia.¹⁴¹

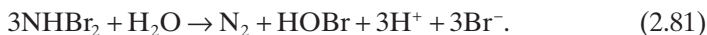
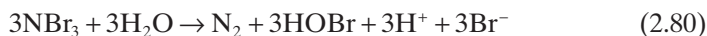
Inman and Johnson¹⁴² examined the influence of ammonia concentration on the relative concentrations and chloramine and bromine species when seawater is chlorinated. They concluded that when ammonia is present at a relatively high concentration (>0.5 mg/l as N) and the chlorine dosage is relatively low (less than 2.5 mg/l), a mixture of NH_2Cl and NHBr_2 will form; but at higher chlorine dosages and longer contact times, NH_2Cl will begin to predominate, especially since it will persist much longer than NHBr_2 . When the

ammonia-N concentration is less than 0.4 mg/l and the chlorine dose is sufficiently high, a mixture of HOBr and NBr₃ will be formed.

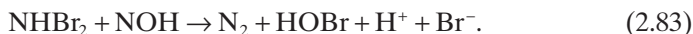
The stoichiometry of the breakpoint reaction between bromine and ammonia is the same as that for the breakpoint reaction between chlorine and ammonia and can be expressed as follows:



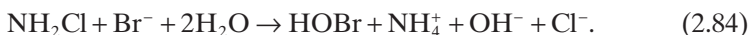
Decomposition of bromamines to diatomic nitrogen may occur primarily by way of decomposition of NBr₃ at Br₂:N ratios greater than 3:2, and NHBBr₂ is known to decompose rather rapidly even at lower Br₂:N ratios.¹²⁶ These reactions can be expressed as follows:



The exact mechanisms are unknown, but various possibilities have been discussed by LaPointe et al.¹⁴³ As in the case of the breakpoint reaction between chlorine and ammonia, some investigators have hypothesized that NOH is an intermediate species that forms by hydrolysis of dibromamine and then initiates decomposition of dibromamine to nitrogen as follows:



It was once thought that chloramines could react with bromide to form HOBr, as exemplified by the following reaction involving monochloramine:



However, this reaction, if it occurs at all at neutral pH, produces extremely little HOBr, as evidenced by the fact that chloramination (under controlled conditions) does not produce brominated trihalomethanes. (Traces of brominated trihalomethanes may be formed in full-scale plants practicing chloramination because bromide may be present in the water used to prepare and carry the concentrated chlorine solution.) This reaction does not proceed at pH 4, which is the basis for a residual chlorine analyzer that responds only to free chlorine and not to chloramines.¹⁴⁴

Although the reactions between bromine and ammonia are in many ways very similar to those between chlorine and ammonia, there are several significant differences:^{126,143}

1. Formation of NHBBr₂ is strongly favored over NH₂Br at neutral pH values, even at relatively low Br₂:N ratios.

2. Bromamine species can be converted from one form to another simply by changing the pH of the solution, that is, they are equilibrium controlled, whereas the distribution of chloramine species is controlled by their relative rates of formation and decay, which varies with pH.
3. NH_2Cl , the predominant chloramine species at neutral pH when the $\text{Cl}_2:\text{N}$ molar ratio is less than 1:1, is relatively stable in water, whereas NHBr_2 , the predominant bromamine species under similar conditions, decomposes rather rapidly to N_2 (Eq. 2.81), which is a distinct advantage in wastewater discharged into a receiving stream.

Due to the predominance of NHBr_2 in chlorinated seawater and its relatively rapid decomposition to N_2 , removal of ammonia nitrogen from seawater does not depend on the molar ratio of HOBr to $\text{NH}_3\text{-N}$ (R.E. Selleck, pers. comm.). Also, since NBr_3 has been found to have significant virucidal activity,¹²³ and since bromamines have been found to be as effective as HOBr as disinfectants,^{126,145} the presence of ammonia in seawater does not pose the same problems as it does for chlorination of municipal drinking water supplies and wastewater effluents.

OXIDATION-REDUCTION REACTIONS OF CHLORINE COMPOUNDS

Fundamental Considerations

Oxidation-reduction reactions, also referred to as “redox” or electrochemical reactions, involve the transfer of electrons from one substance to another. Oxidation occurs when electrons are lost; reduction occurs when electrons are gained. A substance is said to be oxidized when it loses electrons, and such substances are sometimes referred to as electron donors or reductants. An oxidant is a substance able to be reduced by gaining electrons, so oxidants are sometimes referred to as electron acceptors. Redox reactions are always coupled, and the number of electrons lost must equal the number of electrons gained.

Chlorine is an oxidant. When chlorine oxidizes a contaminant, chlorine gains electrons and is reduced to chloride; and the contaminant loses electrons and is oxidized. Considering reactions involving chlorine as redox reactions is helpful in (a) writing balanced reactions to determine reaction stoichiometry since the number of electrons gained must equal the number of electrons lost; (b) determining whether a given reaction is thermodynamically possible under a specific set of conditions; and (c) determining the redox potential associated with a reaction under a specific set of conditions, which can be useful for instrumentation and control purposes. Examples are presented and discussed below.

The oxidation and reduction reactions in any redox reaction may be written as separate “half-reactions.” When two half-reactions are added together in

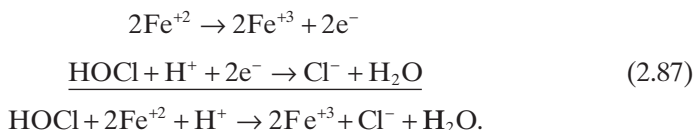
proper fashion, they yield a balanced redox reaction. For example, when HOCl is used to oxidize ferrous iron (Fe^{+2}), the oxidation reaction is



and the reduction reaction is



Multiplying Equation 2.85 by 2 (so the electrons will cancel) and adding it to Equation 2.86 yields the balanced overall reaction:



Half-reactions for free and combined chlorine species, and for selected alternative oxidants, reducing agents, and water and wastewater contaminants, are listed in Table 2.10 along with their standard potentials. The standard potential of a half-reaction, E^0 , is a measure of its potential to transfer electrons under standard conditions (25 °C, 1 atm, with all products and reactants at unit activity) relative to the half-reaction for hydrogen ($2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$), which has been assigned a value of 0 volts. Standard potentials for many other half-reactions may be found in handbooks,^{16,28} in reference books,¹⁴⁶ and in publications pertaining to specific chemicals of interest. The standard potential for a redox reaction, E_{rxn}^0 , is determined by adding together the standard potentials of the half-reactions involved, reversing the sign of the potential if the half-reaction is reversed.

Example. Determine the standard potential, E_{rxn}^0 , for oxidation of Fe^{+2} by HOCl.

The half-reaction for Fe^{+2} shown in Table 2.10 must first be reversed to reflect the oxidation of Fe^{+2} (Eq. 2.85) rather than the reduction of Fe^{+3} ; and, if the half-reaction is reversed, the sign of E^0 must also be reversed (from +0.771 to -0.771). The standard potential for the reaction (Eq. 2.87) is then calculated as follows:

$$E_{\text{rxn}}^0 = 1.482 + (-0.771) = +0.711 \text{ V}. \quad (2.88)$$

Note that the value of E^0 for Fe^{+2} oxidation was not multiplied by 2. E^0 is not proportional to the number of electrons transferred, but is related to the tendency of electrons to be transferred, analogous to voltage rather than current in an electrical system and to pressure rather than flow rate in a hydraulic system.

Since E_{rxn}^0 is positive for the oxidation of Fe^{+2} by HOCl, the reaction will proceed spontaneously (with no added energy), in the direction shown, under

TABLE 2.10. Half-Reactions and Standard Potentials for Selected Chlorine Compounds, Alternative Disinfectants, Contaminants, and Reducing Agents

Half-Reaction	E^0 (V)	Reference
$\text{Cl}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.396	16
$\text{HOCl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$	+1.482	28
$\text{OCl}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.81	28
$\text{Cl}_3^- + 2\text{e}^- \rightarrow 3\text{Cl}^-$	+1.415	16
$\text{NH}_2\text{Cl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{NH}_4^+$	+1.40	147
$\text{NHCl}_2 + 3\text{H}^+ + 4\text{e}^- \rightarrow 2\text{Cl}^- + \text{NH}_4^+$	+1.34	147
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.0873	28
$\text{HOBr} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Br}^- + \text{H}_2\text{O}$	+1.331	28
$\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$	+1.423	28
$\text{OBr}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Br}_2 + 2\text{OH}^-$	+0.761	28
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.5355	28
$\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	+0.536	28
$\text{HOI} + \text{H}^+ + 2\text{e}^- \rightarrow \text{I}^- + \text{H}_2\text{O}$	+0.977	28
$\text{OI}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{I}^- + 2\text{OH}^-$	+0.485	28
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87	28
$\text{ClO}_2(\text{aq}) + \text{e}^- \rightarrow \text{ClO}_2^-$	+0.954	28
$\text{ClO}_2^- + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Cl}^- + 4\text{OH}^-$	+0.76	28
$\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O}$	+1.451	28
$\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{Cl}^- + 4\text{H}_2\text{O}$	+1.389	28
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.076	28
$\text{OH}\cdot + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O}$	+2.8	146
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.229	28
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	+0.695	28
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.776	28
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.679	28
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00000	28
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.8277	28
$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	+0.771	28
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{+2} + 2\text{H}_2\text{O}$	+1.224	28
$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$	+0.01	28
$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_3\text{AsO}_3 + 2\text{H}_2\text{O}$	+0.560	28
$\text{CNO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CN}^- + 2\text{OH}^-$	-0.97	16
$\text{S}_4\text{O}_6^{2-} + 2\text{e}^- \rightarrow 2\text{S}_2\text{O}_3^{2-}$	+0.08	28
$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_2(\text{aq}) + \text{H}_2\text{O}$	+0.158	16
$\text{H}_2\text{SO}_3 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{S}^0 + 3\text{H}_2\text{O}$	+0.449	28
$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	+0.172	28
$\text{SO}_4^{2-} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{SO}_3^{2-} + 2\text{OH}^-$	-0.93	28
$\text{S}^0 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{S}(\text{aq})$	+0.142	28
$\text{S}^0 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HS}^-$	+0.287	16

Following IUPAC convention, each half-reaction is written as a reduction reaction. E^0 values are for 25°C.

standard conditions, that is, at 25°C and with each product and reactant present at unit activity. However, such conditions are rarely pertinent to environmental applications. The following equation, referred to as the Nernst equation, may be used to determine reaction potential under nonstandard conditions:

$$E_{\text{rxn}} = E_{\text{rxn}}^0 - \frac{RT}{nF} \ln(Q), \quad (2.89)$$

where

R = universal gas constant (1.987×10^{-3} kcal/mol-K),

T = absolute temperature in degrees Kelvin ($273.15 + ^\circ\text{C}$),

n = number (equivalents) of electrons transferred,

F = Faraday constant (23.061 kcal/equiv-V), and

Q = reaction quotient.

The reaction quotient, Q , has the same form as the equilibrium constant but is used when a reaction is not at equilibrium. Assuming a temperature of 25°C, substituting appropriate values for R and F into Equation (2.89), and converting from a natural (base e) logarithm to a base 10 logarithm, yields a simplified form of the Nernst equation:

$$E_{\text{rxn}} = E_{\text{rxn}}^0 - \frac{0.05916}{n} \log(Q). \quad (2.90)$$

Example. Determine the reaction potential for oxidation of Fe^{+2} using HOCl under the following conditions: HOCl = 0.709 mg/l as Cl_2 (10^{-5} M); Cl^- = 10 mg/l (2.82×10^{-4} M); Fe^{+2} = 1 mg/l (1.79×10^{-5} M); Fe^{+3} = 10^{-12} M, limited by the solubility of $\text{Fe}(\text{OH})_3(\text{s})$; pH = 6.00; and temperature = 25°C. Ignore ionic strength effects (i.e., assume concentration equals activity).

After writing the balanced reaction (Eq. 2.87), determine the reaction quotient, Q :

$$Q = \frac{[\text{Cl}^-][\text{Fe}^{+3}]^2}{[\text{HOCl}][\text{H}^+][\text{Fe}^{+2}]^2} = \frac{(2.82 \times 10^{-4})(10^{-12})^2}{(10^{-5})(10^{-6})(1.79 \times 10^{-5})^2} = 8.8 \times 10^{-8}$$

Knowing the value of Q , use the Nernst equation (Eq. 2.90) to calculate the reaction potential:

$$E_{\text{rxn}} = 0.711 - \frac{0.05916}{2} \log(8.8 \times 10^{-8}) = +0.919 \text{ V}.$$

Thus, oxidation of Fe^{+2} by HOCl proceeds spontaneously (is thermodynamically favorable) under conditions similar to those typically encountered

in water treatment applications. Equivalent results can be obtained by calculating the free energy of reaction, but reaction potentials are much more widely used than free energy by water and wastewater treatment professionals.

Standard reaction potentials can also be used to estimate the extent of reaction that can be achieved under specified conditions. At equilibrium, Q equals the equilibrium constant (K) and $E_{\text{rxn}} = 0$. Substituting these values in Equation (2.90) and rearranging it yields the following relationship:

$$K = 10^{(nE^0)/0.05916} \quad (2.91)$$

Example. Determine the equilibrium constant for the oxidation of Fe^{+2} with HOCl and determine how much Fe^{+2} will remain in solution at equilibrium under the conditions stated in the previous example.

$$K = 10^{(2 \times 0.711)/0.05916} = 10^{24.04}$$

$$\text{Fe}^{+2} = \left[\frac{(2.82 \times 10^{-4})(10^{-12})^2}{(10^{-5})(10^{-6})(10^{24.04})} \right]^{0.5} = 5.1 \times 10^{-21} \text{ M} \quad (\text{i.e., nondetectable}).$$

There are important practical limitations to the use of calculations based on standard potentials and other thermodynamic data, as described below, and the reader is cautioned to carefully examine the details of a redox reaction before relying on such calculations. Additional information on writing and balancing half-reactions and on making and interpreting calculations involving equilibrium constants, reaction potentials, and free energies can be found in any good water chemistry textbook, including those by Snoeyink and Jenkins,¹⁴⁸ Pankow,¹⁴⁹ Benjamin,¹⁵⁰ and Jensen.¹⁵¹

Practical Considerations

Combining properly balanced half-reactions is an excellent way to determine the stoichiometry of a redox reaction; and thermodynamic calculations, such as those made above for Fe^{+2} oxidation by HOCl , can be helpful in determining whether a reaction proceeds spontaneously in the direction written (or in reverse) and where equilibrium lies. However, thermodynamic calculations have important practical limitations. First among these is that they provide no information about the rate of a reaction (unless the rate of reaction in one cell is known, in which case a chemist can potentially learn something about the rate of the half reaction in the other cell; G. Gordon, pers. comm.). For example, in the case of Fe^{+2} oxidation, HOCl , NH_2Cl , and oxygen (O_2) all yield positive reaction potentials under typical water treatment conditions, but NH_2Cl reacts too slowly to be of practical use in most treatment applications, and oxygen oxidizes Fe^{+2} rapidly only at higher pH values or in the presence of iron-oxidizing bacteria or a chemical catalyst. The rate of most redox

reactions is significantly influenced by pH and temperature and may also be influenced by substances having catalytic or inhibitory effects. Such information is obtained primarily through experimentation and experience. Fortunately, a great deal of reliable information regarding oxidation of commonly encountered contaminants has been reported in the scientific literature, and information pertaining to selected contaminants found in water and wastewater is presented in a subsequent section of this chapter.

Another reaction that is thermodynamically favorable under typical treatment conditions is the oxidation of water by chlorine. Fortunately, this reaction is extremely slow under typical treatment conditions, allowing chlorine to serve as a useful disinfecting agent—unlike fluorine, which reacts much too rapidly with water to be a useful disinfectant. However, oxidation of water by chlorine is catalyzed by sunlight, heat, high chlorine concentrations, and certain metal ions, so chlorine decomposition can be significant in uncovered basins and in concentrated hypochlorite solutions, especially those containing impurities. Similarly, many reducing agents, such as metallic sodium, react rapidly, and sometimes violently, with water, reducing the water to hydrogen. Therefore, only a limited number of reducing agents, including several sulfur compounds listed in Table 2.10, are useful as dechlorinating agents in water and wastewater treatment. See Chapter 11 for additional information regarding dechlorination.

Several other limitations of thermodynamic calculations involving redox reactions are worth noting:

1. Stable intermediates may form even though more highly oxidized or reduced end products are thermodynamically favored. For example, oxidation of hydrogen sulfide (H_2S) with chlorine can produce elemental sulfur particles (S^0) rather than sulfate, and chlorine dioxide (ClO_2) preferentially decomposes to chlorite rather than chloride ion in most water treatment applications.
2. Although it is tempting to compare half-reaction potentials, such comparisons are generally meaningless except for species reacting in very similar fashion, such as HOCl and HOBr . A reaction can proceed spontaneously only if the reaction potential of the overall reaction is positive under the conditions of interest, regardless of the standard potential associated with one of the half-reactions; and a reaction having a higher reaction potential may proceed more slowly than one with a lower reaction potential, or not at all.
3. Although reaction potentials can sometimes be exploited for useful purposes, as in control systems based on oxidation–reduction potential (ORP) measurements (described below), they are not useful indicators of disinfecting power when comparing one disinfectant with another. For example, hydrogen peroxide (H_2O_2) has a relatively high reaction potential in a number of possible reactions, but it is a relatively weak disinfectant because catalase enzymes are able to neutralize it as it diffuses

through the cell wall. Furthermore, oxidation is not the only mechanism involved in disinfection. In the case of chlorine, substitution reactions are believed to play an important role in disrupting the functions of proteins and nucleic acids.

4. Reaction potentials are relevant only if they are based on the actual chemical species involved in the reaction of interest. For example, a reaction potential calculated using the half-reaction for $\text{Cl}_2(\text{aq})$ would probably not be applicable to a reaction involving a low concentration of chlorine at pH 6 since most of the chlorine would be present as HOCl . However, the predominant chemical species is not necessarily the one that dominates the reaction. HOCl may be largely responsible for disinfection of a particular organism at a pH greater than pK_a even though OCl^- is the dominant chlorine species present; and NH_2Cl formation proceeds most rapidly at pH 8.4 (at 25°C) even though neither of the two species thought to be involved in the rate-limiting step (HOCl and NH_3) is predominant at that pH value.

ORP MEASUREMENTS

The reaction potential associated with a particular redox reaction can be measured by allowing the half-reactions to proceed in separate compartments of a galvanic cell and measuring the potential between them using an indicator electrode that is sensitive to the concentration (activity) of only one species involved in the reaction and a reference electrode having a potential that does not change over the range of conditions of interest.¹⁴⁸ Physical chemists construct such systems to determine standard potentials and to study interactions between chemical species, such as dissociation and complex formation. In similar fashion, analytical chemists use an ion-selective or gas-sensing electrode to measure the potential of a redox reaction, with the potential then being used to determine the concentration of a specific chemical species. An example is the potentiometric iodide electrode described in Chapter 3. Analytical chemists have also developed amperometric (or polarographic) methods of analysis based on the measurement of the current (rather than the voltage) associated with a particular redox reaction. An example is the amperometric method for determining chlorine residuals described in Chapter 3.

Indicating electrodes used for analytical purposes are typically designed to isolate the reaction of interest from others that may occur, thereby eliminating or limiting interferences. There are also nonspecific indicating electrodes that can be used to determine the ORP of a solution in which one or more redox reactions is occurring.^{148,152} ORP electrodes are unable to sense many important redox reactions, so there are many applications for which they are not useful, even if only a single redox reaction is occurring. In a complex mixture, such as a drinking water supply or a municipal or industrial wastewater efflu-

ent, the potential measured using an ORP electrode is influenced by all of the redox reactions occurring at the electrode surface, so it is a “mixed potential” that is usually difficult or impossible to fundamentally relate to one particular redox reaction.¹⁴⁸ However, in some systems, ORP is strongly influenced or dominated by one particular reaction of interest and can therefore provide useful information even though the signal is fundamentally semiquantitative in nature. ORP electrodes have been successfully employed in monitoring and controlling a number of processes, including chlorination, chloramination, dechlorination, and even biological processes, including anaerobic digestion and biological nutrient removal.

The potential associated with a particular half-reaction in pure solution can be readily calculated from the standard potential using a modified version of the Nernst equation (Eq. 2.90):

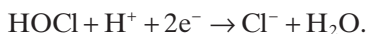
$$E_H = E_H^0 - \frac{0.05916}{n} \log \left[\frac{\{\text{red}\}}{\{\text{oxid}\}} \right], \quad (2.92)$$

where E_H is the half-reaction potential (ORP), E_H^0 is the standard half-reaction potential relative to the standard half-reaction for hydrogen, and the bracketed quantity represents the reaction quotient expressed using the species on the reduced and oxidized sides of the pertinent half-reaction. The standard half-reaction potential for hydrogen has been assigned a value of zero and is the reference potential against which other standard potentials are measured. If a standard hydrogen electrode is used as the reference electrode, the indicating electrode will measure E_H directly, but a standard hydrogen electrode is rarely used, even in the laboratory. A silver/silver-chloride (Ag/AgCl) or calomel reference electrode is typically used instead, resulting in a shift in the measured potential as follows:

$$E_{\text{Measured}} = E_H - E_{\text{Reference}}. \quad (2.93)$$

Example. Determine the theoretical electrochemical potential of a free chlorine residual of 1.0 mg/l as Cl_2 in a pure solution having a pH of 6.0, a temperature of 25 °C, and a chloride concentration of 10 mg/l. Assume that all of the free chlorine is present in the form of HOCl.

The half-reaction for HOCl is



From Table 2.10, E_H^0 for HOCl is 1.482. Substituting into Equation (2.92) and ignoring the effects of ionic strength:

$$\begin{aligned} E_H &= 1.482 - \frac{0.05916}{2} \log \left[\frac{[\text{Cl}^-]}{[\text{HOCl}][\text{H}^+]} \right] \\ &= 1.482 - \frac{0.05916}{2} \log \left[\frac{(10/35,453)}{(1/70,906)(10^{-6})} \right] = 1.266 \text{ V}. \end{aligned}$$

Relative to an Ag/AgCl reference electrode, which has a standard potential of 0.222 V, the measured potential would theoretically be

$$E_{\text{Measured}} = 1.266 - 0.222 = 1.044 \text{ V.}$$

Measured potentials are typically reported in millivolts (mV) rather than volts, so the measured potential for the pure solution in the above example would be 1044 mV if the electrode system behaved ideally. Unfortunately, ORP readings in field applications, including water and wastewater treatment, have been found to correlate very poorly with calculated E_H values. The indicating electrode measures a “mixed potential,” as noted above; the electrodes are subject to drift, polarization, fouling, and poisoning; and some reactions produce no signal while others may be irreversible.³³ ORP also varies with temperature, pH, and ionic strength, but these effects are predictable and can be compensated for. Fortunately, even if an ORP electrode measures a potential that differs greatly from the theoretical value, it may still provide a stable signal that is useful for process control, as described below.

Since measured ORP values have little or no fundamental significance, it is common practice to use the ORP of the untreated stream as a baseline against which to compare values obtained from the treated stream. Some investigators report “differential potentials,” based on the difference between treated and untreated streams, rather than potentials measured relative to the standard hydrogen electrode or a reference electrode. In water and wastewater treatment, it is also common practice to measure the chlorine residual and to then adjust the measured ORP to correspond to the value found on a “calibration” curve. Therefore, the values reported for one system may not be directly comparable with those for another system.

General dissatisfaction with the orthotolidine method of measuring chlorine residuals led a number of investigators to evaluate ORP as a measure of the germicidal efficiency of various chlorine species.^{153–156} In 1933, Schmelkes¹⁵³ examined the ORP of chlorine solutions as a function of pH and the ratio of chlorine to ammonia. As shown in Figures 2.14 and 2.15, he found that free chlorine has a much higher potential than chloramines formed from ammonia or organic nitrogen, ammonia addition lowers the ORP of a chlorine solution, and ORP decreases with increasing pH, as expected based on thermodynamic calculations. These results were consistent with contemporary findings that free chlorine is a better germicide than combined chlorine and that germicidal efficiency increases with decreasing pH. In a follow-up study, Schmelkes et al.¹⁵⁴ found a relationship between ORP and disinfection efficiency, illustrated in Figure 2.16. These results were encouraging and suggested that ORP measurements might help avoid problems associated with false or misinterpreted results from orthotolidene tests. However, subsequent investigations demonstrated that ORP has serious shortcomings as a measure of disinfection efficiency.

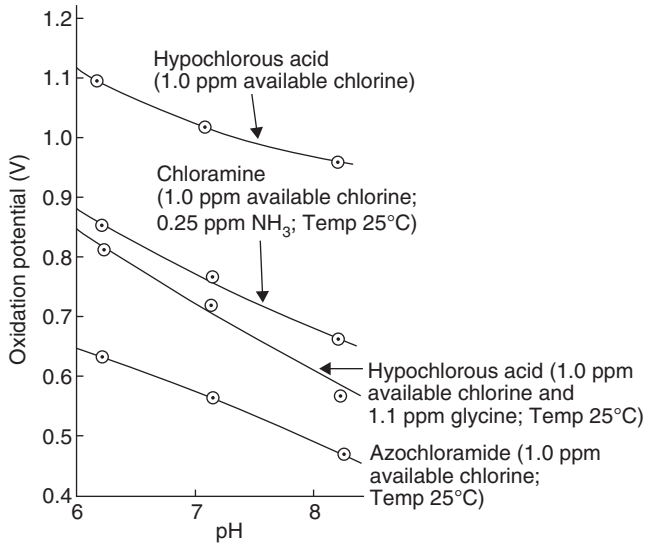


Figure 2.14. Oxidation potentials of chlorine compounds.¹⁵³

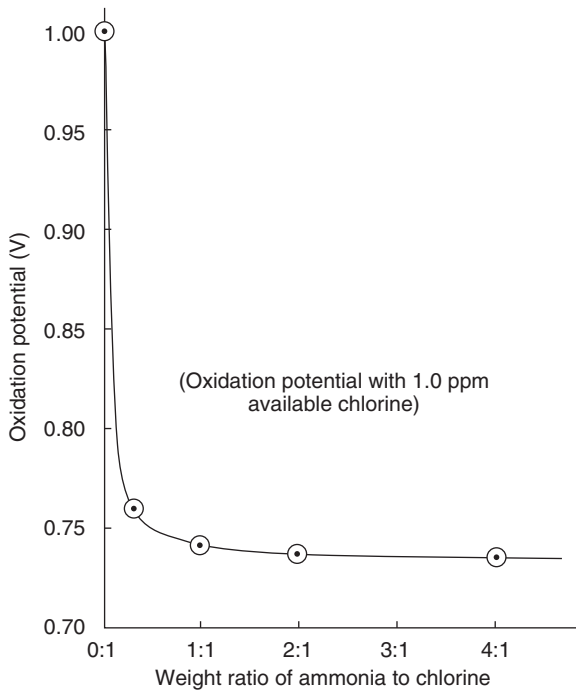


Figure 2.15. Oxidation potential as a function of the weight ratio of ammonia to chlorine.¹⁵³

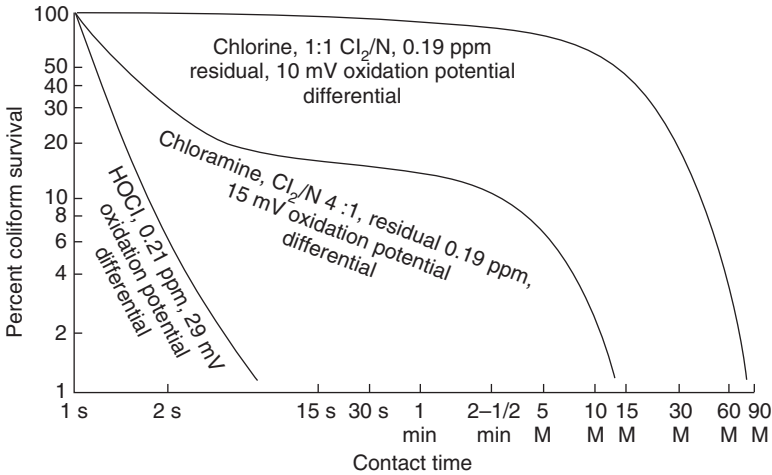


Figure 2.16. Relationship of germicidal efficiency and ORP differential.¹⁵⁴ (“Potential differential” is the difference in potential between chlorinated and unchlorinated streams measured using a dual-cell mercury electrode.)

Over the next few years, Chang and Fair¹⁵⁷ and Chang^{155,156,158} did some notable work on inactivation of microorganisms by chlorine. This work included an investigation of the ORP of germicidally active chlorine in which Chang¹⁵⁶ concluded that interfering substances and uncertainty as to the amount of dissolved oxygen in raw waters and the reversibility of various reactions made it impossible to directly relate ORP measurements to residual chlorine. He did find that free chlorine, inorganic chloramines, and organic chloramines all had their own characteristic oxidation potentials; but he also found that the ORP of a cysticidal concentration of one disinfectant was unrelated to the ORP of a cysticidal concentration of any other disinfectant. This in itself rendered useless the concept of using ORP to evaluate the germicidal efficiency of different chlorine compounds. In a later study, Victorin et al.¹⁵⁹ found that ORP correlated better with disinfection efficiency than did total disinfectant residual when comparing one disinfectant with another; but for individual disinfectants, they found that disinfection efficiency was more strongly correlated to the residual disinfectant concentration than to ORP.

Practical Applications of ORP Measurements

Rideal and Evans¹⁶⁰ described the use of ORP electrodes to control chlorination in 1913. However, ORP proved to be a poor indicator of disinfection efficiency; measured ORP values were poorly correlated with calculated values; and the electrodes initially available to measure ORP were found to be rapidly fouled or poisoned when used in water and wastewater treatment

applications. Therefore, ORP was considered for many years to be unsuitable for process control. However, ORP electrodes are especially sensitive to the concentrations of chlorine and bisulfite in water, making them attractive for process control, so efforts to develop a practical control system based on ORP continued.

Frank Strand, founder of Stranco Corporation of Bradley, Illinois (now a subsidiary of Siemens Water Technologies Corporation), eventually developed ORP electrodes that give stable readings in the complex and highly oxidative environment associated with free chlorine residuals and that are much less subject to fouling and poisoning than earlier ORP electrodes. His first successful applications involved control of chlorination and pH in large indoor and outdoor swimming pools.^{161,162} Stranco control systems are still used for this purpose today, and they were later employed with great success for chlorination and dechlorination processes at water treatment plants and WWTPs and power plants. Control systems for chlorination and dechlorination at water and wastewater treatments plants are described in detail in Chapter 12.

The Stranco swimming pool control system uses an ORP signal to start and stop the chlorinator and a pH signal to start and stop a pump feeding a caustic (sodium carbonate) solution. The system maintains precise control of the pH, ensuring a constant percentage of undissociated HOCl, and it also maintains a high free chlorine concentration (1.5–2.5 mg/l) to rapidly inactivate pathogens and to keep the pool free from algae and other nuisance organisms, making its water clear and sparkling. Maintaining a high free chlorine residual also helps oxidize organic nitrogen compounds, which, if allowed to accumulate, will eventually convert much of the chlorine residual to dichloramine, upset the water quality, and create the need to shut down the pool for draining and flushing.

In 1975, White¹¹⁰ investigated four swimming pools, three of which were using a Stranco control system and one was using conventional pH and chlorine residual controls. At a constant free chlorine residual of 2.1 mg/l, ORP was measured in each pool at pH values from 6 to 10. In each case, ORP was strongly influenced by pH, shifting about 60 mV for a change of one pH unit (Fig. 2.17). This illustrates why it is important for an ORP control system to properly incorporate pH measurements. It is also noteworthy that the ORP readings at Gilroy and Petaluma differed by about 60 mV at identical pH values. In a second series of tests, ORP was measured in each pool's water at a constant pH of 7.5 with free chlorine residuals ranging from 0.1 to 10 mg/l. As shown in Figure 2.18, ORP is very sensitive to free chlorine, especially at low concentrations.

As illustrated in Figures 2.17 and 2.18, each water yields a different ORP reading for a given chlorine concentration. The ORP values of the untreated waters also vary and are said to be “poised” at a particular level. The term “poised” can be used to describe a solution that resists changes in redox potential,¹⁶³ much in the way that a buffered solution resists changes

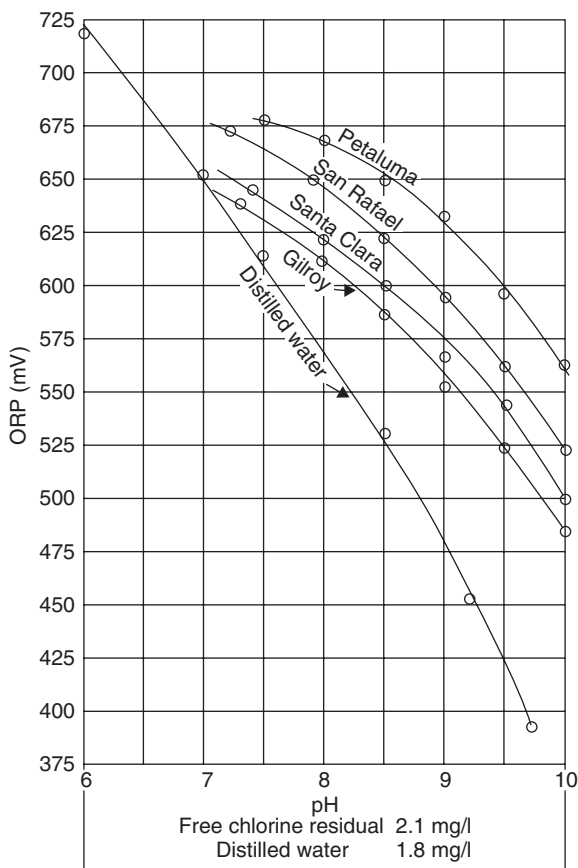


Figure 2.17. ORP as a function of pH at a fixed chlorine residual (2.1 mg/l).

in pH, and “poising intensity” is the electrochemical equivalent of “buffer intensity.”¹⁶⁴ However, in water and wastewater treatment, the water is only weakly buffered with respect to ORP since a small change in chlorine concentration causes a large change in ORP. The baseline ORP (or “poise”) is produced by the interaction of the electrodes with various constituents in the water and the reading typically takes about 24h to stabilize (R.W. Dennis, pers comm.). The control system is calibrated to the natural poise of the untreated water. If the water source or the character of the water is changed, the system must be recalibrated.

REACTIONS OF CHLORINE WITH SELECTED CONSTITUENTS

The reactions of chlorine with ammonia, organic nitrogen, and bromide were discussed earlier in this chapter; its reactions with organic matter

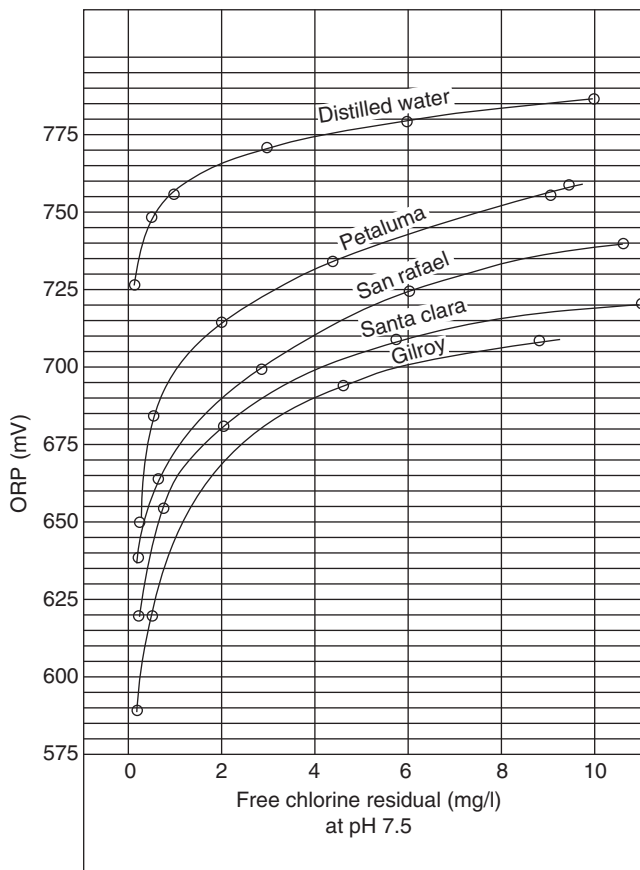


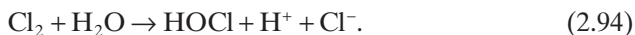
Figure 2.18. ORP as a function of free chlorine residual at a constant pH in five different waters.

are briefly addressed in Chapter 4, and its reactions with various dechlorinating agents are described in Chapter 11. The reactions of chlorine with selected constituents found in water and wastewater are described below. Its reaction with alkalinity, the first constituent discussed below, is an acid–base reaction. The remaining reactions described below are redox reactions, which can also consume alkalinity by releasing protons into solution.

Alkalinity

Alkalinity is a measure of the capacity of water to neutralize acidity. When a chlorine solution prepared from gaseous chlorine is used to chlorinate water or wastewater, it is diluted to the point that molecular chlorine behaves as a

strong acid, so the equilibrium reaction described by Equation (2.3) can be assumed to proceed completely to the right as follows:



Thus, each mole of chlorine added produces 1 mol of protons (H^+ ions), or 1 mol of acidity, which will destroy 1 mol of alkalinity. Dissociation of hypochlorous acid will release a second proton, but the extent of dissociation depends on the pH, temperature, and ionic strength of water, as described earlier in this chapter.

Example. Determine how much alkalinity is destroyed by adding 1 mg/l of Cl_2 to a low ionic-strength water having a pH (after Cl_2 addition) of 8.0 at a temperature of 25°C.

$$(1 \text{ mg/l } \text{Cl}_2) / (70,906 \text{ mg/mol}) = 1.41 \times 10^{-5} \text{ M } \text{Cl}_2.$$

From Table 2.3, $\text{HOCl} = 25.6\%$ at pH 8.0 and 25°C, so $\% \text{OCl}^- = 74.4\%$; and H^+ produced = alkalinity destroyed, so

$$\text{Alkalinity destroyed} = 1.41 \times 10^{-5} (1 + 0.744) = 2.459 \times 10^{-5} \text{ M}.$$

Converting alkalinity to the more familiar units of milligrams per liter as CaCO_3 :

$$\begin{aligned} (2.459 \times 10^{-5} \text{ M})(1 \text{ equiv } \text{H}^+ / \text{mol}) &= 2.459 \times 10^{-5} \text{ equiv/l} \\ (2.459 \times 10^{-5} \text{ equiv/l})(500 \text{ mg } \text{CaCO}_3 / \text{equiv}) &= 1.23 \text{ mg/l as } \text{CaCO}_3. \end{aligned}$$

In similar fashion, addition of NaOCl or $\text{Ca}(\text{OCl})_2$, which are bases, will increase alkalinity, with a dosage of 1 mg/l as Cl_2 increasing the alkalinity by 0.7 mg/l as CaCO_3 .

As chlorine reacts with various constituents in the water, additional acidity may be produced, as is the case for the constituents discussed later in this section and for ammonia, as discussed below. However, without knowing the specific constituents contributing to the chlorine demand of a particular water, it is not possible to precisely determine how much acidity will be produced, nor is this usually necessary, since the operator will ultimately adjust the pH to the desired value, provided that appropriate chemical feeding equipment has been installed. A good rule of thumb for initial estimating, when the nature of the chlorine demand is unknown, is to assume that 1 mol of protons will be produced for each mole of chlorine consumed. When adding molecular chlorine, this rule predicts an overall alkalinity consumption of 1.4 mg/l as CaCO_3 for each milligram per liter of Cl_2 demand and no net effect on alkalinity for the demand associated with sodium or calcium hypochlorite addition.

The acid or base associated with the addition of molecular chlorine or hypochlorite, respectively, will change the pH of the water being treated, but the change in pH will be buffered by the alkalinity in the water. Only a slight change in pH will occur if the water is high in alkalinity and receives only a small dosage of chlorine. If the water is low in alkalinity or if it receives a very high dosage of chlorine, a substantial change in pH may occur. Knowing the initial pH and alkalinity of the water and its temperature and ionic strength, the pH following chlorine addition can be calculated as described in various water chemistry textbooks or by using a suitable software program. A detailed description of the calculations involved is beyond the scope of this handbook.

In water treatment, it is common practice to add acid or base to adjust the pH of the water for treatment and distribution. In wastewater treatment, pH adjustment is less common, except for systems practicing nitrification or employing biological nutrient removal processes, and is usually done before chlorine is added. Since the acidity or alkalinity introduced by the chlorine may be significant, it should be taken into consideration in the design and operation of treatment plants. This is especially important in the case of breakpoint chlorination, which produces additional acidity and often requires relatively high chlorine dosages.

Acidity is generated in breakpoint chlorination (nitrogen removal) from both the hydrolysis of chlorine gas (when Cl_2 gas solutions are used) and the oxidation of ammonia nitrogen. The overall reaction for molecular chlorine is described by Equation (2.48):

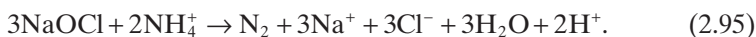


In this case, 8 mol of acidity are produced for every 2 mol of N removed, so the amount of alkalinity destroyed is

$$\begin{aligned} & \frac{8 \text{ mM H}^+}{2 \text{ mM NH}_4^+-\text{N}} \times \frac{1 \text{ mg H}^+/\text{mol}}{14 \text{ mg N/mol}} \times \frac{1 \text{ mequiv H}^+}{\text{mg H}^+} \times \frac{50 \text{ mg CaCO}_3}{\text{mequiv}} \\ &= \frac{14.3 \text{ mg/l as CaCO}_3}{\text{mg/l NH}_4^+-\text{N}}. \end{aligned}$$

Thus, breakpoint chlorination can result in a very large drop in pH for waters low in alkalinity (including nitrified wastewater effluents) or having high ammonia concentrations.

If sodium hypochlorite is used for ammonia removal, the overall reaction is

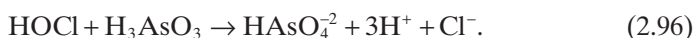


In this case, the amount of alkalinity consumed is only 3.57 mg/l as CaCO_3 for each milligram per liter of NH_4^+ removed.

Arsenic

Some natural waters, mostly groundwaters, contain elevated levels of arsenic in either the +3 (arsenite) or +5 (arsenate) oxidation state. At pH values below 9.29 at 25 °C,²⁸ arsenite is present predominantly in the form of arsenious acid (H_3AsO_3),¹⁶⁵ which is difficult to remove using ion exchange or other adsorptive processes because it is uncharged. Arsenic acid (H_3AsO_4) has pK_a values of 2.26, 6.76, and 11.29 at 25 °C,²⁸ so in most natural waters, arsenate is present as a mixture of H_2AsO_4^- and HAsO_4^{2-} ions.

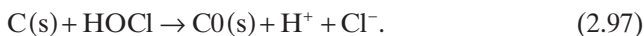
If arsenic is present primarily in the +3 oxidation state, that is, in the form of arsenious acid, it is generally necessary or advisable to oxidize it to the +5 state to facilitate its removal by various treatment processes, including ion exchange.¹⁶⁵ This is readily accomplished using free chlorine¹⁶⁶ as follows:



Since arsenic is typically found only in trace quantities ($\mu\text{g/l}$), it does not exert a significant chlorine demand nor does its oxidation produce a significant amount of alkalinity. The mere presence of free chlorine for a very short period (a few minutes or less at the pH values typically encountered in drinking water treatment) is sufficient for oxidation to take place. Monochloramine reacts much more slowly with arsenite. Dodd et al.¹⁶⁷ estimated the half life of arsenite in the presence of 1–2 mg/l of monochloramine to be about 4 h, but they also noted that about 75% of the arsenite was oxidized within 10 s of adding free chlorine to water to form monochloramine, so oxidation of arsenite by free chlorine evidently proceeds rapidly during the time the chlorine is reacting with $\text{NH}_3\text{-N}$.

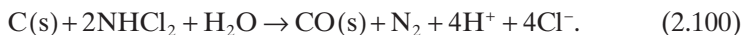
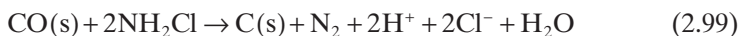
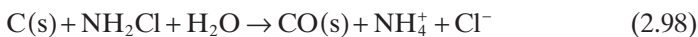
Carbon

Free chlorine reacts rapidly with both powdered activated carbon (PAC) and granular activated carbon (GAC). The reaction is heterogeneous, involving both solid and liquid phases, and can be expressed as follows:^{168,169}



The surface of the carbon is oxidized, chlorine is reduced to chloride, and acidity is produced. If the chlorine is present in the form of HOCl, removal of 1 mg/l of residual chlorine as Cl_2 consumes 0.7 mg/l of alkalinity as CaCO_3 .

Removal of combined chlorine occurs much more slowly than removal of free chlorine;¹⁶⁹ and the reaction can be expressed as follows:^{168,169}



Thus, the amount of alkalinity consumed by the reaction of combined chlorine with GAC or PAC depends on the species present.

Dechlorination occurs not only when GAC is intentionally used for this purpose but also when chlorine is added to a water containing PAC (or vice versa) or when a chlorinated water is filtered through a filter capped with GAC or through a bed of GAC being used to remove synthetic organic chemicals or other contaminants.

Detailed information on dechlorination using GAC and other reducing agents is presented in Chapter 11.

Cyanide

Two-stage chlorination has been commonly employed for cyanide destruction for many decades. Chlorine reacts very rapidly with cyanide to produce cyanogen chloride, but cyanogen chloride is both highly volatile and highly toxic and it hydrolyzes slowly to cyanate below a pH of about 8.5.¹⁷⁰ Therefore, for safety, the first stage of the process is typically carried out at a pH of about 9–10. The first stage reaction is as follows:



Cyanate is much less toxic than cyanide, so oxidation of cyanide to cyanate may suffice. If complete oxidation of cyanide is desired, a second stage is employed. In the second stage, HOCl is the active species, so the pH is typically lowered to about 7 to speed the reaction, although it will gradually proceed at higher pH values since a fraction of the chlorine will be present in the form of HOCl even at significantly higher pH values. The second stage reaction can be expressed as follows:¹⁷⁰

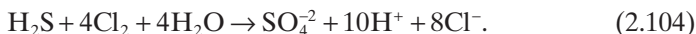


Overall, the two-stage process requires a $\text{Cl}_2:\text{CN}$ molar ratio of 5:2, or 6.82 mg/l of Cl_2 per milligram per liter of CN.

Hydrogen Sulfide

Hydrogen sulfide (H_2S) may be present in anoxic groundwater or in water drawn from the bottom of a strongly stratified lake or reservoir; and it is frequently formed in sewers and anaerobic digesters by sulfate-reducing bacteria. It can also be formed in wells, transmission lines, and water distribution systems in areas where the water is devoid of both chlorine and oxygen due to chemical or biological reactions. Hydrogen sulfide is characterized by its highly obnoxious odor, best described as that of rotten eggs. It reacts rapidly with chlorine to produce particulate sulfur, sulfate, polysulfides, or a combination of these products, depending on pH, time, and the residual chlorine

concentration. The reactions producing sulfur and sulfate can be expressed as follows:

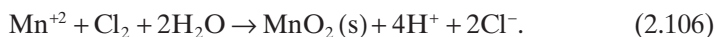
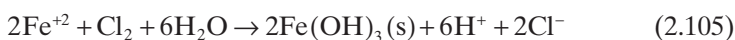


As shown in Equation (2.104), complete oxidation of hydrogen sulfide to sulfate requires a $\text{Cl}_2:\text{H}_2\text{S}$ molar ratio of 4:1, which equates to a chlorine dosage of 8.34 mg/l as Cl_2 for each milligram per liter of H_2S . Thus, high concentrations of hydrogen sulfide can exert a very high chlorine demand. Chlorination of sulfide also consumes a considerable amount of alkalinity—14.7 mg/l as CaCO_3 for each milligram per liter of H_2S oxidized completely to sulfate.

Options for reducing chlorine consumption and alkalinity destruction include air stripping (to remove the majority of the H_2S prior to chlorination) and partial oxidation of sulfide to particulate sulfur, which requires one-fourth as much chlorine. Sulfide particles are typically colloidal in nature and impart a milky appearance to the water, an example of the Tyndall effect. Sulfur particles, if coagulated, can be removed by filtration; and both sulfur and polysulfides can be oxidized to sulfate by sulfur-oxidizing bacteria. Other options include oxidation using hydrogen peroxide or ozone, and removal of particulate sulfur using membrane processes. See Chapter 4 for a more detailed discussion of sulfide control.

Iron and Manganese

Iron and manganese are commonly present in reduced form, that is, as Fe^{+2} and Mn^{+2} , in groundwater, in anoxic hypolimnetic waters, and in water drawn from lakeshore and riverbank infiltration galleries. They are rapidly oxidized by chlorine and by most other oxidants commonly used in water and wastewater treatment, with the notable exception of combined chlorine, which reacts too slowly to be of practical use for treatment but which can slowly react with reduced forms of iron in the distribution system.¹⁷¹ Fe^{+2} and Mn^{+2} can be rapidly oxidized using oxygen if the pH is sufficiently high—about 7.5 or higher for Fe^{+2} and greater than 9 for Mn^{+2} . When oxidized, to Fe^{+3} and Mn^{+4} , iron and manganese precipitate as ferric hydroxide, $\text{Fe}(\text{OH})_3$, and manganese dioxide, MnO_2 , respectively, which are highly insoluble in the pH range typically encountered in water and wastewater treatment. Oxidation of Fe^{+2} and Mn^{+2} using chlorine can be expressed as follows:



On a stoichiometric basis, a chlorine dose of 0.64 mg/l as Cl_2 is required to oxidize each milligram per liter of Fe^{+2} , and a dose of 1.29 mg/l as Cl_2 is

required for each milligram per liter of Mn^{+2} . In practice, the dose actually required for oxidation of Mn^{+2} is less than stoichiometric because Mn^{+2} adsorbs to some extent on both $\text{Fe}(\text{OH})_3$ and MnO_2 , depending on the pH of the water and other factors; but additional chlorine may be required to oxidize other contaminants in water, such as ammonia and natural organic matter.

Oxidation of iron and manganese produces acidity. When using chlorine gas, alkalinity consumption is 2.69 mg/l as CaCO_3 for each milligram per liter of Fe^{+2} removed and 3.64 mg/l for each milligram per liter of Mn^{+2} removed. Thus, oxidation of high concentrations of Fe^{+2} and Mn^{+2} can significantly alter the chemical requirement for controlling the pH of the finished water.

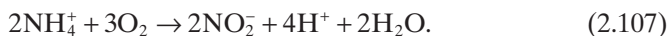
See Chapter 4 for detailed information regarding iron and manganese removal from drinking water.

Methane

Methane gas is relatively insoluble in water, but its solubility is sufficient to pose an explosion or fire hazard if the methane is released into an enclosed space. Some methane-rich waters are characterized by a high chlorine demand (10–25 mg/l). Some formerly thought that chlorine might react directly with methane to form carbon tetrachloride, but this reaction proceeds only at temperatures above about 300 °C. Chlorine does not react with methane in water, and the high chlorine demand observed in some methane-rich waters may be associated with the presence of ammonia, hydrogen sulfide, or nonmethane hydrocarbons in the water.

Nitrite

Nitrite typically appears as a transitory compound when ammonia nitrogen begins to be biologically oxidized to nitrate, for example, at the onset of nitrification in a WWTP or in a water distribution system. This reaction can be expressed as follows:

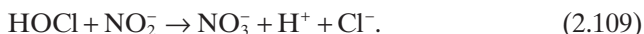


This reaction is generally carried out by bacteria of the *Nitrosomonas* genus. Nitrite can be further oxidized to nitrate by *Nitrobacter* bacteria, which biochemically carry out the following reaction:



Once the population of *Nitrobacter* bacteria becomes established, nitrite is oxidized so rapidly that it is rarely detected.

When nitrite is present, it reacts rapidly with free chlorine to exert a chlorine demand as follows:



Thus, a free chlorine dosage of 5.1 mg/l as Cl_2 is required to oxidize 1 mg/l of NO_2^- -N. It was once believed that nitrite does not react with monochloramine,¹¹⁰ but Margerum et al.⁴² found that this reaction does proceed very slowly— 1.8×10^5 times more slowly than the reaction of nitrite with OCl^- . There is some indication that nitrite can react with dichloramine at pH 4.¹¹⁰

Nitrite can be deceptive in the chlorination process because it not only reacts with free chlorine but also interferes with chlorine residual measurements as discussed in Chapter 3.

CHLORINE DEMAND

Chlorine demand is the difference between the concentration of chlorine added and the concentration remaining. It is exerted primarily by the reaction of chlorine with various constituents in the water, such as natural organic matter, ammonia and organic nitrogen, hydrogen sulfide, iron and manganese, and various other constituents. It can also be exerted by substances in contact with the water, such as iron deposits or biological growths on the walls of basins and pipes, by sunlight in the case of free chlorine, and by gradual chemical decomposition in the case of chloramines. Chlorine demand is often monitored in both water and wastewater treatment because (a) the chlorine dosage must be sufficient to satisfy the demand while also producing the required residual chlorine concentration and the required level of inactivation of pathogens or coliforms; and (b) if the chlorine demand is excessive, steps should be taken to identify the cause of the increased demand and to reduce it to control both chemical costs and by-product formation.

A procedure for determining chlorine demand is described in *Standard Methods*³³ (Method 2350B). This procedure measures only the demand associated with the aqueous phase, as pipe deposits are not included; but if all other factors influencing chlorine demand are controlled, including pH, temperature, time, and sunlight, the results of the test can be compared with field measurements to determine whether pipe deposits may be exerting a significant chlorine demand. Chlorine demand tests can also be used to guide the selection of chlorine dosages and to assess the impacts of changes in treatment on chlorine demand.

In water and wastewater treatment applications, a portion of the chlorine demand is exerted instantaneously by species that react very rapidly with chlorine, including H_2S , Fe^{+2} , Mn^{+2} , NH_3 -N, and a portion of the organic matter present. The remaining residual chlorine concentration typically decays exponentially over time as it slowly reacts with other contaminants, especially organic matter. Feben and Taras^{172,173} found that chlorine demand followed a consistent pattern, in the water supplies of Detroit and other cities, and they developed the following equation to estimate chlorine demand as a function of time:

$$D_t = D_{1.0} \left(\frac{D_{1.0}}{D_{0.5}} \right)^{3.322 \log t}, \quad (2.110)$$

where

D_t = chlorine consumed in t hours (chlorine dose – chlorine residual),

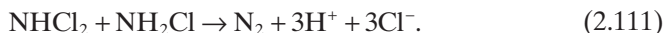
$D_{1.0}$ = chlorine consumed in 1 h, and

$D_{0.5}$ = chlorine consumed in 0.5 h.

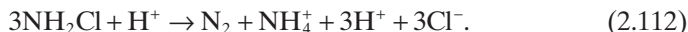
Using this equation, the chlorine demand at the end of any contact time can be determined if the chlorine demand is known after both 30 min and 1 h. If the chlorine demand at exactly 0.5 h or 1.0 h is not known, it can be estimated graphically or mathematically from a log-log plot of chlorine demand versus time.^{172,173}

Several models of chlorine demand based on the reaction of chlorine with organic matter were developed more recently,¹³ but their general applicability to other waters has not been determined. In practice, chlorine demand is relatively easy to measure, so models are more commonly employed for data analysis than for a priori predictions of chlorine demand.

Combined chlorine is generally more stable than free chlorine in a water distribution system, but even in a pure solution it gradually decomposes. A key reaction is the disproportionation of NH_2Cl to form NHCl_2 (Eq. 2.43), which reacts rapidly to form additional end products, including N_2 and NO_3^- , but evidently not NO_2^- .^{174–176} NH_3 , produced in the disproportionation of NH_2Cl , is a major end product of chloramine decomposition and, as noted earlier, can serve as a food source for nitrifying bacteria, leading to increased chloramine decomposition. N_2 , the other major end product of chloramine decomposition in pure solution, is formed by the reaction of NHCl_2 with NH_2Cl , a reaction equivalent to the breakpoint reaction:



The overall chloramine decomposition reaction, based on acid-catalyzed disproportionation of NH_2Cl (Eq. 2.43), is



Nitrate formation occurs through other pathways that are not yet well understood. Nitrate is generally considered to be a minor end product at neutral pH values in pure solution, but higher concentrations are expected to form at higher pH values^{37,174,176} or in the presence of natural organic matter (NOM).¹⁷⁶ When NOM is present, oxidized NOM and halogenated DBPs may also be formed as end products.

Valentine et al.^{174,175} found that chloramine decomposition in pure solution, commonly referred to as autodecomposition, could be reasonably well

represented using the model described by Jafvert and Valentine,³⁷ which is based on the reaction scheme shown in Figure 2.4. For a water utility experiencing difficulty maintaining a combined chlorine residual in the distribution system, it is very helpful to know the autodecomposition rate. If the chloramine decay rate observed in the distribution system is significantly greater than the autodecomposition rate, then one or more additional factors must be accelerating chloramine decay, and further investigation may be required to identify the cause of the problem. Possibilities include natural organic matter, bromide concentrations greater than 0.1 mg/l,^{174,175} nitrite, and biofilm growths associated with nitrification or other biological processes.

Unfortunately, the model developed by Jafvert and Valentine³⁷ is too complicated for routine use by practitioners, and solving the model equations applicable to chloramine autodecomposition requires advanced computational techniques. It is also not possible to provide universal guidelines for all utilities. The rate of chloramine autodecomposition will vary greatly from one utility to another because autodecomposition increases strongly with decreasing pH and increasing temperature and also depends on other factors such as alkalinity and the chlorine to nitrogen ratio, but not ionic strength.¹⁷⁴

To address the limitations of the model of Jafvert and Valentine,³⁷ Valentine et al.^{174,175} developed a simplified model that considers chloramine decomposition in pure solution to be a second-order reaction involving only one decay coefficient. In essence, their model assumes that disproportionation of NH_2Cl (Eq. 2.43) is the rate-limiting step, and this reaction is known to be a second-order reaction as discussed earlier. The value of the decay coefficient is a function of pH, temperature, the carbonate system, the $\text{NH}_3\text{-N}$ concentration, the constants describing the rate of reaction between NH_2Cl and HOCl , and the equilibrium between NHCl_2 and HOCl .

GERMICIDAL SIGNIFICANCE OF CHLORINE RESIDUALS

Chlorine species differ greatly in their ability to inactivate various types of microorganisms, and the chemical mechanisms involved may also differ. The paragraphs below provide a chemical and historical perspective on the germicidal properties of important chlorine species, providing background information helpful in understanding the development and effectiveness of the water and wastewater disinfection practices described in detail in Chapters 4 and 6, respectively.

Chlorination, like most other water and wastewater treatment processes, began to be employed because it effectively accomplished its purpose, and not because its mode of action was well understood. For the past century, it has been extensively studied in an effort to better understand it so that it can be more effectively utilized and more reliably controlled. Much remains to be learned about the chemistry of chlorine and the mechanisms whereby various chlorine species inactivate microorganisms, but fundamental understanding of

the process has dramatically increased since the practice of chlorination first came into widespread use.

Mechanisms of Inactivation

When chlorine first began to be used as a disinfectant (in 1908 in the United States and earlier in several locations Europe), its germicidal power was commonly attributed to the liberation of nascent oxygen from hypochlorous acid $\text{HOCl} \rightarrow \text{HCl} + \frac{1}{2}\text{O}_2$. Other investigators attributed it to the direct chlorination of protoplasm, while proponents of the “toxic substance theory” held that chlorine reacts with lipoproteins in the cell wall to form toxic chloro compounds that interfere with cell division.¹⁵⁸ In 1944, Chang¹⁵⁸ noted that earlier investigators had already dispelled the nascent oxygen theory by showing that hydrogen peroxide and potassium permanganate liberate considerable quantities of nascent oxygen but exhibit only weak germicidal activity, and he demonstrated that there is no liberation of oxygen involved in the inactivation of bacteria by chlorine. He also demonstrated that the effectiveness of various chlorine species for inactivating *Entamoeba histolytica* cysts is related to their ability to penetrate into the cysts and that the penetrating power of HOCl is far greater than that of OCl^- . He also noted that the lowest cysticidal dosages of chlorine employed caused rapid and extensive damage to the cell walls and cytoplasm, and he speculated that this damage alone might be sufficient to inactivate the cysts even before newly formed chloro-organic compounds would have an opportunity to poison the cysts.

In 1946, Green and Stumpf¹⁷⁷ concluded that chlorine reacts irreversibly with the enzymatic system of bacteria, thereby killing the bacteria. They found that a bacterial suspension became sterile when the bacteria lost the power to oxidize glucose. They also found that when enzymes containing sulfhydryl groups were oxidized by chlorine, the oxidation was irreversible, thereby eliminating enzyme action and causing inactivation. In 1953, Ingols et al.¹⁷⁸ concurred with this theory; but, using monochloramine, they found that even when they restored the sulfhydryl groups, the bacteria were not reactivated. This led them to believe that although the sulfhydryl group is vulnerable to strong oxidants, such as hypochlorous acid or chlorine dioxide, changes to other functional groups, able to be caused by weaker oxidants such as monochloramine and dichloramine, may also be important in inactivating bacteria. In 1962, Wyss¹⁷⁹ speculated that inactivation may be caused by “unbalanced growth,” that is, destruction of part of the enzyme system, throwing a cell so out of balance that its own metabolism kills it before the necessary repairs are made.

Many studies have explored the mechanisms involved in the inactivation of bacteria,^{74,177,179–181} cysts,^{74,157,158} spores,^{74,182} viruses, and other organisms by various chlorine species and alternative disinfectants.^{13,183} Although it is generally not possible to precisely explain how a particular chlorine species inactivates a given microorganism, inactivation is believed to occur by means of one

or more of the following mechanisms: inactivation of key enzymes; disruption of nucleic acids, rendering them nonfunctional; and oxidative damage to cell walls or other vital cell components. It should be noted that pathogenic microorganisms are effectively inactivated if they are unable to reproduce; it is not necessary to completely halt all of their metabolic activity (i.e., to actually “kill” them) to prevent them from multiplying and causing disease.

For each of the inactivation mechanisms listed above, the effectiveness of each disinfecting agent is a function of both its rate of diffusion through the cell wall and its reactivity with cells walls, enzymes (proteins), and nucleic acids. Finch et al.¹⁸⁴ and others^{185–187} demonstrated that inactivation mechanisms can interact synergistically. Oxidative damage to cell walls of *Cryptosporidium* oocysts by ozone or chlorine dioxide evidently facilitates the diffusion of monochloramine into the oocysts and the sporozoites inside them, causing greater inactivation than expected based on the individual effects of these disinfectants.

From a practical standpoint, the specific inactivation mechanisms involved in disinfection are less important than the factors that influence the rate and extent of inactivation, which are known to include the following:

1. the type and concentration of organisms being inactivated;
2. the disinfectant species present;
3. the concentration of disinfecting species;
4. contact time;
5. temperature;
6. pH; and
7. interfering substances (particles and substances that exert a chlorine demand).

Disinfection requirements for potable water supplies (Chapter 4) are typically based on “CT” values, calculated by multiplying the disinfectant concentration (C) by the contact time (T). Minimum values have been established for free and combined chlorine (as well as ozone and chlorine dioxide) for specific target organisms as a function of the temperature and pH of the water. Interfering substances are typically removed by pretreatment. Wastewater disinfection requirements (Chapter 6) are usually based on the concentration of coliforms in the effluent, which may also be controlled by achieving a “CT” value known to result in the required level of inactivation under prevailing conditions.

Hypochlorous Acid

HOCl is overall the most effective disinfectant of the chlorine species present in dilute solution at the pH values associated with water and wastewater treatment. Because HOCl is uncharged and has a relatively low molecular weight,

it is better able than other chlorine species to penetrate cells walls; and it reacts more rapidly than other chlorine species, in both oxidative and substitution reactions, with organic matter, including critical components of cells.

Since the dissociation of HOCl to form OCl^- is strongly dependent on pH, and since OCl^- is a much weaker disinfectant than HOCl, the germicidal efficiency free chlorine depends very strongly on pH. Table 2.3 shows the percentage of undissociated HOCl in a chlorine solution as a function of pH values and temperature. Lowering the pH increases the percentage of HOCl, generally enhancing disinfection. Lowering the temperature suppresses dissociation, which would suppress disinfection if this were the only consideration; however, an increase in temperature will also increase the rate of diffusion of chlorine into cells, increase the rate of reaction of chlorine with vital cell components, and increase metabolic activity (accelerating the toxic effects of chlorine on cells), so an increase in temperature actually increases the rate of inactivation rather than decreases it.

As HOCl is consumed at constant pH, OCl^- ions will combine with H^+ ions to form more HOCl, so the percentage of free chlorine present as HOCl will remain unchanged. This is commonly referred to as the “reservoir effect.” This effect occurs because both dissociation of HOCl to OCl^- and the reverse reaction (Eq. 2.9) are extremely rapid (virtually instantaneous), and the balance between HOCl and OCl^- (embodied in Eq. 2.10) depends only on pH if the temperature and other conditions (such as ionic strength) remain constant. The chlorine dosages employed for water and wastewater disinfection are typically small compared with the alkalinity of the water, so changes in pH due to chlorine consumption are usually negligible. However, if high dosages of chlorine are employed, or if it reacts to produce or consume a significant amount of alkalinity, a significant pH change may occur.

Hypochlorite Ion

The OCl^- ion is a relatively poor disinfectant because of its inability to diffuse through the cell walls of microorganisms. Since it is negatively charged, it is electrostatically repelled from cell walls, which are also negatively charged. Since it is ionic, it is strongly hydrated and effectively much larger in size than an unhydrated molecule having a similar molecular weight (such as HOCl), so it also diffuses into cells more slowly than HOCl due to its larger size. Furthermore, chlorine substitution reactions, which presumably play a key role in disrupting the functions of enzymes and nucleic acids, are enhanced by a low pH and the presence of HOCl, whereas oxidative reactions involving chlorine, which typically proceed much more slowly than substitution reactions, are favored by a high pH and the presence of OCl^- . This is consistent with the observations of Fair et al.⁴³ Based on the earlier work of Butterfield et al.,¹⁸⁸ they computed the activation energies associated with disinfection using free and combined chlorine as a function of pH. They noted that the activation energy associated with HOCl (7000 cal/mol) was in

the range associated with diffusion, whereas the activation energy for OCl^- (15,000 cal/mol) was characteristic of chemical reactions.

Fair et al.⁴³ concluded that HOCl is 80 times more effective than OCl^- for inactivation of *Escherichia coli*. They based this estimate on the assumption that the effects of HOCl and OCl^- are additive and on calculations involving the equilibrium expression for dissociation of HOCl (Eq. 2.10) and an equation fitted to inactivation data (chlorine concentration to achieve 99% inactivation vs. pH). According to White,¹¹⁰ Selleck (R.E. Selleck, pers. comm.) found HOCl to be only 20 times more effective than OCl^- for inactivating an unspecified organism, while another study found that the relative effectiveness of HOCl to OCl^- increased from 150 to 300 over a temperature range of 3–23°C for inactivation of *Entamoeba histolytica* cysts.

Given the complexity of the reactions involved in chlorine disinfection and differences among organisms, even those of the same species grown under different conditions, it is not surprising that estimates of the relative effectiveness of HOCl and OCl^- vary from one study to another. Although most studies have found that HOCl is far superior to OCl^- as a disinfectant, Scarpino et al.^{189,190} found that although this was true for bacteria, OCl^- is superior to HOCl for inactivation of poliovirus type 1, and this finding was later confirmed by other investigators.¹³ One factor that has been shown to influence the effectiveness of OCl^- as a disinfectant, and that may therefore explain at least some of the variability in the results are various investigators, is the ion pair formation between OCl^- and cations such as sodium or calcium.^{13,136–139,191,192} Neutral or positively charged ion pairs should be able to diffuse into cells much more readily than OCl^- .

Chloramines

It has long been recognized that chloramines inactivate microorganisms much more slowly than free chlorine. The first person to realize this may have been Alexander Houston¹⁹³ in 1925. The first known scientific laboratory study of the germicidal efficiency of chloramines was conducted by Holwerda⁶⁰ at the Laboratory for the Purification of Water at Mangarai in the Dutch East Indies. He investigated chloramines at pH 4.5, 6.8, and 8.5, with dichloramine most likely being the dominant species at pH 4.5 and monochloramine at pH 6.8 and 8.5 (see Figs. 2.5 and 2.6). Holwerda's findings indicated that combined chlorine required 20–80 times longer than free chlorine to achieve the same level of inactivation. His findings compared reasonably well with those of Butterfield and Wattie,^{194–196} who found that, compared with free chlorine, chloramines required either a 100-fold increase in contact time or a 25-fold increase in concentration to achieve complete inactivation of various types of microorganisms, including *E. coli*, *Ebertfella typhosa*, and *Shigella dysenteriae*. Kabler¹⁹⁷ reported similar findings a few years later. Earlier, in 1940, Weber et al.¹⁹⁸ had noted that ammonia addition significantly increased the time required to kill 99% of *Bacillus metiens*

spores, and they attributed this to the formation of chloramines. Many subsequent studies reached similar conclusions.¹⁹⁹

Clarke et al.²⁰⁰ summarized the results obtained by Butterfield and Wattie, along with those from several other studies, on a log-log plot of residual concentration versus time, as shown in Figure 2.19. (Insufficient data were available to include dichloramine.) These results, which pertain to 99% inactivation of *E. coli* at 2–6°C, clearly illustrate the relative effectiveness of HOCl, OCl⁻, and monochloramine for coliform inactivation. However, these data are not necessarily applicable to other conditions or to other species of microorganisms. It is well known that microorganisms can vary greatly in their resistance to inactivation by a given form of chlorine, that the relative effectiveness of different chlorine species is not consistent from one species of microorganism to another, and that changing conditions can influence the inactivation of some microorganisms more than others.^{13,190,192,201}

The studies summarized in Figure 2.19, as well as other studies, clearly demonstrated the critical importance of both contact time and chlorine residual in achieving a given level of inactivation, especially when comparing one disinfectant with another. This ultimately led to the adoption of

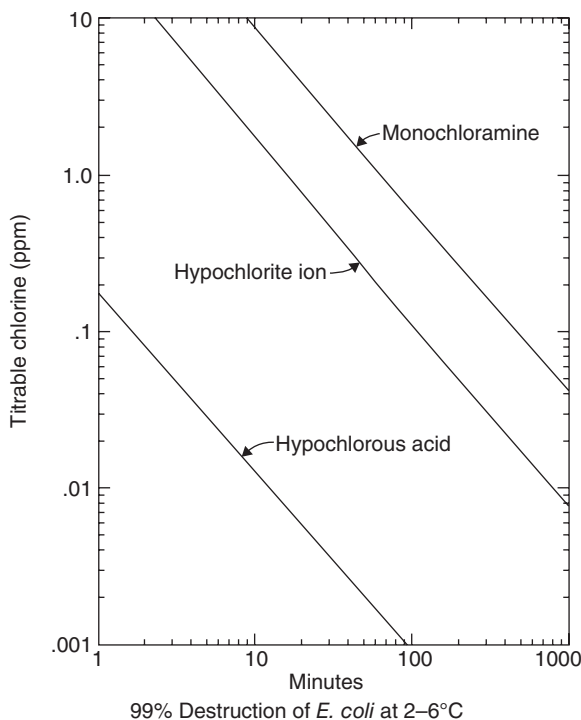


Figure 2.19. Comparison of germicidal efficiency of hypochlorous acid, hypochlorite ion, and monochloramine.²⁰⁰

the “CT” concept for specifying minimum levels of treatment for regulatory and process control purposes as noted above and described in greater detail in Chapter 4. The “CT” concept is clearly rather simplistic, but for practitioners it is easier to understand and utilize than parameters such as Morris’s “specific lethality” constant²⁰² and various exponential expressions used by scientists to correlate inactivation data. More sophisticated models of the inactivation process have been developed,¹³ but they are used primarily for research purposes and to evaluate the soundness of regulatory decisions, and not for process control.

There has been considerable discussion of the possible reasons why combined chlorine is generally much less effective than free chlorine as a disinfectant. Several early investigators thought this might be primarily due to differences in oxidation potential, but this proved to be an inadequate explanation as noted earlier in this chapter. Others thought that perhaps it could be explained by differences in the rates of diffusion of chlorine species through cell walls; but, although such differences exist and clearly influence the relative effectiveness of HOCl and OCl⁻, they are too small to explain the relative ineffectiveness of monochloramine and dichloramine, which like HOCl are also uncharged.

Ingols et al.¹⁷⁸ suggested that reactions between monochloramine and vulnerable enzymes might be reversible, in contrast to those involving free chlorine. However, monochloramine and dichloramine exist in equilibrium with free chlorine (see Eqs. 2.38 and 2.39), so there is actually a trace of HOCl present even in relatively pure solutions of combined chlorine; and trichloramine is unstable in the absence of free chlorine. This suggests another possible reason for the low potency of chloramines, that their potency may be related to the extent to which they hydrolyze to HOCl, which is very limited. Hydrolysis of monochloramine is described by the following equation, which simply represents formation of monochloramine (Eq. 2.38) in reverse:



For this reaction, equilibrium lies strongly to the left. Corbett et al.²⁰³ found the value of the equilibrium constant to be 2.8×10^{-10} at 15 °C, in fair agreement with a later estimate of 1.0×10^{-11} by Morris and Wei,⁷⁷ who calculated that a pure solution of NH₂Cl at a concentration of 2.0 mg/l as Cl₂ contains 0.58% HOCl at pH 7 and 25 °C. More recently, Margerum et al.⁴² estimated the value of the equilibrium constant for Equation (2.38) to be $(3.8 \pm 0.8) \times 10^{10}$, which equates to an equilibrium constant for Equation (2.113) of 2.8×10^{-11} , reasonably close to the value reported by Morris and Wei.

The fact that solutions of combined chlorine contain traces of HOCl, and therefore OCl⁻ as well, makes it very difficult to determine their individual effects on organisms. It should also be kept in mind that the chemical environment inside a cell may differ considerably from that of the surrounding water in terms of pH, ionic strength, and the concentrations of ammonia and organic

nitrogen. Given the complexity of the physical and chemical processes at work, there is no reason to believe that there is one simple explanation for the differences in effectiveness between free and combined chlorine or among the various species involved. The differences are most likely the result of a number of factors acting in concert.

Laboratory studies of disinfection using chloramines have tended to focus on the effects of readily controlled factors such as residual concentration, pH, temperature, and the $\text{Cl}_2\text{:N}$ ratio. Few studies have fully considered the dynamic nature of the reactions of chlorine with ammonia and the implications for disinfection in full-scale treatment facilities where mixing is not instantaneous and the distribution of chlorine species changes over time at a rate that may be fast or slow depending on pH, temperature, the $\text{Cl}_2\text{:N}$ ratio, and water quality. For example, when both chlorine and ammonia are added to the rapid-mix basin at a softening plant at the same time that lime is added, the reaction between chlorine and ammonia is expected to be greatly slowed in the high-pH environment associated with lime softening, especially during the winter months, when the water temperature is very low. Under such conditions, the extent of disinfection is expected to be greater than would occur under laboratory conditions at the same pH and temperature using a pure solution of preformed monochloramine. Given the rates at which certain reactions, such as monochloramine formation, occur under ideal conditions, the order of chemical addition is also expected to significantly influence disinfection. Means et al.,²⁰⁴ based on a series of pilot plant tests, concluded that preammoniation was less effective in producing low bacterial counts than concurrent addition or prechlorination.

Dichloramine. Holwerda⁶⁰ was probably not aware of it, but his results indicated that dichloramine is a significantly more potent germicide than monochloramine. Using a chloramine dosage of 0.5 mg/l at pH 4.5 (mostly dichloramine), disinfection was achieved in 20 min, whereas at pH 8.6 (nearly all monochloramine) it required 60 min. This was based on the observance of gas-forming bacteria. In other tests using plate counts, disinfection required only 10 min at pH 4.5 compared with 60 min at pH 8.6.

Fair et al.⁷⁴ studied the inactivation of suspensions of cysts (*E. histolytica*, 30 cysts/ml) at 23 °C with a contact time of 30 min. They found that at pH 5, a residual of 1.5 mg/l, which they determined to be nearly 100% dichloramine, was required to kill the cysts, whereas at pH 10, with only monochloramine present, the required residual was 220 mg/l. They also found that dichloramine was about 60% as effective as HOCl for killing cysts, and monochloramine only about 22%; however, at pH values above 8, with most of the free chlorine present as OCl^- , chloramines were the more effective cysticidal agents. In a limited number of experiments with *Bacillus anthracis* spores, they found that dichloramine was only 15% as effective as HOCl for a 30-min contact period, whereas the effectiveness of monochloramine was too low to be measured.⁷⁴

Kelly and Sanderson⁵¹ attributed the inactivation of poliomyelitis and Cocksackie viruses to dichloramine rather than to monochloramine. They were able to achieve 99.7% inactivation of poliovirus with a combined chlorine residual in 3 h at pH 6, whereas at pH 10, 6–8 h were required.

It can be concluded from these and other studies that dichloramine is typically at least twice as potent as monochloramine as a germicidal agent. More data characterizing the germicidal effectiveness of dichloramine to monochloramine and free chlorine would be welcome but would be largely of academic interest. Dichloramine formation is avoided in water treatment due to its contribution to taste and odor. When chlorine is used to disinfect municipal wastewater effluents, true dichloramine (as opposed to organic chloramines, discussed below, which titrate as dichloramine) is usually not formed in large amounts. Nonnitrified effluents typically contain a large excess of ammonia nitrogen, such that the residual consists almost entirely of monochloramine, while nitrified effluents containing relatively little ammonia nitrogen may be treated using breakpoint chlorination.

Nitrogen Trichloride. This chlorine compound is known to be an effective oxidizing agent. It was at one time used for bleaching flour¹⁰⁰ (but is no longer permitted for this purpose in the United States), and it has been used as a fungicide and for control of insects on fruit in storage and in cars being transported across international borders. Information regarding its oxidation potential and bactericidal effects is lacking, but it may contribute to the oxidation of organic matter and the inactivation of microorganisms when it is formed in water and wastewater applications. However, its formation in water treatment applications is carefully avoided due to its highly objectionable taste and odor.

Organic Chloramines. The organic chloramines of interest here are those that are formed during chlorination of water and wastewater by the reaction of chlorine with organic nitrogen. These organic chloramines have relatively low hydrolysis constants and typically appear in the dichloramine fraction when measured by forward titration using either the amperometric or the DPD–FAS method. They are nearly always present in chlorinated wastewater effluents but appear to be largely nongermicidal. The following discussion excludes manufactured organic chloramines, such as chloramine T, chlorinated cyanurates,¹⁰⁶ and chlorinated hydantoins,¹⁰⁹ which are used as sanitizing agents, algicides, and “stabilizers” to reduce chlorine photolysis in swimming pools and spas. These compounds have relatively high hydrolysis constants and slowly hydrolyze to release HOCl into solution.

As Marks et al.¹⁸² noted in 1945, organic chloramines can inactivate microorganisms by direct action or by hydrolyzing to form HOCl. They reasoned that since HOCl is a much better disinfectant than unhydrolyzed organic chloramines, the latter mechanism should predominate. Thus, in the presence of organic chloramines, disinfection is expected to depend on the extent of

hydrolysis, which will vary strongly with pH (since most organic nitrogen compounds forming chloramines are either acids or bases), the $\text{Cl}_2\text{:N}$ ratio, and the nature of the organic nitrogen compound.

In 1966, Feng²⁰⁵ reported a great disparity in germicidal efficiency between inorganic chloramines and those formed from organic nitrogen compounds. He reported that methionine, an amino acid indispensable for biological growth and expected to be present in wastewater, reacts with chlorine to form chloramines having a measurable chlorine residual but no germicidal power. He also investigated the lethal activities of chloramines formed from glycine, taurine, and gelatin. He found that taurine chloramines are as lethally active as monochloramine at pH 9.5 but less so at lower pH values; that glycine chloramines are as germicidal as monochloramine at pH 4 but totally inert at pH 7; and that gelatin chloramines are active at pH 9.5 but inert at pH 7 and pH 4.

Sung¹¹² evaluated the effects of 15 organic compounds, representing seven different chemical groups, on the chlorination process. Nine of the 15 compounds interfered with the germicidal efficiency of the chlorination process; and five of the nine were organic nitrogen compounds. Of the organic nitrogen compounds, cystine and uric acid produced the strongest interference, but uracil had little or no interfering effect. When five of the interfering compounds were mixed together, their combined effect was more pronounced than any of their individual effects but did not equal the sum of their individual effects. Sung also chlorinated a simulated wastewater with and without the interfering organic compounds. He found that chlorine residuals in wastewater containing interfering compounds had little or no germicidal effect. Later studies by other investigators, including Wolfe et al.,²⁰⁶ Scully et al.,²⁰⁷ and Donnermair and Blatchley,²⁰⁸ also found that organic nitrogen compounds strongly reduce the bactericidal effectiveness of inorganic chloramines.

Wastewater contains innumerable organic compounds, many of them having characteristics in common with the compounds studied by Feng²⁰⁵ and Sung,¹¹² so it is reasonable to assume that many of them will react with chlorine to produce organic chloramines having little or no ability to inactivate microorganisms. Any organic chloramines formed that do have germicidal power would presumably be able to react with other organic compounds, leading to a gradual decline in disinfecting power. This is consistent with the observation of Esvelt et al.,²⁰⁹ who found that the toxicity of combined chlorine residuals in wastewater effluents diminished over time. However, if the chlorine dosage is sufficient to produce a true free chlorine residual, such that the immediate chlorine demand is satisfied, this might allow organic chloramines having germicidal power to persist for a longer period of time, provided that they are not further oxidized by free chlorine to inert products.

As noted earlier in this chapter (see "Organic Nitrogen and the Breakpoint Curve"), work done at the San Jose/Santa Clara Water Pollution Control Plant¹¹³ over a 2-year period (1980–1982) indicated that, for a nitrified effluent containing a high concentration of organic nitrogen, monochloramine had a

much greater germicidal efficiency than free chlorine because the free chlorine reacted with organic nitrogen to form organic chloramines. The organic chloramines titrated as dichloramine but were relatively nongermicidal. Addition of ammonia caused monochloramine to be formed instead of organic chloramines, greatly enhancing the disinfection process. Similarly, Scully et al.²⁰⁷ found that disinfection of wastewater containing brewery waste having a high organic nitrogen content was faster with preformed monochloramine than with free chlorine, evidently because free chlorine reacted much more rapidly with the organic nitrogen.

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3

Determination of Chlorine Residuals in Water and Wastewater Treatment

HISTORICAL BACKGROUND

Analytical methods evolve over time in response to changing needs, technological advances, and improved understanding of the chemistry of the analytes, and to overcome the limitations of existing methods. This brief historical overview is presented to explain what drove the development of currently used methods, thereby highlighting their advantages, and to point out the limitations of earlier methods, which may be important to consider when evaluating data and studies reported on in older publications.

The Early Years

When chlorine compounds were first introduced, about 1902 in the United States, as a means of disinfecting water, the only method available for testing residual chlorine was the starch–iodide (iodometric) method. Between 1902 and 1908, the proponents and investigators of this process were merely feeling their way along and were not ready to accept the concept of residual chlorine. There was also considerable doubt about the bactericidal efficiency of chlorine. Thus, disinfection by chlorine was evaluated not on the basis of chlorine residual and contact time, as is routinely done today, but entirely on the kill (inactivation) of bacteria or coliforms, with inactivation of the latter being determined by the coliform presumptive test.

After the momentous Jersey City litigation in 1910, which ended with the court ruling unequivocally in favor of chlorination as a successful disinfection process for potable water,¹ workers in this field turned their attention to proper control of chlorination. In 1909, E.B. Phelps² proposed orthotolidine as a qualitative indicator of residual chlorine. Then, in 1913, Ellms and Hauser³ developed a quantitative test for residual chlorine, using orthotolidine, and the colorimetric standards for its use. This was a great contribution since it

White's Handbook of Chlorination and Alternative Disinfectants, 5th edition,
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paved the way for the scientific study of chlorination. Between 1917 and 1920, Wolman and Enslow⁴ conducted studies on chlorine absorption in water and demonstrated the suitability and reliability of the orthotolidine test. Their work was the first scientific approach to the use of chlorine in water treatment. Until about 1930, the use of chlorine in water treatment increased rapidly, which inspired further studies of the various phenomena controlling its application as well as refinements to the use of orthotolidine for measuring residual chlorine. The color standards formulated by Ellms and Hauser were modified by Meur and Hale⁵ in 1925, by Scott^{6,7} in 1935 and 1939, and by Chamberlin and Glass⁸ in 1943.

The air raids over Britain during World War II focused attention on the need for an adequate field test for high chlorine residuals to be used for emergency sterilization of water mains. The most notable contributions to the measurement of high chlorine residuals were made by Chamberlin and Griffin,^{9,10} which also resulted in the need to overhaul the entire procedure of measuring residual chlorine using orthotolidine. This led to the American Water Works Association (AWWA) Joint Committee Report¹¹ issued in 1943 that was based on the research of Chamberlin and Glass,^{8,12} and that in turn became the basis for both the procedure and the color standards of the orthotolidine test appearing in the 13th and earlier editions of *Standard Methods*.¹³ Chamberlin and Glass¹² noted that one of the conditions for the accuracy of the orthotolidine test is that the sample should be added to the reagent, not vice versa.

Following Discovery of the Breakpoint Phenomenon

The discovery of the breakpoint phenomenon in 1939 revealed the existence of two distinct types of residual chlorine—free and combined. Further work indicated that the breakpoint phenomenon could not be properly evaluated or controlled without the ability to differentiate between free and combined residuals. This led to important new contributions to techniques for determining residual chlorine. First came the orthotolidine flash test by Laux¹⁴ in 1940, a modified flash test in 1942,¹⁵ and then the orthotolidine–arsenite (OTA) test developed by Hallinan¹⁶ and Hallinan and Gilcreas¹⁷ in 1944. Over time, many analysts switched from the orthotolidine test to the OTA test.

Connell¹⁸ introduced the orthotolidine titration technique in 1947 in an attempt to differentiate between free and combined residual chlorine. This method was based on the development of a cherry red color when insufficient orthotolidine is present, followed by the conversion of the red chlorine-substituted holoquinone to the yellow holoquinone by rapid addition of sufficient orthotolidine. The method assumes that there is no reaction between chloramines and orthotolidine in the time it takes to perform the titration. Since orthotolidine is the reagent, sample temperature is a limiting factor affecting the accuracy of the free chlorine measurement. This method was never adequately evaluated before orthotolidine was abandoned as a reagent for

determining residual chlorine, and other investigators did not agree that it was proper procedure to convert the red chlorine-substituted holoquinone to the yellow holoquinone.^{9,10,12}

Amperometric Method. In the meantime, an even more important development in chlorine residual measurement was being explored. This was the amperometric method, first introduced by Marks and Glass¹⁹ in 1942. The principle of amperometric titration had been proposed as early as 1897 by Salomon²⁰ and was used in 1905 by Nernst and Merriam,²¹ who showed that the diffusion current is proportional to the concentration of the electroreducible substance. Marks and Glass used a single indicator electrode (gold) with a silver chloride reference electrode. The titrating agent used was sodium arsenite. Marks later found a more discriminating reducing agent (phenylarsine oxide [PAO]), which allowed modification of the procedure to better differentiate the various chlorine residual fractions, including monochloramine and dichloramine.²²⁻²⁴ The first amperometric titrator for residual chlorine developed by Marks was made available in 1949. The dual-indicator-electrode system was introduced by Foulk and Bawden²⁵ in 1926 for titration of iodine with thiosulfate, but not until 1966 was it proposed for residual chlorine determination.²⁶

Diethyl-*p*-Phenylenediamine (DPD) Method. While Marks was investigating the amperometric method in the United States, Palin in England was exploring different colorimetric procedures to differentiate free and combined chlorine residuals. Palin²⁷ first reported on the use of *p*-aminodimethylaniline in 1945 as an indicating reagent superior to orthotolidine. Although this indicator had been reported on in the United States by Moore²⁸ in 1943, Palin's work was considerably more extensive and eventually convinced him that he should discard this indicator in favor of a new approach. In 1949, Palin²⁹ announced a new method using ferrous ammonium sulfate (FAS) as the titrating agent and neutral orthotolidine as the indicating reagent. This approach was shown to be valid for measuring free chlorine, monochloramine, dichloramine, and even nitrogen trichloride. Further refinements were reported by Palin³⁰ in 1954, but owing to limitations of water temperature and errors due to interferences, Palin explored other colorimetric indicating reagents. In 1957,³¹ he reported on his investigation of *N,N*-diethyl-*p*-phenylenediamine, soon to be known as DPD. The DPD method, using various reagents in tablet form, became the most widely accepted method in England and remains among the most popular methods in the United States and throughout the world, especially for field use.

In 1966, the Chester Beatty Research Institute at the Royal Marsden Hospital in London issued a report titled "Precautions for Laboratory Workers Who Handle Carcinogenic Aromatic Amines." This report contained a list of chemicals, including orthotolidine, that were regarded as

potential causes of tumors in the urinary tract, which led to the abandonment of using orthotolidine in residual chlorine tests in the British Isles in 1969 and left Palin's DPD method as the only colorimetric procedure in use there. The 14th edition of *Standard Methods* excluded all but one orthotolidine method, and the remaining one was excluded in the 15th edition; but orthotolidine methods continued to be used for many more years by those already familiar with them.

Methyl Orange (MO) Method. This method, first described by Winkler³² in 1915, never gained popularity or widespread credibility. It is mentioned here as an historical item and also because the U.S. Environmental Protection Agency (USEPA)³³ reported that it demonstrated the best accuracy for measuring both free chlorine and combined chlorine (separately) in synthetic water samples containing low concentrations of free or combined chlorine (less than 1 mg/l) and no interfering substances. The other methods tested were leuco crystal violet (LCV), stabilized neutral orthotolidine (SNORT), DPD titrimetric, DPD colorimetric, amperometric, and OTA.

Chang³⁴ used the MO method in 1944 for measuring free chlorine in his investigation of the relative cysticidal power of free and combined chlorine. Taras^{35,36} investigated this method and described both volumetric and colorimetric procedures in 1946 and 1947. In 1965, the methods proposed by Taras were more fully evaluated by Sollo and Larsen³⁷ in their quest for a better and simpler field method of differentiating between free and combined chlorine residual.

LCV Method. In 1967, Black and Whittle³⁸ reported on a new indicator solution identified as LCV, which possesses excellent properties for quantitative measurement of free chlorine. The LCV method stemmed from investigations comparing the use of free iodine versus free chlorine in both potable water and swimming pools. It was not widely acclaimed even though it was in some ways superior to the orthotolidine method for measuring either free or combined residuals.

An improved version of the LCV method was described by Whittle and Lapteff³⁹ in 1973; but the older version was included in the 15th and 16th editions of *Standard Methods*.⁴⁰ This method was dropped from the 17th edition because it was cumbersome, offered no significant advantages over other methods, and involved the use of mercuric chloride. The LCV method was rated second to the MO method in the USEPA's 1971 report.³³

Improved Field Methods for Measuring Free Chlorine. In 1963, the U.S. Army Medical Research and Development Command began to support research into improving the field method for measuring free chlorine, and in 1967 adopted the modified orthotolidine–arsenite method (MOTA) as an improvement over Hallinan's OTA method.^{16,41} The MOTA method was an attempt to eliminate or minimize interfering substances; however, it was not

successful enough for the Army, as combined chlorine, nitrites, and iron and manganese compounds continued to cause significant errors in the determination of free chlorine.

In 1965, the U.S. Army sponsored an investigation at the University of North Carolina to find a method not only able to accurately measure free chlorine in the presence of combined chlorine under all conditions but also simple to use in field operations^{42,43} (J.D. Johnson and R. Overby, pers. comm.). The chosen method utilized a solution of SNORT, which develops blue merquinone colors in sample-reagent mixtures. The SNORT method was first used by Harrington⁴⁴ at Montreal and then by Caldwell⁴⁵ at Springfield without the benefit of a stabilizer. The SNORT procedure developed for the Army included a test kit with disks, such as the Wallace & Tiernan and Hellige orthotolidine kits. After reviewing the test results in 1976, the Armed Forces Epidemiological Board recommended against the adoption of the SNORT method because of a false-positive free chlorine reading in the presence of combined chlorine, which erased any advantage of the SNORT method over the MOTA method.

In 1972, Bauer et al.⁴⁶ reported on measuring free chlorine using a color chart and a strip of paper treated with syringaldazine. The developer, Miles Laboratory, claimed no interference from combined chlorine. The U.S. Army was impressed with the possibilities of this method and engaged Guter and Cooper to evaluate it.⁴⁷ Their investigation concluded that a syringaldazine solution was the most specific for free chlorine of those employed in the five handheld portable field test kits evaluated. However, as might be expected, organically polluted water resulted in appreciable false-positive free chlorine readings by the majority of the kits.⁴⁸ In the meantime, the U.S. Army continued its own investigation and concluded that the "free available chlorine test using syringaldazine" (or FACTS method) was the most specific method for free chlorine.^{49,50}

The Army continued to pursue its search for a free chlorine test accurate under field conditions, having decided based on its World War II and Vietnam experiences that only a free chlorine residual of a given magnitude would consistently provide safe drinking water. In 1975, an Army investigative unit suggested that the DPD method might be modified to reduce combined chlorine breakthrough into the free chlorine reading.⁵¹ Palin followed through on this suggestion by proposing the addition of glycine immediately after mixing the DPD tablet with the sample. Glycine is supposed to suppress the combined chlorine reaction with the DPD reagent, thereby inhibiting combined chlorine breakthrough into the free chlorine reading. This modification was examined for the Army by Meier et al.⁵² in 1978, but the Army was not satisfied with this modification as compared with the syringaldazine (FACTS) method. Palin made a further modification, which he called Steadifacs,^{53,54} which utilizes a thioacetamide solution that dechlorinates a sample containing combined chlorine without affecting the previously developed DPD color representing free chlorine.

Both the U.S. Army and the Drinking Water Research Center at the Florida International University in Miami carried out more testing and observations of various methods to detect and measure free chlorine.^{55,56} The investigators concluded that measurement of free chlorine by the FACTS method was acceptable in the presence of significant concentrations of chloramines and superior to the DPD method, which suffers appreciably from chloramine intrusion.

In 1982, the USEPA approved the FACTS method for determining free chlorine residuals.⁵⁷ Gibbs et al.⁵⁸ and Cooper et al.,⁵⁹ summarizing their work exploring for the Army the best method for measuring free chlorine in the presence of chloramine under military field conditions, concluded that the FACTS method was superior. Cooper et al.⁶⁰ reported that free chlorine residuals measured by FACTS and amperometric titration were equivalent.

Recent Developments

In the past three decades, there have been relatively few changes in the standard methods used to determine chlorine residuals. Since publication of the 15th edition of *Standard Methods* in 1980, the only major changes (made in the 17th edition) have been to drop the LCV method and to add the low-level amperometric method and the iodometric electrode method. However, there has been continued progress. New test kits have been developed, many of which include calibrated portable spectrophotometers that permit very accurate readings in the field and some of which include provisions for data storage. Other developments include the “miniamperometric titration method” using disposable electrodes (Palintest, patent applied for), an indo-phenol method specific for monochloramine⁶¹ (Hach Chemical Co., U.S. Patent 6,315,950), and improved potentiometric electrode methods⁴⁰ following the pioneering work of Johnson et al.^{62–64} that led to the iodometric electrode method described below. Some of these methods are being incorporated into monitoring kits and process control systems, and some may gradually evolve into standard methods.

GENERAL CONSIDERATIONS

When selecting a method for determining chlorine residuals, one should consider the chlorine fraction to be determined (free, combined, or total); the range of concentrations likely to be encountered; the type of water being analyzed (drinking water, municipal wastewater, industrial wastewater, etc.) and the type of treatment provided; whether the measurements will be made in the field or in the laboratory; the analyst’s skill and level of confidence in a particular method; the presence of interferences and the ability of the method to eliminate or compensate for them; how rapidly the residual must be measured (e.g., relatively stable water distribution system samples versus

those from a rate study involving a water with a high chlorine demand); the shelf life of the reagents and how frequently residuals will be measured; the sensitivity (detection limit) and accuracy required; how the data will be used (e.g., process control versus compliance reporting); and whether an approved method is required. Table 3.1 summarizes some of these considerations for methods commonly used to determine chlorine residuals; but the analyst should carefully consider all important aspects of a particular application, including possible interferences, before choosing a method. Recommendations for method selection for various types of applications are provided below.

Colorimetric and Titrimetric Methods

Both colorimetric and titrimetric methods are available for determining chlorine residuals. In general, colorimetric methods are preferred for field use. Field kits traditionally employed permanent color standards mounted on a disk or slide, so the results depended on the visual acuity of the analyst. Today, however, an increasing number of kits include a simple, portable spectrophotometer calibrated for a particular method. This permits residuals to be measured to the second decimal place, similar to the results that can be achieved using a more sophisticated spectrophotometer in the laboratory. Indeed, many laboratories, especially those designed to facilitate the operation of small treatment systems, are equipped with field kits for determining chlorine residuals.

Titrimetric methods, whether done manually or using an automatic titrator, are generally more accurate than colorimetric methods employing color disks, since a buret can typically be read to one or two decimal places, whereas the user must visually interpolate between the colors on the disk to estimate the chlorine concentration. However, colorimetric methods employing a spectrophotometer are typically as accurate as titrimetric methods. The biggest advantage of titrimetric methods, in general, is that they are subject to little or no interference from color and particulate matter, so a blank is not required. Most colorimetric methods employ a blank to compensate for small amounts of color and turbidity in the sample that might otherwise be interpreted as residual chlorine.

Common Interferences

Common interferences in measuring chlorine residuals include other strong oxidants, such as chlorine dioxide, ozone, and permanganate; oxidized forms of iron and manganese; nitrite; and organic matter, especially organic nitrogen. Glycine can be used to distinguish free chlorine from iodine, bromine, and chlorine dioxide since it reacts only with chlorine.¹³ Manganese interference is stoichiometric and can be compensated for by using a procedural modification described below for the DPD method. Interference by organic

TABLE 3.1. Comparison of Analytical Methods Commonly Used for Measuring Chlorine Residuals

Method	Working Range ^c (mg/l)	MDL ^a (mg/l)	Chlorine Species Measured	Advantages and Limitations ^b
Amperometric titration	0.1–10	0.02	Free and total	Reference method for free and combined chlorine; suitable for quantifying individual chloramine species Not well suited for field use, but portable amperometric titrators are available; requires greater skill than colorimetric methods
Low-level amperometric titration	0.01–0.20	0.01	Total	Developed to determine residuals below 0.2 mg/l Not suitable for differentiating between free and combined chlorine
DPD colorimetric	0.01–4	0.01	Free and total	Suitable for field use by those who understand breakpoint chlorination and use of the DPD method; especially well suited for determining combined chlorine and individual chloramine species; suitable for use in polluted waters (but titrimetric method is better if interfering color is present) Results can be misleading if chlorine concentration exceeds working range; high concentrations of monochloramine interfere with determination of free chlorine; DPD solutions are relatively unstable (but powered reagents are much more stable); requires greater skill than colorimetric methods
DPD titrimetric	0.01–4	0.01	Free and total	Not well suited for field use, but better suited for colored waters than the DPD colorimetric method; otherwise, the same as for the colorimetric DPD method
FACTS	0.1–10	0.1	Free	Developed specifically for field use; measures only free chlorine, so it is especially well suited for applications requiring maintenance of a free chlorine residual
Iodometric I	0.1–10	0.07	Total	Unable to detect the presence of combined chlorine Well suited for determining the strength of feed solutions Amperometric end point required for concentrations below 1 mg/l; not able to differentiate free and combined chlorine
Iodometric II	0.1–10	0.07–0.35	Total	Back titration method developed specifically for wastewater analysis (to avoid a reaction between iodine and organic matter); not able to differentiate free and combined chlorine
Iodometric electrode	0.1–5	0.05	Total	Suitable for measuring total chlorine in both drinking water and wastewater Not able to differentiate free and combined chlorine

^aTypical working range and estimated method detection level (MDL); actual values depend on technique, sample dilution, and the equipment and modifications employed.

^bSee the accompanying text or detailed method descriptions for information regarding interferences.

nitrogen is discussed immediately below; and nitrite interference is discussed later in the context of the amperometric titration method. Other interferences, especially those that pertain to a particular method, are described in subsequent sections of this chapter.

Bromide is oxidized to hypobromous acid (HOBr) in the presence of free chlorine and can in turn react with ammonia to form bromamines, as described in Chapter 2. Using the methods described below, HOBr is measured as free chlorine and monobromamine as combined chlorine. Since drinking water supplies typically contain only traces of bromide (see Chapter 2), and since HOBr and bromamines have germicidal properties similar to those of hypochlorous acid (HOCl) and chloramines, respectively, bromide is not expected to have a significant impact on the determination of chlorine residuals. However, the analyst should be aware that free chlorine usually includes a trace amount of HOBr and combined chlorine a trace amount of bromamines. If high concentrations of both bromine and chloramines are present, bromochloramine (NHBrCl) can be formed, and Valentine⁶⁵ has shown that this compound reacts directly with DPD, so it represents an interference in the determination of free chlorine.

Because chlorine decays over time, samples must be analyzed promptly rather than being stored for later analysis; and, as it also decomposes in sunlight, analyses should be conducted away from direct sunlight.

Organic Nitrogen Interference

It has long been recognized that organic nitrogen reacts with free chlorine, and more slowly with combined chlorine, to form organic chloramines.⁶⁶ Little is known about these compounds or their health effects, in part because individual compounds are present only in minute quantities and are labile (e.g., they tend to break down when introduced into the heated injector port of a gas chromatograph); but it is suspected that when any such compounds reach the bloodstream, they are likely to be dechlorinated (detoxified) by reacting with glutathione. Only traces of organic nitrogen are typically present in water supplies; but Westerhoff et al.^{67,68} found an average concentration of 0.15 mg org-N/l in the finished water from 28 water treatment plants. This level is sufficient to bring into question the nature of the chlorine species in water supplies having low residual chlorine concentrations, especially residuals of 0.2 mg/l or lower.

Municipal wastewater effluents contain much higher concentrations of organic nitrogen, typically about 1–6 mg-N/l,^{67,69,70} depending on the level of treatment; and some industrial and agricultural effluents contain even higher concentrations. Organic nitrogen contributes to chlorine demand;^{71–73} explains, at least in part, variations in the toxicity of chlorinated effluents;⁷⁴ and reacts with chlorine to produce substantial amounts of organic chloramines that can cause significant error in the results of chlorine measurements made using conventional methods and devices^{71–73,75–76} (G.C. White, unpublished observations).

Since individual organic chloramine compounds can titrate as free chlorine, monochloramine, or dichloramine, it would in theory be difficult to have much confidence in the results of residual chlorine measurements unless the types and concentrations of organic chloramine species present were known, as stated by Morris et al.⁷⁵ However, in practice, when residual chlorine is measured according to standard methods and using good judgment in interpreting the results, the measurements can be trusted for the following reasons:

1. Drinking water supplies typically contain relatively low concentrations of organic nitrogen, limiting the total amount of organic chloramine that can be formed.
2. Organic nitrogen can react rapidly with free chlorine, but the end products (organic chloramines) in real-world applications appear to titrate entirely or almost entirely as combined chlorine (especially dichloramine). Therefore, a free chlorine residual produced for the purpose of disinfection can reasonably be expected to meet this objective.
3. Organic nitrogen reacts quite slowly with combined chlorine, giving the combined chlorine time to begin inactivating pathogens. Also, the concentration of combined chlorine typically used for protection of a distribution system (2–4 mg/l) is very high relative to the anticipated organic nitrogen content. Furthermore, many states do not permit drinking water utilities to rely on combined chlorine as the primary means of disinfection, in which case a more powerful disinfectant will already have been employed.
4. It is reasonable to expect that a free or combined chlorine residual measured in a public water supply treated using chlorine dosages and contact times in the appropriate range (e.g., those specified by the Surface Water Treatment Rule) will, even under extreme conditions, actually consist primarily of free or combined chlorine rather than organic chloramines or other titratable by-products. (However, a small residual measured at the ends of a distribution system may still consist largely of organic chloramines.)
5. White^{73,77} (G.C. White, unpublished observations), as a result of numerous studies and many years of experience, was strongly convinced that most, if not all, organic chloramines formed in real-world applications titrate as dichloramine. (Of course, there are notable exceptions, such as the chloroisocyanuric acids; but cyanuric acid does not occur naturally in water supplies and is added to swimming pools specifically because it reacts with chlorine to form compounds whose reactivity and disinfecting power are roughly equivalent to those of free chlorine.⁷⁸) If wastewater disinfection is monitored using appropriate methods for residual chlorine, this “dichloramine” fraction will be properly taken into account, allowing treatment objectives to be met. Recommendations

for measuring residuals in wastewater are given below, and disinfection of wastewater is discussed in Chapter 6.

6. Although most organic chloramines formed during treatment of drinking water or wastewater are expected to be relatively nongermicidal, those that titrate as free chlorine or monochloramine are likely to have germicidal properties, whereas those that titrate as dichloramine, especially at pH 4 or lower, where interference by organic chloramine is most pronounced, can not be relied on for disinfection.
7. Although wastewater effluents may contain relatively high concentrations of organic chloramines, residual chlorine concentrations are typically used for process control, while coliform concentrations are used to verify that the required level of disinfection is met, so a certain level of interference can be tolerated as long as the treatment objectives are being achieved.
8. If significant interference by organic chloramines is likely, analytical methods^{13,79} are available to determine the concentration of organic nitrogen so its potential impact can be assessed.

The guidance below for selecting an appropriate method for determining chlorine residuals includes consideration of interference by organic nitrogen. In general, methods that determine free chlorine and monochloramine at neutral pH values (6–7), including the amperometric method (forward titration), the DPD methods, and the FACTS method, are not very susceptible to interference from organic nitrogen, whereas methods that include dichloramine and those that use acidic conditions (pH 4 or lower) to determine free or combined chlorine, such as the standard back titration methods, the orthotolidine method, the LCV method, and the MO method, are vulnerable to interference by organic chloramines. The extent of interference can be qualitatively assessed by forward titration procedures, either the amperometric method or the DPD–FAS titrimetric method, and by determining whether the dichloramine concentration is unusually high.

Recommendations for Method Selection

Small Water Supplies. Summer camps, resorts, campgrounds, motels, roadside restaurants, isolated residential subdivisions, and so on, are often served by small supplies. Monitoring chlorine residuals in these types of systems is similar to working under U.S. Army “field conditions.” Therefore, the FACTS method, selected by the Army after intensive investigation, would be the method of choice. Test kits are available that include a field spectrophotometer or permanent glass color standards (0.2, 0.4, 0.7, 1.0, 2.0, 5.0, and 10.0 mg/l) and two solutions: buffer and syringaldazine. The FACTS method measures only free chlorine, which is important for small systems because a free chlorine residual is imperative for their inherently short contact times. Operators,

especially those who do not fully understand breakpoint chlorination, can easily mistake a combined chlorine residual for a free chlorine residual if they use a kit that measures both. For those who fully understand both breakpoint chlorination and the DPD method, the DPD colorimetric test is equally appropriate.

Chlorination Stations. Many water utilities, especially those serving rural areas and those drawing high-quality groundwater from multiple wells, do not have a central treatment plant but use one or more chlorination stations to maintain a chlorine residual throughout the system. In such cases, the choice of a method for determining residual chlorine depends on the type of residual being maintained (free or combined), whether the measurements are being used as the basis for manual control or to calibrate online chlorine analyzers (discussed below), and other factors noted above. For a smaller system maintaining a free chlorine residual, the FACTS method may be the most appropriate; but for larger systems and systems maintaining a combined chlorine residual, the best choice is likely to be either a portable amperometric titrator or a portable DPD colorimetric test kit equipped with a spectrophotometer.

Drinking Water Treatment Plants. Practically all drinking water treatment plants have laboratories, which facilitates use of the DPD–FAS titrimetric method. This method, the amperometric titration method, and the DPD colorimetric method (using a calibrated spectrophotometer) all enable the operator to measure free, combined, and total residual chlorine.

Many treatment plants use continuous chlorine residual analyzers, either to verify continuous maintenance of a chlorine residual (for compliance with the Surface Water Treatment Rule) or for process control. Most continuous analyzers use chemical methods virtually identical to those described in the following sections, and several types of analyzers currently being used are described in Chapter 12. It is important to remember that continuous analyzers can lose their calibration (drift), become fouled or plugged, or run out of reagents, so they should be viewed as a secondary source of information. The primary source of information is the analytical method used to calibrate the analyzer. Therefore, the calibration method must be quantitatively precise and qualitatively definitive. Only three methods fit these criteria: amperometric titration, DPD–FAS titration, and the DPD colorimetric method based on spectrophotometric analysis.

Since a continuous analyzer can pick up variations and unexpected “events” that grab samples may miss, the best approach is to continuously measure the residual using an analyzer that is regularly checked, calibrated, and validated. Another approach is to provide reliable autocalibration.

Chloramines. All chloramine installations should have testing equipment capable of monitoring free chlorine, monochloramine, and dichloramine

residuals, as well as ammonia nitrogen. The ability to measure these species provides helpful information relating to the Cl_2 -to- NH_3 -N ratio and operating conditions relative to the breakpoint curve. This is important not only for process control but also for control of tastes and odors and disinfection by-products (DBPs). Dichloramine in particular will adversely affect the taste and odor of the treated water. To measure all chlorine residual species, any of the following methods—amperometric titration, the DPD–FAS titrimetric method, or the DPD colorimetric method—should be used. Additional information regarding breakpoint chlorination, maintaining a suitable Cl_2 -to-N ratio, and minimizing taste and odor is presented in Chapters 2 and 4. Process control is discussed in Chapter 12.

Primary Wastewater Effluents. Primary effluents were sometimes chlorinated in the past, but are now rarely chlorinated except in emergencies or in the case of storm water overflows that are treated only by sedimentation before being chlorinated. The chlorine residuals in such effluents are inevitably combined. Forward titration involving the liberation of iodine will be subject to a strong interference due to the reaction of iodine with the large amount of organic matter in the effluent. Thus, a back titration method should always be used. Two such methods are available: one using amperometric titration and the other using the iodometric (starch–iodide) method. The latter is acceptable when the total residual chlorine concentration is 1 mg/l or higher. Organic chloramines will interfere, but they are expected to form slowly in such effluents. Colorimetric methods have never proved useful in measuring chlorine residuals in primary effluent.

Conventional Secondary Effluents. Conventional (nitrified) secondary effluents contain enough ammonia that the residual almost invariably consists of combined chlorine. For such effluents, the back titration method using an amperometric end point is probably the most commonly used today. Next in popularity is the long-standing iodometric (starch–iodide) method (II) using the back titration procedure, although many former users of this method have found the DPD–FAS titration method preferable.

For treatment plants with moderate to severe disinfection requirements (2.2–240/100 ml most probable number [MPN]), a forward-titration procedure, either amperometric or DPD–FAS titrimetric method, should be used, so that the relative concentrations of mono- and dichloramine can be monitored. White et al.⁷² found that more vigorous mixing at the point of application of chlorine resulted in a larger fraction of monochloramine to dichloramine in the final residual, resulting in more efficient disinfection. Therefore, forward-titration has an important place in monitoring the disinfection process. It is further recommended that use of forward-titration to determine mono- and dichloramine be supplemented by determining total residual chlorine using back-titration. Wastewater disinfection is further discussed in Chapter 6.

Nitrified Secondary and Tertiary Effluents. These effluents may contain either free or combined chlorine residuals, or both, depending on the degree of nitrification, the contact time, the temperature, the dosage of chlorine, and other factors. To properly monitor the disinfection process, it is beneficial to run forward titrations to determine free chlorine, monochloramine, and dichloramine. Total residual chlorine should also be determined to monitor dechlorination. If the effluent is completely nitrified, both ammonia and combined chlorine should be absent; but organic chloramines may titrate as combined chlorine, especially in the dichloramine fraction. When nitrification is incomplete, nitrite may be present, so the analyst should take precautions to avoid nitrite interference as discussed below (“Occurrence and Control of Nitrite Interference”). The methods of choice are the amperometric and the DPD–FAS titrimetric methods.

Detailed Descriptions of Individual Methods

Methods of determining residual chlorine are described below in alphabetical order. For some, especially those that are most widely used, the procedures involved are described in considerable detail. Others, especially those included primarily for historical completeness, are described in less detail. The reader is encouraged to consult the latest edition or the online version of *Standard Methods*¹³ for the most up-to-date detailed instructions for using a method. For obsolete methods, the best sources of more detailed information are the older editions of *Standard Methods* and the articles published by those who developed the methods, many of which are cited above (see “Historical Background”) or by Gordon et al.⁴⁰

Gordon et al.⁴⁰ conducted a comprehensive review of methods for determining disinfectant residuals, including free and combined chlorine, chlorine dioxide, and ozone. Each method is evaluated in terms of what an ideal method would accomplish, limitations and interferences are noted, and the results of studies comparing various methods are summarized. The review also includes additional methods for determining chlorine residuals, such as UV spectroscopy, that are not routinely used in water and wastewater treatment but may be useful in laboratory studies. This review is strongly recommended as a source of additional information.

AMPEROMETRIC TITRATION

This is one of the most widely used methods for measuring chlorine residuals and, despite its limitations, it is generally considered the standard against which other methods are judged. Amperometric titrators are easy to use, and are accurate and reliable if reasonable care is exercised in maintaining electrode sensitivity. Amperometric titrators can also be used to determine chlorine dioxide (Chapter 14), iodine and bromine (Chapter 16), and chlorite.

Principles of Titrator Operation

The amperometric method employs a special adaption of the polarographic principle. It is one of a class of methods involving an electrometric titration in which the current passing through the titration cell between an indicator electrode and an appropriate depolarized reference electrode (at suitable applied electromotive force) is measured as a function of the volume of a suitable titrating solution.⁸⁰ In general, the end point of an amperometric titration can appear either as the cessation of current at the equivalence point (for complete reduction of the titrant), as a sudden increase in current (when the titrant is the oxidant and overcomes the reducing agent in the electrolyte), or as an abrupt change in current at the equivalence point.

In any cell consisting of two electrodes contacting an electrolyte, the impressed voltage will be opposed by a countervoltage, due to accumulation of electrolysis products (polarization) or exhaustion of the material being electrolyzed (depolarization) at the electrode surfaces. The current that can flow in the electrolyte between the electrodes is said to be decreased by concentration polarization, which is sometimes described as concentration overpotential or activation potential. The flow of current in a cell will cause the accumulation of reducing agents at the cathode (negative electrode) and oxidizing agents at the anode (positive electrode). The addition of an oxidizing agent to the cathode solution or a reducing agent to the anode solution will decrease the accumulation at the respective electrode. This phenomenon, known as depolarization of the electrodes, reduces the countervoltage, thereby allowing more current to flow.

Amperometric titrators designed for analysis of chlorine residuals fall into one of two categories: those using a single indicator electrode with a reference electrode and those using dual indicator electrodes. Each type is described below.

The Single-Indicator-Electrode Titrator

A titrator employing a single indicator electrode, a more recent version of the unit first developed by Marks et al.,^{19,22-24} is illustrated in Figure 3.1 and shown schematically in Figure 3.2. This titrator consists of a platinum indicating electrode (the cathode, which is polarized to some extent) and a silver reference electrode (nonpolarizable anode) immersed in a saturated salt solution. The potential of the silver electrode provides an internal voltage and makes it unnecessary to impress an external voltage. To measure low chlorine concentrations, the surface area of the indicating electrode is made large to increase the sensitivity of the cell. In this case, a 0.01 mg/l change in chlorine concentration will produce a current of about $2.5\mu\text{A}$, which will move the pointer about seven divisions. Efficient agitation at the indicating electrode surface, which is necessary to obtain a higher and more uniform diffusion current, is achieved by a high-speed rotating Lucite sleeve, which fits with



Figure 3.1. Amperometric titrator (courtesy of Siemens Water Technologies).

minimum clearance over the cylinder containing the platinum electrode. The electrical path through the water sample (electrolyte) is made short and of low electrical resistance by putting a salt bridge in the narrow space between the turns of the platinum spiral electrode.

To perform a titration, a sample that contains the oxidizing agent—either chlorine or iodine (I_2), with the latter being formed when iodide is initially added to react with an oxidant to produce iodine—is placed in position,

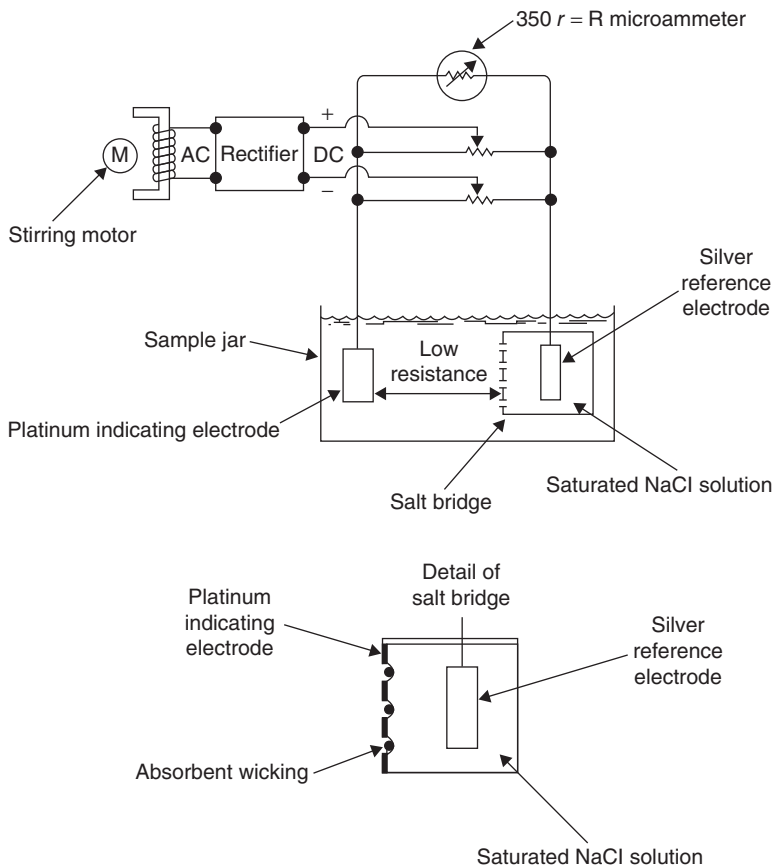


Figure 3.2. Schematic of an amperometric titrator with a single indicating electrode (courtesy of Siemens Water Technologies).

and the agitator is started. The microammeter will deflect to the right, upscale, depending upon the concentration of the oxidizing agent. The reducing agent, PAO, is then added, which decreases the concentration of the oxidizing agent and accordingly decreases the current through the cell. When the oxidizing agent has been completely reduced by the titrating agent (PAO), the end point is indicated by no change in the current upon further addition of reagent.

The reverse of this procedure, known as back titration, is performed by using an oxidizing agent (iodine) as the titrating solution to overcome an excess of reducing agent previously added to the sample. In this case, the end point is observed as the first appearance of a current caused by the exhaustion of the reducing agent by the oxidizing agent.

The Dual-Indicator-Electrode Titrator

The portable amperometric titrator (Chlortrol Model 17T2000) utilizes dual indicator electrodes.²⁶ Figure 3.3 illustrates the essential components of the titrator. This model employs a platinum and copper electrode pair rather than the formerly used dual platinum electrodes. The Pt–Cu pair provides a good current–voltage curve (Fig. 3.4), yielding a usable plateau wherein small voltage variations do not produce significant current changes. At the selected electrode potential (200 mV, total residual chlorine; 100 mV, free chlorine) the cell generates a stable current, as a function of the chlorine concentration, which can be applied to several stages of amplification. This amplification provides the unit with a sensitivity of 0.005 mg/l. A Pt–Pt pair produces a current-versus-voltage curve that is essentially a straight line for free chlorine. Therefore, a small shift in electrode potential generates a significant change in current, making amplifier input–output unpredictable and of limited use.

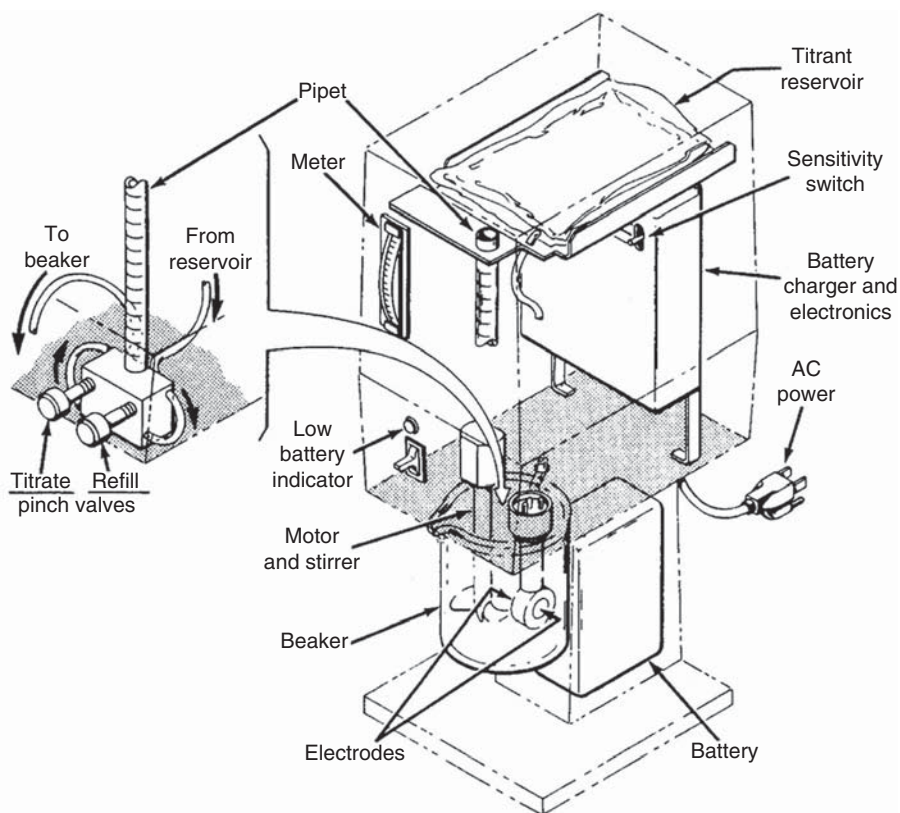


Figure 3.3. Diagram showing the essential components of a dual-electrode titrator (courtesy of Severn Trent Services).

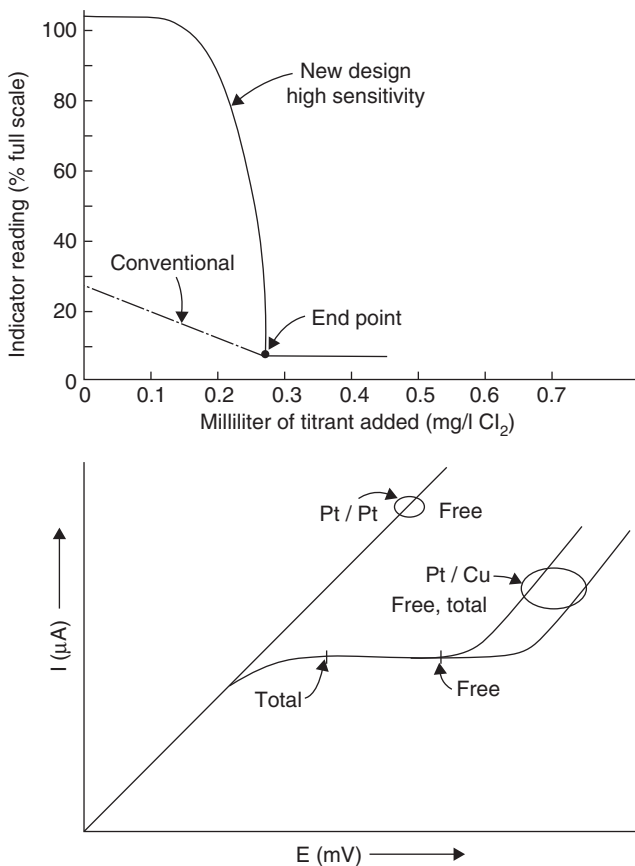


Figure 3.4. Relationship between current and applied voltage across the Pt/Cu electrodes and log function readability versus conventional display (courtesy of Severn Trent Services).

The final display output (meter reading) is made more readable in the critical end point region by applying the cell output to a log-linear amplifier circuit. The upper curve in Figure 3.4 compares the log-amplified output with the conventional display. For any given chlorine concentration, the meter response is minimal at the beginning of the titration, increasing sharply as the end point is approached.

This system employs what is known as a biamperometric titration. The procedure is the same as that used in the single-indicator-electrode system. When the oxidizing agent is being titrated by a reducing agent, both electrodes remain depolarized, and current flows in proportion to oxidizing agent and is indicated on the output meter (microammeter). When the last traces of the oxidizing agent have been destroyed by the reducing agent, the cathode

is without a depolarizer and the flow of current is immediately arrested, signifying the end point. This is indicated by the microammeter. Conversely, if the titrant is an oxidizing agent, such as iodine, which is added to overcome a reducing agent, as in the back titration procedure, the end point occurs at the first appearance of current, as soon as there is an excess of iodine, which depolarizes the cathode. The anode is already depolarized by the iodide ion.

Operating Characteristics

The following statements appear in the 21st edition of *Standard Methods*:¹³ “The method is not as simple as the colorimetric methods and requires greater operator skill to obtain the best reliability. Loss of chlorine can occur because of rapid stirring in some commercial equipment. Clean and conditioned electrodes are necessary for sharp end points” (4500-Cl A. Introduction). “Amperometric titration requires a higher degree of skill and care than colorimetric methods. Chlorine residuals over 2 mg/l are measured best by using smaller samples or by dilution with water that has neither residual chlorine nor a chlorine demand” (4500-Cl D. Amperometric Titration Method). Similar statements appear in older editions, dating as far back as the 13th edition.

Except for the need to properly sensitize the electrodes, these statements are not supported by White’s personal experience or by the experience of the analysts and operators with whom he worked for more than 40 years on both potable water and wastewater applications.⁷³ Measuring residuals up to 20 mg/l without dilution is a routine task with an amperometric titrator. As for the skill required, one needs to know only how to handle a pipette and a buret and how to interpret an ammeter.

An important aspect of this method that is often overlooked is care of the electrodes. Each manufacturer has specific instructions for electrode care, but the most important task is to sensitize the electrodes. For forward titrations, the electrodes should be sensitized by allowing them to soak in a dilute (5 mg/l) free chlorine residual. When back titrations are made, for example, for wastewater samples, the electrodes should be soaked in a dilute (light brown color) iodine solution. When routinely performing *both* forward and back titrations, separate titrators should be used to shorten the time required to completely remove the iodine before measuring free chlorine. The electrodes should be sensitized as described above for about 10 min before use if the titrator is not being used daily. Otherwise, they should be sensitized at weekly intervals.

Frequent use of the titrator builds the operator’s confidence. Colorimetric methods based on permanent color standards, charts, or disks, rather than on spectrophotometric readings, always leave some doubt because color depth acuity varies among individuals and because of the difficulty of visually estimating color depth between standards. Therefore, colorimetric

methods are subject to errors that do not occur with the amperometric method.

Chemistry of the Amperometric Method

The success of this method is largely attributable to the reducing agent PAO ($\text{C}_6\text{H}_5\text{AsO}$). Other reducing agents have been tried and discarded for a variety of reasons. For example, thiosulfate, which is used in the starch-iodide method, does not sufficiently discriminate between free and combined chlorine, and it reacts in stepwise fashion, causing a time lag that interferes with the end point. Sodium arsenite, which had possibilities because it would react with free chlorine only in the absence of potassium iodide and with any iodine released by chloramines in the presence of iodide, would not react quantitatively below pH 6, which is essential for picking up dichloramine, which liberates iodine only at pH much lower than 6.

PAO reacts only with free chlorine (not combined chlorine) at pH 7 in the absence of potassium iodide (KI). PAO reacts with iodine produced by the reaction of monochloramine with iodide in the presence of 50 mg/l KI at pH 7; and it also reacts with iodine produced by the reaction of dichloramine with iodide in the presence of 250 mg/l KI at pH 4. Iodine is liberated quantitatively under these conditions, and the released iodine is then quantitatively titrated using PAO. The reactions of PAO with free chlorine and iodine are as follows:



One mole of PAO reacts with two equivalents of chlorine or iodine. The strength of PAO was selected at 0.00564N so that, when titrating a 200-ml sample, 1 ml of PAO solution is equivalent to 1 ppm of chlorine. Therefore, when the end point of the titration is reached, the volume of PAO used, in milliliters, represents the chlorine concentration in milligrams per liter.

Note. The iodine in "iodine solutions" is actually present mostly in the form of the tri-iodide complex, I_3^- ; but this is of no practical significance since it does not influence the overall reaction stoichiometry.⁸¹

When determining free chlorine, the pH must not be higher than 7.5 to avoid sluggish reactions, nor lower than 6.5 because at lower pH values some combined chlorine may react even in the absence of iodide. In determining combined chlorine, the pH must not be less than 3.5 because substances such as oxidized manganese interfere at pH values lower than 3.5, or higher than 4.5 because the reaction of combined residual chlorine is not quantitative at higher pH values.

The tendency of monochloramine to react with iodide more readily than does dichloramine provides a means of further differentiation. The addition

of a small amount of potassium iodide in the neutral pH range makes it possible to estimate the monochloramine concentration. Lowering the pH into the acid range and increasing the potassium iodide concentration allows separate determination of dichloramine.

Preparation and Procedures for Titration

Apparatus. An amperometric titrator (end point detection device) consists of a two-electrode cell, a microammeter, an adjustable potentiometer, a salt bridge, a titration vessel (200 ml), and a stirrer. Recommended accessories include a graduated cylinder suitable for accurately measuring out a 200-ml sample, a 1-, 2-, or 5-ml buret with 0.01- or 0.05-ml graduations (depending on the normally encountered chlorine concentrations and the desired level of precision), and a finger pump for charging the buret with the PAO reducing reagent.

To prepare the titrator for operation, the operator should check the following:

1. If the unit is equipped with a silver-silver chloride electrode, verify that there are sufficient salt tablets in the cell (two-thirds full) and that enough distilled water has been added to cover the tablets.
2. The electrical contacts between the cell and the microammeter must be clean and making proper contact.
3. The platinum electrode surface has to be free of any deposits. If necessary, it should be cleaned by lightly rubbing it with scouring powder, using only the fingers and without disturbing the porous wicking between the turns of the platinum ribbon.
4. If the titrator has been used only for measuring free chlorine and it is desired to measure combined or total residual chlorine, the platinum electrode must be sensitized to iodine. This will be noticed during a titration when potassium iodide is added. When potassium iodide is added and the needle deflects downscale momentarily and remains there, the cell is said to have lost its sensitivity to iodine. The sensitivity is easily restored by adding enough free iodine to the water in a sample jar to produce a yellowish color, agitating the sample for 2 or 3 min, and allowing the cell to stand in this solution for 10 or 15 min. After this treatment, the cell unit should be rinsed thoroughly to remove all traces of free iodine.
5. All glassware used in this procedure should be free from chlorine demand. The sample jar should be treated with water containing at least 10 mg/l of chlorine for 3 h or longer before use and then rinsed with chlorine-demand-free water.
6. To prevent errors in titration by contaminants in the buret, it is good laboratory practice to fill the buret to the top and to discharge the

contents to waste before beginning a series of titrations. To prevent volumetric errors, all air bubbles should be removed from the buret, including the tip, before titrating a sample.

Reagents. The following reagents are required:

1. standard PAO titrant (0.00564 N $\text{C}_6\text{H}_5\text{AsO}$);
2. pH 7 phosphate buffer for chlorine determination (purchased from a vendor or prepared as described in *Standard Methods*);
3. pH 4 acetate buffer for chlorine determination (purchased from a vendor or prepared as described in *Standard Methods*);
4. potassium iodide solution (5-g reagent-grade potassium iodide in 100 ml of freshly distilled water; stored in the dark at 4°C in a brown glass-stoppered bottle); and
5. electrolyte tablets (made from USP-grade sodium chloride).

Procedures. Procedures for free and combined residuals and for various combined chlorine species are listed below. The analyst must select the procedures needed to determine the type and species of chlorine compounds being analyzed.

I. Free Chlorine

1. Connect the titrator to a suitable power source.
2. Fill the buret with a PAO solution. Remove all air from the buret and tubing and then discharge the PAO. Refill the buret to the top calibration mark.
3. Place a 200-ml sample of the water to be tested in the titrating vessel and position the vessel on the titrator. If the chlorine concentration is high (e.g., if the amount of titrant required exceeds the capacity of the buret), use a smaller volume of sample and dilute it to 200 ml.

Note. If the titrator has been used previously to determine combined chlorine, that is, if pH 4 acetate buffer or KI has been added to the titrator, the apparatus and electrodes must be very thoroughly rinsed to remove all traces of iodide and any remaining pH 4 buffer before analyzing another sample for free chlorine.

4. Add 1 ml of pH 7 phosphate buffer solution to the sample. If the natural pH of the sample is between 6.5 and 7.5, the pH 7 buffer solution is not needed. If necessary (e.g., for samples containing high concentrations of alkalinity or acidity), verify that the buffer is adequate to adjust the pH to between 6.5 and 7.5.

Note. Droppers are usually furnished with commercially available preparations of the phosphate and acetate buffers for chlorine analysis

(and with the KI solution). The droppers are typically scribed to the 1-ml mark for use whenever 1 ml of solution is called for.

5. Start the agitator by turning the switch to "on."
6. Adjust the potentiometer so that the microammeter needle (or digital output) reads near maximum on the scale. If the needle is above maximum when the adjusting knob is rotated completely counter-clockwise, the titration must be started with the knob in this position.
7. Begin adding the PAO solution just below the sample surface. If free chlorine is present as the titrant is being added, the cell current will decrease, causing the microammeter needle to move downscale. If the needle is above the maximum reading at the beginning of the titration, it will remain so until enough PAO solution has been added to reduce the free chlorine residual (and hence the current) to cause the needle to read less than maximum. While adding the titrant, adjust the potentiometer as needed to return the needle on scale. When the end point is approached, that is, when the response of the microammeter to each increment becomes more sluggish, add the titrant in smaller increments. The end point is just passed when a single drop of PAO no longer causes the needle to move downscale (decrease of current). Then read the buret, and subtract the last increment (one drop) of titrant from the reading. The volume of titrant used, in milliliters, is the free chlorine concentration in the sample (or diluted sample) in milligrams per liter as Cl_2 .

Note. In some cases, the needle (reading) will continue to deflect very slightly downscale after the end point has been reached. In such cases, the true end point occurs when for equal amounts of PAO added the deflection changes from large to small. The end point can be more accurately determined by graphical or mathematical analysis of the current readings; but this is rarely necessary for routine analysis.

II. Monochloramine

1. Continue immediately using the same sample as used to determine free chlorine, and note the buret reading at the endpoint in I. Note that this titration is also performed at pH 7.
2. Add 0.2ml of potassium iodide solution to the original sample. The furnished dropper usually delivers 20 drops/ml. Therefore, four drops corresponds to 0.2ml. If monochloramine is present, the needle will deflect to the right (probably off scale) immediately upon addition of the potassium iodide.
3. Proceed with the addition of PAO to the end point as in I. Note the buret reading. The difference between the buret readings at the end

points of I and II is the amount of monochloramine present in the sample (or diluted sample) in milligrams per liter as Cl_2 .

III. Dichloramine

1. Continue immediately using the same sample, and note the buret reading at the endpoint in II. Decrease the pH of the sample to 4 (3.5–4.5) by adding 1 ml of pH 4 acetate buffer solution.
2. Add 1 ml of potassium iodide solution. If dichloramine is present, the needle will deflect to the right at this point.
3. Proceed with the addition of PAO until the end point is reached as before. Note the buret reading. The difference between this reading and the previous reading (at the end of II) is the amount of dichloramine present in the sample (or diluted sample) in milligrams per liter as Cl_2 .

IV. Total Residual Chlorine. This procedure combines free and combined chlorine into a single total reading.

1. Start with a fresh 200-ml sample (or appropriate dilution) and fill the buret with PAO solution to the top calibration mark.
2. Add 1 ml of pH 4 acetate buffer solution.
3. Add 1 ml of potassium iodide solution. At this point, the needle will first deflect to the left and then move upscale (probably off scale). Any chlorine residual, free or combined, will quantitatively release iodine from the potassium iodide.
4. Proceed with the addition of PAO to the end point as before. Note the buret reading. The volume of PAO used, in milliliters, represents the total residual chlorine in the sample (or diluted sample) in milligrams per liter as Cl_2 .

V. Free and Combined Chlorine Residuals. It is often desirable to separately determine the free and combined chlorine residuals. This can be done using only one sample, as follows:

1. Measure free chlorine as in I.
2. Add 1 ml of pH 4 acetate buffer solution, then add 1 ml of potassium iodide. At this point, all of the monochloramine and dichloramine liberates iodine from potassium iodide quantitatively. If combined chlorine residual is present, the needle will deflect first to the left and then sharply to the right upon the addition of potassium iodide.
3. Add PAO until the end point is reached as before. Note the buret reading. This reading represents the total chlorine, and the difference

between this reading and the reading in I is the combined chlorine residual, with all readings in milligrams per liter as Cl_2 .

Note. If free chlorine residuals are to be determined after using pH 4 acetate buffer or potassium iodide (e.g., for determination of combined chlorine), the titration cell and electrodes must be very thoroughly rinsed to remove traces of potassium iodide and pH 4 acetate buffer solution.

VI. Nitrogen Trichloride. It is well established that nitrogen trichloride can exist simultaneously with free chlorine at a pH as high as 8.5 or even 9^{31,82,83} if free ammonia is available to react with the chlorine and if sufficient chlorine is added to reach the breakpoint. It is believed that, in the amperometric method, any nitrogen trichloride titrated will appear partly in the first fraction as free chlorine and partly in the third fraction as dichloramine.²⁴ This is consistent with the finding of Nagy et al.⁸⁴ that nitrogen trichloride reacts with iodide to form NCl_3I^- , which then decomposes to NHCl_2 and ICl . However, Dowell and Bray⁸⁵ found that the starch-iodide titration includes only 80% of the total nitrogen trichloride present, while the acid-orthotolidine method includes only about 60% of the total. Palin's methods have been tentatively shown to account for all nitrogen trichloride present. Sufficient data are not available to clearly establish the ability of the amperometric method to differentiate the total nitrogen trichloride from the other fractions.

Williams (D.B. Williams, pers. comm.) recommended the following method:

1. A carefully collected sample, subjected to a minimum amount of agitation to prevent volatilization of nitrogen trichloride, is placed in the titrator. Before the agitator is started, an excess of pH 4 buffer and an excess of potassium iodide are added to "fix" all the chlorine fractions, including NCl_3 .
2. Determine total chlorine residual. This is reading A.
3. Next, the titrator cell, agitator, and sample jar are thoroughly rinsed. Another sample is placed in the titrator jar. With the sample jar held in the operator's hand and slightly raised under the agitator, to achieve the maximum amount of turbulence, the agitator is turned on to aerate out all the nitrogen trichloride.
4. The sample jar is quickly returned to its normal position. The remainder of the procedure is the same as for determination of free chlorine, monochloramine, and dichloramine (in sequence). The sum of these fractions will be reading B, and the difference (A-B) will be the amount of nitrogen trichloride present (in milligrams per liter as Cl_2), assuming that the entire amount of it will appear in the total chlorine determination (reading A).

If desired, the nitrogen trichloride can be extracted using carbon tetrachloride rather than by aeration; but this approach would be more cumbersome.

Precision and Detection Limits

The precision of the amperometric method for determining free chlorine, combined chlorine, and total residual chlorine is limited primarily by the gradations on the buret, and is about ± 0.05 mg/l. Concentrations as low as 0.01 mg/l can be detected, but not precisely or accurately measured. The low-level amperometric method described below is recommended for concentrations of 0.2 mg/l or lower. For a skilled operator, the precision of the method for monochloramine and dichloramine is about 0.1 mg/l for analyzing samples with minimal amounts of interfering substances.

Low-Level Amperometric Titrations

If necessary, chlorine in concentrations of 0.2 mg/l or lower can be more precisely determined using one-tenth-strength (0.000564N) PAO and a buret with 0.01-ml gradations, and by recording and plotting the current readings to more precisely determine the end point of the titration. This is facilitated by using a titrator equipped to provide accurate current readings. The following modification was made to a Wallace & Tiernan Model A-790 Titrator (A.S. Brooks, pers. comm.):

1. Encase the sample jar in aluminum foil and ground it.
2. Remove the ammeter and insert a Rochester converter that emits a milliamper signal.
3. Connect the milliamper output to an electrician's voltmeter.

This modification enables the user to measure the electrical potential across the electrodes and to read residuals to concentrations as low as 0.001 mg/l.

Low-level titrations should be performed according to the procedure given above (in IV) for total residual chlorine. Free and combined chlorine can be distinguished at low concentrations in synthetic water samples, but most experts question the validity of such measurements in natural waters, especially in municipal and industrial wastewaters containing significant amounts of organic matter, because the results can be influenced by small amounts of interfering substances such as organic chloramines, or by slight intrusion of combined chlorine into the free chlorine titration, which can be increased by the presence of traces of iodide in the water. Similar problems can occur with other methods. Therefore, many states require water supply systems that rely on free chlorine for protection of the distribution system to maintain a residual of at least 0.2 mg/l, and the Surface Water Treatment Rule requires drinking water treatment plants using surface water as a source of supply to maintain a residual of at least 0.2 mg/l entering the distribution system.

Free Chlorine Residuals at Short Contact Times

In special situations, it may be desirable or necessary to determine the free chlorine residual after only a very short contact time, perhaps in seconds or minutes, while the free chlorine is still reacting with other substances such as ammonia nitrogen. This can be accomplished by exploiting the ability of PAO to react with free chlorine at pH 7, but not with combined chlorine.

By adding an excess of PAO solution to a properly buffered sample, the amount of free chlorine in the sample at the time the PAO is added (which will not necessarily be the same as the concentration at the time the sample was collected) can be determined by titrating the remainder of the excess PAO with a freshly prepared and standardized chlorine solution. The apparatus and the reagents are the same as described above except for a 0.00564N chlorine solution standardized with PAO solution, so that 1 ml of chlorine solution is equivalent to 1 ml of PAO solution. (Aqueous solutions of chlorine are unstable, especially in the presence of sunlight, so the chlorine solution must be freshly prepared, standardized immediately before use, and stored in the dark or in a brown glass bottle.)

The procedure for determining residuals at short contact times is as follows:

1. Add 1 ml of pH 7 buffer solution and 5.00-ml PAO to an empty but clean titrator jar.
2. Add precisely 200ml of sample and mix the solution as thoroughly and as rapidly as possible (perhaps at the point of sample collection and not necessarily in the immediate vicinity of the titrator).
3. Place the titrator jar in the titrator and titrate the sample using standardized chlorine solution (0.00564N) as the titrant.
4. At each addition of the titrant, the microammeter needle will momentarily deflect slightly to the right, returning each time. The end point is reached when the needle deflects discernibly to the right and does not return, indicating that all excess PAO has been oxidized by the chlorine solution and that the last addition of titrant has produced a current. Subtract this last addition from the buret reading. This is reading A (in milliliters).
5. If reading A is greater than 4.0 ml, repeat the procedure using less PAO solution. If reading A is less than 0.2 ml, repeat the procedure using more PAO solution.
6. The free chlorine residual in mg/l as Cl_2 = ml PAO – A, where A is the buret reading in milliliters.

The purpose of this procedure is to determine the free chlorine residual after a very short contact time. The contact time between the chlorine and the sample is measured from the time the chlorine is applied to the water being treated until the time the sample is added to the jar containing the PAO. The

time to transport the sample jar to the titrator and to run the titration is not part of the contact time.

Determination of Residual Chlorine in Wastewater Effluents

Chlorinating primary effluent to enhance its acceptability became common practice in the late 1940s. The chlorine dosage was usually insufficient to reach the breakpoint, so the residual was largely combined chlorine (and, as is now known, included significant amounts of organic chloramines). Primary effluent and other organics-laden waters, such as certain industrial wastewaters, present an analytical problem because they exert an immediate iodine demand, that is, the iodine produced by the reaction of combined chlorine with iodide reacts with organic matter and perhaps with other reducing agents that are unaffected by the initially present combined chlorine. In 1948, Wallace & Tiernan suggested a new method of amperometric titration of chlorine residuals in such wastewaters.⁸⁶ To avoid the loss of iodine, the titration procedure is reversed as follows: An excess of titrant (PAO) is added to the sample before adding iodide. Then, when the sample pH is reduced to 4 with buffer and iodide is added, the released iodine is immediately consumed by the PAO. The remaining PAO is back titrated with a standardized iodine solution.

Amperometric Back Titration Procedure. Back titration may be performed by either the amperometric method or iodometric method II (described below). The amperometric procedure is as follows:

1. Sensitize the electrodes with a dilute iodine solution; a light brown color is satisfactory. This will produce sharp end points. Allow the electrodes to soak in this solution in the sample jar for 15–20 min.
2. Thoroughly rinse out the sample jar, removing all traces of iodine.
3. Place a 200-ml sample of wastewater in the titrator and start the agitator.
4. Add 5.00-ml PAO solution while mixing the sample. If the total residual concentration is known to be higher than 5 mg/l, add 10-ml PAO.

Note. In some procedures, thiosulfate may be used in place of PAO, but if thiosulfate is used, the method is subject to interference from nitrite and free chlorine. Thiosulfate can reduce nitrite to nitric oxide, which catalyzes air oxidation of iodide; and free chlorine can react with thiosulfate to produce some sulfate (as well as tetrathionate), which alters the assumed analytical stoichiometry.⁸⁷

5. Add 4 ml of pH 4.0 acetate buffer solution (or a sufficient amount to produce a sample pH between 3.5 and 4.2).
6. Finally, add 1 ml of KI solution while mixing the sample.

Note. Adding the KI solution before adding the PAO will defeat the purpose of this method.

7. Adjust the microammeter pointer to read about 20 on the scale.
8. Add small increments of 0.0282N iodine solution from a 1-ml pipette or buret with 0.01-ml gradations. (A standardized iodate solution may also be used.)
9. As iodine is added to the sample, the pointer will remain almost stationary until the end point is approached. Just before the true end point, each increment of iodine solution will cause a temporary deflection of the microammeter, but the pointer will return to near its original position. The true end point is reached when the addition of a small amount of iodine solution results in a definite and permanent deflection of the pointer.
10. Note the volume of iodine solution used to reach the end point, and calculate the total residual chlorine as follows:

$$\begin{aligned} \text{Total residual chlorine, mg/l as Cl}_2 \\ = \text{ml } 0.00564 \text{ N PAO} - (5 \times \text{ml } 0.0282 \text{ N iodine solution}). \end{aligned} \quad (3.3)$$

The analyst should recognize that many wastewaters contain significant amounts of nitrogenous material, such as protein, that may form organic chloramines. Organic chloramines typically react with iodide under the conditions of this back titration and will thus be included in total residual chlorine, but they may have little or no disinfecting power. When interference from organic chloramines is possible, the analyst should use a forward titration (amperometric or DPD-FAS) to determine the amount of dichloramine, which will include most or all of the organic chloramines present. A back titration procedure can then be used as a check on the total chlorine residual determined by forward titration.

Monitoring the Normality of Iodine Solutions. In the past, the 0.0282N iodine solution was believed to be so unstable that it had to be made up fresh daily. Long-term experience discloses that this was a gross error. If stored in the dark (in a brown bottle) at moderate temperatures, the solution will remain stable for months. However, it is prudent to check its normality weekly or biweekly. The following is a quick and simple field procedure using an amperometric titrator:

1. Sensitize titrator electrodes to iodine by placing them in a sample jar containing a weak iodine solution—one that gives a light brown cast. Leave the electrodes immersed for 15–20 min.
2. Rinse the electrodes thoroughly with tap water.
3. Add 5.00-ml PAO to 200-ml distilled water and place the solution in the titrator.
4. Titrate with 0.0282N iodine solution.

5. The end point is reached when the addition of a small amount of iodine causes the microammeter needle to deflect to the right (upscale) for 15–20 s. At this point, all of the PAO has been oxidized.
6. Read the amount of iodine used from the buret (or pipette). If 1.00-ml iodine solution neutralizes 5.00 ml of 0.00564 N PAO solution, the iodine solution is 0.0282 N. If the iodine solution has deteriorated, the volume of iodine solution used to reach the end point will be somewhat greater than 1.00 ml.

Sample Calculation. Upon standardizing the iodine solution, it is found that 1.20-ml 0.0282 N I_2 is required to neutralize 5.00-ml 0.00564 N PAO in a 200-ml sample. As 1.20-ml I_2 is required to neutralize 5-ml PAO, 1.0 ml of I_2 solution will neutralize only $5.00/1.20 = 4.17$ ml PAO. Thus, the equation for calculating the chlorine residual becomes

$$\text{Total residual chlorine, mg/l as } Cl_2 = \text{ml PAO} - (4.17 \times \text{ml } I_2 \text{ solution}). \quad (3.4)$$

Given a PAO normality of 0.00564, the normality of the I_2 solution is calculated as $(5.00/1.20)(0.00564 \text{ N}) = 0.0235 \text{ N}$.

Nitrogen Trichloride. Nitrogen trichloride (or “trichloramine”) can be produced during the manufacture of chlorine if the electrolytic cell water contains ammonia nitrogen, and it can also be produced in the laboratory; but in potable water and wastewater treatment systems, it is produced only when the chlorine-to-ammonia-N ratio is about 12:1 or greater at pH values up to 9 (Chapter 2). Its occurrence in potable water treatment is rare, but it is readily detected (by virtue of its pungent odor and eye-stinging effects) in swimming pool water treated with chlorine. In the Rancho Cordova study of nitrogen removal by using chlorine, nitrogen trichloride generation was not a problem because of its rapid decay.⁸⁸ Palin^{29,83} and Cooper and Gibbs⁵⁶ spent considerable amounts of time investigating the detection and measurement of NCl_3 in potable water. It was a tantalizing exercise but a seemingly futile one since NCl_3 solutions are made up in the laboratory under controlled conditions. The nitrogen trichloride in a treatment plant is not generated in the same way as the solutions made up in the laboratory, so the methods of detecting NCl_3 in synthetic solutions prepared under laboratory conditions are unlikely to apply under field conditions.

Two factors related to nitrogen trichloride formation should be kept in mind: (a) $HOCl$ must be present for NCl_3 to exist; and (b) monochloramine is always found in the presence of NCl_3 . This is the result of the simultaneous competing breakpoint reactions described in Chapter 2.

Nitrogen trichloride is liquid at room temperature (boiling point = 71°C). It is *practically* insoluble in water (where it decomposes slowly); but it is soluble in liquid chlorine and in solvents such as chloroform, carbon

tetrachloride, and carbon disulfide. The strongest solution of NCl_3 achieved by Cooper et al.⁵⁵ was 13.8 mg/l; and the solutions they prepared were stored at 0°C or used immediately. These solutions and those prepared by Palin were made under carefully controlled conditions and at reacting concentrations substantially different from any field conditions.

From a practical viewpoint, the operator is more interested in whether or not NCl_3 is generated in the treatment process, rather than how much of it is generated. NCl_3 is highly volatile, so an operator can detect its presence more readily than an analyst can. The olfactory nerve can detect concentrations as low as 0.02 ppm⁸² (D.B. Williams, pers. comm.), but the eyes can detect it before the nose can. The slightest concentration will cause the eyes to smart, and prolonged exposure will cause severe tearing. As the concentration of NCl_3 increases, its effects become similar to those of tear gas; but its effects on the respiratory system are much milder than those of gaseous chlorine (G.C. White, unpublished observations).

The only documentation covering the measurement of NCl_3 generated under field conditions at a treatment plant is by Williams⁸² (D.B. Williams, pers. comm.). His method of measuring NCl_3 by amperometric titration is described earlier in this chapter.

Occurrence and Control of Nitrite Interference. In the early 1970s, the Bureau of Sanitary Engineering, California State Department of Health, investigated the disinfection of wastewater effluent by chlorination. A popular method at that time was the starch-iodide forward titration, which called for acidifying the sample to pH 1–2, adding iodide, and measuring the I_2 released by the combined chlorine residual. The procedure was carried out at a pH of 1 or 2 to avoid reactions between iodine and organic matter (R.J. Baker, pers. comm.). In several instances, false residuals as high as 16 mg/l were reported—false because they were measured when the chlorinators had been shut down.⁸⁹ An investigation discovered that the false residuals were caused by nitrite. It has since been confirmed that at pH 3 or lower, nitrite will oxidize I^- to I_2 , at a rate depending on acidity and the reactant concentrations⁹⁰ (R.J. Baker, pers. comm.). It is also possible for I_2 to oxidize nitrite to nitrate, depending on the pH and the concentration of each constituent, and monochloramine is also known to oxidize nitrite in an acid-catalyzed reaction,⁹¹ so both positive and negative interferences may occur.

There is conflicting and incomplete information in the literature regarding the extent to which nitrite interferes with both forward and backward amperometric and iodometric methods, and regarding the effectiveness of methods to control nitrite interference. The problem has received relatively little attention because it is rarely encountered in drinking water applications and often goes unnoticed when chlorinating wastewater. Nitrite is usually not found in drinking water supplies, although trace amounts of it sometimes occur in distribution systems undergoing nitrification. At wastewater treatment plants, elevated concentrations of nitrite are encountered only when the plant is

partially nitrifying or in transition to full nitrification; and a nitrite interference is likely to go unnoticed because the primary concern is the inactivation of coliforms to the required level rather than producing a particular concentration of free or combined chlorine. Also, most wastewater effluents that are disinfected with chlorine are dechlorinated before being discharged, so the final effluent is typically analyzed only to ensure that no trace of chlorine remains rather than to determine the speciation of the residual.

White⁷⁷ has stated that the nitrite interference in forward amperometric and iodometric (starch–iodide) titrations is eliminated by using pH 4 acetate buffer, presumably because the pH remains above 3 when using this buffer; and he indicates that nitrite does not interfere at pH 7 either. *Standard Methods*¹³ also states that nitrite does not interfere with the (forward) amperometric titration method. However, researchers at Hach Chemical Co. found that nitrite interferes with forward amperometric titration when analyzing monochloramine at pH 4, creating a positive interference when the KI is added before the acetate buffer (suggesting that nitrite may be oxidizing iodide to iodine, either at neutral pH or as the pH is lowered) and a negative interference when the pH 4 buffer is added first (suggesting that the liberated iodine is reacting with nitrite at pH 4).⁹² The significance of these findings with respect to the forward amperometric procedure is unclear since in the forward titration, monochloramine is determined at pH 7 and dichloramine at pH 4. Nevertheless, these findings suggest a need for further investigation.

As for the back titration procedure, using either a starch–iodide or amperometric end point, *Standard Methods*¹³ states that interference from nitrite (up to 0.2 mg/l) is controlled by buffering the sample to pH 4 before adding the KI, but provides no supporting information. For nitrite concentrations higher than 0.2 mg/l, *Standard Methods*¹³ directs the analyst to control the interference with phosphoric acid–sulfamic acid reagent but provides no clear instructions as to how this reagent is to be used. The analyst is warned that “a larger fraction of organic chloramines will react at lower pH,” indicating that one interference is being traded for another. The analyst is evidently supposed to assume that the phosphoric acid–sulfamic acid reagent is to be used as a substitute for the phosphoric acid solution in a colorimetric iodate titration to determine the end point; but the instructions for this titration indicate that the analyst should add the reductant (PAO or thiosulfate), an excess of KI (before adding the phosphoric acid!), the phosphoric acid solution (with sulfamic acid added if nitrite is present), and starch and then “titrate immediately.” No time is allowed for reduction of nitrite by the sulfamic acid. Dietz et al.⁸⁷ demonstrated the importance of allowing the sulfamic acid to react with the nitrite (for 2 min) before adding KI, confirming the effectiveness of the procedure used by earlier investigators; and they also noted that thiosulfate should not be used in the back titration procedure when free residual chlorine (FRC) is present since some of the thiosulfate may be converted to sulfate rather than to tetrathionate.

White,⁷⁷ addressing the question of nitrite interference in the back titration procedure using PAO, contended that although iodine can react with nitrite to form nitrate, the iodine liberated by the residual chlorine will be immediately consumed by the PAO, and the oxidation of nitrite by iodine is so slow at pH 4 that nitrite interference is nonexistent. White⁷⁷ did not directly address the possibility that nitrite would oxidize iodine under the same conditions but appeared to believe that this problem is limited to pH values of 3 or lower. Data presented by Harp,⁹² which show that nitrite at concentrations up to 50 mg/l did not significantly interfere with the back titration procedure regardless of whether the buffer was added before or after the KI solution, strongly support White's contention that nitrite interference is not a problem with the back titration procedure.

Harp⁹² also reported that nitrite readily oxidized iodide to iodine when using the phosphoric acid-sulfamic acid reagent and iodate as the titrant, as directed by *Standard Methods*.¹³ This is not surprising, as sulfamic acid must be added and given time to destroy the nitrite before the iodide is added. The proper procedure is as follows:

1. To a 200-ml sample of wastewater, add 1 ml of a 5% solution of sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$), which will convert nitrite to nitrate. Mix the solution and allow it to stand for 10 min.
2. Add 5.00 ml of 0.00564 N PAO solution (for chlorine concentrations up to 5 mg/l as Cl_2).
3. Add a sufficient amount of pH 4.0 acetate buffer solution to adjust the sample pH to between 3.5 and 4.2. (The sulfamic acid will depress the pH, so less buffer than usual will be required.)
4. Titrate amperometrically, as described above, or add excess KI (1 g) and titrate with standard iodine (0.00282 N) (see "Iodometric Method II").

The California State Department of Health's solution to the nitrite interference problem was to destroy the nitrite in the samples with sulfamic acid. However, using sulfamic acid for this purpose should be limited to analysis of samples known to contain only combined chlorine since sulfamic acid can react with free chlorine to form both *N*-chlorosulfamic and *N*-dichlorosulfamic acids. The dichloro compound forms far more rapidly at pH values of 5–8.⁹³ Little is known about the potential for these compounds to hydrolyze and release free chlorine, as do some *N*-chloro compounds, especially at the pH values associated with the once popular low-pH iodometric back titration method. Samples containing free chlorine are not expected to contain an appreciable amount of nitrite since free chlorine rapidly oxidized nitrite to nitrate.

As for the DPD methods described below, *Standard Methods*.¹³ does not list nitrite as an interference, and Harp⁹² states that nitrite interference is minimal

if pH is controlled in the range of 6.0–6.8. Minimal interference is to be expected since the pH is neutral and the liberated iodine will react almost instantaneously with the DPD. The interference of nitrite with the orthotolidine method is discussed below.

Baker's Alternative Procedure.⁹⁴ Since about 1974, when chlorine residuals were discovered to be toxic to aquatic life, measurement of these residuals, especially in wastewater and cooling water discharges, has come under close scrutiny. Baker's procedure is based on the assumption that chlorine species capable of disinfecting potable water, wastewater, cooling water, and the water in swimming pools are also able to oxidize iodide to iodine at pH 7 (R.J. Baker, pers. comm.). Dichloramine and various organic chloramine species that have little or no biocidal effect do not react with iodide at pH 7, but do react at pH 4. In some cases, dechlorination of residuals in the "dichloramine fraction" may be required. Baker's procedure is particularly useful for detecting titratable organic chloramines in nitrified wastewaters that contain only a trace of ammonia but high concentrations of organic nitrogen—and "dichloramine." His procedure is as follows:

1. Titrate for free chlorine with PAO.
2. Titrate for monochloramine at pH 7 in the usual way with PAO.
3. Take another sample, add excess KI (1 ml) and 5.00 ml of 0.00564N PAO, then back titrate at pH 7 with standardized chlorine solution. It is not possible to back titrate with I_2 because it would be consumed by organic matter at pH 7, but not at pH 4.
4. Take the sample from step 3 and lower its pH to 4. The species that titrate in this step are the "dichloramine" species.

DPD METHOD

The DPD method is the only surviving one of the three methods developed by Palin.^{31,95} (The other two were the *p*-aminodimethylaniline method²⁷ and a neutral orthotolidine–FAS titration procedure.³⁰) First introduced in 1956, this method uses an indicator solution of DPD. In the absence of iodide ion, free chlorine reacts instantly with the DPD indicator to produce a red color (a relatively stable semiquinoid cationic free radical⁴⁰ commonly known as a Wurster dye). Subsequent addition of a small amount of iodide ion acts catalytically to cause monochloramine to produce color. Further addition of excess potassium iodide evokes a rapid response from dichloramine. Nitrogen trichloride, if present, reacts partly as free chlorine and partly as dichloramine. The color produced at each stage may be determined colorimetrically or titrated to a colorless end point using a standardized FAS solution. Color (absorbance) does not increase linearly with chlorine concentration, so

colorimetric methods must employ a calibration curve or use a specially calibrated spectrophotometer.

Except for strong oxidants (e.g., ozone or chlorine dioxide), the most significant interfering substance likely to be encountered when using the DPD method is oxidized manganese. Correction for manganese interference can be made as described below for the DPD–FAS titrimetric method.

Whether using a colorimetric or a titrimetric procedure, the analyst should also note the following:

1. It is very important to maintain a pH of 6.2–6.5. Lower pH values cause increased breakthrough of monochloramine into the free chlorine fraction and breakthrough of dichloramine into the monochloramine fraction. At a higher pH, the rate of color formation associated with dissolved oxygen will increase.
2. Monochloramine will slowly break through into the free chlorine fraction. The rate of breakthrough varies with temperature and other factors, but is typically about 3%–6% per minute.⁴⁰ To minimize this and the interference associated with dissolved oxygen, the analyst should promptly measure the color or titrate the sample.⁷⁶ This is especially important at higher sample temperatures, which accentuate these interferences and can also cause color fading.
3. Even when the sample is titrated rapidly, high concentrations of combined chlorine can break through and appear as free chlorine (at a rate of about 2% per minute). The breakthrough can be suppressed using thioacetamide as described below for the DPD–FAS titrimetric method.
4. If iodide is used to measure combined chlorine and the same glassware is used for subsequent determination of free chlorine, the glassware must be thoroughly rinsed to remove all traces of iodide.
5. Each DPD method is developed for a specific (and stated) range of chlorine concentrations. It is critical not to exceed the upper limit since an excess of chlorine will further oxidize the red-colored Wurster dye to form a colorless amine, making it appear that the chlorine concentration is lower than it really is. For example, if the analyst using a test kit with a stated range of 0–4 mg/l measures a chlorine residual of 2.0 mg/l, it is possible that the actual chlorine concentration could be much higher than the upper limit of the test kit. To determine whether the true residual value is 2.0 mg/l, the analyst should dilute the sample 1:1 (with distilled or deionized water free of chlorine, ammonia, and other interfering substances) and then verify that the chlorine concentration in the diluted sample is 1.0 mg/l. If it is not, the residual chlorine concentration may actually be higher or interferences may be present.
6. The order of reagent addition is important. The buffer must be present when the DPD reagent reacts with chlorine in the sample; otherwise the

reaction may not take place at the desired pH (6.2–6.5). Thus, when using liquid reagents, both the buffer and the DPD reagent are added to the titration vessel before adding the sample. When using tablets or powdered reagents, the buffer must be added to the sample either before the DPD is added or at the same time.

7. When analyzing samples containing high concentrations of chlorine, that is, when sample dilution is required, it is important to prevent high concentrations of chlorine from coming into contact with the DPD reagent, which will cause the DPD to be oxidized to a colorless amine. This is accomplished by adding the reagents and dilution water in the proper order and providing adequate mixing. When diluting a sample having a high chlorine concentration, the buffer, DPD reagent, and dilution water should be added to the titration vessel first, then the sample should be added with sufficient mixing to rapidly disperse it throughout the vessel. Alternatively, the sample may first be diluted with chlorine-demand-free water free of interfering substances and then analyzed in the usual manner.

DPD Colorimetric Method

The DPD colorimetric method is the only colorimetric method that can be used to differentiate among the various combined chlorine species. Because it also differentiates between free and combined chlorine, it quickly came to be widely preferred over the earlier orthotolidine methods, especially for field measurements.

Using the DPD colorimetric method with a suitable spectrophotometer, the minimum detectable chlorine concentration is about 0.01 mg/l as Cl_2 . The range of the test is typically about 0–4 mg/l without dilution of the sample, but there are method variations designed to accommodate other ranges of concentration. Concentrations beyond the range of a particular method (or field kit) may be determined by diluting the sample with distilled or deionized water (free of chlorine, ammonia, and interfering substances) and then multiplying the readings by the appropriate dilution factor. Kits should be carefully chosen to accommodate the range of chlorine concentrations likely to be encountered. Concentrations exceeding the stated range, if not diluted, will produce meaningless and, possibly, misleading results. DPD colorimetric methods employ a sample blank to automatically correct for minor amounts of turbidity or color.

The DPD colorimetric method is particularly well suited for use in the field. The necessary reagents can be prepared in the laboratory¹³ or purchased from a vendor, typically as part of a kit that includes reagents in tablet form or in dispensers, as well as means of measuring the color. A calibrated spectrophotometer or permanent color standards may be used in the laboratory. Portable spectrophotometers specifically calibrated for use with the DPD method are available, but many field kits include color charts or a “color comparator” with

color standards mounted on a disk. Most field kits are designed to use the Palin tablet method or a variation of it.

Palin Tablet Method. All of the necessary reagents are incorporated into four tablets that must be completely dissolved before measuring the residual. The contents of the tablets are as follows:

Tablet	Contents
DPD no. 1	DPD indicator with EDTA and buffer
DPD no. 2	Stabilized KI for monochloramine activation
DPD no. 3	Stabilized KI for dichloramine activation
DPD no. 4	All reagents in a single tablet

Depending on the chlorine residuals or species to be determined, the appropriate procedure is selected:

Free chlorine	Use tablet 1
Free and combined chlorine	Use tablet 1, then 3
Monochloramine	Use tablet 1, then 2
Dichloramine	Use tablets 1 and 2, then 3
Total residual chlorine	Use tablet 4

Combined chlorine is determined from the increase in color after adding tablet 3; thus, it is the difference between the free chlorine reading taken after adding tablet 1 and the reading taken after adding tablet 3. Similarly, monochloramine is determined from the increase in color after adding tablet 2, and dichloramine from the increase after adding tablet 3 following monochloramine determination. These procedures mimic those of the DPD titrimetric procedure described below.

Spectrophotometric Methods. Calibrated spectrophotometers are widely used in concert with the DPD colorimetric method. Such devices are often equipped with batteries for portable use or with a power outlet for laboratory use. Most are supplied with a carrying case that also stores reagents in liquid or powder form. Reagents in powder form are more stable and less readily spilled, so they are often used in the field; but solution reagents are easier and quicker to use than powdered reagents or tablets, and the speed of color development in the DPD measurements enhances the accuracy of the method. Therefore, solution reagents are most commonly used in laboratories. Devices specifically designed to determine chlorine concentration normally come with complete instructions.

DPD-FAS Titrimetric Method

This method is very similar to the colorimetric method, with the primary difference that the red color formed by the DPD in each step of the procedure

is determined by titrating the sample with a standardized (0.00282 N) solution of FAS. The minimum detectable concentration is about 0.01 mg/l as Cl_2 , and a typical working range is 0–4 mg/l.

The FAS solution and the other reagent solutions (phosphate buffer, DPD, and KI) can be prepared by the analyst¹³ or purchased from a vendor. Many analysts prefer to use dry reagents, such as “DPD no. 1 powder” (which includes both the phosphate buffer and DPD reagent) and KI crystals, rather than solutions because the dry reagents are much more stable than the liquid reagents. When using reagent solutions, the buffer and DPD solutions must be kept separate (the DPD degrades much more rapidly at the pH of the buffer solution); and the DPD solution must be regularly inspected and discarded when it becomes discolored, that is, when the absorbance at 515 nm exceeds 0.002/cm.^{13,96} The following procedures are based on the use of DPD no. 1 powder and KI crystals. When using solutions, the phosphate buffer solution and DPD solution are used in place of the DPD no. 1 powder, and a 5 g/l KI solution is used instead of KI crystals.

Procedure for Free Chlorine. To a 100-ml sample, add approximately 0.5-g DPD no. 1 powder. Mix the solution rapidly to dissolve the powder, and titrate immediately with 0.00282 N FAS solution to a colorless endpoint (reading A).

Procedure for Monochloramine and Dichloramine. Add to the above solution one very small crystal of potassium iodide (about 0.1 mg) or two drops of KI solution. Mix well and titrate immediately to a colorless endpoint (reading B). Note that reading B is a cumulative reading that includes reading A. Add several crystals (about 0.5 g) of potassium iodide. Mix to dissolve the KI, and after the solution stands (unmixed) about 2 min, continue the titration (reading C, also a cumulative reading). If this (dichloramine) fraction is fairly high, use double the quantity (about 1 g) of potassium iodide.

Procedure for Nitrogen Trichloride. To 100 ml of fresh sample, add one small crystal of potassium iodide. Mix the solution and then add about 0.5-g DPD no. 1 powder. Titrate immediately with FAS solution (reading D, not cumulative). Reading D reportedly includes free chlorine, monochloramine, and about half of the trichloramine, with the other half appearing along with dichloramine in reading C.⁹⁶ However, Palin recovered only about 90% of trichloramine using this procedure.⁹⁶ In the absence of verification of the accuracy of this procedure by others, the results should be considered qualitative and interpreted with caution.

Procedure for Total Residual Chlorine. Total residual chlorine may be obtained in one step by adding DPD no. 1 powder and the full quantity of potassium iodide to the sample and allowing it to stand for about 2 min. A combined DPD and potassium iodide reagent known as DPD no. 4 powder can be used as a single reagent for total chlorine. For a 100-ml sample, use

about 0.5 g of this powder, or if high concentrations of chlorine are present, use about 1.0 g. After allowing the sample to stand for about 2 min, titrate with the FAS solution to obtain the total chlorine (reading E).

Calculations. For a 100-ml sample, 1 ml of 0.00282 N FAS solution equals 1 mg/l of chlorine as Cl_2 :

Reading A = free chlorine

Reading B = free chlorine + monochloramine

Reading C = free chlorine + monochloramine + dichloramine + $\frac{1}{2}\text{NCl}_3$

Reading D = free chlorine + monochloramine + $\frac{1}{2}\text{NCl}_3$

Reading E = total residual chlorine

Therefore,

Free chlorine = A

Monochloramine = B – A

Dichloramine = C – B (if no NCl_3 is present)

Dichloramine = C – D (if NCl_3 is present)

Combined chlorine = (C – A) or (E – A)

Nitrogen trichloride = 2(D – B)

Total residual chlorine = E

Monochloramine Breakthrough. If a substantial amount of monochloramine (≥ 0.5 mg/l as Cl_2) is present with the free chlorine, an alternative procedure is recommended to prevent monochloramine breakthrough into the free chlorine reading. Add 0.5 ml of a 0.25% solution of thioacetamide to the 100-ml sample, immediately after mixing it with the DPD reagent, to stop further reaction of the DPD with combined chlorine. Titrate immediately with FAS to obtain free chlorine. Then determine total residual chlorine using the above procedure (reading E) without thioacetamide. Combined chlorine is determined by the difference between the two readings.

Palin⁵³ called using thioacetamide with the DPD procedure (either colorimetric or titrimetric) the “Steadifac” method. The reaction of the Steadifac solution occurs in a molar ratio of 1:1, from which it may be calculated that 0.5 ml of a 0.25% solution of thioacetamide added to a 100-ml sample can eliminate 11.8 mg/l of chloramine.

Manganese Interference. Oxidized manganese, commonly encountered in drinking water applications, causes stoichiometric interference in the DPD method (and in other methods, but not in the determination of free chlorine by amperometric titration).⁶⁴ This interference can be circumvented by using the following procedure.¹³ Add 0.5 ml of 0.5% sodium arsenite (or thioacetamide) solution, along with 5 ml of buffer solution to the titration flask,

then add the sample and mix. Add 5 ml DPD indicator solution, mix the sample, and titrate with standard FAS titrant until the red color is discharged. Subtract this reading from reading A (free chlorine), obtained by the normal forward titration procedure described above, or from total chlorine, reading E, also described above. If using the combined powdered reagent (DPD no. 1 powder), first add KI and arsenite to the sample and mix the solution, then add the combined buffer-indicator reagent. A similar procedure was used by Sollo and Larsen³⁷ to eliminate manganese interference in the MO method. The procedure initially developed by Palin⁹⁶ included addition of a small KI crystal with the arsenite solution, presumably to speed the reaction of arsenite with combined chlorine; but this is evidently not necessary, as it is omitted in the procedure described in *Standard Methods*¹³ (DPD-FAS method).

FACTS (SYRINGALDAZINE) METHOD

The free (available) chlorine test using syringaldazine, generally referred to as the FACTS method, uses a saturated solution of syringaldazine in 2-propanol as the indicating reagent.¹³ Syringaldazine is stable when stored either as a solid or as a solution. It is oxidized by free chlorine on a 1:1 molar basis, yielding a colored product with an absorption maximum at 530 nm. The color product is only slightly soluble in water; therefore, at chlorine concentrations higher than 1 mg/l, the final reaction mixture must contain 2-propanol to prevent product precipitation and color fading.

The pH of the reagent and sample mixture is critical. It must be held between 6.5 and 6.8 using a buffer.¹³ Otherwise, color develops too slowly or too rapidly, the latter resulting in fading. When analyzing alkaline or acidic samples, special care must be taken to ensure that the amount of buffer added is sufficient to maintain pH within the 6.5–6.8 range.

The minimum detectable free chlorine concentration is 0.1 mg/l or less. The range of free chlorine measurement is 0.1–10.0 mg/l. Interferences common to other methods of determining free chlorine do not affect the FACTS procedure. Monochloramine at concentrations up to 18 mg/l, dichloramine up to 10 mg/l, and oxidized forms of manganese up to 1 mg/l do not interfere. Ferric iron at concentrations up to 10 mg/l does not interfere, nor does nitrite at concentrations less than about 250 mg/l. Strong oxidizing agents such as iodine, bromine, and ozone will produce a color, as does nitrogen trichloride. Temperature has a minimal effect on color development. The largest error observed over a temperature range of 5–35 °C is $\pm 10\%$.

The color depth is converted to milligrams of free chlorine per liter using a filter photometer, a spectrophotometer, or permanent color standards. *This method measures only free chlorine concentrations.* Commercial color kits are available with four permanent glass color standards of 0.5, 1.0, 1.5, and 2.0 mg/l free chlorine.

As noted above (under “Historical Background”), the FACTS method was developed by the U.S. Army as a field procedure that would be very simple to use. All the analyst has to do is buffer the sample, add the syringaldazine solution, and then measure the color.

IODOMETRIC METHOD I

The iodometric method, also referred to as the starch–iodide method, is the oldest method for determining chlorine residuals. It is still widely employed today, primarily to determine the concentration of chlorine in relatively high-strength solutions, such as feed or stock solutions. It is based on the quantitative oxidation of iodide to iodine by free and combined chlorine. The liberated iodine is titrated, usually with a standard solution of sodium thiosulfate, using starch as the indicator.^{97,98} If organic matter is present that reacts with the liberated iodine, as can occur when analyzing chlorinated wastewater effluent, a “back titration” procedure can be used to circumvent this problem. (See “Iodometric Method II” below.) The following equations illustrate the chemistry of the reactions involved:

For free chlorine residuals:



For combined chlorine residuals:



For titration with thiosulfate:



Either sodium thiosulfate or PAO may be used as the titrant. PAO reacts faster than thiosulfate and is more stable. However, sodium thiosulfate is used more often because a standardized thiosulfate solution is simpler to prepare and because it is relatively nontoxic. The strength of the titrant can be adjusted to accommodate the range of chlorine concentrations of interest. Normalities of 0.01 and 0.025 are commonly used, but a 0.1 N titrant is preferable for analyzing high-strength solutions.

Until the discovery of the breakpoint phenomenon, this method was used to measure residuals that released iodine from KI at neutral pH, that is, free chlorine plus monochloramine. An alkaline pH value must be avoided because hypiodite disproportionates to iodate and iodine at pH values of

7–9 or higher, depending on conditions.⁹⁹ Today, the standard practice is to lower the pH to 3–4 because (a) the titration is nonstoichiometric at neutral pH owing to the oxidation of some of the thiosulfate to sulfate; (b) any dichloramine present will also be included in the analysis at pH 3–4, but not at neutral pH; and (c) the oxidation of iodide to iodine by oxygen proceeds very slowly at pH 3–4 but is acid catalyzed⁹⁹ and may become significant at the lower pH values used in earlier versions of this method. Acetic acid was found to be better suited for pH adjustment than either sulfuric or hydrochloric acid, as well as providing much better control of the pH in the desired range.

If ferric or manganic compounds are present, they will give false residual readings. Reducing agents that have not yet reacted with the chlorine residual can also interfere. Nitrite interferes, especially under the acidic condition of the titration, but the interference can be overcome by the sulfamic acid procedure described below for iodometric method II. A blank titration is used to compensate for traces of oxidizing or reducing impurities in the reagent and for the fraction of the iodine that may bind irreversibly to the starch indicator.

Skoog and West⁹⁹ have described the types of starches that can be used as indicators and some of their limitations. “Soluble” starches rich in straight-chained β -amyloses, such as potato starch, work well, whereas those containing branched-chain amylopectins, or α -amyloses, such as cornstarch, form complexes that are not readily irreversible. Amylopectins settle more rapidly and can thus be partially removed by settling and decanting. Starch decomposes readily unless a preservative is added. Mercuric salts can be used, but an excessive concentration of mercury (II) will interfere by complexing the available iodide and converting tri-iodide to iodine, and the starch indicator works by binding the tri-iodide complex. Starch does not work well as an indicator at temperatures much above room temperature, and it must be added after most of the iodine has been titrated to minimize irreversible binding with iodine.

The minimum practical detection limit using a starch–iodide end point is about 1 mg/l, although lower concentrations can be measured by using an amperometric end point. This method is not considered suitable for compliance monitoring and similar purposes because detecting the residual chlorine concentrations typically encountered in water and wastewater requires a relatively large sample volume, the thiosulfate and starch solutions are relatively unstable, and the end point can be a bit “tricky,” especially at higher temperatures. However, it is still very widely used for analyzing high-strength chlorine solutions such as feed solutions and for standardizing chlorine solutions used in laboratory studies of chlorine demand, disinfection, taste and odor control, DBP formation, and so on.

For the convenience of operators and laboratory technicians, a procedure for measuring chlorine concentrations in the range of 100–3000 mg/l as Cl_2 is outlined below.

Procedure for Standardizing Chlorine Solutions

1. Add about 10-ml reagent water, 2-ml glacial (concentrated) acetic acid (or enough to adjust the sample pH to 3–4) and 1 g of KI (USP-grade crystals) to the titration vessel.
2. Add an accurately measured volume of sample to the titration flask. For a solution containing 100–3000 mg/l of free chlorine, a volume of 10–50 ml is suitable. In general, use a sample volume requiring between 0.2 and 20 ml of sodium thiosulfate titrant. Immediately stir the sample to thoroughly mix it with the reagents. Any free or combined chlorine present will immediately release iodine, producing a color ranging to light straw to dark brown, depending on the amount of chlorine initially present.
3. Begin adding 0.100N sodium thiosulfate titrant (purchased commercially or prepared by dissolving 24.82-g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 1-l freshly boiled distilled water, storing for 2 weeks, and then checking the titer against a standard solution of iodate or dichromate).¹³ Continue adding the titrant until only a light straw color remains.
4. Add 1 ml of starch solution, which will react with iodine to produce a blue color. (To prepare starch solution, add 5 g of water-soluble starch to 1 l of boiling distilled water, stir, allow to settle overnight, then decant and use the supernatant. Various preservatives may be used.¹³)
5. Titrate with sodium thiosulfate until the blue color disappears. Read the amount of thiosulfate used at first disappearance of the blue color (reading A) and disregard the reappearance of the color upon standing.
6. Titrate a reagent blank (reading B). (If reducing substances are present, the blank may be “negative,” in which case a standardized iodine solution must be added to produce a blue color before titrating with thiosulfate. Correct the volume of the titrant used by deducting the equivalent volume of iodine solution added to obtain the blue color.)

Calculation. Assuming that 0.100N thiosulfate is used as the titrant, the chlorine concentration is

$$\text{mg/l as Cl}_2 = (A \pm B) \times 0.100 \times 35,450 / (\text{ml sample}). \quad (3.9)$$

IODOMETRIC METHOD II (WASTEWATER)

When determination of residuals in wastewater first became an important consideration, many effluents were receiving only primary treatment. In the forward titration procedure (iodometric method I), the iodine is released before titration, and it was found that during the time required to neutralize the iodine with the titrant, some of the iodine was being consumed by organic

matter. To overcome this interference, a back titration method was devised. It is applicable to both iodometric and amperometric procedures, which yield similar results. Nitrite is not believed to interfere with this method, as discussed above in "Occurrence and Control of Nitrite Interference." The amperometric back titration procedure was described above; the iodometric back titration procedure, referred to as iodometric method II, is as follows:

1. Place 5.00 ml of 0.00564 N PAO solution in a titration flask. (Sodium thiosulfate may be used in place of PAO in this method. PAO gives a much sharper end point when using the amperometric titration method.)
2. Add an excess (about 1 g) of KI and 4 ml of pH 4 acetate buffer solution, or sufficient buffer, to reduce the pH to between 3.5 and 4.2. To minimize interference from nitrite, buffer to pH 4 before adding the KI.
3. Pour in a carefully measured volume of sample and mix with a stirring rod. The volume of sample used is governed by the concentration of chlorine in the sample. For a residual chlorine concentration of 10 mg/l or less, titrate at least 200 ml of sample. For higher concentrations, use proportionately less of the sample.
4. Add 1-ml starch solution for each 200-ml sample.
5. Titrate with 0.0282 N iodine to the first appearance of blue color that persists after mixing, as described in "Monitoring the Normality of Iodine Solutions" above. A standardized iodate solution may also be used as the titrant.

Note. For a 200-ml sample, 1 ml of 0.00564 N PAO represents 1 mg/l chlorine, so 5 ml of PAO solution is sufficient for residual chlorine concentrations up to 5 mg/l. For residual chlorine concentrations of 5–10 mg/l, use 10 ml of PAO. For higher chlorine concentrations, use a smaller sample volume.

Calculation.

$$\text{mg/l as Cl}_2 = (A - 5B)(200/C), \quad (3.10)$$

where

A = ml 0.00564 N PAO solution,

B = ml 0.0282 N iodine, and

C = ml of sample.

IODOMETRIC ELECTRODE METHOD

This method is based on the potentiometric measurement of iodine after total residual chlorine reacts with iodide at pH 4. It measures only total residual chlorine, including iodide-reactive organic chloramines and any other

oxidizing substances that are strong enough to oxidize iodide to iodine, such as oxidized forms of manganese, bromine, chlorine dioxide, and divalent copper ions. Organic matter able to react with the liberated iodine interferes, as does chloride at high concentrations, which can form the I_2Cl^- complex that is not sensed by the electrode.⁹² Silver ions interfere at concentrations above 10 mg/l and mercury ions at concentrations above 20 mg/l,¹³ and the temperature of the standards and samples must be controlled because the measured potential will depend strongly on temperature.

The method is quite simple, requiring only an iodide selective electrode, a platinum electrode (separate or in combination with the iodide selective electrode), an expanded-scale pH/mV meter, pH 4 acetate buffer, and a KI reagent solution (84 g/l KI and 0.4 g/l Na_2CO_3). A semilogarithmic calibration curve is prepared by analyzing standards prepared by oxidizing iodide to iodine with carefully measured volumes of standard potassium iodate (0.00282 N), taking care to use the same concentrations of pH buffer and iodide used when analyzing samples. Total residual chlorine is determined by adjusting the pH of a 100-ml sample (or diluted sample) to 4 using 1 ml of pH 4 acetate buffer, adding 1 ml of KI reagent, and waiting for about 2 min until the iodide is oxidized and the potential is stabilized. The millivolt reading is converted to total residual chlorine, in milligrams per liter as Cl_2 , using the calibration curve.

Polarographic membrane sensors able to directly measure free chlorine are also available. These sensors are similar to the electrodes described above, but the chlorine diffuses through a membrane before reacting with the sensor to produce a signal proportional to the chlorine. No reagents are required, but the output signal is pH dependent; therefore, unless the pH of the water being monitored is very stable, a second electrode must be used to measure pH so that the signal strength can be adjusted (internally) to yield the correct chlorine concentration. A more recently developed electrode circumvents the need for external pH compensation by using an acidic electrode filling solution that internally converts all of the free chlorine to $HOCl$.¹⁰⁰ Some organic chloramines are thought to interfere with these electrodes.¹⁰¹

A typical electrode has a working range of 0.01–20 mg/l, but *Standard Methods*,¹³ calls for dilution of the sample if the chlorine concentration exceeds 5 mg/l as Cl_2 . The practical detection limit is about 0.05 mg/l.

LEUCO CRYSTAL VIOLET (LCV) METHOD

LCV, 4,4',4''-methylidynetris(*N,N*-dimethylaniline), reacts instantly with free chlorine at pH 3.6–4.3 to produce a bluish color. Interference from combined chlorine is avoided by completing the test for free chlorine (taking a color depth reading) within 5 min after adding the reagent. Total residual chlorine can be determined by adding iodide before adding LCV. Iodide reacts with both free and combined chlorine to form iodine. In the presence of excess mercury (II), iodine is almost completely hydrolyzed to hypoiodous acid,

which reacts instantaneously with LCV to form the dye crystal violet. The color of this dye remains stable for several days.

Two separate sets of color standards are required for this method: one for free chlorine (bluish) and one for total residual chlorine (violet). Commercially prepared standards are available in test kits for determining the concentration of free chlorine, but not for total residual chlorine. Color values expressed as chlorine residual can be measured using a calibration curve for either a filter photometer or a spectrophotometer.

The minimum detectable concentration is 10- μ g/l free chlorine and 5- μ g/l total residual chlorine. The practical range for this method is 0–10 mg/l for both free and total residual chlorine.

Interference with free chlorine occurs when the combined chlorine concentration is 5.0 mg/l or higher. The major interference in the FRC measurement is from the *manganic ion*, which increases the apparent chlorine residual reading. When the manganic ion is known to be present, the photometric procedure is used to determine the absorbance due to the manganic ion separately. This measurement is subtracted from the total absorbance to yield that produced by free chlorine alone.

Detailed procedures, including instructions for reagent preparation, can be found in the 13th–16th editions of *Standard Methods*. This method is now considered obsolete for those involved in water and wastewater treatment, although it may still be used in certain niche applications. Methods based on LCV, such as those in *Standard Methods*,¹³ are used to determine both iodide and iodine (Chapter 16).

METHYL ORANGE (MO) METHOD

This method is based on the rapid and quantitative decolorization of MO by free chlorine at pH 2, whereas the bleaching effect of combined chlorine is much slower, except in the presence of bromide. Theoretically, free chlorine bleaches MO quantitatively on the basis of two molecules of chlorine to one of MO, so the weight ratio of reacted MO to chlorine is 2.31:1. One milliliter of 0.005% MO contains 50 μ g of MO, enough to react with 21.6 μ g of chlorine. Experimentally, Taras²⁸ found that 50 mg of MO reacted with 21.9 μ g of chlorine (a ratio of 2.28:1); and he found the following relationship for titration of a series of 100-ml chlorine standards with 0.005% MO:

$$\text{mg/l Cl}_2 = 0.04 + (0.217 \times \text{ml } 0.005\% \text{ MO solution}). \quad (3.11)$$

(Thus, 1.0 ml of 0.005% MO solution is equivalent to 0.217 mg/l of free chlorine.)

The analyst has the choice of the volumetric method,^{18,35} where a titration is carried to the end point using an exact amount of MO titrant, or the colorimetric method of Sollo and Larsen,³⁷ using an excess of MO (necessary

for compliance with Beers law) and either comparing with permanent color standards or determining the light absorbance of the color with a properly calibrated spectrophotometer. Combined chlorine can be determined, by difference, by adding an excess of bromide, which at pH 2 reacts with combined chlorine to form bromine, which in turn bleaches MO. Nitrite does not interfere, and the interference of oxidized manganese can be overcome by using an arsenite modification.³⁷ Because of the low pH of the reaction and the potential for chlorine to react with organic matter under strongly acidic conditions, this method is not suitable for analyzing samples high in organic matter.

The reagent, MO, is a primary standard, is stable, maintains its titer indefinitely, and reacts with chlorine at a wide range of temperatures. However, the useful range of this method is limited to 2 mg/l of free chlorine. This method has been used only in a few laboratory projects and was included in the 13th edition of *Standard Methods* as a tentative method for determining residual chlorine, but has not been included in recent editions.

ORTHOTOLIDINE METHOD

This method is no longer included in *Standard Methods*,¹³ and its use is steadily diminishing, in part because orthotolidine may pose a risk of urinary tract cancer. The method is described here because it is still in use in field kits and for process control and because so much past investigative work relied on it. It offers a simple and reliable means for determining total residual chlorine concentrations in potable water. Its use involves only one reagent, and it covers a range of 0–10 mg/l. Concentrations as low as 0.01 mg/l can be detected, and residuals in the range of 0–5 mg/l can be reliably estimated to the nearest 0.25 mg/l using Nessler tubes or other visual means.

The procedure is very simple. Samples and standards should first be warmed to 20°C since color development is temperature sensitive. As described in the 13th edition of *Standard Methods*, the reagent is prepared by dissolving 1.35 g of orthotolidine in 500 ml of reagent water and adding it to a mixture of 350-ml reagent water and 150-ml concentrated HCl. A small volume of the reagent is first added to the cell (0.5 ml to a 10-ml cell), followed by the sample. Color is measured when it reaches maximum intensity. For free chlorine, this occurs almost instantaneously and then color begins to fade. For combined chlorine at 20°C, color peaks in about 3 min, and begins to fade after about 5 min. This difference in reactivity is exploited in the OTA method described below, which is used to distinguish between free and combined chlorine.

Interfering Substances

The 1943 *Joint Committee Report on the Control of Chlorination*¹¹ declared that the color developed by the reaction of chlorine and orthotolidine could be considered residual chlorine if the water sample contained no more than the following amounts of interfering substances: 0.3 mg/l iron, 0.01 mg/l

manganese (manganic), and 0.10 mg/l nitrite. These limits were never changed, and the substances listed also interfere with other colorimetric methods. Interference from limited amounts of turbidity and color is compensated for by using either a sample blank or a sample that has been decolorized by adding a reducing agent, such as sodium sulfite or sodium thiosulfate.

Hulbert¹⁰² found that nitrite interference was catalyzed by light and proceeded slowly enough in the dark to be minimized by allowing the color to develop in total darkness and then promptly measuring its depth. However, nitrite at concentrations above 1 mg/l will interfere even in the dark. Free chlorine oxidizes nitrite to nitrate, so nitrite interference typically arises when sufficient ammonia and organic nitrogen are present to convert all of the chlorine residual to combined chlorine and organic chloramines. The false-positive interference from nitrite can give the impression that free chlorine is present or that the combined chlorine residual concentration is higher than it actually is.

Because of the low pH (1.3) of the sample–reagent mixture, the orthotolidine method is not acceptable for measuring chlorine residuals in wastewater or in water supplies containing substantial amounts of organic matter. At this pH, chlorine residual species become highly active and are partially consumed before the orthotolidine color develops, causing a negative interference. Investigations have shown that residuals measured in primary effluent using the orthotolidine method can be 2–2.5 times lower than those determined by amperometric titration. Thus, the results of older investigations of wastewater disinfection using this method should be viewed with caution. Another factor to consider in older investigations of germicidal efficiency, particularly those comparing chlorine and ozone, is whether the medium used contained ammonia nitrogen. Some researchers inadvertently used bacterial cultures that contained ammonia nitrogen, which converted the free chlorine to chloramines, thus distorting the results.

OTA Method

The OTA method was developed to distinguish between free and combined chlorine. Samples are chilled to 1 °C to slow the reaction of orthotolidine with combined chlorine; and, immediately after the orthotolidine reacts with free chlorine, arsenite is added to prevent further interference by combined chlorine. Combined chlorine can be determined by difference, that is, by analyzing a second sample without adding arsenite and deducting free chlorine from total residual chlorine. Chilling the samples takes time, which can introduce error as a result of decay of the chlorine residual.

Drop Dilution Method

The upper limit of residual measurement with orthotolidine is 10 mg/l. However, it is often necessary to measure residuals in the 25–100 mg/l range,

for example, when disinfecting water mains, reservoirs, ships' tanks, hospital water systems, and new office buildings. The drop dilution method is ideally suited for such applications because it permits simple and rapid approximations of residuals at concentrations from 10 to 100 mg/l.¹⁰

The drop dilution method consists of adding one or more drops of a chlorinated water sample to a cell or vessel of known volume filled with orthotolidine solution and distilled water. This is easily done using a standard chlorine residual comparator, calibrating the dropper furnished with the comparator (to establish the volume of one drop, typically about 0.05 ml) and then using this dropper exclusively for estimating chlorine residuals. The procedure is as follows:

1. Collect the sample in a small glass container.
2. Add 0.5-ml orthotolidine to one of the comparator cells and fill it to the scribed mark with distilled water. (A typical comparator cell holds 15 ml of sample to the scribed mark.)
3. Fill the other cell with distilled water. (This cell normally compensates for the natural color of the water sample, but the diluted sample is mostly distilled water when using the drop dilution method.)
4. Add one drop of chlorinated sample to the center tube, mix it, and read the result immediately. If no color appears, continue adding drops of chlorinated sample, one at a time, until the reading is within the range of the color disk.

Example Calculation. Assuming that the dropper produces 0.05-ml drops and the comparator cell volume is 15 ml, if two drops of sample produce a comparator reading of 0.25 mg/l Cl_2 , then

$$\text{mg/l } \text{Cl}_2 = 15 / (0.05 \times 2) \times 0.25 = 37.5 \text{ mg/l.} \quad (3.12)$$

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4 Chlorination of Potable Water

Chlorine is widely used for production of potable water. Although the primary reason for chlorine application to water is disinfection, other treatment and operational benefits are evident and discussed in this chapter.

MICROBES IN WATER SUPPLIES

Potable water sources include rivers, lakes, streams, aquifers, and seawater. In the mid-1800s, scientists proved that a cholera epidemic¹ was caused by a polluted drinking water supply. Since then, extensive studies have shown that source waters frequently contain potentially pathogenic organisms that must be eliminated before the water is distributed for potable use.

Although seawater is the largest natural environment inhabited by microorganisms, similar (and dissimilar) types of these organisms abound in inland surface waters such as rivers and lakes in the form of bacteria, algae, protozoa, and viruses—some of which are pathogenic. Groundwaters may also contain harmful organisms but are generally less vulnerable to serious microbial contamination. To help minimize the threat of pathogenic disease from these organisms, disinfection with chlorine has become a common water treatment practice.

Surface Water and Springs

Bodies of water such as lakes, streams, wetlands, and oceans are surface waters, which are susceptible to almost continuous contamination by microorganisms, some of which are pathogens from infected animals or humans. Spring water is groundwater that reaches the surface through fissures or exposed porous soil and unless protected, needs to be treated in the same manner as a surface supply.

Groundwater

Water from wells, or groundwater, is perceived as being less susceptible to pathogenic organisms, such as those that can contaminate surface waters.

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Shallow wells, including those with water quality that is influenced by a surface water body, are typically more susceptible to pathogenic microbes than deeper wells, and as a consequence, deep wells, which are deeper than 100 ft, require disinfection less frequently than shallow wells. The Ground Water Rule (GWR)² and the Surface Water Treatment Rule (SWTR)³ outline a methodology for evaluating the contamination, or risk of contamination of a well supply, and the level of disinfection that would be required.

Well water often contains iron, manganese, and/or sulfur compounds that sustain the life of sheathed organisms such as *Sphaerotilus*, *Crenothrix*, and *Leptothrix*. These chemical compounds and associated organisms must be removed by treatment to make the water esthetically acceptable.

Normally, the microbial content of groundwater is negligible, provided that the well is properly constructed and protected. In general, the low microbial content is due to sufficient percolation that has occurred before water is withdrawn from the well.

WATERBORNE DISEASES

Water can carry bacteria, viruses, and protozoa—all of which may be responsible for various diseases in humans. Not all waterborne diseases are associated with microorganisms. For example, of the 31 waterborne diseases associated with drinking water reported by 19 states in 2001 and 2002, 24 or about 79% percent were identified as being caused by either a microbial or chemical agent. Of the 24 identifiable outbreaks, 19 were attributed to pathogenic organisms, and the remaining five incidents were determined to be associated with chemical poisonings.⁴ The seven outbreaks for which the causative agent could not be established were thought to be the result of microbial contamination. The sole purpose of disinfecting potable water is the elimination of pathogenic organisms to prevent infection from waterborne diseases.

Historically, control of typhoid fever became a great success of disinfecting drinking water supplies. Deaths from typhoid and paratyphoid fevers in the United States decreased by more than 90 percent between 1900 and 1935.⁵ While about 35 deaths per 100,000 population Deaths from these two diseases were reported at the start of the 20th century, by 1970 fewer than eight cases per year were reported nationwide.⁶ Between 1920 and 1936, about 470 outbreaks of waterborne typhoid fever in the United States and Canada caused nearly 1200 deaths and approximately 125,000 cases of illness. During the same period, more than 16,000 cases of waterborne typhoid fever, more than 100,000 cases of gastroenteritis, more than 200 cases of bacillary dysentery, 1400 cases of amoebic dysentery, and 28 cases of jaundice were reported. More than 30% of the outbreaks in the United States originated in well water. The cases of amoebic dysentery and jaundice were unique in water supply and in public health history.⁵

Public health agencies are deeply committed to the theory of multiple barriers or multiple points of control between wastewater discharges and water supply intakes. These barriers or points of control include wastewater treatment, land confinement, dilution, time, distance, source water protection and monitoring, potable water treatment and monitoring, and design, maintenance, and monitoring of the distribution system. Any type of treatment is fallible; so reliance on natural barriers should be maintained as long as possible. However, it is obvious that disinfection of potable water is the last line of defense.

Data published annually or biennially since 1973⁷ regarding waterborne disease outbreaks indicate that more outbreaks occur in noncommunity supplies—such as those of cruise ships, resorts, summer camps, and boarding schools—than in either community or small private supplies. In 1 year as much as 75% of the outbreaks occurred in such supplies. However, it is the community supplies where the greatest numbers of cases are encountered each year. Travelers suffer greatly from waterborne illnesses, particularly in the third-world countries where sanitation and drinking water treatment are often inadequate. Since reporting of waterborne disease outbreaks is voluntary, the true incidence of these outbreaks is thought to be noticeably underestimated.⁷

Waterborne outbreaks are caused by contaminated groundwater or by inadequate or interrupted chlorination of municipal supplies. At one facility in a developing nation (L. Harms, pers. comm.), there was not adequate space for more than one chlorine cylinder to be online at a time. Consequently, the operating staff discontinued chlorination when an empty cylinder was being replaced, while the plant continued to discharge nondisinfected water into the distribution system. In some years, contamination of the municipal distribution system caused a substantial number of outbreaks.

The role of chlorination in improving public health by controlling waterborne diseases cannot be overemphasized and must not be disregarded in today's regulatory environment, which has additional public health concerns regarding the long-term effects of ingestion of chlorinated disinfection by-products (DBPs). Some major diseases known to be transmitted through water are listed in Table 4.1. This is not a comprehensive list, and these diseases are not necessarily transmitted only by water. Food and personal contact are other means by which most of these diseases can spread.

CHLORINE AS A DISINFECTANT

Use as a Biocide

The strong oxidizing characteristics of free chlorine make it an excellent biocide, capable of destroying bacterial cell membranes and oxidizing enzymes and proteins.¹⁰ Free chlorine consists of molecular chlorine, Cl_2 , hypochlorous

TABLE 4.1. Major Waterborne Diseases

Disease	Comments
Typhoid fever	Once a major cause of sickness and death, it has largely been eliminated in developed countries by disinfecting public water supplies. The causative organism, <i>Salmonella typhi</i> , is readily destroyed by chlorination, but is still prevalent in communities that lack safe potable water supplies.
Cholera	<i>Vibrio cholerae</i> , the causative agent of cholera, sometimes called <i>Vibrio comma</i> , has caused major epidemics with a high mortality rate. It is now controlled by improved sanitation and disinfection of public potable water supplies.
Amoebic dysentery	Caused by the cyst <i>Entamoeba histolytica</i> , amoebic dysentery can reoccur because the cyst can lie dormant in the host's intestinal system. It is effectively controlled in water supplies by providing filtration in addition to disinfection.
Gastroenteritis	A wide range of bacteria and viruses can cause gastrointestinal disorders resulting in nausea, vomiting, diarrhea, abdominal discomfort and cramps, fever, and headache. Most of these organisms inhabit the intestines of warm-blooded animals, including humans, and can be transmitted through contaminated drinking water. The more common organisms are the genera <i>Shigella</i> , <i>Salmonella</i> , <i>Campylobacter</i> , <i>Mycobacterium</i> , <i>Pseudomonas</i> , and enterotoxigenic <i>Escherichia coli</i> . Filtration, in addition to disinfection, is often necessary for control. Some <i>Mycobacterium</i> species appear more susceptible to inactivation by chloramines than by free chlorine. ⁸
Schistosomiasis	An eventually fatal disease caused by parasites such as <i>Schistosoma mansoni</i> , it has infected over 100 million people worldwide. It is transmitted primarily by snails in tropical waters used by bathers and swimmers. Transmission by ingestion is also possible but can be readily controlled by disinfection. ^{5,6}
Giardiasis	Caused in humans primarily by cysts of <i>Giardia lamblia</i> , this disease occurs worldwide, including in developed countries such as the United States. It can be contracted by drinking untreated surface waters. Commonly found in most surface water supplies, it is controlled by disinfection with free chlorine as outlined in the 1989 Surface Water Treatment Rule. ³

Table 4.1. *Continued*

Disease	Comments
Cryptosporidiosis	The parasite <i>Cryptosporidium parvum</i> is excreted by cattle and other animals and can be washed into drinking water supplies as runoff. <i>Cryptosporidium</i> oocysts are very hardy in the environment and resistant to inactivation by free chlorine. Cryptosporidiosis can cause severe diarrhea and can be fatal to persons with immunocompromised systems such as AIDS victims, transplant recipients, or patients undergoing chemotherapy. The USEPA has set treatment and inactivation criteria, which include a combination of coagulation, filtration, and inactivation. ⁹
Legionellosis	Several species of the <i>Legionella</i> family of bacteria can cause this respiratory illness that may lead to severe pneumonia, and can sometimes be fatal. Although the infectious agents can be carried in drinking water, the onset of the illness is through aerosols rather than by ingestion. Its ability to colonize appears to increase in warm water, and hotels and other institutions are advised to periodically disinfect storage tanks, cooling towers, condensers, showerheads, and water faucets. <i>Legionella</i> are inactivated by chlorination.
Viral infections	Several viral infections are transmitted by ingesting contaminated water. Of primary concern to the water works industry are enteric organisms that invade the intestines of warm-blooded animals and cause gastrointestinal illnesses. They can be controlled by treatment consisting of a multibarrier approach using coagulation, solids separation, and disinfection with free chlorine. Combined chlorine is not an effective disinfectant against these organisms.

acid, HOCl^- , and hypochlorite ion, OCl^- . The chemistry of free chlorine is explained in detail in Chapter 2.

Although chlorine is a very effective bactericide, the rate and efficiency of disinfection are specific to individual microorganisms and their aqueous environment. The U.S. Environmental Protection Agency (USEPA) has developed guidance for disinfection of drinking water supplies by introducing the CT concept, where C represents the residual concentration of free chlorine after the contact time, T, which is further defined as the time that 90% of the microorganisms within the disinfectant contact vessel are exposed to chlorine. Differences in the aqueous environment are considered by adjusting the CT for pH, temperature, residual concentration, and the amount of disinfection needed.¹¹

The effectiveness of chlorine as a biocide was proved early in the 20th century as water supplies were disinfected with chlorine and the incidence rate of typhoid fever and cholera decreased drastically.

Use to Inactivate Protozoa

Chlorine is an effective disinfectant for some protozoan cysts, but ineffective for others. Two pathogenic protozoa of public health concern are the *Giardia* and *Cryptosporidium* species. The USEPA has developed the CT concept and criteria for inactivation of *Giardia* cysts in terms of chlorine dose, water temperature, pH, contact time, and degree of inactivation.¹¹ However, free chlorine is not very effective for inactivation of *Cryptosporidium* oocysts. For example, at pH 7 and a temperature of 20°C, a 1-log inactivation of *Giardia* cysts is achieved with a CT of 19 (mg/l)(min), while the same degree of inactivation for *Cryptosporidium parvum* oocysts requires a CT of 3600–7200 (mg/l)(min).^{11–13} This concept is more fully discussed later in this chapter.

Use as a Virucide

It is the consensus of virologists that all untreated surface water supplies in the United States and Canada contain or could potentially contain naturally occurring human enteroviruses, and that the best way to protect the public from sickness attributable to the viruses is by the multiple-barrier approach.

A comprehensive study by O'Connor et al., published in 1982,¹⁴ concluded that by using modern treatment practices, it is possible to achieve essentially complete removal and inactivation of viruses. At the time of that study, this meant prechlorination, flocculation, coagulation, sedimentation, and filtration followed by terminal disinfection. Prechlorination enhances the effectiveness of the treatment process for removing and inactivating the viruses because of the extended contact time, but prechlorination has been discontinued at most treatment facilities as a means of controlling DBPs. The coagulation step must be effective to remove virus particles during sedimentation or filtration.

Like the protozoa, enteric viruses also are readily inactivated by free chlorine but not by chloramines, and the difference in the results can be explained by the CT concept. The 1989 SWTR^{3,9} requires that water treatment facilities achieve at least 4-log inactivation, or removal, of enteric viruses. Most facilities found that they needed at least 2-log virus inactivation after receiving 2-log credit for other treatment processes. The Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources¹² for the SWTR requires a CT of only 1 (mg/l)(min) to achieve 2-log virus inactivation with free chlorine at 20°C, but specifies a CT of 321 (mg/l)(min) to achieve the same degree of inactivation with chloramines.

Consensus Indicator Organism

Inactivation of an ideal “consensus” organism would represent inactivation of all other pathogenic bacteria, cysts, viruses, protozoans and other waterborne disease-producing organisms. However, with the information that has been collected about waterborne diseases, it does not seem possible to isolate a consensus organism that would serve that purpose.

The problem is compounded by the lack of any observed relationship between multiple microbial indicators, such as total coliforms, fecal coliforms, or standard plate counts, and viruses or other organisms. Likewise, there is no observed relationship between salmonellae and viruses, nor can enteroviruses or coliphages be used as virus indicators.

For example, a potable water supply can be contaminated by a contribution from a small source that includes viruses but no fecal indicators such as total or fecal coliforms. Likewise, if there is fecal contamination from a populace that is not “shedding” a virus, there will be fecal indicators but no virus. All of this shows why an indicator organism would be useful but to date an appropriate indicator organism has not been identified.

Regulators in the United States have, however, adopted the Total Coliform Rule,¹⁵ which requires monitoring of total coliforms in the distribution system. Total coliforms are used as an “indicator” of the presence, and extent, of fecal contamination, if present.

DISINFECTION REQUIREMENTS UNDER (PROVISIONS OF THE) SAFE DRINKING WATER ACT (SDWA)

The SDWA of December 1974 brought about improved surveillance of drinking water supplies. The SWDA, which applies to all water systems serving 15 connections or at least 25 individuals for a minimum duration of 60 days, was followed by the National Interim Primary Drinking Water Regulations promulgated in 1975 and implemented in 1977. The regulations established maximum contaminant levels for specified microbiological and chemical contamination, as well as turbidity limits and monitoring frequency. Since then, the USEPA has promulgated several additional rules pertaining to disinfection of both filtered and nonfiltered drinking water supplies. These rules are briefly discussed below.

SWTR

Published in the *Federal Register*³ on June 29, 1989, the SWTR established treatment techniques to protect the public’s health from illnesses due to exposure to *Giardia lamblia*, viruses, *Legionella*, and heterotrophic bacteria as well as from associated pathogenic organisms. The primary thrust of the regulation centered on implementing filtration and disinfection requirements.

Although allowing nonfiltered water systems to continue operating if they meet specific requirements, the overall goal of the regulation was to achieve at least a 3-log removal or inactivation of *Giardia* and a 4-log removal or inactivation of viruses. All systems using a surface water or groundwater under the direct influence (GWUDI) of a surface source as their source of supply must provide adequate inactivation as discussed further below. Groundwater under the direct influence of surface water is any water beneath the surface of the ground with (a) significant occurrence of insects or other macroorganisms, algae, or *Giardia lamblia*, or (b) significant and relatively rapid shifts in water quality characteristics such as turbidity, temperature, conductivity, or pH and which closely correlate to changes in surface water conditions.

The SWTR provides specific guidance for achieving inactivation at various conditions (pH, temperature, disinfectant residual, and contact time). It introduced the CT concept, where C represents the disinfectant residual at the end of a defined contact time, and T represents the contact time when at least 90% of the water has been exposed to the residual C. Sometimes T is referred to as T_{10} , where T_{10} is the time elapsed from time zero (0) until 10% of the water has exited the contact chamber. States were encouraged to adopt the CT concept as they evaluated their individual water systems. Although its adoption was not required, most states have incorporated the CT concept in their regulations.

Users of the CT criteria should remember the following:

1. The chlorine species in the residual C is important. The disinfecting powers of free chlorine and of monochloramine differ widely. Therefore, the CT value has to be determined on the basis of a given species. For example, if the water being disinfected contains organic nitrogen (N) or ammonia nitrogen monochloramine will also be present, and it is a less powerful disinfectant than free chlorine.
2. The contact time, T, is as important as C. An accurate method of determining contact time is to use a tracer, although the USEPA does allow the use of conservative factors in determining T. The tracer should be added at the disinfectant application point. Either the step method or the slug dose method is acceptable.¹¹ Drinking water facilities often use food-grade fluoride, although other tracers are also available.
3. Water temperature has a significant effect on the inactivation of most organisms. The lower the temperature, the lower the disinfection efficiency. When Hibler developed the CT values for *Giardia* cysts at 0.5, 2.5, and 5.0°C, he recommended that the values for 5.0°C be used also for warmer waters simply to provide a greater safety factor (C.P. Hibler, pers. comm.).
4. pH is also a consideration. When free chlorine is required, it is essential to maintain the pH of the water being disinfected reasonably steady at a low enough value to achieve disinfection. As the pH increases, the

chlorine species changes from hypochlorous acid, HOCl, to the less effective hypochlorite ion, OCl⁻. The USEPA guidelines for CT values consider this change in species.¹¹

5. Another factor is the effect of sunlight. When free chlorine is used, the contact chamber is normally covered to avoid exposure to sunlight (ultraviolet [UV] rays), which would cause a significant loss of chlorine residual. Therefore, if chlorination is practiced in open basins, such as sedimentation tanks filtration, a dosage change needs to occur to take into account the absence of UV rays after sundown.
6. The contact chamber should be designed with baffles to minimize short-circuiting. Closed pipes flowing full can easily achieve 97% plug flow conditions and at the same time eliminate the loss of residual due to sunlight. Under the USEPA guidelines, pipes are allowed a contact time equal to 100% of the theoretical hydraulic residence time.
7. Adequate mixing at the point of chlorine application is as desirable as plug flow conditions in the contact chamber, as inadequate mixing will result in inadequate disinfection in some portions of the finished water.

Additional disinfection requirements under the SWTR include (a) redundant components for the disinfectant feed system, including an auxiliary power supply with automatic start-up, or automatic shutoff of the disinfectant delivery system if the residual concentration falls below 0.2 mg/l; (b) a disinfectant residual of 0.2 mg/l or more in the water entering the distribution system must be maintained; and (c) a detectable disinfectant residual must be present throughout the distribution system in at least 95% of all samples collected each month. For purposes of compliance, a sample is considered to have a detectable residual if the heterotrophic plate count is 500/ml or less.

Interim Enhanced Surface Water Treatment Rule (IESWTR)

The IESWTR¹⁶ built upon the treatment technique requirements of the SWTR. A maximum contaminant level goal of zero was established for *Cryptosporidium* and systems that achieved specified filtered water turbidity levels were granted a 2-log removal credit. Because *Cryptosporidium* oocysts are not readily inactivated with chlorine, the 2-log removal credit makes sedimentation and filtration important treatment methods for alleviating the health concerns associated with this organism.

At the same time the IESWTR was promulgated (December 16, 1998), the USEPA promulgated the Stage 1 Disinfectants/Disinfection By-products Rule (DBPR).¹⁷ In other words, the USEPA was well aware of the conflict between the IESWTR, which required increased disinfection, and the Stage 1 DBPR, which required reducing the by-products of disinfection with chlorine. Thus, the major requirements of the IESWTR centered on the establishment of treatment and disinfection benchmarks when using chlorine for disinfection.

Hence, if a water system met or exceeded 80% of the maximum contaminant levels (MCLs) for either total trihalomethanes (TTHMs) or the five haloacetic acids (HAA5), it had to prepare a detailed disinfection profile using the CT concept from the tables of the SWTR. Thus, even if a water system was located in a state that did not require the use of CT values to determine disinfection, if it exceeded the 80% limit, not using the CT concept was no longer an option. This requirement has led Colorado to reconsider the use of CT values, and its new design standards under development will include CT criteria (G. Bodnar, pers. comm.).

Other requirements of this rule that pertain to disinfection are (a) any change in disinfection practice has to receive the prior approval of the state, and (b) if a system uses chloramines or ozone as the primary disinfectant, it must also prepare a disinfection benchmark for viruses in addition to the benchmark for *Giardia*.

Stage 1 DBPR

The Stage 1 DBPR¹⁷ set maximum limits for disinfectants as follows: chlorine at 4mg/l, chloramines at 4mg/l, and chlorine dioxide at 0.8mg/l. These limits were termed maximum residual disinfectant levels, or MRDLs. This rule also established new MCLs for TTHMs at 0.080mg/l, HAA5 at 0.060mg/l, bromate at 0.010mg/l, and chlorite at 1.0mg/l.

Long-Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR)

The disinfection requirements of the IESWTR applied only to water systems that served a population of at least 10,000. The LT1ESWTR¹⁸ extended these requirements to smaller systems using surface water. No new disinfection requirements were included.

Long-Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR)

Promulgated on January 5, 2006, the LT2ESWTR⁹ intended to further reduce the risk of waterborne infection by *Cryptosporidium* and other pathogenic organisms. It mandated a 2-year *Cryptosporidium* monitoring program for all surface water systems, with a phased approach depending on system size. The USEPA has prepared several guidance manuals to assist with the implementation of this rule.

This rule includes the following disinfection aspects:

1. Any substantial change in disinfection practice requires the development of disinfection profiles and benchmarks.
2. All filtered water systems are to be classified in one of four bins according to the results of the 2-year source water *Cryptosporidium* monitoring program. If the initial monitoring results yield an average *Cryptosporidium*

concentration of 0.075 oocysts/l or more, additional treatment or inactivation is required.

3. Because *Cryptosporidium* oocysts are not susceptible to inactivation with chlorine, further inactivation is to be achieved using chlorine dioxide, ozone, or UV light irradiation. Specific CT requirements need to be met using ozone or chlorine dioxide, and a dose table is included for systems that are installing UV.

GWR

The GWR,² promulgated on November 8, 2006, applies to those systems that use groundwater sources as their drinking water supply, including consecutive systems that receive finished groundwater from another public water system. It does not apply to public water systems that combine their groundwater with surface water or GWUDI prior to treatment. These systems would be covered under the requirements pertaining to surface water systems. The thrust of the groundwater regulation is to ensure protection against viral pathogens with the goal of providing a 4-log removal or inactivation of these organisms. Disinfection is not mandatory for all groundwater supplies under this rule, but it may be required by the state, or primacy agency at any time for systems having deficiencies.

The GWR contains four major provisions:

1. States are to complete sanitary surveys approximately every 3 years to identify any critical deficiencies in the system.
2. If a positive total coliform sample results occur during routine monitoring, any system that does not already provide a 4-log virus removal/inactivation must begin source water monitoring.
3. Any system that has a significant deficiency or evidence of fecal contamination of its source water must implement corrective action. Disinfection with chlorine is the most common corrective action taken for those systems that are not presently chlorinating.
4. After action is taken, compliance monitoring must be conducted to ensure that the system achieves a minimum of 4-log virus removal/inactivation.

DISINFECTION OF DRINKING WATER WITH CLORINE

Disinfection of potable water with chlorine has had a tremendous impact on public health by minimizing waterborne diseases. Research in the late 20th century that identified DBPs attributable to chlorine has led to the development of modified chlorination procedures in water treatment. Although chlorine is still the most commonly used disinfectant for drinking water supplies,

there are methods for achieving effective disinfection while minimizing by-product formation, as discussed in the following sections.

Historical Background

Chlorination of water supplies started around the start of the 20th century. The first use of chlorine as a continuous process in water treatment was probably in the small town of Middelkerke, Belgium, in 1902. Ferric chloride for coagulation was mixed with calcium hypochlorite, and this process, referred to as the Ferrochlor process, resulted in the formation of ferric hydroxide floc and hypochlorous acid, which served as the disinfectant.¹⁹ At Ostende, Belgium, in 1903, chlorine gas was generated by mixing potassium chlorate and oxalic acid. These installations, which were designed by Maurice Duyk, a chemist for the Belgian ministry of public works, are the earliest known continuous applications of chlorine for disinfection of potable water.

The first recorded use of hypochlorite (as a bleaching powder and chloride of lime) for disinfection of water was in 1896 when a typhoid epidemic occurred at the Austria–Hungary naval base of Pola.²⁰ In 1897, a solution of bleaching powder was used to disinfect the water supply of Maidstone, England, during a typhoid epidemic,²¹ and the first known continuous use of chlorine in England was at Lincoln in 1905.^{22,23}

In the United States, William Jewell's advancements to the electrolytic generation process were used by George W. Fuller in January 1896 during experimental work at Louisville, Kentucky. His installation consisted of 12 electrolytic generators, which required 10 lb of salt to produce 1 lb of chlorine, and was capable of dosing 0.25 mg/l free chlorine into filtered water.²⁴

The first notable chlorination facility in the United States was at the Bubbly Creek Filter Plant in Chicago in 1908, which served the Chicago stockyards.^{23,25,26} The raw water, which was contaminated with sewage, was treated by filtration and dosed with copper sulfate. When the copper sulfate was replaced with chloride of lime, the bacteriological quality of the water improved dramatically (as determined by sampling for *Escherichia coli*).

Throughout the early 1900s, the use of chlorine for disinfection of potable water became more common. An example is the San Francisco water supply, which originates in the Sierra Nevada's range and is conveyed to the city through more than 160 mi of pipeline and aqueducts. In 1937, the pipeline was dosed with chloramines to control biofouling attributed to the filamentous bacteria *Crenothrix* in the groundwater that was seeping into the pipeline. A 1.5 mg/l dose of chloramine produced a combined residual of about 1.0 mg/l at the end of the tunnel 25 mi away. During World War II, when ammonia became difficult to obtain, it was replaced with free chlorine residual.²⁷

As the use of chlorine increased, its other benefits became evident. It was found to improve treatment, keep basins clean, and eliminate some tastes and odors. In North America, chlorine was used throughout the treatment train. Chlorinating the raw water and carrying a residual into the flocculation basins

was common practice for decades. At many plants, chlorine or chlorine dioxide was applied upstream of the filters. Use of the multiple feed points kept treatment processes from deteriorating and helped control tastes and odors.

The benefits of chlorine for disinfection and improved treatment were clearly evident; however, the potential health impacts of long-term exposure to chlorinated DBPs were not recognized until the 1970s.

Points of Application

Although not a common practice today, the application of high doses of chlorine to raw water has many benefits, among them the following: control algae growth that clogs filter media and inhibits flocculation; prevention of septicity in the sedimentation basins; and control of color caused by organic matter in the water. The chlorine dosages used have ranged from 5–10 mg/l to as high as 25–30 mg/l; the record is 120 mg/l at Ottumwa, Iowa.^{28,29} For many of these applications, dechlorination was often required at the facility.

Since the promulgation of the MCLs for TTHMs in 1979 and the Stage 1 DBPR in 1998, the practice of chlorinating raw water has declined substantially. Applying chlorine at the head of the plant results in the formation elevated concentrations of TTHMs and other DBPs in the water. Moving the point of chlorine application downstream to follow organics removal helps curtail DBP formation. Many plants have opted to apply chlorine only at the filters, or after filtration.

When chlorination of raw water upstream of filters was discontinued in an effort to minimize chlorinated DBP formation, many utilities realized that they had been controlling manganese with chlorine. As discussed later in this chapter, continuous dosing of chlorine onto filter media is an excellent method of manganese removal. In plants where chlorine cannot be applied ahead of filters, other oxidants have been used to convert dissolved manganese into its particulate form for removal by clarification and filtration.

Chlorine continues to be commonly used for both primary and secondary disinfection. For primary disinfection, it is generally applied to filtered water and allowed sufficient contact time in the clearwell. However, based on the Information Collection Rule (ICR) data and on review comments to the 1994 draft of the Stage 1 DBP Rule, several plants practice predisinfection not only for disinfection credit, but also to alleviate problems, such as infestation of zebra mussels or tastes and odors. The draft Stage 1 DBP Rule originally included language about not granting disinfection credit for predisinfection (i.e., disinfection CT upstream of DBP precursor removal in the treatment plant). During the comment period for the Stage 1 DBPR, it was learned that predisinfection did not affect DBP precursor removal by enhanced coagulation, and that many plants would need significant treatment modifications if pre-disinfection received no disinfection credit. This resulted in the final Stage 1 DBP Rule allowing predisinfection credit, but requiring compliance with the DBP limits for TTHMs and HAA5s.

Secondary disinfection consists of carrying a disinfectant, either free chlorine or combined chlorine, within the distribution system. Advantages and disadvantages of both are discussed later in this chapter.

Types of Chemical

The two common types of chlorine used in water treatment are chlorine gas and liquid sodium hypochlorite. Both can be delivered in accurate and consistent dosages for disinfection; however, there are distinct differences in the feed systems, water chemistry (see Chapter 2), and the resulting water quality as discussed further in other sections of this handbook.

DBP

Chlorination of waters containing naturally organic materials (NOM) causes the formation of DBPs. Researchers have identified several DBPs,^{30,31} however, the majority of chlorinated organics in drinking water has yet to be fully characterized. The identified DBPs of chlorination include TTHMs, HAAs, haloketones (HKs), haloacetonitriles (HANs), glyoxals, aldehydes, chloropicrin (CP), chloral hydrate (CH), and chlorinated furanones (MX). A full description of these DBPs, their occurrence, and formation is beyond the scope of this handbook; however, some of the main DBPs are discussed herein.

The formation and control of DBPs in drinking water requires a thorough understanding of the disinfection requirements, nature of the source water, and conditions (i.e., pH, temperature, contact time, and type and concentration of disinfectant) of treatment. Some conditions, such as higher pH, favor the formation of TTHMs, whereas those conditions do not enhance the formation of regulated HAA5.

Trihalomethanes (THMs)

Rook discovered chloroform as a DBP in the early 1970s,³² and the total of four THMs, including chloroform, bromoform, bromodichloromethane, and chlorodibromomethane, the total of which, referred to as TTHMs, was limited to 0.10 mg/l by the USEPA in 1979.³³

In general, TTHMs are formed when chlorine reacts with NOM, and the formation of TTHMs continues during the chlorine's contact time with NOM. One strategy for controlling TTHM formation is to minimize the contact time with chlorine. This control strategy is often by the use of ammonia for converting free chlorine into combined chlorine, which forms significantly less TTHMs than free chlorine.³⁴ TTHM formation is favored or enhanced when the pH is elevated, the temperature is elevated, the chlorine dose is high, and the NOM concentration is high.³⁴

When TTHM formation is a concern, water treatment plants (WTPs) can also optimize NOM removal upstream of chlorine addition, thus minimizing this precursor to TTHM formation. Typical NOM removal processes include (a) coagulation, which can be enhanced per the Stage 1 DBP Rule¹⁷ through optimized coagulation practices, such as optimal pH and coagulant type and dose; (b) adsorption onto activated carbon, either in the powdered or granular form; (c) adsorption onto specialty resins that are designed for NOM removal; (d) biodegradation within filters or activated carbon adsorbers; and (e) membrane filtration, including reverse osmosis (RO) and nanofiltration systems. Aeration of TTHMs from water is not effective at practical air-to-water ratios.³⁴

Treating water with alternative oxidants, such as ozone or chlorine dioxide, is another possible control strategy for TTHMs. These oxidants do not form TTHMs, can provide primary disinfection, and can be used upstream of chlorine application to minimize the chlorine demand (see Chapter 2) of the water, thus minimizing TTHM formation.³⁴

Haloacetic Acids (HAAs)

HAAs are also formed when chlorine reacts with NOM in water. There are actually nine HAAs that contain chlorine and/or bromine: monobromoacetic acid (MBAA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), tribromoacetic acid (TBAA), bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA). Only five HAAs—MBAA, MCAA, DCAA, TCAA, and DBAA—are currently regulated by the Stage 1 DBPR due to difficulty in developing appropriate analytical techniques for the remaining four HAAs during Stage 1 DBPR development.

Much research has focused on HAA formation and ways to minimize HAAs in drinking water. The impact of solution pH on HAA formation is complicated because the rate for formation and hydrolysis varies for each individual HAA. For example, formation of TCAA is greatest at low-to-neutral pH, whereas DCAA formation is only slightly decreased under alkaline conditions.³⁵ Because TCAA is often the individual HAA with the highest concentration in chlorinated waters with low bromide concentration, it is clear that it may be difficult to comprehensively control DBPs by pH control alone. Other control strategies, such as alternative oxidants or improved DBP precursor removal, would be necessary.

Total Organic Halides (TOX)

It should be recognized that many DBPs are yet to be identified, as evidenced by the TOX concentration in chlorinated drinking water. TOX represents nonvolatile halogenated compounds in drinking water.³⁶ Chlorinated waters

contain appreciable TOX concentrations, of which nearly half are identifiable as TTHMs, HAAs, or other DBPs.³⁷ This means that a significant fraction of chlorinated DBPs are still unidentified in drinking water.

Bromate

Although bromate is not typically formed by chlorination of drinking water supplies, it can be formed if chlorinated waters that contain bromide are exposed to sunlight.³⁸ For most water systems, finished water supplies are covered and have no exposure to sunlight; however, there are some utilities, such as the Los Angeles Department of Water and Power (LADWP), which have measured elevated bromate concentrations (e.g., 100 µg/l) seasonally in uncovered finished water reservoirs. The LADWP recently installed shade balls, which are 4-in.-diameter polyethylene vapor control balls, into these reservoirs to minimize sunlight penetration into the water.

Chlorine Demand

When chlorine is added to water, some of it will react with dissolved or particulate materials, and the chlorine concentration will decrease over time. The amount of chlorine consumed over a certain period, referred to as the chlorine demand, varies from water to water. It also changes seasonally if the raw water quality undergoes seasonal changes; therefore, chlorine demand tests should be conducted throughout the year.

Determining the chlorine demand is a relatively simple laboratory procedure, as outlined in detail in *Standard Methods*.³⁶ In general, a known dose of chlorine is applied to the water, and the residual is measured over time until the rate of depletion is diminished. Many ions or compounds in water exert a chlorine demand (see also Chapter 2), and a few of these are summarized in Table 4.2.

There are many ways to use the chlorine demand test at a WTP. If the detention time in the disinfection contact basin is known to be 30 min, the chlorine residual after 30 min can be measured by the chlorine demand test to estimate the dose required at the contactor inlet. Also, knowing the duration of detention time (24 h, 48 h, or longer) in the distribution system, the chlorine

TABLE 4.2. Chlorine Demand of Common Ions and Compounds in Natural Waters

Ion or Compound	Chlorine Demand (mg HOCl/mg)
Iron, as Fe ²⁺	0.64
Manganese, as Mn ²⁺	1.30
Total organic carbon	Varies

demand test can be used to estimate the residual that would remain at different locations in the distribution system.

In the 2008 American Water Works Association (AWWA) survey, with 140 water systems responding, the average free chlorine residual of water entering the distribution system was 1.0 mg/l, and the average residual at locations with the maximum retention time while in the distribution system was 0.63 mg/l; thus, the average depletion or demand was about 0.37 mg/l in distribution.³⁹

Chlorine demand, or consumption, also correlates with DBP formation;⁴⁰ thus, for waters whose chlorine demand is associated with NOM, chlorine demand could be used as a rapid and simple means of approximating DBP formation for TTHMs and HAAs.

The chlorine demand of natural waters varies widely, and caution should be used when estimating chlorine demand without actual laboratory testing. In the fourth edition of his chlorine handbook, C. White reported that the water supply to Santiago, Chile, originated from snowmelt and was then naturally filtered before it reached the WTP. The chlorine demand of this water was only 0.2 mg/l after 20 min of contact time. In contrast, the chlorine demand of coagulated water from Missouri River near Kansas City, with 3.6 mg/l total organic carbon (TOC) and dosed with 4.0 mg/l Cl₂, was 2.8 mg/l after 24 h of contact.⁴¹

In a recent survey by AWWA's disinfection committee,³⁹ it was reported that the average total chlorine residual was 2.2 mg/l at the entry point to the distribution system for 117 systems, and the average total chlorine residual at locations within the distribution system that had a maximum retention time was 1.4 mg/l; thus, about a 0.8 mg/l demand, on average within the distribution system.

The chlorine demand of water entering a distribution system is influenced by the treatment it received at the WTP, and treatment can be tailored to remove ions or compounds that contribute to chlorine demand. When NOM is the main contributor to chlorine demand, enhanced coagulation or biological treatment can remove the NOM. Enhanced coagulation is outlined in the Stage 1 DBPR and uses optimized treatment conditions, including coagulant type, dose, and pH, for NOM removal.

Biological treatment has been used for many years in Germany and in Canada. Biological treatment typically takes place in a filter bed. The filter media can be standard sand and anthracite; however, granular activated carbon (GAC) media can support a greater colony of biomass, and thus will remove more NOM. Some utilities have installed postfilter GAC adsorbers to provide biological treatment downstream from ozonation, which degrades the organics to the more biodegradable form called assimilable organic carbon (AOC).

The various benefits of biological treatment are (a) removal of TOC or NOM; (b) reduction of concentrations of bacterial nutrients; (c) removal of micropollutants (such as pesticides and herbicides); (d) improved taste and

odor control (by removing compounds such as geosmin and 2-methylisoborneol [MIB]); and (e) reduction of the overall chlorine demand, which also lowers the concentrations of DBPs formed.

Chlorination–Dechlorination

When reliable chlorine residual controllers became available in the early to mid-1900s, the use of chlorine at high dosages followed by dechlorination became a popular method for controlling tastes and odors, minimizing biofouling in sedimentation tanks and filters, as well as providing high-quality water in the distribution system. This practice was known as “superchlorination.”

Although examples of the superchlorination process are presented below, it is rarely practiced in drinking water treatment today because DBP concentrations in the finished water are limited by drinking water regulations, and many utilities have modified their operating practices to use alternative oxidants or to allow some beneficial biological activity in the WTP. Also, converting from superchlorination to chlorination at a lower dose enables utilities to lower their operation and maintenance costs by lowering the chlorine dose and eliminating the dechlorination chemical and associated equipment (see Chapter 11).

The superchlorination process involves feeding a large dosage of chlorine at the influent of the WTP to maintain free chlorine residual in the treated water through the plant until it is sent to storage. At this point, the residual is quenched automatically by dechlorination, and in many installations, chlorine is dosed to achieve the desired residual for the finished water. One advantage of the superchlorination process was that operators could overdose chlorine to account for changes in raw water quality as well as degradation of chlorine in large basins by sunlight, without concern about excess chlorine in the water entering the distribution system, because dechlorination could automatically quench the excess chlorine concentration.

Waters that contain considerable amounts of ammonia can be superchlorinated to avoid formation of the undesirable chloramine species, nitrogen trichloride. Nitrogen trichloride can be initially formed during superchlorination, depending on the chlorine-to-ammonia ratio; however, during dechlorination, the ammonia that is bound in the nitrogen trichloride residuals remains to form true monochloramine when the free chlorine is added downstream. In this reaction, the objectionable dichloramine and nitrogen trichloride are removed, which is an advantage of this process. Because the downstream chlorine dose is targeted to achieve a chlorine-to-ammonia ratio of 3:1 to 5:1, there is no danger of any nuisance chloramines forming.

Many dechlorinating agents are available for use in drinking water. The recent American Water Works Association Research Foundation (AwwaRF) study,⁴² “Guidance Manual for Dechlorination of Potable Water Releases,” outlines the chemistry of such dechlorinating agents, but it should be noted that the focus is on releases of chlorinated water that require dechlorination,

TABLE 4.3. Dechlorinating Agents Used in Drinking Water

Chemical	Formula	Dose per Milligram per Liter Cl ₂ (mg/L)	Notes
Sulfur dioxide	SO ₂	1.1	Lowers pH, lowers alkalinity, depletes dissolved oxygen
Sodium thiosulfate	Na ₂ S ₂ O ₃	—	pH-dependent reaction
Sodium sulfite	Na ₂ SO ₃	1.8	—
Sodium bisulfite	NaHSO ₃	1.45	—
Sodium metabisulfite	Na ₂ S ₂ O ₅	1.34	—
Calcium thiosulfate	CaS ₂ O ₅	0.99 at pH 7.4; 0.45 at pH 11	Slower reaction kinetics
Ascorbic acid	C ₅ H ₅ O ₅ CH ₂ OH	2.5	Vitamin C, weakly acidic
Sodium ascorbate	C ₅ H ₅ O ₅ CH ₂ ONa	2.8	—

Note: Information adapted from Tikkanen et al. 2001.⁴²

rather than on potable water supply, and any chemical used for dechlorinating potable water in the United States must be National Sanitation Foundation (NSF) 61 certified. The stoichiometric requirements for the various dechlorinating chemicals are summarized in Table 4.3.

Because of concerns about DBP formation, superchlorination followed by dechlorination is rarely, if ever, practiced in WTPs in the United States since the passage of the TTHM regulation and DBPR.

DISINFECTION WITH CHLORAMINES

Historical Background

The use of ammonia with chlorine in water treatment has an unusual history. Both its discovery and its use were largely accidental. Fritz Raschig,⁴³ in 1907, while working with aniline and hypochlorite, noticed that no color developed when these two compounds were reacted in the presence of ammonia. By further experimentation, reacting two parts by weight of chlorine and one part of ammonia, he was able to produce a faint yellow oily-looking compound. He termed this compound “chloramine” in accordance with the following equation:



Raschig’s experimental work provided the basis for the later application of chlorine and ammonia in the water treatment field. Race^{44–46} was probably the

first to use the ammonia–chlorine process. He was in search of a method that would reduce the cost of chlorination, and was influenced by some observations by Rideal,⁴⁷ who noted that during the chlorination of sewage, bactericidal action continued even after all the hypochlorite had “disappeared.” Rideal attributed this continuing action to the influence of the ammonia in the sewage. After successful laboratory experiments with ammonium hypochlorite, Race adopted this method in 1916 for use at the principal treatment plant at Ottawa, Ontario. Race also noted the elimination of aftergrowths following prolonged use of ammonium hypochlorite. The first use of this method in the United States was made in Denver in 1917.⁴⁸

The chloramine process enjoyed great popularity between 1929 and 1939, but fell into a rapid decline shortly after the discovery of the breakpoint phenomenon in 1939 (illustrated in Fig. 4.1 and discussed in detail in Chapter 2). This, coupled with the inability to purchase ammonia during World War II (1941–1945), relegated its use to special cases only.

The process regained popularity as an alternative to free chlorine in the mid-1970s. One of the initial regulations under the SDWA of 1974 limited TTHMs, a by-product of chlorination, to 0.10 mg/l. Many water systems were

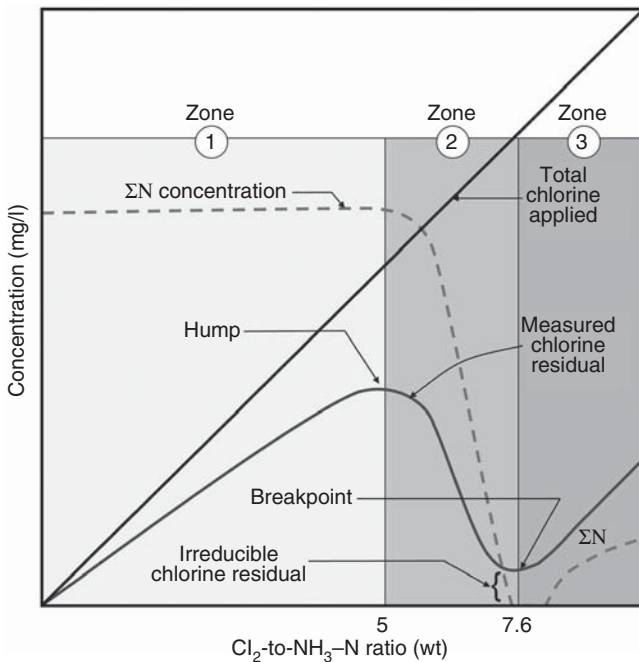


Figure 4.1. The classic breakpoint curve (ΣN is the sum of nitrogen species, including both $\text{NH}_3\text{-N}$ and chloramines).

able to effectively control TTHMs while meeting all other aspects of the SDWA for 30 years by switching to chloramines.^{49,50}

Today, many major water systems such as those serving Denver, Tampa Bay Water, Kansas City, and San Francisco use chloramines as part of their disinfection scheme. However, difficulty with meeting the Lead and Copper Rule (LCR) has caused some chloraminated systems to reconsider using this process. Data from the Washington, DC, water system indicate that before the introduction of chloramines, the existing lead was often in the form of Pb(IV) because free chlorine concentrations had been increased to meet the coliform limits. The high concentration of free chlorine resulted in a higher than normal oxidation–reduction potential (ORP), which drove the lead into the Pb(IV) form. Switching to chloramines decreased the ORP, and the concentration of lead in solution rose as the lead stabilized into Pb(II). Although this change in the lead forms has also been documented elsewhere, it appears to be a site-specific issue.^{51,52}

The Ammonia–Chlorine Process

In the ammonia–chlorine process, ammonia and chlorine compounds are added to water separately. The ammonia is usually added as anhydrous ammonia, as a liquefied gas, or as aqueous ammonia, NH_4OH ; it can also be added as a salt of ammonia, ammonium sulfate, or ammonium chloride.⁵³ Use of the solid form is limited almost exclusively to small systems. The active forms of chlorine in dilute solution in water are hypochlorous acid and hypochlorite ion; together with ammonia, these compounds combine to form chloramines. This procedure can also be called chloramination or the chloramine process, and the chemistry of the process is described in detail in Chapter 2. In general, when the ammonia is applied first, it tends to prevent the formation of compounds that would produce chlorinous taste and odors. However, in many instances, ammonia is added to water containing free chlorine residual (and perhaps in some cases both free and combined chlorine) for the purpose of converting all the free residual to combined residual.

The preferred ratios of chlorine to ammonia N, expressed as milligrams per liter chlorine as Cl_2 to milligrams per liter ammonia as N, are between 3:1 and 5:1. As shown on Figure 4.1, higher ratios result in the loss of chlorine residual and the formation of dichloramines, compounds notorious for causing tastes and odors. Ratios lower than 3:1 will result in additional chemical use and an increased potential for nitrification to occur. If the addition of chlorine continues until a ratio of about 8:1 to 10:1 is reached, a “breakpoint” will occur and the residual will transition into predominantly free chlorine residual. The resulting curve is referred to as the “breakpoint curve.”

Operators using the ammonia–chlorine process must understand this fundamental breakpoint curve. Normally, if loss in chlorine residual is noticed, the first reaction is to increase the chlorine dose; however, this may be exactly the wrong response depending where on the breakpoint curve the plant is

operating. Increasing the chlorine concentration may lead to a further drop in chlorine residual if the plant is operating at the right of the hump on the curve (at a chlorine-to-ammonia ratio greater than 5:1). Before adjusting the chlorine dosage, the operator should calculate the current chlorine-to-ammonia ratio to determine where on the breakpoint curve the system is operating.

Basic Chemistry of Ammonia N Reactions with Chlorine

The basic reactions between ammonia and chlorine,⁵⁴ which result in the formation of chloramines, are listed below (see also Chapter 2 for a more detailed discussion of these and related reactions). Only monochloramine is normally present at pH values greater than 8, when the chlorine-to-ammonia ratio is 5:1 or less and trichloramine (nitrogen trichloride) alone is normally detected at pH below 3.



Reaction 1 above predominates at pH of 8.5 or higher, and produces a preponderance of monochloramine. Reaction 2 predominates at lower pH values (4.5 and 6.0), with the distribution of monochloramine and dichloramine depending not only on pH but also on temperature, time, and the Cl_2 :N ratio. Only traces of trichloramine are formed (reaction 3) under typical water treatment conditions; but trichloramine is very objectionable and highly volatile, so its formation should be minimized by controlling pH and maintaining a suitable Cl_2 :N ratio.

Preformed chloramines for chloramination of public water supplies are feasible but seldom applied. A key to the success of their use is pH control. If they can be prepared at pH10, there is very little problem of keeping them in chlorine solutions of 3000 mg/l or less.

Operation of the Chloramination Process

The preferred sequence of chemical addition is usually ammonia followed by chlorine, but in most surface water facilities, chlorine is added as the primary disinfectant to ensure adequate disinfection, and ammonia is added later as the secondary disinfectant to be carried through the distribution system. Both the ammonia and chlorine chemicals must be well dispersed and mixed rapidly because the reaction between ammonia and chlorine solution at pH7–8.5 is nearly instantaneous. Slow or poor mixing can result in side reactions between the chlorine and organic matter, which would interfere with the formation of true chloramines.

Three to five parts of chlorine are added for each part of ammonia nitrogen present. When treating waters with substantial amounts of naturally occurring ammonia, that fraction of ammonia needs to be considered in the chloramination process. Most drinking water supplies contain less than 0.2 mg/l of ammonia nitrogen and less than 0.3 mg/l of organic nitrogen. These concentrations will seldom interfere with the chloramination process, but they should be regularly checked, as they may vary. Surface waters that freeze over during the winter should be frequently checked for ammonia, as the freezing causes a buildup of ammonia nitrogen; and some groundwaters contain elevated levels of ammonia nitrogen.

If the ammonia–chlorine process precedes rapid sand filtration, addition of ammonia in excess can promote the growth of nitrifying bacteria in the filter beds, as chloramines will not react to destroy nitrite, and the excess ammonia act as a nutrient. The resulting bacteria and the nitrite will have to be destroyed, usually with free chlorine. This problem can be avoided by maintaining a proper ratio of chlorine to ammonia, including the natural ammonia content of the water, and an adequate chloramine residual (0.5–1.0 mg/l) at the discharge of the filters. When using a combination of chlorine and ammonia N, the operator should not use colorimetric methods for residual determination because if nitrite does develop, they cause a false chlorine residual reading. Instead, the amperometric forward titration procedure or the diethyl-*p*-phenylenediamine (DPD)–ferrous ammonium sulfate (FAS) titrimetric method should be used to monitor the process.

Operators of chloramine systems must be aware that as the chlorine residual concentration drops, ammonia is released. If the chlorine residual drops too low or disappears, populations of nitrifying organisms may increase because the excess ammonia stimulates their growth; and other microbial populations may flourish in the absence of an adequate residual. Although this problem has been largely eliminated by improved monitoring, it can still be encountered in dead-end or stagnant locations.

When chloramines are used, the distribution system should be monitored at strategic locations for monochloramine and dichloramine residuals. In some cases, identifying only the total chlorine residual is not enough, particularly if the water contains any organic, or ammonia N. In the presence of organic N, monochloramine will, within 30–40 min, hydrolyze to react with the organic N to form nongermicidal organochloramines that titrate quantitatively in the dichloramine fraction of the forward titration procedure. Although the formation of organochloramine contributes to biological instability, its more serious effect may be the loss of the monochloramine residual, which may lead to reappearance of free ammonia N, and thus to biological instability in the form of nitrification or regrowth in the distribution system, resulting in foul taste, odors, or dirty and off-colored water at the consumer's tap. Operators should receive instruction on how to determine free and total chlorine residuals when using field kits that utilize the DPD method.

Issues of Concern

Although the ammonia–chlorine process has been used successfully in the United States for many decades, there are several concerns associated with its use: (a) blending chloraminated water with water disinfected with free chlorine; (b) disinfection efficiency; (c) nitrification; (d) effect on kidney dialysis patients; (e) effects of aquatic life; (f) changes in lead concentrations when switching to the use of chloramines; (g) control of DBPs; and (h) potential odors.

Blending Chloraminated Water with Water Containing Free Chlorine Residuals. Blending two waters disinfected with different disinfectants requires special attention. Many systems use both free chlorine and chloramines in the same distribution system without difficulty; others have frequent problems, especially in the locations where blending takes place. A key to successful operation is maintaining a chlorine-to-ammonia ratio of 5:1 or less in these locations. If the ratio exceeds 5:1, dichloramines are formed, causing tastes and odors as well as a drop in chlorine residual. Other water quality problems may occur when blending two different water supplies. The quality of the blended water should be matched as closely as possible to that of the water currently in the distribution system. The possibility that the blended water may increase corrosion of pipes and appurtenances must also be considered.

Two approaches are used to avoid development of tastes and odors and loss of chlorine residual. One approach is to isolate pressure zones in the distribution system, with each zone receiving only one type of chlorine residual, that is, either free chlorine or chloramines. The other approach is to combine the waters in proportions that maintain the chlorine-to-ammonia ratio in the blended water at less than 5:1. Some complex water systems, such as the Metropolitan Water District of Southern California (MWD), have developed computer programs that adjust flows of incoming source waters with free chlorine and chloramine residuals to maintain the desired ratio at sensitive locations.

A recent AwwaRF Project⁵³ found that while blending of chlorinated water with chloraminated water was not a common practice, it was most frequently done by water systems that used both surface water and groundwater supplies. Of the 63 water systems surveyed that were using chloramines, only six blended waters with the two types of residuals in their distribution systems. In general, these systems found that if the chlorine-to-ammonia ratio was not closely controlled, normal operation was interrupted by sporadic episodes of tastes and odors complaints.

The MWD has spent considerable resources in an effort to provide its customers with satisfactory blended water. In 1984, MWD discontinued the use of free chlorine as its primary disinfectant to meet USEPA regulations pertaining to THM formation. Although treatment with activated carbon was preferred, it found that too expensive and chose chloramines instead. Because it anticipated taste and odor problems, MWD carried out a laboratory study

to determine the effects of blending chloramine residuals with chlorine residuals by developing blend-residual curves to simulate the systems involved.⁵⁵ The potential problems of blending are related to a mixture that proceeds through the breakpoint curve, which allows the formation of dichloramine and possibly nitrogen trichloride, both of which are notorious for causing conditions leading to consumer complaints. MWD decided on a 3:1 ratio of Cl_2 -to- NH_3 -N for chloramination. Using this ratio and accounting for the almost negligible concentration of naturally occurring ammonia N, it developed an induced breakpoint curve for each of its two supplies: (a) the Northern California water supply, known as the state project water (SPW); and (b) the Colorado River water, labeled CRW. The induced breakpoint occurred for the SPW at pH 7.5 and at a Cl_2 :N ratio of 11:1, and for the CRW at pH 7.9 and a ratio of 9.2:1, both breakpoints occurred after 4 h in the dark at 25 °C. An additional series of breakpoint curves due to blending were then developed. Two of these curves, shown on Figures 4.2 and 4.3, illustrate the same two waters at contact times of 5 min and at 4 h. These figures demonstrate that at short contact times, all of the chlorine species may exist together in the breakpoint region.

From this experimental work, MWD staff developed a computational model that allows the prediction of acceptable blends of chloraminated and chlorinated waters without experimentally determining each case. They anticipate the need of further analyses to check for chlorine-to-ammonia ratios higher than 5:1, which become bacteriologically significant at ratios of about 6.5:1. At this point forward, the chlorine residual begins to decrease rapidly until it drops to nearly zero at the breakpoint, where disinfection ceases. This situation, which is more serious than a consumer complaint about taste and odor, develops into nitrification in covered reservoirs, producing nitrites that cause severe algae blooms, as well as serious dead-end problems.

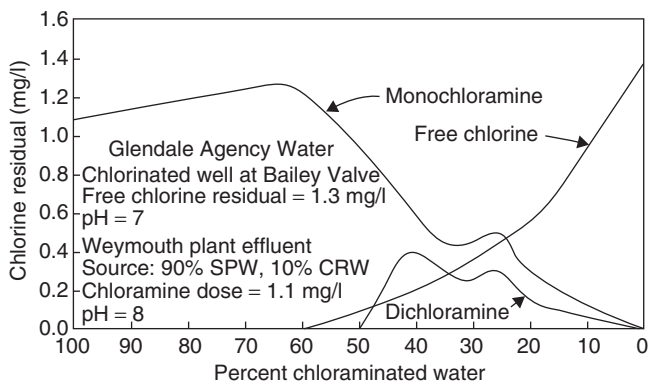


Figure 4.2. Chlorine residual curves for Glendale, California, chlorinated well water blended with chloraminated effluent from the Weymouth WTP after 5-min contact time⁵⁹ (courtesy of the Metropolitan Water District of Southern California).

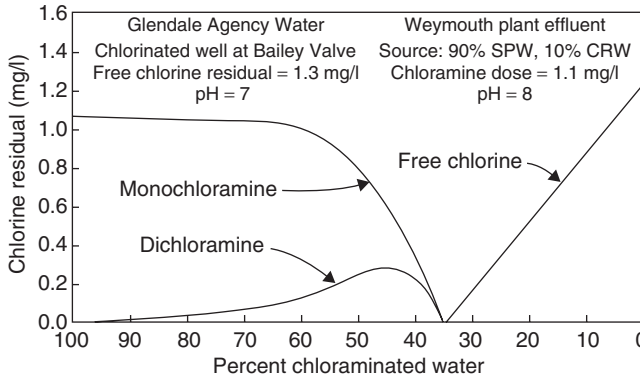


Figure 4.3. Chlorine residual curves for Glendale, California, chlorinated well water blended with Weymouth treatment plant chloraminated effluent after 4-h contact time⁵⁹ (courtesy of the Metropolitan Water District of Southern California).

Disinfection Efficiency. It is well accepted within the water works industry (and well documented, as discussed in Chapter 2) that free chlorine is a more effective disinfectant than chloramines. However, some field situations indicate that chloramines are nearly as effective for inactivation of bacteria as free chlorine and may penetrate more deeply into the biofilms within the distribution system.^{56–60} There are probably two reasons for these results at specific locations, which are seemingly contrary to fundamental laboratory research.⁶¹ First, many water systems operate at a pH in the range of 7.5 to 9.5 and have adequate mixing and contact times exceeding 30 min. In the pH range above 7.5, the majority of free chlorine is present as hypochlorite ion, OCl^- , not as hypochlorous acid, HOCl .⁵³ Although the germicidal efficiency of hypochlorous acid is much better than that of monochloramine, the germicidal efficiency of hypochlorite ion approaches that of monochloramine and in practice, the difference between the two may be difficult to distinguish. Second, in waters containing organic N, free chlorine will combine with the organic N to produce a nongermicidal organochloramine. Thus, in these situations, the free chlorine is not available as a bactericide. And third, higher concentrations are typically present (1–4 mg/l entering the distribution system versus 1.5 or less free chlorine; and monochloramine is a lot more stable, so the difference in the far reaches of the distribution system is typically greater) and combined chlorine is less reactive so it penetrates deeper into the biofilm before reacting with organic matter, reduced inorganic species such as iron, and live and dead cells.

Chloramines are much weaker disinfectants for both viruses and protozoa. Consequently, chloramines are normally unable to meet the requirements for inactivation of *Giardia*, *Cryptosporidium*, or enteric viruses in surface water systems. Disinfectant criteria, CT values, for inactivation of these organisms as indicated by the USEPA, are in Tables 4.4 and 4.5.⁶²

TABLE 4.4. CT Values for *Giardia* Cyst Inactivation Using Chloramines (CT Values Given in [mg/l][min])

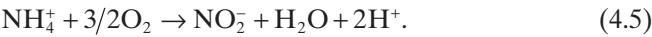
Inactivation	Temperature (°C)				
	5	10	15	20	25
0.5-log	365	310	250	185	125
1-log	735	615	500	370	250
1.5-log	1100	930	750	550	375
2-log	1470	1230	1000	735	500
2.5-log	1830	1540	1250	915	625
3-log	2200	1850	1500	1100	750

TABLE 4.5. CT Values for Inactivation of Viruses Using Chloramines (CT Values Given in [mg/l][min])

Inactivation	Temperature (°C)				
	5	10	15	20	25
2-log	857	643	428	321	214
3-log	1423	1067	712	534	356
4-log	1988	1491	994	746	497

Nitrification. Nitrification is a two-step microbiological process carried out by two distinct groups of autotrophic bacteria, in which ammonia (NH₃) is oxidized sequentially to nitrite (NO₂⁻) and then to nitrate (NO₃⁻). These bacteria obtain their energy from oxidation of reduced forms of inorganic nitrogen and derive most of their cellular carbon by fixing carbon dioxide by the Calvin cycle.⁶³ Heterotrophic bacteria are also able to carry out nitrification, but at a much slower rate than by autotrophic nitrification.⁶⁴⁻⁶⁶

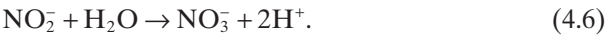
In the final step, ammonia is oxidized to nitrites as follows:



Hydroxylamine is an intermediate in this energy-yielding reaction, and very small amounts of nitrous and nitric acids are produced.⁶⁷

Although *Nitrosomonas* bacteria are the ones most frequently considered being the operatives of this step, other genera, which include *Nitrosolobos*, *Nitrosococcus*, *Nitrosovibrio*, and *Nitrospira* have been known to oxidize ammonia to nitrite autotrophically.⁶⁸

In the second step, nitrite is oxidized to nitrate without detectable intermediates:



In soil and freshwater, this step is carried out exclusively by members of the genus *Nitrobacter*. In nature, nitrite usually does not accumulate during

nitrification unless a specific inhibitor of nitrite oxidation or a selective toxin for *Nitrobacter* is present.⁶⁹ However, distribution systems that use chloramines should be monitored for nitrite as increases in nitrite can be an early warning of nitrification. Recent data show that growth of nitrifiers is inhibited by sunlight,⁷⁰ which indicates that a dark environment such as a buried pipeline or a covered reservoir is favorable to their growth, and that nitrifying bacteria secrete organic compounds that can stimulate the growth of heterotrophic bacteria.⁶⁸⁻⁷¹

Uncontrolled production of nitrites can be stopped by switching to free chlorine or other oxidants, as chloramines cannot oxidize nitrites. Many utilities view use of free chlorine as a last resort since it frequently leads to the development of tastes and odors, as well as increasing the concentrations of regulated chlorinated by-products such as THMs and HAA5. Thus, it is preferable to prevent nitrification instead of attempting to mitigate them after formation. One promising control method is the use of low doses of chlorite ion, about 0.1 mg/l or less, as described by McGuire et al.^{72,73}

Five parts of chlorine are required to oxidize one part of nitrite. Nitrite may proliferate in a covered reservoir if the water entering the reservoir has been chloraminated: First, the chloramine residual will begin to decay sharply, and heterotrophic plate count (HPC) levels will escalate. MWD tackled this problem at its two covered reservoirs, after they were returned into service, by adding sufficient chlorine to the reservoir influent to raise the chlorine-to-ammonia ratio to at least 4:1.

The groups of autotrophic microorganisms that oxidize ammonia to nitrite are often called ammonia-oxidizing bacteria (AOB), and the subsequent group that oxidizes the nitrite to nitrate is called nitrite-oxidizing bacteria (NOB). This two-step nitrification process has several adverse effects on water quality, which include the following:

1. Diminished chlorine residuals: A loss of chloramine residual is a serious consequence of nitrification. In addition to the potential public health consequences associated with a low disinfectant residual, the additional amounts of chlorine and ammonia needed will increase chemical costs.
2. Increased biological growth: Both nitrogen and phosphorus are micro-nutrients that are capable of promoting excessive biological growth even in small amounts. As nitrifying organisms die and decay, they release additional nutrients that will stimulate the growth of heterotrophic bacteria; thus, routine measurements of HPCs are likely to show an increase. Some tastes and odors may accompany this increase.
3. Loss of dissolved oxygen (DO): DO concentrations are seldom an issue for drinking water supplies, but if it becomes very low or depleted, other chemical reactions can occur that are detrimental to water quality. An example would be an obnoxious taste or odor of sulfur.
4. Increases in nitrite and nitrate: Because the SDWA has established MCLs for both nitrite and nitrate in plant discharges, it is wise for public health

reasons to limit their concentrations within the distribution system as well. An increase in nitrite is associated with a decrease in monochloramine.⁷⁴

5. Lower pH and alkalinity: The biological reactions from the metabolism of both AOB and NOB organisms produce acids that reduce both the alkalinity and pH of the water, leading to corrosion and unstable water quality.

MWD Investigation. To better understand how nitrification develops, MWD of Southern California conducted a study to examine the factors that influence the AOB in a chloraminated distribution system.⁷⁵ Samples were collected over an 18-month period from three sources: (a) raw surface water, (b) two covered finished water reservoirs that had experienced nitrification, and (c) conventional treatment plant effluent. Sediment and biofilm samples were collected from the interior wall surfaces of two finished water pipelines and one of the covered reservoirs. The AOB were enumerated by the most probable number (MPN) technique; isolates were isolated and identified, and the resistance of naturally occurring AOB in chloramines and free chlorine was examined.

Results of the monitoring program indicated that the AOB concentrations (genus *Nitrosomonas*) in both raw and finished water varied seasonally, being highest during the summer. The MPNs of AOB in the two floating-cover reservoirs ranged from <0.2 to >300/ml. This is correlated significantly with temperature and the concentrations of HPC bacteria.

When the water temperature was below the range of 60–65°F, AOB were not detected in the chloraminated reservoirs. The study indicated that nitrifiers occur throughout the chloraminated distribution system. Higher concentrations of AOB were found in samples of the reservoir and pipe sediments than in the pipe biofilm. The AOB were found to be about 13 times more resistant to monochloramine than to free chlorine. After 33 min of exposure to 1.0 mg/l of monochloramine (pH 8.2, 74°F) only 99% (2 logs) of an AOB culture were inactivated. Chloramine residuals currently in use are 1.5 mg/l at a 3:1 chlorine-to-ammonia N ratio. Results of this study have indicated that this residual concentration may not be adequate to control the growth of AOB in the distribution system because it was found that the AOB not only could survive but also were capable of growing in the reservoir water columns in the presence of 1.3–1.5 mg/l chloramine residual. These organisms seem to grow best in an environment of mild alkalinity, pH 7.5–8.5, a water temperature of 77–82°F, darkness, an extended detention time, and the presence of free ammonia, all of which were available in the MWD covered reservoirs.

The fact that AOB were recovered when the nitrite concentration was below the detectable level suggests that the measurement of AOB is a more accurate indicator of nitrification than nitrite analysis, particularly when the nitrites have already been converted to nitrate. The AOB concentration correlated closely with the HPCs⁷⁵ in one of the reservoirs, suggesting that in some chloraminated systems these heterotrophs may be good indicators of the presence of nitrifiers. Considering the lengthy incubation period required for

enumerating the AOB, such a surrogate indicator would be most useful because the presence of free ammonia is at the root of the problem, and waters with chlorine-to-ammonia ratios between 3:1 and 5:1 should be evaluated for taste and odor acceptability at the consumer's tap. Higher ratio values translate to lower ammonia concentrations in the reaction.

Keys to Operating without Nitrification Problems. Because nitrification can adversely affect water quality, prevention is preferred over remedial action. Successful operation of a chloraminated system without nitrification is more likely achieved by observing the following guidance:⁵³

1. Regular monitoring: The plant discharge should be regularly monitored to establish baseline values for ammonia, nitrite, nitrate, HPC, pH, alkalinity, and chloramine residual, which should then be compared with samples taken from the distribution system as a means of timely detection of nitrification.
2. Maintaining low ammonia levels: Although chloraminated plant discharge will contain some excess free ammonia, the level of free ammonia should be maintained below 0.3 mg/l as $\text{NH}_3\text{-N}$.
3. Increased monitoring at elevated water temperatures: Nitrification is most likely to occur during periods of higher water temperatures that are conducive to accelerated microbial activity.
4. Maintaining adequate chloramine residual: Most systems that do not encounter nitrification problems operate with a chloramine residual of 2–3 mg/l, and some large distribution systems are operated with residuals as high as 4 mg/l.
5. Controlling water age: Water that remains in the distribution system for extended periods is likely to develop quality problems, including nitrification. While sufficient water must be maintained in the distribution system for routine and emergency uses, it may not be necessary to completely fill all possible storage during periods of low demand. Modeling the distribution system is an effective means of managing water age as well as early detection of water quality problems.

Shock-Chlorination. With some groundwaters and surface waters that contain significant concentrations of ammonia, such as at Champaign–Urbana, Illinois, breakpoint is not routinely achieved because it is not cost-effective. In such systems, a chloramine residual is maintained throughout treatment, and occasionally, the system is shock-chlorinated to disinfect both the plant and the distribution system and to eliminate nitrifying bacteria that might be flourishing in the high-ammonia water.

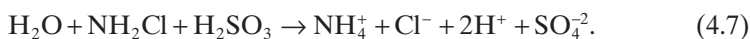
Effect on Kidney Dialysis Patients. Kjellstrand et al.⁷⁶ reported that chloramine residuals in tap water pass quite easily through RO membranes in dialysis machines, and that they directly induce oxidant damage to red blood cells,

which results in methemoglobin formation and damage to the hexose-mono-phosphate shunt (HMPS), which is used by red blood cells to defend themselves against oxidant damage, which induces hemolysis and shortens their survival time. They also sensitize the patients to oxidant drugs such as primaquine, sulfonamides, and others.

It is important for water purveyors to notify hospitals and dialysis centers of any change in their disinfection procedures, including the use of chloramines. Since the medical community is required by law to protect the identity of all patients, the water system cannot directly notify dialysis patients of such changes, and it is up to the medical profession to ensure their patient's safety. The water used for dialysis is routinely monitored for both chloramines and free chlorine, as either would have detrimental effects on the dialysis procedure. One key issue is that GAC is often used to remove chloramines or free chlorine from water for dialysis systems, and because chloramines react far more slowly with GAC than free chlorine, if the GAC canisters are designed for free chlorine removal, they may be inadequate for chloramine removal, especially if the chloramine residual is higher than the free chlorine. The responsibility of the water system is to notify the appropriate individual at each medical facility and follow-up to ensure that the notice was actually received.

Effect on Aquatic Life. Both chloramine residuals and un-ionized ammonia are toxic to fish in even very low concentrations. The mechanism of chloramine toxicity is as follows: Chloramines pass readily through the permeable gill epithelium, causing insignificant cell damage. Having entered the bloodstream, they chemically bind to the iron in hemoglobin in red blood cells, which cripples the cells' ability to bind oxygen. This condition is known as methemoglobinemia. It is similar to the oxidation of hemoglobin caused by nitrite toxicity.^{77,78}

When monochloramine is dechlorinated by a reducing compound that produces sulfurous acid (H_2SO_3), ammonium and chloride are formed as follows:



Ammonium chloride ionizes to form ionized NH_4^+ and un-ionized NH_3 nitrogen (ammonia). Therefore, all ammonia utilized to produce monochloramine is returned to the water as shown in Equation (4.7), $\text{NH}_4^+ + \text{Cl}^-$. This represents total ammonia. To avoid toxicity to fish, un-ionized ammonia must be limited. Information and chemicals to eliminate this problem for aquariums are available at pet shops.

Increased Lead Concentrations. Several studies indicate that even low concentrations of lead in their blood can have serious consequences in the cognitive development of children.^{79,80} Consequently, the USEPA has regulated the concentration of lead in drinking water under the LCR as part of the SDWA, which along with other factors, has succeeded in substantially reducing the lead

content in children's blood. However, after switching from using chlorine to disinfection with chloramines in November 2000, the Washington, DC, system began to encounter serious problems with lead concentrations in its tap water.

Investigators who have evaluated this situation have concluded that most of the lead solids in a water distribution system occur in a form of Pb(II) such as PbCO_3 . However, in the presence of a strong oxidant such as chlorine, especially at high concentrations, the resulting high ORP drives the lead into a Pb(IV) state, forming solids such as the highly insoluble PbO_2 . With a lower ORP level is present, as when chloramines are introduced into the system, the lead tends to revert back to the Pb(II) form and in so doing, is released into the drinking water.^{51,52}

Although most systems that are considering switching from free chlorine to chloramines are not likely to encounter the same situation as in Washington, DC, where over 20,000 lead service lines were in use, the potential for an increase in lead concentrations in the drinking water should not be ignored. Utilities considering such a change would be wise to evaluate the possible consequences of the change, which should include identifying the form of the lead scales in their distribution system.

DBPs from Chloramination. Chloramines are often the most economical solution for utilities that experience high concentrations of DBPs such as HAA5, TTHMs, and HANs from disinfecting with free chlorine. Under most conditions, chloramines produce considerably lower concentrations of this DBPs.^{62,81} As with any oxidation–reduction reaction, however, some by-products from the reaction are formed, and some free chlorine will be present, as monochloramine will slowly hydrolyze. Among the by-products of concern are *N*-nitrosodimethylamine (NDMA), cyanogen chloride, CP, HAAs, and dihaloacetic acids (DXAAs). Although currently, none of these DBPs except for HAAs, are regulated by the USEPA, there are some concerns, as discussed below:

1. NDMA: In addition to being a by-product of chloramination, other sources, such as ion exchange and cationic polymers, can contribute NDMA to drinking water. A survey by the California Department of Health Services detected NDMA in drinking water at concentrations up to 63.7 ng/l, but the mean concentration of all samples collected was 1.8 ng/l.⁸² Because of its presence at extremely low levels, NDMA in drinking water is not expected to be regulated soon.⁵³
2. Cyanogen chloride: Cyanogen chloride is a reaction by-product of chlorine, ammonia, and organics. If ingested by humans, it can be metabolized to cyanide, which is toxic in high concentrations. At this time, a safe limit for cyanide in drinking water is thought to be around 70 $\mu\text{g/l}$.⁸³
3. HAA/DXAA: Research funded by the AwwaRF has shown that the type of NOM and its removal are far more influential in the formation of HAA/DXAA than the chloramine residual.⁸¹ Hong et al. found that

TABLE 4.6. Taste and Odor Concentration Limits for Chloramines

Compound	Concentration
Monochloramine (NH ₂ Cl)	<5
Dichloramine (NHCl ₂)	<0.8
Nitrogen trichloride (NCl ₃)	<0.02

Concentrations were provided by White as personal observations.

the direct reaction of monochloramine with dissolved organic matter was the principal means of HAA formation during chloramination.⁸⁴ These findings reinforce the importance of removing organic material before disinfection with either chlorine or chloramines.

4. CP: Chloropicrin can be formed during chloramination, but in practice, at very low nanogram per liter concentrations. In general, if chlorine is not added before NOM removal, the CP concentrations will be low. Experiments conducted by Duguet et al.⁸⁵ on waters with high TOC concentrations of 6–14 mg/l and very high chlorine residuals resulted in CP formation at concentrations of about two to three orders of magnitude less than chloroform.

Potential Odors of Chloramination. Chloramines are not likely to produce tastes and odors when applied at concentrations less than those listed in Table 4.6.

Nitrogen trichloride produces a strong odor. Its solubility in water is negligible. It is difficult to capture and measure in a sample because it is readily released from water by the slightest agitation. There is no mistaking its presence in water, and even at concentrations too low to get a response from the olfactory system, it will cause the eyes to water. The odor of NCl₃ is different from the odors of free chlorine and the other chloramines. It can be removed from water by aeration; however, the air quality near the aerator has to be considered.

Williams^{86–88} demonstrated over a period of 20 years that if the ratio of monochloramine to dichloramine was higher than 2:1, the objectionable tastes caused by dichloramine will be minimal. This ratio of concentrations of these chloramine compounds for acceptable palatability is, however, site specific and should be verified under local conditions.

DISTRIBUTION SYSTEM

The distribution system typically consists of pipes, storage tanks, pumping stations, valves, and meters. The point of entry to the distribution system is generally from a well or the clearwell or high-service pumping station at a treatment facility. Where the WTP is located a great distance from the first

customer, the detention time in the pipeline may be used for disinfection. In such cases, the pipe where disinfection takes place is considered to be part of the treatment. Any drinking water consumed at the WTP would still require disinfection, and some utilities have installed separate, small-capacity disinfection systems for the in-plant drinking water supply.

The use of chlorine or chloramines in the distribution system is referred to as secondary disinfection. The water leaving the WTP has already received primary disinfection, but a disinfectant residual to protect the quality of the finished water as it travels through the distribution system infrastructure to customers is maintained with the secondary disinfectant.

As water travels through the distribution system, its quality undergoes changes brought about by factors such as detention time, pH, temperature, disinfectant residual variations, biological activity, and chemical reactions—both in the bulk liquid phase and on pipe surfaces. For example, the formation of TTHMs continues as chlorinated water travels in the distribution system. If the TTHM concentration needs to be lowered at the customer's tap, one option is to lower the hydraulic residence time in the distribution system. Because TTHM formation is also affected by other variables, these variables should be investigated as well.

Maintaining a palatable drinking water extends beyond the treatment plant outlet. Water quality problems in the distribution systems include tastes and odors, color, dirty water, precipitation on pipe surfaces, changes in bacteriological quality, and corrosion of pipes and fittings. The solution to these problems is often is site specific.

The deterioration of water quality in a distribution system is usually attributed to three causes: (a) biofouling by microorganisms producing tastes, odors, and colored or dirty water; (b) undesirable end products of chemical or microbologically induced corrosion, such as metallic and brackish tastes, failure of water heaters and residential water piping, and excessive lead and/or copper content in tap water; and (c) the presence of coliform organisms in the distribution system, indicating recontamination of an otherwise safe water. Each of these phenomena contributes to consumer complaints.

Ridgway and Olson⁸⁹ and Ridgway et al.,⁹⁰ using a scanning electron microscope, have produced photographic evidence of large colonies of diverse microbes adhering to interior walls of distribution system mains and the surfaces of suspended particulate matter in drinking water. Such colonization can apparently take place during the summer even despite intermittent low-level free chlorine residuals (0.1–0.2 mg/l), which may occur in low-use areas of the system. There is ample evidence that microorganisms attached to pipe walls or present in partially anaerobic sediments in the invert of the pipe in low-flow and dead-end portions of the distribution system are responsible for taste, odor, and color problems of potable water systems.

Proliferation of bacterial colonies in distribution systems leads to biofouling that can harbor and encapsulate organisms such as *Klebsiella pneumoniae* and *Enterobacter cloacae* even in the presence of free chlorine residuals. This phenomenon is not yet understood, but it is believed to occur in older systems

where slime layers of bacterial colonies are layered with particulate matter followed by scale of silica and/or calcium.

Because taste and odor problems do not necessarily end at the treatment plant, consideration must be given to the off-flavors that may develop in the distribution system.

Regulatory Compliance for Distribution Systems

Several drinking water regulations affect the way chlorine is used in water treatment and distribution, and the requirements may vary from state to state. The appropriate state or federal agency (for states that do not have primacy) with jurisdiction over the water system should be contacted regarding specific criteria that need to be met.

Specific requirements for primary and secondary disinfection were presented earlier in this chapter, but requirements for distribution systems are shown in Table 4.7.

Regrowth

Regrowth is the increase in microorganisms within the distribution system, either suspended in water or attached to pipe surfaces, even after treatment and disinfection. It is usually described in terms of biofilm, breakthrough, and growth. The microbes may or may not in themselves be health hazard concerns, but they are indicators of the overall water quality and may contribute to tastes and odors, add color to the water, or degrade overall water quality. The occurrence of coliform bacteria in otherwise high-quality drinking water has long plagued the water industry.⁹¹ The AWWA Committee on Water Supply reported on the problems of “*E. coli*” regrowth in 1930.⁹² The coliform group, which is discussed in more detail later, is quite fragile and relatively easy to inactivate when compared with more resistant pathogenic organisms. Their presence in treated water supplies indicates a potential for a serious waterborne disease outbreak.

There is ample evidence that the interior of most distribution system pipings is colonized by microorganisms. Electron microscopy of encrustations present within the system has revealed several common characteristics:

1. a hard but porous surface,
2. a multitude of crystals beneath the surface veneer,
3. microorganisms predominating near the surface layer, and
4. microcolonies of similar-shaped organisms, indicating growth at the biofilm surface.⁹³

Inductively coupled plasma spectrometric analysis of tubercles scraped from a cement-lined ductile iron pipe showed that the material was 98.7% iron.⁹⁴ Microanalysis has shown that the tubercles are composed predominantly of iron, calcium, silicon, phosphorus, aluminum, and sulfur.^{89,95}

TABLE 4.7. Drinking Water Regulatory Compliance That Is Impacted by the Distribution System

SWTR	The disinfectant residual (a) entering the system must be at least 0.2mg/l, and (b) it must be measured within the system at the same time and location as for coliform sampling and (c) it must be detectable in at least 95% of the samples collected monthly. Acceptable HPC data may be substituted for detectable residuals. If the sample collected has an HPC count less than or equal to 500/ml, the sample is deemed to have a detectable residual. Unfiltered systems must provide either redundant disinfection system components or an automatic shutoff of water delivered to the distribution system if the residual disinfectant falls below 0.2mg/l.
IESWTR	Disinfection profiling
LT1ESWTR	Requirements of the IESWTR for systems serving less than 10,000 people
Stage 1 DBPR	Based on a running annual average (RAA), maximum residual disinfectant levels (MRDLs) are to be no greater than 4.0mg/l for free chlorine, 4.0mg/l for chloramines, and 0.8mg/l for chlorine dioxide. Disinfectant levels may be temporarily increased above the MRDLs if for the protection of public health. Disinfectant levels in portions of the distribution system may exceed the MRDL if the RAA of MRDLs is still met. Monitoring for disinfectant residual is to be conducted at the same location and time as sampling for total coliforms. MCLs for TTHMs are lowered to 0.080mg/l and established for HAA5 (0.060mg/l), which typically increase in concentration with contact time in distribution.
GWR	The GWR applies to those systems using groundwater and may or may not require disinfection. Systems are responsible to provide 4-log removal/inactivation of viruses and must initiate corrective action, such as disinfection, if their source water is found to be contaminated or deficient (i.e., vulnerable to contamination) or if routine coliform monitoring identifies a positive sample.
LCR	Samples, the number of which is based on the population served, taken throughout the distribution system must have less than 15µg/l lead and less than 1.3mg/l copper in 90% of the samples collected.
TCR	Samples, the number of which is based on the population served, taken throughout the distribution system must demonstrate acceptable presence/absence of total coliform bacteria, with follow-up testing for <i>Escherichia coli</i> or fecal coliforms.

Allen et al.⁹³ showed large populations of bacteria in main encrustations collected from seven water utilities throughout the United States. Diatoms, algae, and filamentous and rod-shaped bacteria were commonly encountered. These observations clearly indicate that distribution systems can be populated by a variety of microorganisms. It is not clear at this time why coliform regrowth is an apparent problem only in certain systems. As the water industry develops a more comprehensive database on bacterial nutrients, it may be able to better answer this question.

Examination of distribution system biofilms has revealed large variations in the number of HPC bacteria. Tuovinen and Hsu⁹⁶ found viable counts that ranged between 40 and 3.1×10^6 bacteria per gram in tubercles from distribution system piping in Columbus, Ohio, that included organisms such as sulfate reducers, nitrate reducers, nitrite oxidizers, and various unidentified HPC microorganisms. Nagy and Olson⁹⁷ observed a correlation between the number of years in service of a pipeline and the density of bacteria. They estimated that the concentrations of HPC bacteria increased by 1 log for every 10 years of service.

Donlan and Pipes⁹⁸ inserted coupons into cast iron corporation cocks as sampling devices for various areas of a suburban Philadelphia distribution system. When water temperatures were 20–25 °C, bacteria colonized and grew on the coupons to 10^4 – 10^8 cells/cm² within 28–115 days. At lower water temperatures (5–9 °C), their densities dropped to 102–105 cells/cm² within 29–84 days. The investigators found that water velocity and chlorine residuals did not correlate with biofilm viable counts.

Seidler et al.⁹⁹ recovered *Klebsiella* growing in slime layers on staves of redwood distribution storage tanks. Olson¹⁰⁰ reported recovering *E. coli* from the organic surface layer of a mortar-lined pipe in the MWD of Southern California distribution system, and Victoreen¹⁰¹ isolated *E. cloacae* and *Serratia marcescens* from tubercles in the Wilmington, Delaware, distribution system. Investigators in New Jersey showed that coliform bacteria found in a water utility's distribution system originated in the biofilm.⁹⁴ Monitoring results showed that the numbers of coliforms continued to increase with distance away from the treatment plant. Calculations revealed that the increase could not have been the result of growth in the water but must have come from the biofilms in the transmission line near the treatment plant. Identification of coliform bacteria showed that species diversity increased as the water flowed through the study area. Because coliform bacteria occur at specific, discrete locations within the distribution system, they may not be detected by a random sampling of pipe surfaces.⁹⁴

Explanation of Terms Involving Regrowth

Biofilm, breakthrough, and growth are key components of regrowth.

Biofilm. Biofilm is the most important factor affecting regrowth. It is a surface deposit consisting of microorganisms, microbial products, and detritus.^{102–104} It

may occur on pipe surfaces, sediments, inorganic tubercles, suspended particles, or on virtually any substratum immersed in the aquatic environment. It may be evenly distributed or may appear in random patches.

Biofilm develops as a result of the accumulation of microorganisms and nutrients at an interface, followed by metabolic growth, product formation, and finally, detachment, erosion, or sloughing from its surface.^{103,104} The rate of its formation depends on the chemical-thermodynamic properties of the interface, the physical roughness of the surface, and the physiological characteristics of the attached microorganisms.¹⁰⁵ Shear forces generated by fluid velocity and the effects of disinfectants on extracellular polymer substances (EPS) may contribute to the release of biofilms from surfaces.

The attachment of bacteria to surfaces in flowing water has important ecological consequences:¹⁰⁵

- Macromolecules tend to accumulate at liquid solid interfaces, creating favorable conditions for growth in an otherwise nutrient-deficient environment.
- Low concentrations of nutrients in the water combined with high flow rates can result in large quantities of nutrients being transported to fixed microorganisms.
- EPS provide an anchor for attached bacteria and may be a factor in nutrient capture.
- Bacteria embedded in EPS matrices are protected from disinfectants.

Breakthrough. Breakthrough is the result of an increase of bacteria in the distribution system passing through or avoiding the treatment process, and is considered to be associated with the traditional causes of waterborne illnesses.

Breakthrough is indicated by the presence of coliform bacteria along with high concentrations of HPC bacteria in the finished water. Breakthrough of coliform organisms in treatment plants may occur even when effluent samples appear to be of good microbiological quality. This may be due to the repair of the cellular lesion in badly injured coliform bacteria that have been resuscitated in the biofilm.¹⁰⁶ Several reports^{107,108} describe how the detection of injured coliform bacteria in plant effluents has helped the operator to detect and correct these microbiological problems.

Research has shown that increased resistance to disinfection results from attachment or colonization of microorganisms on various surfaces, including macroinvertebrates (such as Crustacea, Nematoda, Insecta, and Platyhelminthes),^{109,110} turbidity particles,^{111–115} algae,¹¹⁶ and carbon fines.^{116,117} Bacteria on these particles may survive disinfection and enter the system. Solving this type of problem requires intensive examination of the entire treatment process by operating personnel. The sources of contamination in the Grand Rapids, Michigan, system¹¹⁸ included a turbid discharge from one of the plant's filters, seepage of rainwater into the filter beds, cross-connections,

and leaks in the clearwell. Each one of these contamination events resulted in a prolonged occurrence of coliforms in the distribution system.

Breakthrough and regrowth are characterized by a large initial occurrence of coliform organisms, followed by a gradual decline in their numbers. The only solution to breakthrough and regrowth is to locate and eliminate its source.

Growth. This is an increase in the number of bacteria in the distribution system resulting from cell reproduction. Significant growth always occurs at the expense of the organic or inorganic substrate. Therefore, understanding the nutritional conditions within the pipe network is critical to the control of growth within the system.^{119,120}

Regrowth of Coliforms. The frequency and persistence of coliform “regrowth” in the distribution network is a major concern to many water utilities. It has occurred in systems considered biologically stable even though the water leaving the treatment plant is free of coliforms and cross-connections are nonexistent.

The American Water Works Service Company, Haddon Heights, New Jersey, reported in 1984 that six of its Midwestern water utilities had been encountering coliforms in their distribution systems.¹²¹ In all cases, traditional corrective measures had failed to reduce the bacteria concentrations in distribution systems that habitually maintained free chlorine residuals of 2–3 mg/l (R.H. Moser, pers. comm.) until the chlorine residual was increased to 6 mg/l.

In one of the affected systems, the treated water was dosed with a zinc phosphate compound as it entered the distribution system. This treatment seems to have eliminated the coliform organisms. R.H. Moser (pers. comm.) believed that the coliforms were harbored in the gasket material at the pipe joints, and the zinc compound deposits a metallic film at the pipe joints, encapsulating the surviving organisms. This explanation derives from the fact that the distribution system piping involved in the coliform reappearance phenomenon had been “poly-pigged” preceding treating the distribution system piping with zinc phosphate, which removed tubercles and other scaly deposits that could harbor or encapsulate microorganisms.

V.P. Olivieri (pers. comm.), who investigated the regrowth problem, believed it is the result of a microbiological process; that is, the development of a biofilm by the microorganism that protects the organism from the chlorine residual. He also believes that the microorganism develops this film in response to the hostile environment that consists of free chlorine residual and a starvation level of nutrients. The protective film was damaged or destroyed by the cleaning described above and the organisms became exposed to the disinfectant.

In 1990, Schotts and Wooley¹²² conducted a study of bacterial–protozoan interaction in the presence of chlorine, and found that when the bacteria were alone, they were killed by free chlorine residuals in the range of 0.25–1.0 mg/l. However, when the same bacteria were ingested by protozoans, significant concentrations of them survived for up to 24 h in the presence of free chlorine

residuals of 1.0–10 mg/l. This discovery provides a rational explanation for the survival and proliferation of coliforms in distribution systems in the presence of free chlorine residuals as high as 10 mg/l. The bacteria used in this investigation were potential human pathogens such as *K. pneumonia*, *Klebsella oxytoca*, *E. cloacae*, *Enterobacter agglomerans*, *Citrobacter freundii*, *E. coli*, *Campylobacter jejuni*, *Legionella gormanii*, *Salmonella typhimurium*, *Yersinia enterocolitica*, and *Shigella sonnei*. The protozoans were *Tetrahymena pyriformis*, *Acanthamoeba castellanii*, and *Bodo edax*.

The phenomenon of coliform regrowth is best characterized by the persistent appearance of coliform organisms in high-quality drinking water. Several factors distinguish the growth of coliforms in distribution systems:

1. Coliforms in treatment plant effluent are undetected or very low even when using sensitive methods.
2. High densities of coliforms are routinely detected in distribution system samples.
3. Coliforms in the distribution system samples persist despite the maintenance of a disinfectant residual.
4. The problem with regrowth may last for a long period of time, sometimes for several years.⁹⁴

Most of the time, when coliforms are detected, it is difficult to determine whether they are present due to regrowth or unrecognized contamination.

Factors Influencing Microbial Growth

There are many factors that influence the growth of microorganisms within a water distribution system.

Environmental Factors. There are two key environmental factors: temperature and rainfall.

Water temperature is perhaps the most important rate-controlling factor in microbial growth, as it affects directly or indirectly all other factors. Significant microbial activity is often observed at a temperature of 15 °C or higher.

Rainfall has been suggested by some investigators^{123,124} to be a catalyst for coliform growth. Lowther and Moser¹²⁴ found that TOC concentrations in raw water were at their highest after turbidity had been increased by rainfall. LeChevalier et al.¹²³ observed a 7-day lag between rainfall events and the appearance of coliform bacteria in distribution system water samples.

Rainfall also carries large numbers of microbes such as *Aerobacter aerogenes* into the system. While these are not fecal coliforms, they do yield positive results in the coliform test.

Positive coliform tests are common in some systems following storm events and research has shown that many are fecal.¹²⁵

Availability of Nutrients. Microorganisms must obtain all the substances they require for growth from the environment. Limiting the availability of any growth nutrient will curtail growth. However, for coliforms and HPC bacteria, the macronutrients, carbon, phosphorus, and nitrogen necessary for building the cells are normally available. LeChevalier et al.^{94,123} showed that AOC concentrations in drinking water declined rapidly as the water flowed through the distribution system. Removal of AOC occurred very quickly, within a short distance from the treatment plant. A reasonable relationship was found between AOC concentrations and the growth of HPC bacteria, suggesting that AOC is also a limiting nutrient. Trace nutrient availability can alter the particular species that grow, but overall growth is generally limited by macronutrient availability.

Reliability of Disinfectant Residuals. Growth of HPC and coliform bacteria may occur in some sections of a distribution system where an effective disinfectant residual cannot be maintained.^{126,127} This situation can be resolved by thoroughly flushing the system, increasing the disinfectant dosage to produce an adequate residual throughout the system, and monitoring it for both disinfectant residual and DO. The monitoring may reveal the need for booster or rechlorination to reach remote parts of the system or other zones that may be prone to dead-end problems, such as insufficient DO concentration. It may also be necessary to remove chlorine demand-causing compounds by modifying treatment practices and by “pigging,” relining, or replacing portions of the piping.

Type and Concentration of Disinfectant Residual. Several investigators found that maintaining substantial free chlorine residuals did not always correlate with reduced bacterial counts in the distribution system.^{94,128–131} Nagy et al.¹³² reported that a 1–2 mg/l chlorine residual reduced the concentration of bacteria on the biofilm in the Los Angeles Aqueduct by 2 logs, but the concentration of the remaining bacterial was still unacceptable. It was necessary to lower the bacteria level by 3 logs, which required chlorine residuals of 3–5 mg/l. During the persistent coliform episode at Muncie and Seymour, Indiana, coliforms could not be reliably controlled with free chlorine residuals less than 6 mg/l.^{124,129}

Others have found chloramines to be more effective than free chlorine. LeChevalier et al.^{58,59} indicated that various disinfectants may interact differently at biofilm interfaces. In a comparison study,⁶⁰ investigators found that low concentrations (1.0 mg/l) of either free chlorine or monochloramine could reduce viable counts of biofilms grown on copper, galvanized, or polyvinyl chloride (PVC) pipe by more than 2 logs. However, for organisms grown on iron pipe, free chlorine residuals of 3–4 mg/l were ineffective, and only monochloramine residuals higher than 2.0 mg/l were successful in reducing the biofilm. C.N. Haas, M.W. LeChevalier, and M. Geoffry (unpublished observations) modeled the interaction of free chlorine and monochloramine with biofilm surfaces and suggested that free chlorine, owing to its high reaction rate, was largely consumed before it penetrated the biofilm. Because mono-

chloramine will react with fewer compounds,^{133,134} it can penetrate the biofilm layer and inactivate the attached organisms better than does free chlorine. The inability of a disinfectant to penetrate the biofilms in distribution system piping can explain the occurrence of coliform bacteria in highly chlorinated water.

Corrosion and Sediment Accumulation. Corrosion by-products can protect bacteria from the disinfection action of free chlorine. Chlorine is known to react with ferrous iron to produce insoluble ferric compounds. The sediment and debris that accumulates in distribution system piping can serve as habitat for microbes as well as protection for them against disinfectants. Dixon et al.¹³⁵ found that residual aluminum in filter effluent can form a hydrous floc deposit on pipe walls, which then increases the concentration of organics while protecting the bacteria from the disinfectant.

Corrosion inhibitors can improve the disinfection efficiency of free chlorine in iron piping. LeChevalier et al.⁶⁰ demonstrated that polyphosphate and zinc orthophosphate combined with pH and alkalinity adjustment resulted in up to 100-fold improvement in disinfection of biofilm by free chlorine. Before using these inhibitors, their effects on overall water quality should be thoroughly investigated.

Polyphosphates are sequestering agents that may actually increase the concentrations of other metals such as lead and copper, both of which are regulated under the LCR; thus, solving the biofilm problem could cause violation of the LCR, and because zinc is a controlled pollutant in some wastewater discharges, the use of zinc orthophosphate may cause violation of National Pollutant Discharge Elimination System (NPDES) permits. Therefore, most water systems, considering changes in corrosion control, should conduct, as a minimum, a desktop corrosion control study followed by further evaluation at bench-scale or pilot-scale, if confirmation is necessary. Some utilities have found it preferable to evaluate the proposed treatment techniques on portions of piping removed from their distribution system.

Hydraulic Effects. The hydraulics of a distribution system can affect the microbiological growth in the piping. Increasing the velocity allows greater flux of nutrients to the pipe surface, greater transfer of disinfectant and greater shearing of biofilm from the pipe surface, whereas stagnation in the system leads to a loss of the disinfectant residual, which will lead to microbial growth, and may also lead to the development to anaerobic condition that cause septicity because of insufficient DO in the water. This is the reason why dead-end areas show significant deterioration in microbial quality. Reversal of water flows can easily shear biofilms, and water hammer events can dislodge tubercles from pipe surfaces.⁹²

Operation of the Distribution System

Operating a distribution system requires a balance between the supply needs and the water quality. Knowing how the various portions of the system

function helps operators control the finished water quality, including the concentration of chlorine maintained for secondary disinfection. This is not only a public health requirement but is also essential to maintaining the aesthetic quality of the water while minimizing the bacterial regrowth potential.

An adequate chlorine residual in a distribution system is essential for the protection of public health. A public water supply can become contaminated through cross-connections with nonpotable water lines or breaks in a water main and a sewer line at crossover points, which may lead to outbreaks of waterborne disease. Maintaining chlorine residual in the distribution system will help minimize such health risks.

Some of the operating procedures for maintaining an acceptable water quality involve controlling the water age within the system and periodic flushing of the mains.

Monitoring

Maintaining satisfactory water quality within the distribution system requires frequent monitoring of all areas of distribution. In this section, the different types of monitoring are discussed, as they relate to maintaining secondary disinfection within the distribution system.

Nitrification Control. Nitrification is normally only a problem only for water systems located in warmer climates that use chloramines. Systems located in the northern tier of the United States seldom experience problems from nitrification because both AOB and NOB are slow-growing organisms that thrive only in a warm environment. This is not to say that water systems in colder climates can ignore the possibility of nitrification or do not need to monitor for it.

To prevent nitrification, the system should be monitored for a variety of water quality constituents, including pH, alkalinity, water temperature, chlorine residual, nitrite, nitrate, and ammonia. Table 4.8 shows a sample monitoring plan presented by Harms and Owen⁵³ to provide early warning of nitrification.

The following action plan was also suggested for systems using chloramination:⁵³

1. Operate at a chlorine-to-ammonia N ratio of 4.5 ± 0.5 and a systemwide chlorine residual concentration of 2 mg/l or higher. If water temperature is higher than 20°C during periods of low water use, operate distribution system to shorten water age.
2. Compile background information on water quality in the distribution system using monitoring data from sampling stations used for sampling of total coliforms or for water quality constituents under the LCR, and analyze for the constituents listed in Table 4.8.

TABLE 4.8. Sample Monitoring Program for Nitrification Control

Constituent	Monitoring Frequency
pH (units)	Daily or online at the WTP; field pH to be measured in all coliform samples from the distribution system
Chloramine residual (mg/l)	Same as for pH
Alkalinity (mg/l as CaCO ₃)	At least daily at the WTP; measured in coliform samples from the distribution system
Temperature (°C)	Same as for pH
Heterotrophic plate counts (cfu/ml)	Determined from coliform samples
Ammonia (mg/l as N)	At least daily at the WTP; determine once or twice monthly in the system during periods of cold water, weekly in warm water
Nitrite (mg/l as N)	From the distribution system, same as for ammonia
Nitrate (mg/l as N)	From the distribution system, same as for ammonia

3. Catalog and present data spatially and temporally. Do indications of water quality degradation routinely appear at particular sites? If so, investigate the site and identify contributing factors such as low water use, cross-connection, pipe material/condition/age, and so on and correct if possible. If not possible, schedule more frequent flushing.
4. Compare results with predictions of water age and the related water quality degradation. This is useful for both chlorinated and chloraminated systems. Minimizing consequences of water age improves overall water quality and system condition.
5. Use data (from step 4) and the predicted water quality to develop a flushing program.
6. Continue the routine monitoring described in step 2 unless a significant loss of chloramine residual occurs or nitrite concentration increases by more than 0.05 mg/l.
7. If loss of chloramine residual occurs without any accompanying sign of nitrification, check the configuration of the distribution system (valves, tanks, water age, etc.) and flush the affected areas.
8. If the distribution system is configured normally and indicators point to severe nitrification, increase chloramine concentration from the WTP and flush to increase disinfectant concentrations throughout the distribution system.
9. If the distribution system is configured normally and indicators point to severe nitrification that was not corrected by increasing the

chloramine residual, initiate breakpoint chlorination for 1–2 weeks, then resume chloramination.

10. If breakpoint chlorination is needed more frequently than annually, consider the addition of chlorine dioxide or modifications to finished water quality. Small amounts of chlorite ion may control nitrifiers.^{72,73}

Stagnant, Low-Flow, or Dead-End Area Surveillance Program. Chlorine residual, temperature, and pH are typically measured when sampling for coliforms and HPCs within a water system. The locations of problem areas in the distribution system are often well known. When chlorine residuals decline, the first response will be flushing the problem area. In a system containing a large number of known problem areas, flushing may be done on a regular basis. The development of hydraulic and water quality models of distribution systems has greatly increased the ability to identify trouble spots. Where possible, the flushing should be unidirectional. The requirement of a “detectable residual” in distribution systems has led to the increasingly widespread use of flushing. Some utilities have installed new pipes simply to improve circulation for maintaining chlorine residuals in a particular zone. Stagnant portions of distribution systems using chloramination are particularly susceptible to nitrification as chloramines will eventually decay and release the ammonia, and disinfectant residuals tend to decline. Such conditions promote the growth of AOB and NOB. In addition to flushing, all valves in the affected area should be checked to verify that the system functions as intended. Inadvertent closure of valves can create unnecessary dead ends. Flushing also removes tubercles and sediments, thus allowing the disinfectant better access to biofilms that may contain nitrifying organisms.

Control of Water Age

Water age refers to the length of time the water remains in the distribution system. In high-turnover systems, it may be as short as 24–48 h. Systems with a longer water age are at higher risk of losing the chlorine residual, which may lead to deterioration of water quality, such as (a) higher TTHM formation as free chlorine continues to react with organics in the water, (b) regrowth, (c) increased corrosion, (d) low DO concentration, and (e) turbidity or color episodes. Keeping the water in the pipes and tanks fresh maintains a disinfectant residual and reduces the potential for these problems.

HAA5 formation also increases with longer contact times with chlorine residuals. However, some utilities have observed a decrease in the HAA5 concentration in their distribution systems. In Newport News, Virginia, the HAA5 concentrations in portions of the distribution system with the longest residence times were lower by as much as 33% than at the point of entry into the system.^{136–138} It is believed that microbial regrowth in the distribution system is degrading the various HAA compounds.¹³⁹ This has not been observed in all distribution systems, so although it may be an advantage of a longer water age, it is outweighed by the benefits of a shorter water age.

Operators should fully understand the demands on the system so that they can store just enough water in the distribution system to meet the customers' needs and the fire protection requirements. Treating and pumping excessive amounts of water into the system results in a longer water age, and the associated deterioration of water quality. Another factor to consider, especially when planning any new storage facilities, is the type of storage (e.g., standpipe, elevated tank, reservoir) in the distribution system, and the location of these tanks relative to high-demand areas.¹⁴⁰ Daily drawdown and refilling of the storage tanks and reservoirs is one way of improving water age.

Secondary Disinfectant Residuals

Operating the distribution system with either chlorine or chloramines, and at different concentrations, will impact the water quality. Obviously, maintaining a residual concentration is an important operational goal for the distribution system.

Type and Concentration of Secondary Disinfectant. Results from some research indicate that monochloramine may be more effective for biofilm control than free chlorine.^{59,60} As chlorine is a stronger oxidant than chloramines, this is presumed to occur only when the biofilm is sufficiently thick to prevent the complete penetration of the chlorine. Experience indicates that secondary disinfection with 100% combined chlorine residual can effectively control bacteria levels in the distribution system.^{49,141–149}

LeChevalier et al.⁶⁰ showed that the threshold level at which monochloramine was effective for controlling biofilms on iron pipes: a 2.0 mg/l monochloramine residual. This number will certainly vary in accordance with site-specific conditions of water quality and pipe conditions.

The 2 mg/l concentration agrees well with other utilities controlling nitrification with chloramines at concentrations of 2–3 mg/l. The Hackensack, New Jersey, Water Company began using chloramine in its distribution system in 1982 (L. Fung, pers. comm.) with an initial chloramine dose of 2.0 mg/l, but because of sporadic presumptive coliform occurrences and evidence of nitrification in the distribution system, the company increased the chloramine dose to 3.0 mg/l in 1986. During the early summer, only a few coliform bacteria were discovered, and in August, chloramine doses were increased to keep the average distribution system residual at 2–3 mg/l for the remainder of the summer, which eliminated both coliforms and nitrification.

Other utilities experiencing coliform regrowth problems have relied upon high free chlorine residuals, in general, 3–6 mg/l, to control coliform regrowth.^{94,128,130,131,141,142,150,151}

Maintaining Disinfectant Residuals. It is impossible to prevent all microbial growth in the distribution system; however, maintaining a disinfectant residual in the distribution system is one method of maintaining the quality of water at the customer's tap. Maintaining a residual within in the distribution system

requires an understanding of the operation of the system (water age, dead ends) as well as the conditions that contribute to residual decay.

One of the factors that affect the persistence of disinfectant residual is temperature.¹⁵² Plowman and Rademacher¹⁵³ found that when the water temperature was between 44 and 60 °F, the loss of combined chlorine residual was low but it became rapid during the summer, when the temperature rose to 68–73 °F. There would be both biological and chemical contributions to the increased decay with temperature; and the chemical contribution should be both a function of homogeneous reactions in solution as well as heterogeneous reactions on the surfaces of pipes and particles.

If it is difficult to maintain chlorine residual in some parts of the distribution system, and using a booster station may make it possible to deliver chlorine to these areas. The method of delivery is sometimes referred to as relay chlorination. Water is rechlorinated based on automatic residual monitoring, typically with a chlorine or ORP analyzer.

The booster station should be designed taking into account the flow reversals in the distribution system. For example, when dosing 0.8–1.2 mg/l free chlorine in a pipe, the residual concentration could fluctuate between 0.3 and 2.0 mg/l throughout the day, depending on the rate of decay and the direction of flow through the pipe. Understanding this variability is essential, especially in parts of the distribution system where balancing reservoirs can increase the water age and contribute to the depletion of the residual.

When there is difficulty maintaining a residual in a distribution, plant operators can perform the following tasks to help identify the cause of the problem.

1. Measure the DO, chlorine residual, pH, and alkalinity to identify the zones of degradation at multiple locations within the distribution system.
2. Implement a flushing program in areas of the distribution system with the poorest water quality, starting with the zones of least DO.
3. Strive for a free chlorine residual of 0.5–1.0 mg/l or a combined chlorine residual of 1.5–2.0 mg/l throughout the system.
4. Ask the media to inform consumers about the reasons for the program and how they can help by flushing their own service pipes.
5. Keep a continuous record of complaints.
6. Repeat the DO survey as necessary.
7. Measure chlorine at locations throughout the distribution system.
8. Make spot checks by comparing distribution system residuals with adjacent consumer tap residuals. If these checks reveal a wide disparity, implement a flushing program and continue monitoring the residuals.

Proper planning and design of the distribution system, placement of balancing reservoirs, and avoiding dead ends will help prevent wide fluctuations in distribution system residuals. A periphery-type grid system will result in better circulation in the distribution system.

Flushing

Flushing of the distribution system involves wasting water from the system. It is routinely practiced by many water utilities: The 2008 AWWA Disinfection Committee reported that nearly 50% of utilities surveyed flush the entire system yearly, and others flush certain areas as needed to help maintain a chlorine residual in the distribution system.³⁹ Procedures for designing and conducting a flushing program are outlined in AWWA publications.¹⁵⁴ Generally, fire hydrants are used for flushing, but other infrastructure, such as valves and outlets, can be designed into the system for flushing distribution systems into sewers. In practice, it is difficult to flush transmission mains and trunk lines without extreme effort, high costs, and usually considerable disruption of service to the consumers.

HPC and coliform bacteria are likely to occur in distribution system sections that lack a disinfectant residual.^{126,127} This problem can be resolved by flushing followed by increasing the disinfectant dosage sufficiently to produce residual throughout the system, and continued monitoring for disinfectant residual, DO, pH, temperature, and alkalinity.

Some utilities have corrected the poor water quality in the dead ends of their systems by implementing a routine monitoring and flushing program. Distribution systems that contain many problem areas may be flushed on a regular basis, especially during the summer, to help improve water quality. In sections of the distribution subject to chronic problems, a continuous bleeding system may be installed to prevent stagnation, and in extreme cases additional pipes or loops of pipes have been installed to improve circulation.

Flushing with chlorinated water will not completely eliminate regrowth of all microbes as observed in a study of *Legionella* contamination in both hot and cold water systems of the distribution system of a newly constructed WTP.¹⁵⁵ *Legionella* is not considered to be chlorine resistant, and its persistence is attributed to heavily colonized components of the distribution system, such as valves and their interior parts.

Flushing programs do not always improve the water quality. Increased flushing of the New Haven, Connecticut, distribution system actually increased the coliform content of the water.¹⁴¹ This was attributed to pieces of the biofilm being sheared off pipe surfaces by changes in the velocity or the oxidative quality of the water. Similarly, 3 days after flushing the system at Muncie, Indiana, coliforms at a density of 126/100 ml were detected a few blocks from the plant,¹⁴² and flushing of some sections of the Seymour, Indiana, distribution system did not eliminate the coliforms.¹²⁴

When using chloramines in the distribution system, it is imperative to maintain a residual throughout the system and to enforce a flushing program because if the residual is depleted, the ammonia nitrogen returns and serves as a nutrient to promote proliferation of the bacteria. In many locations, any release of a chlorinated or chloraminated water from flushing will require that the water be dechlorinated prior to discharge (see Chapter 11).

Treatment Plant Performance Impacts on Distribution System Water Quality

Biological treatment in the WTP encourages microbial activity within the treatment process with the goal of having microorganisms remove enough nutrients to limit significant bacterial growth in the treated water. This type of treatment has been used for many years in Germany, and more recently in Canada and the United States.

The benefits of biological treatment include removal of TOC; reduction of bacterial nutrients; partial removal of selected micropollutants; improved taste and odor control; reduction of chlorine demand, which automatically reduces DBPs; and a general improvement of subsequent processes in the treatment train.¹⁵⁶⁻¹⁵⁸

Not all of these advantages are important to all water utilities, such as those with high-quality source water, such as San Francisco; Denver; and Portland, Oregon. Practicing biological treatment at this level also requires special operator skills for it to be effective. Biological treatment lends itself to the consideration of other oxidants such as ozone. Ozone disrupts complex organic molecules, which then make the TOC more amenable to biological removal.

DISINFECTION OF NEW INFRASTRUCTURE

New WTPs, water mains, storage reservoirs, and buildings must be disinfected before being placed into service. Unless specified otherwise by applicable state or local regulations, the following disinfection procedures prepared by AWWA may be followed:

- C0651-05 Disinfection of Water Mains¹⁵⁹
- C0652-02 Disinfection of Water Storage Facilities¹⁶⁰
- C0653-03 Disinfection of Water Treatment Plants¹⁶¹
- C0654-97 Disinfection of Wells¹⁶²

Typical Disinfection Chemicals

Free chlorine is the most common disinfectant used for potable water systems, as it is readily available and can be easily applied and tested.

1. Chlorine gas: 100% pure chlorine in either liquid or gaseous form. It must be dissolved in water before being applied.
2. Liquid hypochlorite solution: From 5% to 16% available chlorine, typically as sodium hypochlorite (note: a 1% hypochlorite solution is equivalent to 10,000 mg/l free chlorine).
3. Granular or tablet hypochlorite: Calcium hypochlorite in granular or tablet form contains 65% available chlorine by weight and is very

effective for disinfection of infrastructure. The tablets are available commercially, and are attached to the pipe or tank walls to release chlorine into the water as they dissolve.

The form of chlorine applied depends on the type of system and the means of delivery. Feeding disinfectants to basins already filled with water should be discouraged, as it is difficult to achieve appropriate mixing and contact.

Further information about the various forms of chlorine is available in AWWA B300 (Hypochlorites) and B301 (Liquid Chlorine) and in Chapters 8, 9, and 10. Guidelines on chemical dosages are included in the Appendix B of AWWA C650. Container volumes and available concentrations are varied and generally depend on availability.

While chlorine is the most commonly used disinfectant and is discussed in AWWA standards, alternative disinfectants such as ozone, chlorine dioxide, or chloramines are also available. However, these are generally not recommended. Chloramines are not used for disinfecting infrastructure because they are not an aggressive enough disinfectant. Ozone is more aggressive but is not generally used because it does not maintain a residual for sufficient time to guarantee that all biological activity has been stopped. Before using an alternative disinfectant, regional jurisdictional authority should be consulted.

Disinfectant Feed Systems

Permanent chlorine feed systems, as opposed to temporary feed systems, should be used wherever possible in order to achieve disinfection because of the safety features installed with permanent systems. When permanent systems are not available or cannot provide the required disinfectant dosage, temporary systems may be used and are typically provided by the contractor or an outside vendor. When selecting a temporary feed system, it is important to evaluate the types of feed systems that are available, means of connection and dose control, and safety outside firms specializing in disinfection should be considered if a temporary system is required.

When using chlorine gas, a conventional vacuum eductor with a booster pump is required due to the health hazards associated with chlorine. This system will dissolve the chlorine gas in water to produce a hypochlorite solution, the strength of which will vary based on the mass of chlorine fed per volumetric flow of water. It is important to check with the local special hazards authority prior to the installation or use of chlorine gas, because there are often special requirements and permits for these systems.

Bulk hypochlorite, in either the NaOCl or $\text{Ca}(\text{OCl})_2$ form, is often used because it can provide the range of concentrations that are required for disinfection of infrastructure. These solutions are however, sensitive to sunlight and heat, which causes the available chlorine in the bulk solution to degrade, or diminish, over time. It is recommended that local chemical suppliers be

contacted during the planning stages of infrastructure disinfection to determine what chlorine solution strengths are available, and the volume options for delivery. Because of the issues with degradation over time, bulk hypochlorite should not be delivered until the infrastructure is ready for disinfection.

Pumps that are designed specifically for hypochlorite solutions are recommended, but they are not required because the hypochlorite solutions can be easily removed from the pump casing by flushing with water after chlorine dosing is performed. Any equipment needed should be designated for potable water service and should be disinfected prior to use with a 200 mg/l chlorine solution.

Disinfection of Water Mains

The methods of applying chlorine to water mains are described in AWWA C0651, and they are continuous feed, slug dosage, and by tablet dissolution. In general, the infrastructure is usually pressure washed before and, possibly, after installation, and then filled with water and flushed using 1–3 vol of water. Next the disinfectant is applied and the infrastructure is flushed again with dechlorinated water preceding bacteriological testing.

The continuous-feed method involves continuous feeding of chlorine (gas or liquid) until the entire main contains chlorine solution. The dosage recommended by the AWWA is 50 mg/l as Cl_2 , but the requirement is a residual of at least 10 mg/l throughout the main at the end of 24 h. There is no specific requirement for the initial chlorine dose to be applied, but it should be minimized because disposal of the disinfecting and flushing water can be challenging at project locations where disposal options are limited.

For large systems with large diameter pipes, the slug method is typically used because the continuous feed system dosing is impractical. This consists of a single dose, or slug, of chlorine being applied (typically with tablets), filling the infrastructure with water to eliminate air, and then allowing the volume of chlorinated water to travel through the infrastructure so achieve a minimum of 100 mg/l Cl_2 to disinfect all of the interior surfaces for at least 3 h.

The tablet method is generally used for disinfecting short sections (less than 2500 ft) of small-diameter (up to 24 in.) pipe where mixing and distribution of the disinfectant are hindered by hydraulics. The tablets are placed in the pipes and dissolve as the pipe is filled with water to provide disinfection.

Appendix B and C of AWWA C0651 provide chemical dosing requirements for various volumes to be treated and information on chlorine neutralization dosing, respectively.

After the appropriate contact period, the infrastructure is flushed with potable water. Note that if the chlorine-laden water from the disinfection or flushing procedures is being disposed to the sewer, the WTP staff should be notified. They may request that the water be dechlorinated prior to disposal to the sewer.

Procedures for Disinfecting Storage Tanks

Elevated tanks, covered ground storage tanks, and ship tanks are most conveniently disinfected using portable chlorination equipment. Procedures and requirements are listed in AWWA C0652. Portable chlorination equipment must be used carefully and under expert supervision.

Three methods of disinfection are used for disinfecting water storage facilities. Full basin chlorination is used when the basin is relatively small or when water disposal concerns are easily mitigated. The basin is filled completely with a chlorine solution such that the residual is not less than 10 mg/l after 6 h if gaseous chlorine is used, or after 24 h if liquid or tablet hypochlorite is used. Spray application of water-contact surfaces is used for large basins or when disposal of highly chlorinated water is difficult. A 200 mg/l chlorine solution is sprayed onto all surfaces that will be in contact with potable water. The surfaces must remain in contact with the disinfectant spray for 30 min, after which the basin is filled to overflow with potable water. The third method is two-step chlorination, which is typically used at locations where chlorine solution is delivered in bulk for disinfection, as opposed to utilizing continuous-feed or permanent-feed systems. The bottom 5% of the basin is filled with a 50 mg/l chlorine solution. After 6 h, the basin is filled to overflow with potable water and allowed 24 h of contact time. The minimum chlorine residual after filling is 2 mg/l, and additional chlorine can be added to achieve 2 mg/l.

AWWA C0652 Appendix B provides estimated chemical requirements for various volumes, and Appendix C provides information for determine the amount of neutralizing chemical required.

After disinfection, the tank is flushed with clean water in preparation for bacteriological testing. Total coliform samples should be taken at multiple locations within the tank. Representative sampling of tanks will require the use of any hatches, drains, sample taps, or other access points.

Procedure for Disinfecting Water Treatment Plants

Newly installed or refurbished water treatment structures that are downstream of filters require disinfection, as described in AWWA C0652. Piping, however, shall be disinfected by methods described in AWWA C0651, and media filters, by AWWA C0653.

For filter media disinfection, a chlorine solution is added by a backwashing or forward flow procedure. Note that filters or postfilter contactors that contain GAC should be disinfected prior to the installation of the GAC media because chlorine reacts with GAC.

During the backwash procedure, chlorine is added to the backwash water as it enters the filter. The minimum chlorine residual for adequate disinfection is 25 mg/l as the backwash flow passes through the filter. After 25 mg/l chlorine is detected in the backwash water, the backwash flow is terminated and the filter media soaks in the chlorinated water for at least 12 h. After 12 h, if the

chlorine residual is less than 15 mg/l at both the top and bottom of the filter, the backwashing procedure must be repeated until the 15 mg/l concentration is achieved.

In the forward flow method, chlorine is added to the water as it enters the filter bed, and the target concentration is at least 25 mg/l when the filter is operated in the filter-to-waste mode. Once a chlorine residual of >25 mg/l is detected in water at the bottom or exit of the filter, filter operation is terminated and the filter is allowed to soak in the chlorinated water for at least 12 h. After 12 h, if the chlorine residual is less than 15 mg/l at the top and bottom of the filter, the forward flow method is repeated until the 15 mg/l concentration is achieved.

AWWA C0653 Appendix A provides the estimated chemical requirements in order to determine the amount of neutralizing chemical required after the completion of disinfection. Calculating the amount of neutralizing chemical is based on the chemistry presented earlier in this chapter, and in Chapter 11. All disinfection water should be wasted to either the plant's sewer connection or water recovery systems.

After disinfection, the basins and pipes are flushed with water, possibly water that is being produced through the treatment plant. Total coliform samples from water at the top and bottom of all disinfected filters and at reasonable locations throughout the basins and pipes shall be collected.

Disinfection of New Buildings

New building piping is disinfected according to the guidelines of AWWA C0651-05 for disinfection of water mains; however, building water service is generally governed by building codes and may be subject to additional requirements. Slug disinfection is not recommended, as the high chlorine concentration is corrosive to copper piping and joints.

The disinfectant should be added at or as near as possible to the building water service entrance and should be distributed throughout the building's distribution system by opening faucets at various locations in the building. Injection of the disinfectant should be continued until sufficient residual is measured either at several locations along the system or at the most distant point, and the building service valve should be shut off to isolate the system for the duration of the contact period.

At the end of the contact period, the building service valve should be reopened and samples should be taken at various locations to ensure that adequate residual remains. After disinfection has been verified, the piping system should be thoroughly flushed to remove the disinfectant and corrosion by-products. The system can then be put into service and lead and copper samples can be collected for the LCR. It may also be necessary to consult the wastewater authority to determine whether the chlorinated waste should be neutralized. Total coliform samples should be taken at all points where there is the potential for human consumption and/or at the end of pipe runs.

Procedure for Disinfection of Wells

The disinfection of wells for potable use is covered in AWWA C0654. Other suggested resources are

- *Water Well Rehabilitation, A Practical Guide to Understanding Well Problems*,¹⁶³
- *Chemical Cleaning, Disinfection & Decontamination of Water Wells*,¹⁶⁴ and
- *The Nalco Water Handbook*.¹⁶⁵

All aboveground piping must be disinfected according to AWWA C0651. The most convenient way to disinfect wells is to use portable chlorination equipment and/or tablets since permanent systems are generally not equipped to feed into the well casing. The portable equipment must be used carefully and under expert supervision.

The following methods can be employed for disinfecting wells and well equipment:

- *Chlorination of new gravel*: For new wells, the well casing should be flushed of all drilling fluid as described in AWWA A100. Chlorine may be introduced either by adding chlorine tablets to the gravel as it is being installed or by adding chlorinated water into the well casing until the chlorine concentration of water in the well casing reaches 50 mg/l.
- *Chlorination of makeup gravel*: Before adding gravel to an existing well, the gravel should be soaked in a 50 mg/l chlorine solution for at least 30 min.
- *Chlorination of existing gravel*: When an existing well has become contaminated and requires disinfection, the well casing, screen, gravel pack and contacting formation should be filled with a pH-buffered, 200–300 mg/l chlorine solution. The volume of this solution should be 1.5–2.0 times the standing well volume. It is critical that this chlorine solution be dispersed throughout the well bore, especially to the bottom portion where the problematic bacteria reside. Proper placement of the solution can be accomplished by utilizing a small diameter pipe or, if administered to the top of the well, should be followed by an amount of water equal to the standing well volume to displace the solution into the well. If the permanent pump is removed from the well, use of a surge block tool with chemical injection ports will allow for proper placement of the chlorine solution and the application of surging action to disperse the solution into the well bore. The minimum contact time for this process is 2–5 h; however, allowing the solution to remain in the well overnight can be beneficial. When the disinfection process has been completed and the solution is ready for discharge, a chlorine residual test should be performed. If chlorine residual is greater than the level allowed by regulatory agencies, the solution should remain in the well until the chlorine residual has dissipated or the solution should be pumped to the surface and dechlorinated prior to discharge.

- *Chlorination of well equipment:* All equipment and materials to be permanently installed in the well require disinfection with a 200 mg/l chlorine solution that is buffered for optimal disinfection.

The estimated chemical requirements for well casings of various sizes and depths are listed in AWWA C0654, Appendix A. Information for determining the amount of neutralizing chemical required is presented in Appendix B.

Prior to starting production from a new well or rehabilitated well, the water within the well must be disinfected, and the dose of chlorine varies by state agency. The buffered chlorine solution is placed in the well and allowed to react overnight. The next day, the solution is pumped from the well, dechlorinated if necessary, and bacteriological samples of the disinfected well water are collected.

If a well tests positive for total coliforms, the disinfection procedure can be repeated. If unsafe samples persist, a variety of procedures are available, and these are selected based on the characteristics of the well. Pumping the well to waste, or flushing, for long periods of time can be beneficial in removing dislodged biofilm. For deep wells with sumps, the application of slow dissolving chlorine/bromine tablets can be beneficial. The tablets allow the disinfectant to reach the bottom of the well, which can be the most problematic area of the well.

Note that coliforms and most of the organisms that yield a positive result to the coliform test are facultative anaerobic bacteria. Therefore, they can reside in the lower portions of the well, which are void of excess oxygen. In wells where it is difficult to get acceptable total coliform sample results, special attention should be given to administering disinfection chemicals to the lower portion of the well, especially with a well sump below the screen (R. Miller, pers. comm.).

Procedures for Maintaining Disinfection while Inspecting In-Service Water Storage Facilities

Occasionally, inspections of in-service storage tanks or basins are required. AWWA Standard C0652 provides guidelines to verify that the water quality is not compromised during these inspections, and outlines procedures for entry and inspection of existing infrastructure by divers or equipment. This procedure requires special equipment and training and is best accomplished by specialty contractors. All equipment used in inspections must be designated for potable water use only and must be disinfected with a 200 mg/l chlorine solution prior to entering the water storage facility. The chlorine residual of the water in the storage facility should be checked at the beginning of the inspection and repeated at the end of the inspection. If there is no apparent decrease in the chlorine residual, then the water may be tested for total coliforms. If the chlorine residual has decreased, the chlorine concentration in the storage facility must be increased to the preinspection concentration (but <2.0 mg/l), and then a total coliform sample can be collected.

OTHER USES OF CHLORINE IN WATER TREATMENT

In addition to being an effective disinfectant, chlorine has several other benefits in drinking water treatment.

Tastes and Odors

The attitudes of the water industry professionals regarding the relationship between chlorine and the tastes and odors in drinking water have undergone a considerable change since the early 1900s when utilities first began to use chlorine to disinfect drinking water.

Many customers found the taste and odor of chlorine offensive. Many utilities used it at low dosages (0.25 mg/l) and were able to kill the bacteria while minimizing complaints about the chlorine tastes. At the time, the public was strongly opposed to the use of chlorine, perceiving it as forced medication, and believing that bad-tasting water was synonymous with chlorination.

This attitude inspired the waterworks profession to explore the mechanics of chlorination, with emphasis on improving or eliminating the tastes and odors. In the 1920s, Howard^{166–168} evaluated chlorine doses beyond the marginal bactericidal doses (superchlorination), and Bushnell¹⁶⁹ reported that increasing them to 3–5 mg/l eliminated the foul odors that were thought to be caused by gnats breeding in a covered reservoir.

Griffin¹⁷⁰ continued the exploration of very high dosages (25–30 mg/l) under a variety of conditions and practically revolutionized chlorination. Not only did his work lead to the discovery of the breakpoint phenomenon but it also proved that the free chlorine residual was not necessarily the cause of the off-flavor.

These discoveries helped change the perception that chlorine was synonymous with undesirable taste and odor. Subsequent research focused on identifying how chlorine can remove or control other tastes and odors, even if it must be applied in very high dosages.

The origins of tastes and odors in water supply are of two categories: natural and synthetic. Natural sources include aquatic growth, such as algal and bacterial metabolites; organic compounds from decaying vegetation and sources; and inorganic compounds, such as hydrogen sulfide, sulfates, and other sulfurous compounds. Synthetic sources of taste and odor in water supplies include domestic and industrial wastes, in particular, manufacturing plants and pulp and paper mills.

Substances that cause odors in drinking water are volatile, and generally are soluble in both water and organic liquids. Only a very few inorganic substances have odor, but they serve as nutrients to odor-producing algae. They can be destroyed or rendered less offensive by chlorine, or masked by the chlorine odor.

Hundreds of articles about taste and odor have been published, among them three thorough references by Middlebrooks (1965),¹⁷¹ Spitzer (1976),¹⁷² and Lin¹⁷³ (1977). Another valuable reference is the AwwaRF study, *Advances*

in *Taste-and-Odor Treatment and Control*,¹⁷⁴ which identifies common tastes and odors in drinking water and presents data on the effectiveness of various treatments in removing them.

Tastes and odors are quantified either by direct measurement of the compound such as geosmin or 2-MIB, or by a surrogate method, such as the Threshold Odor Test, detailed in *Standard Methods*. This reference and papers by Gerstein¹⁷⁵ and Sigworth¹⁷⁶ describe in detail how to construct continuous and batch-type odor monitoring devices. The threshold odor test is an organized evaluation of human detection of odors in specially prepared water samples. The water sample is diluted in consecutively higher amounts with odor- and taste-free water until the panel identifies a nondetection of odor in a sample, and a threshold odor number (TON) is then calculated based on the dilution. For satisfactory results, the TON should be less than 5, but some states have established secondary MCLs at lower TON values (CaDPH secondary MCL is 3 TON).

Tastes and Odors from Algae and Actinomycetes

The tastes and odors produced by algae and actinomycetes can be described as aromatic, fishy, grassy, earthy, musty, or septic. TONs caused by algae or actinomycetes may be as low as 1 or as high as 40, with some instances of 90 or more. Algae odor is generally objectionable, even when the threshold number is low.

In previous editions of this handbook, White compiled information about the types of tastes and odors produced by different types of algae. This information is summarized in Table 4.9.

Green algae are not often associated with tastes and odors in water; however, some species do produce odors. *Dictyosphaerium*, one of the worst offenders among the green algae, will produce a grassy-to-nasturtium odor as well as a fishy odor when present in larger concentrations. Some of the swimming green algae, such as *Volvox*, may also produce fishy odors. Green algae growth may help to somewhat inhibit blue-green algae and diatoms, and thereby be helpful in the control of water quality.

Jenkins et al.¹⁷⁷ have reported several odorous organic sulfur-containing compounds produced in decaying blue-green algae cultures and in reservoirs containing blue-green algal blooms. These compounds include methyl mercaptan, dimethyl sulfide, isobutyl mercaptan, and *N*-butyl mercaptan.

Actinomycetes are an order of filamentous, branching bacteria that were long been suspected of being the source of earthy odors in water supplies, and were therefore subjected to intensive investigation,^{178–182} but the general consensus among more recent investigators is that the majority of earthy-musty odors are associated with cyanobacteria rather than actinomycetes, even though actinomycetes are generally present.

Appreciable progress has been made in evaluating the relationship between volatile products of actinomycetes and the musty-earthy odors affecting water

TABLE 4.9. Tastes and Odors Caused by Algae

Type of Alga	Taste and Odor Impact
<i>Synura</i>	A very potent odor producer. A few colonies per milliliter will cause a perceptible odor resembling ripe cucumber or muskmelon. It can also produce a bitter taste, leaving a persistent dry, metallic sensation on the tongue. When present in large numbers, it may cause a fishy odor.
<i>Dinobryon</i>	Imparts a prominent fishy odor when the standard areal count reaches 30/ml. This organism develops in the southern end of Lake Michigan in June and July of almost every year.
<i>Asterionella</i> (500 units or more) and <i>Tabellaria</i>	Imparts an aromatic geranium-like odor that changes to fishy when present in large numbers.
<i>Synedra</i>	Produces an earthy-to-musty odor, and also inhibits proper floc formation.
<i>Stephanodiscus</i>	Contributes a vegetable oil taste but produces very little odor.
<i>Anabena</i> , <i>Anacystis</i> (formerly known as <i>Microcystis</i> , <i>Polycystis</i> , and <i>Clathrocystis</i>), and <i>Aphanizomenon</i>	Blue-green algae ^a that cause a very foul “pigpen” odor as well as a grassy-to-moldy odor in the water. They may develop into large luxuriant blooms. The foul odor develops from products of decomposition as the algae begin to die off in large numbers.

Compiled by White in previous editions of the *Handbook of Chlorination and Alternative Oxidants*.

^aThese are now known to be bacteria and are more properly referred to as cyanobacteria, but they were classified as algae for many years, and are still commonly referred to as blue-green algae, especially by practitioners in the field of drinking water treatment.

supplies across the country. Two earthy-musty smelling compounds have been isolated: geosmin and 2-MIB, both of which are metabolites of actinomycetes and blue-green algae (cyanobacteria) and have exhibited very low threshold odor concentration.^{181,183,184} Work done by Dougherty and Morris¹⁸⁵ in 1967 on the Cedar River identified the causative agent, which they called “mucidone.” They classified this compound as a metabolite of actinomycetes; so it was probably geosmin. Their work using chlorine and activated carbon indicated that oxidation by chlorine is relatively ineffective, but that 25 mg/l of powdered activated carbon removed it to an acceptable level. They also concluded that to be effective, an oxidant would have to break the carbon-carbon double bond of the taste and odor compound produced by actinomycetes.

The success of heavy doses of chlorine in the raw water for the correction and control of tastes and odors that presumably originated in algae and/or seasonal reservoir conditions is well documented¹⁸⁶⁻¹⁹⁰ in literature: Offensive

tastes caused by *Synura*, *Synedra*, *Dinobryon*, *Asterionella*, *Anabena*, *Ceratium*, and *Anacystis* blooms have been found to be controlled by prechlorination that produces a free chlorine residual of 1–5 mg/l. It should be noted, however, that prechlorination can also aggravate taste and odor problems by lysing algae and releasing their odorous metabolites when they would otherwise have been coagulated and removed by sedimentation.^{174,191}

Many utilities have had to discontinue prechlorination to achieve compliance with the TTHM Rule and the Stage 1 and Stage 2 DBPR. Also, chlorination of algae-laden waters produces TTHMs,^{192,193} and this has resulted in many utilities abandoning prechlorination, even at low dosages. Because most of the tastes odors that are caused by algae are not effectively controlled by low dosages of chlorine, such as those used for posttreatment primary disinfection, other treatment processes (activated carbon, ozone, or advanced oxidation with hydrogen peroxide and irradiation by UV light) have been installed for taste and odor control.

Synthetic Sources of Tastes and Odors

Among the worst tastes and odors are those that are produced in the manufacture of chemicals, dyes, pharmaceuticals, coke (quench water), ammonia recovery, wood oil, phenols, cresols, petroleum products, textiles, and paper products. Of the chemicals that contribute to off-flavor in potable water, those that have historically received the most attention are phenols because of the intensification of the off-tastes by low doses of chlorine. Although significant progress has been made by the federal and state agencies to control the discharge or release of these synthetic chemicals, water industry professionals should be aware that microquantities of chemicals that can produce objectionable tastes and odors when chlorinated in water supplies¹⁹⁴ (Table 4.10). The reaction between chlorine and phenolic compounds has been thoroughly investigated^{195–198} because it imparts an extremely objectionable medicinal taste to the water.

In some instances, low dosages of chlorine cause an increase in the taste and odor intensity of the water, but higher chlorine dosages result in a decrease in the taste and odor. Many researchers^{168,196,199–201} have observed this trend, and showed that the taste intensity could be removed completely with very high dosages of chlorine. Research using gas chromatography by Burtshell et al.¹⁹⁷ indicated that the phenolic compound that was always present when a phenolic taste was detected was 2,6-dichlorophenol.

To eliminate phenolic tastes from water, the treatment system must achieve a stable free chlorine residual and be allowed sufficient time for a complete reaction. Like disinfection efficiency, these reactions are affected by pH, temperature, and contact time. The colder the water, the longer the contact time and the more chlorine is required.

Because of the taste and odor intensity problem when applying low dosages of chlorine, and the high chlorine dose requirement to completely remove

TABLE 4.10. Chemicals That Produce Tastes and Odors²⁰⁸

Chemical	Average	Range (mg/l)
Acetic acid	24.4	5.07–81.2
Acetophenone	0.17	0.0039–2.02
<i>n</i> -Amyl acetate	0.08	0.0017–0.86
Aniline	70.1	2.0–128
Benzene	31.3	0.84–53.6
<i>n</i> -Butanol	2.5	0.012–25.3
<i>p</i> -Chlorophenol	1.24	0.02–20.4
<i>o</i> -Cresol	0.65	0.016–4.1
<i>m</i> -Cresol	0.68	0.016–4.0
Dichloroisopropylether	0.32	0.017–1.1
2,4-Dichlorophenol	0.21	0.02–1.35
Ethylacrylate	0.0067	0.0018–0.0141
2-Mercaptoethanol	0.64	0.07–1.1
Methylamine	3.33	0.65–5.23
Methylethylpyridine	0.05	0.0017–0.225
β -Naphthol	1.29	0.01–11.4
Phenol	5.9	0.016–16.7
Pyridine	0.82	0.007–7.7
Quinoline	0.71	0.016–16.7
Trimethylamine	1.7	0.04–7.15
<i>n</i> -Butyl mercaptan	0.006	0.001–0.06

phenolic and other industrial tastes and odors, it is recommended to investigate methods of removing the industrial compounds, or chemicals, during treatment, prior to chlorine addition. Studies by Ryckman and Grigoropolous¹⁹⁸ and Erdei¹⁸⁰ indicate the necessity to remove ammonia, organic nitrogen, phenolic compounds, and other organic extracts from drinking water because they interfere with the chlorination process and make it difficult to produce palatable water. Other processes such as activated carbon may be needed to sufficiently treat these waters to acceptable quality.

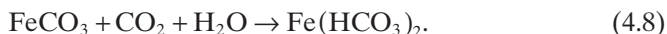
Taste and Odor of Chlorine

Chlorine and chloramines impart a taste to drinking water. This is discussed in Chapter 2.

Iron and Manganese

Both iron and manganese cause serious problems in potable and industrial water systems and both are relatively abundant in the earth's crust.²⁰² Because these problems are common, it is pertinent to discuss the occurrence of these elements in water supplies, their significance, and the role of chlorination in controlling iron and manganese.

Iron exists mainly as insoluble ferric oxide, and manganese as manganese dioxide; and both may be present in a variety of sulfide forms in anoxic environments. Iron also occurs as ferrous carbonate (siderite), which is slightly soluble. As groundwaters usually contain substantial amounts of carbon dioxide (30–50 mg/l), appreciable amounts of ferrous carbonate may be dissolved to form more soluble ferrous bicarbonate as follows:



The predominant forms are ferrous (Fe^{2+}) and manganous (Mn^{2+}), and colloidal and complexed forms, especially organic iron, may also be present in significant amounts. Insoluble ferric compounds will dissolve into solution only under reducing conditions, such as in the absence of oxygen. This is true also for the oxidized compounds of manganese.

The occurrence of iron and manganese in water supplies is usually limited to well water and impounded surface supplies. Both can also be released from sediments in reservoirs or lakes during seasonal turnovers. Acidic mine drainage waters, where the pH is lower than 5, contain significant quantities of both iron and manganese compounds in solution.

Biological activity appears to be a powerful factor in the dissolving of iron and manganese,^{203,204} and anaerobic conditions must prevail for appreciable amounts of iron and manganese to enter the water supply.²⁰⁵

Even flowing water that does not normally contain iron or manganese is likely to contain them when it is impounded. Sources of iron and manganese in impounded waters include the sediment, vegetation, subsurface rocks and gravel, as well as runoff. Also recognize that if a WTP recycles any flow, including treated or untreated filter backwash, possibly through an on-site impoundment, there is the risk of recycling iron and manganese into the treatment facility.

The natural seasonal cycles of a reservoir also impact the iron and manganese concentration of source water. Decomposition of organic matter in the lower strata (the hypolimnion) of a reservoir eliminates dissolved oxygen and produces carbon dioxide, enhancing the solubility of the iron and manganese compounds in the flooded soil and rocks. These soluble minerals are then mixed into the water column during the seasonal turnover. During mixing, some iron and manganese can be oxidized and precipitated or coprecipitated, and will eventually sink to the lower layers of the reservoirs, and dissolve again in the absence of oxygen. Thus, when the lake is stratified, water at the surface of a reservoir is most likely to contain low concentrations of iron and manganese, and the hypolimnion is likely to contain higher concentrations.

Raw water intake ports in impoundments should be located at several depths. Withdrawal should be made at the upper levels when iron and manganese concentrations are high at lower depths and at the deeper levels when algae proliferate near the surface. Utility staff should recognize that high concentrations of iron and manganese may be present in the hypolimnion at the same time as an algal bloom in the epilimnion. Water from the hypolim-

nion may also have high concentrations of sulfide or ammonia, but the epilimnion may also have higher concentrations of total coliforms, especially if the reservoir is used for recreation.

The concentrations of iron and manganese are typically less than a few milligrams per liter, but much higher concentrations have been known to occur. For example, manganese has been found at concentrations of 20 mg/l or higher in the Tennessee Valley Authority lakes.²⁰⁴ The time for the appearance of significant amounts of iron and/or manganese in man-made lakes varies greatly with the location and conditions. Elevated levels of iron and manganese are frequently present in alluvial aquifers. Relatively high concentrations may initially be present in water drawn from wells or infiltration galleries used for riverbank filtration; but the levels will gradually decline in proportion to the amount of oxygenated water being drawn in through the riverbank.

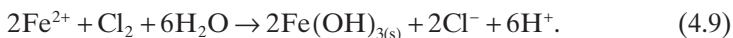
Although there is no evidence that humans suffer from drinking water containing iron or manganese, these substances have presented challenges to the water industry. Waters containing ferrous iron stain everything with which they come in contact a yellowish to reddish brown. Manganese-bearing waters that are free of iron will produce black stains. Waters containing ferrous iron usually contain some manganese as well, a combination that produces dark brown to black stains. Depending on their concentration, consumers' complaints will start first with staining and streaking problems in the laundering process; next, there will be red water or dirty water; finally, there will be large visible chunks of material that have sloughed off the distribution system pipes. Most industrial processes, such as those in the textile, pulp and paper, and beverage industries, cannot tolerate iron or manganese in the water.

In addition to their physical presence, both iron and manganese promote the growth of *Crenothrix*, a filamentous organism in the distribution system. It forms heavy, gelatinous, stringy masses that slough from pipe surfaces, causing a variety of problems to both domestic and industrial consumers. In addition to degradation of esthetic quality of the water, they also impair the hydraulic capacity of the system.

The USEPA has secondary MCLs for iron and manganese at 0.3 and 0.05 mg/l, respectively. Manganese at concentrations above 0.02 mg/l is likely to cause problems in the distribution system (especially chlorinated swimming pools) and will lead to customer complaints. Many waterworks professionals believe that all public water supplies should be free of manganese, and most domestic systems tolerate concentrations up to 0.01 mg/l.

Oxidation of Iron

Chlorine, either free or combined, reacts to oxidize ferrous iron as follows:



The soluble ferrous bicarbonate ($\text{Fe}(\text{HCO}_3)_2$) is oxidized to ferric hydroxide ($\text{Fe}(\text{OH})_3$), which can be removed by sedimentation and filtration. Although

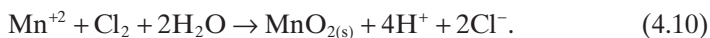
this reaction occurs over a wide range of pH values (from 4 to 10), the optimum pH is 7.0.²⁰⁶ The reaction consumes 0.9 mg/l alkalinity as calcium carbonate (CaCO₃) for each milligram per liter of iron (as Fe) that is oxidized.

If the iron present is in a complexed organic form, free residual chlorine is more effective at oxidizing it than combined chlorine. A dosage of chlorine in excess of the stoichiometric dose will be needed to oxidize the iron in the presence of organic carbon. The amount depends on the pH and the type and concentration of organics.

Preaeration of raw water will not only oxidize some of the iron but will also strip some carbon dioxide, causing the pH to rise, which is beneficial for further oxidation of iron by chlorine. Although chlorine is usually applied after aeration, it is nearly always desirable to prechlorinate to keep *Crenothrix* organisms from growing in the aerator. *Crenothrix* organisms can proliferate in waters containing as little as 0.1 mg/l iron.

Oxidation of Manganese

Chlorine will oxidize soluble (manganous) manganese to the insoluble (manganic) form as follows:



The stoichiometric chlorine requirement for manganese oxidation is 1.3 mg/l chlorine for each milligram per liter of manganese as Mn.^{206,207} For each part of manganese oxidized, 3.4 mg/l alkalinity as CaCO₃ is consumed. In practice, a chlorine dose much higher than the stoichiometric level is often required to satisfy any chlorine demand by other constituents (iron, organics).²⁰⁸

Oxidation of manganese by free chlorine can require long reaction times (longer than an hour at nonalkaline pH,²²² and the reaction is impaired by low temperatures. In view of the concern over trihalomethane formation, the use of chlorine for oxidation of manganese in raw water should be carefully compared against the use of other strong oxidants such as chlorine dioxide and potassium permanganate.

Chlorine reacts with manganese to form manganese dioxide (MnO₂), which is notorious for forming intermediate colloidal forms rather than particulate forms. Manganese dioxide can still be removed on the filter beds, but the mechanism of removal depends on the form of manganese. Because manganese is typically oxidized into colloidal forms that can pass through conventional filter media, it is generally recommended to operate with a chlorine residual over the filter media, which oxidizes any adsorbed MnO₂ deposits and acts as a catalyst to continually adsorb MnO₂ from the water.²⁰⁹

Manganese in carrier water can also plague chemical feed systems. Manganese precipitates readily at pH 2 in heavy concentrations of chlorine, as evidenced by the troublesome deposits of manganese in chlorination equipment.

Iron and manganese problems are typical of small-community water supplies or individual wells. Most of such wells contain *Crenothrix* and are periodically treated with chlorine to control their growth. Following chlorination, however, iron and manganese will be oxidized, which results in the deposition of iron particles and manganese in the dead ends of the distribution system. This problem can be overcome by adding about 2 mg/l of a sequestering agent, such as sodium hexametaphosphate with the chlorine in the well. This procedure has been successful in waters with iron concentrations as high as 0.6–0.8 mg/l; however, there are some instances where precipitated iron will need to be removed by a conventional treatment process.

Coagulation Aid

Prechlorination to produce a free residual is nearly always effective in improving coagulation or reducing the coagulant dose, or both.^{210,211} It is not clearly understood how chlorine acts as a coagulant aid, although it is probably through its oxidizing effect on organic matter. Although prechlorination has been practiced widely in the past, the regulations limiting trihalomethanes and haloacetic acids, both of which are by-products of the reaction between chlorine and organics, have caused many utilities to stop using it.

Historically, chlorine has also been used in some color and turbidity removal processes. Chlorine can be added to ferrous sulfate in the form of either a solution of pickle liquor or copperas. Chlorine converts the ferrous ion to ferric, which hydrolyzes to form ferric hydroxide, a fluffy gelatinous floc. Copperas is a granular, free-flowing material, and is easily handled in a dry chemical feeder. The chlorine is added downstream from the solution chamber outlet of the copperas feeder. This method has a special application where the optimum pH for coagulation is in the range of 8–9. One part of chlorine is required to react with 7.8 parts copperas to convert all of the ferrous to ferric ion as follows:



Chlorinated copperas has been known to form a tough, rapidly settling floc.²¹² Chlorinated ferrous sulfate is not commonly used for surface water treatment due to concerns with chlorinating DBP precursors in the treatment plant.

Filtration Aid

In the years following implementation of chlorination and filtration of water supplies, there were many differing views on the impact of chlorine on the performance of media filters. At one time, it was thought that the efficiency of filtration depended in part on the establishment of a thin film of organic material on the sand grains, and that a chlorine residual would destroy this

organic film, thereby decreasing the efficiency of the filter.²¹³ However, later research has shown that chlorination or prechlorination can extend the filter run time and protect against mudball formation. A chlorine residual also prevents growths that contribute to slime buildup on the filter media. The distinction between a prechlorinated filter and a chlorinated filter is that a prechlorinated filter may not have a chlorine residual throughout the depth of the filter bed, whereas a chlorinated filter will have a detectable residual in the water leaving the filter.

Early evidence of the benefits of prechlorination was reported by Baumann et al.²¹⁴ The authors indicated that a prechlorinated filter operated considerably longer than a control filter, which was not prechlorinated. Other observations included that (a) prechlorination reduced the depth of suspended solids into the filter sand; (b) less sand was removed during the cleaning process; (c) oxidizable tastes and odors were destroyed; (d) oxidizable organic matter was confined to the sand surface; and (e) the bacterial quality of the filter effluent was considerably better than that of the unchlorinated control filter effluent.

Free chlorine is an aid to both coagulation and filtration. In the past, prechlorination was used extensively; however, concerns about DBP formation have caused its use to decline.

Applying chlorine to a filter bed can minimize microbial growth, which can shorten filter runs and cause the formation of mudballs. These organic growths can create an environment where nitrifying bacteria, such as *Pseudomonas*, can convert the available nitrogen to nitrite. The nitrite may contribute to proliferation of other bacteria in the filter bed and degrade the quality of the filtered water. This can be prevented by dosing the filter with free chlorine. Combined chlorine will not oxidize the nitrite to nitrate; only free chlorine (i.e., HOCl or OCl⁻) can do this.

A filter fouled by microbial growths can often be restored by chlorination. In the fourth edition of this handbook, White outlined a procedure for restoring a filter by chlorination. At first, the residual in the filtered water will be a combined residual (predominantly monochloramine). This suggests the presence of amounts of ammonia, possibly organic N, in the filter media. As the chlorine dose is gradually increased, the organic material will become more and more oxidized; and over a short period (possibly 1 or 2 weeks), a trace of free chlorine residual may begin to appear in the filtered water. When the free chlorine content is 80%–85% of the total residual, it may be assumed that the filter is relatively free from organic growth. Backwashing will become more effective, filter runs will be considerably longer, and the bacterial quality will return to an acceptable level. Filter media that cannot be cleaned by chlorination should be discarded.

Chlorine is often applied to filters in an effort to improve their performance, but if the problem persists, the problem could be that the diatom concentration in the feed water is limiting filter productivity. Diatoms, such as *Asterionella*, *Fragilaria*, *Tabellaria*, and *Synedra*, which are present during all seasons of the year, are the most serious filter-clogging algae. Filter run

times can be dramatically reduced by an influx of diatoms into the water supply, as evidenced during a diatom proliferation in Chicago, where filter run times decreased from 41 h to 4–5 h.²¹⁵ When diatoms are the cause of filter clogging, free chlorine residual usually does not improve filtration.

Chlorination of other types of filter-clogging algae can help prevent operating problems. If filter-clogging blue-green algae such as *Anacystis*, *Rivularia*, *Anabena*, and *Oscillatoria* invade a filter, they form a loose, slimy layer over the sand grains, which interfere with the flow through the filter. These types of algae can be controlled by maintaining free chlorine residual.

Chlorinating algae-laden waters can result in higher formation of DBPs,^{192,193} and can cause the algae to release more taste- and odor-causing compounds as a result of environmental stress (i.e., lysing of the cells).

Control of Mollusca in Seawater

Members of the family Mollusca, which includes snails and other single-shelled Gastropoda and the clams, oysters, mussels, and other bivalves, are the most troublesome of the seawater-fouling organisms.^{216,217} The most common of these is the edible black mussel *Mytilus edulis*, which is found throughout the world and has been responsible for intake fouling problems in the British Isles, in the North Atlantic, and on the western coast of the United States.

The earliest known experiments to control marine growths were conducted in 1919 for the Portobello Generating Station in Edinburgh, Scotland. The first work in this field in the United States was done about 1926 by W.J. O'Connell Jr.²¹⁸ Control of marine growths was started in 1929 at the Northpoint station of the Long Island Lighting Company. Early plant-scale work was done at the Lynn Gas and Electric Company plant in Massachusetts.²¹⁹

The black mussel (Fig. 4.4) varies in size, but has a maximum length of 4 in. Its life cycle is typical of many other fouling invertebrates: within 5 h of egg fertilization, the embryo is completely free-swimming in seawater (at 68°F). At the end of 48 h, the organism has attached to some stable, hard material, and the shell begins to develop. At the end of 69 h, the fleshy portions of the



Figure 4.4. The black mussel.

organism are completely enclosed by the elementary single shell, and the organism is capable of rapid swimming and is able to crawl on solid surfaces, vertical walls, and the tops of horizontal tunnels. Some time later, the true bivalve shell develops.

The black mussel, which is now attached by long, clear threads (i.e., byssus threads), is capable of motion or migration. Under conditions of poor feeding, inadequate oxygen supply, or mechanical or chemical irritation develop, the organism will break the byssus threads from their point of attachment, and crawl by a "foot," which projects out near the hinge. This is similar to the locomotion of a snail. The mussel can also move by secreting new byssus threads and breaking off older ones.

Under normal conditions, the adult mussel will leave the shell open about 15–20° about three-quarters of the time. Water containing food is forced through the digestive tract, and any solid or suspended matter is deposited on the mucous surfaces. The usable material is then digested, and the rest is rejected. If any unfavorable conditions develop, or if anything disturbs the organism, the shell will close in a fraction of a second, and only after an extended period will the mussel open slightly and feed cautiously. This ability to close the shell so quickly and so tightly makes adults difficult to kill.

The American oyster is a common member of Mollusca and is responsible for severe fouling of power plant inlets on the South Atlantic and in the Gulf Coast states. It is easily recognized by its rough shell and white interior. Its life cycle is similar to that of the edible mussel.

Hard-shelled organisms are most effectively controlled by continuous chlorination.²²⁰ Maintaining a free residual of 0.5–1.0 mg/l throughout the intake pipe will usually prevent their growth and attachment on the pipe walls. The chlorine dosages and contact time are site specific. The chlorine dosage will vary seasonally, especially in areas of wide seasonal temperature variations.

Zebra Mussels

Before the invasion of North America waterways by the zebra mussels, the main troublesome organisms were the black mussels and barnacles that infest intake systems. The intake systems most affected by them were at steam-powered electric power generating stations. The arrival of the zebra mussel led to additional research to determine whether chlorine was effective in controlling them on intake structures.

The invasion of the zebra mussel into North American freshwaters is a recent phenomenon.²²¹ Their source is believed to be the Caspian Sea, from which they have gradually spread over the last 150 years (S.G. Moore, pers. comm.) to European freshwater harbors, and now the United States. With lengths less than 1 in., the zebra mussel, *Dreissina polymorpha*, is smaller than the black mussel, and has a distinctive striped pattern on the shells.

The zebra mussel is regarded as the most potentially damaging natural intrusion into the United States. In Europe, polluted freshwater is believed to

have initially prevented the survival, but with the recent environmental cleanup throughout Europe, the zebra mussels found an environment in which to thrive. Populations of 100,000 zebra mussels per square foot are not unusual, and this far exceeds the typical density of native black mussels in the United States.

It is believed that in 1985 or 1986, a ship from Europe discharged ballast water that contained young zebra mussels (veligers) between Detroit and Lake Huron. Unfortunately, the freshwater ports in the Great Lakes have provided the zebra mussels with a hospitable environment, and the population is now established and expanding. Some experts believe the population in the United States of zebra mussels could increase 10-fold each year, and that zebra mussels could eventually inhabit about two-thirds of U.S. waters. In parts of Lake Erie, zebra mussels have been found in densities as great as 70,000 per square foot.

Damage to U.S. water systems by these organisms has already occurred. With females producing over 30,000 eggs per year, their rapid growth, their ability to attach to almost any clean hard surface, and their tendency to form large clumps, zebra mussels can easily clog submerged pipe intake lines. Water intakes are popular spots for the zebra mussels because of the continuous flow containing algae, phytoplankton, and other organisms that serve as a food source.

A plan to control the zebra mussels should be prepared before any are detected. Once they are detected, control measures should be implemented immediately. As with the black mussel, a continuous dose of chlorine has been found to be effective for minimizing zebra mussel attachment onto intake screens and pipes. With concerns about DBP formation when applying chlorine to feed water, alternative oxidants have been evaluated for zebra mussel control. Combined chlorine is relatively ineffective for zebra mussel control, but chlorine dioxide has been shown to effectively control zebra mussels at water plant intakes.

One of the most important components of the chlorination system is the diffuser. A variety of designs are available from the electric power industry. The theory and the practice of diffuser design are covered in Chapters 8 and 9.

Model studies conducted at Worcester Polytechnic Institute found the diffusers shown on Figures 4.5 and 4.6 to be the most satisfactory.²¹⁷

Some power companies have installed duplicate intake pipes so that one can be taken out of service for cleaning or inspection.

Quagga Mussels

Quagga mussels, in the same genus as the zebra mussel, *Dreissena*, are also spreading across the United States and creating problems for raw water intakes and submerged infrastructure. After being first discovered in the Great Lakes in the late 1980s, quagga mussels have spread westward, with sightings in California in the autumn of 2007.²²² They have been found in the Missouri,

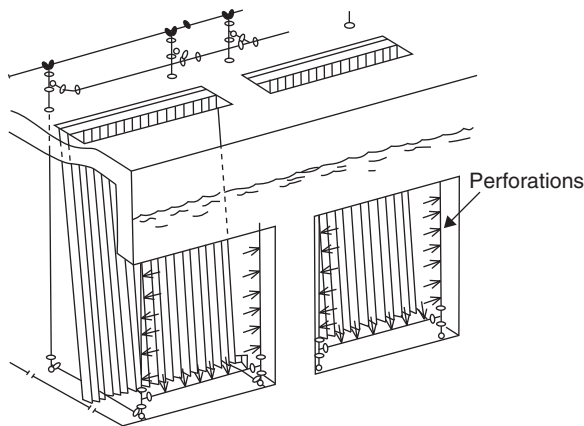


Figure 4.5. Perforated chlorine solution diffuser for installation ahead of bar racks.

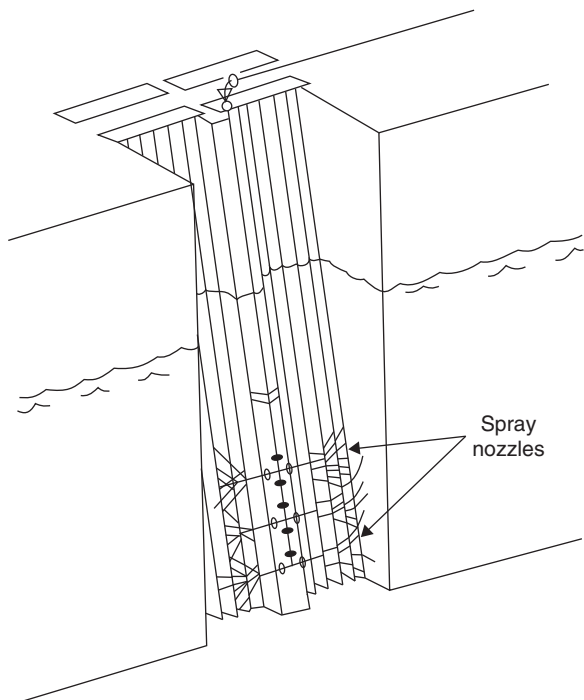


Figure 4.6. Chlorine solution diffuser with spray nozzles.

Arkansas, and Mississippi rivers, as well as in the St. Lawrence Seaway. Chlorine can be used to control quagga mussels.²²¹

Aquifer Recharge

Reclaimed waters are frequently used to replenish underground aquifers in areas that are short of freshwater. Injection wells are also used for (a) maintaining oil well production (S.G. Moore, pers. comm.), (b) prevention of seawater intrusion into freshwater aquifers, and (c) prevention of land subsidence as a result of withdrawal of oil from underground deposits.

In the 1950s and 1960s, the consensus^{223,224} was that the water injected into underground aquifers should be sterilized, or free of bacteria, to prevent the growth of filamentous organisms that might plug the aquifers. The free chlorine was also expected to inhibit the growth of native bacteria that might thrive on the oxygen and nutrients added in the injected water. Since implementation of the Clean Water Act, more treatment and disinfection requirements have been established by the USEPA and state regulatory agencies for aquifer recharge. For example, in Florida, where aquifer recharge has been practiced extensively, there are water quality and disinfection requirements for any water that is used for groundwater recharge.²²⁵ Each state will have requirements for the quality of water entering the aquifer.

Some of the concerns with chlorination and aquifer recharge include introduction of DBPs, contaminants, pathogenic microorganisms, especially viruses, into a groundwater that might reach a drinking water well supply. This would be especially concerning for private wells that are used as potable water but are not disinfected. There are also concerns about changing the chemical stability of the aquifer after recharge of chlorinated water. Changes in the reduction/oxidation character of the aquifer could lead to the mobilization of arsenic or other metal ions and precipitation of solids, which would impede water flow.

Hydrogen Sulfide Control

Hydrogen sulfide (H_2S) is one of the most troublesome compounds in a potable water supply. With H_2S in the source water, it is difficult to produce a potable supply that is free of taste and odor. Not only the treatment process but also the distribution system and the consumers' hot water systems must be monitored for H_2S .

H_2S in the water will turn silverware black, make bathing in tubs or showers unpleasant, and stain plumbing fixtures and laundry. H_2S occurs mainly in well waters but can enter surface supplies through groundwater intrusion. It can be present in hypolimnetic water. Seawater can also contain some H_2S .

Sulfides in well water are produced through chemical and bacterial reactions under anaerobic conditions. Sulfate can be reduced to sulfides by organic

matter under anaerobic conditions, and metallic sulfides can be converted to H_2S by the action of carbonic acid.

Sulfate-reducing bacteria (*Desulfovibrio desulfuricans*) convert sulfates and other sulfur compounds to H_2S . They function at pH 5.5–8.5 and are found in water at temperatures of 0–100°C, especially in the range of 24–42°C.²²⁶

Sulfide-oxidizing bacteria (*Beggiatoa* and *Thiobacillus*) are also present in waters with H_2S . *Beggiatoa* are filamentous, white sulfur bacteria that obtain energy for growth by oxidizing sulfide to colloidal sulfur, which is then stored in their cells. H_2S at concentrations as low as 0.2 mg/l will promote the growth of *Beggiatoa*.²²⁶

Hydrogen sulfide is a flammable and extremely poisonous gas. Exposure for even 30 min or less to H_2S at concentrations as low as 0.1% by volume of air may be fatal to humans. The gas is highly soluble in water to the extent of 4000 mg/l at 20°C and 1 atm. The minimum detectable concentration by taste in water is 0.05 mg/l.²²⁶

In aqueous solutions, it hydrolyzes as follows:



The bisulfide ion (HS^- ; hydrosulfide) further dissociates as follows:



At 18°C, the acid dissociation constant for Equation (4.12) is

$$K_h = 9.1 \times 10^{-8} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}, \quad (4.14)$$

and for Equation (4.13):

$$K_h = 1.2 \times 10^{-15} = \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]}. \quad (4.15)$$

Figure 4.7 illustrates the distribution of H_2S , HS^- , and sulfide (S^{2-}) as a function of pH. At pH 7, H_2S constitutes about 50% of the total dissolved sulfide, whereas at pH 5, it is practically 100% of the total. At pH 9, however, it is nearly all hydrosulfide ion. Figure 4.7 shows that the existence of H_2S in sulfur-bearing waters is pH dependent, which has been well documented.^{203,227–229}

Whenever the equilibrium between the hydrosulfide ion and the hydrogen sulfide in solution is upset, as when H_2S is removed by oxidation, the shift will be to form more H_2S from the remaining dissolved sulfides to reestablish the equilibrium. The stored sulfur gradually disappears by metabolic action, being itself oxidized to sulfate to yield more energy. H_2S can be removed from water by aeration, chlorination, coagulation, filtration, and softening.

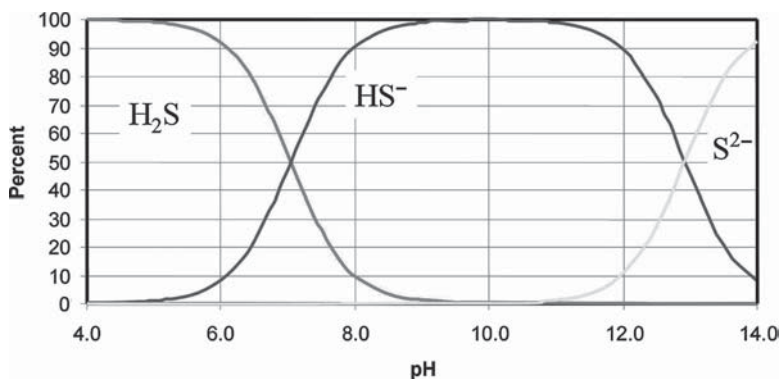
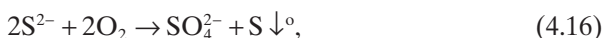


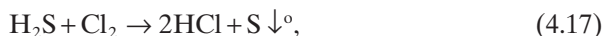
Figure 4.7. Effect of pH on hydrogen sulfide–sulfide equilibrium.

The chemistry of the oxidation and removal of H_2S is extremely complex. Oxidation of H_2S forms elemental sulfur, sulfate, or both, as follows:

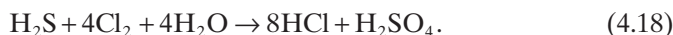
Aeration or oxidation by dissolved oxygen in the water:



and chlorination:



and



Theoretically, Equation (4.17) requires 2.1 mg/l chlorine for each milligram per liter of H_2S , and Equation (4.18) requires 8.5 mg/l for each milligram per liter of H_2S . This reaction was amply demonstrated in field experiments by Powell.²²⁹

The reactions represented by these equations suggest that if enough chlorine is added to satisfy the natural chlorine demand of the water and to react with the H_2S , then free sulfur will be formed (as shown by Eq. 4.17). If more chlorine is added to satisfy the stoichiometric requirements of Equation (4.18), then all the H_2S would be converted to sulfates. However, this is not the case.

As reported by Choppin and Faulkenberry,²³⁰ oxidation of the alkaline sulfides is not simple and may yield polysulfides, sulfites, and thiosulfates in addition to elemental sulfur and sulfates. Hot water supplied from systems that provide treatment for H_2S removal may still have a sulfurous odor, even though the sulfur is not present in the form of H_2S . Monscivitz and Ainsworth²³¹ believe that the sulfurous odor is caused by polysulfides (HS_n^-), which will eventually oxidize to sulfates in the presence of dissolved oxygen; however,

in the absence of dissolved DO as in the dead ends of distribution systems, the polysulfides may be converted back to H_2S .

When chlorine in any amount is added to sulfur-bearing water, colloidal free sulfur will be formed. The free sulfur yields a milky blue turbidity (the Tyndall effect), which can be removed by filtration. Other reactions will produce polysulfides, which must be treated to prevent sulfurous odors in finished water. Monsevit and Ainsworth²³¹ suggest conversion of colloidal sulfur and the remaining polysulfides to sulfates by first adding sulfite (SO_3^-), which forms thiosulfate (S_2O_3^-), followed by conversion of thiosulfate to sulfate through chlorination. The reactions are as follows:



The reaction of Equation (4.19) is very rapid. The formation of tetrathionate ($\text{S}_4\text{O}_6^{2-}$) is not significant, as it will be converted to sulfate within a short time, with no contribution to any threshold odor. The sulfite ion may be added as sulfur dioxide in an aqueous solution or as sodium metabisulfite. This reaction, taken to completion, is recognized as the typical dechlorination reaction.

Thus, complete removal of H_2S can best be accomplished by oxidation with chlorine, followed by conversion of the resulting colloidal sulfur and polysulfides by metabisulfite or sulfur dioxide to thiosulfates, and then conversion of thiosulfates to sulfate by rechlorination. Above pH 9.0, polysulfides do not form, which is probably one reason why lime-softened sulfur-bearing waters will not produce threshold odors.

Probably, the most important factor in H_2S removal is contact time. Given adequate time and an effective oxidizing agent, all dissolved sulfides can be converted to sulfates. With a raw water concentration of 5 mg/l H_2S , aeration, followed by coagulation and filtration, coupled with free residual chlorine of up to 0.35 mg/l, complete removal of H_2S can be obtained.²³²

Derby²³³ reported in 1928 on the satisfactory removal up to 7 mg/l of H_2S by conventional lime softening and chlorination. Concentrations as high as 32 mg/l have been successfully removed by pre- and postchlorination, coagulation, and filtration.²³⁴

Water supplies that contain H_2S or sulfides may cause sulfur bacteria to grow in the distribution system. Although the forms of sulfur-oxidizing bacteria in an aerated environment provide benefits by converting the sulfide ion to sulfates, they may proliferate in the distribution system, slough off into dead ends, and ultimately contribute sulfur compounds that under anaerobic conditions will restart the H_2S production cycle. It is important to maintain chlorine residual in the distribution system as protection against sulfur bacteria.

Color Removal

Historically, chlorine has been shown to lower the color of waters where color removal by coagulation and filtration has failed. Adequate free chlorine residual produces a polished, sparkling look to the water by bleaching the organic matter it contains. Other methods of color removal are typically used since the promulgation of the initial THM regulation and DBPR because chlorine reacts with color-causing organics to produce DBPs, which could easily exceed allowed concentrations.

Color removal by chlorine is most effective at a pH between 4.0 and 6.8. Highly colored, low-turbidity waters are usually either naturally acidic or so lightly buffered that the application of chlorine may be sufficient to reduce the pH to the optimal range. In these cases, the lower pH may cause the color to disappear, and for such waters it should be verified that the color does not return when the pH is increased for corrosion control. This can be predicted by a simple laboratory procedure.

Color removal by free residual chlorine is usually instantaneous, and temperature does impact the reaction significantly. The optimum dosage is site specific, and the amount of color removal will vary with local conditions.²⁰⁶

Where color is accompanied by turbidity, and coagulation is practiced, prechlorination to produce a free residual will oxidize part of the color and act as a coagulant aid. Prechlorination is not always a feasible option, and other color-reducing mechanisms, such as improved coagulation or alternative oxidants, may be needed.

Desalination

Seawater contains a variety of organisms, which must be removed and/or inactivated before using it as feedwater to desalination technologies, such as RO and thermal or evaporative distillation processes, and chlorine is often used as a predisinfectant. Chlorine can be fed continuously or intermittently, as in cooling water treatment, to combat a variety of problems (i.e., mussel fouling of intakes, pathogen inactivation, control of slime growths). If prechlorination is used at RO plants, the free chlorine residual must be removed ahead of the membranes because free chlorine reacts with many membrane materials and will eventually degrade them.

Some seawaters contain H_2S , which may be a by-product of decaying vegetation. Hydrogen sulfide in an evaporative desalination plant can cause severe corrosion to almost any metal. Sometimes the concentration of H_2S varies over a wide range, which makes it difficult to control. Chlorination of the raw water is typically effective, unless the H_2S concentration is higher than 5.0 mg/l, in which case, chlorination combined with air stripping may be more economical.

The desalinated water should be chlorinated like any potable surface water, even though evaporation has a pasteurizing effect and RO membranes remove microbes. In some facilities, finished water may be blended with raw

seawater (either during treatment or when the plant is shut down), thus most systems include postchlorination for adequate disinfection prior to distribution.

Reflecting Pools

Water fountain displays used to enhance the appearance of public buildings and recreation centers must be treated to prevent the growth of unsightly algae; however, the treatment chemical must not impart any offensive chemical odors to the water. The water displays usually include cascades that provide a certain amount of aeration. It is important to maintain a free chlorine residual in the system and to prevent the formation of chloramines because chloramines, particularly dichloramine and nitrogen trichloride, cause offensive odors, especially when aerated.

The best approach is to maintain continuously a free chlorine residual of 0.75–1.25 mg/l, and to never use an algicide that contains nitrogen compounds. With an adequate free chlorine residual, algicides will not be needed. The chlorination equipment, regardless of the type, must be controlled by an amperometric residual analyzer that is calibrated for a free chlorine residual to assist in preventing the formation of chloramines.

All recirculated waters will need continuous addition of caustic, sodium carbonate, or sodium bicarbonate to maintain the elevated pH when using chlorine gas, and most waters will require these chemicals even if hypochlorite is used because hypochlorite may not raise the pH to 9, except in water softened by the lime soda process.

Restoration of Wells

Most wells lose efficiency with time, and as demand for water continues to increase, it is just as important to maintain the efficiency of existing wells as it is to drill new ones. The decline in well production has several causes, such as lowering of the groundwater table or static water level; worn, corroded, or encrusted pumps; and plugging of the aquifer (including the gravel pack and screen). Plugging of the aquifer is categorized as any of the following: (a) mechanical plugging by natural sands, silts, or clays; (b) mineral plugging by the deposition of mineral scales such as iron oxide and calcium carbonate; or (c) bacterial plugging by the bacteria themselves as well as the polysaccharide slime, or biofilm, that they produce. These plugging mechanisms occur primarily within the borehole of the well; however, the biofilm can extend beyond the borehole into the natural formation of the aquifer.

Mechanical plugging generally occurs from overpumping the well or not having properly developed the well in the construction process. Mineral plugging is influenced by groundwater chemistry and biology. The impact of biology stems from the biofilm, which can convert dissolved substances into less soluble forms (e.g., Fe^{+2} to Fe^{+3}) and also provide a “sticky” surface for

mineral accumulation. The potential for mineral deposition is well understood, and predictions can be made from such measurements and calculations, such as the Saturation Index and ORP. Bacterial plugging is the most difficult mechanism of well fouling to predict and control. Even the construction activities of a well provide opportunities for naturally occurring microorganisms to proliferate.

Although there are thousands of different bacteria that inhabit well systems, not all cause biofouling that result in well blockage. The groups of bacteria that typically cause problems are (a) iron-related bacteria, (b) slime-forming bacteria, and (c) sulfate-reducing bacteria. In addition to these groups of bacteria that plug wells and reduce production, there is the coliform group that is used as a surrogate measure for the presence or absence of pathogenic organisms, which are a threat to human health. Well rehabilitation procedures must address the removal of all types of bacteria.

In the current groundwater industry, there are many technologies used to restore well production. Many times, multiple processes are used to more effectively clean and disinfect the well system. A well that has mechanical plugging is usually treated with physical surging and swabbing. This procedure is also referred to as well development or redevelopment. Chemicals such as phosphates and dispersion polymers can also be beneficial in mobilizing these plugging materials for easy removal from the well.

Mineral and bacterial plugging can be treated with both chemical and physical methods. Many types of acids are used to dissolve both the mineral scale and organic biofilms in a well. Additionally, there are additives to acids and chlorine to help improve cleaning and disinfection.

The typical mineral acids used for these procedures are muriatic, sulfamic, or phosphoric, sometimes with organic acids, such as hydroxyacetic, acetic, or citric acid. The concentration of acid that is used in well rehabilitation ranges from 5% to 15%. The concentration depends on the well volume and the cause of well plugging, but a general rule of thumb is to target a pH of <3 (R. Miller, pers. comm.). The chlorine concentration is generally 200–500 mg/l as Cl_2 . The chlorine solution is typically buffered to pH 6.5–8.5 so that the most biocidal form of chlorine is present during well rehabilitation.

Physical tools are used to remove deposits that are on the internal portions of the well screen and casing. Freeing the screens and casings of deposits also aids in the penetration and agitation of chemicals in the well and into the aquifer.

Wire brushes with surge block tools are used to scrape deposited materials from the casing, screen, or open-hole formations. Once the materials are dislodged, they are bailed or air lifted from the well. The surge block tool is used to agitate chemical solutions and flush the chemical in and out of the screened area of the well.

Tank surging procedures are used when removing the permanent pump is not desirable. In this process, a chemical solution is mixed in a tank at the surface, and the chemical solutions are either gravity fed into the well through

the permanent pumping equipment or pumped into the well with a pump at the surface. After a short contact time, the chemicals are pumped back into the tank by the permanent pump. This process is repeated over several hours. Heating the chemical solution during tank surging (a patented process) has also been shown to be beneficial.

Carbon dioxide (CO_2) is also used for well rehabilitation. Early trials were performed with solid dry ice; however, current technologies apply carbon dioxide to the well through engineered injection equipment. The CO_2 expands within the well and aquifer, and provides exceptional energy for agitation and dislodging of plugging materials. The subsequent formation of carbonic acid from this process also provides some dissolving and solubility benefits for certain chemical deposits.

Percussive devices are used in well rehabilitation to provide high-energy horizontal pressure waves that effectively remove deposited material from the screen and rock formation interface. Additionally, the waveform moves into the surrounding materials and provides a flexing action to the gravel pack and formation materials. Engineered and patented percussive devices were developed in the 1950s with pressure compensators that create and control the surging action.

The most recent technologies introduced to the water well rehabilitation industry are gas impulse devices. These processes incorporate special equipment to apply a high-pressure, low-volume, gas release down into the well. The process provides a high-energy gas release for shearing, dislodging, and pulverizing materials within the borehole of the well. Additionally, a waveform is generated that can agitate and carry any treatment chemicals throughout the borehole and into the formation. The major advantage of this process is the continual repeatability of the energy release as the tool can release gas impulses every few seconds.

The primary consideration of water well rehabilitation is that there does not appear to be a single technology that is the answer to all well problems. In most cases, effective well rehabilitation is provided by an investigative evaluation of the problems and the selection of technologies, processes, and procedures that provide the most probable resolution to the specific problems identified.^{163,164,235,236}

CHLORINATION IN THE UNITED KINGDOM

Chlorine remains as the predominant primary disinfectant used in the United Kingdom. Until about 2005, there were only a few plants, albeit small and typically groundwater facilities, where UV disinfection followed by chlorination was practiced. More recently, a number of larger UV plants have been installed for groundwater and surface water facilities, and the main reason is that UV has a smaller footprint (i.e., the contact tank required for chlorine disinfection could be removed from the site). Other oxidants such as ozone

or chlorine dioxide are rarely used for disinfection. The function of ozone is usually oxidation.

Chlorine is used either as elemental chlorine drawn as a gas or a liquid from cylinders, which are 30–70 kg, or drums, which are 800–1000 kg. The type of chemical used depends on the requirements of the works. Sodium hypochlorite, at 10%–15% by weight chlorine, or sodium hypochlorite that is generated on site to a concentration of 0.7%–0.9% w/v (7–9 g/l) by electrolysis of brine (a solution of sodium chloride) are other common chlorine chemicals used in the United Kingdom. The quantity of chlorine that is stored at a facility is dictated by the Control of Major Accident Hazard (COMAH) Regulations (1999).²³⁷ The type of accident response required for a treatment plant depends on the level of control required for substances which are toxic (e.g., chlorine and anhydrous ammonia), oxidizing (oxygen), or dangerous for the environment (e.g., chlorine, petroleum products, anhydrous ammonia). The levels of control for chlorine are categorized as 10 t, for the lower tier, and 25 t, for the upper tier. For the lower tier, COMAH requires that the operator demonstrate general care in handling, safe operation and reporting of all incidents to the Health & Safety Executive (HSE). For the upper tier, operators must have on-site and off-site emergency plans, submit a safety report to the HSE, and inform the public of the potential hazard. These regulations have resulted in almost all U.K. water utilities minimizing bulk storage, and for utilities that require large volumes of chlorine, most are changing from chlorine gas to sodium hypochlorite, which is either purchased or generated on-site.

The design of chlorine facilities is covered by HSE guidelines HSG28²³⁸ for bulk chlorine installations and HSG40²³⁹ for drum and cylinder installation. Occupational exposure limits for chlorine are defined in EH40.²⁴⁰ Almost all chlorine storage facilities are fully enclosed. In the event of a major leak, the gas is contained in the building and allowed to discharge to the atmosphere under controlled conditions, with police, fire, and ambulance service in attendance. It is common in chlorine facility design to locate the vacuum regulator in the container storage area and to restrict the chlorine gas under pressure to within the storage area. Also, efforts are made to minimize the transfer of chlorine solution across the site by locating the chemical feed system close to the point of application, and the chemical transfer is conducted under vacuum.

There are some large and many small installations where chlorine gas has been replaced by sodium hypochlorite, which must comply with the British European standard.²⁴¹ Sodium hypochlorite contains bromate as an impurity that contributes to the overall bromate concentration in the finished water. This may be problematic at installations where ozone is used to treat water. For these installations, sodium hypochlorite that is manufactured from low-bromide salt is used, and this helps lower the overall bromate concentration in the finished water. To combat the problem of chlorine solution concentration decay at warm temperatures and over long storage periods, some large

installations have installed chillers on storage tanks, and typically operate them during summer months. At smaller installations, the solution inventory is managed to minimize the storage period.

There are over 150 installations in the United Kingdom where sodium hypochlorite is generated on-site. Chlorate and bromate are by-products of the process. Low-bromide salt is used in the process where a low-bromate concentration is required. For chlorate (ClO_3^-), the U.K. drinking water standard is less than 0.7 mg/l as ClO_3^- . There are no guidelines for the design of these installations, except that the plant should conform to the Explosive Atmosphere Directive (ATEX) 94/9/EC²⁴² and that a hazardous area classification should be prepared in accordance with the British Standard, which does not conflict with European Standards (BSEN), specifically 60079-10:2003.²⁴³

In the United Kingdom, continuous prechlorination is rarely practiced due to the potential for DBP formation. For the same reason, the use of chlorinated ferrous sulfate as a coagulant has been discontinued for about two decades. In some instances, intermittent chlorination is used to discourage algae growth in open structures. Intermediate chlorination is used for manganese oxidation and adsorption during filtration, but this application, for surface waters, occurs after a high proportion of the DBP precursors have been removed by coagulation and clarification. There are also many facilities in the United Kingdom that use dedicated, chlorinated secondary filters for manganese removal from surface water plants.

The disinfection requirements of the United Kingdom follow a CT approach, but there are differences in the design criteria and implementation at facilities. Disinfection to achieve free chlorine residual and a CT of 15–60 mg-min/l, with 30-min contact is common. Some utilities require a minimum contact of 20 min, a minimum HOCl concentration of 0.2 mg/l, and a maximum pH of 7.5, while other utilities aim for a minimum of 5 mg-min/l for at least 20 min in the case of groundwater or 30 min in the case of surface water. The free chlorine residual is assessed at the highest water pH and temperature. In most facilities, disinfection occurs in a dedicated contact tank that is equipped with baffles to minimize short-circuiting. New tanks are now designed using computational fluid dynamics (CFD) modeling for optimized disinfection. Providing contact time in pipes is also allowed and practiced in the United Kingdom.

Some works practice superchlorination, where water is dosed with a high concentration (i.e., up to 2.5 mg/l) of chlorine. It is often used on groundwaters that have unpredictable incidences of pollution, which suggests an influence from surface water. It is also used (a) for heavily polluted surface waters where pretreatment is not adequate and (b) as a predisinfectant for waters that generate taste and odors at lower doses of chlorine. Superchlorination is followed by partial dechlorination to the target residual.

The quality of water entering the disinfection stage is critical for the efficiency of disinfection, and the following are considered important: (a) ammonia < 0.1 mg/l; (b) pH 6.5–8.0; (c) turbidity < 1.0 NTU; and (d) total

coliforms < 100/100ml. Iron and manganese concentrations of 0.10 and 0.05 mg/l, respectively, are considered appropriate and acceptable for disinfection and finished water quality.

The regulatory requirement in the United Kingdom is that water leaving the WTP has to be suitably disinfected, without specifying the type of disinfectant and the level of disinfection. The proof of adequate disinfection is the absence of coliforms, and this applies to throughout the distribution system. To define a residual leaving the WTP, the water utilities have to consider the type, the size, and the quality of the distribution system and the water quality leaving the WTP, which will be a function of the type of water. They also have to consider the consumer complaints about chlorinous taste and odor due to too much chlorine residual at the tap.

For example, a high-quality groundwater from a chalk aquifer will have about 0.3–0.4 mg/l residual leaving the treatment facility, whereas a surface source could have a residual up to about 2.0 mg/l because of chlorine decay in the distribution system. A fixed chlorine residual value, therefore, cannot be given for the water leaving the works. Some extensive work done by one water utility on a specific distribution system found accelerated degradation due to temperature and organic content originating from algae in the water during summer months.

The chlorine residual in water leaving WTPs varies between utilities. Where water feeds service reservoirs in the distribution system, the residual leaving the works is typically 0.5–2.0 mg/l and those leaving service reservoirs 0.2–0.5 mg/l. Facilities to boost the chlorine residual at service reservoirs are provided if this is considered necessary to maintain a required residual in distribution. Where water is fed directly into distribution, the residual leaving the WTP is normally limited to about 0.5–0.75 mg/l, with a target of 0.2–0.5 mg/l in the distribution.

The residual at consumers' tap varies between 0.2 and 0.5 mg/l, although some aim for less than 0.05 mg/l, but usually 0.02 mg/l. In practice, the desired residual is a balance between a minimal value to reduce complaints of chlorinous tastes and odors and greater values for guarding against bacteriological failures. At high residual values, chlorinous complaints could be a problem typically in the summer when warmer temperatures result in an increase in chlorinous taste and odor complaints, but due to higher losses in the distribution system, control to meet the bacterial quality and please the consumers becomes difficult. Most utilities with large distribution systems have booster chlorination systems either at service reservoirs or in the distribution system.

Chloramination is practiced for three reasons: (a) to produce a persistent residual where long transmission mains are used or for large distribution systems; (b) DBP control; and (c) for biofilm control in distribution system. Thames Water chloraminates the water transferred in the London Ring Main (85-km long, mostly 2.54 m in diameter and average daily flow about 1000 million liters). Anglian water chloraminates water conveyed long distances by

transmission mains. Several other water utilities chloramine selected supplies for DBP (primarily THM) control.

CHLORINATION IN GERMANY

The use of chlorine in German potable water systems differs significantly from those in the United States and the United Kingdom.²⁴⁴ There is no regulatory obligation for disinfectant residuals in distribution, but when it is used, only chlorine or chlorine dioxide, at very low levels (e.g., <0.3 mg/l for chlorine and <0.2 mg/l for chlorine dioxide). The bacteriological water quality in distribution systems is monitored frequently. Over 60% of the water supply in Germany is a groundwater, so disinfectant use at those utilities is often low. There are limits to the amount of chlorine that can be used within any WTP, and most utilities operate without a residual in the distribution system. The TTHM standard is 10 μ g/l at the outlet of the treatment plant and 50 μ g/l at the consumers' taps.

TREATMENT STRATEGIES

The following water treatment scenarios reflect typical water plant design and operation philosophies for coagulated surface water, softened surface water, and groundwater that contain iron and/or manganese. The disinfection concepts represent typical or common approaches, but other oxidants, application points, and operating philosophies could be used for treatment.

Disinfection of Coagulated Surface Water

For typical surface water, treatment consists of possible preoxidation, coagulation, clarification, filtration, and disinfection. Although chlorine has historically been used as a preoxidant, chlorine is presently not often used as a preoxidant in surface water supplies due to the potential for high DBP formation potential of raw water, which contains the highest concentration of NOM in the treatment plant. Chemicals that are currently used for preoxidation include KMnO_4 , ozone, and ClO_2 .

For waters with high concentrations of dissolved iron and/or manganese, it is common for WTPs to operate with a chlorine dose and residual onto the filter media, provided that the filter media is not GAC. The chlorine acts to promote the oxidation of iron and manganese, as well as catalyze the adsorption of oxidized manganese onto the filter media. This approach is not often used with GAC filter media because GAC reacts with chlorine, and chlorine affects the adsorption capacity of GAC (which was likely installed for NOM removal or taste and odor control).

Disinfection with chlorine in a postfilter clearwell, reservoir, or pipeline is common. The requirements of the SWTR dictate the inactivation requirements for virus and *Giardia*, and outline the CT requirements for dif-

ferent temperatures. A disinfectant residual of free or combined chlorine is then established and carried into the distribution system.

Disinfection of a Softened Surface Water

Disinfection with chlorine in softened water is similar to that of coagulated water, except that special attention must be made to the pH of disinfection. The pH during softening can be quite high (e.g., typically 10.0–11.0), and the formation of TTHMs is greater at higher pH values. Many softening facilities have discontinued any prechlorination due to problems with meeting the Stage 1 and 2 DBPR limits for TTHMs. Chlorination generally occurs in the final clearwell or reservoir, after the treated water pH has been lowered to the pH for distribution (e.g., pH 8–9). Some utilities that previously practiced prechlorination have constructed postfilter chlorine contact basins.

Treatment and Disinfection of a Groundwater that Contains Iron and Manganese

For groundwaters that contain iron and/or manganese, chlorine is often the oxidant and disinfectant used for treatment. Iron is normally susceptible to oxidation with free chlorine, but the oxidation of manganese with chlorine is usually only effective if the pH is greater than 9 and there is a substantial excess of free chlorine. Studies indicate that soluble Mn(II) is rapidly oxidized by potassium permanganate, chlorine dioxide, and ozone in low-dissolved organic carbon (DOC) waters over a pH range of 6–9. Mn(II) can also be removed by adsorption on $\text{Fe}(\text{OH})_3$ solids that are formed by oxidation of Fe(II) if the ratio of Fe:Mn is sufficiently high.

Some wells are dosed with chlorine inside the well casing to minimize biological growth and help maintain production levels. This chlorine dosing location provides some oxidation time for iron and manganese prior to the water coming to the surface. Other well systems are chlorinated once the water reaches the surface. If the pH is low, or the iron and manganese concentrations are appreciably high, providing additional contact time with chlorine can be beneficial. There are waters, however, where no contact time is required with chlorine for adequate treatment.

Oxidized iron and manganese are typically removed by filtration or green-sand filtration. Chlorine residual is carried through the filter media, and if necessary the chlorine residual is boosted prior to entering the distribution system.

ACKNOWLEDGMENTS

The authors would like to thank Roger Miller of Layne Christensen, Don Ratnayaka and Tim White of Black & Veatch, and Stephen J. Randkte of the University of Kansas.

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5 Chlorination of Wastewater

INTRODUCTION

The use of chlorine in wastewater treatment falls into the following categories: (a) odor control in wastewater and foul air; (b) prevention of septicity; (c) control of activated sludge bulking; (d) destruction of cyanide; and (e) disinfection. Each of these categories will be discussed in detail.

History

Chlorine was used as a deodorant long before its value as a germicide was recognized. Until the late 19th century, the belief persisted that diseases were spread by odors, and that control of odors would stop the spread of disease. Although bacteria were discovered in about 1680, it was not until about 1880 that investigations revealed that certain bacteria—now described as pathogens—caused specific diseases. It was later discovered that chlorine compounds could destroy these organisms.

The earliest recorded use of large-scale chlorination of wastewater took place in 1854 in London, when the Royal Sewage Commission used chloride of lime to deodorize that city's sewage. A subsequent investigation for the Metropolitan Board of Works, London,¹ showed that a dosage of 400lb of chlorinated lime per million gallons (15 mg/l) could delay putrefaction of the raw sewage for 4 days.

The first known application of chlorine for disinfection was described by William Soper of England in 1879, who reported using chlorinated lime to treat the feces of typhoid patients before disposal into a sewer. The first plant-scale use of chlorine for disinfection of sewage occurred in Hamburg, Germany, in 1893 to control a waterborne typhoid epidemic. The first recorded use of chlorine for this purpose in the United States was in 1894 at Brewster, New York.² The Brewster installation was unique in that it made chlorine on the spot by the Woolf process—and electrolytic decomposition of a brine solution—and discharged the resultant hypochlorite solution into the sewage.

The results of using chlorinated lime reported by British and German investigators were confirmed by studies made in the United States by Phelps

White's Handbook of Chlorination and Alternative Disinfectants, 5th edition,
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and Carpenter in 1906–1907 at the Massachusetts Institute of Technology.³ Plant-scale studies by Phelps and others in Red Bank, New Jersey and in Baltimore, and Boston in 1907–1908 marked the beginning of effective chlorination practice in the United States. Clark and Gage^{4,5} established many of the basic principles of chlorination at the Lawrence Experiment Station prior to 1911. The practical value of chlorinating raw, septic, or treated sewage with chlorinated lime was soon confirmed by studies at installations in Philadelphia, Chicago, Providence, and elsewhere. By 1911, eight sewage treatment plants in New Jersey were reported to be using chlorinated lime to protect water supplies, shellfish beds, and bathing beaches.

Until 1913, when a suitable gas chlorinator became available, chlorination for disinfection and control of sewage odors grew very slowly because the chlorinated lime was expensive and difficult to use and deteriorated in storage. Liquid chlorine became commercially available in 1909 at Niagara Falls. The first chlorinator for metering and applying chlorine gas was developed by George Ornstein of the Electro Bleach Gas Company in 1912, and in the following year, based on his patent, Wallace & Tiernan marketed the first successful gas chlorinator, which revived interest in the chlorination of sewage. Among the first municipalities to employ liquid chlorine for disinfection of sewage effluent were Altoona, Pennsylvania, and Milwaukee, Wisconsin, in 1914, followed by El Dorado, Kansas, in 1915 and Philadelphia in 1916. Since then, the use of chlorination in wastewater treatment has grown tremendously owing to the development of suitable equipment, and is now an integral part of wastewater treatment practice in the United States and Canada. Chlorine is also used widely in odor control, prevention of septic conditions, control of activated sludge bulking, destruction of cyanide, and disinfection.

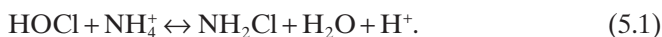
Active use of chlorine for disinfection of wastewater in the United States began in about 1945. Most of the wastewater treatment plants (WWTPs) that practiced disinfection at that time belonged to the U.S. Armed Forces. During World War II, it was military policy to chlorinate the sewage effluent at all Army bases in the United States. The first chlorine residual-controlled disinfection system for municipal wastewater was installed in 1961 at Napa, California. Later, the Federal Water Pollution Control Act (1970) recommended that municipal WWTPs practice some disinfection.

Other uses of chlorine in wastewater treatment practice include controlling odors and preventing septicity; improving grease and scum removal; preventing ponding in trickling filters and propagation of filter flies; controlling activated sludge bulking and foaming; destroying phenols; and scrubbing foul air.

Chlorine Chemistry in Wastewater

Chlorine added to wastewater can react with a variety of constituents, including bacteria, viruses, ammonia nitrogen, organic nitrogen, hydrogen sulfide,

tannins, cystine, uric acid, humic acid, pickle liquor, cyanides, and phenols. Plant effluent, except highly nitrified effluent, contains appreciable amounts of ammonia nitrogen (10–40 mg/l). Hypochlorous acid (HOCl) is a weak acid. In chemical terms, this means that the compound dissociates based on the liquid pH. So, as chlorine gas is added to water, HOCl is formed and the amount of HOCl versus OCl^- is determined by the pH. Undissociated ammonia exists in equilibrium with the ammonium ion (NH_4^+), and the distribution is dependent on pH and temperature of the effluent. At near-neutral wastewater pH, ammonia exists in its ammonium form and, at ammonia nitrogen-to-chlorine weight ratios greater than 1:5, reacts with chlorine (HOCl) to form chloramine:



If the pH drops below 7, dichloramine (NHCl_2) begins to form, and at a much lower pH, nitrogen trichloride (NCl_3) is produced.

The reaction of chlorine with inorganic compounds such as ammonia is faster and takes precedence over disinfection (reaction with bacteria). The kinetics of chlorine–ammonia reactions in wastewater is pH dependent. For example, at 25 °C, pH 7, and a molar ratio of 1:5 (HOCl: $\text{NH}_3\text{-N}$), 99% of the ammonium is converted to monochloramine within 0.2 s. The reaction is most rapid at pH 8.3. Because the chlorination process proceeds in the neutral pH range, the speed of the chlorine–ammonia reaction to monochloramine is finite, but almost instantaneous and takes precedence over bacteria penetration. In a wastewater containing 30 mg/l of ammonia, the molecules of ammonia can outnumber bacteria by a factor of about 10^{13} , which is a significant factor in the kinetics of wastewater disinfection.

All municipal wastewaters contain organic nitrogen compounds such as uric, humic, and amino acids, and tannins, most of which remain stable for long periods, even in the presence of free chlorine, and upon reaction with chlorine are converted to organochloramines that do not possess any germicidal properties. In analyses for determination of chlorine residual, these compounds show up in the dichloramine fraction of the complete forward titration procedure by either the amperometric or the diethyl-*p*-phenylenediamine (DPD)–ferrous ammonium sulfate (FAS) method. They cannot be identified by an analyzer measuring total residual.

Consumption of chlorine by wastewater increases with the biochemical oxygen demand (BOD) of the waste, which explains the diurnal variation in the chlorine demand of most domestic wastes from as low as 2:1 up to a high of 5:1. Rule-of-thumb estimates of 15-min chlorine demand for various wastewaters are summarized in Table 5.1. These values can be used to calculate chlorinator capacity for disinfection. As these are 15-min chlorine demands, the appropriate adjustments should be made to arrive at the appropriate chlorine dosage.

TABLE 5.1. Fifteen-Minute Chlorine Demand of Various Wastewaters

Type of Wastewater	Chlorine Demand (mg/l)
Raw fresh domestic waste	12–15
Raw septic domestic waste	15–40
Primary effluent	12–16
Biofilter effluent (secondary)	4–8
Trickling filter effluent	4–10
Well-oxidized secondary effluent	3–8
Multimedia filter effluent	3–6
Slow sand filter effluent	2–4
Nitrified filtered effluent	2–10
Septic tank effluent	30–45

ODOR CONTROL

Unpleasant odors are caused by bacteria and enzymes acting on proteinaceous matter under anaerobic conditions. Ammonia, hydrogen sulfide, volatile fatty acids, and mercaptans are also products of putrefaction. Odor-producing substances in wastewater systems usually persist only within the confines of the treatment plant and can be greatly reduced by liberal use of landscaping capable of masking and absorbing odors. However, experience has shown that when hydrogen sulfide is controlled, other obnoxious odors are also controlled. Other odor-producing compounds such as cadaverine, indole, mercaptans, and skatole are more difficult to detect and analyze, and so it is assumed that detection and measurement of hydrogen sulfide will indicate when putrefaction may be occurring and, consequently, when conditions in the wastewater could produce foul odors. The sulfide production mechanism in free-flowing sewers is schematically illustrated on Figure 5.1.

Hydrogen sulfide is highly soluble in water,⁶ with an aqueous solubility of 3618 mg/l at 20 °C and 1 atm. H₂S is denser than air. It has an odor threshold of 11 µg/m³ in air and a Henry's law constant of 9.8 atm-l/mol at 25 °C. Hydrogen sulfide is a weak acid, and in aqueous solutions it hydrolyzes as follows:



The hydrosulfide ion (HS⁻) further dissociates as follows:



At 18 °C, the hydrolysis constant for the dissociation of hydrogen sulfide is

$$K_h = 9.1 \times 10^{-8} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}. \quad (5.4)$$

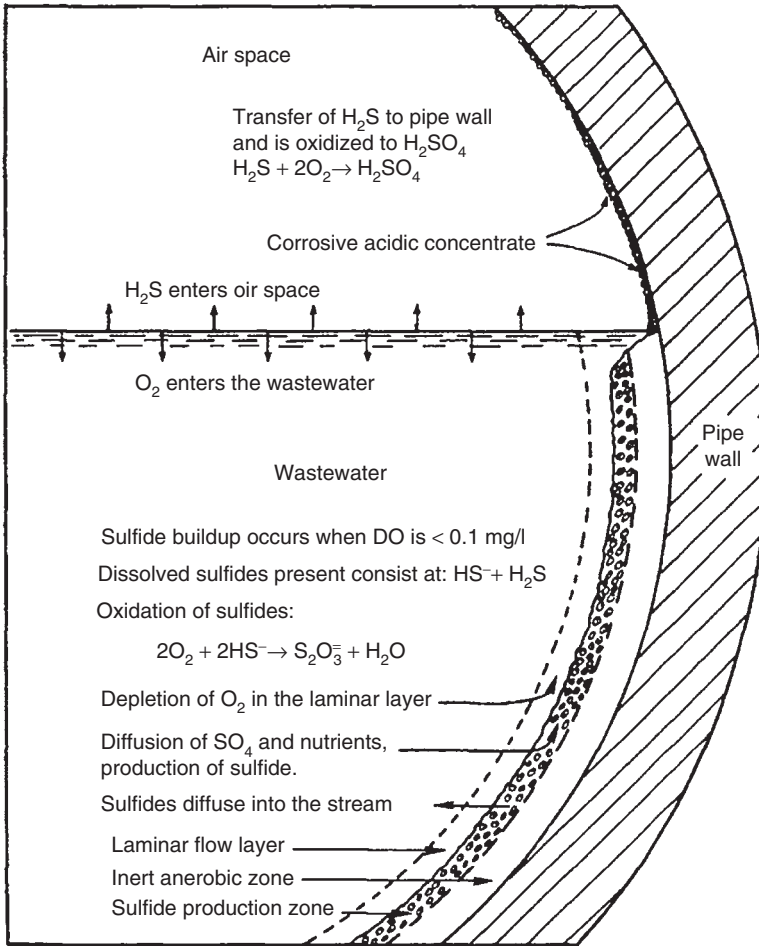


Figure 5.1. Processes occurring in free-flowing sewers under sulfide buildup conditions.

Figure 5.2 illustrates the distribution of H_2S , HS^- , and S^{2-} as a function of pH. At pH 7, approximately 50% of the total dissolved sulfides is H_2S ; at pH 5, it is practically 100% of the total; at pH 9, dissolved sulfides are nearly all S^{2-} . At neutral and acidic pH, significant quantities of H_2S can partition into air, causing odor problems in the WWTP.

Prechlorination of Wastewater

The chemistry of the oxidation and removal of hydrogen sulfide by chlorination is complex, and oxidation can proceed to form either elemental sulfur or

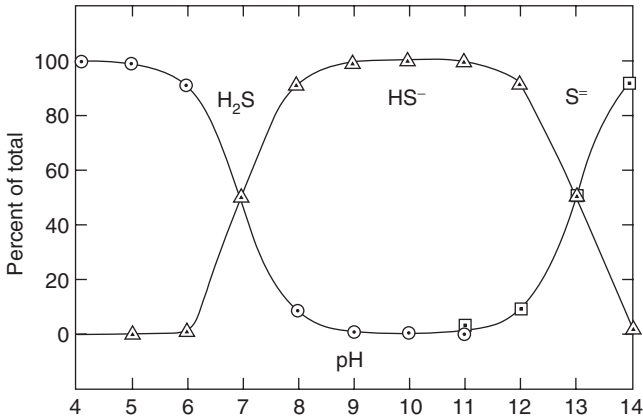


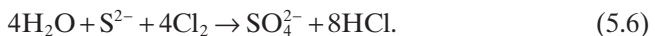
Figure 5.2. Effect of pH on the hydrogen sulfide-sulfide equilibrium.

sulfate, or both. In dilute aqueous solutions, chlorine reacts instantaneously with sulfides to form colloidal sulfur or sulfates, depending on the pH, the temperature, and the ratio of chlorine to sulfides present.



This reaction requires 2.2 mg/l chlorine per milligram per liter of sulfide as hydrogen sulfide. A high pH is required for this reaction to go to completion. At pH 10, the amount of sulfide oxidized to free sulfur is only slightly more than 50%.

The addition of 8.87 mg/l chlorine to each part of sulfide can theoretically oxidize the sulfides to sulfates:



The chlorine-sulfide reaction that is most often observed is the oxidation to sulfate. The chemistry of this reaction is complex and depends on the wastewater pH and temperature. Some free sulfur and polysulfides are probably formed along with the sulfates. Given sufficient time in an oxidizing environment, the polysulfides are converted to sulfates, but in a reducing environment they easily revert to hydrogen sulfide.

The practical way to determine the optimum chlorine dosage for a wastewater containing sulfides is the chlorine demand test. *Standard Methods'* chlorine demand test (Method 2350 B) procedure can be used to determine the chlorine consumed during a 5-min contact period, which is sufficient time for all the chlorine-sulfide reactions to go to completion. Chlorine dosage is adjusted until a measurable residual is detected at the end of 5 min. Other chlorine side-reactions occur, and it is not uncommon that the actual chlorine

dose required for sulfide oxidation is higher than the theoretical value needed for oxidation of sulfide to sulfate.

With the advent of biologicalal phosphorus removal, the side reactions of chlorination to remove hydrogen sulfide in the collection system must be considered. Chlorine will react with any readily oxidizable materials that include readily degradable BOD, such as organic acids (volatile fatty acids or VFA). The VFA are needed for biologicalal phosphorus removal. If the VFA are chemically oxidized with chlorine, they must be added or produced in the WWTP for biological phosphorus removal. The cost of chlorination must be compared against the cost of producing or adding organic acids to choose the most economically desirable method solution that can be made.

A prechlorination facility is one enhancement that can be installed at every WWTP to control hydrogen sulfide odors at the headworks. It can be used as a standby system for disinfection and/or as a supplement for chlorination of return activated sludge (RAS). In the absence of chlorine demand tests, the equipment should have the capacity to deliver at least 15 mg/l for peak dry weather flow of fresh domestic wastewater. If the wastewater is a mixture of industrial wastes and septic domestic waste, the chlorine dose might escalate to 30 or 40 mg/l.

Continuous measuring of chlorine residual is not necessary for hydrogen sulfide control. A chlorine residual analyzer cannot function on raw wastewater because of its high chlorine demand. The oxidation–reduction potential (ORP) method has been tried at different plants with little success. However, the Stranco HRR Control System has been found to be ideal for both odor control and disinfection of wastewater (Chapter 12).

The preferred method for odor control is based on the controlling of chlorine dose to prevent liberation of H_2S from an aerated sample of chlorinated wastewater. The H_2S liberated from an aerated sample of wastewater is directly proportional to the dissolved sulfides in the wastewater. Proper chlorination control using the air sampling technique can be readily achieved, provided that the sample is aerated properly. An example of adequate aeration is the typical wastewater sampling device. The wastewater is pumped at a rate of 2–3 gpm to the sampling device, and it discharged to waste over a weir. The air suction cone of the H_2S detector is suspended above the weir so that any H_2S aerated out of the sample is trapped by the detector.

A successful installation of this kind consisted of an automatic proportional sampler of prechlorinated raw wastewater.⁷ Chlorination control was maintained by keeping the concentration of the dissolved sulfides always slightly below the critical limit of 0.3 mg/l. The air entering the H_2S detector suction line was pumped through the analyzer, where it came into contact with a lead acetate-saturated tape, on which it produced a black spot with a density proportional to the amount of H_2S in the atmosphere. The density of the spot was converted into an electric signal that was fed into a controller, which operated the chlorine metering orifice in response to a field-observed empirical set point. This system enabled the operator to adjust the set point to measure the

chlorine in accordance with a preset acceptable H_2S concentration in the atmosphere adjacent to the wastewater surface.

The chlorine control system must be equipped with a bias feature, which limits the minimum dosage of chlorine to approximately 8 mg/l. Without this feature, when no H_2S was being generated, the control system would eventually reduce the chlorine feed rate to near zero, and with sudden reappearance of H_2S , the control system would be unable to react in time to prevent a breakout of H_2S in the treatment plant area. There are several ways to maintain the minimum dosage.

It is wise to use two H_2S detectors: one to control the chlorine dosage and the other to monitor odors in the plant area. The latter analyzer should be the portable type. The control analyzer should be fitted with an H_2S range of 0–3 mg/l that can be converted in the field to 0–10 mg/l. The portable odor analyzer should have the same capability. Both units should have built-in recorders of H_2S concentration since a historical record is of prime importance to the operator.

Local conditions will determine the need for a flow pacing signal in addition to the H_2S signal. A flow signal is highly desirable and should be considered. It is well worth the expense even if the flowmeter range is limited to 3 to 1. The flow must be measured near the plant influent. Automatic dosing of chlorine for odor control using an H_2S analyzer to detect the odor potential of the wastewater is the surest way to successfully control odor by chlorination, as it eliminates the need for human response as a detection device.

Scrubbing of Foul Air

Scrubbing towers have been widely used at WWTPs to control odors and minimize air pollution. For worker health and safety, ventilation air must have low H_2S gas concentrations at all times. Scrubbing towers are also used in pumping stations and other collection system structures where high concentrations of H_2S can accumulate.

Chemical scrubbing towers can be operated with only chlorine or with a combination of chlorine and caustic. For severe cases in odor-sensitive areas, the wet scrubber may be followed by an activated carbon tower impregnated with either potassium or sodium hydroxide. The most successful type of wet scrubber is the countercurrent packed tower illustrated on Figure 5.3. Foul air enters the scrubber at the bottom, and the scrubbing water enters from the top. The scrubbing water is continuously recirculated by a centrifugal pump, with its suction connected to the bottom of the chemical mixing tank. The pump discharges the liquid into the top of the tower, and foul air is blown into the bottom of the tower by a centrifugal fan. The packing medium in the tower is designed to bring the water into intimate contact with the foul air to achieve maximum odor removal.

Past practice has been to use secondary effluent in scrubbers located at treatment plants, and freshwater in collection system installations.

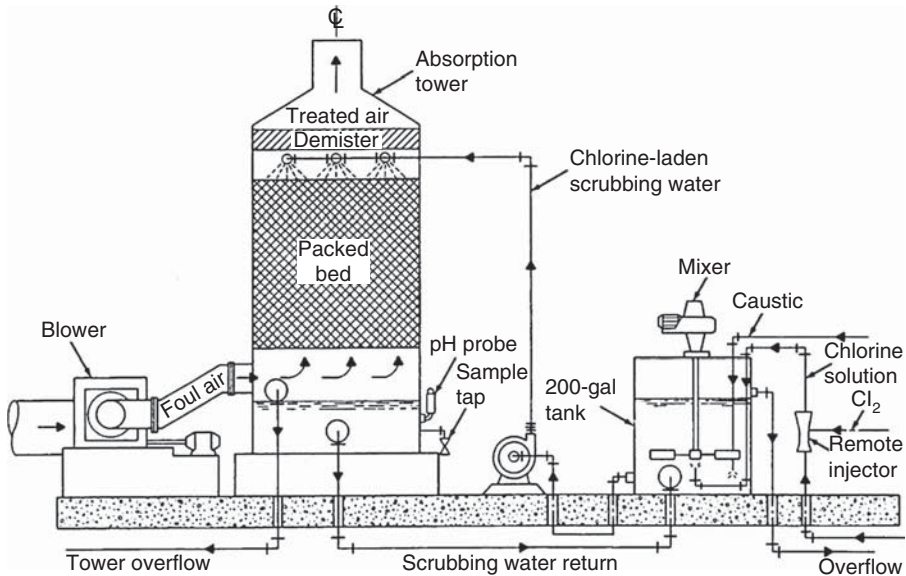


Figure 5.3. Wet scrubber system for removal of H_2S from foul air.

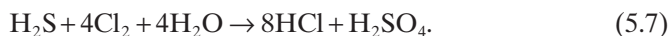
The secondary effluent may add ammonia to the system, which will consume significant amounts of chlorine, and the suspended solids in the secondary effluent will also exert a chlorine demand that must be met before sulfide oxidation begins. The biggest problem with secondary effluent is its hardness: When the pH of the water in the scrubber rises above 8, softening reactions occur, followed by scale formation that will eventually clog the media or interfere with the circulation of the water. Chemical cleaning of the media is a time-consuming task. The scaling problems can be alleviated by using softened potable water as makeup water for the wet scrubber systems. The scrubbers operate as a recirculated system, using blowdown, either continuous or intermittent, with a constant makeup water supply. A proper chemical balance of pH and chlorine concentration must be maintained in the scrubber so chlorine and caustic are added in the mixing tank as the only makeup fluids used in the system, and are usually sufficient to eliminate the need for continuous addition of makeup water.

There are several advantages to a chlorine scrubber over a caustic or a caustic-and-chlorine scrubber. A chlorine scrubber is operated at neutral pH so there is no precipitation of the calcium or magnesium ions that occurs in caustic towers. Even though hypochlorite is added and the pH does rise, acid is added by absorption of hydrogen sulfide into water, which causes the pH to drop. Caustic-only scrubbers are not commonly used, as the caustic raises the pH to absorb hydrogen sulfide into solution. In caustic-only scrubbers, the hydrogen sulfide is not oxidized so whenever the pH of the blowdown is lowered, hydrogen sulfide can be released from solution.

Scrubbers using a combination of caustic and chlorine can be better than 98% efficient in removing hydrogen sulfide; however, the caustic-and-chlorine scrubbers operate at a pH of around 9–10, which is conducive to the formation of carbonate scale that must be periodically removed using an acidic solution. Corrosion therefore caused by the accumulation of high concentrations of chloride in the scrubber solution can be an issue; both pH and ORP or chlorine residual in the scrubbing water must be controlled. If the temperature of the scrubbing water, that is, the wastewater effluent, is 22 °C (72 °F), the aqueous solubility of H₂S at a pressure of 1 atm is 3.432 mg/l. Figure 5.4 is the schematic of the odor control system at the Irvine Ranch Water District Reclamation Plant.

Chlorine does not actually remove the H₂S; rather, it chemically converts the H₂S and hydrosulfide ion (HS⁻) to sulfates through oxidation. At pH 7, approximately one-half of the total dissolved sulfide exists as hydrogen sulfide, and the remaining half is hydrosulfide ion (HS⁻). As the H₂S is oxidized, more H₂S is formed from the remaining dissolved sulfides to reestablish the equilibrium between HS⁻ and H₂S. The ratio of HS⁻ to H₂S is governed by the solution pH.

There are two important reactions between chlorine and hydrogen sulfide: The first and most significant is the reaction that converts the H₂S to sulfates. This requires 8.32 parts of chlorine to each part of hydrogen sulfide:



The pH range for this reaction is 6.0–9.0. The optimum pH is 6.0. For each part of H₂S removed, 10 parts of alkalinity (as CaCO₃) is consumed.

The other important reaction is an intermediate one, which precipitates free sulfur:



This reaction requires only 2.1 parts chlorine for each part H₂S and consumes 2.6 parts of alkalinity (as CaCO₃). The pH range for this reaction is 5.0–9.0, and the optimum pH is 9.0.

The removal of hydrogen sulfide in a wet scrubber is a two-step process. The first step is absorption of the H₂S from the malodorous air stream into the scrubbing solution. The second step is chemical oxidation of the H₂S to sulfate. The intent of the scrubbing is to convert as much H₂S as possible to sulfate while maintaining the pH in the scrubber system at 7.0 or higher in order to efficiently absorb H₂S into solution. The blowdown from the system always appears milky as a result of the formation of colloidal sulfur. Maintaining the pH in the system above 7.0 minimizes long-term corrosion.

In addition to absorbing the hydrogen sulfide and other odor-producing compounds, the scrubbing water will also absorb some of the carbon dioxide in the foul air. This will tend to lower the pH, and the acid added from

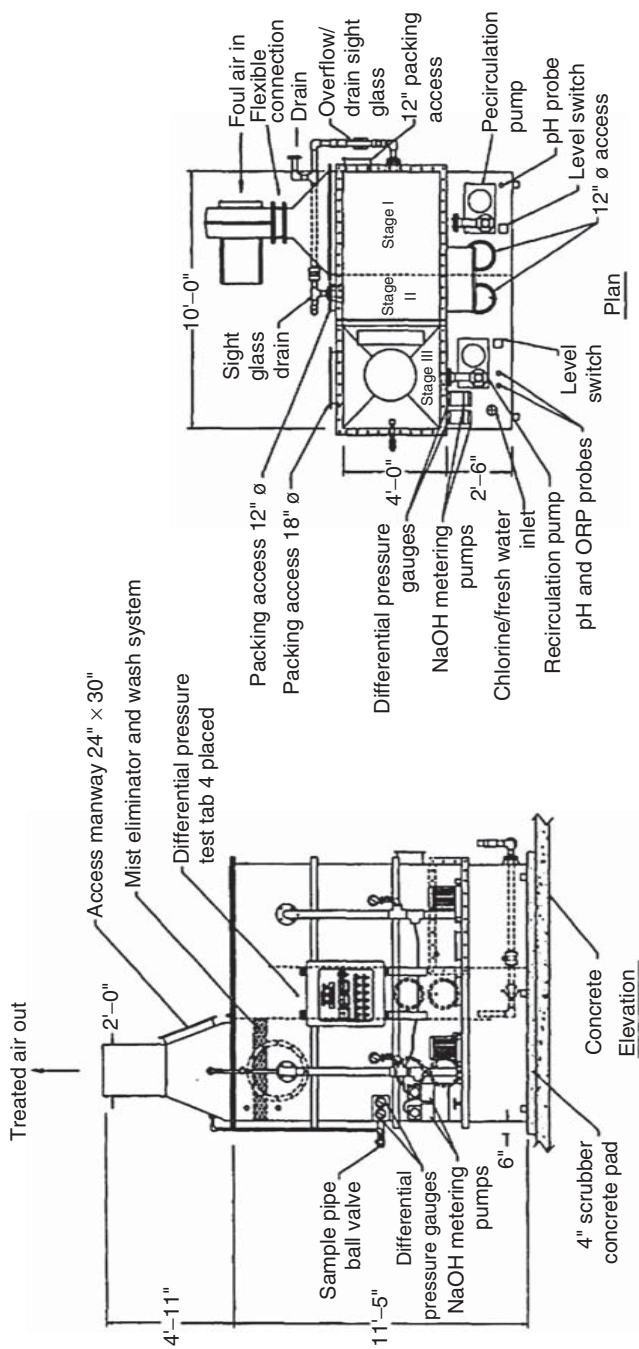


Figure 5.4. Schematic of a foul air scrubbing system (courtesy of R-J Environmental Inc.).

absorption of carbon dioxide can be countered by continuous pH control. Loss of alkalinity in the system must be prevented by adding caustic.

Another facet of chemistry important to the application of chlorine is the presence of ammonia nitrogen in the scrubbing water. If nonnitrified plant effluent is used, the $\text{NH}_3\text{-N}$ concentration will be in the range of 12–22 mg/l. Chlorine in the scrubber will react with ammonia and will proceed through breakpoint chlorination. This adds to the chlorine demand in the scrubber and increases operating costs.

Multistage hybrid systems that utilize both oxidant and caustic can also be used for scrubbing foul air (Fig. 5.5). These systems incorporate the advantages of both the Cl_2 and NaOH (or NaOCl) oxidant systems while reducing the oxidant demand by incorporating a first-stage caustic (NaOH) scrubber. The single-pass, three-stage absorption system consists of a gas conditioning/pretreatment section, followed by two vertical cocurrent/countercurrent packed bed absorption sections. In the first stage, hydrogen sulfide is absorbed into a high-pH solution, and in the next two stages, chlorine is used to oxidize the sulfide absorbed into solution. Each stage is designed to provide an overall performance of at least 99.0% removal of hydrogen sulfide.

The objective of the first stage is to absorb the H_2S into the scrubber water solution with NaOH according to the following reaction:



An air exhaust fan draws foul air from the sources through a network of collection ducts and passes it through the scrubber system. The foul air first

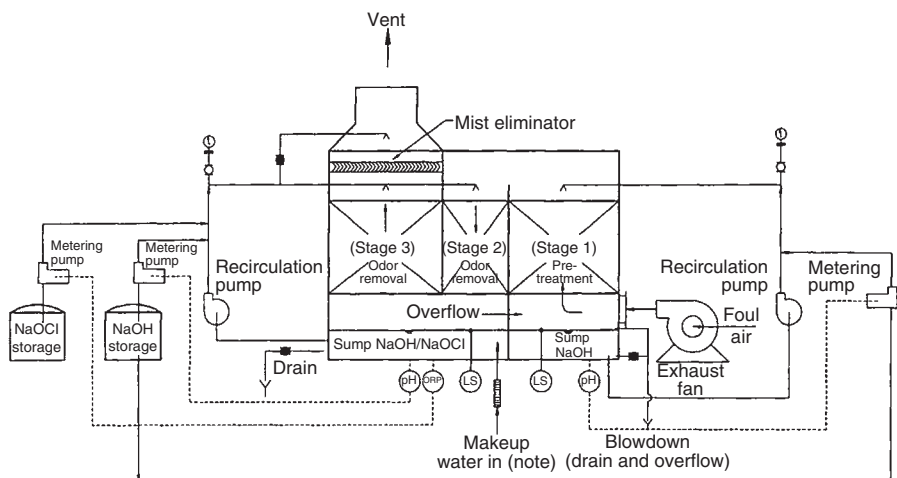


Figure 5.5. Foul air scrubbing system process diagram (courtesy of R-J Environmental Inc.). LS = level sensor.

enters the preconditioning section, in a countercurrent flow, and contacts a recirculation stream including the chemical blowdown from the second and third stages. Most of the chemical content of this stream is consumed by recirculation in the pretreatment stage before being blown down. A NaOH pump and a pH controller are included in the first stage to remove most of the hydrogen sulfide and reduce oxidant demand in the second and third stages.

In the second stage, the gas flows cocurrent and it is contacted with fresh NaOH/Cl₂ or NaOH/NaOCl solution, which oxidizes much of the odorous material; the final polishing takes place in the third stage, where gas and liquid are contacted countercurrent. This arrangement of gas absorption assures (a) odor removal with efficiencies above of 99% and (b) complete utilization of chlorine oxidant before to discharge from the system.

The composition of the chemical sump contents is maintained at preset pH and ORP by adding NaOH and Cl₂ or NaOCl, under control of pH and ORP controllers. Water losses by evaporation and blowdown are compensated for by adding water through a manual rotameter. An overflow above the liquid level prevents the chemical sump from being overfilled. A low-level alarm sounds when sump level drops below the set point.

CHLORINE AND BIOLOGICAL TREATMENT

The principal uses of chlorine in the biological treatment of wastewater include control of septicity and odor in trickling filters, prevention of sludge bulking in activated sludge systems, and reduction of BOD by direct oxidation of oxygen-demanding organics in both raw and treated wastewaters.

Trickling Filters

Trickling filters, especially those operating intermittently, need to be treated with chlorine for odor control. During the downtime, the wastewater becomes septic and the slime in the trickling filter goes anaerobic and generates odorous gases, which are released into the atmosphere during the filtering cycle. In 1928, Morris Cohn of Schenectady, New York, was one of the first plant superintendents in the United States to experiment with chlorine for controlling odors at trickling filters.⁸

Chlorine is applied to the dosing tank of the trickling filter unit. Occasionally, effective odor control can also be achieved by applying it at the prechlorination point. Proper control is usually obtained by satisfying only a fraction of the immediate chlorine demand (approximately 25%–30%). The chlorine dose varies from 2 to 6 mg/l. Dosages lower than the chlorine demands are difficult to control. Some operators take dissolved oxygen (DO) readings at the dosing tank influent. If there is some DO at this point, the chlorine dose is sufficient; if no DO is detected, the chlorine dose is increased, and secondary

effluent is recirculated through the filter until the DO can be detected. High-rate trickling filters are generally odor free, as their continuous operation produces a more stable biological environment. However, rock media trickling filters can be subject to ponding, infestation, and filter flies. Both problems can be mitigated by the proper use of chlorine.

Ponding is the result of clogging of the interstices in the media by filamentous growths or accumulation of solids. If the filter is overloaded and the clogging solids have become deeply embedded, it may be too late for chlorine to help since chlorine works by causing the organisms in the zoogeal mass to loosen so that they can be flushed out of the filter bed, which requires heavy doses of chlorine.

Some filters never undergo ponding; with others, it can occur seasonally to various degrees, making it necessary for operators to determine the best way to apply it. Sufficient chlorine should be applied at the filter influent to produce an amperometric residual between 4 and 8 mg/l at the nozzles. Ponding of high-rate filters can be prevented or eliminated by maintaining a chlorine residual of about 0.5 mg/l. The small amount of chlorine continuously applied seems to create a stable environment that will not allow excessive growths and does not interfere with the normal biological processes within the filter.

The trickling filter presents an ideal for the propagation of the filter fly, *Psychoda alternata*, which develops rapidly during the warm season. Since chlorine has no effect on the adult fly, there is no entirely foolproof way of eliminating this nuisance. However, chlorine has been somewhat effective in removing or at limiting the thickness of the zoogeal film in the top layer of the filter, where the pupae and larvae of the fly are hatched. Since the extent of the infestation depends on the thickness of the film, and best control is achieved by partial removal of the film, chlorination should be limited to only the fly season.

BOD Reduction

The effectiveness of chlorine in reducing the biochemical oxygen demand of wastewater is often overlooked. As early as 1859, chlorine in the form of chloride of lime was applied to wastewater in England to delay its putrefaction while it was being carried in receiving waters to the open sea. Since then, effluent chlorination has been used successfully to reduce its BOD and thus maintain the assimilation capacity and the desired DO concentration of the receiving waters.

Chlorination of WWTP effluent can help meet effluent standards based on the receiving stream's assimilation capacity. Susag⁹ illustrated how effluent chlorination was more economical than installation of additional treatment facilities to maintain the assimilation capacity of the Mississippi River during critical periods. The "Minneapolis-St. Paul Sanitary" District treatment plant utilizes a high-rate activated sludge process, which has a predicted BOD removal efficiency of 75%. This treatment level was considered adequate for

93% of the time in 1980. When chlorination of effluent was evaluated as an additional means of BOD reduction, its cost was found to range between 8% and 40% of the cost of providing additional biological treatment capacity. However, since chlorine is toxic to a variety of aquatic organisms, dechlorination is required, which reduces the incentive to use chlorine for BOD removal. No information is available on the effect of dechlorination on BOD reduction by chlorination.

Chlorination of wastewater for any purpose reduces its BOD. This effect is shown most dramatically in prechlorination of a strong wastewater (high BOD). Rawn¹⁰ reported a 25% BOD reduction as a result of a comprehensive up-sewer chlorination procedure for the Los Angeles County Sanitation District. The full value of this treatment was, however, not in BOD reduction alone. The chlorinated wastewater arrived at the treatment plant in a fresh, rather than in a septic, state, which had the ultimate effect of increasing the capacity of the plant threefold.

Observations made by researchers and operators about the effect of chlorination on BOD reduction^{8,9,11-14} include the following:

- Each milligram per liter of chlorine results in a 2 mg/l reduction of BOD.
- The reduction of BOD appears to be permanent.
- BOD reduction increases with chlorine dose.
- BOD reduction per milligram per liter of chlorine absorbed is greatest at the dosage producing the least residual, and decreases with increasing chlorine dosage, irrespective of total initial BOD.
- When chlorine is applied up to the first appearance of chlorine residual, the highest BOD reduction per pound of chlorine is produced is correlated to the strength (BOD) of the waste.
- Chlorination of activated sludge effluents can result in up to 80% removal of the residual BOD.

The work by Susag⁹ indicated that chlorine does not act solely as an oxidant of oxidizable organic matter. Chlorine reacts to reduce and retard BOD, partly by oxidizing organic matter and partly by substitution and addition to unsaturated and saturated compounds to produce compounds that are either inert or resistant to bacterial action. One drawback of chlorination for BOD removal is disinfection by-product formation. Federal and state water quality standards regulate chlorination by-products. For treatment plants discharging to low-flow streams, those that have a small mixing zone, compliance with chlorine by-product limits may be difficult. Table 5.2¹⁵ presents a summary of chlorine by-product water quality standards.

Control of Sludge Bulking

Poor settling or “bulking” of sludge is responsible for many of the upsets that occur in the activated sludge process and can seriously impair the overall

TABLE 5.2. Trihalomethane Federal and State Water Quality Standards

Compound	Federal WQS (µg/l)			State 1 WQS (µg/l)		State 2 WQS (µg/l)	
	Freshwater Acute	Human Health		Freshwater		Human Health	
		Water and Organisms	Organisms Only			Water and Organisms	Organisms Only
Chloroform (CHCl ₃) ^a	28.9	5.7	470	470.8	5.7	470	470
Chlorodibromomethane (CHBr ₂ Cl) ^a	NR	0.41	34	34	0.41	34	34
Chloromethane (CH ₃ Cl) ^b	NR	NR	NR	470.8	NR	NR	NR
Bromodichloromethane (CHBrCl ₂) ^a	NR	0.27	22	22	0.56	46	46
Bromoform (CHBr ₃) ^a	NR	4.3	360	360	4.3	360	360
Bromochloriodomethane (CHClBrI)	NR	NR	NR	NR	NR	NR	NR
Chlorodiiodo-methane (CHClI ₂)	NR	NR	NR	NR	NR	NR	NR
Dibromiodomethane (CHBr ₂ I)	NR	NR	NR	NR	NR	NR	NR
Bromodiiodomethane (CHBrI ₂)	NR	NR	NR	NR	NR	NR	NR
Iodoform (CHI ₃)	NR	NR	NR	NR	NR	NR	NR

^aSafe Drinking Water Act limits the sum of these four compounds to less than 80ppb rather than setting limits for each individual compound.

^bChloromethane is not a THM, but falls under the more general heading of a halogenated organic chemical.

WQS, water quality standards; NR, not regulated.

efficiency of the treatment plant. Effluent discharged during serious bulking episodes have been known to result in violation of discharge permits and to cause adverse impacts to the receiving waters as well as seriously upset the stability of the biological process.

Activated sludge contains large populations for several types of microorganisms. There are two important morphological groups: (a) the floc formers and (b) the filamentous sludge bulkers. The floc-forming bacteria include the following genera: *Zoogloea*, *Pseudomonas*, *Arthrobacter*, and *Alcaligenes*. The filamentous group (the causative organism of sludge bulking) includes members of the genera *Sphaerotilus*, *Thiothrix*, *Microthrix*, *Parvicella*, *Beggiatoa*, and others. Satisfactory operation of the activated sludge process depends on maintaining the correct ratio of floc formers to filamentous organisms by controlling the population of the filamentous bacteria.

Bulking of sludge can be monitored by routinely performing two tests: (a) measuring sludge volume index (SVI) and (b) daily microscopic evaluation of organisms in the return sludge. The three most common causes of poor settling include (a) low DO concentration, (b) low food-to-microorganism ratio (F/M), and (c) nutrient deficiency (inadequate concentrations of nitrogen or phosphorus or both). These conditions produce bulking sludge by allowing filamentous organisms to proliferate. Filaments, because of their high ratios of surface area to volume, are more efficient in competing for DO and nutrients when their concentrations are low than are the other dispersed bacteria.

Chlorine has long been used for control of sludge bulking. Tapleshay¹⁶ began investigating the use of chlorine for prevention and control of sludge bulking. He theorized that chlorine restores the balance between the organic matter and the biological life in the sludge. His investigation encompassed 50 treatment plants in the United States, and found that the best method of control was possible when the chlorine dose was correlated to the sludge index as follows:

$$\text{lb/day Cl}_2 = \text{SI} \times F \times W \times 0.0000834, \quad (5.10)$$

where

SI = sludge index (Mohlman), the amount of dry solids in the return sludge,

F = return sludge rate (mgd), and

W = suspended solids in return sludge (mg/l).

Chamberlin¹⁷ found that the usual chlorine dose required to control bulking averaged about 5 mg/l based upon the RAS flow. This application of chlorine usually produced a turbid effluent for the first 12h as the reaction began to stabilize, which caused some plant operators to discontinue chlorination for controlling bulking sludge. Where chlorination was continued, the turbidity gradually decreased along with the SVI. A decided improvement was noted

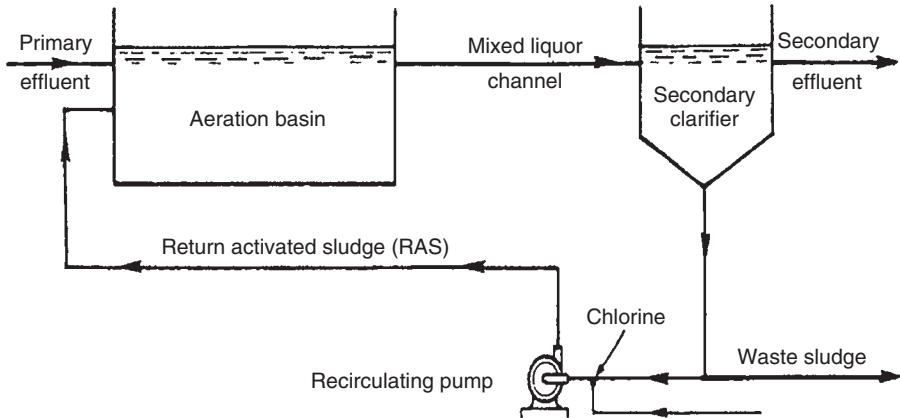


Figure 5.6. Chlorination of RAS for control of sludge bulking.

in 3 or 4 days. In these early years, some wastewater treatment facilities relied solely on intermittent chlorination, whereas others practiced continuous chlorination.

The application of chlorine to a bulking sludge system is illustrated in the following scenario. The return sludge at a 10 mgd plant shown schematically on Figure 5.6 is to be subjected to chlorination for control of bulking. The 2.5-MG aeration basin has a nominal hydraulic detention time of 6 h. When RAS flow is included, the hydraulic detention time in the aeration basin is 4.4 h. The 1.3-MG clarifier has a surface area of 12,500 ft² and surface overflow rates of 800 (average) and 1050 (peak) gpd/ft². The concentrations of mixed liquor total suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) are 1375 and 1030 mg/l, respectively. The average total suspended solids (TSS) and average volatile suspended solids (VSS) concentrations in the clarifier are 2000 and 1500 mg/l, respectively. The RAS flow is 3.5 mgd, and the TSS concentration in RAS is 5300 mg/l. The F/M is 0.30, mean cell residence time (MCRT) is 6.3 days, and sludge yield is 0.7-lb VSS per pound of BOD removed.

It is recommended that operators start adding chlorine at a dose of 1 lb/day/1000 lb VSS, where VSS is the total inventory in the entire system (i.e., aeration basins, clarifiers, and mixed-liquor channel). If more chlorine appears to be needed, it is prudent to increase the dose by about 10%–20% per day. A sample calculation for the chlorine feed rate is as follows:

$$\begin{aligned}
 \text{VSS in aeration basins} &= \text{MLVSS mg/l} \times 8.34 \times \text{aerator volume} \\
 &\quad \text{in million gallons} \\
 &= 1030 \text{ mg/l} \times 8.34 \times 2.5 \\
 &= 21,475 \text{ lb.}
 \end{aligned}
 \tag{5.11}$$

$$\text{MLVSS in clarifiers} = 1500 \text{ mg/l} \times 8.34 \times 1.3 = 16,260 \text{ lb} \quad (5.12)$$

$$\text{Total VSS inventory} = 37,735 \text{ lb.}$$

Therefore, the daily feed rate of chlorine is

$$= (37,735/1000) \times 4 \text{ lb Cl}_2 = 150 \text{ lb/day.} \quad (5.13)$$

The next step is to check the number of exposures (the number of times the sludge is exposed to chlorine) of the RAS to the chlorine applied. The minimum number is considered to be 3.

$$\begin{aligned} \text{Volatile solids in RAS} &= \text{RAS flow} \times 8.34 \times \text{RASTSS} \times \text{Volatile fraction} \\ &= 3.5 \text{ mgd} \times 8.34 \times 5300 \text{ mg/l} \times 0.75 \end{aligned} \quad (5.14)$$

$$\text{RASVSS} = 116,000 \text{ lb/day.}$$

Since the total inventory is 37,735-lb VSS, the exposure frequency is calculated to be $116,000/37,735 = 3.05$ times/day. As the exposure frequency is marginal (3 times/day), it is suggested that if chlorination is not effective within 48 h in this case, the sludge return rate should be increased, provided that other system operating parameters are in order. This can be done if the clarifier solids flux loading remains within permissible limits.

The chlorine dosage can be calculated as

$$\frac{150 \text{ lb/day}}{Q_{\text{RAS}} \times 8.34} = \frac{150}{3.5 \times 8.34} = 5.1 \text{ mg/l.} \quad (5.15)$$

A chlorine dose of 6–7 mg/l should be applied. Jenkins et al.¹⁸ recommend using 0.2–0.8 g of chlorine per kilogram of MLSS per day for systems with hydraulic retention times of 5–10 h. The chlorine must be applied at a point where there is effective initial mixing, such as the suction side of a centrifugal RAS pump, to assure that the filaments in the entire sludge mass will be inhibited, rather than only small amounts of the sludge in passing clumps. Chlorine should be applied continuously until the target SVI is achieved. Intermittent chlorination allows filaments to pass through undamaged and to proliferate in the parts of the aeration basin where they have an environmental advantage. Chlorination alone does not always correct a bulking problem. The root cause of the problem—low DO or insufficient nutrients—must be corrected for the system to fully recover.

When chlorination of the RAS is initiated, temporary deterioration in the effluent quality will occur. In single-stage activated sludge systems, the turbidity may double, the suspended solids may increase by 20%, and the BOD by not more than 10%–15%. However, after RAS chlorination has been initiated, if a substantial increase (>40%) occurs in the effluent BOD, it is a warning signal that chlorine is inhibiting the biological processes, and the dose must be reduced.



Figure 5.7. Activated sludge basin foaming (approximately 1.5-ft foam) after a chlorine overdose for filament control.

Excessive use of chlorine must be avoided, as it can kill too many desirable microorganisms. Excessive foaming after application of chlorine is an indication that too many desirable bacteria have been killed, and the foaming is caused by their rapid regrowth. The amount of foam can be proportional to the chlorine overdose; in one instance, an overdose resulted in a more than 1.5-ft-thick layer of foam on an activated sludge basin (Fig. 5.7). An overdose can be remedied only by either seeding the basin with activated sludge from another facility or waiting for the foaming event to subside and for the microbes to repopulate the system. Mechanically breaking the foam with water spray helps recovery as the foam tends to float the active biomass and the biomass becomes trapped in the foam.

OTHER USES OF CHLORINE IN WASTEWATER TREATMENT

Other uses of chlorine in wastewater treatment include the control of septicity in the collection system, in plant unit processes and in conveyance of sludge; and in the removal of oils, grease, and ammonia from plant effluent.

Septicity Control

Prechlorination of wastewater prevents the development of septic conditions, thereby allowing the various biological treatment processes to work efficiently. Application of chlorine ahead of the primary clarifier improves clarification and eliminates septicity in the settled sludge, preventing it from rising in the clarifier. Chlorine can be used to control the less severe cases of septicity in

the settling basins as well as in the long trunk sewers that convey treated effluent from several plants to a common discharge point. Although some plant operators believe that prechlorination interferes with anaerobic digestion, there is no scientific evidence to support this. Prechlorination may interfere with biological phosphorus removal by either stopping VFA formation in the sewer or through chemical oxidation of any VFA in the wastewater at the point of chlorine addition. Prechlorination must be used carefully in systems that use biological phosphorus removal.

The problem of septicity is closely allied with the generation of hydrogen sulfide. However, septic conditions can also occur where hydrogen sulfide formation is not a factor, such as when the solids float to the surface in a sedimentation basin because of the formation of carbon dioxide and methane gas in the sludge blanket of the basin as a result of anaerobic conditions. The use of chlorine to relieve this type of condition raises the question of how much chlorine is sufficient. The amount of chlorine needed to prevent septicity over a given time span can be determined by the methylene blue stability test. This test is based on the fact that methylene blue is decolorized under anaerobic conditions caused by reducing bacteria, loss of oxygen, or the formation of hydrogen sulfide. Thus, so long as the blue color persists, no septicity or sulfide odor is present. The first step of the methylene blue stability test is the determination of the 15-min chlorine demand of the wastewater, as a guide to finding the optimum chlorine dose for a given situation. If the chlorine consumption in 15 min is 14 mg/l, then it would be appropriate to dose four samples at 3, 5, 10, and 15 mg/l, respectively, to prevent septicity for at least 3 h.

Wastewater samples collected in 250-ml glass-stoppered bottles should be dosed with chlorine at the four concentrations listed above. An equivalent unchlorinated control sample should also be included. The contents of the bottles should be mixed vigorously for 5 s before storing the bottles in the dark at a temperature of 25–30°C for an hour. After 1 h, approximately 0.5 ml of 0.10% solution of methylene blue should be added to each bottle, and the samples should be observed at hourly intervals over a 6- to 8-h period to compare the status of the blue color in each sample against the control sample. At the onset of septic conditions, the blue color will begin to fade and the optimum chlorine dose will be somewhere between the doses corresponding to a faded and the nonfaded sample. The duration of these occurrences is the probable length of time that the “optimum” chlorine dose keeps the wastewater fresh and thus prevents septicity. Chlorine can keep raw wastewater from becoming septic for up to 24 h. It is important to remember that the chlorine will inhibit or kill the microorganisms creating the septic conditions, and once the chlorine addition has been stopped the microbes will again flourish.

Septicity control is also needed in sludge conveyance pipelines. If the sludge becomes septic during transport, hydrogen sulfide is generated in amounts sufficient to cause odor and corrosion in the manhole or tank at the end of

the pipeline. However, the dose of chlorine required to prevent septicity in pipelines can be as high as 50–125 mg/l, which is high enough to cause corrosion of the sludge pumps. A way around this problem is to convey the sludge mixture with raw or treated wastewater. The oxidizability of raw wastewater and sludge is higher than that of raw wastewater alone. Thus, whenever sludge is to be transported, the feasibility of mixing it with wastewater should be investigated. To determine the feasibility of any sludge conveyance system, the probable condition of the sludge at the terminus must be investigated. Septic conditions and H_2S generation should be avoided if at all possible. This can be done conveniently with reasonable doses of chlorine. The sludge or the sludge and wastewater mixture should be subjected to the methylene blue stability test to determine the chlorine dose necessary to prevent septicity. Other techniques besides chlorination are available for controlling sulfide in force mains.

It is good practice to periodically purge the sludge pipeline with caustic to remove biological slimes, which harbor the microbes that ferment BOD into volatile acids and hydrogen sulfide. It will also help prevent the increase in hydraulic friction head. The recommended dosage is 400 lb of 50% NaOH per 450 gpm applied over a 30-min period, once every 4–6 weeks.

Before embarking on a program to eliminate septicity from a collection system or force main, the WWTP staff should be consulted. If the WWTP practices or is planning to implement biological phosphorus removal, using chlorine to eliminate or retard septicity may not be the most economical solution. VFA, the short-chain organic acids such as acetic, propionic, and others, are necessary substrates for the organisms that make biological phosphorus removal work. Oxidation of these acids will interfere with the process. Elimination of the biological slime that ferments more complex organics into VFA will also interfere with biological phosphorus removal by not fermenting the more complex portions of the soluble organic material in the wastewater to VFA.

While chlorination to remove septicity or the biological slime that generates the organic acids is necessary to prevent excessive odors and corrosion in the collection system, elimination of these materials from the system will interfere with WWTP operation. The VFA must then be produced through fermentation at the WWTP or added as an external carbon source to support biological phosphorus removal. An economic comparison should be made between chlorination or other means of odor, corrosion, and septicity control and the cost of operating a biological phosphorus-removal process to determine the preferred approach. If chlorination is selected, it must be realized that the VFA load into the WWTP will change and that the cost of adding or producing VFA should be added to the cost of chlorination to take into account all economic factors.

There will always be competition between a city's or utility's wastewater treatment and collection system managers for budget. The fact that there may be a greater capital investment in the collection system makes it an

asset to be protected. Septicity, odor, and corrosion may be localized issues or may be system-wide, which is why there is no hard-and-fast rule about where chlorination should be practiced. Protecting the integrity of the collection system should be of prime importance and must be one of the principal factors in evaluating the methods of controlling corrosion of a system, which includes force mains and pumping stations. However, long-term compliance with the permitted phosphorus limits is also important, so weigh these factors to make the best decision possible after evaluating the economic factors.

Removal of Oils and Grease

Excessive amounts of oils and grease are a nuisance at wastewater treatment facilities. These materials can blind screens, accumulate on the interior structures and piping, destroy paint on steel structures, cause odors, and interfere with secondary treatment processes and sludge digestion. If discharged into receiving streams, oils and grease can hamper oxygen transfer and disturb fresh water ecology. Most National Pollutant Discharge Elimination Systems permits include a general condition prohibiting the discharge of materials that float or produce a sheen on the receiving stream. The typical oil and grease numerical limit for direct discharge is 10 mg/l.

The use of chlorine to improve grease removal was first reported by Faber¹⁹ at the Woonsocket, Rhode Island, plant, where the preaeration air used for grease removal was dosed with 2 ppm of chlorine gas. With a contact time of approximately 6 min, the effectiveness of grease removal increased by 189%–442%. Keefer and Cromwell²⁰ evaluated chlorine doses of 1–10 ppm introduced into the diffused air lines for grease removal with liquid contact times of 5, 10, and 15 min at the Baltimore, Maryland, WWTP. Best results were obtained with a chlorine dose of 5 ppm and a contact time of 5 min. Increased removals with chlorine over those achieved by using air alone ranged from 148% to 800%. The success at these facilities led to the implementation of aerochlorination at the two activated sludge plants at Lancaster, Pennsylvania. The chlorine was applied as a solution immediately ahead of the air diffusers in the preaeration channel. The chlorine doses used averaged about 2 mg/l, with 2–3 min of contact. With this treatment, 70%–80% of the grease was removed, as compared with 50% removal using air alone. Although data on the use of aerochlorination for grease removal are limited, they do indicate a definite increase in removal over air alone. Chlorine appears to break up emulsions, allowing the grease to float, which facilitates its collection.

In conventional wastewater treatment, prechlorination can increase the amount of scum from the surface of clarifiers. The scum appears to accumulate in a more dense or compact and more readily removable mass, and improves the general appearance of the clarifiers. Chlorine for grease removal may be applied as a solution ahead of the primary clarifiers (prechlorination) or ahead of the aeration tanks. It is not necessary to satisfy the chlorine demand of the

wastewater. Often a chlorine concentration as low as 2–5 mg/l can bring about an improvement in grease removal.

Aerochlorination seems to be more effective than conventional prechlorination. Dry chlorine gas is mixed with the diffused air being discharged into the aeration basins using conventional vacuum feed solution-type chlorination equipment; however, instead of water, air is forced through the injector to operate the equipment. With this method, a mixture of 2–10 mg/l chlorine gas and 0.02–0.20 ft³ of air is applied per gallon of wastewater, with a 3- to 20-min aeration period.

Removal of Ammonia

Nitrogen in its various forms can deplete the DO in receiving waters, stimulate aquatic growth (algae), and at sufficiently high concentrations, be lethally toxic to aquatic life. In 1970, the European Inland Advisory Commission conducted a study of the effect of ammonia nitrogen on freshwater fish, the results of which indicated that the allowable limit for un-ionized ammonia N, rather than total ammonia N, should be limited to 0.025 mg/l. Un-ionized ammonia is far more toxic than ammonium ion. Unfortunately, ammonia N probes cannot detect concentrations lower than 0.03 mg/l. However, the un-ionized ammonia concentration can be calculated from measurements of total ammonia, pH, total dissolved solids, salinity, and temperature according to the following expressions:

$$\text{NH}_3\text{-N} = \frac{\text{Total ammonia}}{10^x + 1}, \quad (5.16)$$

where

$x = pK_a - \text{pH}$, and

pK_a = the equilibrium constant between NH_3 (ammonia) and NH_4^+ (ammonium ion).

Removal of ammonia nitrogen by chlorine is an extension of the breakpoint reaction. The use of chlorine to remove ammonia nitrogen has been studied on two levels: (a) where chlorination was the sole process and (b) where chlorine was used following a biological nitrification process. In the first instance, ammonia nitrogen concentrations were in the range of 15–25 mg/l, and in the second instance, the range was 0.5–2.5 mg/l.

The speed to complete the breakpoint reaction is a function of the concentration of the reactants (i.e., chlorine and ammonia). Lower ammonia concentrations result in slower reaction rates. Therefore, larger contact chambers are required for the removal of lower concentrations of ammonia N.

Stone et al. conducted a full-scale demonstration of nitrogen removal by breakpoint chlorination at the Rancho Cordova secondary WWTP in

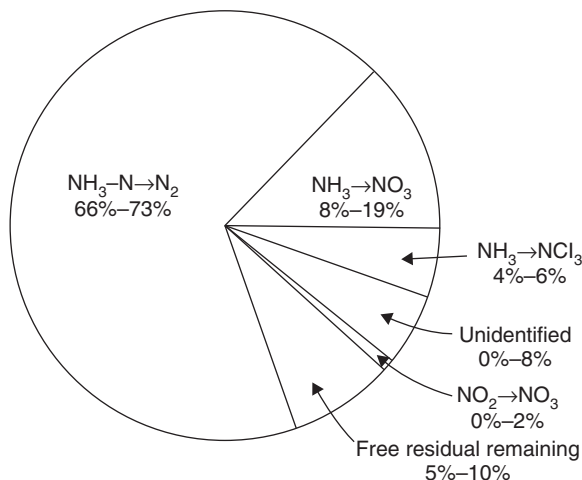


Figure 5.8. Chlorine consumption during nitrogen removal by breakpoint chlorination.

Sacramento County, California, between December 1975 and March 1976.²¹ During this time, the automatic chlorination facility was operated 24h a day, 5 days a week. The process flow rates varied from about 0.1 to 1.2 mgd. Influent ammonia nitrogen concentrations were ordinarily in the range of 15–25 mg/l. The breakpoint process succeeded in constant removal of about 97% of ammonia nitrogen.

The observations and conclusions from the Rancho Cordova demonstration program included the following:

1. The dosage of chlorine to reach breakpoint and to maintain a controllable free residual in the process stream averaged 10mg/l for each 1.0mg/l ammonia nitrogen in the process influent, which was the plant effluent.
2. Approximately 70% of the breakpoint chlorine dosage was consumed to produce nitrogen gas (N_2) from ammonia ($\text{NH}_3\text{-N}$) at pH set points between pH 7 and 8. The oxidation of $\text{NH}_3\text{-N}$ to NO_3^- consumed 8%–19% of the total chlorine dosed to the system. As indicated on Figure 5.8, about 96% of the total chlorine dosage accounted for reactions between chlorine and nitrogenous species in specific chemical pathways and the free chlorine residual remaining in solution following breakpoint.
3. Nitrate (NO_3^-) production in breakpoint chlorination was not pH sensitive, with about 1.0mg/l NO_3^- (as N) produced from NH_4^+ across a final pH range of 6.5–8.5. The production of NO_3^- from NO_2^- was wholly dependent on the influent NO_2^- concentration.
4. Nitrogen trichloride (NCl_3) production was insensitive to pH across a range of final system pH values from 7 to 8. The median value for

NCl_3 produced was about 0.4 mg/l (as N) when treated effluent after breakpoint chlorination was used as the injector water. While the amount of chlorine consumed in forming NCl_3 was relatively small (4%–6% of the total dosed), NCl_3 generation affects the minimum achievable ammonia concentration in breakpoint, as it decays slowly in dilute solution, and it is converted to ammonia upon dechlorination with sulfite ion.

5. If the breakpoint process influent is used as injector water, reactions between chlorine and ammonia can occur in the injector water and consume chlorine in undesirable side reactions. Therefore, injector water should always come from the reacted process effluent. At Rancho Cordova, when secondary effluent (process influent) was used as the injector water source, the NCl_3 formed in the injector discharge increased the NCl_3 in the process effluent by about 0.2 mg/l.
6. The rate of reaction for breakpoint chlorination varied depending on the pH control point (final system pH), with fastest rates observed at a set point of pH 7.0. The time to completion was between 60 and 90 s at pH 7.0. Reaction rate slowed considerably at pH set point 6.5, with gradual reductions in rate as pH increased from 7.3 to 8.5.
7. Variations in the amount of mechanical mixing intensity in the zone of breakpoint chemical application had no effect on overall system chemical consumption and effluent quality. Mechanical mixing to facilitate rapid and thorough blending of process chemicals and the influent stream was important in dampening free residual oscillations for control.
8. Sodium hydroxide (NaOH) was used throughout the study as alkalinity supplement. The amount of NaOH required to neutralize breakpoint acidity (1.53 lb NaOH/lb Cl_2) was essentially identical to that predicted from chemical stoichiometry.
9. The small amount of NCl_3 formed did not present any odor problem, partly owing to the closed pipe reactor and the reliability of the control system.
10. The continuous $\text{NH}_3\text{--N}$ process influent analyzer signal built into the chlorination control system was not needed for the successful operation of the process.
11. The key control parameters, in addition to the plant flow signal, were the chlorine dosage trim signal from the free residual analyzer and the ability of the NaOH feed system to maintain a set point of the process pH within ± 0.2 pH units.
12. The DPD–FAS titrimetric method for determination of the chlorine residual species proved most reliable and time saving.
13. The reaction time at high $\text{NH}_3\text{--N}$ concentrations was so rapid that nuisance residuals had little chance to form.

Removal of lower ammonia nitrogen concentrations with chlorine requires longer contact periods. For example, 0.5 mg/l ammonia N will require at least 20 min of contact time. If the ammonia N concentration falls below 0.5 mg/l, the contact time will have to be longer. However, for an ammonia N concentration of 2.5 mg/l, the contact time required is about 10 min. The key control parameter in the case of low ammonia N concentrations is the signal generated by the free chlorine analyzer. The analyzer must be able to detect free chlorine over a range of 1–15 mg/l in the presence of about 25% combined chlorine. The chlorine dose correction called for by the analyzer must have a frequency related to the contact time required to complete the breakpoint reaction. As long as the $\text{Cl}_2:\text{N}$ ratio is optimum (10:1), the formation of nitrogen trichloride will not be significant enough to cause a nuisance.

INDUSTRIAL WASTE TREATMENT APPLICATIONS USING CHLORINE

Chlorine has been used to treat industrial wastewaters containing cyanides, phenols, and textile dyes. Some of these applications are described below.

Free and Combined Cyanides

Cyanides are toxic to aquatic life. They interfere with normal biologic processes of natural purification in streams, are detrimental to agricultural uses of water, and are a menace to public water supplies. Intermittent exposure of activated sludge to cyanide can inhibit nitrification; however, with continued exposure, the biomass will become acclimated to low concentrations of cyanide. Cyanides are toxic to living organisms by reducing or preventing utilization of oxygen in a manner similar to asphyxiation. The action at the toxic level is both rapid and fatal.

Cyanide in receiving streams can result in fish kills either directly or indirectly by destroying the organisms upon which the fish feed. The toxic threshold for some species of fish is reported to be 0.05–0.10 mg/l of cyanide as (CN) radical.^{22,23} This toxicity increases with rise in temperature and decrease in DO. The toxic action appears to be related to photosynthetic activity in surface waters because fish have been found to thrive in water containing cyanide at concentrations as high as 1000 mg/l in the absence of sunlight.⁸ Doses lethal to animals and humans amount to only 4 mg/l per pound of body weight.

Cyanide wastes are known to impair the biological processes used at waste treatment plants, although these processes do reduce the cyanide concentration. The U.S. Environmental Protection Agency requires all cyanide wastes discharging into municipal wastewater collection and treatment systems to be reduced to cyanates, which are several hundred times less toxic than cyanides. Cyanide is one of the pollutants that must be

regulated by technically based local limits under the Industrial Pretreatment Program.

Although cyanide compounds are widely used in industry, the following five industrial processes are responsible for most of the cyanide wastes that cause stream pollution and present problems at waste treatment plants: (a) metal plating; (b) case hardening of steel; (c) neutralizing of acid “pickle scum”; (d) refining of gold and silver ores; and (e) scrubbing of stack gases from blast and producer gas furnaces. Cyanide is also made at treatment plants that incinerate sludge. Multiple heart incinerators often produce cyanide from incomplete combustion or from a low temperature profile. The cyanide will be trapped in the scrubber water and, when recycled to activated sludge, the cyanide can inhibit nitrification. Incinerators with after burners and fluidized bed incinerators can be operated to eliminate or minimize cyanide formation.

Cyanide in wastes occurs in two basic forms: free cyanide (NaCN or KCN) and combined or complex cyanide ($\text{Na}_2\text{Au}(\text{CN})_2$). When chlorine in its various forms (represented as Cl_2 below) is applied to wastewater containing free cyanide such as sodium cyanide, the following reaction takes place, producing cyanogen chloride:



This reaction is instantaneous and independent of pH. Cyanogen chloride is also a toxic waste, and, as it volatilizes readily, its formation as the end product is to be avoided. With proper pH control, CNCl can be converted to a more stable compound. In the presence of alkali, CNCl decomposes to cyanate at pH 8.5–9.0:



Complete conversion of free cyanide to cyanate with chlorine at pH 8.5–9 takes 10–30 min. At higher pH, the reaction time is shorter; for example, at pH 10–11, it takes only 5–7 min. If the pH drops below 8.0, cyanogen chloride begins to form.

The theoretical requirements for destruction of free cyanides to cyanates are as follows: 2.73 parts of chlorine for each part of free cyanide as CN ; 1.125 parts of NaOH or 1.225 parts of $\text{Ca}(\text{OH})_2$ per part of chlorine applied. In actual practice, more chlorine is required because other chlorine-consuming substances are usually present. As the waste usually contains sufficient alkalinity, the alkali requirement averages less than 1 part of alkali per part of chlorine. If the waste contains ammonia, it is not economically desirable to chlorinate beyond the breakpoint to a free chlorine residual, as the chloramines will react to destroy the free cyanide. For chloramine treatment, an additional 15 min should be allowed. Since the pH value is critical to the reaction, it should be measured after chlorination.

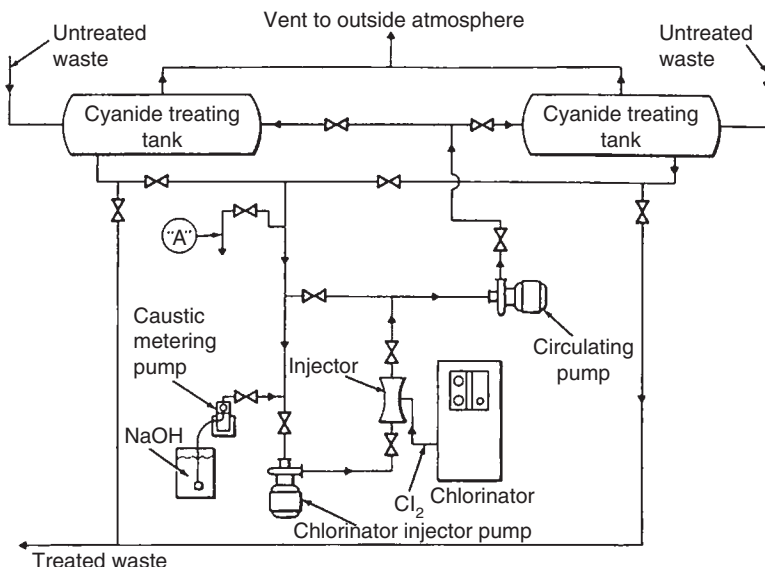
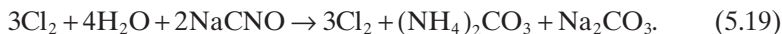


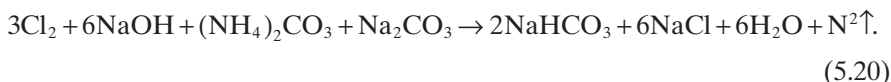
Figure 5.9. Schematic of a batch-type chlorination system for the destruction of cyanides. Free chlorine residual at point "A" denotes complete destruction of cyanides to carbon dioxide, nitrogen, and nitrous oxide.

When partial oxidation of cyanides to cyanate is sufficient, either a flow-through or a batch treatment system may be used. The process schematic of a batch system is illustrated on Figure 5.9. A flow-through system can be more economical than a batch system because it is possible to control the reaction between chlorine and cyanide to form cyanate before the reaction between chlorine and cyanate can begin. This economic advantage may not be the primary consideration when the free cyanide must be completely destroyed.

The cyanates produced by destruction of the cyanides at pH 8.5–9.0 are not readily decomposed by water or by the excess alkali in the treated waste unless free chlorine is present. Cyanates hydrolyze slowly in the presence of chlorine to form ammonium carbonate and sodium carbonate:



In this reaction, chlorine acts as a catalyst to complete the reaction within 1–1.5 h. The chlorine must be free available HOCl. After hydrolysis, the chlorine and the caustic rapidly oxidize the ammonium carbonate to nitrogen gas, and the carbonates are converted to bicarbonates as follows:



Although not shown above, small amounts of inert nitrous oxide (N_2O) and volatile nitrogen trichloride (NCl_3) are also formed as part of this reaction. Complete destruction of cyanides and cyanates to carbonates, nitrogen, and nitrous oxide theoretically requires 6.82 parts of chlorine per part of free cyanide as CN , and 1.125 parts of NaOH or 1.225 parts of $\text{Ca}(\text{OH})_2$ per part of chlorine applied.

In practice, slightly more chlorine is required to deal with other chlorine-consuming compounds. Any ammonia initially present will have to be destroyed by breakpoint phenomenon in order to ensure the formation of free chlorine. This requires approximately 10.0 mg/l chlorine per milligram per liter of ammonia nitrogen.

Owing to the frequently high initial alkalinity of these wastes, the alkali requirements are usually less than 1 part (0.6–0.8 part) of alkali per part of chlorine.

Either a flow-through or a batch system may be used for the complete destruction of cyanides and cyanates. In either case, the minimum holding time for all reactions to go to completion is 1.5 h. In a flow-through system, short-circuiting becomes critical; therefore, it is necessary to monitor the ORP of waste at several points. A process schematic of a flow-through system with appropriate process controls is illustrated on Figure 5.10. Chlorinator no. 1 is controlled by an ORP controller; this is first-stage oxidation of cyanide to cyanates. Caustic pump no. 1 is controlled by a pH controller. Chlorinator no. 2 is controlled by chlorinator no. 1; this is second-stage oxidation of cyanate to carbon and nitrogen. Caustic pump no. 2 is controlled by chlorinator no. 2. Chlorinator no. 3 and caustic pump no. 3 are backup units operated by alarms on the ORP monitoring system.

In the electroplating industry, the plating baths and rinse waters contain excess cyanide above that required to form the soluble metal cyanide complexes. The excess cyanide is known as free cyanide; in the complex metallic form, it is referred to as combined cyanide, which can be of cadmium: $\text{Cd}(\text{CN})_2 \cdot 2\text{NaCN}$; of copper: $\text{Cu}(\text{CN})_2 \cdot 2\text{NaCN}$; of silver: $\text{AgCN} \cdot \text{NaCN}$; or of zinc: $\text{Zn}(\text{CN})_2 \cdot 2\text{NaCN}$.

The chlorine and alkali requirements for the destruction of cyanides and cyanates in metal plating wastes is based on the total cyanide, that is, on the sum of free and combined cyanide. The chlorination of metallic cyanide wastes differs from chlorination of free cyanides in the following ways:

1. The metals are more or less converted to insoluble oxides, hydroxides, or carbonates.
2. These insoluble compounds require additional facilities for sedimentation and sludge disposal.
3. Additional chlorine is required to oxidize certain metals, specifically copper and nickel, to a higher oxidation state.

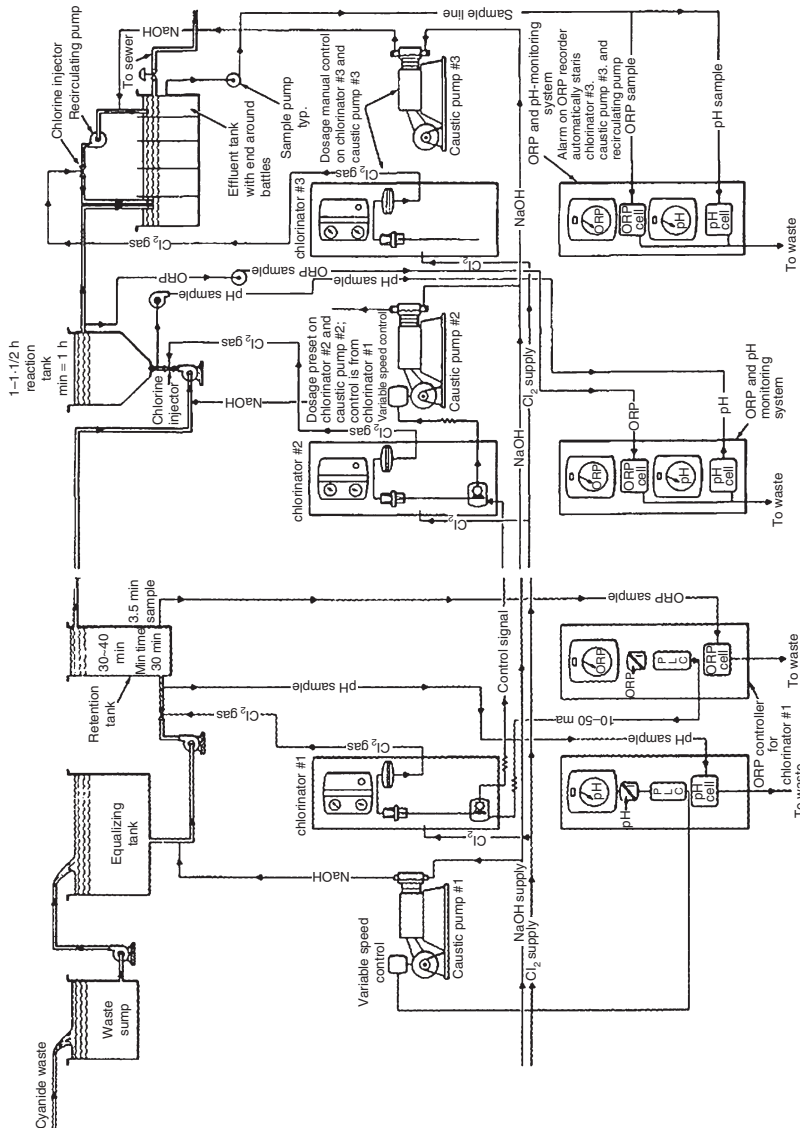
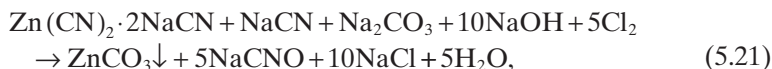


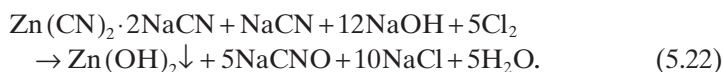
Figure 5.10. Schematic of a fully automatic alkaline-chlorine waste destruction system for continuous flow-through treatment.

4. When nickel is present, it can interfere with the conversion of cyanides to cyanates.
5. When iron is present as ferrocyanide, it is readily oxidized to ferricyanide, which resists destruction by the alkaline chlorine process.

The chlorination of plating wastes to the soluble alkali cyanates and the insoluble metallic precipitate is shown by the following reaction, which forms insoluble zinc carbonate:



or by the reaction forming insoluble zinc hydroxide:



Both of these reactions are rapid in the presence of free chlorine residual. If chloramines occur, the reaction will not go to completion, and insoluble metallic cyanides may be found in the sludge. This can be avoided by monitoring to a free chlorine residual or to the proper ORP level (Fig. 5.11). The chlorine demand for this reaction must include breakpoint chlorination of any

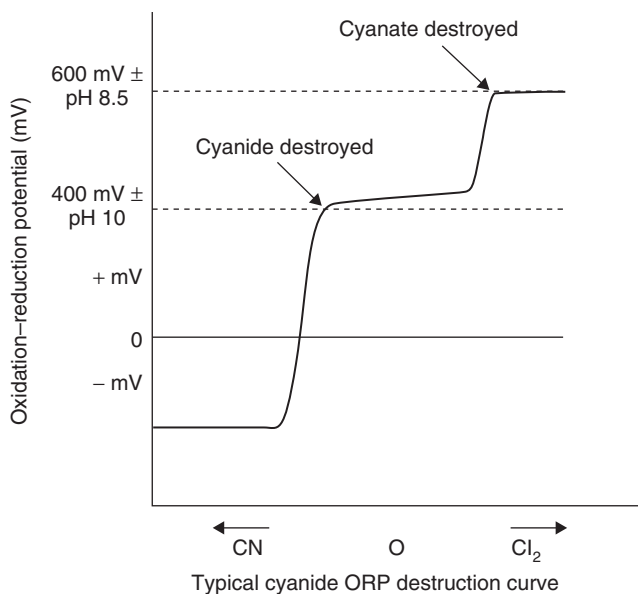


Figure 5.11. Typical ORP versus cyanide destruction curve.

ammonia in the waste. The volume of sludge will be 1% of the initial waste volume when the total cyanide concentration is between 50 and 75 mg/l.

When copper or nickel plating rinse waters (which are cyanide free) are mixed with cyanide wastes and treated, additional chlorine is consumed in converting the cuprous copper and nickelous nickel to higher forms as follows: 0.56 part of chlorine per part of cuprous copper; 2.25 parts of chlorine per part of nickelous nickel; and 1.125 parts of NaOH or 1.225 parts of $\text{Ca}(\text{OH})_2$ per part of chlorine applied.

Nickelous nickel forms a cyanide complex that interferes with the destruction of cyanides to cyanates. It is reported that this complex cyanide cannot be completely oxidized to cyanate in a short time, even in the presence of free chlorine residual. However, it creates no problem when the cyanides are to be completely destroyed to carbon dioxide, nitrogen, and nitrous oxide. In a flow-through system, where the cyanides are to be converted to the cyanates, the presence of nickel may be solved as follows:

1. Separate nickelous waste from the cyanide waste.
2. Apply nickelous waste to inlet of settling basin along with the cyanide waste after chlorination (nickelous waste does not contain cyanide).
3. Allow the nickelous oxide or hydroxide formed by the reaction with the alkali to settle out. Any excess free chlorine in the chlorinated cyanide waste will rapidly convert the nickelous nickel to black nickelic oxide, which hydrolyzes to insoluble hydroxide.

Photographic process wastes contain potassium and sodium ferricyanides among other chemicals deleterious to receiving waters. Both ferrocyanide and ferricyanide are toxic to some fish in the presence of sunlight at concentrations as low as 2 mg/l and should therefore not be discharged without treatment to bodies of water used for beneficial purposes.

While the ferrocyanide is readily oxidized to ferricyanide by chlorine, it apparently cannot be destroyed directly by alkaline chlorination. It must therefore be first decomplexed. The addition of mercuric chloride to the waste has been suggested to decomplex the iron cyanide. This would form mercuric cyanide, which can be destroyed by alkaline chlorination, but the mercury would then have to be recovered or precipitated.

One source of cyanide at WWTPs is the blowdown of incinerator scrubber water. If the sludge is incinerated at low combustion temperatures, cyanide can be formed and will be captured in the scrubber water. The scrubber water has a low pH and contains high concentration of dissolved carbon dioxide. The low pH and high acidity of the scrubber water blowdown may require more caustic than needed for the oxidation reaction. The intermittent return of cyanide in the scrubber water may interfere with nitrification in the secondary treatment process. The cyanide can be eliminated from the scrubber blowdown by adding an afterburner to the incineration system.

Phenols

Phenolic compounds are toxic to aquatic life, and in minute quantities are deleterious to water supplies because of their taste- and odor-producing characteristics. Wastes from many chemical plants; coke, gas refining, rubber production, and animal husbandry such as sheep dips and livestock disinfection, contain these objectionable substances. Phenols are the hydroxyl derivatives of benzene that include various phenols, cresols, and related compounds of higher order.

Phenols can be completely destroyed through oxidation by chlorine, chlorine dioxide, or ozone. In the past, economic considerations have eliminated both chlorine dioxide and ozone as practical means for destruction of phenols in wastewaters; however, the cost of making chlorine dioxide and ozone is becoming more economically affordable. Biological oxidation of phenols can be accomplished under rigorously controlled conditions. However, slug discharges of phenolic compounds to conventional activated sludge or high-rate trickling filter systems may not remain in the system long enough to fully oxidize the phenols, in which case, phenols will appear in the effluent. If the effluent from such a system is disinfected by chlorination, chlorophenols will be formed, which is the worst possible situation since chlorophenols at concentrations as low as 0.1 mg/l can impart an off-flavor in a water supply. Chlorophenols are also more toxic to aquatic life than are straight phenols, and are regulated under water quality standards.

Destruction of phenols by chloro-oxidation is the preferred chemical method, and it is economically practical if the phenolic content of the waste does not exceed 200 mg/l. The chloro-oxidation process must be carried out at pH between 7 and 10 and with a minimum of 100 mg/l free chlorine residual. Although the ratio of chlorine to phenol to accomplish destruction has been estimated to be between 6:1 and 10:1, generally larger amounts of excess chlorine are required. As a result of the enormously high chlorine demand of phenolic wastes, 3-min residuals should be on the order of 1000–3000 mg/l. Under these conditions, it is likely that other chlorinated by-products will also be formed.

Chamberlin and Griffin²⁴ found that 5000 mg/l of chlorine was required to destroy 100 mg/l of phenols in a coke plant still waste. If the theoretical ratio is valid (10:1), the waste contained other compounds that had a chlorine demand of about a 4000 mg/l. It should also be recognized that the contact time for the reaction largely depends on the amount of excess chlorine available. The chlorine residual in the destruction process should be at least 100 mg/l. Although this seems unusually high, extremely obnoxious odors will develop during the treatment process if the residual is not maintained at this level, indicating incomplete oxidation by chlorine. Some free chlorine residual must be present to avoid the odors. Temperature can also influence the speed of the reaction: The rate of phenol destruction increases with rising temperature.

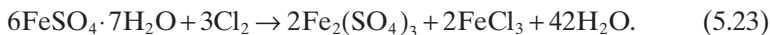
Depending on the amount of excess chlorine residual, the contact time may vary from about 5 to 10 min, with residuals of 1000–3000 mg/l, to nearly 2–5 h, with residuals of 50–100 mg/l. A stepwise reaction with chlorine first forms trichlorophenols, which are subsequently cleaved by chlorine to yield aliphatic acids as the end product of the phenol destruction. This high residual–contact time relationship makes the treated effluent toxic because of too high a chlorine residual. The effluent must either be held in a contact tank for the chlorine residual to decay to nontoxic levels or the treated effluent must be dechlorinated prior to discharge.

The chlorination facility for destruction of phenols is similar to a cyanide destruction facility. The waste is pumped from a holding tank through the chlorine injector at a constant rate to a chlorine contact or holding tank. Since phenol destruction takes place only at pH 7–10, the pH of the solution discharged from the chlorine injector must in this range by adding caustic at a rate of about 1.125 parts NaOH per part of chlorine. Depending on the buffering action of the waste, this rate may vary from 0.8 to 1.5 parts NaOH per part chlorine. Therefore, the caustic feeder should be automatically modulated by a pH control system capable of feeding approximately 0.235 gal of 50% NaOH per pound of chlorine. Since the chlorinator recirculates a constant amount of waste to be treated, the chlorinator control is done by manual dosage setting.

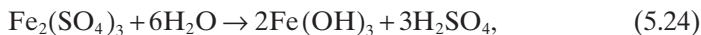
Textile Wastes

Wastes from the processing of cotton and wool, which usually have a high BOD (500–1500 mg/l) and are often highly colored, are generally treated by both chemical precipitation and biological processes. Chlorine is used in the treatment of these wastes to produce ferric chloride coagulant and to bleach the color out of the treated effluent.

Since chlorine is used as a bleaching agent, it can also be used to convert the ferrous ion in the form of copperas (ferrous sulfate) to ferric sulfate as follows:



The ferric sulfate hydrolyzes to ferric hydroxide, which forms a brown, heavy, gelatinous floc, as follows:



and similarly,



For textile waste pretreatment, copperas (FeSO_4), which is a granular material, is fed through a volumetric feeder into a solution mixing chamber, and the solution is pumped or ejected into the discharge of the chlorinator injector solution line, where the ferric sulfate is formed. The solution is then delivered

to the chemical mixing chamber to produce the floc for the treatment process. A common chlorine feed facility can be used. A second chlorine stream can be diverted to the effluent for bleaching color from the treatment plant effluent, or for a disinfectant if combined wastes are involved.

Applications to Other Industrial Waste

Before raw wool is processed by the textile manufacturer, it must be cleaned. The wastewater from the cleaning process is an alkaline and highly putrescible emulsion of grease, organic matter, and fine solids in suspension. Its strength may range from approximately 5000–10,000 mg/l suspended solids, 5000–15,000 mg/l grease, and 5000–6500 mg/l of BOD.

Hypochlorite is often used to recover the grease in the wool scouring process. The hypochlorite process reacts with the alkalinity and the soluble soaps to produce a precipitate, separating the waste into its solid and liquid phases, and is reported to remove about 98% of the grease, of which 70%–75% can be recovered and sold. Thus, practically all of the suspended solids and grease can be removed, together with 80%–90% of the BOD.

Chlorine is also widely used in rendering plants to convert poultry, fish, and animal by-products into animal feed and recovered grease. This is accomplished by cooking the by-products for several hours at high temperatures. The cooked material is pressed to remove the grease, and the pressings are ground. The cooking process gives off odorous vapors, which are captured by condensing them in large quantities of water and by burning the noncondensable vapors. About 150 gpm of water is required for a 5-ton cooker. The water used to scrub the stack gases is chlorinated to about 6–8 mg/l, which eliminates the odors and substantially increases grease removal.

Washing of trucks, barrels, and floors can produce strong liquid wastes, which are often treated with alum and chlorine. Alum reacts with the bicarbonate alkalinity to form a floc, and the CO_2 thus produced reduces the pH. Chlorine oxidizes the reduced material and coagulates the protein, which is most effective at pH 4.0–4.5. The optimum doses of alum and chlorine are 80 mg/l and 260–350 mg/l, respectively. BOD can be reduced by 35%–90% with chlorine dosages of 260–350 mg/l.

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6 Disinfection of Wastewater

INTRODUCTION

The United States' public health agencies have remained deeply committed to the theory of multiple barriers or multiple points of control between a sewage discharge and a water supply intake. These barriers include wastewater treatment, land confinement, dilution, time, distance, and potable water treatment. To achieve strict control of the spread of disease, the U.S. Environmental Protection Agency (USEPA) and state regulatory agencies mandate that municipal wastewater effluents be adequately disinfected before being discharged into the environment.

Wastewater disinfection is defined as the partial destruction of pathogenic microorganisms in the wastewater stream by physical or chemical means. This is best accomplished by using chemical agents such as aqueous solutions of chlorine, chlorine dioxide, hypochlorite, bromine, bromine chloride, ozone, peracetic acid (PAA), bromochlorodimethylhydantoin (BCDMH), or combinations of these chemicals. Ultraviolet (UV) light is another common means of disinfecting wastewater treatment plant (WWTP) effluents. Other means that have been used in special situations and with varying degrees of success include gamma radiation, sonication, heat, and silver ions. The objectives of wastewater disinfection include prevention of the spread of disease and protection of potable water supplies, bathing beaches, receiving waters used for boating and water contact sports, and shellfish beds. Since residual chlorine is needed to meet disinfection goals and chlorine is a toxic material to aquatic life, dechlorination is typically a companion process and the objective of dechlorination is the protection of aquatic life.

History

It was the fouling of one of the most beautiful expanses of resort beach areas in California that captured the attention and energies of the California State Department of Public Health. Beginning about 1920, the Bureau of Sanitary

Engineering entered into a 20-year battle with the City of Los Angeles to clean up the discharge from its Hyperion WWTP, which was solely responsible for the fouling of a 10-mi stretch of this magnificent beach. In order to convince the City of Los Angeles that the 170 mgd of wastewater discharged from the Hyperion outfall was polluting the beach area, the Bureau of Sanitary Engineering, California State Department of Health, launched in 1941 a year-long study of 10 miles of beach in Santa Monica Bay.

The report of this investigation led to the immediate quarantine of this stretch of beach, on the grounds that both the beach and the surf waters were polluted with sewage and were therefore dangerous to human health. After a length of time considered sufficient to correct this hazardous condition of gross pollution, the California State Board of Public Health took the City of Los Angeles to court on a suit based on pollution as determined by the “coliform count” in the bathing waters. Other factors were considered, but it was the coliform count that became the most persuasive piece of evidence.

In its lawsuit against the city, the State Board of Health maintained that 1000 *Escherichia coli* per 100 ml as the limiting standard in the surf waters ensured the safety of the bathers. The State of California won the suit because the judge hearing the case held that the coliform limits used by the Board of Public Health were reasonable, after it was demonstrated that there was clear evidence of pollution and physical nuisance in areas where these bacterial limits were exceeded. This historic case established a statistical baseline for coliform concentration that defined the difference between polluted and pollution-free recreational contact waters in the open surf and has been accepted by the sanitary engineering profession in the United States as a landmark achievement.¹

The Coliform Standard

A comprehensive study of inland recreational waters by Stevenson² concluded that a most probable number (MPN) coliform concentration of 2300/100 ml may be a threshold quality associated with an increase in the incidence of disease. In later years, a geometric mean fecal coliform content of 400/100 ml was determined to be equivalent to the 2300/100 ml total coliform number. In theory, two different standards could be set for potable water and for a wastewater discharge. One was a standard of assured safety where there is no health concern, whereas the other standard was the threshold of unsafe water (2300/100 ml) and might be used as an indication that quarantine or abatement action should be undertaken.

The California State Department of Health recommended discharge limits that would produce a water quality where there is no health concern. The limits reflected an inherent factor of public health safety, whether for potable water, wastewater discharges to variable-use receiving waters, or water reuse situations. These concepts are described as follows:

1. The limit for surf waters should be about 500 times the pollution allowed by the U.S. Public Health Service standards for potable water (2.2 MPN/100 ml).
2. There should be no scientific evidence to indicate that water quality within this standard causes ill health.
3. This amount of indicator organisms should be seldom reached or exceeded in saline waters in the absence of recent waste contamination.
4. A less severe standard might show "approved" areas to lie within areas visible of grease and detritus of waste origin and would therefore seem to be lacking in common sense and decency.

The application of this standard for disinfection first appeared as a required chlorine residual concentration after a specified contact time that would produce the desired receiving water quality. At the time, it was thought that disinfection would meet this standard if a 0.5–0.75 mg/l orthotolidine residual was achieved at the end of a 30-min contact time. Contact chambers were built to give a theoretical 30-min detention time at average flow, based on the volume through the chamber. Effective mixing and contact chamber short-circuiting was never considered. During this period (1947–1957), a great many chlorination facilities were placed into operation, and it became obvious that a given chlorine residual and contact period often resulted in effluents of quite different bacterial quality at different plants. After many years of testing and surveillance of these installations, the California Bureau of Sanitary Engineering concluded that a practical, feasible, and superior way was to prescribe a coliform count directly to the plant effluent, rather than a chlorine residual value as evidence of disinfection.

The numbers in effect in California are 80% of samples less than 1000/100 ml for coastal bathing waters (equivalent to a median of 230/100 ml), a median of 70/100 ml for shellfish growing areas, and a median of 23/100 ml for confined waters used for bathing or other water contact sports, assuming that the dilution is at least 100 to 1. The requirement for discharge into ephemeral streams or other locations of public exposure to effluents receiving little dilution is an essentially coliform-free effluent, a median MPN not greater than 2.2/100 ml. There is a subtle implication of the necessity for good operation and adequate treatment to achieve the 23/100 ml limit. This has been found to be a reasonable standard, but it requires a properly operated treatment plant with an effective disinfection system to consistently achieve it.

The severe effluent limit of 2.2/100 ml implies the necessity for some type of advanced treatment (i.e., filtration) before disinfection to reliably meet this level of disinfection effectiveness, and thereby suggests some virus-removal capability for the system beyond that which normally occurs. These are not alternative requirements, only implications of what might be needed to meet the requirement.

There may be cases where the quality of the plant effluent bears no relation to the receiving water quality. For example, a receiving water might have a consistent coliform concentration as high as 2300/100 ml or even higher. If the California Department of Health had decided that wastewater being discharged to such a receiving water needed to be disinfected, the discharger would not be allowed to simply meet the water quality of the receiving water (2300/100 ml or better) because this would not be evidence of effluent disinfection. Advances in analytical methods now allow differentiation between coliforms of human origin and coliforms from nonhuman sources.

One of the most useful features of a modern wastewater disinfection facility is its ability to serve as a means of monitoring the combined wastewater treatment processes. If all the unit processes are not performing properly, chlorination alone will not be able to produce an effluent that meets the National Pollutant Discharge Elimination System (NPDES) discharge limits. This important attribute of disinfection is often overlooked. This is true in California, where the requirements are the strictest in the nation because it is a mostly arid state, with its wastewater effluent disposed of mainly by surface discharge into coastal bathing areas. Therefore, the consensus organisms to eliminate and control are total coliforms rather than fecal coliforms, which are allowed by the USEPA in many states.

In 1973, the USEPA adopted the secondary treatment regulations to implement the Clean Water Act. These regulations included a limit for fecal coliform bacteria. Three years later, the USEPA replaced the fecal coliform limit with a provision that allowed each state to develop site-specific or water use-based effluent standards for wastewater treatment facilities. Today, state agencies enforce standards ranging from 2.2 to 5000 MPN/ml of fecal or from 2.2 to 10,000 MPN/100 ml of total coliforms from stream to stream, and even for the same stream at different times of the year. The most commonly used limit is 200 MPN fecal coliforms/100 ml.

Unlike other pollutants that are regulated by monthly averages, the coliform standard is based upon a geometric mean. The geometric mean can be based on a 30-day reporting period or on a 7-day period. The regulatory agency should be contacted about the intent of the 7-day geometric mean. Is it to be calculated based upon a 7-day calendar period, or is it a 7-day floating mean? The use of the geometric mean for a long-term average value is to the benefit of the permittee. A straight arithmetic average will be greatly impacted by a single high effluent value, which often happens in disinfection. A geometric mean is calculated by multiplying together all of the reported data and then taking the root of that value with the root equal to the number of reported data points. Some regulatory agencies further tighten the standards by imposing a maximum instantaneous or daily value.

The determination of fecal coliform is the latest in a long history of selective tests to separate the strains of coliform bacteria found in wastewater. It has been largely adopted by the USEPA for various disinfection requirements: shellfish areas, recreational waters, and so on.

Coliforms from the intestines of dogs and cats are mainly *E. coli*. The fecal coliforms from humans and livestock account for about 97% of the total. Fish do not have permanent coliform flora in their intestines. The presence of coliforms in fish is evidence of pollution in the water of their habitat. Fecal coliforms are not abundant in soil (as *E. coli*), as they die off rapidly in the soil. The presence of fecal coliforms in significant numbers is indicative of fresh pollution (Table 6.1). All fecal coliforms in a stream may be accepted as being of fecal origin. Determination of fecal coliforms provides a superior indicator of fecal pollution to measuring total coliforms. So the relationship between the various organisms can be summed up as follows:

1. Total coliforms is the largest group and encompasses all of the target organisms.
2. Fecal coliforms are a subset of total coliforms but are a group of organisms that can come from sources other than humans.
3. *E. coli* is a subset of fecal coliforms and is specific to mammals. When *E. coli* is present in a wastewater, it is probably of human origin. *E. coli* in the environment can come from other mammals.

The California Department of Health has used enumerations of both total and fecal coliforms in its surface water studies since 1960. Although the use of a fecal coliform number as a river water quality objective is appropriate, the use of a fecal coliform limit for measurement of disinfection effectiveness may not be. All available data indicate that the fecal coliform strains are more fragile than the total coliform group and can be more easily destroyed or inactivated by disinfection or by natural purification processes. It has been amply demonstrated on the basis of chlorine demand tests that fecal coliforms can be completely destroyed while significant numbers of total coliforms remain.

There is only sketchy information on the relative resistance of pathogenic agents to chlorination. The data suggest that bacterial agents may be as hardy as coliforms, whereas most viruses are more resistant. The total coliform group is a more conservative indicator of effective disinfection, and total coliforms

TABLE 6.1. Comparison of Fecal and Total Coliform Concentrations through a WWTP³

Process	Total Coliform (#/100 ml)	Fecal Coliform (#/100 ml)
Raw wastewater	10^7 – 10^8	10^6 – 10^7
Primary effluent	10^7 – 10^8	10^6 – 10^7
Secondary	10^5 – 10^6	10^4 – 10^6
Filtered	10^4 – 10^6	10^3 – 10^5
Nitrified	10^4 – 10^6	10^3 – 10^5

are more numerous in wastewater than the fecal coliform group. It is conservatively estimated that the ratio of fecal coliforms to total coliforms in saline waters is 1:70. However, there is a considerable difference in the fecal-to-total coliform ratio from saline to freshwater areas. Instead of the 1:70 ratio, it is estimated that in wastewater effluents the ratio of fecal to total coliforms is about 1:3.

While fecal coliforms have been the indicator of choice for disinfection standards, they are being replaced as the indication of sufficient disinfection. The USEPA has made a change from fecal coliforms to *E. coli*. A commonly used conversion between the fecal coliform and *E. coli* standards is 126 colony-forming units (cfu)/100 ml *E. coli*, which is equivalent to 200 MPN/100 ml of fecal coliforms. The USEPA has tasked each state to develop their guidelines for *E. coli*, so there is no national trend. Some states are using indicator organisms other than *E. coli*. Disinfection standards are changing. To keep current on the issues that impact your part of the world, check with your local regulatory agency/governing agency for guidance.

VIRUSES

While the incidence of typhoid fever in the United States dropped from approximately 2000 cases in 1955 to only 300 cases in 1968, the frequency of infectious hepatitis remained at a static level of 50,000–60,000 cases per year.⁴ This indicated that although waterborne bacterial infections had been all but eliminated by the late 1960s, waterborne viral infections continued to remain a cause of concern. The problem of viruses in water supplies has received a great deal of attention over the years and is well documented.^{5–10} In evaluating the virus hazard, two factors concerned the protectors of the water supplies: the origin of infectious hepatitis and the origin of the significant increase in gastroenteritis. Gastroenteritis is not a reportable disease, as distinguished from relatively well-defined illnesses such as infectious hepatitis, shigellosis, salmonellosis, and typhoid. Yet it can be estimated that the number of gastroenteritis cases occurring per year is hundreds of thousands and possibly millions.

During the period of 1961–1970, a total of 26,546 cases of gastroenteritis in the United States were attributed to contaminated water.⁸ Of the 52 waterborne-disease outbreaks in the United States in 1971–1972, 22 were outbreaks of gastroenteritis, amounting to 5615 cases from a total of 6817 cases of waterborne illnesses.⁹ The concern here was that these cases might have been the result of some unidentified viruses. More than 100 viruses excreted in human feces have been reported to be found in contaminated water. Another aspect of viral infections that is a cause for great concern was included in the evidence examined by McDermott, who pointed out that the poliomyelitis virus had hurdled the technical barriers of water treatment in Paris, France, that consist of coagulation, filtration, and disinfection with both chlorine and ozone.

The concerns about viruses in water were confirmed and substantiated by a 1970 report of the Committee on Environmental Quality Management, American Society of Civil Engineers (ASCE) Sanitary Engineering Division, which concluded the following:⁵

1. The hepatitis virus could be transmitted by drinking water.
2. It was likely that enteric viruses and other possible causative agents of viral gastroenteritis could be transmitted by drinking water.
3. The coliform index was not a reliable index for viruses. Greater assurance of the absence of viruses would be a turbidity less than 0.1 JTU and an HOCl residual of 1 mg/l after a contact period of 30 min.
4. A risk of hepatitis infection could result from the consumption of raw or steamed shellfish taken from sewage-polluted waters; the Public Health Service Coliform Standard (70 coliforms/100 ml) had been shown by experience to be a reliable indication of risk-free shellfish waters. A high level of protection could be provided by process treatment using the activated sludge and chlorination of the effluent to produce an amperometric chlorine residual of >5 mg/l after 30 min of contact.
5. Multiplication of viruses in polluted water did not appear to be a significant possibility.
6. Viruses were present in certain river waters, and failure to isolate them may have been a result of their low concentrations and the relatively ineffective sampling and concentration procedures employed.
7. Enteroviruses and the virus of infectious hepatitis could survive for prolonged periods under conditions prevailing in drinking water reservoirs. Long detention times, therefore, could not be considered a safety factor.
8. Enteric viruses differed in their resistance to free chlorine. Adenovirus 3 was less resistant than *E. coli*, whereas poliovirus type 1 and Coxsackie viruses A2 and A9 were more resistant.

The concentration of enteric virus in raw sewage in the United States can range from 2 or 3 to more than 1000 infectious virus units/100 ml with peak levels occurring in late summer and early fall.⁶ If the concentration of coliform bacteria in raw sewage is estimated at 10^7 – 10^8 /100 ml organisms, then the concentration of enteric viruses is perhaps five to seven orders of magnitude lower.^{11,12}

Although enteric virus concentrations in drinking water are generally very low, as little as one virus infectious unit can produce an infection in humans.⁷ Most isolation of enteric viruses have been made from heavily polluted surface waters, but Berg¹³ detected enteric viruses in Missouri River water that had a fecal coliform concentration as low as 60/100 ml. Although virtually nothing is known about the levels of enteric viruses in U.S. potable water supplies, monitoring of the potable water supplies of Paris¹⁴ in the 1960s revealed that about 18% of the 200 samples examined contained

enteric viruses at an estimated average concentration of one infectious unit/300l.¹⁴

Although there is little quantitative information available on enteric virus levels in sewage-contaminated surface and groundwaters, there is sufficient evidence that wastewaters are a primary source of enteric virus contamination in the human environment. With the possible exception of a few poliomyelitis outbreaks, there is no evidence of waterborne outbreaks in the United States caused by other specific viruses. The most prevalent waterborne disease in the United States continues to be gastroenteritis of unknown etiology. It therefore continues to be important that wastewater treatment processes and reuse systems address themselves to this virus hazard.

Virus Inactivation

The Sanitation Districts of Los Angeles County have been active participants in various water reuse programs since the mid-1950s. Discharges of disinfected secondary effluent have been spread in percolation basins to replenish groundwater used for domestic supplies. Conveyance of this water to the percolation sites is through open flood control channels, and in transit, it is unintentionally used for recreational activities, including body contact sports. About 80 mgd of chlorinated secondary effluent in flood control channels is subject to such unplanned recreational use. The flood channels are classified as “unrestricted recreational impoundments” by the California State Department of Health; therefore, wastewater discharged to them must comply with Title 22 of the California Administrative Code, which contains the effluent quality and treatment system standards for recreational reuse. In order to qualify for such use, secondary effluent must be coagulated, settled, filtered, and disinfected to achieve a median total coliform MPN of 2.2/100 ml or less to protect swimmers against viral illnesses. This level of treatment is expensive from both capital cost and operational standpoints. Therefore, to find alternatives, the Los Angeles County Sanitation District conducted a comprehensive study of methods of tertiary treatment that might be more cost-effective than the required Title 22 System and still produce an effluent with the required degree of public health protection.¹⁵

The investigation focused on four systems using similar wastewater effluent. The nonnitrified effluent contained 20 mg/l $\text{NH}_3\text{-N}$, with suspended solids on the order of 1.5 mg/l and turbidity ranging between 1 and 1.5 FTU when measured using Fromazin polymer. The pH was 7.5, and total dissolved solids (TDS) concentration was 580 mg/l. At this pH, the undissociated HOCl content in system D was about 50%. The four tests are summarized as follows:

- A. The Title 22 treatment protocol defined by the California Department of Health was a 40 gpm secondary effluent ($\text{NH}_3\text{-N}$, 20 mg/l) treated with alum and ionic polymer followed by flash mixing, flocculation, sedimentation, dual-media filtration, and disinfection.

- B. A 25 gpm secondary effluent, similar in quality to system A, was treated with alum and ionic polymer followed by flash mixing, dual-media filtration, and disinfection.
- C. A 100 gpm secondary effluent, similar in quality to systems A and B, was treated by using two-stage carbon adsorption followed by disinfection.
- D. A 25 gpm nitrified secondary effluent ($\text{NH}_3\text{-N}$, 0.1 mg/l), similar in quality to the others, was treated with alum and anionic polymer followed by flash mixing, dual filtration, and disinfection.

Systems A, B, and C could be disinfected by either ozone or chlorine. System D was disinfected with chlorine only since nitrification was not considered to enhance the performance of ozone. Chlorine was applied in systems A, B, and C to produce two levels of chlorine residual at the end of the contact chamber (5 and 10 mg/l). These residual concentrations required chlorine dosages of about 10 and 15 mg/l, respectively. In system D, the free chlorine residual at the outlet of the contact chamber was maintained at 4 mg/l. This required a chlorine dosage of 10 mg/l.

Careful attention was given to the degree of mixing at the point of disinfectant application. A 1/3-hp flash mixer was installed in a 32-gal confined mixing chamber, providing a G factor of 450s^{-1} . A conventional perforated-type diffuser was installed to discharge chlorine about 3 in. from the mixer impeller. The chlorine contact chambers were designed for plug flow. After an optimization study to achieve a coliform MPN of 2.2/100 ml, a detention time of 120 min was selected. A tracer study of the prototype contact chamber revealed a modal time of 98 min and a minimum time of 58 min. So, to compare with laboratory studies, it might be stated that the bacterial kills and virus inactivation were accomplished with a 1-h, rather than a 2-h, contact time.

The ozone system was arranged to dispense a dosage of 10 mg/l in system A, 10–50 mg/l in system B, and 6 mg/l in system C. In each case, the ozone contact time was 18 min. The ozone contactors consisted of six 14-in.-diameter, 18-ft-high polyvinyl chloride (PVC) columns.

Virus inactivation data from this study are illustrated in Figures 6.1 to 6.3. The effectiveness of the combined chlorine residual was a surprise and advanced a totally new concept: that chloramines have viricidal efficiency potentially equal to that of free chlorine.

None of the samples used in these tests conducted in the mid-1970s were analyzed for organic nitrogen because it was not until early 1982 that organic nitrogen content was found to seriously affect free chlorine dosages. It was discovered that using free chlorine in system D (nitrified secondary effluent) increased the predisinfection effluent concentration of chloroform from 0.06 to 1.98 mg/l, whereas in the other systems using only combined chlorine increased the chloroform content by about 0.01–0.06 mg/l. This observation, plus the demonstrated effectiveness of chloramines as a viricide, led to the conclusion that there was no benefit from free residual chlorination of tertiary effluents, where indirect potable reuse is called for.

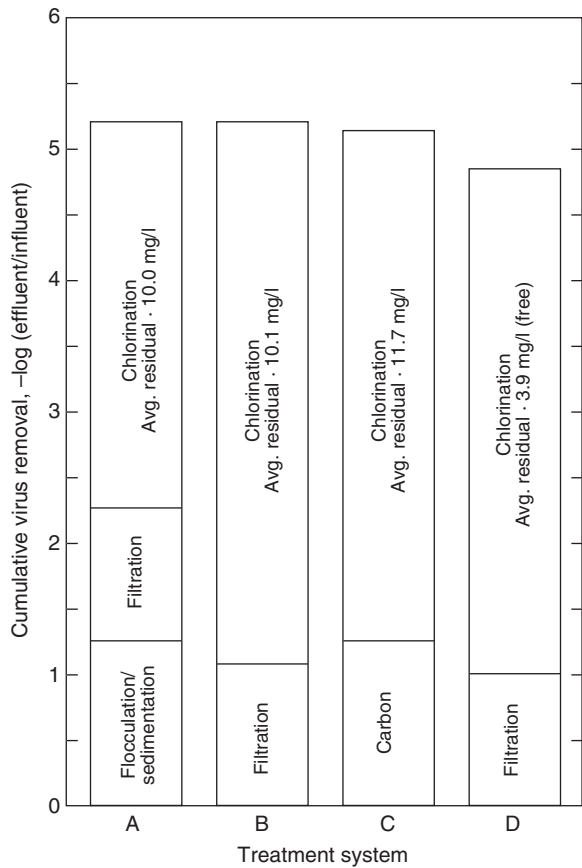


Figure 6.1. Virus removal at high chlorine residual concentrations.

A dominant feature of Figure 6.1 is that the majority of virus removals occurred in the disinfection step. The data presented in this figure indicate that reliance must be placed on the disinfection step rather than on the filtration or carbon absorption steps before disinfection. Other important conclusions drawn from the Pomona study included the following:

1. Virus inactivation in tertiary treatment systems employing combined chlorine residuals of 5–10mg/l ranged from 4.7 to 5.2logs. These results were obtained in poliovirus seeding experiments. Additional virus removal using the 10mg/l residual over the 5mg/l residual was minimal, but the coliform kill was consistently better at the higher residual.
2. The system using free residual chlorination produced about 4.9logs virus removal when the average free chlorine residual concentration was 4mg/l.

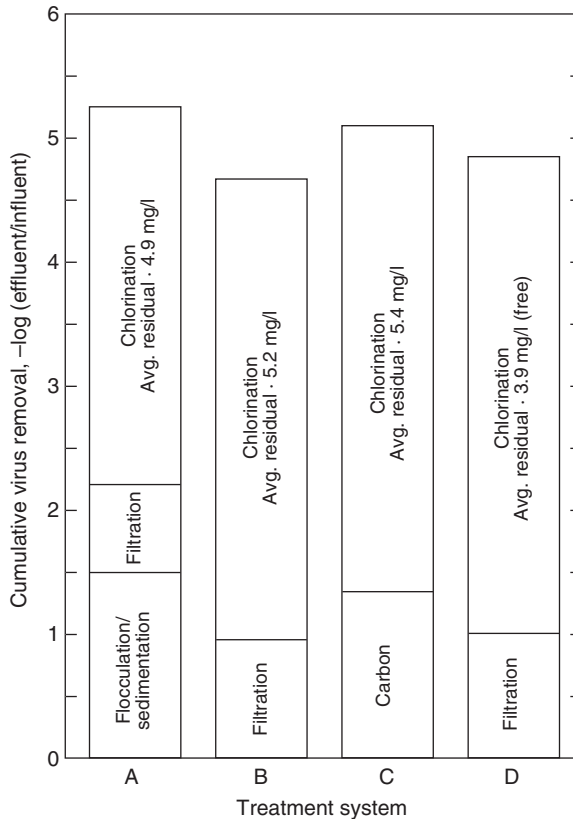


Figure 6.2. Virus removal at low chlorine residual concentrations.

3. All chlorination studies indicated consistent capability by all systems to meet the 2.2/100ml MPN coliform limit.
4. In the experiments using ozonation, virus removal ranged from 5.1 to 5.5 logs; however, meeting the 2.2/100ml MPN coliform limit was hampered by variations in water quality.
5. Based upon the results of the virus experiments, it was concluded that system B (direct filtration) or system C (carbon adsorption), tertiary treatment systems were more cost-effective than system A (the one required by the California State Department of Health).
6. Direct filtration system B was evaluated as the least costly option with chlorination, with an estimated total capital and operating cost of \$0.137/1000gal, as compared with system A at \$0.215/1000gal with chlorine, system C at \$0.172/1000gal with chlorine; and system D at \$0.199/1,000gal with free chlorine. The systems using ozonation were more costly.

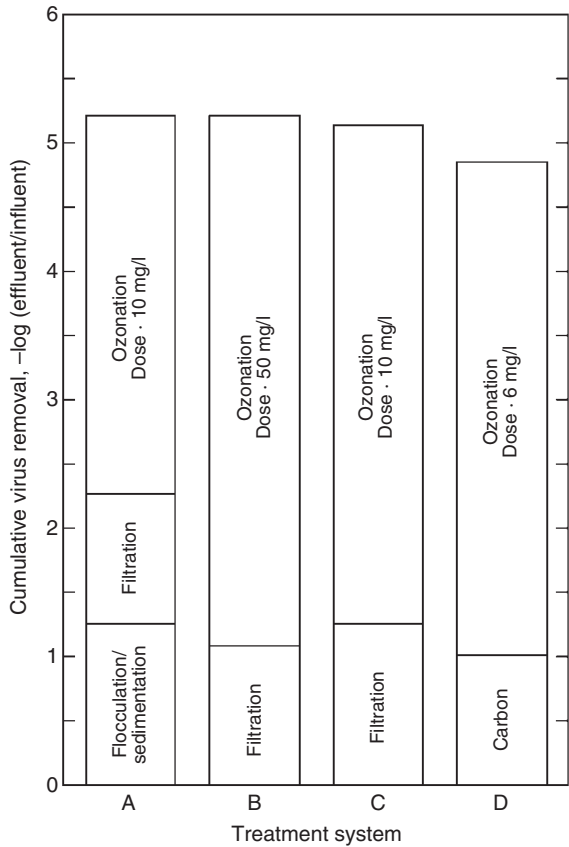


Figure 6.3. Virus removal using ozone.

Ludovici et al.¹⁶ performed a large number of pilot-plant experiments using tertiary effluent from the Tucson, Arizona, WWTP. This effluent had a pH ranging from 7.3 to 7.6; $\text{NH}_3\text{-N}$ concentration of 2.8–5.5 mg/l; an organic nitrogen concentration of 1.4–5.6 mg/l; a biochemical oxygen demand (BOD) of 1.5–8.5 mg/l; and a chemical oxygen demand (COD) of 15–33 mg/l. Although no turbidity information was given, the effluent was considered to be of high quality, except for the 5.6 mg/l organic nitrogen concentration, which was expected to have some inhibiting effect on the chlorination process. The effluent was seeded variously with poliovirus 1, Cocksackie B1, and Cocksackie B2. The chlorine dosages were 2 and 4 mg/l, meaning that all the residuals reported at the end of a 30-min contact time had to be combined chlorine. They were 0.31–1.2 mg/l for the 2 mg/l dose and 0.99–2.76 mg/l for the 4 mg/l dose in the poliovirus 1 tests. The mean virus reduction for the 2 mg/l dose was 96.19%, and 99.3% for the 4 mg/l dose—all at a 30-min contact time. The Cocksackie B1 and B2 viruses were much more susceptible to the combined chlorine residuals: A mean of 99.8% reduction was achieved with a 4 mg/l dose for

Coxsackie B1, and a 100% reduction for Coxsackie B2 with the same chlorine dose.

Other virus inactivation studies were conducted at Louisville, Kentucky, by Pavoni and Tittlebaum,¹⁷ who applied ozone to a 40,000 gpd activated sludge plant effluent seeded with F2 virus (bacteriophage) at a concentration of 1011 plaque units per milliliter and a rate of 1 ml to 1 l of sewage. They reported “virtually 100 percent efficiency (inactivation) after a contact time of 5 minutes with a total ozone dosage of approximately 15 mg/L and a residual of 0.15 mg/L.”

Nupen et al.¹⁸ treated a high-quality effluent for water reuse and found that a free chlorine residual beyond the breakpoint, which produced a pH of about 6.0 and a residual of at least 0.6 mg/l, inactivated poliovirus in 35 min. A major difficulty in the inactivation of viruses is their variable sensitivity to disinfectants. Liu¹⁰ reported the resistance of 16 types of human enteric viruses to free chlorine in treated Potomac River water. The criterion used was time in minutes required for 99.99% inactivation by a 0.5 mg/l free chlorine residual at pH 7.8 and 2°C. Resistance of the viruses occurred in the following order: polio type II (36.5 min) > Coxsackie B5 (34.5 min) > *E. coli* type 29 (18.2 min) > *E. coli* type 12 (16.7 min) > polio type III (16.6 min) > Coxsackie B3 (15.7 min) > adenovirus 7a (12.5 min) > polio type I (12.0 min) > Coxsackie B1 (8.5 min) > adenovirus 12 (8.1 min) > Coxsackie A9 (7.0 min) > *E. coli* 7 (6.8 min) > adenovirus 3 (4.3 min) > reovirus 2 (4.2 min) > reovirus 3 (4.0 min) > reovirus 1 (2.7 min).

The results of the experiments discussed above illustrate the importance of predisinfection processes in treating wastewater effluents. Raw water used for potable supplies is usually of much higher quality than filtered tertiary wastewater plant effluent. Therefore, two different standards of disinfection related to virus inactivation need to be recognized: one for potable water and the other for wastewater. For the latter, significant virus destruction is not possible unless the effluent is of tertiary quality. As for raw potable water, it is the consensus that a 1.0 mg/l free chlorine residual concentration at the end of 30-min contact time at a pH not to exceed 8.0 will probably destroy all pathogenic viruses.

Sorption of viruses to exposed surfaces may not necessarily provide protection from disinfection.¹⁹ Therefore, a higher turbidity could be tolerated in high-quality effluents in the context of virus inactivation. However, it is likely that total encapsulation of the viruses would be the principal mechanism by which particles protect viruses in water.

For tertiary effluents, a combined chlorine residual between 5 and 10 mg/l with a 2-h contact time is likely to be as good or better than a 4 mg/l free chlorine residual for the same contact time. Other disinfectants, such as chlorine dioxide, might prove to be better viricides than either chlorine or ozone. There is no question of the efficacy of ozone as a viricide, but on a cost-effectiveness basis, it seems to be little better than chlorine, with the disadvantage that it may not produce an effluent that meets the coliform limit.

METHODS OF WASTEWATER DISINFECTION

Wastewater effluent disinfection can be disinfected by natural (predation and normal die-away), physical (ultrasound, heat, radiation), or chemical (oxidation) processes. This section discusses briefly the common methods of disinfection used in wastewater treatment, which includes chlorination; use of chlorine dioxide, bromine, iodine, peracetic acid and BCDMH; ozonation; and UV light.

Chlorination is the oldest disinfection method and continues to be an important method of disinfecting municipal wastewater. Chlorine is available in several different forms, and the characteristics of these forms greatly influence the disinfection system. Liquid or gaseous chlorine can be used in disinfection processes; both are manufactured commercially by electrolysis of a saturated salt solution.

“Available chlorine” can be in the form of sodium or calcium hypochlorite. The most popular form is NaOCl or household bleach. $\text{Ca}(\text{OCl})_2$ can be difficult to manage, owing to excessive maintenance problems caused by calcium ion deposits throughout the system. NaOCl is a clear liquid that is available in concentrations of 5%, 10%, and 15% by weight (available chlorine). $\text{Ca}(\text{OCl})_2$ is available either as a granular white powder or in tablet form in strengths of either 35% or 65% chlorine by weight. Imported sodium hypochlorite is being used in some large WWTPs as a measure to avoid the hazard of liquid–gaseous chlorine delivered and stored in containers under vapor pressures of 80–110 psi.

Complete systems are available for on-site manufacturing of hypochlorite solutions by electrolysis, which also eliminates the hazards associated with handling the liquid–gas chlorine in pressurized containers. Electrolytic cell systems are available for use with seawater, brackish water, or concentrated salt brines. The hypochlorite is produced in much the same way as the liquid–gas chlorine, except that there is no need to separate the chlorine gas and the sodium hydroxide, which are the products of the electrolysis. This also eliminates the need for the sulfuric acid drying step required in the manufacture of liquid–gas chlorine. In addition to the formation of NaOCl, hydrogen gas is a product of the electrolytic action. It is diluted with air and vented to the atmosphere in concentrations well below the lower explosive limit. Equipment for this method of on-site production includes electrolytic cells, rectifiers, electric switchgear, brinemaker, brine-treatment unit (where required), water treatment system for cell water, cooling equipment, and storage tanks for brine and hypochlorite. For economy, the process is operated at a constant rate, and excess hypochlorite solution is stored for high-demand periods.

Another method of on-site manufacture of hypochlorite is the use of tank car quantities of chlorine gas supplemented by either calcium hydroxide or sodium hydroxide solution to produce an 8000–9000 mg/l hypochlorite solution. This system is economically appealing from an equipment cost standpoint, when the average chlorine feed rate exceeds 5–6 tons/day.

Chlorine dioxide (ClO_2) can also be used to disinfect effluent. It is a highly selective oxidant that is unstable as a compressed gas, and must be generated at the point of use. It cannot be stored in steel containers as can chlorine. Historically, chlorine dioxide has been generated on-site as an aqueous ClO_2 solution by reacting to a solution of sodium chlorite with the aqueous solution of a conventional chlorine injector discharge. New technology that reacts chlorine gas with specially processed solid sodium chlorite has substantially overcome several limitations of the older chlorine dioxide method of generating, making it more acceptable for wastewater treatment, especially for tertiary treatment of water intended for reuse. Chlorine dioxide does not combine with the ammonia nitrogen normally present in wastewater. Therefore, in a nitrogen-laden wastewater, it can inactivate both bacteria and viruses in the same manner as free chlorine. There is only limited experience with using chlorine dioxide for disinfection of wastewater, and it is significantly more expensive than chlorine.

Bromine, bromine chloride, and iodine have been used in various ways as alternatives to chlorine. Bromine and bromine chloride are more soluble in water than chlorine. However, bromine is too hazardous to handle in the treatment of wastewater. Bromine chloride is much easier to handle than bromine because it has a vapor pressure of about 30 psi at room temperature. The materials required to meter bromine chloride are considerably different from those for metering chlorine; so completely different types of instruments and equipment are required for feeding and metering this gas.

Bromine compounds have an advantage over chlorine compounds since bromine residuals decay more rapidly than chlorine residuals. This alleviates the concern of toxic effects of residuals on aquatic life in the receiving waters. However, this characteristic makes the control of bromine or bromine chloride residual very difficult. Furthermore, the bromine compounds are more expensive than those of chlorine.

Effective and rapid disinfection of combined sewer overflows (CSO) has been achieved using 1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH), a bromine disinfectant. BCDMH is a powder and when dissolved in water produces hypobromic acid, an active biocide. This bromine compound is commonly used in industrial, spa, and pool applications. It is comparable with NaOCl in terms of toxicity and disinfection and there are no halogen-related derivatives prompting subsequent dehalogenation. The speed of reaction reduces the need for disinfectant contact tanks, a critical factor in land-constrained areas. The required retention time is 3 min or less compared with ~15 min for NaOCl . Performance data has shown that an injection rate of 2–7.5 mg/l (chlorine equivalent) reduces 10^3 – 10^6 cfu/ml of coliform to less than 3000 cfu/ml. Since 2004, a total of six facilities have been constructed to provide rapid disinfection of CSO in metropolitan Tokyo. Results have been favorable prompting further expansion and use of this technique within Japan.

Iodine is a gray-brown crystalline solid that is only slightly soluble in water. It has been used as an effective means of water treatment on an emergency basis. There are so many unknown factors about iodine as a wastewater

disinfectant that this lack of information, coupled with its high cost and uncertain availability, makes it difficult to consider it as a practical wastewater disinfectant. The higher molecular weight of both bromine and iodine also puts them at a distinct competitive disadvantage with respect to chlorine.

Another disinfectant—ozone—is an unstable gas that must be produced at the point of use. It is made commercially by the reaction of an oxygen-containing gas (air or pure oxygen) in an electric discharge. It is a powerful oxidant and has been used since the early 1990s to remove odors and color as well as to disinfect potable water supplies in Western Europe and Canada. More recently, it has been investigated for possible use in polishing tertiary effluents, for both color removal and disinfection. From these investigations, it appears that ozone in combination with either chlorine or chlorine dioxide could solve the disinfection issues related to both bacterial and viral contamination in tertiary wastewater effluents. It may be particularly well suited for wastewater that is being considered for reuse.

UV light systems are finding increasing use in disinfection of wastewater effluents. UV light, which has a sterilizing effect on microorganisms, can be produced by special lamps. The disinfection reaction occurs on the thin film surfaces of water where microorganisms can be readily exposed to the radiation. With wastewater, this lethal action cannot be exerted through more than a few centimeters from the surface. Beyond this limiting distance, the absorption of the rays by the water and by the suspended solids dissipates the UV energy. The concept is applicable where the water or the wastewater to be disinfected is of high quality. The process must be carefully monitored, and in many cases, supplemented by terminal chlorination for drinking water. In the past, it was assumed that UV disinfection in wastewater is limited to where the NPDES permit limits fecal coliforms are not less than 200/100 ml. However, recent experience has shown that UV systems can be used to meet strict reuse standards as long as the UV dose has been determined by a dose-response test. The total suspended solids (TSS) and turbidity of the water must be monitored to ensure proper disinfection by UV.

Peracetic acid is a promising new disinfectant that is being evaluated more frequently as an alternative to chlorine. Researchers debate whether its disinfection action occurs as a result of active oxygen release or the hydroxyl radical. Regardless, it is an effective disinfectant that is not mutagenic or carcinogenic, decomposes to harmless acetic acid, oxygen, and water, and thus does not yield harmful disinfection by-products (DBPs). In addition, its use requires no subsequent processes, that is, dechlorination. The main disadvantages are the increase of organic content in the treated effluent, the potential for microbial regrowth caused by the remaining acetic acid, limited effectiveness against viruses and parasites, and the strong dependence on wastewater quality. Literature indicates that peracetic acid has mostly been used on effluent discharged to marine waters, which are subject to less stringent discharge limits than to reuse and recharge applications. It may not be cost competitive when high doses are required, that is, to meet California standards of

2.2 cfu/100 ml total coliforms and >5 log inactivation of poliovirus. It has been shown that under the right conditions (high PAA dosages, sufficient contact times, and adequate concentrations of organic and mineral constituents in the final effluent), halogenated by-product formation may be a problem. Aquatic toxicity issues and costs of full-scale operation are not well documented. While PAA shows promise as a disinfectant, many questions remain to be answered before implementing its full-scale application.

Literature indicates that hydrogen peroxide could be used for disinfection; however, no full-scale facilities have been built utilizing this type of disinfection alternative. Typically, when hydrogen peroxide is used it is combined with another disinfection alternative such as UV or ozone.

CHEMISTRY OF WASTEWATER DISINFECTION BY CHLORINE

Chlorine is a strong oxidant that reacts with a wide range of organic materials. As chlorine oxidizes the organic material in cell walls or in other cell components, it kills the target organism. The effectiveness of chlorine as a disinfectant depends on both its concentration and the contact time. Increasing the chlorine dose or extending the contact time results in more organisms being killed. A common NPDES permit limit for discharge to many watersheds is a 30-day geometric mean of 200 cfu/100 ml. Nationally, the USEPA is converting disinfection permit limits from fecal coliform to *E. coli*. As permits are renewed, these new limits will come into effect. In many cases, there will be no real change in operation; it will just be a change in analytical procedures and reporting. NPDES permits for environmentally sensitive areas such as watersheds used for water supplies and reuse systems can have lower limits that range from a 30-day geometric mean of 22 total coliforms/100 ml to non-detect for fecal coliforms. In order to design a successful disinfection system, the designer must clearly understand chlorine chemistry to ensure that the system dispenses enough disinfectant to produce an effluent that meets the NPDES permit limits.

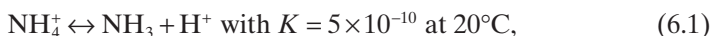
Reactions with Wastewater Constituents

Several constituents in wastewater react immediately with injected HOCl or hypochlorite solution. Consequently, free chlorine ($\text{HOCl} + \text{OCl}^-$) is probably consumed or converted to some form of chloramine in a matter of seconds after mixing with the wastewater stream, owing to the presence of ammonia nitrogen. Simultaneous with the $\text{Cl}_2\text{--NH}_3$ reaction are the other inorganic reactions of chlorine with reduced substances such as S^{2-} , HS^- , SO_3^{2-} , NO_2^- , Fe^{2+} , and Mn^{2+} . These substances react with both the free chlorine and combined chlorine (monochloramine— NH_2Cl , dichloramine— NHCl_2), reducing them to the stable chloride ion, which is nonbactericidal. At this point, there is no measurable residual. Chlorine consumption in the first minute of reaction is probably the result of the reactions with inorganic substances. The reactions

that occur in the next 2 or 3 min are probably due to organic chlorine demand. These reactions are much slower reactions. The 10-min chlorine demand of a fresh domestic wastewater may be as low as 5 mg/l to produce a measurable residual; however, this amount may escalate to 40 mg/l if the same wastewater becomes septic.

The most significant chemical reactions between chlorine and the various chemical constituents in wastewater effluents are those with the various nitrogenous compounds, either inorganic (ammonia— NH_3 , nitrite— NO_2^-) or organic (proteins and their degradation products). These reactions are described in greater detail in Chapter 2.

With the exception of highly nitrified effluents, there is usually an appreciable amount of ammonia nitrogen in all wastewater effluents. The range is on the order of 10–40 mg/l. The ammonium ion (NH_4^+) exists in equilibrium with ammonia nitrogen and hydrogen. The distribution is dependent on pH and temperature. The relative distribution can be defined as follows:



where K is the acid dissociation constant of ammonium. The negative logarithm of the acid dissociation constant ($-\log K$ or $\text{p}K$) represents the value at which NH_3 and NH_4^+ are present in equal proportions. The $\text{p}K$ value is 9.3 at 20°C . Above pH 9.3, ammonia in solution exists predominantly in its NH_3 form, and below pH 9.3, it exists primarily in its NH_4^+ form. At ± 1 pH unit, the reaction is forced to either extreme with approximately 90% conversion. At ± 2 pH units, the conversion is nearly complete, approaching 99%. So at a pH of 7.3, approximately 99% of the ammonia is present as ammonium ion.

At normal wastewater pH, the predominant chlorine reaction proceeds as follows:



when the chlorine-to-ammonia nitrogen weight ratio is 5:1 or less. If the pH drops below 7, dichloramine (NHCl_2) will begin to form; and at a much lower pH, nitrogen trichloride (NCl_3) will form. However, as soon as the 5:1 weight ratio of chlorine to ammonia nitrogen is exceeded, a new set of reactions begin to take place. These reactions are described fully in Chapter 2.

The disinfecting power of chlorine in wastewater is greatly enhanced by good mixing at the point of application. Good mixing ensures the maximum formation of monochloramine.^{20,21} If mixing is poor, the chlorine species tend to split between monochloramines and organochloramines. With poor mixing (hot spots of high concentrations of chlorine), the localized ratio of chlorine to ammonia can be high enough to force these reactions to proceed. Dichloramines, nitrogen trichloride, and organochloramines have weak or no germicidal properties. Pure dichloramine does not form at neutral pH and a chlorine-to-ammonia nitrogen weight ratio of 6:1 or less.

In raw untreated municipal wastewaters, organic nitrogen compounds are present in both soluble and particulate forms. Most of them occur as insoluble compounds. The soluble compounds are mainly in the form of urea and amino acids. Secondary biological treatment reduces the soluble organic nitrogen compounds to ammonia with a small fraction, typically 0.5–1.5 mg/l as a non-biodegradable soluble organic nitrogen compound. Filtration can remove the suspended solids fraction of organic nitrogen to low levels, and effluent quality is simply a function of solids capture by the filter. Soluble organic nitrogen fractions will pass through the filter.

Chlorine is known to react and combine with urea, amino acids, and proteinaceous organic nitrogen compounds to form nongermicidal organochloramines. Very little is known about the kinetics of these reactions and their reversibility. Extensive investigations surrounding the presence and identification of this species of chlorine compounds in swimming pools and potable water have demonstrated that they titrate as dichloramines in forward titration procedures using either amperometric or diethyl-*p*-phenylenediamine (DPD)–ferrous ammonium sulfate (FAS) methods (*Standard Methods* Method 4500-Cl).²²

The germicidal efficiency of combined chlorine residual has a tendency to decrease with time. This decrease has been noticed in some secondary effluents. It is most noticeable in primary effluents when the contact time exceeds 45–60 min. The decrease in germicidal efficiency is related to the presence of organic nitrogen and a noticeable shift in the chloramine species with time. The monochloramine concentration has been observed to decrease after 45–60 min, while the “dichloramine” increased. In effluents containing 0.5 mg/l or more organic nitrogen, the monochloramine formed in the presence of ammonia nitrogen in the wastewater slowly hydrolyzes with time to react with organic nitrogen compounds and to form organochloramines, thereby decreasing the overall germicidal efficiency of the remaining residual.

Sung²³ conducted a controlled laboratory study of 15 organic compounds representing seven groups to evaluate their individual and combined effects on the chlorination process. Nine of the 15 compounds were found to interfere with the germicidal efficiency of the chlorination process. Of these nine, five were organic nitrogen compounds. Cystine and uric acid were the most severe inhibitors of the nitrogen group. When five of the interfering compounds were mixed together, their combined effect was more pronounced than any of their individual effects, but did not equal the sum of their individual effects.

Sung²³ compared the germicidal efficiency of simulated wastewater and found that the resulting chlorine residuals in wastewater containing the interfering compounds had little or no germicidal effect. The greatest interference was caused by cystine, tannic acid, humic acids, uric acids, and arginine. Cystine is an amino acid connected by two sulfur groups that is known to react with chlorine. Tannic, humic, and uric acids are capable of exerting a significant chlorine demand when present in water or wastewater. Arginine is

a basic amino acid. The reaction between chlorine and arginine is almost instantaneous. These reactions are relevant when chlorinating raw wastewater or primary effluent in a bypass condition; however, secondary treatment should have removed these materials to nondetect levels, as they are BOD (food for the microorganisms).

Organochloramines are nongermicidal and interfere with the accuracy of chlorine residuals measured by current chlorine residual analyzers. Their effects are easy to calculate if the sample is from a nitrified wastewater effluent. In this situation, most of the organochloramine is measured as dichloramine and 10% as monochloramine. If the sample is from a nonnitrified wastewater effluent, the free chlorine will be totally absent, and the monochloramine fraction will probably titrate 100% in the forward titration if the sample is measured within 5 min of the dosing. In order to allow the monochloramine to react with the organic N, it is suggested that another forward titration be made after 40–50 min of contact time. This time the organochloramine should show up in the dichloramine fraction.

Biological treatment systems effectively remove almost all of the soluble BOD and most of the soluble COD. All treated WWTP effluent contains some nonbiodegradable soluble COD, typically 10–50 mg/l. As the nonbiodegradable COD is partially oxidized by chlorine, some of it can be converted into a biodegradable material. For WWTPs that have permits with a 30 mg/l BOD limit, conversion of nonbiodegradable COD into biodegradable COD or BOD is of no consequence. However, for WWTPs that have permits with effluent BOD limits (less than 10 mg/l), formation of BOD through oxidation of COD by chlorine may become an important compliance issue.

Chlorine Dose and Effluent Quality

The basic concept of adequate disinfection of wastewater is expressed by the Selleck–Collins model.²⁴ The model states that good mixing at the point of chlorine application, and plug flow conditions in the contact chamber (no short-circuiting) yield a predictable coliform reduction with given chlorine residual at the end of a specified contact time. This is the *CT* relationship commonly referred to as the chlorine concentration–contact time envelope.

The original model was subsequently fine-tuned using plant-scale studies that reinforced the practical aspects of the original model.²⁵ The Selleck–Collins model is represented by the following equation:

$$y = y_0[1 + 0.23Ct]^{-3}, \quad (6.3)$$

where

y = MPN in chlorinated wastewater at end of time t ,

y_0 = MPN in effluent prior to chlorination,

C = total chlorine residual (mg/l) at the end of contact time, and

t = contact time (min).

This mathematical model was developed from a pilot-plant system that achieved excellent mixing in a highly turbulent regime and an ideal plug flow contact chamber. Good mixing occurs when the velocity gradient, G , is approximately 500s^{-1} , and the contact time t is at least 30 min. Contact times longer than 1 h should be avoided in effluents containing organic nitrogen in concentrations above 5 mg/l. Long contact times in such effluents allow the monochloramine fraction of the chlorine residual to hydrolyze and become converted to organochloramines.

The following examples illustrate the utility of the Selleck–Collins model for sizing chlorination equipment for a new plant and for evaluating an existing plant. These examples demonstrate the effect of effluent quality as it relates to the y_0 coliform concentration.

Assuming that a primary effluent has MPN of $38 \times 10^6/100\text{ml}$ total coliforms before chlorination (y_0) and the treated wastewater has to be discharged into a surf water in California that has a y fecal coliform limit of 1000/100 ml, the CT value can be determined from the Selleck–Collins model:

$$\frac{1000}{38 \times 10^6} = [1 + 0.23Ct]^{-3} \quad (6.4)$$

$$CT = 142,$$

and for $t = 30\text{min}$,

$$C = 4.73.$$

To allow an immediate chlorine demand of 6–8 mg/l plus a die-away in the contact chamber of 1 mg/l, the required chlorine dosage will be about $5 + 8 + 1 = 14\text{mg/l}$.

Similarly, the median coliform concentration in a well-oxidized secondary effluent will be about $2 \times 10^6 = y_0$. Assuming a discharge into a confined body of water, the total coliform limit might be 23/100 ml MPN. In this case, CT calculates to 188. This magnitude calls for a contact time longer than 30 min. So, C for a 45-min contact time is 4.2. Assuming an initial chlorine demand of 5 mg/l and a 1.5 mg/l residual decay in the contact chamber, the required dosage will be $4.2 + 1.5 + 5 = 10.7$ or 11 mg/l.

In the case of filtered effluents, the ease of treatment depends on whether or not filtration was preceded by coagulation and sedimentation. A conventional water reuse situation would consist of filtration of secondary effluent preceded by coagulation and sedimentation. The y_0 of such an effluent would probably range between 3000 and 10,000 coliforms/100 ml. In California, whenever tertiary effluent is required, the coliform limit is usually the same as that for potable water, namely, 2.2/100 ml. Assuming $y_0 = 10,000$ and $y = 2.2$, then C calculates to 2.25 mg/l for $t = 30\text{min}$. Thus, a tertiary effluent with the predisinfection processes described above would require chlorine dosages on the order of 5–7 mg/l.

A filtered effluent with chemical coagulation but without sedimentation produces an effluent with coliform concentrations on the order of 50,000/100 ml. In this case, using $y = 2.2/100$ ml, C calculates to 3.96 mg/l for $t = 30$ min. This is almost twice the residual required in the preceding case.

The Selleck–Collins model^{25,26} was further refined in 1978 to

$$y/y_0 = (RT/b)^{-n} \quad \text{or} \quad \log(y/y_0) = -n \log RT + n \log b, \quad (6.5)$$

where

y_0 = initial bacterial concentration before chlorination,

y = bacterial concentration at end of time T in minutes,

R = chlorine residual at the end of time T (mg/l),

T = contact time in minutes,

n = slope of the curve, and

b = the x intercept when $y/y_0 = 1$ or $\log(y/y_0) = 0$ (Fig. 6.3)

The parameter b is sometimes called the lag time of bacterial kill because kill does not occur until $RT > b$ (see Fig. 6.3). When data are not available to plot a bacteria kill regression curve, the suggested value for b is 4 in working with total coliforms and 3 for fecal coliforms. When these values are used for b and for $n = -3$, the equation $y/y_0 = (RT/b)^{-n}$ becomes practically identical to the original Selleck–Collins model, which is $y/y_0 = [1 + 0.23Ct]^{-3}$, where $C = R$ and $t = T$. The insertion of 1 in the latter equation was used to force the regression plot into a straight line at low values of bacteria reduction.

An extensive study conducted by Roberts et al.²⁷ found b and n values of 3.95 and 2.79 for secondary effluent from Palo Alto, and 4.06 and 2.82 for secondary effluent from San Jose in California.

Up to 2 h of contact time may be needed to sufficiently reduce the coliform concentration for the WWTP effluent to meet strict reuse limits. In addition to meeting the strict discharge limits, state standards may require that the WWTP that uses chlorine for disinfection maintain and record a measurable chlorine residual in the chlorine contact basin effluent. WWTPs using free chlorine for disinfection may find it nearly impossible to maintain a residual chlorine concentration without having several chlorine injection points in the chlorine contact basin. Simply increasing the influent chlorine dose may only produce more DBPs without an increase in the effluent chlorine residual. Covering the chlorine contact basin may reduce dissipation of chlorine through exposure to sunlight as well as by discouraging the growth of algae that may consume chlorine.

Chlorination of Nitrified Effluents

Since the discovery of the breakpoint phenomenon in 1939, it has been known that concentrations of organic nitrogen as low as 0.3 mg/l can adversely affect

chlorination of potable water. However, in wastewater treatment, such adverse effects were neither known nor seriously considered until the advent of nitrified effluents. When chlorine is applied for disinfection to nitrified effluents with little or no ammonia, the free chlorine is consumed by the various reducing compounds found in municipal wastewaters. As an example, organic color is bleached by free residual chlorine (FRC) and can consume as much as 10–15 mg/l of the FRC in a few minutes. The organic nitrogen acts as an equally formidable competitor for the free chlorine because the resulting reaction forms organic chloramines that do not possess germicidal properties.

Organic nitrogen compounds are common to all wastewater effluents. The concentration levels of these compounds vary with the effluent quality. Activated sludge effluents usually contain between 3 and 6 mg/l, while filtered secondary effluents contain between 0.75 and 1.5 mg/l of organic nitrogen. These compounds react with both free chlorine and chloramines to produce nongermicidal organochloramines.

When chlorine is used as a disinfectant in wastewater systems, the actual chemistry of disinfection varies depending on the amount of ammonia remaining in the treated effluent. Ammonia is one of the chemicals that chlorine readily reacts with. As soon as chlorine is added to the wastewater, it reacts with the ammonia present in that wastewater to instantaneously form monochloramine:



While monochloramine is the product of a side reaction that consumes chlorine, its formation is not bad because monochloramine is itself a good disinfectant. As indicated by this reaction, as long as there are more moles of ammonia in the wastewater than chlorine, almost all of the chlorine will react with the ammonia to form monochloramine. Because monochloramine is a very weak oxidant, it does not react with other organic material, thus minimizing the formation of DBPs, and because it is a relatively stable compound, it remains in the form of monochloramine through the chlorine contact chamber. When monochloramine is the primary disinfectant, it is relatively easy to maintain chlorine residual and to achieve effective disinfection.

However, in nitrifying WWTPs, ammonia is nitrified and converted to nitrate, and less ammonia remains in the effluent to react with chlorine. In a nitrified effluent with a very low ammonia nitrogen concentration, monochloramine will form and then begin to disappear.²⁸ Once the molar ratio of chlorine to ammonia exceeds 1:1, the two combine to form dichloramine:



The reaction to form monochloramine is nearly instantaneous and the reaction to form dichloramine is slower so any chlorine added in greater than a 1:1 molar ratio with ammonia nitrogen will result in the conversion of some

monochloramine to dichloramine. Once the ratio of chlorine to ammonia nitrogen exceeds a molar ratio of 2:1, all of the monochloramine will be converted into dichloramine.

Chlorine can also react with organic ammonia to form organochloramine; therefore, the residual in this case contains free chlorine, dichloroamine, and organochloramine. The organochloramine fraction can be identified only by forward titration procedures, either amperometric or DPD–FAS titrimetric. It titrates as dichloramine, which makes it a false positive or produces an artificially high reading for dichloramine. As this fraction is not germicidal, it has to be subtracted to evaluate the effectiveness of any such residual for disinfection.

When the molar ratio exceeds 2:1, trichloramine is formed:



The formation of trichloramine is commonly called breakpoint chlorination. Breakpoint chlorination was originally researched as a method to remove ammonia. It is seldom used as the primary means of ammonia removal because of the high dose of chlorine required to completely remove ammonia and because of the other unwanted chlorinated products formed during the process. However, when a WWTP removes ammonia by nitrification, the residual ammonia left in the effluent (at a much lower concentration than the influent ammonia) can undergo breakpoint chlorination whenever the mole ratio of chlorine to residual ammonia exceeds 3:1.

To understand the chemistry of breakpoint chlorination, three forms of chlorine must be defined: free chlorine, combined chlorine and total chlorine.

- Free chlorine is the amount of hypochlorite (OCl^-) in solution.
- Combined chlorine is the measure of monochloramine (NH_4Cl) in solution.
- Total chlorine is the sum of free chlorine plus combined chlorine.

The reaction between free chlorine and organic nitrogen is much faster than the same reaction between monochloramine and organic nitrogen. Therefore, the absence of ammonia in a nitrified effluent results in greater loss of free chlorine to the organic nitrogen reaction than occurs when ammonia is present, owing to the slow reaction between organic nitrogen and monochloramine.

Breakpoint chlorination is a stepwise reaction that begins with the formation of monochloramine. As more chlorine is added to a solution, all of the ammonia is converted to monochloramine and the reaction is almost instantaneous. As still more chlorine is added, dichloramine will begin to form. Dichloramine formation is slow, requiring about 20 min to proceed to completion. However, as a higher free chlorine residual is present (and all ammonia is converted to monochloramine), dichloramine will be formed more rapidly

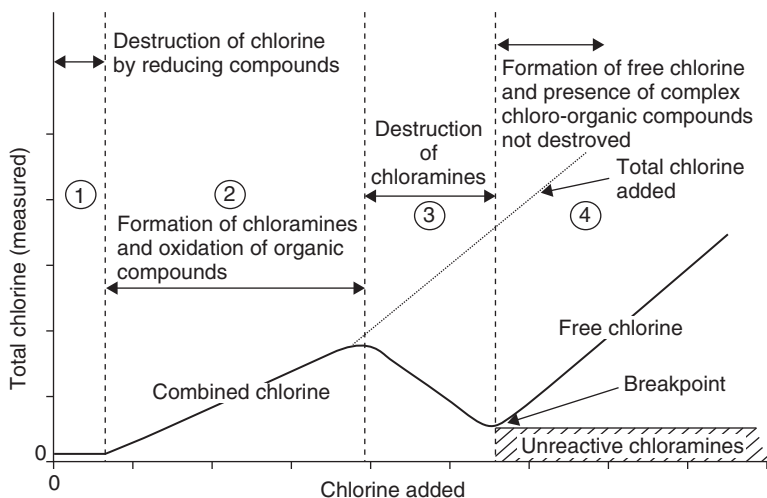


Figure 6.4. Breakpoint chlorination curve.

because the rate of dichloramine formation is a function of the free chlorine residual concentration. If enough chlorine is added, dichloramine will react with free chlorine to form trichloramine. Trichloramine formation is also a rapid reaction. As trichloramine is formed, it can be easily vented out of solution at any point of turbulence.

Figure 6.4 is a graphic representation of breakpoint chlorination. In zone 2, monochloramine is formed and, when analyzed, is defined as combined chlorine. As more chlorine is added, the system transitions into zone 3. The effective chlorine residual actually declines as dichloramine and trichloramine are formed (combined chlorine concentration declines as monochloramine is converted into dichloramine and trichloramine). In zone 3, the transition zone, most of the chlorine residual measured is combined chlorine. There will be some free chlorine, but for the most part only combined chlorine will be measured. The free chlorine will continue to react with dichloramine until all of the dichloramine is converted to trichloramine. Once all of the dichloramine is converted to trichloramine, any free chlorine added can remain as free chlorine (zone 4).

While breakpoint chlorination is not the intended goal of wastewater disinfection, it is one of those unwanted side reactions that happen. Breakpoint chlorination cannot be stopped, but it can be understood and it can be taken into account in developing the control scheme for wastewater disinfection processes (Chapter 12).

In general, one of three conditions of breakpoint chlorination will occur in disinfection. The easiest to understand and the condition that usually predominates is a high ammonia concentration in the WWTP effluent. As long as chlorine is added at a molar ratio of less than 1:1 chlorine to nitrogen, the

reaction is predictable and results in the formation of monochloramine. This reaction is easy to control.

The second condition is a very low ammonia concentration (less than 1 mg/l as nitrogen) in the treated effluent. Many activated sludge systems that are designed to fully nitrify will produce an effluent ammonia concentration between 0.01 and 0.5 mg/l as nitrogen. Under this condition, breakpoint chlorination will probably be complete. With a low effluent ammonia concentration, it may be difficult to maintain free chlorine residual because of the side reactions that consume free chlorine. However, with a low effluent ammonia concentration the chlorine demand is more easily predicted.

The third condition is most troublesome from the process control perspective; if the effluent ammonia concentration varies, either seasonally or diurnally, between 1 and 5 mg/l as $\text{NH}_3\text{-N}$, the disinfection mechanism will vary between monochloramine and free chlorine. A good process control system must be able to cope with both chemistries and detect when the transition from one to the other occurs. For example, during breakpoint chlorination, there are conditions when adding more chlorine would be the wrong control response because it would reduce the residual chlorine concentration by producing more dichloramine and reduce disinfection effectiveness. By adding more chlorine and progressing through zones 3 and 4 of the breakpoint curve, more chlorine would be used for disinfection, whereas the correct response might have been to reduce the chlorine dose and to increase the monochloramine concentration by forming less dichloramine and still produce a disinfected effluent.

When a treatment plant is in the nitrification mode so that the ammonia N either is not detectable or has a concentration less than 0.5 mg/l, there is sure to be free chlorine residual in the effluent. If the effluent contains organic color in any of these situations, a significant amount of free chlorine will be consumed by the bleaching effect of free chlorine. The chlorine lost by bleaching is variable and could be as high as 15 mg/l.

As nearly all wastewater effluents contain organic color, the method of choice to eliminate this problem is to add ammonia nitrogen and use chloramine for disinfection. A ratio of one part of ammonia nitrogen to six parts by weight of chlorine will produce chloramine (the actual amount of chlorine to be added would also have to account for the instantaneous chlorine demand). This residual should be coupled with a minimum detention time of 50 min for maximum disinfection efficiency. On a stoichiometric basis a one-to-one mole ratio of chlorine to ammonia nitrogen equates to a mass ratio of 5.07:1 chlorine to nitrogen (71 mol wt of Cl_2 divided by 14 mol wt of nitrogen). At the chlorine-to-ammonia nitrogen mass ratio of 6:1, the chlorine residual is on the downslope of the breakpoint curve; that is, the residual is decreasing. As the ratio increases above 6:1 with a declining ammonia nitrogen concentration as a result of nitrification, the operator has lost the battle to meet the effluent coliform discharge limit, owing to insufficient chlorine residual (monochloramine is being converted to dichloramine and the chlorine residual is declining). This

is a common occurrence in smaller plants (1–6 mgd) across the United States that experience excursions of ammonia nitrogen concentration from 1 to 10 mg/l, resulting from biological process instability. The inability to control the fluctuations in the ammonia nitrogen concentration is the crux of the problem. Many plants go in and out of the breakpoint region, which occurs at chlorine-to-ammonia nitrogen mass ratios starting at 5:1 with full breakpoint demand satisfied at a mass ratio of 15 to 1.

It may be necessary to add ammonia nitrogen in an attempt to maintain the proper amount of chlorine to ammonia ratio not greater than 6 to 1. If this is too difficult to achieve, a ratio of 5 to 1 or 4 to 1 may be used, in which case the chlorine dosage may have to be increased by 5%–10% because the germicidal efficiency of chloramines decreases somewhat at the lower ratios.

White et al.^{20,21} investigated chlorination of effluent at several plants with nitrified tertiary effluent. These plants were required to meet an NPDES concentration of 2.2/100 ml MPN total coliform. In spite of higher quality effluents ($y_0 = 30,000$ –60,000 influent total coliform count before disinfection), none of the plants conformed to the Sefleck–Collins mathematical model. The chlorine dosages required to achieve a 2.2/100 ml coliform limit were often twice those needed in plants with a similar treatment process that did not nitrify. These results were unusual because the residuals in the nitrified effluents usually contained 50%–60% free chlorine as measured by amperometric titration and DPD–FAS titration.

The San Jose, California, pollution control plant was thoroughly investigated over a 2- to 3-year period. The chlorine dosage required to achieve a 2.2/100 ml coliform count in the nitrified effluent varied from 17 to 22 mg/l. The total chlorine residual at the end of 49 min of contact time required to meet this goal was consistently about 9 mg/l, and contained about 50%–60% free chlorine. About 90%–95% of the remainder titrated as dichloramine, and the rest as monochloramine. The Selleck–Collins model predicted a total chlorine residual of 2 mg/l at 49 min contact time to achieve a 2.2/100 ml coliform count.

A laboratory study using ammonia nitrogen to determine the chlorine-to-ammonia ratio with the best germicidal efficiency found the most effective ratio to be 6:1, chlorine to ammonia nitrogen by weight. This result confirmed the finding of Selleck et al.,²⁶ who showed that the most effective germicidal chloramine residual was produced when the chlorine-to-ammonia nitrogen ratio was on the “breaking” side of the breakpoint curve, as shown in Figure 6.5 between points A and B. It was further found that a chlorine dosage of 12 mg/l would produce a combined residual concentration of 7 mg/l at the end of 49 min of contact time, which was sufficient to achieve a 2.2/100 ml coliform count in the effluent. Plant operation using these chlorine and ammonia nitrogen dosages proved to be consistent with the laboratory findings. This treatment consistently produced an effluent that met the coliform limit without exceeding the 0.025 mg/l unionized ammonia N concentration in the receiving waters. The chlorine dose and the residual concentration to

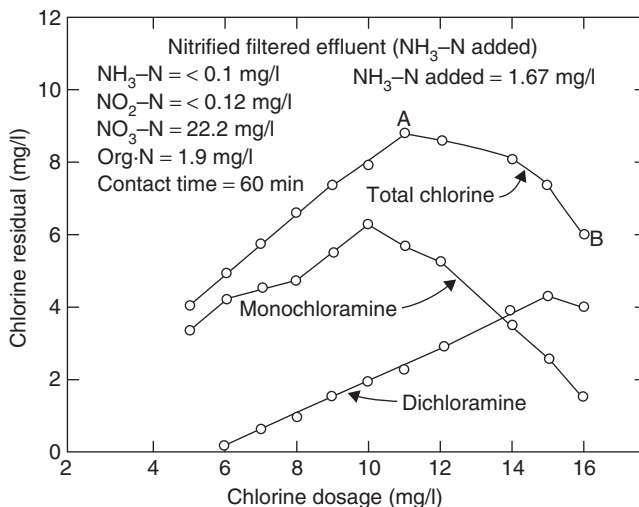


Figure 6.5. Breakpoint curve for chlorination of nitrified effluent amended with ammonia.

meet the disinfection standards were consistently reduced by 5 and 2 mg/l, respectively.

FORMATION OF DBPS

The formation of DBPs is becoming a nationwide issue. As the states evaluate each WWTP's discharge for compliance with water quality standards, the four primary DBPs are subject to very restrictive limits. This is where the dilemma begins. The WWTP must use enough chlorine to achieve the required level of disinfection while minimizing the formation of DBPs to comply with its water quality-based discharge permit. Therefore, it is critical that treatment plant personnel understand disinfection as well as chlorine chemistry.

Organochlorine DBPs are formed during chlorination of wastewater effluent containing organic matter.^{29,30} The formation of these compounds is a concern because their presence in potable water poses a possible risk to public health. The carcinogenic nature of several DBPs has been demonstrated by laboratory tests on animals, although a direct cause-and-effect link with cancer in humans has not yet been established.

The USEPA has made a concerted effort to collect as much data as possible on the public health risk of DBPs. Its primary concern is the formation of trihalomethanes (THMs) such as chloroform and bromoform as a result of chlorination practices. These compounds are known carcinogens; so it is prudent to pursue a course of practice that would reduce or eliminate their formation.

The Safe Drinking Water Act (SDWA) requires potable water treatment facilities to remove THMs to an aggregate concentration of not more than 80ppb. Water treatment plants typically adjust their processes and operating conditions to avoid or minimize the formation of THMs, but may not concentrate on the removal of the precursors. Therefore, any THM precursors in the finished public water supplies will eventually appear in the domestic wastewater as do any additional humic and fulvic acids discharged into the wastewater collection system. Treated wastewater effluent may contain higher concentrations of THM precursors than were initially present in the domestic water supply.¹⁹ This becomes extremely important when chlorine compounds are used for disinfection because THMs are also being regulated in wastewater effluent.

The reactions that form THMs are not instantaneous and are complicated by the many factors that affect both the rate of THM formation and their total yield. The primary variables are the concentration of THM precursors; the concentration of free chlorine; the contact time; and the temperature and pH of the water being chlorinated, and the concentrations of bromide and iodide ions it contains. Bromide and iodide ions are oxidized by free chlorine to species capable of participating in organic substitution reactions resulting in the formation of pure- and mixed-halogen THMs. It appears that bromine substitution is favored over chlorine, even though chlorine is present in large excess compared with the initial bromide concentration.

There are 10 typical THM compounds; however, only four of them are regulated. The four THM compounds regulated by the SDWA and the six nonregulated THMs³¹ are listed in Table 6.2. Table 6.3 presents a comparison of SDWA standards with federal and state water quality standards.

The water quality program has evolved since 1972 when the USEPA first developed the federal water quality standards. Today, the USEPA requires that the delegated states either adopt the USEPA program or develop their

TABLE 6.2. Trihalomethane Compounds

Compound	Formula
1. Chloroform ^a	CHCl ₃
2. Bromodichloromethane ^a	CHBrCl ₂
3. Dibromochloromethane ^a	CHBr ₂ Cl
4. Bromoform ^a	CBBr ₃
5. Dichloriodomethane	CHCl ₂ I
6. Bromochloriodomethane	CHClBrI
7. Chlorodiiodomethane	CHClI ₂
8. Dibromiodomethane	CHBr ₂ I
9. Bromodiiodomethane	CHBrI ₂
10. Iodoform	CHI ₃

^aRegulated under SDWA.

TABLE 6.3. Comparison of THM Limits

Compound	Federal WQS ($\mu\text{g/l}$)			State 1 WQS ($\mu\text{g/l}$)	State 2 WQS ($\mu\text{g/l}$)		
	Freshwater	Human Health			Freshwater	Human Health	
	Acute	Water and Organisms	Organisms Only			Water and Organisms	Organisms Only
CHCl_3^a	28.9	5.7	470	470.8	5.7	470	
CHBr_2Cl^a	NR	0.41	34	34	0.41	34	
CH_3Cl^b	NR	NR	NR	470.8	NR	NR	
CHBrCl_2^a	NR	0.27	22	22	0.56	46	
CHBr_3^a	NR	4.3	360	360	4.3	360	

^aSafe Drinking Water Act Limits the sum of these four compounds to less than 80ppb rather than placing separate limits for each individual compound.

^bChloromethane is not a THM, but it falls under the more general heading of a halogenated organic chemical.

WQS, water quality standards; NR, not regulated.

own water quality program and review its applicability every 3 years. It has taken time but the states are beginning to implement all phases of water quality-based permitting. As NPDES permit renewal applications are submitted, there is usually a requirement to submit monitoring data for a long list of compounds, often referred to as the priority pollutant scan. The four THMs listed in Table 6.3 usually are included in the USEPA priority pollutant scan. The data from the scan can become the information that the state uses to determine whether a facility has a “reasonable potential to exceed water quality standards.” If the data shows that the facility does have a “reasonable potential to exceed water quality standards,” numerical limits may be developed by the state for inclusion in the permit for the applicable pollutants.

Since water quality standards apply at the edge of the mixing zone, if the regulatory agency has allowed the permittee the use of a mixing zone, not all WWTPs discharging these pollutants at the same concentration will receive numerical limits in their NPDES permit. The size of the mixing zone and the background concentration of the pollutants in the receiving stream strongly affect the “reasonable potential to exceed” analysis. However, facilities located on effluent-dominated streams may find that the state will require them to meet water quality standards at end-of-pipe, which may prove to be difficult or impossible.

For WWTPs that either do not nitrify or whose discharge permit limit for NH₃-N is higher than 5mg/l, THM formation may not be a problem. When chlorine is added, monochloramine is formed rapidly, so the exposure time of free chlorine to the THM precursors will be limited.

Another approach is to allow the activated sludge process to fully nitrify, and to add ammonia to the chlorine feed to form chloramine. This approach is favored neither by plant operators nor by the regulators because it involves returning to the process the ammonia that has been removed. However, it provides the advantage of always knowing how much ammonia will be present in the WWTP effluent. In addition, facilities whose permit includes a strict ammonia limit have found that when chloramines are used for disinfection, ammonia re-forms during the dechlorination process, which complicates compliance with the limits for ammonia and total nitrogen.

Other methods of controlling THM formation involve other areas of the WWTP. Coagulants can be added to improve the removal of THM precursors in primary clarification. Filtration ahead of disinfection will remove solids that contain THM precursors. Removal of bromide or iodide from the system will also reduce the THM formation potential, as does increasing the sludge age. Of course, reducing chlorine contact time is a possible approach, but one that may not be practical because of regulatory or code restrictions.

THM formation is due to the presence of reactive chlorine. Switching to a different disinfection method or chemical can avoid THM formation. However, any oxidative system will produce by-products. Those by-products may or may not have harmful effects to human or aquatic life. It has taken many years of research to determine that THMs should be regulated. It will probably take a number of years to determine if other disinfectants produce harmful or unwanted by-products. However, switching to a different disinfection system may be a short-term solution to meet current regulations.

A study by Stone (R.W. Stone, unpublished observations) investigated halomethane formation in the following situations: (A) activated sludge process effluent containing 20 mg/l ammonia nitrogen chlorinated to the breakpoint with dosages of 200 mg/l or higher and resulting in substantial free chlorine residuals (7–12 mg/l); (B) same effluent, but with chlorination for disinfection (3–4 mg/l residual at 30-min contact); (C) same effluent except nitrified and filtered and chlorinated; (D) a primary effluent dosed with 11 mg/l chlorine; and (E) a nitrified oxidation pond effluent downstream from the activated sludge effluent.

The results of this investigation revealed a rapid formation of chloroform (CCl_4) during breakpoint chlorination (system A). At a pH of 7, 0.88 mg/l CCl_4 formed in 2 min and 1.23 mg/l in 5 min. The activated sludge effluent chlorinated for disinfection purposes (system B) formed only 4 $\mu\text{g/l}$ of chloroform in 4 h. The highly polished activated sludge effluent (system C) dosed with chlorine at 11 mg/l led to the formation of three times more halomethane compounds than formed in system B. This was caused by the free chlorine residuals in the highly polished effluent. In this environment of FRC, there is a steady formation of halomethane.

Chlorination of the primary effluent (system D) to 14 mg/l produced no chloroform, a small amount of dichloroethane, and a significant amount of

dibromochloromethane. Overall, a steady increase in total halomethane concentration was noted to a level of approximately $0.0021 \mu\text{g/l}$ at 4 h contact time. This was almost the same as measured for the polished activated sludge effluent (system C) at the same contact time, even though differences in the form of chlorine residuals existed. The residual in the primary effluent was all combined chlorine.

Chlorination of the oxidation pond effluent (system E) to a concentration of 6.7 mg/l yielded no THM through a 4-h chlorine contact period, even though chlorine residuals of $2.5\text{--}3.5 \text{ mg/l}$ were maintained throughout that time. The low concentration of ammonia nitrogen in the nitrifying pond effluent ensured that the chlorine residual throughout the 4-h contact period was a mixture of both free and combined residuals.

A sample of the chlorine injector water was analyzed for THM concentration to determine whether high concentrations of chlorine ($1000\text{--}3000 \text{ mg/l}$) in the injector water could cause THM formation before injection of the chlorine solution into the process liquid. Undisinfected activated sludge effluent served as the water source for the injector. Approximately $0.0023 \mu\text{g/l}$ THM was observed in the injector water. However, dilution of the injector water into the process stream resulted in a 200 or 300 to 1 dilution so that the net impact of THM formation due to the chlorination system itself was negligible. It was likely that the low pH value and the short contact time in the injector water system kept THM concentrations below those observed for breakpoint chlorination of the process stream.

OTHER DISINFECTION CONSIDERATIONS

Other considerations for disinfection of wastewater include regarding the regrowth and clumping of organisms, toxicity of chlorine residuals, and the need for dechlorination. These considerations are discussed in some detail below.

Regrowth of Organisms

Numerous studies have demonstrated the regrowth phenomenon of coliform and fecal coliform organisms after disinfection. Regrowth of these organisms, which has been observed both in wastewaters and in receiving waters downstream from a disinfected effluent discharge, may be possible because the organisms that prey on them have been destroyed. Regrowth may also depend on the presence of certain nutrients in the wastewater or in the receiving waters. Pathogenic bacteria such as *Salmonella* and *Shigella*, which are of the same family as the coliform group, are also known to regrow. If the disinfection process is as effective against pathogens as it is against coliforms, a disinfection requirement resulting in reduction of coliforms to a level of 23 or 230/100 ml can virtually assure the

absence of pathogenic bacteria. This would significantly reduce the pathogen regrowth potential, whereas a more liberal limit of 200 or 400 fecal coliforms would not.

At Roseville, California, a study was performed investigating particle size and solids settling on effluent quality.³² Once a new UV system was installed, it was noticed that solids were accumulating in the UV channel. The plant effluent was filtered and particle size analysis verified that the filter was removing particles larger than 10 μm . The settled solids were sampled and found to contain between 20,000 and 160,000 MPN/100ml. It was also found that small white worms were rowing in the accumulated solids. The settled solids were either shielding bacteria or providing an environment for regrowth. Resuspension of these solids could raise the effluent bacterial concentration from 2 MPN/100ml to 170 MPN/100ml. Hydraulic surges could resuspend solids and cause effluent violations. Frequent cleaning or flushing of the channel can minimize solids accumulation, bacteria accumulation, and regrowth.

Toxicity of Chlorine Residuals

Free and combined chlorine residuals are toxic to most fish and aquatic life even at very low concentrations. Most oxidants such as chlorine and ozone are known to be irritants to both freshwater and saltwater fish. The resistance of fish to toxic substances varies according to the size of the fish. Fingerlings are very susceptible, whereas carp and other large fish are highly resistant to toxic agents. The resistance is also proportional to the size of the fish scales: The larger the scales, the greater the resistance.

When wastewater is chlorinated, other toxic compounds may also be formed. For example, if thiocyanate is present, this can be converted by the chlorination process to the highly toxic cyanogen chloride. It is also well known that under certain conditions, an array of chloro-organic compounds are formed during the disinfection of wastewater with chlorine, and some of these compounds may also be toxic to aquatic life. Very little is known about how these complex reactions affect aquatic life.³⁰

Esvelt et al.³³ evaluated the average daily emissions of toxicity to the San Francisco Bay system and reported that 56% of it was attributable to municipal sources, and the remaining 44% to direct industrial discharges. His study was conducted long before the effects of chlorine residuals in effluents were clearly understood. The total chlorine residuals encountered (as measured by the back titration procedure with an amperometric endpoint) ranged from 1 to 8 mg/l. The test fish used throughout the project were golden shiners. The 96-h TL_{50} using continuous-flow online bioassay in municipal wastewaters was determined to be 0.2 mg/l total chlorine residual. TL_{50} represents the tolerance limit where 50% of the fish subjected to the exposure are killed. This investigation produced the following important conclusions:

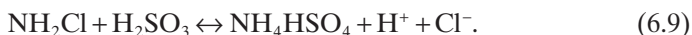
1. Chlorination increased the toxicity of treated municipal wastewaters in all instances.
2. A chlorinated and dechlorinated effluent (with a slight excess of sulfite ion) was less toxic than either the unchlorinated or the chlorinated effluent.
3. Dechlorination completely removed the chlorine-induced toxicity.

Arthur et al.³⁴ conducted a comprehensive study of the toxicity of chlorine residuals to aquatic life in the receiving waters. All experiments were carried out in freshwater systems on both fish and invertebrates. The disinfection system using both chlorine and ozone was able to produce an effluent with coliform counts less than 1000/100 ml. The chlorinated effluent was found to be more lethal than either the ozonated effluent or the chlorinated-dechlorinated effluent, which confirmed the findings of previous investigators. Fish were more sensitive than the invertebrates to the chlorinated effluent in the 94-h tests. The respective 94-h TL_{50} values of total residual chlorine to fish and invertebrates ranged from 0.08 to 0.26 mg/l and from 0.21 to more than 0.81 mg/l, respectively.

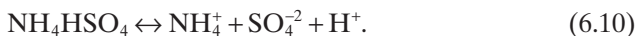
Need for Dechlorination

Residual chlorine in the WWTP effluent can be highly toxic to aquatic life, and the NPDES permits of many WWTPs include dechlorination requirements. Shortly after Esvelt et al. published their study,³³ the Water Quality Control Board of California, in cooperation with the Department of Fish and Game, began issuing orders for certain WWTPs to supplement their chlorination systems with dechlorination facilities. In 1972, the first WWTP in California to add dechlorination (by sulfur dioxide) was in the city of Burlingame. The order specified chlorine residual not to exceed 0.1 mg/l.

Free chlorine reacts with the dechlorinating chemical (sulfur dioxide) and reduces the chlorine to chloride ion. Combined chlorine is monochloramine, which is converted to chloride ion when a dechlorinating agent is added. The unique aspect of dechlorination of monochloramine is that as it is converted, ammonia is formed as a reaction product.



The above equation (which appears in many textbooks) gives the appearance that the ammonium compound is a solid; however, in water, the ammonia compound dissociates into sulfate and ammonium ion.



So, the ammonia that was removed when chlorine was added is re-formed when the residual combined chlorine is dechlorinated. If part of a facility's

ammonia control strategy involves breakpoint chlorination, enough chlorine must be added to complete the breakpoint reactions, or the ammonia will be re-formed during dechlorination or during the natural degradation of the monochloramine.

WASTEWATER REUSE

Wastewater reuse has been practiced in the United States since about 1920. While California's population was rapidly growing in the 1920s and 1930s, the city of Berkeley was nearly devastated by a big fire (in 1923), owing to the lack of sufficient water at a sufficient pressure. One of the first wastewater utilities to put its entire discharge to beneficial use was the activated sludge plant in the Golden Gate Park of San Francisco. This operation began in about 1930. By 1935, there were 62 communities in California using treated wastewater for crop irrigation.

In 1968, the California State Board of Public Health adopted standards for the quality of reclaimed water used for crop and landscape irrigation and recreational impoundments. The concentration of coliform bacteria was selected as the key parameter for regulating the quality of the reclaimed water. The coliform bacteria concentrations allowable for different reclamation uses were supplemented by terms such as "oxidized wastewater," "filtered wastewater," and other descriptive terms that broadly identify the type of reclaimed water required without specifically identifying numerous quality criteria. Joplin³⁵ described these standards as follows:

- Primary effluent. It can be used for surface irrigation of processed food crops, orchards, and vineyards; and for irrigation of fodder, fiber, and seed crops. Virtually no public contact or ingestion is possible.
- Oxidized effluent (secondary). With a median coliform MPN of 23/100 ml, it can be used for landscape irrigation, spray irrigation of processed food crops, landscape impoundments, and milk cow pastures. Public contact is possible, but ingestion is very unlikely.
- Oxidized effluent (secondary). With a median coliform MPN of 2.2/100 ml, it can be used for surface irrigation of produce (makes this operation impractical) and restricted recreational impoundments. Public contact and minor ingestion are possible.
- Filtered effluent (tertiary). With a median coliform MPN of 2.2/100 ml, it can be used for spray irrigation of produce and unrestricted recreational impoundments. Public contact and minor ingestion are likely.

By 1970, there were about 600 reclamation projects operating continuously in the United States, about half of them in California. The first use, of course, was irrigation of crops irrigation, such as fiber, fodder, and seed crops, and

there was little opportunity for public contact. Landscape irrigation, which included parks, playgrounds, golf courses, freeways, rights-of-way, and so forth, also has a fairly long history, but in recent years has there been a sudden increase in such installations. Where crop irrigation installations have increased by 40%, landscape irrigation installations have multiplied ninefold, thus there is a trend toward the use of reclaimed water where the public may have more exposure and more contact with it.

California Wastewater Reclamation Criteria (Title 22—Effluent Reuse Regulation)³⁶ for uses where an oxidized, coagulated, filtered, disinfected effluent is required, are as follows:

1. filtered effluent turbidity equal to or less than 2 NTU;
2. total coliform count equal to or less than 2.2/100ml; and
3. virus inactivation efficiency, 4-log removal (99.99% reduction) based upon poliovirus.

The Michelson Water Reclamation Plant (MWRP) located in Irvine, California, is owned and operated by the Irvine Ranch Water District (IRWD).^{*} The district was formed in 1961 to provide both irrigation and a domestic water supply for a developing community. In 1963, the agency decided to expand the system to include wastewater collection and treatment and thus produce reclaimed water. This decision resulted in the building of the MWRP, which was placed into service about 1967. The IRWD has been a leader in developing rules and regulations for the use of reclaimed water. It uses a dual distribution system, with one set of pipelines for potable water and another for reclaimed water.

The MWRP meets and exceeds the stringent water quality criteria established by the California Department of Health Services. The high-quality “polished” water that leaves the plant earned the IRWD the first “unrestricted use permit” to be issued by the State of California. Consequently, the reclaimed water from MWRP can be used for almost everything except drinking. The reclaimed water is currently used for irrigation of crops, golf courses, parks, school grounds, greenbelts, street medians, and freeway landscaping. Recently, the IRWD pioneered another use for it: furnishing the toilets in high-rise office buildings. Additional office towers and other buildings are scheduled to use it in the future.

The MWRP is a 15 mgd activated sludge plant, whose actual daily production of reclaimed water varies according to seasonal and operational demands. The reclaimed water distribution system is made up of about 150 mi of piping sized 54 in. down to 2 in. in diameter, as well as pumping stations and three storage reservoirs for the irrigation water. The IRWD maintains a state-

^{*}R. Young. Michelson Water Reclamation Plant. Irvine Ranch Water District, 15600 Sand Canyon Ave., Irvine, CA 92718; Customer Service Ph 1-949-453-5300.

certified laboratory that monitors every step of the reclamation process. Samples are collected and analyzed daily, and these results are reported regularly to the California State Health Department and to other regulatory agencies as required. The drinking water supplied to the district's consumers is also monitored and analyzed regularly at the laboratory.

Henderson, Nevada, a suburb of Las Vegas, has used a wastewater treatment program to produce three classes of effluent targeted at irrigation, aquifer recharge, and replenishment of Lake Mead.³⁷ The population of the Las Vegas region has grown rapidly since the early 1990s, which has placed enormous pressure on southern Nevada's limited water supplies as well as on its wastewater treatment utilities, making water resource management crucial.

Henderson's 10mgd wastewater treatment facility has operated since 1994 to provide secondary and tertiary treatment by filtration, phosphorus removal, and nitrification. This plant differs from most other reuse systems by having the flexibility to use a combination of wastewater treatment processes. It is designed to meet any one of the three water quality standards and operates like a water treatment plant attached to the end of a WWTP, with the effluent being removed at the appropriate level of quality for each reuse option.

The Henderson plant is designed to treat its entire flow to the highest quality level, but controls are provided to divert portions of the effluent from further treatment, depending on disposal or reuse alternatives, to avoid the expense of treating the wastewater to an unnecessarily high quality.

The reclamation system is designed to be easily expanded to 20mgd. For example, the discharge into Lake Mead has the most stringent nutrient load limits, with an effluent phosphorus concentration not to exceed 0.25 mg/l. To meet this limit, the effluent is treated with aluminum sulfate and other chemicals to precipitate phosphorus. Effluent to be used for irrigation does not require phosphorus removal; therefore, it bypasses that treatment. Likewise, effluent for groundwater recharge is removed before the filtration step.

Effluent for irrigation is subject to the strictest requirements: BOD and TSS, 30.0 mg/l; total coliforms, 2.2/100 ml; and turbidity, 2.0 NTU. For groundwater recharge, the only limits apply to BOD and TSS, both 30 mg/l. The limits on discharges into both Lake Mead and Las Vegas Wash are BOD and TSS, 30 mg/l; fecal coliforms, 200/100 ml (1000 total coliforms); total ammonia nitrogen (April through September), 0.7 mg/l; total phosphorus (March through October), 0.25 mg/l; pH, 6.0–9.0; total residual chlorine, 0.30 mg/l.

Current disinfection standards for reclaimed water in California require a long (90 min) retention time in a chlorine contact basin, whereas Arizona has selected UV as the method of disinfection, which does not involve any chlorine residual control.

Reclaimed water from WWTPs is currently used for nonpotable applications, including decorative lakes and ponds, and for irrigation of golf courses, parks, and greenery along roads and highways. Reclaimed water is also being injected into freshwater aquifers in coastal regions to prevent saltwater intrusion.

Arizona has developed “scalping” water reclamation plants, which are designed to remove reclaimed water without any solids handling. They “scalp” reclaimed water from the wastewater collection system, and return all the waste products to the sewer for treatment at the wastewater treatment facility located downstream. This procedure makes it possible to use reclaimed water to augment the potable water supply. Local developers have funded new water reclamation plants to supply the water required for new communities featuring lakes and golf courses.

In Florida, the disinfection criteria for reuse is confusing. If a new facility is being built and no historical data is present, the design *CT* value is 120. For operating facilities that have historical data on fecal removal through the WWTP, the design *CT* value can be much lower. Florida has a further requirement that the effluent can never be higher than 5 mg/l TSS. Some facilities are having difficulty meeting the 5 mg/l instantaneous TSS limit after filter backwashes. As a backwashed filter is placed back into service, it is common to have a turbidity surge as flow is applied onto the filter. Many water plants address this phenomenon by wasting the filtrate for the first few minutes of operation. In a wastewater application, this filtrate can be captured and refiltered.

The disinfection criteria in the Florida Regulations³⁸ are stated as follows:

1. Fecal coliform values shall be below detectable values.
2. Design shall include provisions for rapid and uniform mixing and produce a residual chlorine value of 1 mg/l at all times.
3. The minimum contact time shall be 15 min at peak hourly flow.
4. For a reclaimed water or effluent containing 1000 and up to and including 10,000 fecal coliforms per 100ml before disinfection, the *CT* value shall be at least 25.
5. For a reclaimed water or effluent containing 1000 fecal coliforms or less per 100ml before disinfection, the *CT* value shall be at least 40.
6. For a reclaimed water or effluent containing more than 10,000 fecal coliforms per 100ml before disinfection, the *CT* value shall be at least 120.

The Florida regulations are significantly different from those in Arizona and Title 22. For this reason, it is recommended that you always check with your local regulatory agency to determine what rules are currently in force and to see if any have changed since your last project. Reuse rules are changing as more experience is gained, so the rules will evolve.

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7 Chlorine Contact Basin Design

INTRODUCTION

Disinfection is defined as the process of eliminating pathogenic microorganisms by physical or chemical means. This is best accomplished by chemical agents such as aqueous solutions of chlorine, chlorine dioxide, sodium hypochlorite, calcium hypochlorite, ozone, or combinations of them. Other means of disinfection include ultraviolet light, membrane technology, and so on. This chapter deals with the design of facilities used in disinfection by chlorine or sodium hypochlorite. The important aspect of chemical disinfection is the design of the contact basin, which is vital for providing sufficient residence time or contact time between the water being disinfected and the chemical disinfectant.

Disinfection can be accomplished by physical means such as membrane pores that are small enough to prevent the passage of the pathogen, or chemical means such as aqueous solutions of chlorine. Chlorine contact systems disinfect water by exposing it to chlorine for a sufficient period (contact time) for the chemical to react with and inactivate the pathogens. The U.S. Environmental Protection Agency (USEPA) has established requirements for inactivating or destroying various types or categories of pathogenic microorganisms such as *Giardia*, *Cryptosporidium*, and viruses.

The inactivation criteria for chemical-based disinfectants are established by defining the disinfectant dose applied within a specific time frame to inactivate the target pathogen. The disinfectant dose is presented in units of concentration, abbreviated C. The required contact time is given in units of time, abbreviated T. Hence, the disinfectant requirement is abbreviated as a CT value. Other factors affect the CT value as well. As described in Chapter 2, the potency of the chlorine is affected by temperature and pH of the water, so the CT value varies with temperature and pH, and affect the basis for designing chlorine contact systems.

DESIGN ELEMENTS

Chlorination and Dechlorination Doses

The process of establishing the chemical doses to obtain a given concentration for chlorination and dechlorination is described in Chapters 3 and 11.

Dispersion of Chlorine

Injection of chlorine into the water to be disinfected involves mixing to ensure good contact between the pathogens and the injected chemical. Rapid mixing basins and mixing equipment are an essential part of the chlorination process. The basin is typically sized for contact times of 5–15 s; therefore, the volume of a rapid mix chamber can be calculated by multiplying the process flow rate by the selected residence time. For example,

Assume:

Process flow rate = 15 mgd

Selected residence time = 15 s

Volume of rapid mix chamber = (15 s)(15 mgd)(1,000,000 gal/MG)/(86,400 s/day)

Volume of rapid mix chamber = 2,604 gal, or 348 ft³.

In the chlorination of water, the intensity of mixing is a key factor in disinfection efficiency. The fluid mechanics of mixing is represented by the velocity gradient. It is expressed as follows:

$$G = \sqrt{\frac{P}{\mu \cdot V}},$$

where

G = mean velocity gradient (1/s),

P = power requirement (ft lb/s),

V = mixing chamber volume (ft³), and

μ = absolute fluid viscosity (lb-s/ft²).

When water flows through a pipe or along any solid surface or through another fluid moving at a lower velocity or in the opposite direction, the motion is resisted by drag. The nature of the drag is fluid shear, and the cause of this phenomenon is the viscosity of the fluid. The work of shear results in the dissipation of energy as heat, and it is described as “head loss” or friction loss. The velocity gradient is related directly to the total shear per unit volume per unit of time. The G value provides an understanding of turbulence within a mixing system.

The G value does not solely describe the intensity of mixing, but is also a good indicator of turbulence. Typical G values for mixing of chlorine into the process water vary from 500 to 1000. White believes that the G value should be approximately 1000 for superior mixing, and that the intensity of mixing required is partly dependent on the extent of pathogen destruction required, although others have used a G value significantly lower than 1000 with satisfactory results. The power required to obtain good mixing can be calculated once the rapid mix basin volume has been established and a velocity gradient has been chosen.

Mixing Technologies

The means of mixing is an important part of the chlorine injection system. Sizing procedures for the mechanical mixers are proprietary secrets, but as general guidelines, the mixing equipment manufacturers advise that mixers for dispersing chlorine solution in a flowing stream are sized on the basis of 0.3–0.6 hp/mgd of flow.

Mechanical mixers have been widely used in both potable water and wastewater treatment for mixing chlorine solution into the process water. Ideally, the mixing device should be able to homogenize the chlorine solution and the water in the basin in a fraction of a second. This arbitrary mixing time is for either closed conduit or open-channel flow using propeller mixers. Based on a comparison of existing installations using various types of mixing, achieving complete mixing in 3 s would be rated as adequate. Figure 7.1 illustrates the use of a mechanical mixer in open-channel flow.

The use of mechanical mixers in closed conduits running full is not necessary, provided that certain design criteria are followed. White found through laboratory studies and a plant-scale field demonstration that if the chlorine is injected at the center of the flow, it would be completely mixed within a distance equal to 10 pipe diameters, provided that the Reynolds number was 2,000 or greater. This rule of thumb is valid for pipes up to 30 in. in diameter. The dosing and sampling arrangement is illustrated in Figure 7.2. For pipes larger than 30 in. in diameter, the designer should use an across-the-pipe diffuser such as illustrated in Figure 7.3. The designers should be alert to opportunities to capitalize on hydraulic turbulence for mixing chlorine into water.

Static mixers can be used to an advantage where adequate pipe length is not available. The mixer elements are made in lengths equal to 1.5 times the pipe diameter. The manufacturer's rule of thumb is to base the number of elements required on flow velocity. For velocities 2 ft/s or more, two elements are recommended. For velocities as low as 0.5 ft/s, four elements are required for proper mixing. The G factor can be calculated for each situation, but it is not the principal criterion.

The Pentech system, which was made available for water chlorination in the mid-1970s by the Pentech Division of Houdaille Industries Inc., utilizes either direct injection of chlorine gas under a vacuum or chlorine solution

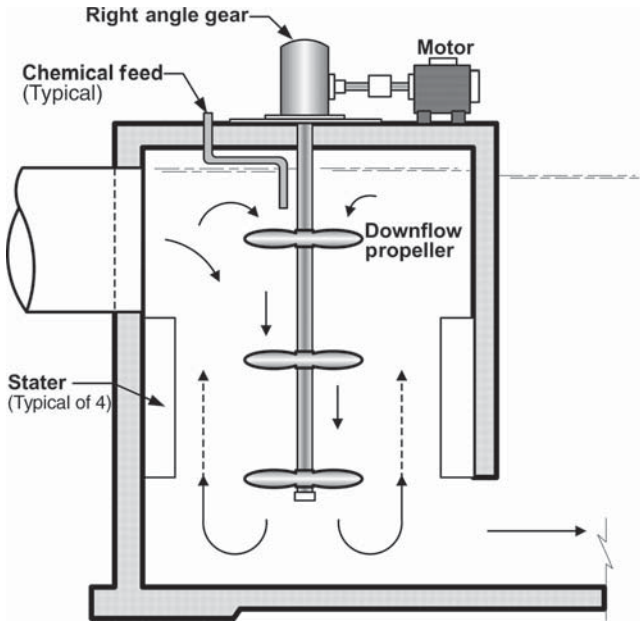


Figure 7.1. Propeller mixer.

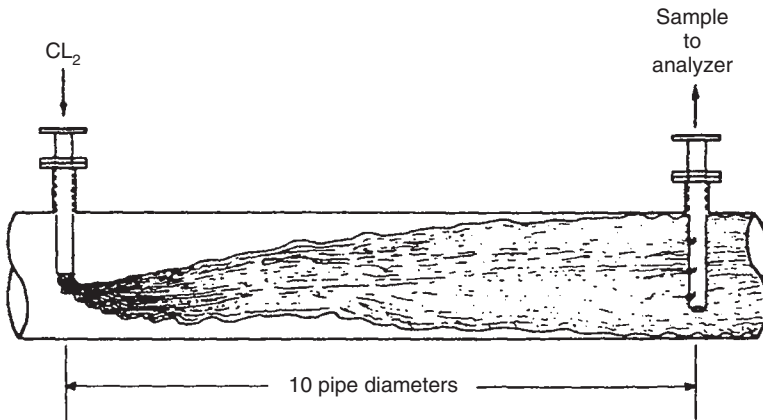


Figure 7.2. Pipeline as a mixing device.

discharged by a conventional chlorinator. When chlorine gas is injected directly, the pump shown becomes the “injector pump,” and the jet nozzle assembly takes the place of the injector. The system is illustrated in Figure 7.4.

The entire effluent stream is forced through the reactor tube, which produces plug flow in a highly turbulent regime. This system provides an almost

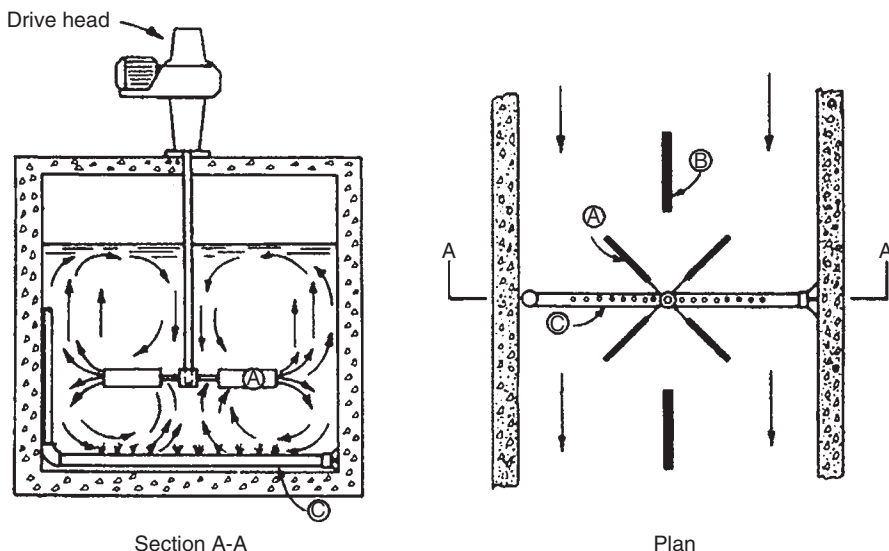


Figure 7.3. Mechanical mixer (courtesy of Kenics Corp., Danvers, MA).

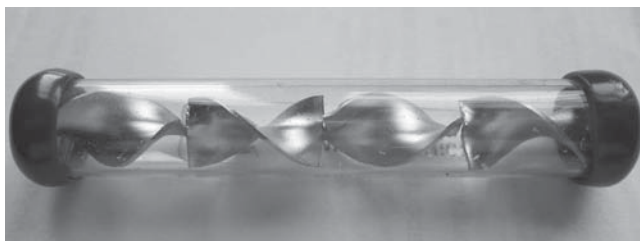


Figure 7.4. Pentech injector mixer (courtesy of Pentech-Houdaille).

instantaneous dispersion of chlorine throughout the mass of water. Pentech claims that this mixing system will generate a G number as high as 10,000 and that total mixing occurs in about 0.2s, with the ability to cope with variable flow rates and to provide a system hydraulic gradient that does not introduce a significant head loss.

The Capitol Controls Co. Chlor-A-Vac™ Series 1420 and 1520 Chemical Induction Unit is a self-contained, high-powered, and highly efficient mixing device that handles both vapors, such as chlorine gas, and a variety of chemical liquids, such as sodium hypochlorite, sodium bisulfite, potassium permanganate, and so on. This unit has worldwide coverage, largely because Capitol Controls Co. is owned by the international Severn-Trent Water Co. of Great Britain.

The induction unit is ideal for use in all-vacuum gas feed systems. It can replace other chlorinator injector systems and also eliminates the need

for a diffuser or a mechanical mixer. The Series 1420 unit is illustrated in Figure 7.5.

It is available in eight capacities to accommodate a range of gaseous and liquid chlorine feed rates, plus a Chlor-A-Vac Mosquito® designed to meet the needs of small plants. The Mosquito® unit can feed up to 100lb/day of chlorine gas or 4gpm of a liquid chemical.

The seven Series 1420 Chlor-A-Vac units cover a range of 750–10,000lb/day of chlorine, and 27–65gpm of liquid chemicals. Literature describing these units and a variety of installation diagrams are available from Capitol Controls, which can also provide operating information from existing installations.

Another chemical induction unit sold on the open market is the Water Champ, manufactured and sold by Siemens, formerly known as US Filter. The device consists of a motor-driven open impeller that creates a vacuum in a precisely structured chamber surrounding the impeller. The vacuum is created by the fluid passing over a polyvinyl chloride (PVC) disk and through the impeller, creating a vacuum slightly upstream from the impeller. The PVC disk or “vacuum enhancer” position can be adjusted to increase or decrease the amount of vacuum generated. This vacuum is transmitted to the chlorinator in a PVC pipe similar to that used in all conventional remote injector systems.

The internal mechanism that creates the vacuum used by the Water Champ is fully illustrated in Figure 7.6.

The chlorine gas or other gas or liquid is injected directly into the process stream without any dilution water. This particular feature is what makes this device unique among all injection systems. In the case of chlorine gas, it has been found that in the absence of dilution water, the reaction with the process stream is more complete, and therefore the results are chemically superior. It has been observed at many installations that with the Water Champ the chlorine transfer efficiency is increased, which reduces both the amount of chlorine required for disinfection and the amount of chemical required for dechlorination.

The rotating speed of the impeller is 3450rpm, which directs the chemical into the process stream in a downward direction at a rate of 60ft/s. The downward velocity component is sufficient to create a major vertical velocity component after striking the bottom of the chamber (Fig. 7.7). The energy release results in thorough mixing throughout the entire channel in seconds. Figure 7.8 illustrates how the process flow pattern converts a portion of the upward velocity component into a horizontal component, producing a scouring action in the bottom of the channel, which is important to wastewater disinfection because it reduces significantly the undesirable deposition of suspended solids in chlorine contact chambers.

The mixing is so rapid and thorough that there is no off-gassing at the point of application, and the reaction between chlorine and water is greatly improved.

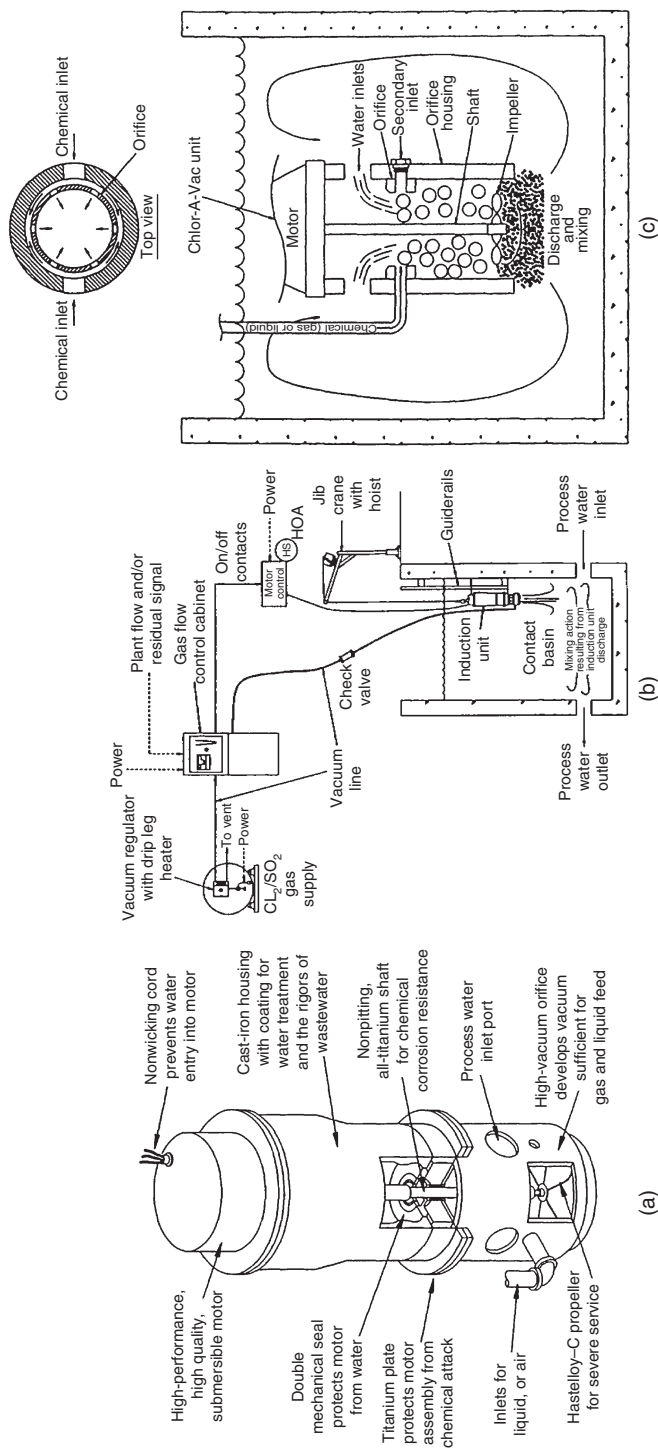


Figure 7.5. (a) Chlor-A-Vac series 1420 induction unit; (b) Chlor-A-Vac series 1420 flow diagram of induction unit (all courtesy of Capitol Controls Co.). HOA: hand/off/automatic; HS: hand switch.

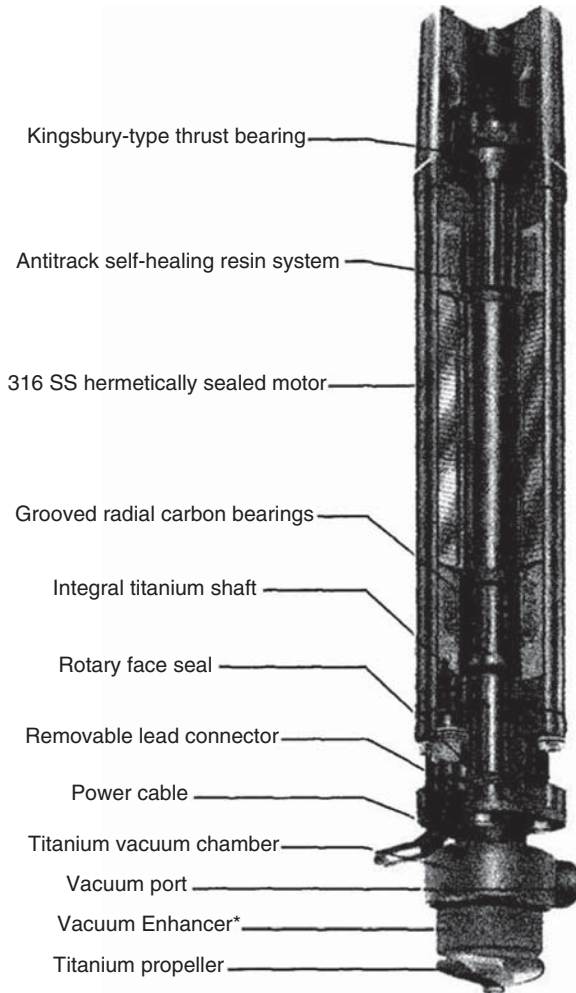


Figure 7.6. Water Champ vacuum induction system (courtesy of Gardiner Equipment Co., Inc.).

*Patented vacuum induction system.

Chlorine Contact Chamber Sizing

The chlorine contact chamber must be designed to provide the optimum distribution residence time or contact time between the disinfectant and the microorganisms to be inactivated or destroyed. Achieving this efficiency involves consideration of a number of factors. Therefore, the chlorine contact should be considered an integral part of the overall treatment process, much like sedimentation, filtration, aeration, or sludge digestion. A chlorine contact chamber is not a mixing chamber and should not be used for that purpose.

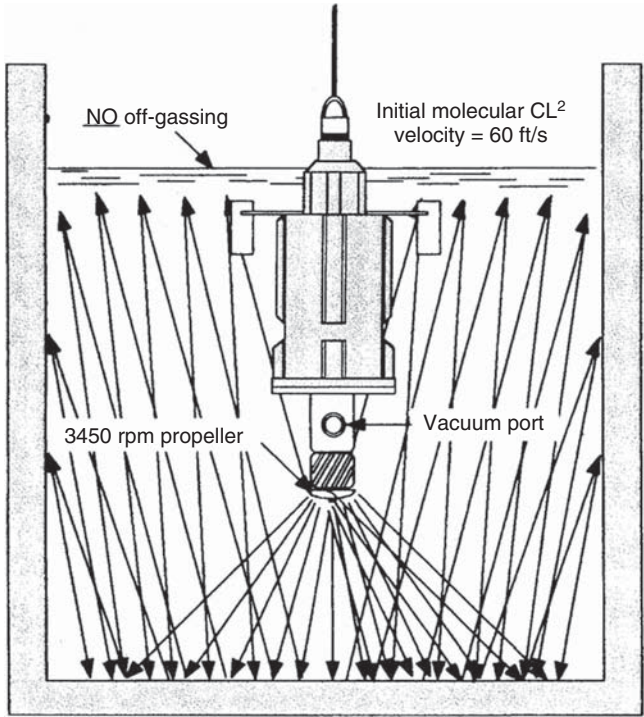


Figure 7.7. The Water Champ (courtesy of Gardiner Equipment Co., Inc.).

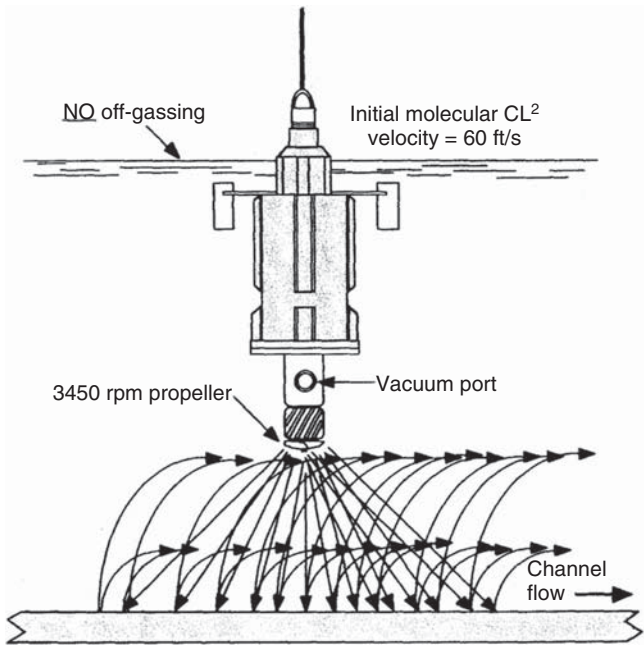


Figure 7.8. The Water Champ (courtesy of Gardiner Equipment Co., Inc.).

The applied chlorine should be thoroughly mixed with the water before it enters the contact chamber.

Before sizing a chlorine contact chamber, the designer will need to establish the design criteria for the system, which includes determination of the end use of the effluent. Will it be discharged into a receiving stream, or will it be applied for reuse such as irrigation for golf courses or agricultural land, or is the plant treating drinking water that will be pumped into a distribution system?

Wastewater

For traditional treatment before discharging the water into receiving waters, the criteria are established based on the flow rate of the receiving water. For instance, in Missouri, because of the large volume of flow in the Missouri and Mississippi rivers, the state has not required disinfection, although this philosophy is changing, whereas the southwestern states, where plant effluent can constitute a large portion of the flow in the receiving stream, require disinfection with chlorine as well as dechlorination. Disinfection requirements are site specific and specific to the discharge permit issued to each wastewater treatment plant. There are some basic guidelines for designing a chlorine contact chamber. The Recommended Standards for Water Works (formerly known as the Ten States Standards) is a compilation of standards prepared by the public health agencies of a group of states in an effort to promote consistency of water and wastewater treatment plant design. For wastewater plant chlorine contact chambers, the Standards suggests a residence time in the chlorine contact chamber of 15 min at design peak hourly flow or at the maximum rate of pumping after the disinfectant is mixed into the process water. The chlorine contact chamber should be constructed with baffling to reduce short-circuiting of flow.

Reuse Water

California was the first state to establish standards for chlorine contact basin effluent, and these standards have been adopted for reuse water across the United States. The term "Title 22 reuse water" stems from the California Code of Regulations, which defines and issues standards for reuse water in the state. Title 22 reuse water has a coliform limit of 2.2 most probable number (MPN) of total coliforms per 100ml average over 7 days, 23 MPN/100ml in any sample over 30 days, and no sample may exceed 240 MPN/100ml. Also, the chlorine contact basin should have a modal contact time of 90 min to ensure adequate virus kill. Model contact time is defined as the amount of time a tracer is injected at the entrance to the chamber, and the highest concentration of tracer is measured at the effluent of the chamber.

Potable Water

Disinfection is required for all drinking water supplies. The disinfection regulations established in the United States require 3-log reduction of *Giardia* and 4-log reduction of viruses. Some states have more strict requirements. Disinfection credit is granted based on treatment processes, which also can be state dependent.

The Recommended Standards for Water Works also recommends that the chlorinator capacity be sufficient to produce a free chlorine residual of at least 2 mg/l after a contact time of at least 30 min when the maximum flow rate coincides with the maximum chlorine demand.

The layout of a chlorine contact chamber has a significant impact on disinfection. The field study by Sepp and Bao¹ indicated that the length-to-width ratio is not in itself an accurate descriptor of plug-flow characteristics. Their pilot tank had a much higher length-to-width ratio than the plant-scale tanks, but it did not have a correspondingly smaller dispersion number. Studies by Marske and Boyle,² and Trussell and Chao³ have indicated that the dispersion number usually decreases with increasing length-to-width ratio, but the correlation is poor. Other factors must be taken into account such as the depth-to-width ratio, extent of dead space, and eddy currents caused by poor plug-flow characteristics at the baffle turning points.

The field investigation by Marske and Boyle² evaluated seven different chamber configurations. Those with longitudinal baffles proved to be the most efficient. The configuration used most today, shown in Figure 7.9, is a longitudinally baffled chamber with a length-to-width ratio of 72:1, which has a modal time of 0.7. The modal time of this chamber could be increased to 0.9, as has been demonstrated by others, with some slight changes such as elimination of its square corners. This work by Marske and Boyle² substantiates the claims that long, narrow channels and/or conduits make the best chlorine contact chambers. At a minimum, the length-to-width ratio should be 10:1, but up to 40:1 decreases the possibility of short-circuiting.

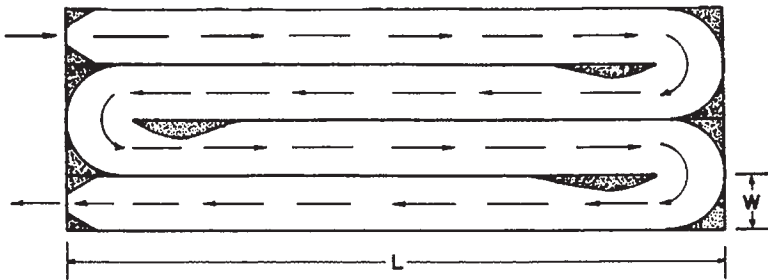


Figure 7.9. Chlorine contact chamber with longitudinal baffling and optimum plug flow characteristics. Flow length:width = 72:1; length-to-width-ratio = 18:1; modal time = 0.70; percent plug flow = 95 (from Marske and Boyle).

The contact chamber analysis by Trussell and Chao³ shows that depth can have an effect on the dispersion index, but not nearly to the same extent as the length-to-width ratio. Based on the results of the plant-scale study versus the mobile pilot-plant study by Sepp and Bao,¹ the data indicate the height-to-width ratio should be 1.0 or less. Therefore, a compromise is a square cross section at peak flow (maximum water surface) and a slightly rectangular section at lower flows. To reduce any potential wind effects, chlorine contact basin sidewater depth should be not less than 10 ft.

Circular chambers are not acceptable as chlorine contact chambers unless they are specially designed with an outer annular ring. The poorer performance of a circular configuration versus a longitudinally baffled chamber with serpentine flow and the special annular ring is clearly shown in the Marske and Boyle investigation. Any other circular chambers would be expected to perform just as poorly.

Marske and Boyle² also studied the following physical characteristics used in the design of a contact basin: (a) the depth of the basin as it relates to the effect of surface wind; (b) the effect of outlet weir configuration; and (c) the effect of turbulence. The effects of these physical characteristics are summarized below.

Two tracer tests conducted on a very long, narrow contact channel approximately 3 ft deep indicated that wind may cause surface currents that result in some short-circuiting. Consequently, a unidirectional shallow basin or a trench may not provide the plug-flow distribution of residence times that would be expected from the geometrical configuration. In this case, the designer would be well advised to replace this type of chamber with a closed conduit.

Tracer tests, performed on a 3.5-ft-wide Cipolletti weir and on an 18-ft-wide sharp-crested weir, indicated that all hydraulic performance parameters were improved when the sharp-crested weir was installed. Consequently, it is recommended that contact chamber overflow weirs be extended across the entire width of the final channel of the contact chamber.

There is no need to produce turbulence such as is required in the mixing phase. Turbulence in a contact chamber will not improve destruction of coliforms; it may, in fact, be detrimental to the disinfection process. Turbulence during the contact period may reduce the chlorine residual by aeration, and may cause back-mixing.

Longitudinal baffles are superior to horizontal baffles. The latter cause many times more back-mixing in the chamber than do longitudinal baffles. Sometimes it is impossible to design a contact chamber with longitudinal baffling because of seismic design considerations. In such cases, the horizontal baffling is usually integrated into the design as structural members, and all dead spaces and short-circuiting can be minimized by eliminating all corners.

In wastewater, whenever the effluent coliform limit is 2.2 MPN/100 ml, the specifications for the concrete in the contact basins should call for a smooth, porcelain-like finish free from any pits or recesses, where bacteria and dirt would accumulate and which would require frequent cleaning. Contact cham-

bers designed with either longitudinal or horizontal baffling to meet an effluent coliform limit of 2.2 MPN/100 ml must be kept as free from slime and algae deposits as possible.

No-Tracer Test Design

If it is not possible to conduct tracer studies to determine the disinfectant contact time needed to achieve the desired disinfection goal, a no-tracer theoretical time can be determined using a “rule of thumb” fraction, T_{10}/T , which typically ranges from 0.3 to 0.7. This value is determined using data from tracer studies and depends on the configuration of the basin being used. The theoretical disinfection contact time is determined by multiplying the fraction T_{10}/T by the theoretical hydraulic detention time, which will give an estimate of the actual disinfection value. Since this approach gives only an estimate, it should be used only when the tracer method cannot be used.

The detention time depends on the design of the basin. While other design criteria such as the length-to-width ratio affect the detention time, baffling within the basin has the largest effect. The types of baffling used in a basin include inlet, intrabasin, and outlet baffling. Baffling conditions are categorized as poor, average, or superior. The best, or superior, mixing occurs with inlet and outlet baffles that reduce the flow velocity and spread the water uniformly across the basin; an intrabasin baffle also helps in achieving the best mixing scenario. Average mixing is achieved with either an inlet or an outlet baffle along with intrabasin baffles. Poor mixing occurs with no baffles or with only a single inlet or outlet baffle and no intrabasin baffles.

Wet Weather Disinfection for Wastewater

Wet weather disinfection presents significant challenges to utilities contending with combined sewer overflows or excess flow. Separate chlorine contact facilities may be required to process water from a storm event. Typically, states require the use of the Recommended Standards as the design criteria of chlorine contact basins, which recommend a residence time in the chlorine contact chamber equal to 15 min at the peak hourly design flow. For facilities using sodium hypochlorite in the wet weather flow treatment systems, there is a concern with degradation of the sodium hypochlorite at higher concentrations of 12–15 trade percent during extended storage. Alternatives include on-site sodium hypochlorite generation or diluting the sodium hypochlorite on-site to 6% or less to reduce the effects of chemical degradation.

The chlorine demand may vary significantly during a storm event; it is advisable to overdose the chemical for chlorination and dechlorination (if required) to ensure a proper level of treatment. The required residence time in the chlorine contact basin may be reduced by conducting chlorine dose and response studies at the site. It has been shown that effective treatment can be

accomplished in a period as short as 5 min, although regulators would need to agree to such a design feature before it is implemented.

Chlorine Contact Basin Construction

Typical construction materials for a chlorine contact chamber include concrete with smooth surfaces to reduce the potential for pits in areas where bacteria and algae can become attached. Although rarely done, corners should be rounded to avoid “dead spots” within the basin. Other materials used should be evaluated for longevity and resistance to attack by sulfide or chloride. Of particular concern is the initial chemical mixing area where the chemicals will be present at highest concentration. The use of corrosion-resistant coatings may be considered for this area.

The ease of cleaning the basin should also be considered. Providing walkways and access points will make it easier to remove debris and algae from the basin. If covers are provided, all portions of the basin should be accessible for cleaning and protection against intrusion by birds and animals.

Disinfection By-products

Disinfection by-products are an important consideration in wastewater treatment and discharge to receiving bodies of water. Chapters 4 and 6 include additional discussion of the federal water quality standards applicable to water treatment.

Sampling and Reporting

Sampling is required for process control and, ultimately, for reporting to the governing regulatory body. The permit governs what is to be reported and when. Most states require a discharge monthly report (DMR), which includes chemical use and chlorine residual concentration. More specific recommendations on process control and sampling are found in Chapters 12 and 3, respectively.

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2. Marske, D.M. and Boyle, V.D. Chlorine contact chamber design—A field evaluation. *Water and Sew. Wks.*, 1973;**120**:70.
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8 Chlorine Feed Systems

Chlorine is delivered to water treatment plants (WTPs) and wastewater treatment plants (WWTPs) as a mixture of liquid and gas. Although fire codes define chlorine as a “gas” because of its properties at standard atmospheric conditions, it is stored as a liquid. Chlorine liquid is much denser than chlorine gas. In order to keep physical storage volumes small, it is more effective to store liquid than gas. Liquid and gaseous forms of chlorine act in different ways and must be handled differently. In addition, chlorine systems frequently straddle the liquid/gas two-phase transition boundaries. Because of this, the liquid, the gas, and the unique properties of a material bridging a liquid/gas boundary condition must be considered when designing or working on a chlorine system. Chlorine is extremely dangerous. A thorough understanding of its properties and the means and methods used to store and feed chlorine are critical for designing or operating a chlorine system in a safe manner.

Chlorine gas exists in chlorine systems in two different ways, under positive pressure and under vacuum. This difference affects many aspects of design and operation, including the equipment and the piping and valve materials used in the system, and considerations of system layout.

Chlorine can be stored on-site in many different ways. The method of storage is generally selected based on the amount of chlorine necessary for storage and the maximum amount required to be instantly available. Various methods are used to determine the necessary amount of storage, but generally, 30 days of storage is supplied at average dosages (in this context, dosage means the amount of chlorine fed in milligram per liter or parts per million) and average plant flows. A secondary requirement is 7 days’ supply at maximum dosages and maximum plant flows. Some facilities use neither of these criteria and instead use 14 days at maximum dosage and average plant flow or 14 days’ supply at average dosage and maximum plant flow. Different situations may influence these requirements (both up and down), including proximity to a source of supply, likelihood of supply interruption, or interruption due to natural disaster, but these criteria serve as a reasonable starting point. There are five different methods of storing chlorine on-site. From smallest to largest: 150-lb cylinders (cylinders), 2000-lb containers (ton containers), 17-ton tank trucks, 90-ton tank cars (railcars), and on-site storage tanks.

When selecting a storage and feed system, the maximum instantaneous flow rate must be considered because the amount of chlorine that can be fed is related to the amount of heat that can be conducted into the chlorine in the container. If insufficient heat is conducted to the chlorine, chlorine flow will decline and eventually stop. Under normal conditions, chlorine feed reaches a maximum rate that cannot be exceeded. The amount of heat that can be conducted to the container is directly related to the ambient temperature, container surface area, and the convective flow conditions around the container. This relationship can be expressed by the following equation:

$$Q = hA\Delta T, \quad (8.1)$$

where

Q = amount of heat transferred to the container,

h = rate of heat transfer to the container,

A = surface area of the container, and

ΔT = temperature difference between the container and the surroundings.

As can be seen, the higher the temperature difference (ΔT) between the chlorine and the surroundings, the larger the area of the container (A), and the higher the rate of heat transfer to the container (h), the greater the amount of heat (Q) transferred to the container, and the greater the amount of chlorine that can be fed from a given container.

It can be surmised that there are ways to increase the maximum rate of flow from a chlorine container. Keeping the container in a room at a temperature elevated above ambient temperature is an option (heat should never be directly applied to a chlorine container for safety reasons). This is not a strategy that should be planned on during design of a chlorine system, but for an operator in a bind, it can supply temporary relief. The rate of heat transfer (h) to the container is strongly influenced by how rapidly air falls around the ton containers. Air falls around the ton containers as the air around the containers cools and becomes denser than the surrounding air, creating a natural convective air current. Anything that speeds up the movement of air over a container will likewise increase the maximum rate of flow from the container. A fan would be effective in this situation. However, this too is not a strategy that should be planned on during the design of a chlorine system, but it may provide temporary relief during an emergency. Both of these strategies can be effective; the effect of the first is fairly simple to quantify, the second is very difficult to quantify.

Considering all this, it is clear that ambient conditions play a strong role in the design of a chlorine system. For an economical design, not only should the minimum, average, and maximum chemical demand be determined but also when these demands occur. For instance, if the maximum chlorine demand

occurs in the summertime when the ambient temperature is above 100°F, a higher ambient temperature can be taken into account. However, it is also necessary to determine the maximum chlorine feed conditions under various conditions. With some creativity and understanding of the whens and whys associated with specific chlorine feed conditions, design of a chlorine system can be further optimized.

In deciding which and how many types of chlorine storage devices to use, maximum instantaneous demand determines how many cylinders, containers, trucks, or tank cars must be connected to the system, and average demands determine how many of them must be stored on-site.

CYLINDERS

Chlorine cylinders can vary in size, but the largest ones hold 150 lb of chlorine. All chlorine cylinders must conform to Department of Transportation (DOT) specification 3A480 or 3AA480.¹ A chlorine cylinder has a single opening equipped with a slow-opening valve. Cylinders have a maximum outside diameter of 10.75 in. (273 mm) and are 59-in. (1499 mm) tall.¹

A 150-lb cylinder can contain more than 150 lb of chlorine; however, this should never be allowed to happen because liquid chlorine is an incompressible fluid, which expands when heated. If it does not have sufficient volume to expand, the pressure inside the fixed volume increases and can easily exceed the pressure-holding capability of the cylinder, which would result in a catastrophic failure. According to the Chlorine Institute, "By DOT regulation, the weight of chlorine that is loaded in a container may not exceed 125% of the weight of water at 60°F that the container will hold."¹ The density of chlorine at 60°F is about 88.9 lb/ft³, and the density of water at 60°F is 62.4 lb/ft³; therefore, a 1-ft³ container would be allowed to hold 78 lb of chlorine (62.4 lb/ft³ × 1 ft³ × 125%), about 0.87 ft³ of chlorine. As a general rule, cylinders are not allowed to be more than 85% full.

Chlorine cylinders must be moved with care. With proper slings a crane could be used, but hand trucks with restraint chains are the preferred means of moving chlorine cylinders. Once in position, usually against a structure such as a wall, the chlorine cylinder must be restrained with an immobilization chain (see Fig. 8.1). Cylinders not in use must also be chained in place.

Connection to cylinders is done in one of two ways: vacuum regulators directly connected to the cylinder valve (discussed later), or with a yoke assembly for pressurized withdrawal. A yoke assembly consists of a yoke, a flexible connection, and a valve. The yoke completely envelops the cylinder valve and is tightened onto the valve with a wrench, as indicated on Figure 8.2, which compresses a lead gasket between the yoke face and the valve face, ensuring a tight leak-free fit between the cylinder and the chlorine feed system. A flexible connection is connected to the yoke, which is then connected to an isolation valve on the chlorine system.

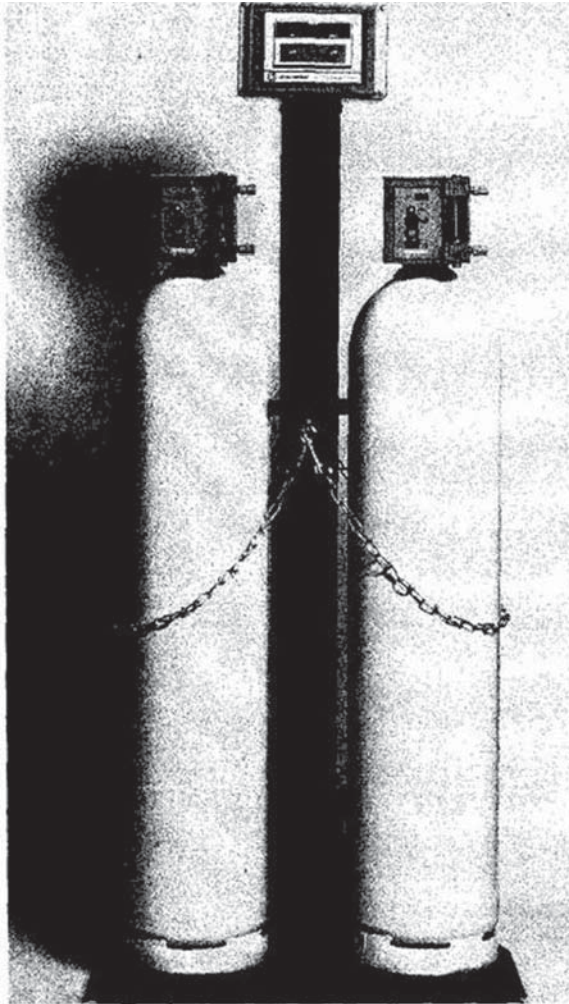


Figure 8.1. Chlorine cylinder scale.

The valve on a chlorine cylinder is slow-opening type with an integral fusible link (Fig. 8.3). The valve body is constructed of a silicon-lead-bronze alloy, suitable for use with chlorine. The fusible link is constructed to fail open at a predetermined temperature (the metal in the link melts). The fusible link on the valve is very important for a chlorine cylinder, as in the event of a high-temperature excursion (fire); the pressure in the cylinder will increase. The failure of the fusible link allows the chlorine to be released in a controlled fashion. Without the fusible link, an explosive decompression of the cylinder can occur, resulting in uncontrolled release of chlorine and launching of the cylinder. In one such situation, an empty oxygen container was launched and

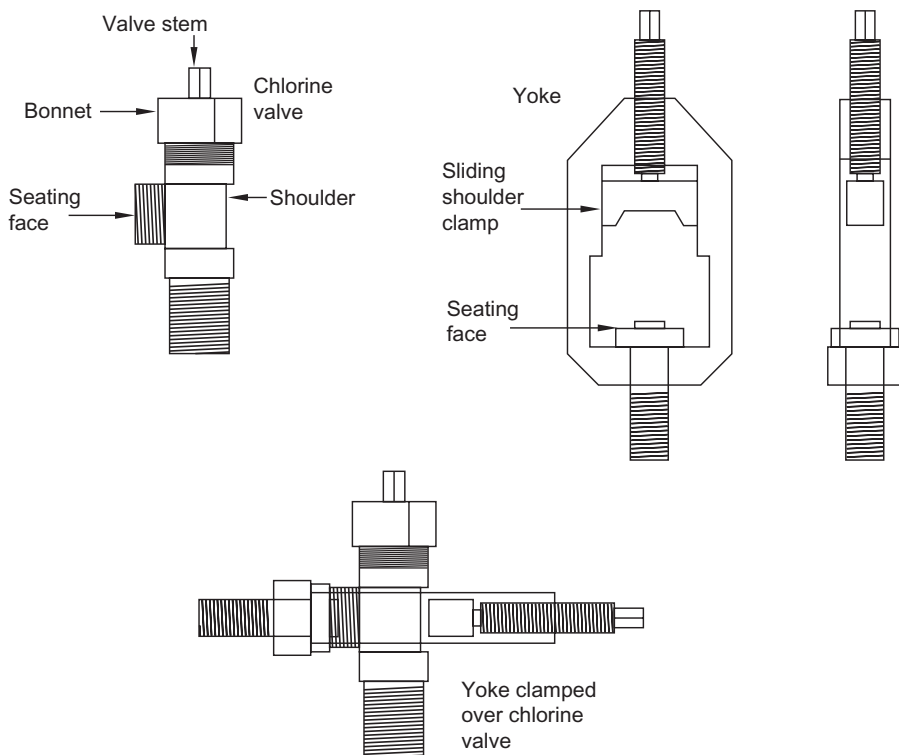


Figure 8.2. Chlorine valve and yoke assembly.

traveled several miles as a result of explosive decompression (and the container was “empty”!). With a chlorine cylinder, this could result in damage to the surrounding enclosure, spreading of the released chlorine over a large area, and damage to other structures or injury to people in the area where the cylinder landed.

It is very important that the valve on the cylinder be of the slow-opening type. When a new cylinder is connected to the chlorine system, the pressure in the cylinder will be high (about 85 psig), while the pressure in the system is low (vacuum). By using a slow-opening valve, the system is allowed to slowly pressurize. If a quick-opening valve such as a ball valve were used, the system would pressurize rapidly, with a very fast-moving pressure front. Any amount of liquid chlorine ahead of this pressure front would serve as a plug, and when it hits a bend in the pipe, it will not change direction easily because of inertia and will try to continue in its original direction. If the pipe is sufficiently strong, the liquid will change direction; otherwise, the liquid will not change direction and will penetrate the pipe wall causing a chlorine leak. Clearly, slow-opening valves are important. Similar design considerations are typically used in steam systems.

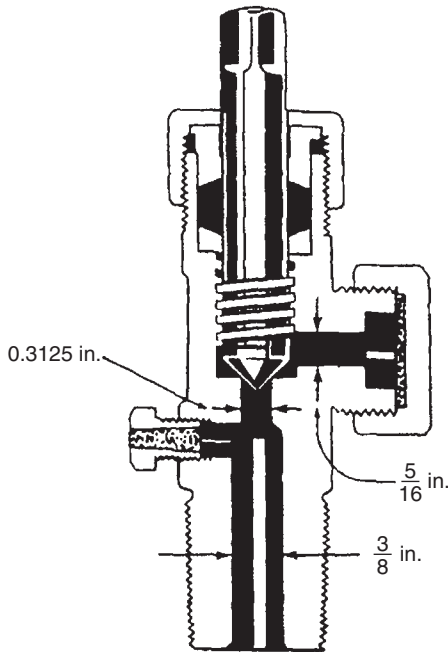


Figure 8.3. Chlorine cylinder valve with fusible plug.

Chlorine can be fed from cylinders as a liquid or a gas. To feed chlorine as a gas, the cylinder is connected to the valve in the upright position. To feed liquid chlorine, the cylinder must be inverted. This creates additional safety issues and should therefore be avoided. There are limits how quickly chlorine can be withdrawn from a cylinder. In the case of chlorine gas, the maximum amount of chlorine withdrawal is 1–1.5 lb/day/°F. At 60 °F, this corresponds to 60–90 lb/day.

In most applications, it is important that chlorine be fed continuously without interruption. This requires multiple hookups of cylinders (one bank in use and one bank on standby). The switchover from one bank to the other can be done automatically in several ways, but knowing when switchover occurred or when a cylinder is truly empty requires a dedicated for each cylinder.

Either hydraulic or electronic scales may be used for weighing chlorine cylinders. Hydraulic systems are rarely used in new applications because it is difficult to get electronic signals from them (although possible), but they have the advantage of having large faces indicating the amount of chlorine left in a cylinder, which can be seen from a distance. Most modern systems are equipped with electronic scales which rely on a load cell to generate an electronic signal that can be easily forwarded to other administrative or control devices. A load cell is a calibrated strain gage. As the strain gage is flexed by

the change in weight of the chlorine cylinder, the electricity flowing through the strain gage changes (piezoelectric effect). This electrical change is detected and changed to another secondary signal by a transmitter. Some transmitters can accept and retransmit a signal only from a single scale, while others can accept signals from multiple scales. As a result, much economic optimization can be achieved by proper selection of the transmitters for weighing systems.

TON CONTAINERS

Ton containers hold 2000lb of chlorine and must conform to DOT specification 106A500X.¹ A chlorine ton container has multiple openings on one end of it, and can have up to four connections on the head for valves and multiple dedicated connections for fusible links. When four valves are used, they are arrayed radially 90° apart around the cylinder centerline on the head. When there are only two valves, they are 180° apart. Inside the ton container, each valve is attached to a tube that extends to the outer edge of the inside of the container. Ton containers can vary in physical size but have a maximum outside diameter of 30 in. (762 mm) and are 82.5-in. (2096 mm) long.¹

Ton containers have one significant safety feature that cylinders do not have—concave heads. Concave heads are designed to reverse themselves when the container reaches an overpressure condition. This provides additional volume and thus lowers the pressure in the container. This temporary relief scenario is expressed mathematically as Boyle's law:

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \quad (8.2)$$

where

P_1 = initial pressure in the container,

P_2 = pressure in the container after head reversal,

V_1 = initial volume in the container, and

V_2 = volume in the container after head reversal.

When a ton container's head reverses, the volume in the container (V_2) increases and the pressure in the container (P_2) decreases.

The concave heads also provide additional protection for the valves and fusible links, as they are recessed from the edge of the container and are protected from falling objects. The valves are covered during transport by a steel housing that is removed for operation in order to access the valves. The concave heads are attached to the container shell to form a thick protective chime that doubles the shell thickness in this area and provides a strong location for lifting the container.

Ton containers are sufficiently large and heavy that they must be handled with mechanical equipment. Generally, they are delivered by truck and must be lifted off the truck with a crane or hoist equipped with special lifting beams and hooks.

Monorail cranes are used most often, as they are relatively inexpensive and less complex than bridge cranes. For very large systems, monorail cranes generally do not have sufficient flexibility and can result in very long narrow buildings. Common design of chlorine facilities involves the monorail extending beyond the building envelope. In this situation, the truck pulls up along the outside of the building underneath the crane. A chlorine ton container is then either removed or placed on the truck with the crane. Loading and unloading of multiple containers can require moving of the truck during loading and unloading.

Bridge cranes are used for very large systems where moving the truck during loading and unloading would present a problem or when the containers must be loaded and unloaded inside a building.

When developing a vertical control diagram for a chlorine facility using ton containers, it is necessary to consider the height of the truck bed; the height of a ton container; the height to accommodate the lifting beam and lifting beam hooks, the crane hook, and trolley; and the stack-up height of the crane (see Fig. 8.4).

Spare and empty ton containers should not be stored directly on the floor but should be placed on trunnions, which come in two varieties—fixed trunnions and roller trunnions (see Fig. 8.5). Operators usually prefer roller trunnions

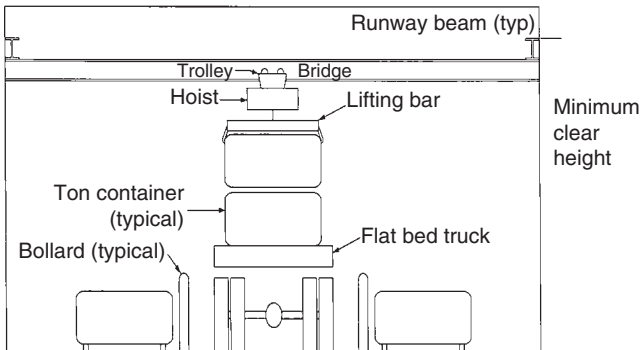


Figure 8.4. Chlorine unloading vertical control diagram.



Figure 8.5. Trunnion for ton container.

nions, as they allow ton containers to be turned for inspections. Roller trunnions are more expensive than conventional trunnions. Rails embedded in the floor can also be used instead of trunnions.

In very large facilities, ton containers are sometimes stacked. While this is not the preferred method, the ton containers are sufficiently tough to tolerate it. Under no conditions should two ton-containers be placed on another.

Chlorine can be fed from ton containers as a liquid or a gas. Each ton container has up to four valves that are nearly identical to the valves on cylinders, with the exception that they do not have an integral fusible link. Ton containers should always be laid on their side, with two valves in a vertical orientation (one directly above the other) and the other two in a horizontal orientation (side by side). If the ton container has two valves, the valves should be in a vertical orientation. The liquid will lie in the bottom of the container and the gas will collect at the top. To feed chlorine as a gas from a ton container, the top valve must be used. The tube inside the vessel will convey the gas in the top of the container to the valve. To feed liquid chlorine, the bottom valve must be used. The tube inside the vessel will convey the liquid at the bottom of the container to the valve.

Like in the case of cylinders, there are limits to how rapidly chlorine can be withdrawn from a ton container. The maximum amount of gaseous chlorine that can be withdrawn from a ton container is 6–8 lb/day/°F. At 60°F, this corresponds to 360–480 lb/day.¹ The maximum amount of liquid chlorine withdrawal is 400 lb/h (9600 lb/day).

These limits will determine how many ton containers should be hooked up to each bank. To feed 300 lb of chlorine a day while changing out the containers only once a week, two ton containers should be used ($300 \times 7 = 2100/2000 \leq 2$). Likewise, to feed 2500 lb of chlorine per day while changing out the containers only once a week, nine containers should be connected ($2500 \times 7 = 17,500, 17,500/2000 \leq 9$). In addition, it is also necessary to consider how rapidly chlorine can be withdrawn from a bank of containers.

When feeding 300 lb of chlorine per day, only one container needs to be connected from an instantaneous feed rate perspective ($300 < 360$). Of course, the container will need to be changed out more frequently than once a week.

When feeding 2500 lb of chlorine per day, and withdrawing gaseous chlorine directly from the ton containers, the seven ton containers must be connected from an instantaneous flow rate perspective ($2500/360 \leq 7$). When withdrawing liquid directly from the ton container, only one ton container needs to be connected for an instantaneous feed rate perspective ($2500 < 9600$). Of course, the ton containers would have to be replaced several times a day!

Generally, instantaneous feed rates are considered when evaluating maximum chlorine feed rates, and frequency of changeout is considered when evaluating average feed rates.

Like with cylinders, yokes must be used to attach to ton container valves with flexible connections, valves, or vacuum regulators. Frequently, several ton containers are connected to a common header. Usually, there is a valve on the

header, and the flexible connection is attached to this valve. Some operators connect the flexible connection directly to the yoke; others connect it to an auxiliary valve, which is then connected to the yoke. Either arrangement is sufficient. Additional valves add safety but create more work.

Flexible connections are the single weakest part in a chlorine system and should be inspected on a regular basis and replaced if there is any doubt about their suitability. According to the Chlorine Institute, "Copper tubing with a diameter of 1/4 inch or 3/8 inch is recommended. Flexible metallic hoses or fluoroplastic hoses as described in Institute Pamphlet 6 are also acceptable materials."¹ Fluoropolymer is a generic term for Teflon-like materials. Chlorine will permeate and penetrate fluoropolymer materials, so if a metallic hose with a fluoropolymer liner is used, the metal will be subject to attack by chlorine.

There are some special dangers associated with hookup of multiple ton containers to feed liquid chlorine when a header is connected to the liquid side of more than one ton container. The pressure inside of the ton container is directly related to the temperature of the ton container—the higher the temperature, the higher the pressure. If several ton containers are connected on the liquid side, it is very likely that each of them will be under a different pressure. Because of the pressure difference, liquid will flow from the higher-pressure container to the lower-pressure one until the pressures equilibrate. If the valves are then closed, one of the containers will be overfilled. If there is any rise in temperature (such as the sun hitting the ton container), the pressure will increase. Because the container is now filled with an incompressible liquid, the pressure can easily exceed the container's pressure-holding capability, causing a release of chlorine. If the fusible plug does not fail first (fusible links are temperature-activated, so they probably will not fail), a valve may be blown off or the container may explode. Regardless of the mode of failure, the container would be emptied.

Opening and closing of the valves in this manner may seem unlikely but is actually fairly common occurrence.

This situation is fairly simple to avoid. When hooking up multiple ton containers for liquid service, their gas sides should be connected to a separate common header and the gas side valves should be opened to allow the pressure to equilibrate, and then the liquid side valves should be opened. While this involves some additional work, it eliminates a serious safety hazard (Chlorine Institute Drawing #183).

TANK TRUCKS/TANK CARS

Tank trucks used for chlorine service have capacities of 15–22 tons, 17 tons being the most common. There are two parts of the tank truck: the vessel and the appurtenances for the trailer (wheels, axles, chocks, etc.). The vessels must conform to DOT specification MC331. Older vessels conforming to MC330 may still be used.¹ The tank trucks can be used to transfer chlorine to a storage

tank or, more commonly, chlorine can be fed directly from the tank truck. Like from ton containers, it is possible to withdraw either liquid or gaseous chlorine from a tank truck. On top of the tank truck is an armored manway with four slow-opening angle valves and a pressure-relief valve. Two angle valves are for liquid service and two are for gas service (see Fig. 8.6). The liquid service valves are connected to pipes extending to the bottom of the vessel, so that liquid can be withdrawn. Seventeen-ton truck trailers generally do not exceed 38 ft in length and are the width of a standard truck trailer.

Railroad tank cars resemble tank trucks, except that they are much larger, with the most common capacity being 90 tons. They have connections identical to those of tank trucks, and like tank trucks they can be used either to fill storage tanks or, kept on-site for direct withdrawal of chlorine.

When chlorine is fed directly from tank trucks or cars, the tanks are brought to the site, placed in a bay, and disconnected from the transfer or the locomotive. Because of their high cost, users will need to purchase tank truck trailers for their use, unlike the cylinders and ton containers, the rental cost of which

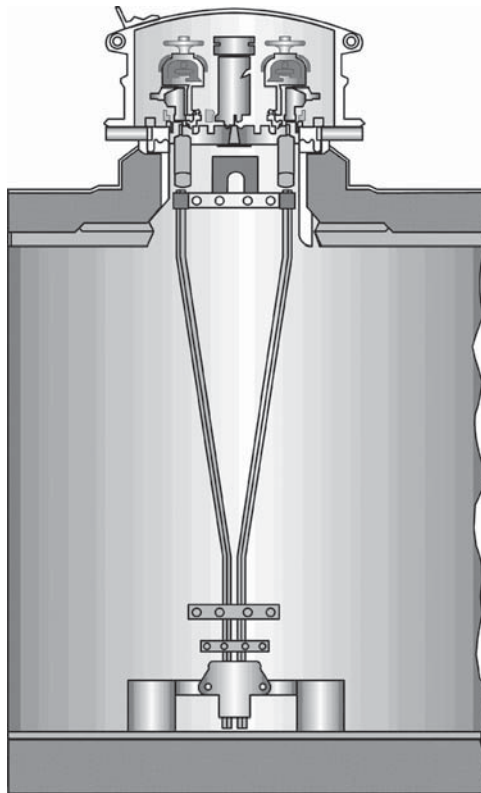


Figure 8.6. Cross-section of a tank car manway and one-inch-diameter liquid withdrawal rubes.

is included with the cost of the chlorine. Tank cars usually remain the property of the railroad utility or the chemical supplier.

Each tank truck or car is equipped with two liquid valves, two gas valves, and a pressure-relief valve. The relief valve serves the same purpose as the fusible link in ton containers but includes a spring to keep the valve closed. The relief valve is directly connected to the vapor space of the vessel, so that in the event of a release, only vapor will escape from the vessel, whereas on a ton container, failure of a fusible link at the bottom of the container will result in a liquid release.

Like on ton containers, the valves on the tank truck/cars are of the slow-opening type and similar in concept, but are physically larger and are made of different materials. They also include some additional safety features. Under each valve is an excess flow valve; the excess flow for the gas valves differ slightly from those for the liquid valves, but both are intended to close if the angle valves are sheared off. The excess flow valves are raising ball check valves (see Fig. 8.7) that seat when there is a rush of chlorine over a preset amount and are available in several capacities. The size used on a tank truck is set by DOT regulation.

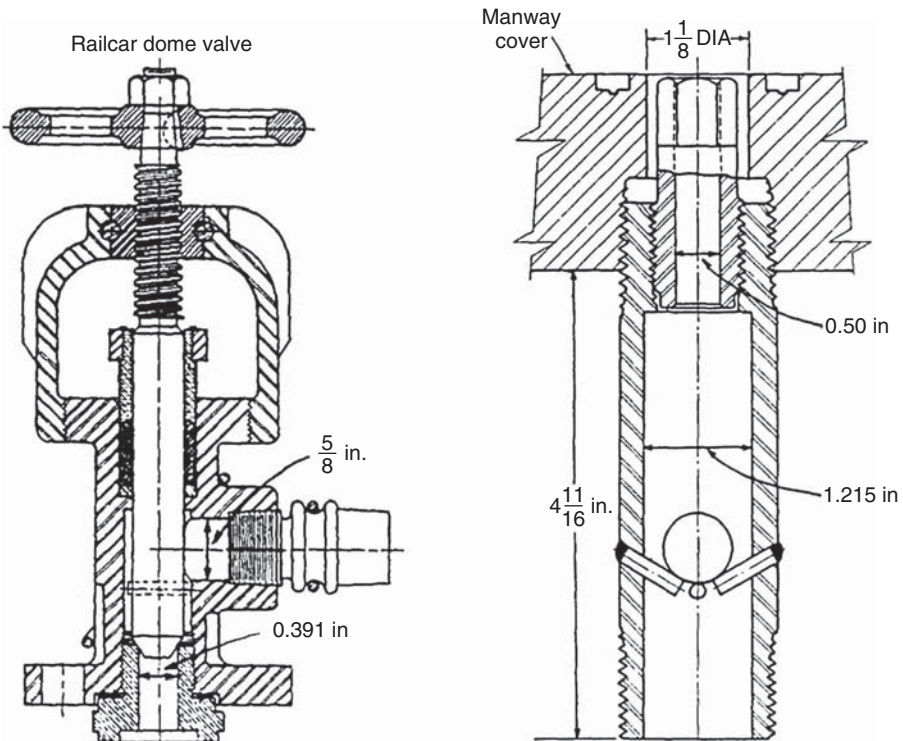


Figure 8.7. Tank car shutoff valve and excess flow valve.

The hoses used for connection to tank trucks and cars are similar to those used for ton containers but are larger in diameter and longer, as additional flexibility is required. They are usually attached directly to the angle valve using a threaded connection.

As with ton containers, hose failure is the most likely cause for a catastrophic chlorine leak. In the event of a hose failure, the excess flow valves are intended to seat and stop the leak. Unfortunately, this has not always been the case (specifically in propane trailers). It has been determined that the pressure drop through the hose can create sufficient back pressure to prevent the excess flow valves from seating. Because of this, federal law requires the use of passive means during unloading to close the angle valves on tank trucks (Docket 49 CFR §178.337-11 and 173.315(n)). The equipment for this application is described later in this chapter.

Unlike tank trucks, tank cars move by rail. Their use is feasible only where a rail line is available close to or adjacent to the site. If rail cars are used, several units should be kept on-site to ensure an uninterrupted supply of chlorine. Tank cars remaining at a site for long periods may be subject to dunnage charges.

The only reliable way to determine how much chlorine remains in a tank truck or tank car is to weigh it. Tank trucks equipped with load cells truck are weighed using scales, identical to the scales used at truck weighing stations. For tank cars, a similar technology is used except that the load cells are placed under the track, so a separate scale is not needed.

Since both tank trucks and tank cars are on wheels, unintended movement is a concern. Therefore, before they are connected to the process, the wheels should be chocked to prevent movement. Tank cars are often provided with an alarm, which consists of a plug on a cord that is normally kept taut; when the tank car begins to roll, the plug is pulled open and the alarm sounds.

STORAGE TANKS

Unlike other types of chlorine storage, be they cylinders, ton containers, tank trucks, or rail cars, all of which are movable, storage tanks are stationary. Their physical size is not limited by any regulations, but they should be larger than the maximum volume delivery anticipated to be delivered, whether by tank truck or rail car, to ensure that the entire load can be accepted.

Storage tanks should be constructed of carbon steel and should meet the same requirements as tank trucks (DOT specification MC331). All connections should be on top of the tank, and platforms and stairs should be provided for ready access to the shutoff valves. The tank should be supplied with the full complement of excess flow valves and pressure-relief valves, and should be placed on scales to monitor the weight of its contents (Chlorine Institute Pamphlet #5).

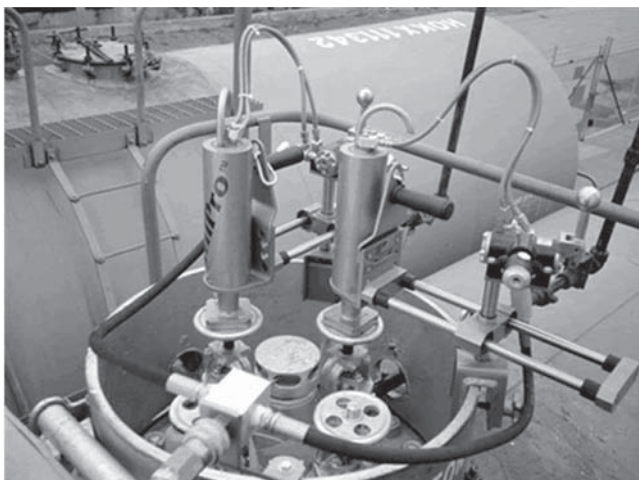


Figure 8.8. Pneumatic automatic shutdown system.

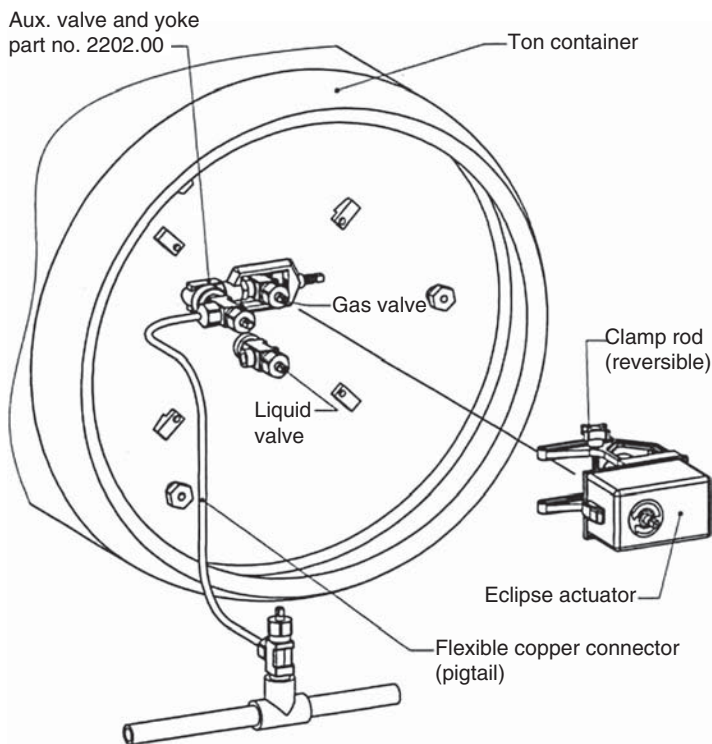
Transfer of chlorine to storage tanks, like any chemical transfer, is inherently dangerous and hazardous, as it requires operators to directly handle the chemical. During the transfer, dry air is usually used to pressurize the delivery vessel to force out the chlorine. This generates a large amount of stored potential energy that is automatically renewed by the air supply. Connection failures are likely to result in large releases and a greater potential for personnel exposure. The passive means of closing the valves on the delivery tank above are required in this case as well. Similar means of automatic shutoff should be provided on storage tanks.

Passive means of closing the valves on chlorine cylinders, ton containers, tank trucks, tank cars, and storage tanks can be either electric or pneumatic operators (both are commercially available). Electric shutoff actuators should include a battery backup for use in the event of loss of power. Similarly, pneumatic operators should be provided with an air backup. The air backup should be “stored air” in a dedicated air receiver supplied by a dedicated air compressor. The air receiver must be of sufficient size to close all valves, and must supply air to nothing else. For large systems, pneumatic operators are preferable (Fig. 8.8). For small systems, electric actuators are a good choice (Fig. 8.9). The choice between pneumatic and electric actuators is based primarily on economic considerations.

LIQUID CHLORINE FEED

Vaporizers

When liquid chlorine is withdrawn from a storage vessel, it must be vaporized before it is fed to the process. Two types of vaporizers are available: the coiled

**Note:**

CGA 820/820C required for mounting Valve Actuator to liquid or gas valve.
Open Yoke and Yoke to Pigtail Adapte are available options from Halogen.

Figure 8.9. Electric automatic shutdown system.

tube type manufactured by Portacel, and the pot style manufactured by Siemens/Wallace & Tiernan and by Severn Trent Services/Capital Controls. Portacel is no longer available in the United States, only in Europe. In any case, heat is transferred to chlorine to vaporize it indirectly through a water bath. Simply stated, liquid chlorine enters the device and gaseous chlorine leaves the device.

The gaseous chlorine that leaves the vaporizer will be at or very close to its dew point. This means that if its temperature drops, it can recondense into a liquid. Some of the equipment downstream from a vaporizer is incompatible with liquid chlorine, so liquefaction of the chlorine can lead to severe operating problems and failures. Therefore, the chlorine gas leaving a vaporizer should contain a certain amount of superheat (the more, the better!). Superheat is the amount of heat the gas contains above its dew point. Vaporizers include “superheat sections” to raise the gas temperature further; however, their effectiveness is questionable.

It may seem remote that chlorine gas would cool off after leaving a vaporizer, but it is commonly observed because of the Joule–Thompson (JT) effect. Whenever a gas decreases in pressure, heat must be added for it to maintain its temperature. If no ready source of heat is available, the gas will become cold (this is isenthalpic expansion). JT effects can be commonly observed by letting air out of a tire. As the air escapes the tire, its volume expands and its pressure drops to atmospheric pressure from the higher pressure in the tire. The released air will be cool, and it is common to see frost form on the tire valve precisely because of this effect. In this case, the released air is removing heat from the tire valve, and the frost results from condensed water vapor. In the case of chlorine, the chlorine cools and recondenses. Pressure drop through piping and pieces of equipment (filters, valves, etc.) can be sufficient to cause this effect. Although rare, reliquefaction sometimes occurs in liquid chlorine systems; hence, the question as to the effectiveness of superheat sections in vaporizers.

The tube-type vaporizer consists of a coiled tube immersed in a water bath (see Fig. 8.10). Liquid chlorine enters at the bottom of the coil and vaporizes as it rises through the tube. In this type of vaporizer, the chlorine vaporizes throughout the tube and the generated gaseous chlorine bubbles up through the liquid chlorine in the tube. The bubbles will rise along the top of tube, so it is important that the tubing have an appropriate pitch to encourage appropriate gas/liquid disengagement. Superheat is supplied to the gas from the tubing that is above the gas liquid level in the tube. This level can vary depending on the hydraulic conditions across the vaporizer.

In tube-type vaporizers, there is a danger that surges in liquid chlorine from the storage device could push a slug of liquid chlorine all the way through the tubing and out of the device. This could result from the sudden opening of a valve on the supply side. It is, therefore, very important to provide a separation

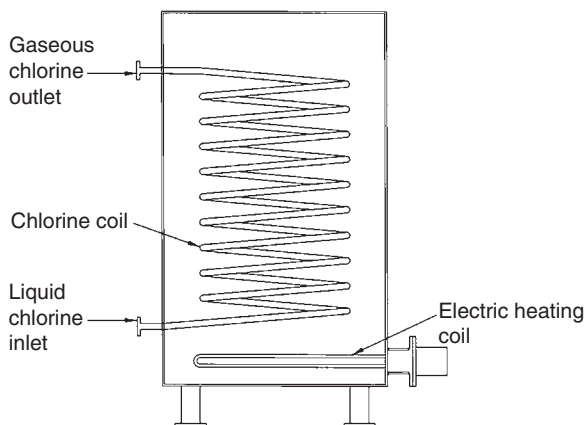


Figure 8.10. Coiled tube-type vaporizer.

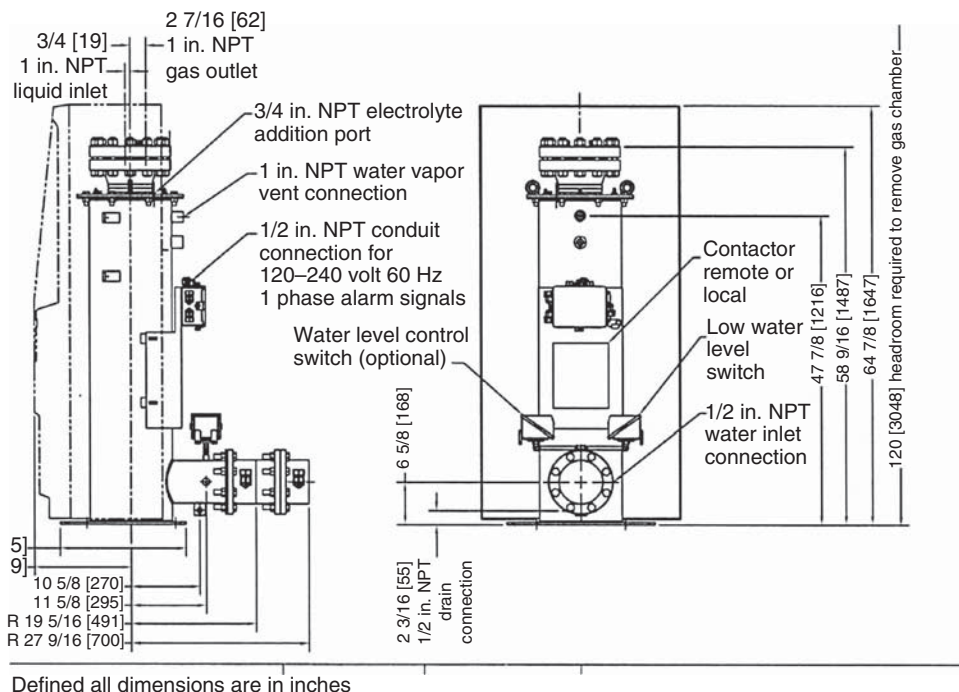


Figure 8.11. Pot-type vaporizer. NPT: National Pipe Thread.

device or knockout pot immediately downstream from this type of vaporizer. Heat can be supplied to the water bath in the same manner as to a pot-type vaporizer.

The pot-type vaporizer consists of a vessel inside of a vessel (see Fig. 8.11). Chlorine is vaporized in the inner vessel. The outer vessel serves as the water bath, with heat from the water bath transferred to the chlorine through the wall of the inner vessel. The inner vessel consists of an inlet and an outlet connection, a vaporizing section, and a superheat/disengagement section. This inner vessel is designed per the American Society of Mechanical Engineers Boiler and Pressure Vessel Code Section VIII Division 1 pressure vessel. In the case of the Severn Trent/Capital Controls vaporizer, this vessel is designed for lethal service and is stamped as such. The liquid chlorine supply is connected to the inlet connection and is conducted to the bottom of the vessel through an internal drop pipe. The liquid chlorine is heated in the lower part of the vessel and vaporized. At this point, the chlorine gas is at its dew point so that a drop in temperature, whatever the cause, will result in the chlorine gas liquefying and creating a two-phased mixture. To avoid this, the superheat/disengagement section supplies extra heat transfer area for the chlorine gas to collect additional heat so that the gas is not at its dew point. This section also supplies an area of low

velocity so that entrained liquid can fall out of the gas and back to the liquid surface (tube-type vaporizers do not have this feature). The gaseous chlorine leaves the vessel through the top outlet connection.

Because the chlorine is heated by the water bath, the water bath must be heated. This is generally done using an electric immersion. In the Severn Trent/Capital Controls equipment, the heating element is positioned directly in the water bath under the inner vessel. In the Siemens/Wallace & Tiernan arrangement, the heating element is positioned vertically in an adjacent small vessel. A small pump pumps water from the water bath past the heating element. Similar equipment is used for tube-type vaporizers.

Both of these designs are well proven, but the Siemens/Wallace & Tiernan method is considered to be a safer design. If the water bath empties, the heating element can get very hot and start transferring heat radiantly to the inner vessel. If the inner vessel gets too hot, the mechanical integrity of the vessel can be damaged and the inner vessel can fail, resulting in a chlorine leak. If the water bath runs dry, the heating element can distend and touch the inner vessel, which could result in a vessel failure. Both of these vaporizer designs have multiple safeguards, including low-water cutoffs, high-temperature switches, and electrical overload protection. The above situation has never occurred in the Severn Trent/Capital Controls design in more than 50 years of operating experience, but has occurred in a Siemens/Wallace & Tiernan design. Siemens/Wallace & Tiernan modified its design in the 1970s and added the pump around and external vessel.

The operation of the outer vessel can have significant effects on the performance of the vaporizer. The outer vessel is essentially open to the atmosphere, so over time water will evaporate from the surface. This requires addition of more water, but also concentrates salts and hardness in the water. These salts can plate out on the inner vessel and make heat transfer through the vessel (or tube) walls less efficient. It can also lead to corrosion of the inner vessel (or tubes). As corrosion occurs, wall thickness decreases, resulting in less pressure-holding capacity. Over time, vessels and tubes can be damaged. Vaporizers are supplied with sacrificial anodes that help keep the salts in solution and limit the corrosive properties of the water. The sacrificial anodes must be periodically replaced. A good solution is to use softened water in the vaporizers and to maintain a constant flow through of the water. This will help keep the level of salts low in the vaporizer by eliminating the amount in the water bath and constantly purging some of the concentrated water. Distilled or deionized water should never be used in the vaporizer. Very pure waters are aggressive and can rapidly corrode the steel vessels, which would result in failure of the inner vessel and cause a chlorine release.

Two factors that affect the amount of chlorine a vaporizer can vaporize are the size of the heating element and the surface area of the vessel or tubing. The vaporizers available from a given manufacturer are physically the same regardless of the capacity. The sole difference is the size of the heating element. Heating element sizes are relatively easy to modify, so it is easy to convert a

6000ppd vaporizer to a 10,000ppd unit. Of course, its electric power supply may need to be modified as well. Commercially available vaporizers are limited on the upper end by the surface area of the inner vessel. The largest size available is 10,000ppd, although Severn Trent/Capital Controls has indicated that under certain circumstances, its vaporizer may be capable of producing 14,000ppd of chlorine gas. This may supply leeway for the short term, but reliquefaction is more likely.

Because vaporizers are large and heavy, it takes time for them to heat up. To ensure the continuous operation of a chlorine system, when one vaporizer is in use, a second vaporizer should be kept warm so that it can be quickly brought on line.

The Chlorine Institute recommends that vaporizers be taken out of service at least once a year for cleaning and inspection, which should be considered when laying out a chlorine room. In some cases, a small crane may have to be used to move the vaporizer.

A specific scenario that must be considered when installing a vaporizer: It is possible for a vaporizer to get valved in on both sides and still continue to operate. In this scenario, pressure in the vaporizer builds as more and more liquid chlorine vaporizes. If this is not dealt with, the vaporizer will eventually explode. On the discharge of each vaporizer, a relief indication control assembly must be installed, which consists of a rupture disk, a high-pressure switch, and a relief valve. When the vaporizer gets blocked in and the pressure rises, the rupture disk blows and the high-pressure switch is actuated. The pressure switch will then alarm so that an operator could shut down the vaporizer. If the vaporizer is not shut down, pressure will continue to build and the relief valve will open, relieving the pressure buildup in the system. The discharge of the relief valve should be routed to the inlet of the chlorine scrubber. The material of the piping from the discharge of the relief valve to the chlorine scrubber must be carbon steel. To help prevent this situation from occurring, lockable line valves should be installed on the line vaporizer filling and discharged.

APPURTENANCES

Pressure-Reducing Valve

The gaseous chlorine discharged from the vaporizers is nominally at the same pressure as the chlorine in the storage containers. In order for chlorine to be fed safely throughout a facility, the chlorine pressure must be reduced to vacuum. This is done in two stages: using first a pressure-reducing valve and then a vacuum regulator.

The purpose of the pressure reducing serves is to drop the pressure of the chlorine gas and to serve as a secondary safety device for the vaporizer and the overall chlorine system. When liquid chlorine is withdrawn from a

container, a back pressure must be maintained, or the chlorine would flood the vaporizer and overwhelm the balance of the chlorine system. When a proper back pressure is maintained, the level in the chlorine vaporizer will remain relatively constant. Flooding could occur during start-up if back pressure is not first built up from the vaporizer. The pressure-reducing valve is equipped with an integral hydraulic actuator. A small electric pump keeps the valve open by keeping a hydraulic cylinder pressurized, which resists the closing force of the integral fail closed spring. In the event of a power failure, the hydraulic pressure is relieved and the valve closes. In addition, the pressure-reducing valve is interlocked with the vaporizer so that if the vaporizer is off or not operating, the valve is closed.

After passing through the pressure-reducing valve, chlorine proceeds through a vacuum regulator, which reduces the pressure to a vacuum. Vacuum regulators operate in the same manner as pressure-reducing valves but drop the pressure down further.

On the discharge of a vaporizer, the pressure is reduced in stages—the reason for this is the JT effect discussed above. If the pressure is reduced all at once, the chlorine may reliquefy, damaging the downstream piping and the vacuum regulator. In the piping system, the pressure-reducing valve should be placed as close as possible to the vaporizer, with a length of piping between the pressure-reducing valves and the vacuum regulators. This will allow the gas, which has cooled down after the pressure-reducing valve due to the JT effect, to draw a small amount of heat from the surroundings. This additional amount of heat usually is sufficient to avoid reliquefaction.

Gas Filter

An additional appurtenance the chlorine system should include is a gas filter. While the quality of chlorine today is much improved, it can still carry impurities (sometimes picked up from the piping system or vaporizer) that can cause fouling in vacuum regulators and chlorine feeders. A chlorine gas filter is a small carbon steel vessel with an integral glass filter (see Fig. 8.12). Inevitably, gas filters will generate pressure drop. Chlorine reliquefaction sometimes occurs in these devices as a result of the JT effect.

Expansion Tanks. One appurtenance that is unique to liquid chlorine feed is an expansion tank. Liquid chlorine has a high coefficient of expansion even relative to other liquids. If liquid chlorine becomes trapped, for instance between two valves, and heats up, its pressure will rise, and eventually result in a chlorine release. To prevent this, expansion tanks must be installed on any piping where the chlorine can become trapped between two closed valves. The expansion tank relieves the pressure buildup in the pipe by adding volume to the pipe section. Normally, the expansion tank is sealed from the pipe by a rupture disk. When the pressure rises, the rupture disk fails and liquid chlorine is released into the expansion tank, which reduces the pressure in the line.

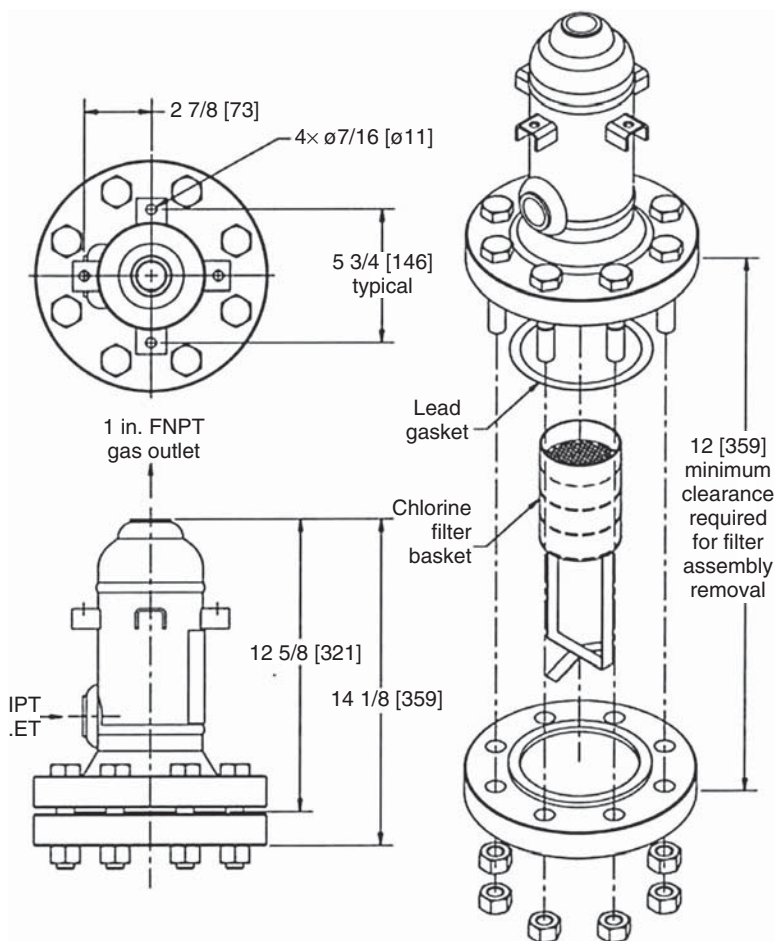


Figure 8.12. Chlorine filter.

Expansion tanks are supplied with integral high-pressure switches that alarm when the rupture disk fails (see Fig. 8.13).

Gas Chlorine Feed

A gaseous chlorine feed system does not include all of the equipment used in liquid chlorine feed systems, as the gaseous chlorine is drawn directly from the container into a vacuum regulator. After the vacuum regulator, there is no difference between liquid and gas chlorine systems. Vacuum regulators may be wall mounted or container mounted; they consist of a large diaphragm over an orifice and a set spring that controls the extent of diaphragm movement (degree of opening) (see Fig. 8.14).

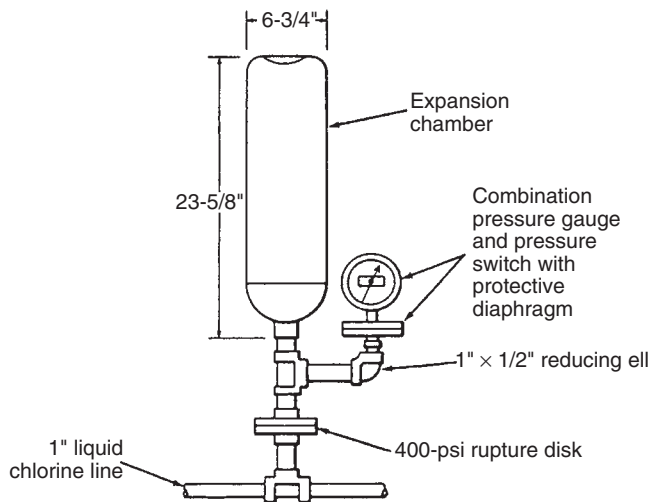


Figure 8.13. Liquid chlorine expansion tank.

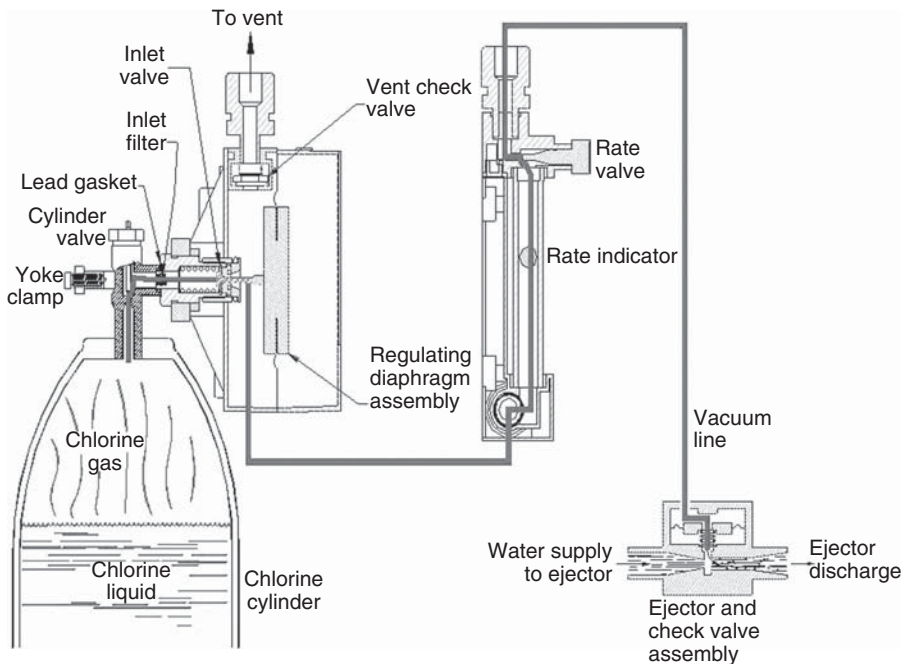


Figure 8.14. Vacuum regulator.

The vacuum is established farther down in the system by the eductors (discussed later), and the vacuum regulator simply provides the pressure drop from positive pressure to vacuum. Without the vacuum induced by the eductors, the vacuum regulators stay closed and stop the flow of chlorine. This ensures that chlorine leaving the storage area is under vacuum, so that if a vacuum line breaks, rather than chlorine escaping, air enters the pipe.

Vacuum regulators are sized to allow only a certain amount of chlorine to pass through them. However, the spring that controls the flow within the vacuum regulator is slightly different in each vacuum regulator because of differences in manufacturing methods and the inherent sensitivity of the device. This means that different vacuum regulators under the same conditions can pass different amounts of chlorine.

Vacuum regulators can be either wall mounted or container mounted. Container-mounted devices have the operating advantage that pressurized chlorine never leaves the cylinder or ton container, which greatly enhances the safety of the system. In addition, there is only one pressurized connection between the ton container or the cylinder and the vacuum regulator. Container-mounted devices are often mounted in parallel, with several units on separate ton containers or cylinders, with the discharges tied together, as indicated on the schematic below (Fig. 8.15).

With this arrangement, all vacuum regulators sense the same level of vacuum on the discharge side. Because of the different springs in the vacuum regulators and the different pressure in each cylinder or ton container, each vacuum regulator will pass differing amounts of chlorine from each cylinder or ton container. The net effect is that one ton container can be emptied much sooner than another. A cylinder or ton container may freeze up as gas is withdrawn from it too rapidly. In addition, one cylinder or ton container may

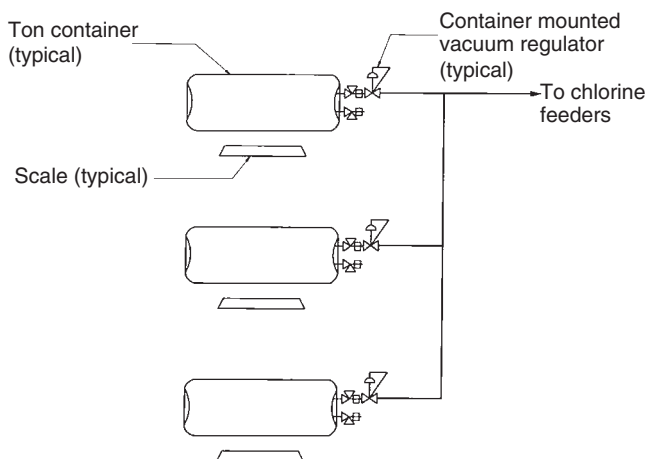


Figure 8.15. Container-mounted vacuum regulator header.

become completely empty before the others. This can result in flow interruption. Therefore, when container-mounted vacuum regulators are used, each container must be placed on a dedicated scale. This allows the operator to know when to change out the empty container without interruption in chlorine feed. For container-mounted vacuum regulators to operate correctly, the vacuum manifold must be of the proper size, and the vacuum regulators must be properly sized and balanced.

If vacuum regulators are mounted in parallel on the discharge of several vaporizers, a single vaporizer may become overtaxed, which would result in the lack of superheat to be applied to the chlorine gas leaving the vaporizer, and in extreme cases, liquid chlorine to be entrained in the gas, which can lead to severe operating problems and unsafe conditions. Under no conditions should vacuum regulators whose total capacity exceeds the capability of the vaporizer be placed in parallel on a system fed from vaporizers.

For very small chlorine feed systems and where automatic control is not needed, container-mounted vacuum regulators can be supplied with integral flow control devices. These sonic-type vacuum regulators can also be supplied with integral switchover devices to ensure uninterrupted chlorine supply (see Fig. 8.16).

Regardless of the type of vacuum regulator used, a switchover device is necessary to ensure uninterrupted flow of chlorine. These devices switch to a new container or bank of containers when those in operation become depleted. Switchover devices for large systems consist of automated valves that operate based on either pressure or weight since the containers are mounted on scales. Pressure-based switchover is a better choice because if the containers freeze

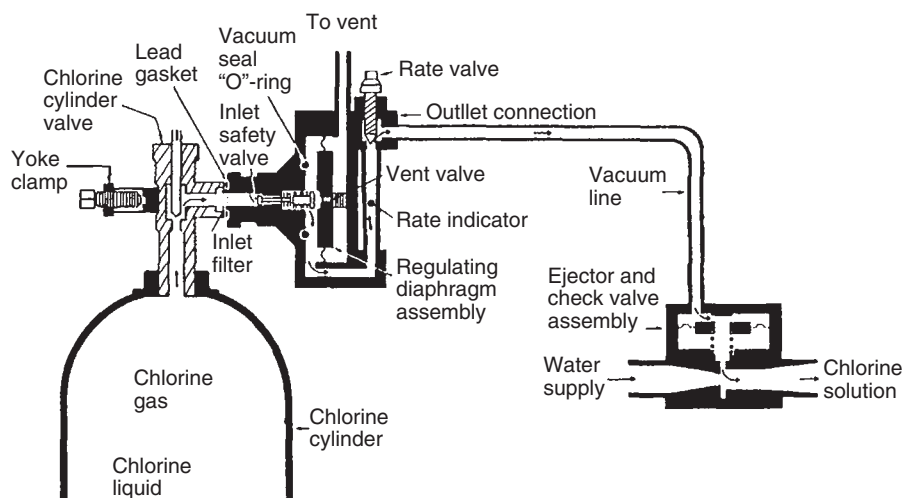


Figure 8.16. Sonic-type vacuum regulator.

up, a fresh bank will be brought on line, allowing chlorine feed to continue. Weight-based automatic switchover does not accomplish this.

CHLORINE FEEDERS AND EDUCTORS

Chlorine is metered as it passes through the feeders. However, the motive force for the flow is generated in the eductors. The eductor generates the vacuum needed for the system through the Bernoulli effect. When water under pressure is passed through a restriction, the fluid velocity increases, creating the required vacuum. This property can be optimized through properly designed nozzles working in conjunction with recovery throats. This is exactly what an eductor does—it acts as a hydraulic pump or a compressor.

In essence, the eductor generates the vacuum for the system and draws the chlorine from the source. The vacuum generated by the eductor causes the vacuum regulator to open. The chlorine feeder is placed in the flow path between the vacuum regulator and the eductor and regulates the flow of chlorine. Both the eductor and vacuum regulator do not regulate the flow in any way other than by establishing an upper limit based on their capacities. The eductor simply creates vacuum, and the vacuum regulator opens in response to that vacuum. The control is accomplished by the chlorine feeder.

In addition to generating a vacuum and making it possible for the chlorine to be safely distributed, the eductor mixes the chlorine with water before it is fed to the process as chlorine solution. Manufacturers limit their eductors as to the amount of chlorine they can receive to keep the chlorine-to-water ratio from exceeding a certain concentration as a safety feature that prevents extreme off-gassing of chlorine in the process and helps the mixing of the chlorine solution into the main process.

The eductor simply generates vacuum. If it does not work properly, no chlorine will be fed to the process. The three main factors that determine whether an eductor will function are (a) the back pressure on the eductor, (b) the flow of the motive force water, and (c) the pressure of the motive force water to overcome the back pressure. If the back pressure is too high, the eductor will stall. If the back pressure is too low, the eductor will surge. If the flow or the pressure of the water is too low, the vacuum regulator will not function because of energy to generate the vacuum. The following instruments should be available around an eductor: a pressure gauge on the water supply, a rotameter on the water supply, and a pressure gauge with a protective diaphragm on the discharge.

It is very difficult, if not impossible, to perfectly match the pump to the eductor; therefore, the pump will create a vacuum on the discharge of the eductor, mimicking a low back pressure on the eductor. To correct this, the water must be bypassed around the eductor to avoid starving the pump. Because the bypass must be dynamic, it is provided with a flow-control valve that is controlled based on the downflow pressure (see Fig. 8.17).

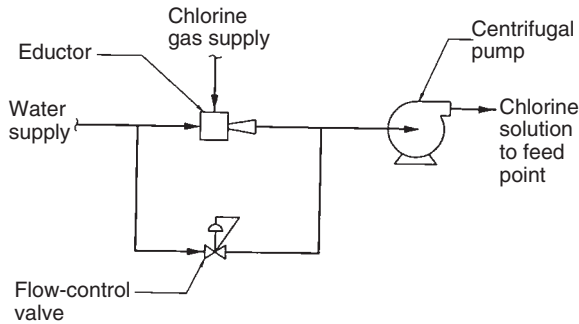


Figure 8.17. Pumped chlorine solution assembly.

In addition to eductors, chlorine induction units (CIUs) can be used to generate the vacuum for the chlorine system. A CIU is really a pump that is placed directly in the channel or the line where the chlorine is fed, to pump water past orifices integral to the machine and thus generate a vacuum (see Fig. 8.18).

CIUs can achieve better mixing under certain conditions, but they are expensive and must be used judiciously. The main problem associated with CIUs involves placing them into the water. Generally, lifting devices (winches) and rail units have to be used to orient the CIU correctly in the flow, without damaging or displacing its chlorine feed and power supply lines.

Chlorine feeders are either sonic or pressure-balanced type. The sonic feeders are small and are usually mounted to the vacuum regulators, which are mounted directly to the ton containers or cylinders. The pressure-balanced-type feeders are used on larger systems and are either floor or wall mounted.

Sonic feeders operate by controlling the area across a critical orifice. Whenever, the gas' pressure drops by about half as it passes across an orifice, the gas will reach maximum velocity, which corresponds to the speed of sound in the gas. The sonic feeders have a fixed opening (orifice) with a needle that moves in and out of the opening to control the area of the orifice and therefore the flow of the gas. Sonic units are used only on very small systems and do not include any means of automatic flow control.

Pressure-balanced chlorine feeders may be wall or floor mounted. In terms of operation, there is no difference between the two types. A pressure-balanced feeder consists of a pressure-regulating valve on its inlet, a rotameter, a variable orifice control valve, and a discharge pressure-regulating valve. The pressure-regulating valves on the suction and discharge ends of the feeder work together to maintain a specific pressure drop across the orifice control valve, which assures that the flow across the variable orifice control valve is predictable based solely on valve position (see Fig. 8.19). The rotameters provides a visual indication of the flow across the chlorine feeder. There is no feedback flow control, which means that chlorine flow is controlled inferentially. Proper operation of the chlorine feeder is verified visually by



Figure 8.18. Chlorine induction unit—Water Champ.

observing the rotameter and through process feedback from a chlorine residual analyzer.

Chlorine Diffusers

The chlorine diffuser is where the chlorine solution generated in the eductor is mixed with the main process water. To achieve proper mixing, pressure energy must be changed to velocity across the diffuser. This is usually accomplished through a pipe with a specific number of holes of a specific diameter spanning a pipe or channel. The greater the pressure drops across the diffuser, the greater the mixing energy as the chlorine solution enters the process flow.

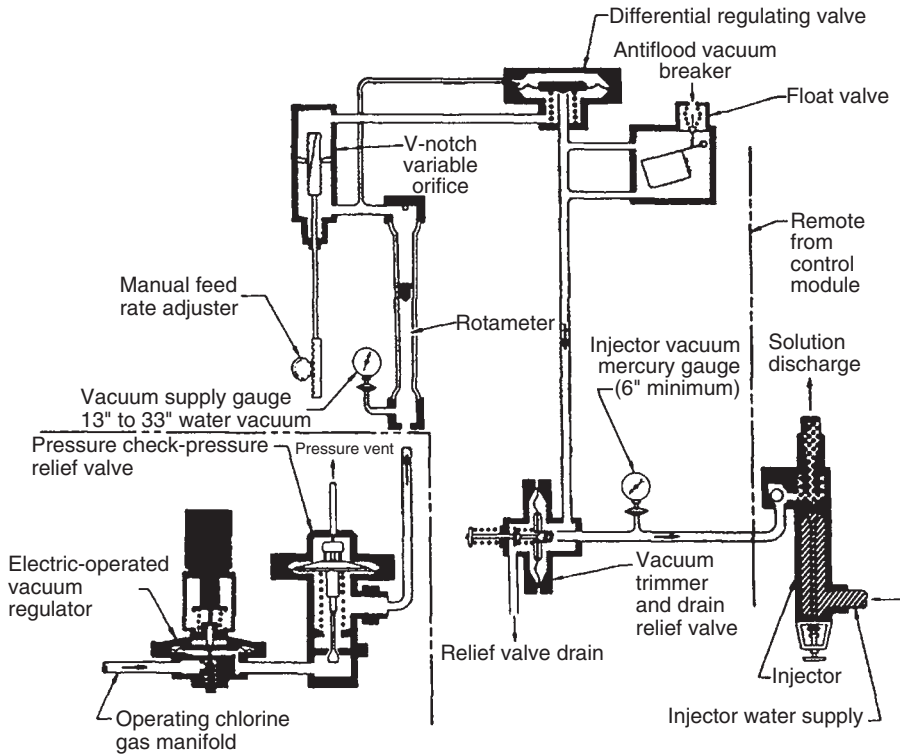


Figure 8.19. Pressure-balanced chlorine feeder flow diagram.

A pressure drop of 5 psi across diffusers using the methods described in the Cameron Hydraulic Data is recommended when using this type of diffuser. Information on sizes and quantities of orifice is available from chlorine feed system manufacturers.

Pipe and Valve Systems

The Chlorine Institute's *Pamphlet 6, Piping Systems for Dry Chlorine* provides excellent guidance on piping, fittings, bolting, gasketing, and so on for all chlorine systems. It is recommended that this document and others from the Chlorine Institute be referred to when designing, installing, or working on a chlorine piping system.

Chlorine systems at WTPs and WWTPs include four different piping zones that must be considered: pressurized liquid chlorine, pressurized gaseous chlorine, gaseous chlorine under vacuum, and chlorine solution.

Piping for pressurized liquid and gaseous chlorine is generally fabricated of carbon steel (ASTM A105, seamless schedule 80). Piping can be connected by threaded connections, socket welding, or butt welding. Butt welding is the

best but its use is not possible on the small piping used at WTPs and WWTPs. While threaded connections are acceptable, socket welding is preferable because it is durable and least likely to leak. Use of carbon steel piping on pressurized liquid chlorine involves some special design considerations.

Often, when a chlorine container is emptied, a vacuum is created all the way to the storage device. When liquid chlorine vaporizes, the remaining liquid and piping will become chilled, and the piping can be as cold as the chlorine liquid. At atmospheric pressure (0 psig, or 14.7 psia) liquid chlorine temperature is -29.15°F . However, as a vacuum is created often, the chlorine will actually be even colder. Normal carbon steel can tolerate temperatures only down to -20°F . With repeated low-temperature excursions, it becomes brittle and cannot hold pressure, and the piping made of this material will fail.

Chlorine Instruction *Pamphlet 6* recommends alloy steel piping (ASTM A333 grade 1). Only socket welding and butt welding can be used for this piping. According to *Pamphlet 6*, the use of threaded fittings is not acceptable. Another solution is to keep the pipe from becoming chilled. This can be done by eliminating any pockets in the piping and making sure that the pipe slopes to the container and to the vaporizer with a high spot in the middle (see Fig. 8.20). In this way, there will still be some chlorine that will evaporate, but because it is not trapped in the pipe, there is a greater likelihood that the thermal mass of the pipe and the ambient heat will be sufficient to keep the temperature of the pipe from dropping below -20°F .

Most guidelines for valving on pressurized chlorine systems recommend slow-opening valves similar to those valves on ton containers, but generally, chlorine piping systems are equipped with ball valves, which are quick opening, rather than slow opening as recommended. Usually, these valves have carbon

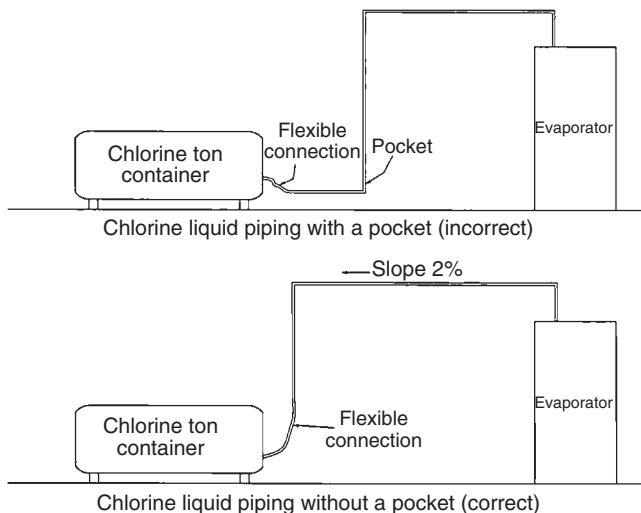


Figure 8.20. Pockets in chlorine liquid lines.

steel bodies, Monel® balls and stems, and Teflon® seats. These valves should be operated only when the piping system is not being actively used. They should be lined out before bringing a chlorine source on line. If they are opened when there is a differential pressure across them, pipe failures can occur. Frequently, there will be liquid in the line behind the valve. When the valve is opened, the piping system will pressurize very quickly with a very fast-moving pressure front. The speed of the front is limited only by the speed of sound in chlorine gas. The liquid chlorine ahead of the pressure front acts as a plug, and when it reaches a bend in the pipe, it will not want to change direction because of inertia and will try to continue in the same direction. If the pipe is sufficiently strong, the liquid will change direction. If the pipe is not sufficiently strong, the liquid will not change direction and will penetrate the pipe wall, resulting in a chlorine leak.

On the vacuum side, downstream from the vacuum regulator, metallic piping should not be used. Chlorine is kept at a vacuum in these sections of the system so that if a leak occurs, air enters the piping system instead of chlorine escaping. When air enters the piping, so does water. Few metals have much resistance to wet chlorine. Carbon steel and most types of stainless steel will be rapidly destroyed in the presence of wet chlorine. As a consequence, plastics are commonly used for chlorine vacuum service, as they have good resistance to chlorine. In the United States, polyvinyl chloride (PVC) pipe is used most commonly; elsewhere, the use of polyvinylidene fluoride (PVDF) is common.

None of these plastics are pure components. Other materials are added to the resins in order to enhance their properties. Frequently, these are elastomers, which are very sensitive to strong oxidizers such as chlorine. PVC comes in three varieties: PVC type I, PVC type II, and chlorinated PVC (CPVC). PVC type 1 is sometimes referred to as uPVC or unplasticized PVC. Of these three, only PVC type 1 is suitable for chlorine vacuum service. The other types are vulnerable to chlorine and will be attacked by chlorine.

Chlorine will diffuse through almost any plastic, and as it do so, will react with the plastic and change it. In the case of PVC type I, the material properties of the PVC are damaged significantly very quickly. However, because the piping is under vacuum and circular, it is held together rather than blown apart.

In terms of connections for PVC piping, solvent-welded connections are preferable wherever possible. Threaded connections should be avoided to the greatest extent possible because threads compromise wall thickness and therefore pipe strength. However, threads are the only way to connect piping to certain pieces of equipment.

For PVC piping in chlorine service, three types of valves can be used: ball, diaphragm, and butterfly.

Full-bore ball valves are most commonly used (see Fig. 8.21). In larger sizes (more than 2 in.), they can be hard to operate. As these valves age, chlorine will permeate the O-rings that seal the stem against the body. The O-rings will

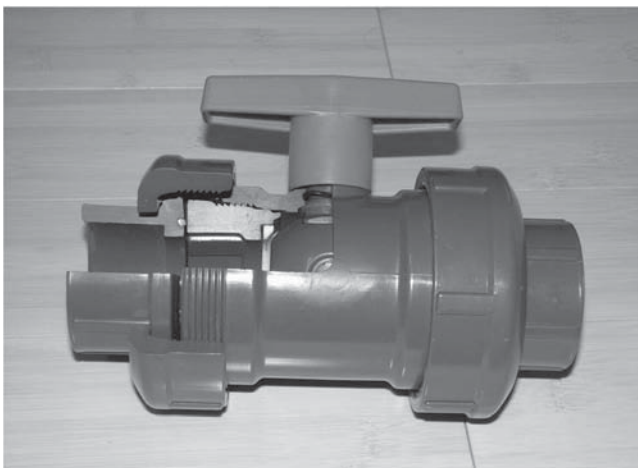


Figure 8.21. Plastic ball valve.

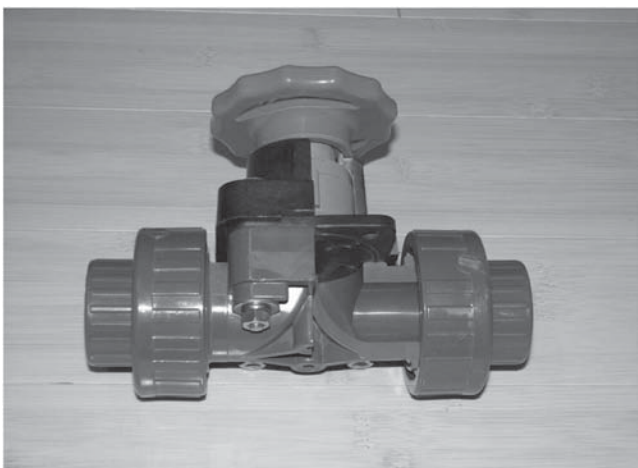


Figure 8.22. Plastic diaphragm valve.

swell, making the valves even more difficult to operate. Trying to open a stuck ball valve can result in failure of the valve (many valves have a breakaway stem) or pipe fracture.

Diaphragm valves (Fig. 8.22) are sometimes used in chlorine service, but the diaphragms are subject to attack from the chlorine, so special attention must be paid when selecting diaphragms. These valves have an internal weir, which creates a pressure drop across the valve. If diaphragm valves are used, special attention should be paid to pipe sizing to accommodate them.

Butterfly valves (Fig. 8.23) should be considered only for larger pipe sizes (more than 2 in.), but they do have limitations that must be considered. Butterfly valves rely on an interference fit between an elastomeric liner and a disk for tight shutoff. The elastomeric liner will be attacked by the chlorine and will be damaged, compromising the valves' ability to close. In addition, some butterfly valves are lugged where the bolting goes through the body of the valve. In these cases, enhanced bolting materials must be used as the chlorine will diffuse through the body of the valve and corrode the bolts.

None of these valves performs perfectly in chlorine service, so choices between the three types of valves must be made on a case-to-case basis.

For chlorine solution piping, most of the same considerations apply as for PVC piping in vacuum service. CPVC is actually resistant to chlorine solution but is still not recommended. After the eductor, chlorine actually takes a small amount of time and distance to go into solution. At this point, the chlorine solution is fizzy and there is enough chlorine that is not in solution to attack the adjuncts in CPVC piping.

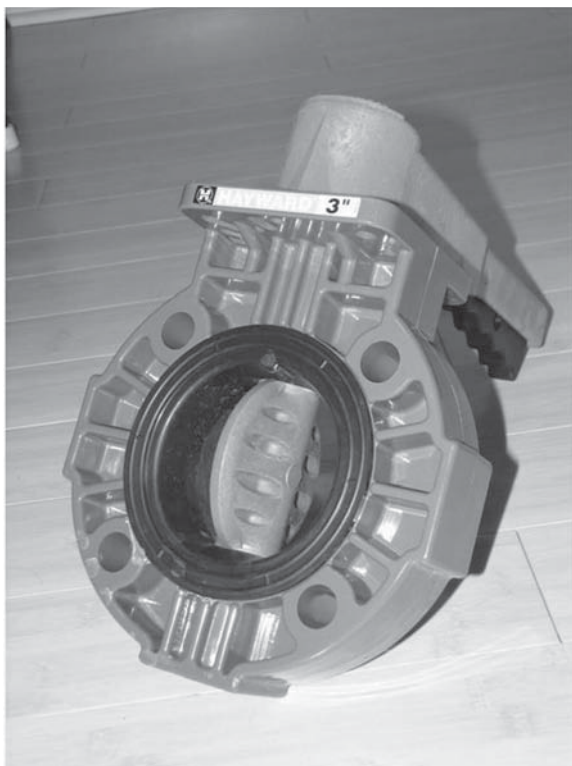


Figure 8.23. Plastic butterfly valve.

Chlorine Scrubbers

For most chlorine systems, fire codes require chlorine scrubbers. When chlorine scrubbers are activated, they generate an air flow that places the chlorine storage room under a negative pressure, ensuring that no leaking chlorine escapes the building. Chlorine scrubbers capture the chlorine by contacting it with some type of media. Two types of media can be used.

Systems that use sodium hydroxide create contact between the sodium hydroxide and the chlorine to generate sodium hypochlorite as a waste product. This is usually done in one of two ways. The more common method is to recirculate the sodium hydroxide through a packed bed. The sodium hydroxide is kept in a reservoir, with a packed bed directly above it. The sodium hydroxide is pumped from the reservoir to the top of the packed bed and distributed over the packed bed. The air from the room is drawn through the packed bed by a fan. The second method involves the use of an eductor to contact the chlorine-laced air with the sodium hydroxide and to create a vacuum in the room. The amount of sodium hydroxide stored in the reservoirs should match the connected load of the chlorine; for example, if there are five ton containers connected to the feed system at one time, there must be sufficient sodium hydroxide stored in the system to neutralize the five ton containers' worth of chlorine (10,000lb). Figure 8.24 shows a schematic of all three systems.

In the second type of system, the chlorine is captured on the surface of engineered media.

All of these systems have advantages and disadvantages. In the sodium hydroxide systems, the level of sodium hydroxide must be monitored, and occasionally, it must be recharged and replaced. The sodium hydroxide reacts with the carbon dioxide in the air to form sodium carbonate. Once the sodium carbonate reaches a certain level, the solution in the reservoir is no longer

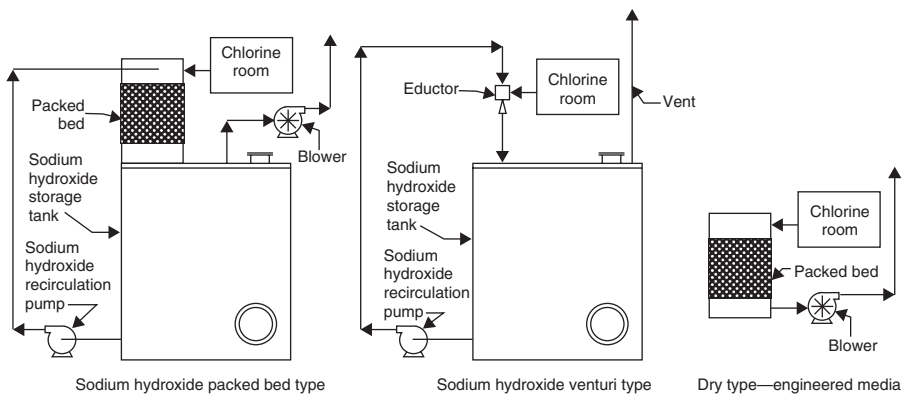


Figure 8.24. Chlorine scrubber types.

effective in neutralizing chlorine leaks. Sodium hydroxide-type systems require a significant amount of attention and maintenance. The systems using engineered media are simpler to operate and require very little maintenance until used. Once used, the spent sodium hydroxide or the engineered media must be replaced. The engineered media must be supplied by specific manufacturers. The sodium hydroxide can be purchased on the general chemical market.

Regardless of the type of system used, the air flow to the units must be carefully monitored to maintain the chlorine storage room at a negative pressure in the event of a chlorine leak.

REFERENCE

1. Chlorine Institute. *Chlorine Institute Pamphlet 1*, 6th ed. Washington, DC: Chlorine Institute, 2000: pp. 5, 8, 10.

9 Hypochlorination—Sodium Hypochlorite

Recently, hypochlorites (sodium hypochlorite and calcium hypochlorite) have become popular alternatives to liquid and gaseous chlorine for disinfection of water and wastewater as well as for other applications. Hypochlorites, which are available in both liquid and dry form, are considered much safer disinfectants than chlorine gas. They are not toxic gases that would pose significant risks to both plant operating staff and the surrounding community. Hypochlorites available commercially include sodium hypochlorite, calcium hypochlorite (liquid and dry), lithium hypochlorite, and chlorinated lime water. This chapter will focus mostly on sodium hypochlorite, which is vastly more common than other forms of hypochlorite.¹

BACKGROUND AND HISTORY OF HYPOCHLORITES

One of the first known uses of chlorine for disinfection was in the form of hypochlorite, known as chloride of lime. Snow used it in 1850 in an attempt to disinfect the Broad Street Pump water supply in London after an outbreak of cholera caused by sewage contamination. Sims Woodhead used “bleach solution” as a temporary measure to sterilize potable water distribution mains at Maidstone, Kent (England) following a typhoid outbreak in 1897.

Subsequent to Scheele’s discovery of the element chlorine in 1774, the compounds made from it were used expressly for bleaching (particularly textiles) for sanitation. Prior to the discovery of chlorine as a bleaching agent, textiles were bleached by the cumbersome method of using the sun’s rays, known as crofting. The textiles to be bleached were spread on large grass fields.

In 1785, Berthollet prepared a bleaching agent by dissolving “Scheele’s gas” in water. In 1789, he improved this bleaching liquid by mixing it with a solution of caustic potash (KOH). This work was carried out at a French chemical plant in Javel, a former town in France, now a part of Paris. This solution was called Javelle water and it is known still by that name.

White’s Handbook of Chlorination and Alternative Disinfectants, 5th edition,
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A short while later, Labarraque replaced the expensive potassium hydroxide with caustic soda obtained from soda ash. This development resulted in what was probably the first use of sodium hypochlorite as bleach. Because of common usage, it too became known as Javelle water. It completely replaced Berthollet's expensive potassium hypochlorite, and soon crofting went out of existence as well. About 1810, the introduction of the Leblanc process for the manufacture of soda ash made the sodium hypochlorite process even more secure by making available more soda ash at a greatly reduced price. Other methods for producing sodium hypochlorite have been developed, but chlorination of caustic soda remains the most popular.

In 1798, Tennant patented a liquid bleach for the Union Alkali Company by passing chlorine through a milk of lime solution, which became known as "bleach liquor." Tennant continued his experimentation and developed a bleaching powder by passing chlorine gas over slaked lime. This product was patented in 1799 as Tennant's bleach, and had a tremendous impact. Here was a solid form of chlorine bleach that could be easily transported and needed only to be dissolved in water to be available for use. It was a boon to the textile industry, and became a cornerstone of the early chemical industry. Much of today's chemical engineering heritage dates to early efforts to make soda ash, caustic soda, and chlorine into a bleaching powder for bleaching cloth.

Freshly prepared bleaching powder contains about 36% available chlorine. Its storage life is short, especially in warm climates. Adding quicklime to bleaching powder resulted in a product known as "tropical bleach," which is fairly stable at tropical temperatures and contains 25%–30% available chlorine. Developed in about 1920, it is still used in significant amounts in underdeveloped parts of the world.¹

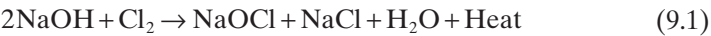
Liquid bleach (sodium hypochlorite) came into widespread use in about 1930s. Today it is the most widely used of all the chlorinated bleaches. Sodium hypochlorite is commonly available in various concentrations. Sodium hypochlorite is an excellent disinfecting agent that is used in home and commercial cleaning and laundry operations, in the health service industry in clinics and hospitals, and at home for disinfecting various kitchen and bathroom surfaces. Sodium hypochlorite (5–5.25 "trade percent" concentration) is commonly available in retail sale and commonly referred to as liquid bleach, household bleach, or soda bleach liquor. Commercial sodium hypochlorite is typically marketed available as 12.5 trade percent, but is known to be available as high as 15 trade percent. Of all the hypochlorite forms, it is clearly the most frequently used for domestic, commercial, industrial, and municipal water and wastewater applications.¹

Dry calcium hypochlorite appeared on the U.S. market in 1928.¹ This bleaching compound, which contains up to 70% available chlorine and is sold under the trade names of HTH, Induchlor, and others, has largely replaced Tennant's bleaching powder in the United States.¹

SODIUM HYPOCHLORITE

Sodium hypochlorite, often referred to as liquid bleach, is the most widely used of the hypochlorites in both potable water and wastewater treatment. Although it requires much more storage space than does dry chlorine or the solid calcium hypochlorite and is more costly to transport over long distances, but it is more easily and safely handled. However, sodium hypochlorite does require special understanding of its properties and characteristics such as degradation and piping and valve selections for optimum use and safety considerations.

Today, sodium hypochlorite is manufactured using a modification of Labarraque’s method by mixing one part of elemental chlorine (Cl₂) with two parts sodium hydroxide to form sodium hypochlorite (NaOCl), as well as sodium chloride (NaCl) and water (H₂O).¹



On the basis of molecular weight, 1 lb of chlorine reacts with 1.128 lb caustic soda to produce 1.05 lb of sodium hypochlorite and 0.83 lb of sodium chloride. The generation of sodium hypochlorite from this reaction is highly exothermic (meaning heat is released during production). The quantities of chlorine and caustic soda required to make 1000 gal of sodium hypochlorite of various strengths are listed in Table 9.1.¹

Sodium hypochlorite (NaOCl) cannot exist without water. Attempts to evaporate the water from sodium hypochlorite solutions will result in its destruction to sodium chlorate, sodium chloride, and evaporated water. Sodium hypochlorite must be produced in an aqueous solution of water where it is chemically stable. Sodium hypochlorite is then kept in aqueous solution

TABLE 9.1. Quantities of Chlorine and Caustic Required to Manufacture 1000 gal of Sodium Hypochlorite of Various Strengths¹

Available Chlorine			As NaOCl		Specific Gravity	Excess NaOH	Cl ₂ Required	Caustic Soda Required		Water Required for Diluting (gal)	
g/l	Trade %	Wt %	g/l	Wt %	At 70°F	g/l	lb	lb	gal	Solid	50% Liquid
								Solid	50% Liquid		
10	1.0	0.98	10.5	1.0	1.014	1.0	83	104	16	991	979
25	2.5	2.4	26.2	2.5	1.035	2.5	209	261	40	979	949
50	5.0	4.7	52.5	4.9	1.070	5.0	417	523	80	958	897
100	10.0	8.8	105.0	9.2	1.140	10.0	834	1045	160	915	794
120	12.0	10.3	126.0	10.8	1.168	12.0	1001	1254	192	898	753
150	15.0	12.4	157.5	13.0	1.210	15.0	1251	1568	240	873	691

for storage, delivery, and use to maintain this stability. Sodium hydroxide is added in slight excess during the chemical reaction as a pH stabilizer. This excess serves to keep the pH high, which enhances the chemical stability of the sodium hypochlorite solution. Sodium hypochlorite solution is most stable at pH between 11 and 13. At pH values higher than 13, sodium hypochlorite degradation is accelerated because of the increased ionic strength of the solution with excess sodium hydroxide.

Further explanation of sodium hypochlorite's stability at various pH values will be discussed later in this chapter.

Sodium hypochlorite is often manufactured in batch or continuous processes. Early processes used the batch method in which chlorine and caustic are mixed in a batch reactor. The excess caustic was calculated rather than determined by continuous monitoring. Additionally, heat exchangers were not used to quickly remove the generated heat. As a result, hypochlorite was manufactured with a high chlorate ion (ClO_3^-) content under improper pH conditions and hot spots in the reactor. Chlorate is undesirable in drinking water so it becomes necessary to find methods to reduce introduced chlorate to the water.

In the 1970s, many manufacturers switched to a continuous process in which chlorine and caustic are continuously fed to a reactor. Platinum electrodes are used for continuous pH monitoring, and in-line heat exchangers are used to quickly remove generated heat. As a result of these better controls, chlorate generation in hypochlorite production was greatly reduced. However, it should still be noted that there are various chemical processing methods within the continuous processes that can still produce the undesired chlorate ion.

Concentration Properties, Feed Calculations, Codes, and Hazards

Commercial sodium hypochlorite is typically delivered to water and wastewater treatment facilities at concentrations between 10 and 15 trade percent with 12.5 trade percent being the most typical. Trade percent is commonly used to express the concentration of sodium hypochlorite solutions, but it does not accurately reflect the concentration of sodium hypochlorite or chlorine in solution.

Concentration. The actual concentration of hypochlorite and chlorine in sodium hypochlorite solution is expressed in many ways; not all of which are useful to a sodium hypochlorite system designer or user. The concentration can be expressed in the following terms:

- sodium hypochlorite trade percent (most common),
- weight percent available chlorine,
- pounds of available chlorine per gallon of sodium hypochlorite per gallon of solution,
- trade percent available chlorine,

- weight percent sodium hypochlorite, and
- weight of available chlorine, grams per liter (g/l) of chlorine in sodium hypochlorite solution.

Most reports consider the measurement of grams per liter of chlorine to be the purest method of expressing chlorine content because this method is independent of specific gravity.² While this is true, it is not commonly expressed by suppliers and manufacturers on their delivered product.

The most straightforward method for the sodium hypochlorite feed system designer is determining the pounds of “available chlorine” per gallon of a given trade percent sodium hypochlorite solution simply because sodium hypochlorite flow rates are usually derived from dosages expressed as milligrams per liter of chlorine. Available chlorine is simply a measurement of the oxidizing power expressed in terms of an equivalent quantity of chlorine. Water and wastewater plants have traditionally used chlorine dosages for disinfection. In addition, most state and federal regulatory agencies using milligrams per liter or parts per million of chlorine in determining the contact time values required for bacterial and virus inactivation. Accordingly, the industry has standardized the dosage of chlorine as the basis, even as use of sodium hypochlorite (and other hypochlorites) became increasingly popular.

To determine the pounds of available chlorine in a gallon of sodium hypochlorite, the weight percent of chlorine must be derived from the trade percent of sodium hypochlorite. This is accomplished by dividing the trade percent concentration by the specific gravity of the solution, as shown below for a given 12.5 trade percent sodium hypochlorite solution with a specific gravity of 1.175.

- Weight percent available chlorine = $12.5 \text{ trade percent} / 1.175 = 10.64$

or

- Weight percent available chlorine = $\text{g/l available chlorine} / \{10 \times \text{specific gravity}\}$.

Second, the weight percent of available chlorine is multiplied by the density of the 12.5 trade percent sodium hypochlorite solution, which is 9.8lb/gal as shown below:

$$\begin{aligned} &\text{Pounds of chlorine per gallon of solution} \\ &= 10.64 \times \text{weight percent available chlorine} \times 9.8 = 1.04 \text{ lb/gal of chlorine.} \end{aligned}$$

Although not as useful to a sodium hypochlorite system designer or user, some other concentration forms can be derived.

Because sodium hypochlorite is a pesticide listed by the Federal Insecticide, Fungicide, Rodenticide Act (FIFRA), by means of its inherent ability to inactivate biological organisms, the weight percent of actual sodium hypochlorite is listed on shipping containers.³ To obtain the actual percent concentration of sodium hypochlorite (which is not synonymous with the trade percent concentration), the weight percent of available chlorine result must be multiplied by the ratio of the molecular weights (MWs) of sodium hypochlorite (74.44 lb/mol) and chlorine (70.91 lb/mol). The ratio of these is 1.05.

$$\begin{aligned} &\text{Actual weight percent sodium hypochlorite} \\ &= 10.64 \times \text{weight percent available chlorine} \times 1.05 = 11.17. \end{aligned}$$

Occasionally used to express the strength of sodium hypochlorite is the trade percent available chlorine. This is similar to the weight of available chlorine (g/l), only the volume is 100 ml instead of 1 liter. To obtain the trade percent available chlorine, the weight of available chlorine (g/l) must be divided by 10 as follows:

$$\text{Trade percent available chlorine} = \text{g/l} / 10.$$

These equations and conversions can be combined in many different ways to derive the preferred concentration expression.

The trade percent, specific gravity, weight percent of available chlorine, density, and weight of chlorine per gallon of solution for various concentrations of sodium hypochlorite solutions are listed in Table 9.2. The exact specific gravity and density of sodium hypochlorite solutions depends on temperature as well as on the content of sodium chloride and on the quantity of excess caustic. While specific gravity of different solutions may vary slightly, the overall product quality is not affected.

TABLE 9.2. Relationship of Various Strengths of Sodium Hypochlorite Solutions

Trade %	Specific Gravity	Available Cl ₂ (g/l)	Density (lb/gal)	Available Cl ₂ (wt %)	NaOCl (wt %)	Available Cl ₂ (lb/gal solution)
0.8	1.01	8	8.44	0.80	0.84	0.067
2	1.034	20	8.62	1.93	2.03	0.17
4	1.062	40	8.86	3.77	3.95	0.33
6	1.089	60	9.08	5.51	5.78	0.50
8	1.116	80	9.31	7.17	7.53	0.67
10	1.142	100	9.53	8.76	9.20	0.83
12	1.168	120	9.74	10.27	10.79	1.00
12.5	1.175	125	9.80	10.64	11.17	1.04
15	1.206	150	10.06	12.44	13.06	1.25

Example System Design Calculation. When calculating the amount of sodium hypochlorite to deliver to the application point of traditional water and wastewater treatment plants, the following example calculation is the simplest method.

- plant flow rate = 30 mgd,
- chlorine dosage = 5 mg/l as chlorine,
- $30 \text{ mgd} \times 5 \text{ mg/l chlorine} \times 8.341 = 1251 \text{ ppd chlorine}$, and
- $1251 \text{ ppd chlorine} / 1.04 \text{ lb Cl}_2 \text{ per gallon} = 1203 \text{ gpd}$

Using the information provided and this example calculation, it is possible to calculate the storage and feed requirements for a sodium hypochlorite system from plant flow rates and chlorine dosages.

Freezing Point. The freezing point temperature of sodium hypochlorite solutions is dependent upon on the concentration. In general, up to 18 trade percent, the freezing point decreases with increasing concentration. Table 9.3 provides freezing points for sodium hypochlorite solutions by weight percent sodium hypochlorite. Figure 9.1 provides a freezing point graph of sodium hypochlorite by trade percent.¹

Freezing of the solution generally does not affect its quality after it is thawed; however, freezing of sodium hypochlorite expands its volume (similar to water), so freezing inside piping, valves, pumps, or tanks can cause significant damage to equipment. In some cases, it may result in precipitation of sodium chloride and/or sodium hypochlorite from the solution and fouling or clogging of pumps, piping, and valves. Care should be taken with thawed hypochlorite solutions to ensure that precipitates are not present.³

Vapor Pressure of Sodium Hypochlorite. The vapor pressure of sodium hypochlorite solution is often confused with the evolution of oxygen gas from decomposition. The decomposition of sodium hypochlorite is discussed later in this chapter in which one of the decomposition by-products is oxygen gas.

TABLE 9.3. Sodium Hypochlorite Freezing Points

NaOCl (wt %)	Freezing Point (°F)	Freezing Point (°C)
0.8	30	-1.0
2	28	-2.2
4	24	-4.4
6	18.5	-7.5
8	14	-10
10	7	-13.9
12	-3	-19.4
15.6	-21.5	-29.7

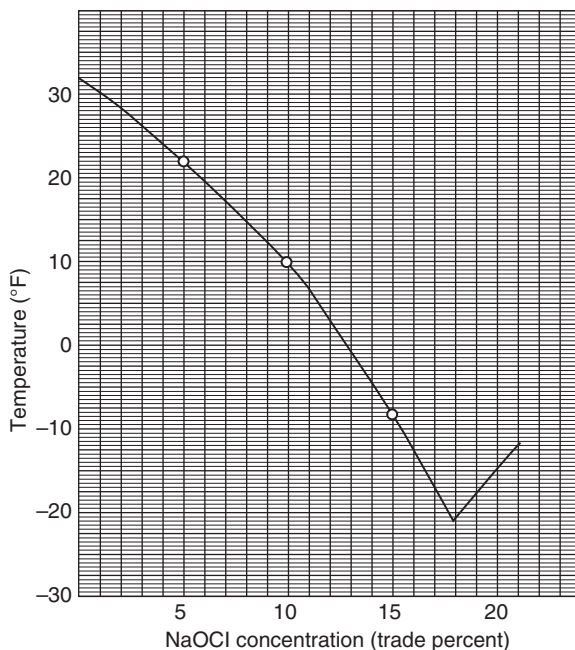


Figure 9.1. Freezing-point temperatures of sodium hypochlorite by trade percent.

Sodium hypochlorite solution, like water and other solutions of inorganic salts, when enclosed with a headspace above the liquid, will exert a vapor pressure on the closed container. The vapor pressure is mostly a function of the solution temperature. As the temperature of the solution rises, the vapor pressure increases. A solution in an enclosed environment at constant temperature will soon develop an equilibrium where water (and other constituents) will continuously move in and out of the vapor and liquid phases by evaporation and precipitation to maintain a constant vapor pressure. Evaporation and precipitation are physical processes rather than chemical reactions. The pressure exerted by the vaporized molecules is considered vapor pressure, which in the case of most inorganic aqueous solutions (and sodium hypochlorite) at ambient temperatures is generally low, less than 2 psi. Because the vapor pressure exerted by sodium hypochlorite is low, independent of oxygen gas generated by decomposition, it is of little consequence. The typical vapor pressure values of 12.5% sodium hypochlorite solution at various ambient temperatures are listed in Table 9.4.

The exact composition of the chemicals in the headspace above sodium hypochlorite solutions is not known. It is believed that oxygen makes up some of the vapor from decomposition; however, it is generally believed to be a very small fraction of the total because decomposition to form oxygen gas proceeds very slowly. The majority of the vapor pressure imparted by sodium hypochlorite solution is water, which is the predominant constituent in the solution,

TABLE 9.4. Vapor Pressure of 12.5% Sodium Hypochlorite Solution³

Temperature (°F)	Temperature (°C)	Vapor Pressure (mmHg)	Vapor Pressure (psia)
48.2	9	3.7	0.071
60.8	16	8.0	0.15
68	20	12.1	0.23
89.6	32	31.1	0.60
118.4	48	100	1.93

and it is believed that hypochlorous acid and chlorine monoxide are also present in the vapor headspace.²

The release of oxygen gas through decomposition follows a chemical reaction that does not follow the physical laws of evaporation, precipitation, and vapor pressure. The decomposition of sodium hypochlorite is a slow but continuous process that does not slow or stop to develop equilibrium in an enclosed environment. A portion of the oxygen gas formed is absorbed by the solution as a dissolved gas, similar to how CO₂ is dissolved in soft drinks. The solubility of gases in liquid is mostly temperature dependent (among other dependent factors such as ionic strength and the solubility of other gases). Eventually, the solution will become saturated with oxygen until it can no longer absorb the oxygen generated. If sodium hypochlorite solutions are confined without means of expansion, the decomposition reaction will slowly generate oxygen gas than cannot absorb or escape. As a result, tremendous pressure can accumulate over long periods of time, whereby the pressure may result in a catastrophic failure of whatever physical means is containing it. There have been piping and valve failures at facilities using sodium hypochlorite where a Schedule 80 chlorinate polyvinyl chloride (CPVC) pipe has exploded from the tremendous buildup of pressure. Figure 9.2 shows a photograph of a 3-in. Schedule 80 CPVC piping that burst as a result of pressure buildup inside the piping for approximately 75 days at 72 to 78 °F. According to pipe manufacturers, the pressure rating of 3-in. Schedule 80 CPVC piping at 73 °F is 370 psi; however, the pressure rating of fittings and valves is limited to 150 psi so the overall rating of a CPVC piping system is limited to 150 psi at 73 °F.

Additional Chemical Properties. Some other noteworthy properties of sodium hypochlorite solutions are as follows:³

• Boiling point	Decomposes
• Appearance	Clear, pale yellow, or greenish liquid
• Odor	Chlorine odor (swimming pool smell)
• Feel	Sodium hypochlorite and diluted solutions of it often feel slick or slippery to the touch because of the high concentration of sodium content



Figure 9.2. Pipe fragments from sodium hypochlorite decomposition without pressure relief.

Fire Codes Requirements. Most water and wastewater treatment plant designs in the U.S. follow the International Building Code (IBC) and the International Fire Code (IFC), which classify commercial sodium hypochlorite as a corrosive chemical. Accordingly, sodium hypochlorite storage systems that exceed the threshold quantity listed in the IFC must include protective measures, which include segregated secondary spill containment structures, continuous ventilation, and fire sprinklers. The threshold quantity for sodium hypochlorite solution at concentrations of 1% or higher is 500 gal.

IFC requires secondary containment of tanks to be sized for the content of the single largest tank plus either a 25-year, 24-hour rain event for outdoor facilities or 20 min of fire sprinkler water for indoor facilities (0.25 gpm/ft² is typically used for sizing). It is recommended that containment be designed to encompass the storage tanks, any transfer or metering equipment, and as much piping as possible. Leaks or ruptures in the storage tank have the potential to release the entire tank contents. However, ruptures or failures in piping (especially on the pump suction side) also have the potential to release the tank contents if left unattended long enough. A properly sized and designed chemical containment structure will capture the spilled chemicals before release to the environment.

Safety shower/eyewash units should be installed as specified in plumbing codes. Plumbing code should be consulted to determine the number of safety shower/eyewash units required and their relative location based on the installation. Plumbing codes required safety shower/eyewashes to be in close proximity to the hazard and accessible without restrictions. For example, the

unit must be in the same room as the hazard. It is not allowable for a potentially exposed person to go through doors or stairways to access the shower from the location of the hazard. Accordingly, multiple safety shower/eye-washes are often required because exposure areas may exist indoors and outdoors and in multiple locations.

IFC. Code also requires that incompatible chemicals be separated to prevent spilled chemicals from mixing. Some notable incompatibilities are discussed in the “Special Hazards” section below. The most notable incompatibilities are with acids, organics, and ammonia.

In water treatment plants, acid chemicals such as hydrochloric acid are used for cleaning membranes. Additionally, hydrofluosilicic acid and sulfuric acid are often used as process chemicals. Sodium hypochlorite tanks, pumps, and piping should be separated in containment areas from these chemicals, which are capable of disrupting the pH balance of sodium hypochlorite solutions in a manner that can evolve dangerous chlorine gas.

Special Hazards. Sodium hypochlorite adds alkalinity to the water or wastewater being treated, unlike elemental chlorine, which will remove alkalinity. It is important to understand this when using sodium hypochlorite or elemental chlorine in the destruction of cyanides or sulfides. If the destruction is carried out at low pH (acidic conditions), toxic hydrogen cyanide or hydrogen sulfide can be released.² Hydrogen sulfide is not only toxic but also flammable and corrosive, which can present additional hazards.

Sodium hypochlorite solutions will react vigorously when mixed with acidic solutions. Acids will cause the hypochlorite ion to convert to elemental chlorine in the following reaction:



If the concentration of elemental chlorine exceeds the solubility of chlorine in the solution at a particular temperature, chlorine gas will be liberated as well as large amounts of heat. In general, sodium hypochlorite should not be mixed with other chemicals, especially acids. Mixing sodium hypochlorite with ammonia or ammonia salts can also result in the generation of hazardous or toxic gases.

Sodium hypochlorite may also react violently with many organic compounds, including oils, fuels, and grease. It must not be mixed with organic substances unless it is known that they are compatible.

Because sodium hypochlorite is a corrosive solution that can moderately burn the eyes and skin, irritate the respiratory system, and burn the nose and throat, it should only be handled while wearing personal protective equipment (PPE), including goggles, face shield, impervious gloves, and a chemically resistant apron or suit. If exposed to sodium hypochlorite, the exposed areas should be flushed thoroughly with clean water.

Dry hypochlorites such as calcium hypochlorite will react in much the same manner as sodium hypochlorite, and should be stored in a cool, dry location, preferably in the dark. As discussed later, all hypochlorites are sensitive to light and will decompose when exposed to ultraviolet (UV) light.⁴

Higher concentrations of sodium hypochlorite solution that are allowed to dry completely under heated conditions, such as around pump seals, can contain crystals of sodium chlorate, a chemically unstable substance which can explode or ignite on impact, causing serious injury or property damage. While such incidents are rare, care should be taken to wash down equipment contaminated with dried sodium hypochlorite and to remove all residues from PPE, clothing, and shoes as any subsequent sodium chlorate residue can be ignited even after it has redried.³

DEGRADATION

Sodium hypochlorite degrades slowly over time to form sodium chloride, sodium chlorate, and oxygen. The degradation process reduces the available chlorine content and produces undesirable byproducts.

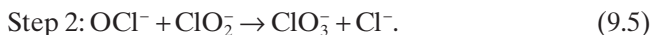
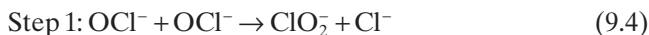
In general, the reaction is slow and occurs over days and weeks at ambient conditions. This is a major problem with this type of chlorination system. It is also important for the end user to understand the degradation process, mechanisms, and rate because the major decomposition pathway produces the undesired chlorate ion. The end user should dedicate laboratory time to monitoring the degradation rate in available chlorine in order to monitor deliveries and understand how degradation is impacted by storage conditions.

The degradation will continue until the bleach is completely degraded to chlorides, chlorates, and oxygen; however, the rate of degradation is greatly influenced by physical and chemical conditions such as initial concentration, temperature, and exposure to UV light, pH, and the presence of heavy metal ions.¹ Proper purchasing specifications for sodium hypochlorite as well as proper storage and handling of sodium hypochlorite will maintain its stability for several months.

The degradation of sodium hypochlorite follows several reaction mechanisms. The first of these, which is the predominant reaction, is the chlorate ion (ClO_3^-) formation reaction in which three molecules of OCl^- degrade to form one molecule of ClO_3^- .



The quantity of chlorate ion present in a given sodium hypochlorite solution can be evidence of decomposition. The chlorate ion formation reaction is most strongly influenced by the initial hypochlorite concentration, temperature, and pH of the solution. The decomposition of sodium hypochlorite to chlorate ion is actually a two-step reaction involving chlorite ion as an intermediate by the following reactions:



The second reaction is the oxygen production reaction. It is very slow and has little influence on the overall decomposition. However, metal ions and/or UV light can catalyze this reaction to degrade more hypochlorite to form oxygen gas by increasing its rate.



Studies have been done on the relative rates of decomposition by the two reaction mechanisms. In the absence of catalysts or UV light, the rate of decomposition to chlorate ion was 8.3 times faster than the rate of decomposition to oxygen.⁵

Despite being a minor byproduct of degradation, the oxygen formation reaction poses a major problem for the sodium hypochlorite user: The formation of oxygen gas can result in a tremendous pressure buildup in a piping system, and hypochlorite solutions saturated with oxygen (from degradation) can change temperatures and release oxygen gas as bubbles in the solution, which can create major problems with pumping.

Users of sodium hypochlorite (especially water treatment plants) must understand the degradation process and its impacts on the formation of chlorate and oxygen gas to understand how it impacts their operation. An extensive study was undertaken by the American Water Works Association (AWWA) in 1995, *Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite Ion is the Chlorinating Agent*.⁵ This study should be consulted for methods and detailed discussions on how to reduce chlorate ion formation. It is generally considered that there are two ways chlorate can become introduced into drinking water through sodium hypochlorite disinfection: (a) through improper manufacturing methods or monitoring of key parameters (pH and heat), which can be managed by limiting the chlorate ion content as well as excess sodium hydroxide content, and (b) through degradation of sodium hypochlorite solutions in storage.

In July 2009, AWWA commissioned a study titled “Hypochlorite—An Assessment of the Factors That Influence the Formation of Perchlorates and Other Contaminants” to examine the factors that influence the formation of perchlorates, bromate, and other contaminants from sodium hypochlorite degradation.¹³ This study should be consulted for a better understanding of chlorate and perchlorate formation from degradation and for guidelines for municipal users to implement to minimize the formation of these contaminants. The details of the report could not be incorporated into this chapter; however, its recommendations are discussed later.

Estimating the Degradation Rate

Under typical storage conditions at pH 11–13, the degradation is considered to be a second-order reaction with respect to the concentration of OCl^- . The rate coefficient (k) is exponentially dependent upon temperature and must be recalculated if the temperature changes.

$$\text{Rate} = k(C)^2. \quad (9.7)$$

At constant temperature, the rate of sodium hypochlorite degradation is not constant with time but depends on the actual remaining concentration as time passes. Therefore, the degradation curve is not linear. The rate declines with time. In order to accurately estimate the degraded concentration after a given time, a mathematical technique known as integration is necessary. Integration reduces the time increments to infinitesimal increments to recalculate the rate at infinitesimal time increments and then totalizes the degradation to derive the remaining concentration.

The same degradation mechanism is observed in the radioactive decay of radioactive substances. Radioactive decay is often conceptualized in terms of half-lives, which is the amount of time necessary for half of the active ingredient to decay. The half-life is much easily understood by those not familiar with integral calculus. Some references express sodium hypochlorite degradation in terms of half-life.

Fortunately, the complex mathematics have been reduced to an equation known as the Arrhenius equation, where natural logarithms (a function found on most scientific and financial calculators) capture the rigors of integration to model the degradation progress as a function of initial concentration and temperature.

The rate of degradation of sodium hypochlorite with respect to the major influences of initial concentration and temperature can be *estimated* from the following equations. It should be noted that the decomposition of sodium hypochlorite is a complex mechanism dependent on many factors. The equations are useful and are limited to initial concentrations of 10–15 weight percent available chlorine; temperatures between 55 and 85 °F; and 28–140 days. For additional information or computer models on sodium hypochlorite degradation for parameters outside these stated or in various combinations of degradation parameters, consult the methods used in Reference 5.

Equation (9.8) can be used to estimate the rate of decomposition of the temperature-dependent rate constant (K), which is determined using Equation (9.9).

$$\text{Ln}(C) = \text{Ln } C_0 - KC_0^3t \quad (9.8)$$

$$\text{Ln}(K) = 18.56 \text{Ln}(T) - 129.65 \quad (9.9)$$

where:

K = rate constant,

T = temperature ($^{\circ}\text{R}$),

C = concentration,

C_0 = initial concentration (percent available chlorine),

C = final concentration (percent available chlorine), and

T = elapsed time (days).

The following are graphical depictions of the degradation curve of various initial concentrations of sodium hypochlorite (12.5% and 15%) for various temperatures for a period of 0–120 days using the equation above. Although the exact degradation rate is influenced by many factors, these curves provide a reasonable depiction of sodium hypochlorite's degradation with respect to initial concentration and temperature (Figs. 9.3 and 9.4).

Concentration Effects

The rate of decomposition is dependent on the initial concentration of the sodium hypochlorite solution. The rate of degradation slows with time as the solution degrades such that the quickest decomposition occurs just after the solution is manufactured. An increase in the decomposition rate is an increase in the chlorate ion production.

Under the same circumstances, higher initial concentrations of sodium hypochlorite will degrade at a more rapid rate to produce a lower concentration of hypochlorite over time than what would be observed by starting with a lower initial concentration. For example, for a given temperature of 100°F and elapsed time of 60 days, 15% sodium hypochlorite will degrade to approximately 8.4%, whereas, 12.5% sodium hypochlorite, under the same condi-

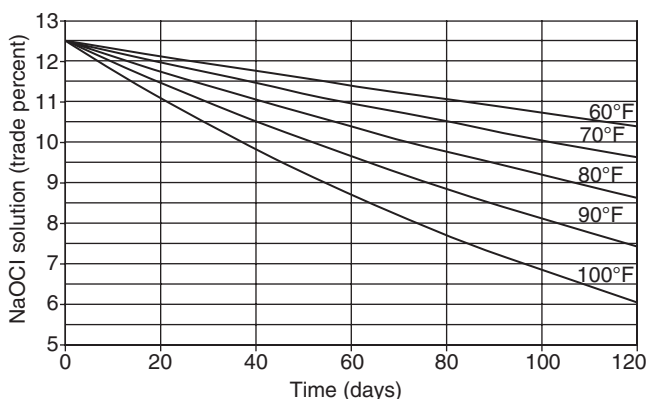


Figure 9.3. 12.5% sodium hypochlorite solution degradation over time (days) at various temperatures.

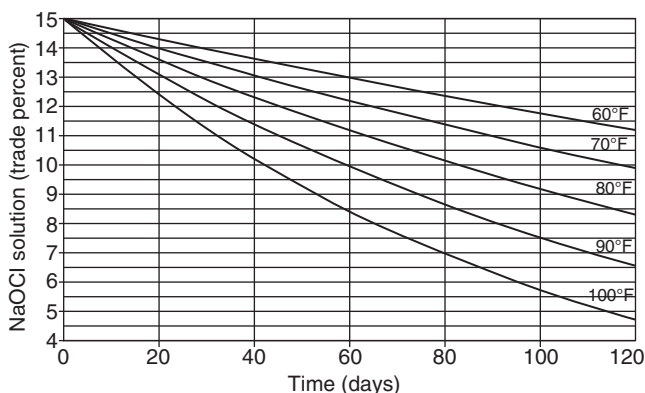


Figure 9.4. 15% sodium hypochlorite solution degradation over time (days) at various temperatures.

tions, will degrade to 8.75%. The higher initial concentration of hypochlorite degraded to a lower concentration over the same time period. Beginning with a higher concentration does not gain the end user any storage time, and in fact, aggravates the degradation problem.

The second-order reaction law predicts that a solution of 120 g/l (12 trade percent) available chlorine will degrade four times as fast as a solution of 60 g/l (6 trade percent) available chlorine under the same conditions of temperature and pH. This is further complicated by a phenomenon called ionic concentration (or ionic strength) of the solution. The ionic strength is the total concentration of all inorganic constituents dissolved in the solution, which include chloride, chlorate, and hydroxide ions. The additional ionic strength of these solutions results in laboratory data that indicates that the predicted decomposition rate of four times as fast will actually be nearly five times as fast.^{2,3,5,6}

The ionic strength of a solution is a function of the initial concentration. When a 120 g/l solution degrades to a 60 g/l solution, the total ionic strength remains constant. Accordingly, when the 120 g/l solution degrades over time to a 60 g/l solution, its degradation rate will exceed the degradation rate of a solution diluted to 60 g/l because the dilution reduces the overall ion strength of the solution.²

Some users purchase sodium hypochlorite solution at high concentrations to reduce the transportation costs and dilute it on-site (thereby lowering the ionic strength) to slow the degradation rate. This is also recommended in Reference 13. In theory, this appears reasonable; however, it requires a detailed understanding of the factors that influence the degradation rate. For example, the dilution water should be demineralized or deionized to eliminate certain metals that may catalyze the degradation reaction at a rate even faster than it would be without dilution.

A catalyst is a substance that lowers the activation energy required to initiate and sustain a chemical reaction so that it can occur under reduced energy

conditions. Various metals, and combinations of metals, are commonly used as catalysts in the chemical industry.

Often, users do not have available adequate demineralizing or deionizing equipment or storage capacity for the additional water and diluted sodium hypochlorite. (The demineralizing or deionizing water systems should be constructed of nonmetallic piping and valves. Piping materials suitable for ultrapure water systems include polyvinylidene fluoride [PVDF] and Teflon.)

Additionally, the diluted sodium hypochlorite should have a pH between 11.86 and 13. A dilution process that disturbs the pH stability of sodium hypochlorite will result in a decomposition rate that is quicker than if the sodium hypochlorite were not diluted at all. The chemical supplier should be consulted for the proper amount of additional caustic required to maintain this pH range. Sodium hydroxide added to diluted solutions should be free of heavy metals or other impurities that will catalyze the decomposition further.

Because of the high pH of sodium hypochlorite, dilution with water containing alkalinity will induce precipitation and scaling of calcium and magnesium carbonate from the mixture. If the point of dilution occurs inside small diameter piping, this piping can often accumulate significant amounts of scale on the interior portions of the pipe.

Temperature Effects

All chemical reactions require energy, commonly called activation energy, to initiate and sustain them. Hypochlorite degradation reactions are no exception. In a sodium hypochlorite solution, sufficient intrinsic energy is available to sustain degradation at a low rate. Additional energy, generally as heat, will increase the rate of reaction, as demonstrated in the equations and the resulting degradation curves. A change in the temperature will change the rate constant. An increase in the rate constant will increase the degradation rate even if all other variables remain constant.

In general, chemists predict that a 10°C (18°F) rise in temperature will double the rate of most chemical reactions. However, studies with sodium hypochlorite have shown that for every 10°C rise in temperature, the decomposition rate increases by a factor of 3–4 in a solution of 5–16 weight percent hypochlorite. Sodium hypochlorite stored at 15°C (59°F) will degrade at a rate 14 times more slowly than at 35°C (95°F). Additionally, at a temperature of 5°C (41°F), in the absence of heavy metal contamination, degradation is almost completely eliminated.⁷ Accordingly, there is tremendous advantage to managing the storage temperature of sodium hypochlorite solutions. The temperature effect and the concentration effect are further illustrated in Table 9.5.

Some sodium hypochlorite manufacturers will rapid-cool their product after manufacture to stabilize the degradation by lowering its temperature. This is accomplished by passing the solution through a plate and frame heat exchanger using chilled water as the cooling medium.² Heat transfer is best accomplished through metal; therefore, heat exchangers are constructed of

TABLE 9.5. Storage Temperature of Sodium Hypochlorite Solutions

Trade %	Half-life (days)	
	25°C	35°C
15	144	39
12	180	48
9	240	65
6	360	97
3	720	194
1	2160	580

exotic metals for chemical resistance; however, exotic metals often contain heavy metals such as nickel, copper, and iron, which can provide a catalyst for degradation.

Sodium hypochlorite tanks, totes, or drums should be stored in air-conditioned or below-grade rooms at maintained lower temperatures. In Nevada, a utility provided a room cooled by water-evaporative coolers to take advantage of the region's low humidity to maintain a lower storage temperature without the energy required for refrigerated air-conditioning. This was especially efficient since building/fire codes required the storage area to have continuous fresh air ventilation.

Uncovered storage outdoors, exposed to direct sunlight, will increase the average temperature of the solution which thereby increases the degradation rate. If indoor storage or sunshades cannot be provided, the containers should be coated or painted in a light color to reduce absorption of heat from sunlight. As a practical guide, the average daily temperature (day and night) of the hypochlorite storage should be used to estimate the degradation rate.

pH Effects

The pH of sodium hypochlorite is a sensitive issue and an important factor in its stability. The subject of excess sodium hydroxide is a source of great discussion regarding the stability of sodium hypochlorite both independently and in conjunction with other parameters that affect its stability. Earlier recommendations state a minimum pH of 11. Later studies recommend a minimum pH of 11.86.

In water, sodium hypochlorite disassociates into ion form by the following equation:



The symbol " $\leftrightarrow$ " indicates that the process is reversible. Dissolved in water, the sodium ion remains elemental and does not undergo further change.

However, the hypochlorite ion establishes another reversible reaction with free hydrogen ions in solution according to the following reaction:



The H^+ ion represents the presence of hydrogen ions, which are associated with acidity. An equilibrium state in this reaction is established and maintained at pH between 11.86 and 13.² At pH 10.5, the ratio of OCl^- to HOCl is approximately 1000:1, which keeps the concentration of HOCl very low. For this reason, sodium hypochlorite is manufactured, shipped, and stored with a slight excess of sodium hydroxide to maintain the pH between 11.86 and 13, which corresponds to an excess of sodium hydroxide of 0.025%–0.35%.^{2,3}

If the pH drops below 11.5, the H^+ ion becomes more abundant and the reaction (Eq. 9.11) is driven to the right to form hypochlorous acid, HOCl . Hypochlorous acid then reacts with hypochlorite (OCl^-) through an acid-catalyzed decomposition reaction as follows:



This reaction is not reversible and is considered to be the dominant acid catalyzed decomposition reaction between pH 5 and 10.8. It should not be confused with the acid destruction reaction in which sodium hypochlorite is mixed with a strong acid at pH below 4 to form elemental chlorine.

Extensive studies on sodium hypochlorite stability indicate that a minimum of 0.025% caustic is necessary to keep sodium hypochlorite stable which corresponds to pH 11.86. Thus, the study recommends pH levels between 11.86 and 13 for the most stable range of storage. At pH higher than 13 (0.4% caustic and higher), sodium hypochlorite degradation is accelerated because of the increased ionic strength of the solution with excess sodium hydroxide, which is also directly proportional to the degradation rate.³

UV Light Effects

Ultraviolet (UV) light is known to increase the degradation rate of sodium hypochlorite by a process called photolysis. The rate of photolysis is proportional to the amount of light absorbed by sodium hypochlorite solution. For sodium hypochlorite, this process is greatly pH dependent. At the maximum sunlight intensity of 330nm, a solution of OCl^- has a molar absorptivity 15 times greater than a HOCl solution of equal strength. Since sodium hypochlorite is stored at high pH where it is mostly OCl^- , it is reasonable to expect that light has an impact on stability.⁵ However, a high pH is necessary to maintain its stability; therefore, lowering the pH of sodium hypochlorite solution is not a reasonable means of reducing the effect of sunlight on it.

The presence of UV light shifts the balance of reaction rates between the two primary decomposition reactions to the oxygen producing reaction. As light intensity increases, the degradation will shift predominantly to the oxygen reaction. However, UV will also catalyze the chlorate formation reaction. The

effect of UV light on sodium hypochlorite solutions will reduce the half-life from a matter of days to a matter of hours. In a study, a solution of 13.5 weight percent NaOCl at pH 12.92 was exposed to UV light at an intensity equivalent to sunlight. In 73 h, 99% of the OCl^- ion had been destroyed to oxygen and chlorate. As evidence of the chlorate catalyzation, chlorate formation in this test was 10 times higher than chlorate formation in the absence of UV light.⁵ The amount of light absorbed is a function of depth and thickness. The majority of the light is absorbed at the liquid surface, which likely was the case in the small laboratory samples used in this study. Large storage volumes with lower surface-to-volume ratios will have an overall reduced effect of UV light because the light cannot penetrate into the solution to degrade. Nevertheless, the effects of UV light are readily notable and storage should be kept shielded from sunlight or other sources of intense UV light.

The influence of light on a solution of sodium hypochlorite is easy to measure by placing one sample of it in a clear container into direct sunlight, and another container in a location shielded from sunlight, but at the same temperature. After an equal amount of time, measure the grams per liter of chlorine in both containers for comparison. In general, bulk solutions of 10%–15% available chlorine solution will undergo a reduction in half-life of about three or four times by the influence of sunlight. For stronger solutions, up to 20%, the result is a reduction of half-life of about six times.¹ While this is not the extreme degradation seen in the laboratory example above, it still denotes that UV light as a significant effect.

Exposure to direct sunlight will have a double effect on sodium hypochlorite stability: (a) the sun's heat will increase the degradation reaction rates as discussed above (it takes only a 10°C rise in temperature to triple or quadruple the reaction rate), and (b) it will provide UV light, which provides the electromagnetic radiation that also increases the degradation rate.

Impurities

Minimizing impurities, both during the manufacture and in storage, is very important to the chemical stability of sodium hypochlorite solutions. Raw materials and source water used in producing hypochlorite must be low in heavy metals, which would catalyze the decomposition of sodium hypochlorite, thereby accelerating the decomposition. Such metals are iron, nickel, copper, cobalt, or manganese.

The predominant reaction by metal catalysts is the oxygen formation reaction, which causes the greatest operational trouble. Higher temperatures, low pH, and higher solution strength will usually follow the chlorate ion formation reaction.^{1,4,8} Poor quality sodium hypochlorite with high metal content should be avoided.

The AWWA has a detailed standard for hypochlorite used in water treatment, which includes physical characteristics such as particle size and density, and chemical criteria such as concentration limits, chlorine content, and allowable impurities. It also specifies that hypochlorites must contain no soluble or

organic substances that would have deleterious or injurious effects on the health of those consuming the water.⁴ Water treatment plants should, at a minimum, require their hypochlorite to meet AWWA standards.

Many of the metals mentioned can be inadvertently introduced into hypochlorite from sodium hydroxide and/or the dilution water during the manufacturing. The quality of the sodium hydroxide used to manufacture sodium hypochlorite is especially important. The principal contaminant that may be contributed is nickel, which can be released from the diaphragm and membrane cells used to make sodium hydroxide. It is also present in the stainless steel piping and valves in the processing facilities. If not removed from the sodium hydroxide feedstock, nickel can be carried into sodium hypochlorite solutions. Soft water, which can remove most metals, is generally used in the production of sodium hypochlorite to enhance its stability.

Iron has been viewed as a bad offender for catalyzing the degradation of sodium hypochlorite. Sodium hypochlorite solutions typically contain 0.5–2.0 mg/l of iron in solution. The source of iron is usually in the caustic used in preparing sodium hypochlorite solutions. Early reports indicate that even minute quantities of iron (as low as 0.5 mg/l) will cause rapid deterioration of sodium hypochlorite solutions. Iron was mostly present in the sodium hydroxide solutions used as a manufacturing feedstock.

The AWWA funded a study to research the effects of iron on hypochlorite stability. The AWWA studied samples of sodium hypochlorite containing 41 mg/l of iron over 60 days. The results indicated that this solution did not degrade at a much higher rate than solutions containing lower concentrations of low iron. Because iron has very limited solubility in water, it was concluded that even a solution saturated with iron probably would not likely contain enough iron to enhance decomposition.³

Flexible connections and the brass-bodied chlorine line valves often contain copper, which must be protected against corrosion to the greatest extent possible. This can be done by keeping copper parts internally free of moisture. Moisture in the presence of chlorine gas will result in an extremely corrosive mixture that will corrode copper, causing it to be introduced into the chlorine feedstock used to manufacture hypochlorite. Keeping copper out of the chlorine feedstock can be a difficult task and, because it is a manufacturing issue, it is out of the control of the end user. Historical references indicate that the content of copper in sodium hypochlorite solutions should be below 1 mg/l.⁷ However, Powell Fabrication and Manufacturing recommends that copper and nickel be kept below 50 µg/l.

Some large municipalities have gone beyond the AWWA standard to mandate specific requirements for sodium hypochlorite deliveries to their plants. For example, some require the excess caustic to be within a range of 0.1%–0.4% by weight. Additionally, they require chlorate ion (ClO_3^-) to be less than 1500 mg/l; iron less than 0.5 mg/l; and nickel and copper less than 0.05 mg/l.⁶

Suspended Solids

Recently, suspended solids content has been identified as a source of impurities that degrade sodium hypochlorite. Although typically not visible in the product and often do not impact its color, suspended solids can contain heavy metals that contribute to degradation. Suspended solids can also accumulate in the system over time, as particles grow and settle out in tanks and piping, causing plugging and serving to host metal catalysts that degrade the solution. The suspended solids concentration can be tested by filtering 1 liter of the sodium hypochlorite through a $0.8\mu\text{m}$ filter at 20 inches of mercury vacuum and recording the time to filter the entire 1 liter volume, which should be less than 3 min.²

As traditional manufacturing methods allow little flexibility in controlling the level of suspended solids in the product, the manufacturer can filter it immediately upon generation using high-efficiency filtration systems where the solution is passed through a media bed of perlite or diatomaceous earth. A more recent method involves producing ultrapure chlorine using a membrane cell process. Gaseous chlorine from this process is reacted with sodium hydroxide generated from another set of cells using softened or demineralized water. This process can produce a very clean sodium hypochlorite solution.

Some users require their sodium hypochlorite manufacturers to filter the product before delivery to remove metals, suspended solids, and other particulate material. The practice not only enhances the stability of the sodium hypochlorite but also minimizes cleaning and flushing of storage tanks. It is recommended that suppliers use 0.2- to $0.5\text{-}\mu\text{m}$ filters to remove suspended solids.⁶ Studies have shown that there is a direct correlation between removing suspended solids and remaining nickel and copper, which are the principal decomposition catalysts. Users can verify the filtration of their delivered solutions using a standardized suspended solids test.

A utility in Modesto, California, suspected that manufacturing impurities may be accelerating the degradation of its sodium hypochlorite solutions, and began to subject all sodium hypochlorite shipments to sampling and laboratory filtration. Suppliers of shipments found to have impurities known to cause degradation were requested to filter their sodium hypochlorite before delivery. Samples are still routinely taken from shipments and from stored sodium hypochlorite after a period of days to monitor the degradation. Since implementing this program, the utility has noted a significant improvement in the quality and reduced degradation of its sodium hypochlorite.

Settled Particulates

Metals and insoluble particulates will tend to accumulate in the bottom of sodium hypochlorite storage tanks. The accumulated particles can also contain catalysts that will repeatedly accelerate the decomposition of fresh deliveries

of sodium hypochlorite. It is therefore recommended that the tanks be periodically drained and flushed of particles that accumulated on the tank bottom. To provide an uninterrupted supply of sodium hypochlorite; it is therefore necessary to have at least two storage tanks.

To further support the two-tank necessity, a report by Powell Fabrication and Manufacturing provides a discussion of a scenario where an end user utilizes a single tank for sodium hypochlorite storage. Powell describes a scenario in which an 8000-gal tank is filled with 12 trade percent sodium hypochlorite. After 1 week, this tank is drawn down until 2000 gal of sodium hypochlorite remains, which has degraded to 11.4 trade percent with a higher level of chlorate. Then the tank is filled again with fresh hypochlorite and after an additional week at the same conditions, the sodium hypochlorite has degraded to 10 trade percent with additional chlorates. As this cycle is repeated, the final concentration after mixing new hypochlorite is continually lowered and the concentration of chlorate is continually higher. This is obviously an undesired situation. Powell recommends that end users use two tanks for storage where each tank is kept in service until all the sodium hypochlorite has been used to the extent possible.

Other Impurities

Magnesium and calcium will form insoluble salts in sodium hypochlorite, which will appear as white precipitates, causing the solution to look cloudy; however, this has no effect on the chemical stability of the solution.³

IMPACT ON TREATMENT PROCESS

Sodium hypochlorite will have an impact on the treatment process that end users must consider; this is especially important when switching from chlorine gas disinfection to sodium hypochlorite. The following paragraphs discuss these effects so that design features can be provided to deal with them.

Sodium Carbonate

Sodium carbonate is also present in sodium hypochlorite solutions by nature of the manufacturing processes. It is also formed when air comes into contact with sodium hydroxide. Carbon dioxide from air is absorbed by sodium hydroxide and reacts to form sodium carbonate. Mostly, sodium carbonate is not considered a problem unless the solution also contains a high level of suspended solids. In solutions with high suspended solids, the sodium carbonate will tend to precipitate on to the suspended solids until large-enough particles are formed that they will no longer stay suspended. At such time, the particles will adhere to tank and piping walls causing scaling and plugging problems. Sodium carbonate concentrations up to 1% are generally not considered to be problematic.

Sodium Bromate

Bromate can enter drinking water sources from several pathways both of which involve the oxidation of naturally occurring bromide to bromate. First, it can from the reaction of ozone with bromide ions found in some raw water sources. Second, it can come from sodium hypochlorite. Recall that salt is a feedstock in the manufacturing of caustic and chlorine, which are then feedstocks to sodium hypochlorite manufacture. Many sources of naturally occurring salt deposits contain bromide in sufficient quantities to add considerable bromate to the drinking water.

Bromate in drinking water became regulated in the United States in December 2001 when the U.S. Environmental Protection Agency (USEPA) established for it the maximum contaminant level at $10\mu\text{g/l}$, which became applicable to all drinking water systems in January 2004. Only 50% of the bromate can originate from sodium hypochlorite, and the allowable amount is set to be lowered to 30% by being reduced by 10% each year. However, few sodium hypochlorite manufacturers can reduce the bromate content in their product to allow potable water producers to meet the new rules.

For example, if a potable water system feeds a total of 12mg/l chlorine, the maximum allowable concentration of bromate in its sodium hypochlorite product cannot exceed 25mg/l to meet the 30% rule.⁹

One solution is to use evaporated salt in manufacturing sodium hypochlorite. As evaporated salt contains very little bromide, therefore, the sodium hypochlorite will be low in bromate. If end users are trapped by new rules, one solution would be to require the sodium hypochlorite manufacturer to use evaporated salt.

pH and Alkalinity Addition

As discussed earlier, commercial sodium hypochlorite contains sodium hydroxide for pH stability. When sodium hypochlorite, with a pH of 11 to 13, is introduced to a water or wastewater treatment process, the sodium hydroxide can elevate the pH of treated water depending upon the water quality and the treatment process. In some cases, it may be necessary to add an acid to counteract the pH elevation.

To avoid the hazardous nature of gaseous chlorine storage and feed, many municipal treatment plants have switched from gas chlorine to sodium hypochlorite. In these cases, the treatment plant was often not designed to accommodate the inherent pH elevation. In many cases, it is necessary to add an acid, such as sulfuric acid or even carbon dioxide, to return the process water's pH to the original level so that downstream process units can still function properly.

Scaling

When sodium hypochlorite is introduced to a water or wastewater treatment process, the sodium hydroxide will also react with the water's background concentrations of calcium and magnesium hardness and induce scale

formation in the immediate area of the application point. In cases of high hardness, this scaling can accumulate quite quickly and cause operational problems. Sodium hypochlorite diffusers need to be designed for periodic removal so that scale can be removed.

Designers often use carrier water with sodium hypochlorite to increase the velocity of the chemical in the feed pipe to the feed point. Carrier water is sometimes viewed as a method to eliminate scaling at the application point. Carrier will not reduce or eliminate the formation of scale unless softened or de-mineralized water is used for carrier water. The introduction of carrier water to un-softened water will likely induce scale formation in sodium hypochlorite feed piping. The sodium hypochlorite feed piping is often much smaller in diameter than in the process piping, thus less tolerant of scale formation. The smaller diameters intensify the scaling problem and could only make matters worse.

Chlorate/Perchlorates

Sodium hypochlorite contains undesirable impurities such as chlorates, perchlorates, and bromate.¹³ The concentrations of these contaminants increase as sodium hypochlorite degrades. As discussed earlier, there is growing concern over the introduction of these contaminants from sodium hypochlorite into drinking water and its impact on human health. In October 2008, the USEPA issued a finding that a maximum contaminant level (MCL) was not necessary for perchlorates. However, the AWWA recommended in the July 2009 Study that the National Sanitation Foundation (NSF) give further consideration to establishing a maximum allowable level of chlorate and perchlorate in bulk sodium hypochlorite. Currently, these are only regulated in drinking water at a state level in California, New Jersey, and Massachusetts.¹³

In September 2009, USEPA issued its final Contaminants Candidate List 3 which included chlorate. This final list deviated from the draft list which did not include chlorate. This means USEPA could elect to regulate chlorate in future regulatory considerations.

Recommendations

The quality of delivered hypochlorite is critical to its stability. End users can take an active role in the specification and purchase of high-quality sodium hypochlorite from the manufacturer and local distributor. The stability of sodium hypochlorite can be enhanced and preserved through a number of means. The following recommendations should be used for sodium hypochlorite system designs and by end users for best results:

- Specify the minimum trade percent sodium hypochlorite, microgram per liter chlorine, weight percent chlorine, weight percent sodium hypochlorite, or some other means to quantify the chlorine content.

- Monitor the chlorine content of the sodium hypochlorite solutions during storage to assess degradation rates and address specific site issues that may be inadvertently accelerating the degradation.
- Use dilution only with a complete understanding of all the factors that influence degradation. Avoid introducing catalyzing impurities or disrupting the pH balance of the solution. Use softened or deionized water.
- Specify the minimum and maximum excess caustic (0.025%–0.35%) to maintain the pH between 11.86 and 13.
- Require the sodium hypochlorite to be cooled and filtered by the manufacturer immediately after production to slow the degradation rate and remove impurities that catalyze the degradation. Filters should be within 0.2–0.5 μm to remove suspended solids.
- Store sodium hypochlorite in a naturally cooled environment or in an air-conditioned room. However, underground storage tanks (UST) are not recommended because they are subject to the strict USEPA regulations.
- Specify the maximum allowable content of chlorate, iron, copper, and nickel in the delivered product; this will reduce the degradation during shipment and storage. Additional consideration should be given to each end user's facility to ensure that additional contamination is not picked up through handling and storage materials of construction. Care must be taken in the selection of tanks and piping materials to avoid introducing these contaminants.
- Specify the maximum acceptable chlorate level in delivered sodium hypochlorite to minimize the time difference between product manufacture and delivery to the end user.
- Provide a minimum of two storage tanks to allow all the hypochlorite from a particular tank to be used before switching to another tank. This minimizes the chlorate content and reduces the dilution of remaining sodium hypochlorite when a new delivery is mixed with an old delivery. Having two tanks will allow the user to completely empty one tank before switching to the other tank.

TANK SELECTION

Sodium hypochlorite is stored in atmospheric tanks equipped with connections for vent, outlet, overflow, drain, level transmitter, visual site gauges, and manways. It is not necessary nor is it recommended to store sodium hypochlorite in pressurized vessels as there would be significant additional cost. With atmospheric tanks, there are a variety of tank materials on the market for chemical storage. Most common tank materials are metallic such as carbon steel, stainless steel, or aluminum. Tanks can also be constructed of exotic metals such as hastelloy or titanium, but these are rare due to the excessive

cost of exotic metals. Metallic tanks can be constructed by a variety of methods, including welding and bolting.

Sodium hypochlorite has a high concentration of chloride and chlorite. Aqueous solutions high in chlorides and chlorites are very corrosive to most metals. Sodium hypochlorite is very corrosive to carbon steel, stainless steel, cast iron, ductile iron, and most other metals used in construction such as copper and brass and aluminum. The only metals suitable for direct contact with sodium hypochlorite are titanium, tantalum, silver, gold, and platinum, with titanium being the only one of these practical as a construction material for tanks in sodium hypochlorite. However, because titanium is rare in the environment, it is very expensive.^{2,3}

Hastelloy is an alloy, which is a combination of various elemental metals. While it is very expensive, it is considered to have only limited chemical resistance to sodium hypochlorite. Hastelloy contains large quantities of heavy metals, including nickel, which is a key contributor to catalyzing the degradation of sodium hypochlorite; therefore, it is not a suitable material for extended exposure to sodium hypochlorite.

In general, thermoplastics such as polyvinyl chloride (PVC) and CPVC are compatible with sodium hypochlorite, although there are some temperature limitations. Many proprietary compounds such as Teflon and Tefzel are also compatible and used frequently for sodium hypochlorite. However, chlorine (both as chlorine and as sodium hypochlorite) will slowly permeate thermoplastics, Teflon, and other resistant materials without detriment to the material itself. Permeated chlorine can be corrosive to materials surrounding the tank or piping.

Engineers, designers, and end users can confirm the general compatibility of materials data for sodium hypochlorite by reviewing chemical resistance tables/guides provided by sodium hypochlorite manufacturers, tank manufacturers, pump manufacturers, and valve and piping manufacturers. The tables are generally based on the results of laboratory testing and are modified based on experience.

In general, metallic materials have excellent structural and mechanical properties. However, carbon steel and stainless steel are readily attacked by chloride; they cannot be used for sodium hypochlorite. Carbon and stainless steel tanks must be lined with rubber, PVC, or Teflon to shield the steel from the chemical.

Fiberglass-reinforced plastic (FRP) tanks are commonly used for sodium hypochlorite storage. FRP tanks consist of a chemically resistant resin used in conjunction with fiberglass strands for structural strength. There are various processes used in the actual fabrication, including filament winding, hand layup, or spray up. While there are many tank fabricators, there are only a few resin manufacturers, among them Ashland, Interplastic, and Reichhold.

Another construction material used for storage tanks is high-density polyethylene (HDPE). HDPE is available in linear and cross-linked polyethylene.

For sodium hypochlorite service, all these tank materials will be discussed in detail below under the respective heading.

In the selection of tank materials, the service temperature is an important factor because higher temperatures increase the corrosion rate of metallic materials and affect the structural strength and chemical resistance of plastic, thermoplastic, and fiberglass.

Sodium hypochlorite tanks should be located indoors, especially in hot climates, to keep them as cool as possible. If this is not possible, a canopy should be provided to shield the tank from the sun's heat and UV light. If neither indoor storage nor a canopy is available, the tanks should be painted a light color. Unpainted FRP tanks are typically dark brown and are not suitable for sodium hypochlorite storage if unprotected by a light-colored paint.

The materials suitable for storing sodium hypochlorite include rubber-lined carbon steel, FRP, HDPE, and titanium.

Lined Steel

A lined steel tank is a tank constructed of carbon steel by typical methods of rolling and welding sheets of carbon steel. After the structural steel layer is completed, the interior of the tank is lined with a chemical-resistant product such as rubber, PVC or Teflon that will be in contact with the tank's chemical contents. Because of the existing infrastructure to provide welded steel structures in a variety of shapes and sizes, there is a great deal of flexibility in the size, shape, diameter, and height in a lined tank.

Lined steel tanks are structurally stronger than tanks of nonmetallic materials, and the lining makes them resistant to sodium hypochlorite solution. However, they are also more expensive than tanks of other materials.

Chlorobutyl rubber linings are most commonly used in steel tanks for sodium hypochlorite. The lining is typically ¼-in. thick and has a life expectancy of 3–6 years. For these reasons of short life and high cost, they are typically used for sodium hypochlorite, but only for pressurized storage or in chemical manufacturing.⁹

Sodium hypochlorite manufacturers have encountered several problems with rubber-lined tanks for bulk storage. Sodium hypochlorite is an aggressive chemical, which degrades the rubber lining. The life span of a typical liner in sodium hypochlorite service is approximately 3–6 years. After that time, the liner will then need to be reapplied and chemically cured within the tank. During this process the tank is taken out of service for an extended duration. A second disadvantage manufacturers have experienced with rubber-lined tanks is that the inner liner flakes off over time, contaminating the sodium hypochlorite stored in the tank. These flakes may be problematic to downstream chemical feed equipment in water and wastewater treatment plants.⁸

In addition, with rubber-lined tanks, pinholes can occur in the rubber lining during installation or lining repair, allowing sodium hypochlorite to contact

the structural steel component, which will lead to rapid corrosion of the steel tanks and associated loss of structural integrity. However, testing and inspection of rubber-lined steel tanks for pinholes is easy and is much more reliable than the visual inspection used in locating small cracks in FRP tanks. The steel walls of rubber-lined tanks allow the use of electronic spark testing equipment.⁸

Rubber-lined tanks are still used at some sodium hypochlorite facilities despite the high maintenance cost associated with repairing the liners. However, most sodium hypochlorite manufacturers prefer to use FRP tanks.⁸

Regardless of the lining material, the exterior of steel tanks should be painted to protect them against external corrosion. Since carbon steel is dark and will absorb heat from direct sunlight, the paint for outdoor tanks should be a light color to reflect heat.

FRP

FRP tanks are manufactured from the inside outward by first constructing a corrosion barrier around a mandrel of a selected size and shape. The corrosion barrier is generally 100–120 mils thick and consists of a resin-rich two-ply synthetic surface veil followed by a corrosion layer of chopped mat or strand. Typically, the corrosion barrier is fabricated using hand layup or spray up methods. Filament winding is not recommended for the corrosion barrier because failures in the veil can allow sodium hypochlorite to “wick” into the filament winding and compromise the structural integrity of the tank.⁹ The structural wall, which is fabricated around the outside of the corrosion barrier, is often filament wound by coating a continuous fiberglass filament with wet resin and immediately winding diagonally around the tank to produce a rigid structural layer.

FRP tanks have good resistance to sodium hypochlorite. Depending on the resin used, temperature ratings may vary between 120 and 150 °F. Appropriate resin selection is critical; depending on selection, the temperature rating may be less than 150 °F, in which cases it would be recommended that the tanks be insulated in some outdoor applications.

FRP tanks used for sodium hypochlorite should use a benzoic peroxide (BPO)/dimethyl aniline (DMA) cure system with a postcure, and the resins should be nonthixotropic (thixotropic agents control the viscosity or flowability of the resin). An additional 10 mils of resin should be applied on the inside wall, for a total of 20 mils, and the tank should be postcured at 180 °F for 4 h. A correctly designed and fabricated FRP tank will have an estimated life of 10–20 years.⁸

FRP tanks improperly constructed will be chemically attacked by the sodium hypochlorite, which will cause the interior surface to become partially liquefied (often reported as sticky or gummy). This loss of resin integrity will eventually lead to a leak. Replacing the interior lining will give only temporary relief from leaks.

HDPE

Another material often used for sodium hypochlorite tanks is polyethylene.

Polyethylene tanks are fabricated by applying heated polyethylene to a mold by a process called rotational molding. Unlike steel or FRP tanks, HDPE tanks can be fabricated only in the sizes of the molds owned by the manufacturer.

HDPE tanks are not usually obtainable in custom sizes of equal diameter and height increments as FRP and steel. For example, one can readily order a 12-ft-diameter FRP or steel tank and be reasonably certain that a fabricator can provide it. With HDPE, the closest tank size might be 11 ft and 6 in. in diameter because the manufacture may not possess a 12-ft-diameter mold. Furthermore, not all HDPE tank manufacturers have the same size molds so perhaps only a few could provide one that is 11 ft and 6 in. in diameter. Other manufacturers might have 11 ft and 9 in. or 11 ft and 11 in. diameters. As a result, it can be difficult to competitively specify an HDPE tank without compromising during bid time.

Two types of polyethylene are used in HDPE tanks: linear and cross-linked. Linear polyethylene consists of long chains of polyethylene molecules that are not bonded together. Cross-linked polyethylene consists of molecule chains that are intermittently bonded at various intervals. Cross-linked HDPE tanks are generally more expensive of the two types because of the higher cost of cross-linked resin material and the more complex fabrication process.⁹

Both linear and cross-linked HDPE tanks are used for 12.5% sodium hypochlorite. There is no agreement among leading HDPE tank manufacturers regarding which type is better for sodium hypochlorite. Cross-linked HDPE is seen as more resilient and less likely to burst or rupture because of its greater strength. However, the chemical compatibility of linear HDPE is considered superior. Some manufacturers produce tanks with a cross-linked HDPE structural layer and an inner linear HDPE liner. However, there is some concern about the integrity of the bond between the two layers.⁹

The service life of HDPE tanks depends on the manufacturer, resin material, and service conditions. Many manufacturers estimate the service life of HDPE tanks to be about 5–7 years. Regardless of the tank manufacturer and resin material used, sodium hypochlorite has an adverse effect on the polyethylene directly exposed to the chemical. The sodium hypochlorite oxidizes the antioxidants and plasticizers that make the polyethylene flexible, causing the inner layer of the tank to become brittle and, under some service conditions, to crack or flake off like in the rubber-lined tanks.⁸

Most HDPE tanks are equipped with a bulkhead fitting for connecting piping. The fittings are available in both threaded and bolted type and may be fabricated of thermoplastic materials such as PVC or of exotic metals such as titanium. Both types of bulkheads rely on the compression of gaskets on the interior and exterior tank walls and surfaces for sealing. The bulkhead fitting requires a flat surface for developing a seal. Often, tanks are round and thus have curved surfaces at locations where outlet nozzles are needed. As a

result, the installer is required to tighten the bulkhead fitting to the extent that it locally flattens the tank wall to obtain a seal. This can be difficult on small tanks as the curvature might be significant. The bulkhead fitting can be an acceptable fitting for tank nozzles that are not routinely submerged in the chemical contents such as overflows or vents. For tank outlet nozzles, the bulkhead fitting becomes more difficult, especially for small-diameter tanks where the curvature is more pronounced. For large-diameter tanks, the angle observed at the outlet nozzle is not great and bulkhead fittings can be somewhat effective, but are more susceptible to failure than the molded fittings used on FRP tanks, where the connection is an integral molded part of the wall and no gaskets are required on the interior wall for sealing.

Some manufacturers can provide one integrally molded flush bottom outlet on certain tank sizes so that users can avoid the bulkhead fitting at locations where liquid could leak. However, the integrally molded fitting is not available on all tank sizes, and there is little crossover between manufacturers on the specific size tanks where the fitting is available, which again makes competitive bidding a challenge.

Bulkhead-type fittings cannot be used in the sidewalls for large nozzles, such as manways. As a result, manways cannot be installed on the sidewalls but only on the tank roof.⁸

Using HDPE tanks for sodium hypochlorite storage presents some challenges: HDPE tanks can be made from various resins, most common of which are a black pigment and a natural translucent pigment. Some fabricators have a special resin specifically for sodium hypochlorite service with an opaque white resin. Translucent HDPE will transmit UV light, which is a major factor in the degradation of both sodium hypochlorite and the structural integrity of unprotected outdoor HDPE tanks. Therefore, the resin used in manufacturing outdoor HDPE tanks must contain a UV inhibitor. The inhibitor is provided by the resin manufacturer, and its composition and concentration in the resin are proprietary. However, upon request, manufacturers will certify that certain resins do contain adequate UV inhibitor to protect the tank, but the UV inhibitor does not provide additional UV protection for the sodium hypochlorite.

HDPE tanks are best located indoors, where the tanks and their contents are protected from the sun's heat and UV light. However, they have a relatively short service life even indoors, and the building the houses a tank must be designed to accommodate its replacement every 5–7 years.

Black HDPE tanks will reflect UV rays but will absorb heat exposed to sunlight, which will cause the temperature of the tank contents to rise. Therefore, black is not an acceptable color for sodium hypochlorite tanks outdoors. Some tank fabricators will provide their tanks a light colored outer shell that reflects heat and blocks UV rays, which reduces the impacts of UV and heat, but it adds to the tank's cost. The tanks should be fabricated according to American Society for Testing and Materials (ASTM) D 1998–2006, the latest ASTM standard for HDPE tanks. They should be designed for a specific gravity of 1.9. Even though this is much higher than the specific gravity of

commercial sodium hypochlorite, it translates into a thicker tank wall. ASTM also calls for a 0.942 density resin.¹⁰

Comparing FRP and HDPE tanks, HDPE tanks are generally less expensive than FRP tanks, which offsets their shorter service life. However, when taking into account the accessories such as integrally molded outlets, UV protection and/or insulation, and HDPE liners, prices of tanks in the 3000- to 10,000-gal size range are comparable to the cost of FRP tanks. Above 10,000 gal, FRP tanks are more economical, and below 3000 gal, HDPE tanks are more economical. HDPE tanks are more difficult to repair than FRP tanks and they do not have the mechanical and structural strength of FRP. As a result, HDPE tank walls tend to distort in shape (bulge) after several years of service with a dense liquid such as 12.5% sodium hypochlorite. As a result of the distortion, it is critical to have flexibility in the piping systems directly flanged bolted to the tank. It is necessary to have flexible connections to allow the tank to bulge and flex during filling and emptying cycles. Failure to use flexible connections could result in stress and failure of the piping and/or the tank and will, in many cases, void the manufacturer's warranty.

Titanium

Titanium is an excellent choice for storage of sodium hypochlorite. It is resistant to sodium hypochlorite and its structural properties are similar to those of more common metals such as carbon steel and stainless steel. It is also the only material for sodium hypochlorite tanks that has a service life of 30 years or longer. However, titanium is very expensive, and therefore it is not usually used for sodium hypochlorite tanks.^{3,9}

Other Tank Materials

Other structural materials that are sometimes used for sodium hypochlorite tanks include concrete or wood staves (slats of wood held together by metal bands similar to a wood barrel used in wine aging operations). In such tanks, the chemical is separated from the tank structure by a flexible PVC liner. These unusual structures reflect abundance of some structural materials in the area. Little practical experience or feedback on their use is available. Foreseeable problems include tears or holes in the thin liner that can leak and spill valuable sodium hypochlorite, which could potentially result in an environmental impact. Additionally, unnoticed leaks could compromise the integrity of the structural layer, resulting in a catastrophic failure.

Level Instrumentation

Level instrumentation is a necessary part of sodium hypochlorite storage tanks since the chemical should be stored in an opaque container. There are a

number of electronic instruments available for this service, including ultrasonic, radar, and differential pressure sensors. All are effective and reasonably reliable methods for sodium hypochlorite level measurement. Each type is accurate to within fractions of an inch. Ultrasonic- and radar-type sensors are mounted to a flange on top of the tank, and since they are not in contact with the liquid, they are minimally affected by its corrosiveness. Differential pressure sensors read the pressure of the chemical at the bottom of the tank, which can be converted into feet of sodium hypochlorite. Differential pressure sensors are in direct contact with the liquid and must be specially designed to be corrosion resistant.

The tanks should be also fitted with sight gauges in case the electronic instrument is out of service. Sight gauges may be of the clear type or the magnetic type. The clear type consists of a clear plastic or Teflon tube where the liquid level is directly visible with a graduated strip adjacent to the tube. The magnetic type consists of a magnetic float inside a sealed tubing assembly, and the position of the internal float is indicative of the liquid level in the tank. Because the float tubing is sealed, the magnetic flag type is equipped with a series of vertical magnetic flags that turn 180° over as the magnetic float passes by. The flags are painted with a two-color system, where the floats are different colors on each side. The vertical location of the color change is easily identified as position of the liquid level.

Truck Unloading

Sodium hypochlorite is often off-loaded from the delivery truck to the end user's tank by applying air pressure to the top of the transport truck to push the chemical out of the truck. U.S. Department of Transportation (DOT) and most state regulations limit the weight limit of truck deliveries to 45,000lb, which equals approximately 4600 gal of 12.5% sodium hypochlorite; thus, the maximum truck delivered is not likely to exceed 5000 gal. It is recommended that this chemical storage be sized for 125% of a maximum truckload to assure sufficient volume to receive a truckload before the tank is completely empty. This excess volume also provides a reasonable time period between when a new truckload can be accepted and when a new truckload actually arrives. As discussed earlier, end users are recommended to have two storage tanks and to use all the sodium hypochlorite solution in one tank before switching to another tank.

Typically, the truck-unloading air pressure is 15–25 psig and 40 scfm, which results in an off-loading rate of approximately 50 gpm. In most cases, the delivery truck is equipped to supply the air, but occasionally, it is supplied by the user. The storage tank must be adequately vented to prevent it from becoming pressurized, which is most likely to happen at the end of the unloading cycle when a burst of air can momentarily pressurize the tank and compromise its corrosion barrier. Most FRP tank manufacturers recommend a 6-in. vent connection when the truck unloading line is 2 in. in diameter.

Top Access

Most tanks can be provided with top shells of flat, domed, or coned construction. In general, dome tops are the least expensive. Flat tops require special reinforcement to support personnel weight. Domed tops can support the weight of a person without special reinforcement. Domed and cone-shaped tops generally have a height equal to about 25% of the tank diameter. A 12-ft-diameter tank that has a diameter of 12 ft will have a 3-ft-high dome or cone. IBC 2003 recommends at least 80 in. from the apex of the dome or cone to the bottom of any covering superstructure. While this is rarely attainable, sufficient room for top access must be provided.

Tanks taller than 5 ft should be provided with a ladder for top access. The ladder should be of FRP or FRP-coated steel for sodium hypochlorite service and should be clip-mounted to the tank wall for lateral support. The ladder bottom should rest on the floor of the containment area, rather than be attached by clips to the tank wall, so that personnel weight rests on the floor. The ladder should extend at least 40 in. above the sidewall of the tank. The Occupational Safety and Health Administration (OSHA) requires ladders longer than 16 ft to be equipped with a safety cage. Most tank fabricators are well informed of the OSHA requirements for ladders and handrails and can provide the required components if the specifications are written to require it.

A tank with top access must be provided with a handrail system that meets OSHA requirements. The handrail should consist of an upper and an intermediate rail, with a bottom kickplate to prevent tools from sliding off the edge of the tank. The handrail should encompass the entire tank perimeter and should be attached with clips integrally molded into the tank/top wall. The top handrail height should be carefully considered to avoid interference with room beams, electrical conduits, lighting systems, and so on.

In some instances, horizontal tanks are used for bulk storage rather than vertical tanks. Horizontal tanks have the advantage of holding a larger volume with a lower profile; however, they are more expensive than vertical tanks because of the multiple tank heads and the less efficient use of freeboard. Generally, horizontal tanks will require walkways for their entire length for access to manways and other top-mounted appurtenances.

Underground Storage Tank (UST)

USTs are infrequently considered for chemical storage. If an underground tank is selected, it will be subject to numerous federal regulations (40 CFR §280): the tank must be double-contained and the interstitial space must be electronically monitored for leaks, with the results regularly reported to the government. The law also requires financial verification and funds for future cleanup to be established in advance in the event that the tank leaks and the owner becomes financially insolvent. Because of the burdensome regulations, USTs are not recommended for sodium hypochlorite storage.

TRANSFER AND FEED EQUIPMENT

Sodium hypochlorite can be fed and/or transferred in a number of ways, depending on the application. The various types of pumps and equipment for transfer and metering and how they can be used in handling sodium hypochlorite are described below.

Transfer Pumps

Typically, transfer of liquid chemical from one tank to another does not involve volumetric metering or monitoring. Centrifugal pumps are a good choice for this task. Centrifugal pumps are generally driven directly or magnetically by a constant speed electric motor, but can also be pneumatically driven. Centrifugal pumps for sodium hypochlorite are available in a variety of materials of construction, including titanium (which is the only suitable unprotected metal for sodium hypochlorite), thermoplastic-lined cast or ductile iron, thermoplastic materials, and fiberglass. The pumps can also be lined in proprietary materials such as Teflon or Tefzel. As expected, titanium pumps are very expensive. Thermoplastic and thermoplastic-lined pumps have traditionally been the choice for transferring sodium hypochlorite.

Magnetic drives offer a distinct advantage over direct drives. The pump drives consist of two magnets (one connected to the motor and one connected to the impeller) that are not in direct contact with each other. A magnetic field transfers torque from the motor to the impeller. Thus, there is no direct shaft connection between the motor and the impeller, which eliminates the need for a shaft seal. A seal is somewhat expensive and requires replacement as a maintenance item. Shaft seals are known to leak or drip the pumped solution.

Diaphragm Metering Pumps

The diaphragm pump was developed in recognition of reciprocating-action piston and plunger pumps. Piston and plunger pumps, while a good technology for positive displacement pumps, inherently leak the pumped fluid by the dynamic seals. In addition, the pump will allow leakage of piston or plunger lubricant into the process fluid. For noncorrosive services such as water or cement, this leakage is not objectionable. However, with sodium hypochlorite, routine leakage of lubricant or sodium hypochlorite is not acceptable because sodium hypochlorite is a corrosive liquid that will react with oil-based lubricants and will corrode concrete and most metals. Diaphragm pumps were developed as an alternative reciprocating pump that utilizes a diaphragm seal between the piston/plunger and the process fluid. Diaphragm pumps are provided by a variety of manufacturers who collectively possess a great deal of experience with this type of pump service.

Diaphragm metering pumps have long been used for metering chemicals in municipal, power, and industrial applications. They have broad range of

flow capabilities, which can be achieved by adjusting the frequency of diaphragm cycling (stroke speed) by adjusting the motor speed and adjusting the length of diaphragm movement (stroke length). The range of flow is referred to as turndown, which is expressed as a ratio of maximum pump output to the achievable minimum output.

Diaphragm pumps are available in many sizes and variations. The standard diaphragm pump includes a flexible flat diaphragm (usually of natural or synthetic rubber) operated by a motor or an electromagnetically driven solenoid. The diaphragm is cycled back-and-forth by the motor through a gearbox and plunger, which converts the rotational motion of the motor to a back-and-forth action. In a solenoid pump, the timed reversal of electromagnetic fields causes a plunger to move back-and-forth to achieve this action. The diaphragm resides inside of a pump head (often called a liquid end) with inlet and outlet check valves. Liquid is drawn into the head by a momentary vacuum created by the retracting diaphragm and pushed out by the forward motion of the diaphragm. Check valves allow flow through the head in only one direction. These pumps operate from the principle that liquids are incompressible. Diaphragm pumps are positive displacement pumps where the frequency and distance of diaphragm movement can be directly correlated to the pump's output flow regardless of the discharge pressure. For a given pump, a linear pump curve can be generated where the pump's output can be accurately estimated from the stroke speed for a given stroke length. Figures 9.5 and 9.6 show a cutaway of a typical diaphragm metering pump and a cutaway of the liquid end indicating the suction and discharge stroking actions that are inherent to pump operation.

Diaphragm pumps are available with mechanically or hydraulically operated diaphragms. In a mechanical diaphragm, the force on the plunger is directly point-loaded to a reinforced location at the center of the diaphragm. This is a wear point especially in high-pressure applications where the friction

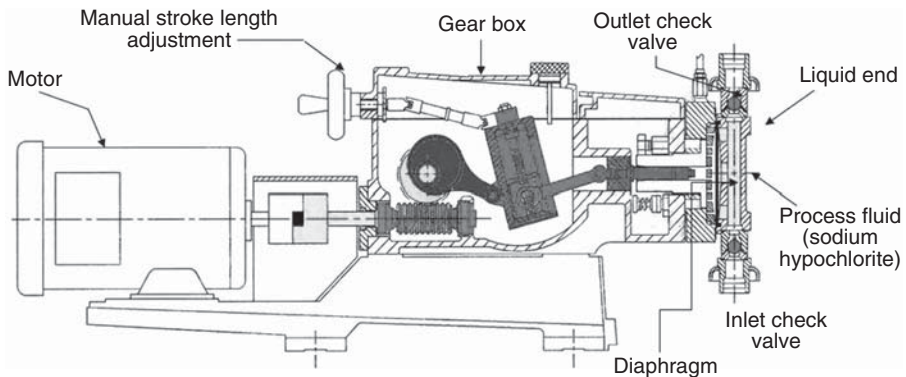


Figure 9.5. Diaphragm metering pump.

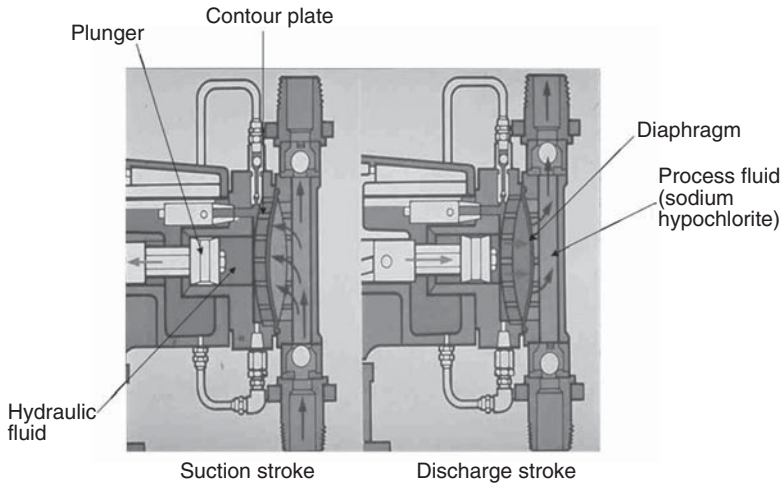


Figure 9.6. Pump head suction and discharge strokes—hydraulic flat diaphragm.

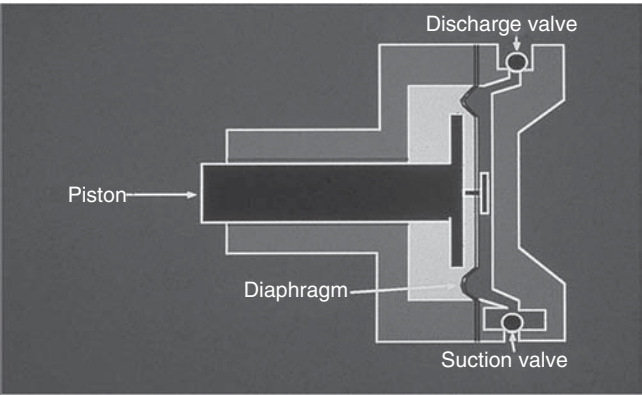


Figure 9.7. Mechanically actuated diaphragm metering pump.

is great. In a hydraulically operated diaphragm, a sealed oil-filled housing exists between the gearbox plunger and the diaphragm. The plunger acts against the incompressible oil (through an internal mechanical seal) to push against the back side of the diaphragm. No air can exist in this oil-filled housing. The overall effect of actuating the diaphragm is the same as a mechanical diaphragm; only the force is equally distributed over the diaphragm as opposed to being point-loaded onto a single location (Figs. 9.7 and 9.8).

Chemical metering pumps are often controlled by one or more electronic analog or digital signals programmed in proportion to the pump's flow ranges.

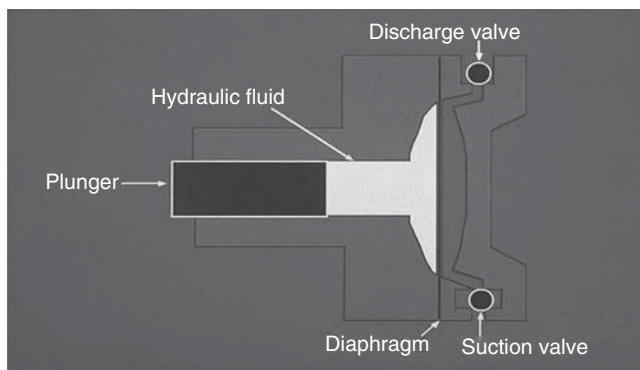


Figure 9.8. Hydraulically actuated diaphragm metering pump.

An increase in the signal valve to the pump will cause the motor speed (or stroke length) to increase, thus increasing the output flow. Water and wastewater plants use this method extensively to adjust chemical flow rates to automatically respond to hourly and daily changes in plant flow and chemical demand.

Pump manufacturers use a variety of materials of construction for wetted parts of the pumps (i.e., parts exposed to pump liquid). Pump manufacturers have the experience and knowledge to select the materials of construction and provide compatibility data to support their materials selection. It is important to note that there are many wetted parts to the pump and all should be selected carefully to offer the best resistance to the solution. Typically, Teflon or Viton rubber has been the most successful diaphragm material for sodium hypochlorite pumps.

Diaphragm pumps require back pressure in order to provide sufficient force to quickly and completely seat the check valves on each stroke. If back pressure is not present from the process, a back pressure valve is used in the downstream piping to artificially generate the back pressure. Additionally, diaphragm metering pumps require other piping appurtenances to protect the pump and piping system such as pulsation dampeners and pressure relief valves. Pulsation dampeners soften the pulsating effects of diaphragm metering pumps to prevent damage to the piping system from continuous pulsating. In addition, to reduce the inertial losses caused by the reciprocating action, they provide a more continuous flow of chemical to the process. Pressure gauges are invaluable on suction and discharge strokes for troubleshooting and understanding the process. Calibration columns are necessary to calibrate the flow of the pump and develop calibration charts so that operators can estimate the pump output at various pump stroke speeds and stroke lengths. The following diagram presents the piping and appurtenances for a successful diaphragm pump application (Fig. 9.9).

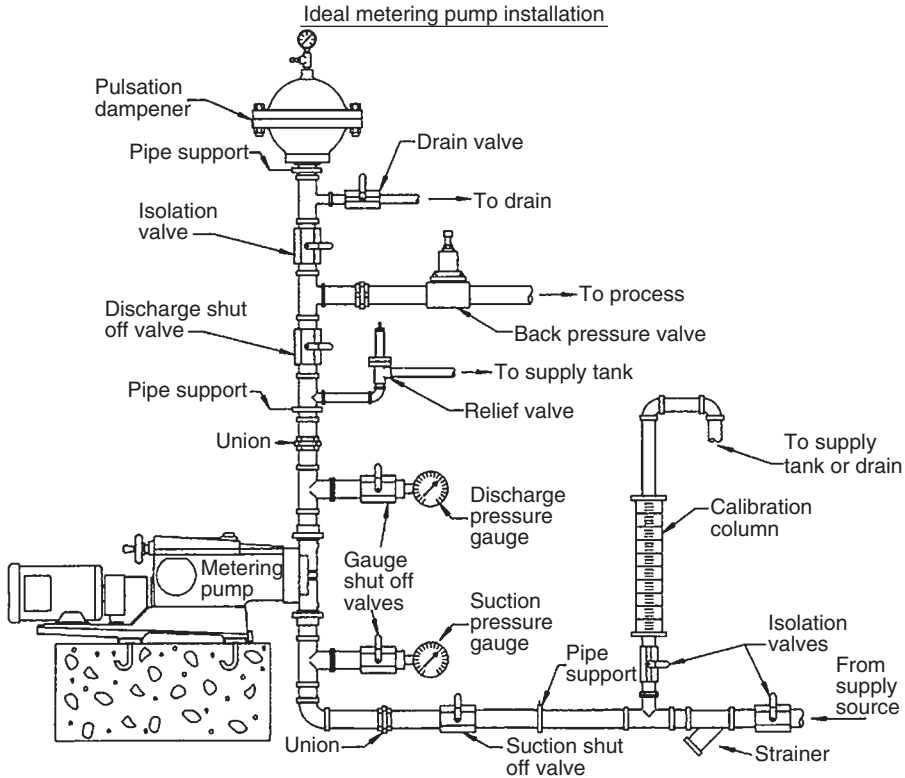


Figure 9.9. Typical diaphragm pump piping system.

Problems with Vapor Locking

The momentary vacuum created by the suction stroke is not adequate to create sufficient suction lift, so diaphragm pumps must operate with flooded suction to allow liquid to flow into the pump head on the suction stroke. Flooded suction is especially important in sodium hypochlorite solutions because of its off-gassing characteristics.

Oxygen is one of the degradation products of sodium hypochlorite, and during pumping, it may be released from solution. The mechanical turbulence of the liquid through piping valves and pump head can disrupt the equilibrium of dissolved oxygen in the solution and can cause gas to effervesce. This is commonly called “off-gassing.” The disruption can also be further induced by lower pressure induced by a pump suction stroke.

The diaphragm pump can draw liquids into the liquid end on the pump suction stroke; however, if there is any gas in the suction piping, the momentary vacuum created by the suction stroke will cause only an expansion of

the gas resulting in a reduced flow of liquid. If gas accumulates, the flow of liquid will cease. In such case, although the diaphragm pump will operate in a seemingly normal manner, it will pump no liquid. This condition is known as “air-binding” or “vapor locking.” Many end users of sodium hypochlorite have experienced this problem, especially with diaphragm metering pumps. Accordingly, the problem has been studied in great detail by diaphragm pump manufacturers.

Contour Plates. When sodium hypochlorite gained popularity with water and wastewater treatment plants as an alternative disinfectant to liquid and gaseous chlorine, end users began to understand the mechanisms that resulted in the release of oxygen gas. As mentioned earlier, mechanical turbulence can disrupt the gas dissolution equilibrium and cause gas to be released. One of the contributors to disrupting the equilibrium of gaseous oxygen in the liquid was found to be the perforated contour plate inside the diaphragm pump’s head that limits the movement of the diaphragm. The contour plates were identified as locations where sodium hypochlorite solution was drawn through the perforations at high velocity, releasing oxygen gas inside the metering pump head, which caused the pumps to become vapor locked. Additionally, gas bubbles attached to the contour plate instead of passing through. Use of pumps with contour plates should not be considered for sodium hypochlorite service without degassing devices.

Stroke Length Limits. In response to the contour plate theory, diaphragm pump manufacturers issued operational recommendations to keep sodium hypochlorite moving through the pump head. One such recommendation was to operate with the pump stroke length between 50% and 100%. Longer stroke lengths were seen as a way to keep new solution incoming and push most of the bubbles out. In normal chemical diaphragm pump applications, the stroke length is adjustable from 10% to 100% for a 10:1 turndown of chemical output flow rates. For the most part, this turned out to be an effective method to prevent air-binding, but it reduced the turndown by stroke length for sodium hypochlorite pumping from 10:1 to 2:1. Additional turndown can be obtained through variable pump motor speeds. Use of stroke lengths greater than 50% is still recommended.

Tubular Diaphragms. Some diaphragm pump manufacturers, including Pulsafeeder and Siemens Wallace & Tiernan, have a line of tubular diaphragm liquid ends for high-viscosity liquids, slurries and chemicals prone to off-gassing. Essentially, the motor and gearbox components are identical to those of the flat diaphragm pump, except the tubular diaphragm pump is equipped with an elastic tube, which does not require a perforated baffle plate. The tubular diaphragm is applicable only to hydraulically actuated diaphragm pumps. In this case, both pressure and vacuum strokes are exerted

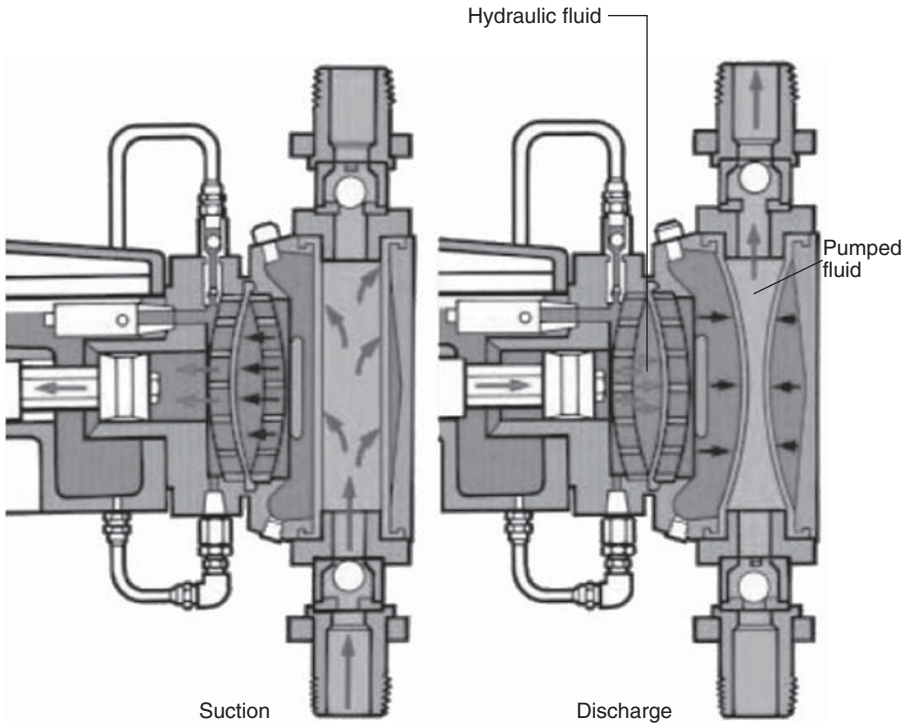


Figure 9.10. Tubular diaphragms.

by the hydraulic oil to expand (suction) or collapse (discharge) the tubular diaphragm with equal pressure around the outside of the tube. Inlet and outlet check valves are still used to control flow one-way through the pump head. The tubular diaphragms have been effective in reducing the effects of off-gassing. Figure 9.10 shows a diagram of a tube-type diaphragm.

Jesco America Corp. has also developed a unique tubular diaphragm pump in which the process fluid operates from the outside of the diaphragm (Fig. 9.11).

Specialty Hypochlorite Pumps. Some pump manufacturers have introduced specially designed diaphragm pumps for sodium hypochlorite.

Pulsafeeder Corp. has patented a sodium hypochlorite pump that it calls “Pulsar Hypo Pump.” The Pulsar Hypo Pump is a mechanically or hydraulically actuated diaphragm pump similar to other pumps; however, its liquid end is fitted with a small bypass port to vent gases from the pump’s liquid end and to pass them to the pump discharge line. The bypass port is equipped with a solenoid-operated flapper and a timer that controls the frequency and dura-

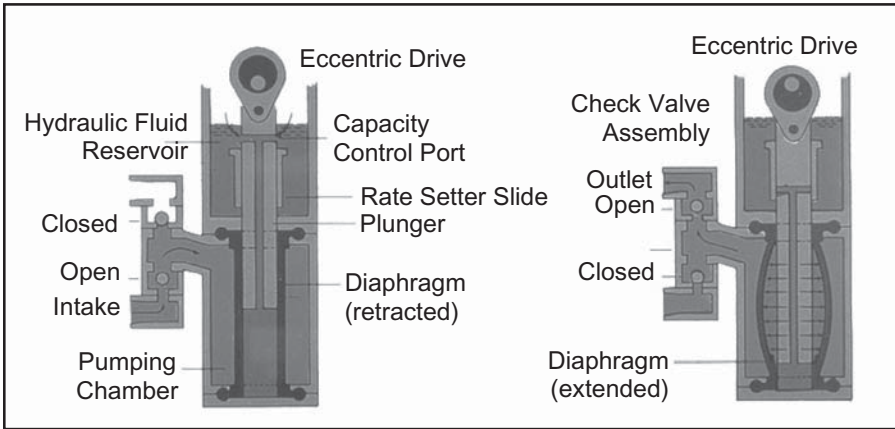
**Suction Stroke****Discharge Stroke**

Figure 9.11. Jesco America Corp. tubular diaphragm (courtesy Jesco America Corp.).

tion of the flapper opening. A cutaway of the Pulsafeeder Hypo Pump is presented on Figure 9.12.

Milton Roy has a pump similar to the Pulsafeeder Hypo Pump that also bypasses the gases and some liquid from the pump's head to prevent vapor locking. It is also controlled by a solenoid-operated flapper and a timer. Additionally, Milton Roy's Milroyal pumps with HPD diaphragms do not have a contour plate so they effectively operate similar to a tube diaphragm.

Jesco America Corp. has developed several features that reduce the effects of off-gassing by bypassing the gas or using tubular diaphragms. The diagram on Figure 9.13 indicates Jesco's electrically operated degassing valve, which it fitted to the outlet check valve of a diaphragm pump.

Peristaltic Pumps

Peristaltic pumps have recently become popular for metering sodium hypochlorite. They are of the positive displacement type, utilizing a flexible tube or hose inside a circular housing. The pumped liquid is pushed through the hose or tube by a rotor with shoes or rollers that compress (occlude) the tube against the inside wall of the housing as the rotor turns. Tube-type pumps are equipped with rollers that roll over the tube to provide the occlusion. Hose-type pumps are equipped with a sealed housing with shoes that slide over the tube using a lubricant such as glycerin. Tube-type pumps need no lubricant.

Various sizes of tubing or hose can be used for a wide range of flow rates. The speed of the rotor can be varied to adjust the output of the pump for a

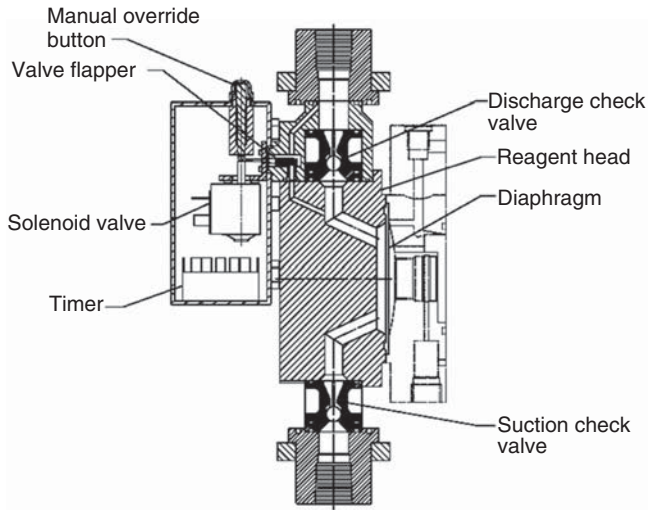


Figure 9.12. Pulsafeeder "Hypo Pump."

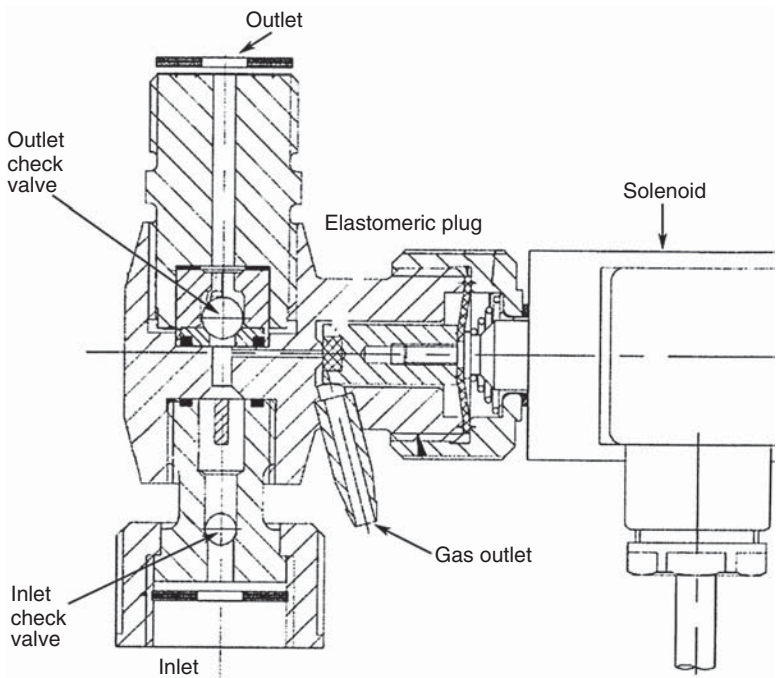


Figure 9.13. Jesco electric degassing pump head.

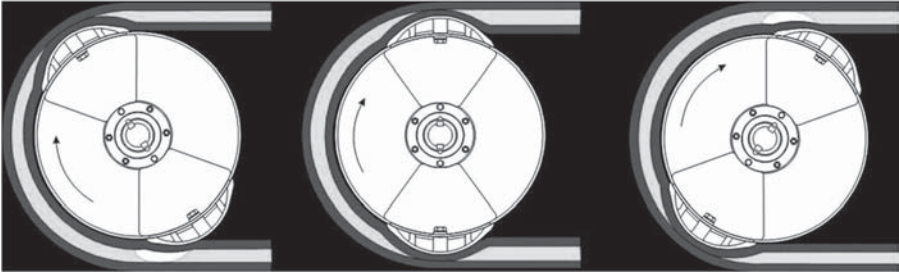


Figure 9.14. Peristaltic pump.

given tube or hose inside diameter (ID). A diagram that indicates the operation of a peristaltic hose pump is presented on Figure 9.14.

Unlike diaphragm pumps, the peristaltic pump does not require inlet and outlet check valves or contour plates. Lacking check valves that require suction and discharge stroking actions on an incompressible fluid, the peristaltic pump can pass liquid and gas bubbles with little problem. Accordingly, peristaltic pumps are not as vulnerable to vapor locking and off-gassing nor do they require additional piping appurtenances (backpressure valves, etc.) as do diaphragm pumps. Peristaltic pumps do not require a back pressure valve to keep a constant back pressure against the pump for positive check valve closure.

The long, continuous vacuum created by the rotor continuously draws liquid through the hose as the rollers or shoes evacuate it. The peristaltic pump has excellent suction lift capabilities. Some manufacturers boast of up to 30 ft of lift; however, at some point, the hose or tubing will collapse under near-vacuum conditions.

Tube Pumps. The tube pump is the smaller version of the peristaltic pump. The flexible plastic tube is available in diameters ranging from 0.5 to 25 mm, and in a variety of elastomeric and synthetic materials including, but not limited to, butyl, neoprene, marprene, and hypalon. Tube pumps are capable of metering flows ranging from fractions of a gallon per hour (gph) up to approximately 7 gpm. A photograph of a typical case drive tube pump is presented on Figure 9.15.

Turndown/Pressure Capabilities. Tube pumps are available with several types of drives. In the case drive, the motor is usually a “servo brushless direct current (DC)” motor integral to the pump case, with the pump controls mounted directly on the pump housing. The motors are generally capable of substantial turndown claimed to be 1000:1.

The discharge pressure of the tube pump is limited by the tubing material, generally to about 30 psi. Recently, heavier tubing elements have been developed to meet market demand, and specialty tubing elements can be found to provide a discharge pressure up to 100 psi, although there is a compromise



Figure 9.15. Case drive tube-type peristaltic pump.

to the output flow at this higher pressure because the integral servomotors are not as powerful as external motors.

Tube Failure. The fastest wearing component of the tube pump is the tube, which can be worn to the point of failure by the rollers, causing the pumped chemical to begin to leak. This is a major concern with sodium hypochlorite, which is corrosive to metals and concrete. In addition, sodium hypochlorite is often a critical chemical to the end users' process such as in water or wastewater disinfection.

An undetected tube failure on the suction side of the pump may cause loss of the entire tank contents, as chemical metering facilities are often unattended and may not be checked by operators for extended periods.

To alleviate this problem, many tube pump manufacturers offer leak detection devices. These are usually electronic-type leak detection devices that reside at the bottom of the pump housing where they detect aqueous liquids by a float or electric conductivity. The leak detection is often wired to an alarm that alerts operators to the need for investigating the problem upon early detection.

For most pumps, tube replacement is a simple task. The tube is typically held in the housing by a latching mechanism that quickly opens to release the tube. Upon releasing the latch, the tube can simply be replaced or the position of the tube can be moved so that different sections of the tube inside pump head. Tubing is often sold on rolls in various lengths up to 50 ft. The appropriate length of tube is determined and cut by the end user.

Hose Pumps. The hose pump is the larger version of the peristaltic pump. It is equipped with a thick multilayered rubber hose and can operate at

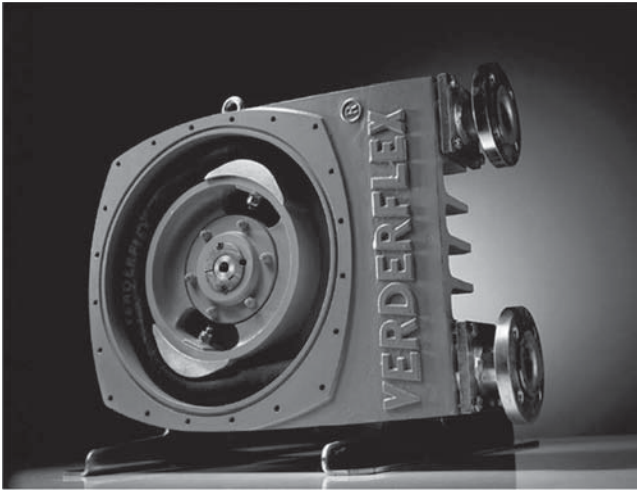


Figure 9.16. Hose-type peristaltic pump.

much higher discharge pressures than the tube pump. The hose is rated for burst pressures in the 600-psi range, which is often much higher than the piping used. Hose pumps are typically used for feed rates of 1 gpm and higher. Hose pumps are not applicable to fractions of a gallon per hour flows. Most sodium hypochlorite metering applications often need flows below 1 gpm at the low end. A photograph of a typical hose-type peristaltic pump is presented on Figure 9.16.

Electric Drives. Similar to the diaphragm pump, the hose pump is equipped with an external motor, either constant speed or variable speed. It does not include an integral control panel, thus an external control panel is required for the operator interface. The variable speed drives are limited in turndown capability. Most silicone controlled rectifier (SCR) drives are limited to 20:1 turndown from maximum speed. Standard adjustable frequency drives are limited to 10:1 turndown. Highly variable, adjustable frequency drives (AFDs) called vector drives are also available which are capable of 100:1 turndown.

Replacing the Hose. Hose replacement first involves draining the lubricant from the housing. The hose for each specific model of pump is of a fixed length with special end connections and must be purchased from the manufacturer. The hose at the pump's suction and discharge ends is held in place with clamping assemblies that must be removed. The pump motor is then activated to extrude the hose from the housing, and a new hose is lubricated and inserted into the pump housing while the pump motor is activated. The motor will pull the hose into the housing until it reaches the proper location and the motor

is deactivated. The clamping assemblies are replaced and the housing is refilled with lubricant.

Hose and Tube Life. The life expectancy of hose and tubes in peristaltic pumps is directly related to the number of occlusions. The number of occlusions depend on many factors such as rotor revolutions per minute (rpm), hose or tube diameter for a given flow rate, and the number of rollers or shoes. Additional factors include fluid abrasiveness and corrosiveness. Peristaltic pump manufacturers will often quote only a range of weeks or months for the lifetime of their tubes or hoses in continuous duty. A reasonable lifetime for hoses and tube in continuous service is 3–6 months.

In general, the most direct method of managing hose and tube wear is through pump rotor revolutions per minute. Most manufacturers of peristaltic pumps limit the maximum tube pump speed to about 200–275 rpm. The hose pump speed is usually limited to 70–100 rpm. If possible, to meet the required flow range, it is best to select a larger diameter tube or hose and to operate at a lower rpm than to select a smaller diameter that requires a higher rpm.

Liquid Dosing Systems

Some equipment manufacturers offer water-induced vacuum systems where high-pressure water passed through an eductor to create a vacuum. Sodium hypochlorite solutions are metered to the eductor through a liquid dosing device similar to the chlorine feeder used to meter chlorine gas. The liquid dosing unit utilizes an electromagnetic flowmeter and a specially modulated control valve operated by a servomotor, which continuously monitors the flow rate and continuously adjusts the valve position as needed. The unit operates with a controller to achieve a set point or to follow a continuous analog signal from a control system that is calibrated to the desired flow range. The flow of motive water remains constant.

This vacuum-operated system is impervious to the off-gassing and vapor locking problems encountered with diaphragm metering pumps. However, the motive water often contains alkalinity and hardness, which will induce scaling at the eductor where motive water and sodium hypochlorite mix. To resolve this, the manufacturers provide a carbon dioxide feed system that adds carbon dioxide to the motive water to counteract the elevation of pH caused by the sodium hypochlorite. The carbon dioxide system is an added cost item since it must be operated and maintained by plant personnel and the supply of pressurized carbon dioxide in portable containers must be periodically replenished.

The modulated valve and servomotor provide a more limited turndown than diaphragm and peristaltic metering pumps. In general, approximately 5-to-1 turndown is all that can be expected from these units with a reasonable degree of accuracy. However, because of their low power use, the liquid dosing units can be equipped with battery backup to operate for up

to 12h in the event of a power failure, provided that motive water is still available.

Motive water use can be an issue in areas where water is expensive or not available at the required pressure and flow rate. Often, motive water booster pumps are needed to supply sufficient water at a constant pressure. Although the water use rate is highly variable and depends on back pressure from the application point, a rough rule of thumb is 15 gpm of water per gallon of 12.5% sodium hypochlorite.

Because liquid dosing units utilize eductors, they are limited by back pressure from the application point. Typically, most eductors are limited to 15–20psi of back pressure. Beyond this back pressure, the water flow rate and pressure become excessive and often require special eductors that utilize high inlet pressures. High operating pressures may preclude the use of thermoplastic piping and require piping of exotic metals.

The liquid dosing units are considerably more expensive than diaphragm or peristaltic metering pumps.

SODIUM HYPOCHLORITE PIPING

Many types and materials of piping are available for sodium hypochlorite. The criteria for selecting sodium hypochlorite piping materials include the following:

- chemical resistance,
- structural and mechanical properties,
- temperature limits,
- installation and joining method, and
- cost.

Most metals are not compatible with sodium hypochlorite, which precludes the use of carbon steel, stainless steel, copper, aluminum, and other metals unless the piping interior is lined with a chemical-resistant material such as PVC, CPVC, Teflon, or glass.

In evaluating piping materials, pipe size, operating pressure, temperature, and connection methods must be considered because they are interrelated. Higher temperatures increase the corrosion rate of metals and decrease the pressure ratings of thermoplastic resins.

The pressure rating of a given piping material is dependent on temperature as well as on the nominal pipe size. In general, metallic piping has a much higher pressure rating than thermoplastic piping materials. For example, at 73°F, a 1-in. socket-end Schedule 80 thermoplastic pipe such as CPVC has a pressure rating of 630psi. At 100°F, the same CPVC Schedule 80 thermoplastic pipe is limited to 390psi. While these may sound like relatively high pressure ratings, the valves, fittings, flanges, and unions of the same

thermoplastic materials (which are required in a piping system) are rated at only 150psi. Therefore, the effective pressure limits of thermoplastic piping materials at ambient conditions is 150psi.¹¹

The method of connecting joints and fittings is important to consider from the standpoints of the potential for leaks, personnel safety, maintenance, and the ease of installation and replacement. A number of joining methods are available, including flanged, socket welded (both metal and plastic), thermofusion, or threaded.

Flanged connections require a gasket for sealing the flanges. The flanged connection uses (four or more) bolts that point-load force onto the gasket to make a seal. Overtightening or uneven tightening of the bolts can distort the flange and result in a poor seal or fracture the flange. Plastic flanges must be joined by metallic bolts, nuts, and washers, which can easily be overtightened, causing the plastic flanges to crack and gaskets to fail or leak more readily than thermofused or solvent welded joints. Therefore, flanged joints should be used only where absolutely necessary to facilitate disassembly such as at pump inlet and outlet connections and tanks nozzles.

Titanium is the only suitable metal for long-term contact with sodium hypochlorite. Metallic socket-welded pipe joints are the best for chemical service because they have the lowest potential for leaks; however, welded metallic pipe is the most rigorous to perform because welding of metallic piping involves joining two sections of piping together using extreme heat generated by electric arc welding. Once formed and cooled, socket-welded joints are structurally very strong. Metallic piping is generally provided with socket ends for 2 in. and smaller sizes. Pipes of larger sizes are provided with butt-welded ends beveled for effective penetration by electric arc welding. Valve connections in titanium piping must be flanged and installed after the piping has been welded and cooled because the valve seats are often of synthetic rubber or Teflon, which would be destroyed by the heat of welding. Alternatively, some metallic valves are of three-part construction so that their socket ends (or butt ends) can be removed for welding. However, in these valves, the welded end of the piping is attached to the valve body by a bolted O-ring-style connection, which offers another opportunity for leaks to develop.

For thermoplastic piping such as PVC and CPVC, solvent-welded joints are commonly used because they are the easiest to install and are least likely to leak when compared with other joining methods such as threaded or flanged connections. In this type of connection, each segment of pipe is manufactured with a male end and a female end, fabricated in close tolerance so that the male end will insert into the female socket with space sufficient for solvent cement. Before assembly, the pipe and socket interior are treated with a primer, and after the primer has dried (a few seconds), solvent cement is applied around the pipe exterior and socket interior. The two ends are immediately joined and held in place until the solvent cement is solidified. However, the solvent cement may require up to 24 h of curing before exposure to sodium hypochlorite solution depending upon the temperature.

Thermofusion welding is used on polypropylene, polyethylene and PVDF piping. Thermofusion welding of plastic pipe is somewhat easier than metal welding since the melting-point temperature of plastics is much lower than that of titanium. In both cases, the same concept is followed, using heat to melt the two pipe ends together. Once the ends are heated, two pipe ends are fused together while still molten and allowed to cool and solidify to form a joint. However, to make a stable joint, thermofusion welding requires a trained pipe joiner and special heating equipment. Because the joints are heat-fused, valves and appurtenances must be connected by flanged ends, which are also heat-fused. Flanged connections provide an opportunity for leaks through flanges or gaskets. Both metallic and thermofusion welding are more difficult and considerably more costly than solvent welding.

Threaded connections in all piping materials are difficult to make leak-proof. In thermoplastic piping, threads also lower the pressure rating of the pipe because threading reduces its wall thickness. Because of the high potential for leaks, the use of threaded connections is not recommended. For comparison with the pressure ratings of CPVC pipes described earlier, a threaded Schedule 80 CPVC piping has a maximum pressure rating of 320 psi compared with 630 psi of a socket-welded pipe.

The most costly material is not necessarily the best choice for a particular application. The cost of a material should therefore be evaluated against its projected benefits and service life.

The materials most frequently used with sodium hypochlorite include PVC, CPVC, lined steel, FRP pipe, hastelloy, and titanium.

While sodium hypochlorite degradation is very slow, it cannot be stopped even under ideal conditions. Regardless of the material, the piping system must include pressure-relief valves at locations where the sodium hypochlorite could be trapped between valves or equipment, even where such valves or equipment may be normally open or operating.

Thermoplastic Piping (PVC and CPVC)

PVC is the most common of all thermoplastic piping materials. PVC pipe is joined by solvent cementing, threading, or flanging. Chemical resistance data on PVC to sodium hypochlorite are not consistent among pipe manufacturers, but most of them agree on a temperature limit of 140°F. In many southern and arid regions, where piping is exposed to direct sunlight, even if painted for protection against UV, the temperature can easily exceed 140°F. In these instances, consideration must be given to insulation to prevent the piping material from reaching 140°F.⁸

The maximum temperature for CPVC sodium hypochlorite service is 180°F. Chemical resistance data on CPVC regarding sodium hypochlorite are not consistent among manufacturers, but most resin and pipe manufacturers agree on a temperature limit of 180°F. This tolerance to high temperature indicates that CPVC pipe needs no insulation even in direct sunlight.⁸

Regardless of the temperature limits, the chemical resistance of PVC and CPVC is essentially the same. The differences between the two plastics lie in their basic physical properties, including the following:

- CPVC is 12% denser.
- CPVC has a 6% greater tensile strength.
- CPVC has an 8% greater flexural strength.
- CPVC has greater resistance to UV light.
- CPVC maintains its strength at a much higher temperature.

Both PVC and CPVC have traditionally been used in sodium hypochlorite chemical service. Both have excellent chemical resistance. However, CPVC is generally preferred over PVC for higher temperature ranges. In high-temperature applications, CPVC pipe is recommended over PVC because of its greater strength and higher temperature ratings with a relatively small increase in cost.

The difference between the two materials chiefly lies in the service temperatures to which they are suited. CPVC retains its chemical resistance to sodium hypochlorite and greater strength up to temperatures of 180°F. PVC retains its chemical resistance to sodium hypochlorite (but less strength than CPVC) up to temperatures of 140°F. In most materials, rigidity and ductility are trade-offs, and CPVC and PVC are no different. The molecular properties that give CPVC a higher service temperature rating also make it more rigid and less ductile than PVC. This increased rigidity and decreased ductility results in a material that is stronger, but may be more susceptible to impact and stress failures. For most cases, the best plastic pipe material for sodium hypochlorite service will be either PVC or CPVC, with CPVC having a higher strength at elevated temperature.⁸

UV radiation from the sun causes unprotected thermoplastic to become harder and more brittle. Much like steel, as thermoplastic pipe hardens, it becomes more vulnerable to fracture under stress. The physical property degradation of CPVC is minimal, whereas PVC is more significant. To protect thermoplastic pipe from sunlight, it should be coated with a UV-blocking paint (opaque latex paint suitable for outdoor use is acceptable).

Although thermoplastic piping has good resistance to sodium hypochlorite, the chemical industry does not normally use it for sodium hypochlorite service because of safety concerns associated with its low mechanical and structural strength. Where temperatures can exceed 150°F, CPVC is recommended because of its higher temperature resistance, better mechanical properties, and ease of installation, as well as its lower cost than FRP, titanium, or lined steel pipe.

Thermoplastic Solvent Cement. Use of inappropriate solvent cement on thermoplastic piping for sodium hypochlorite can cause problems and has been the cause of many sodium hypochlorite piping leaks. Solvent cement consists

of a small amount of the thermoplastic material (in this case CPVC) dissolved in a solvent. Fillers are often added to give the cement desirable flow properties (thixotropic agents). The most commonly used thixotropic agent is an expanded silicon dioxide. However, sodium hypochlorite attacks expanded silicon dioxide, which causes leaks at solvent-welded joints. Special solvent cements are available that lack the thixotropic agent as manufactured by IPS and Oatey. These special solvents consist of only CPVC and the suspending solvent.⁸

Pipe Supports. Most plastic pipe has low mechanical strength, and thus needs closely-spaced structural supports. The pipe supports should be of the sliding type to prevent lateral movement but to allow axial movement from thermal expansion. Rigid pipe supports should be used only at anchor points. None of the pipe supports should clamp down tightly on the pipe, as this would cause localized stress, which can lead to brittleness and fracture. Heavy items such as control valves and flowmeters should be supported separately from the piping.⁸

Lined Steel

With the proper liner, lined steel can have excellent resistance to sodium hypochlorite and a service life of 20–30 years.² However, lined steel piping for used chlorine or sodium hypochlorite (especially in high-pressure applications) should be periodically inspected for corrosion damage on the exterior. Common liner materials are PVC, CPVC, Teflon, Tefzel, Halar, and various rubbers.

Lining of steel piping is a difficult process. Because of the difficult accessibility restrictions inside small-diameter piping, the interior lining must be applied by the fabricator using special equipment. Lined pipe cannot be field applied or repaired during or after installation. All lined steel pipes must be shop-fabricated and joined by flanged connections to protect the future piping assembly from corrosion. Lined steel pipe can not be field-welded because of heat damage to the lining. Additionally, threading of steel pipe will also destroy the lining in the area of the connection so that unprotected steel will be exposed to sodium hypochlorite. All lined steel piping segments must be fabricated, flanged, and lined off-site in sections of specific length and shipped to the jobsite.⁸

In order to deliver piping and appurtenance of appropriate length to the site, detailed isometric or three-dimensional engineering layout drawings indicating exact piping segments and appurtenance locations must be generated prior to fabrication of the pipe. In a complex system, this effort can require a great deal of engineering and technician labor to generate the drawings and provide a numbering system for each segment. As a result, there is a considerable schedule delay and expense involved in this effort when compared with

field-cut and fabricated piping systems. Unlike lined steel, thermoplastic piping systems are generally field-fabricated.

As pointed out earlier, it has recently been observed that chlorine in sodium hypochlorite will slowly permeate most plastics and thermoplastics. While this permeation is slow, it can have detrimental effects on the exterior steel structural piping because chlorine, when wet, is very corrosive to steel.

FRP Piping

FRP can be highly resistant to sodium hypochlorite as discussed in the section on FRP tanks; therefore, FRP piping is often used in corrosive environments and for underground applications. However, to make it resistant to sodium hypochlorite involves the use of special resins, fabrication techniques, and curing procedures.⁸

FRP piping is not widely used in sodium hypochlorite service. FRP piping is fabricated in standard lengths, and field joining involves using virgin resin material similar to that used in pipe fabrication. While the resin is easily applied in piping joining, the BPO/DMA procedure and 4-h 180°F postcure to make the joint resistant to sodium hypochlorite is not always practical in the field.

FRP-Armored Piping

FRP-armored piping consists of FRP as the outer structural layer and with CPVC as the interior corrosion-protective layer. This pipe has a considerably higher pressure rating than ordinary CPVC pipe. FRP-armored pipe eliminates the need for the special BPO/DMA processing and postcuring because the solution is not in direct contact with the FRP. The pipe is joined by solvent welding the inner CPVC layer, overlaying the joint with fiberglass, and bonding it with resin to fabricate the outer layer of the joint. The installation of FRP-armored piping is more labor intensive, and thus more costly, than installation of CPVC piping.

A disadvantage of FRP-armored piping is that it is available only within flanged valve connections, and the valves must be CPVC because FRP-armored valves are not available. Therefore, any advantage associated with the higher pressure rating of this pipe is lost since Schedule 80 CPVC valves are rated only to 150 psi. Consequently, use of FRP-armored piping is very uncommon.⁸

FRP or FRP-armored piping could use FRP or composite valve materials. These valves are available in full port and drilled balls for sodium hypochlorite service.

Titanium

Titanium has excellent resistance to sodium hypochlorite. It offers the advantages of metallic piping, which include structural strength and impact

resistance as well as a very high pressure rating that makes it useful for high-pressure sodium hypochlorite applications where thermoplastic piping is not suitable.

Titanium is the only piping material that has a rated life expectancy of 30 years or longer in sodium hypochlorite service. However, it is a rare elemental metal and is very expensive.

Titanium piping is joined by socket welding. Titanium must be provided with adequate and carefully designed expansion joints. A titanium piping system should also be equipped with titanium valves, which, however, are not readily available.

HDPE

HDPE piping is available in a variety of sizes and wall thicknesses. It is corrosion resistant and is widely used in water distribution for buried applications. HDPE piping is joined by thermofusion whereby the ends of the sections of HDPE piping to be joined are melted using a heated plate.

Pure HDPE is compatible with sodium hypochlorite, which makes it a suitable tank material. However, additives are necessary for pipe fabrication to make the piping malleable. The additives are often attacked and oxidized by sodium hypochlorite. Published information on the compatibility of HDPE piping with sodium hypochlorite is inconsistent among pipe manufacturers. Some indicate satisfactory resistance; others indicate limited resistance rating at 73°F and not recommended ratings at 140°F.

To resolve the differences of opinion by the various manufacturers, the organization called Plastic Pipe Institute (PPI) was formed. PPI generated chemical compatibility charts in agreement with the manufacturers. These charts indicate that HDPE piping is not recommended for use with commercial sodium hypochlorite of 12.5% trade concentration. It may be suitable for use with lower concentrations of sodium hypochlorite solution, but this should be verified with the pipe manufacturer.

PVDF

PVDF piping is joined by thermofusion, thus the valves connected to the piping must be flanged. PVDF has a higher thermal expansion coefficient than CPVC and much lower mechanical strength. A properly designed PVDF piping system will require more structural pipe supports and expansion loops or joints than thermoplastic piping.⁸

PVDF piping is generally considered to be very chemical resistant; however, the resistance varies depending on the resin used in manufacturing the pipe. The supplier of PVDF piping should be consulted for compatibility data on sodium hypochlorite. The PPI compatibility chart indicates that PVDF is suitable for sodium hypochlorite at temperatures up to 68°F.

Polypropylene (PP)

PP piping is not commonly used for sodium hypochlorite service. PP piping, like HDPE and PVDF, is joined by the thermofusion process. PPI compatibility charts do not indicate compatibility data for PP piping in sodium hypochlorite service.

Hastelloy

Hastelloy has limited chemical resistance to sodium hypochlorite solutions. Additionally, it contains high concentrations of nickel, which is known to catalyze the degradation of sodium hypochlorite; however, hastelloy piping is used in some sodium hypochlorite applications. It is more readily available than titanium piping and is often less expensive.

In high-pressure applications where sodium hypochlorite must be injected into the process at pressures above 150 psi, hastelloy piping can be a viable option. As the sodium hypochlorite is continuously moving through the piping, its contact time with nickel content is relatively short; thus, the degradation loss inside the piping is negligible.

The pressure rating of hastelloy piping at ambient temperatures is adequate for most applications and far exceeds that of thermoplastic or plastic piping. Hastelloy is commonly joined by electric arc socket welding, which produces excellent piping joints that will remain leak free for many years. Hastelloy valves are readily available.

Hastelloy piping should only be used as a last resort in high-pressure applications where other piping materials are unsuitable or impractical. It should not be used for construction of sodium hypochlorite tanks because of the long contact time with the nickel content.

Gaskets, Seals, and O-Rings

According to chemical manufacturers, gasket manufacturers, and valve manufacturers, few materials are suitable for gaskets, seals, O-rings, and diaphragms in sodium hypochlorite service. Natural rubber, as well as many rubberlike elastomeric materials, including Nitrile and Buna N (NBR), should not be used. Ethylene-propylene-diene (EPDM) has shown limited resistance to sodium hypochlorite at ambient temperatures; however, at elevated temperatures, such as in tropical and desert climates, EPDM is not considered resistant.

Appropriate materials for sodium hypochlorite service are fluorocarbon and fluorosilicone materials, which include Viton (FKM), fluorosilicone (FVMQ), Kalrez, and Teflon. While Teflon has excellent chemical resistance to sodium hypochlorite, Viton and Kalrez are better suited as gaskets for plastic pipe flanges because they are softer and more pliable, which results in a better seal. The high torque needed to compress Teflon is likely to fracture

plastic pipe flanges; therefore, Teflon gaskets are not recommended for plastic flanges.

Viton. Viton is one of the most widely used elastomers in the world. It has good resistance to abrasion and tearing and it tolerates a wide range of temperature. However, it has a tendency to swell when exposed to hypochlorite; and over time, this swelling can lead to a need for high torque to open and close the ball valves. Nevertheless, Viton is still recommended most frequently for flange gaskets and O-rings in sodium hypochlorite piping. The end user should be aware that there are many formulations of Viton so it is imperative to check the resistance of the formulation used.

FVMQ. Fluorosilicone is another seal material that is resistant to sodium hypochlorite. It is not as widely used or as recommended as Viton because of its poorer abrasion resistance and lower mechanical strength. The cost of fluorosilicone is similar to that of Viton.

Kalrez. In Kalrez, the elastomeric properties of Viton are combined with the chemical resistance of Teflon to yield a unique material resistant to most chemicals. Kalrez has a lower permeability to sodium hypochlorite and thus has a lower swelling rate than Viton. Kalrez is recommended for use in sodium hypochlorite service if Viton proves unacceptable. The key disadvantage of Kalrez is its cost. For example, a single Kalrez O-ring has a higher cost than the entire valve assembly with a Viton O-ring.

Teflon. Teflon has good resistance to sodium hypochlorite at various concentrations and over a wide temperature range. In addition, Teflon is less expensive than other elastomers. However, Teflon does not have sufficient flexibility for many service applications. Teflon is often used as valve seat material

SODIUM HYPOCHLORITE VALVES

The correct type of valves is essential for proper operation of the sodium hypochlorite system. There is a wide variety of valves available with ball valves, plug valves, and diaphragm valves being the most widely used. These valves can be joined to the pipe by a variety of connections, including flanged, socket welded, solvent welded, and threaded.

Another type of valve connection is the true union connection, which is a three-part valve in which the valve body can be removed from the piping system by union connections. The piping end is connected to the valve by variable means such as socket ends, threads, or flanges. The union connection is a threaded union using an O-ring for a seal. Unlike the flanged connection, the union-type connection allows uniform compression of the O-ring around its entire circumference. Operators and maintenance staff like the true union

connection because valves can be easily removed and replaced without altering the piping. A photograph of a true union-type ball valve specifically for sodium hypochlorite service is shown in Figure 9.17.

Valves should be of materials similar to the piping material in which they are installed. For most low-pressure applications, the materials of choice are PVC or CPVC. With the exception of the valve seat, O-rings, and the stem sealing system, all components in contact with sodium hypochlorite can be expected to be manufactured from either PVC or CPVC.

Ball Valves

By a considerable margin, ball valves are the most commonly used isolation valve in chemical service. The ball valve is operated using a handle with only a 90° turn. When the valve is open, the ball valve provides a straight-through flow of process fluid, resulting in very little friction loss (pressure loss; often called headloss) through the valve. Ball valves can be specified as “full port” ball valves. The full port simply means that, for a given nominal pipe size, the interior diameter of the ball is the same as the ID of the corresponding pipe diameter. Therefore, the valve itself provides effectively no constriction of diameter.

The major manufacturers of ball valves include Asahi America, Hayward, Nibco Chemtrol, and Spears. Most manufacturers offer several models of their



Figure 9.17. Ball valve.

valves. Spears manufacture three different true union ball valves. Regardless, each manufacturer offers ball valves with nearly the same features, including threaded-end or solvent-weld true union ends as well as valves with spigot ends and flanged ends. Each offers the full port option as well. The valves are rated for pressure applied in either direction, a feature sometimes called “true block.” Each valve manufacturer’s product may also incorporate minor differences, such as an elliptical ball, number of O-rings on the valve stem, or a floating seat. All manufacturers rate the nonshock working pressure of their valve at least 150psi.

Spears also provides the “SR” series ball valve, which incorporates a stainless steel reinforcing ring around the threaded end connections in order to prevent over stressing the threaded connection due to overtightening. In this case, the Spears valve has a rated working pressure of 235psi.

In recent years, it has been recognized that there are problems using ball valves in sodium hypochlorite service. Most plastic ball valves are provided with a Teflon seat that services as the sliding seal between the ball and valve body. The seat is not continuous (it does not extend through the entire valve body) because the contact area between the ball and the seat would be too large, which would result in excessive friction when the valve is being operated. Therefore, the valve is designed with a cavity between the body and the ball inside the valve where sodium hypochlorite can be trapped. Because sodium hypochlorite degrades to form oxygen gas, the trapped sodium hypochlorite between the body and ball can continue to generate oxygen and increase the pressure inside to the point of catastrophic failure. See cutaway diagram of a ball valve in Figure 9.18.

Some end users and producers of sodium hypochlorite have experienced ball valves exploding from the tremendous accumulation of pressure. To avoid

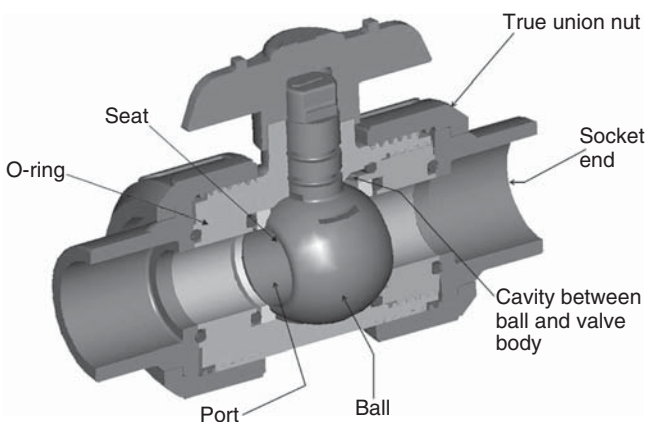


Figure 9.18. Ball valve cutaway.

this, ball vents can be “vented” by drilling a small-diameter hole in the ball on the upstream side as shown in Figure 9.17. If drilled only through one side of the ball, this hole does not impact the valve’s ability to shut off flow when closed. It is recommended that this hole be drilled by the valve manufacturer, not the end user. Care must be taken in drilling the hole so that it can be “deburred” in a manner that will not later damage the valve seat when the valve is operated. Damaging the seat could result in leakage across the valve and in difficulty in operating the valve. This is especially true with metallic valves since the drilling burrs are metal shavings that would easily damage the Teflon seats.

Sodium hypochlorite contains sodium hydroxide for pH stability. Sodium hydroxide has a tendency to precipitate and leave a crusty residue, which may appear inside the ball valve at the interface of the sliding ball and seat. The resulting friction can make the valve very difficult to operate. In some instances, operators have broken the handles and/or valve stems in attempts to open or close the valve. Drilling the ball for venting reasons does not remedy this problem. For this reason, it is imperative that the valves have true union connections so that a malfunctioning valve can be easily removed for cleaning or replacement. It is recommended that ball valves (even true union ball valves) not be used on tank outlet nozzles where shutoff can be critical and where the valve cannot practically be removed without draining the tank.

The valve manufacturer should be consulted on the materials available for seats and O-rings. In general, Teflon seats and Viton O-rings have proven to be the most resistant to sodium hypochlorite. However, recent formulations of EPDM have been shown to be equally resistant.

Regardless of the type of valve used with sodium hypochlorite, it should be carefully examined to ascertain that its construction will not allow sodium hypochlorite to become trapped.

Diaphragm Valves

Diaphragm valves incorporate a horizontal flat flexible diaphragm and a vertical ridge (or weir) molded into the body of the valve. The valve is operated by turning a handwheel that raises and lowers the diaphragm. A photograph of a diaphragm valve is on Figure 9.19, and a diagram is presented on Figure 9.20.

Unlike the ball valve that is opened and closed by a quarter-turn of the handle, the diaphragm is opened and closed by multiple turns of the handwheel. However, the diaphragm valve does not have an unvented cavity that can trap sodium hypochlorite. It is also not affected by precipitation of crystalline sodium hydroxide because it has no internal sliding surfaces where a precipitate can interfere. For this reason, the diaphragm valve is often used on sodium hypochlorite systems.

In the construction of a diaphragm valve, the components in contact with the process fluid include the inlet and outlet ports, the lower body housing



Figure 9.19. Diaphragm valve.

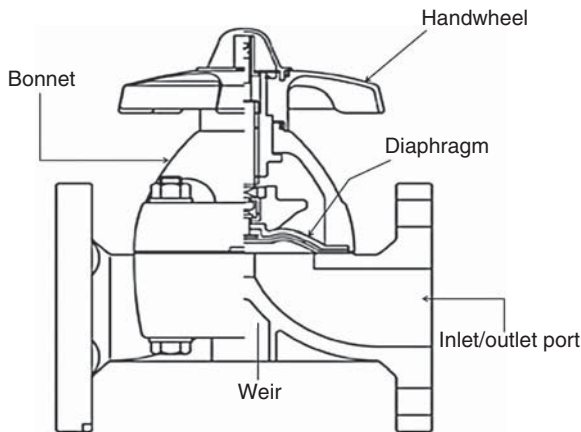


Figure 9.20. Diaphragm valve internals.

and the underside of the diaphragm. The construction materials available are similar to ball valves, which are PVC, CPVC, PP, and PVDF. Available valve ends include flanges, true unions, sockets, and threaded. Most manufacturers rate the working pressure of their valves between 150 and 235 psi.

The diaphragm material is critical to successful application with sodium hypochlorite. Diaphragms materials range from natural rubber to Viton

rubber; the material most commonly used for sodium hypochlorite service is either Teflon or Viton. The disadvantages of Teflon are inflexibility and material creep. However, Teflon is inherently inflexible, which makes for a fundamentally difficult application to a diaphragm valve where flexibility is crucial. Teflon will also tend to be slightly malleable such that it will experience material creep. Creep occurs when chronic stresses on certain areas of a Teflon diaphragm thin the Teflon material in one location and thicken in another. Such distortion will result in a poor seal between the diaphragm and the weir.

While Viton is considered to be resistant to sodium hypochlorite, it is not suitable for the high stresses involved in stretching the diaphragm during opening and closing. Pure Viton diaphragms are not recommended for sodium hypochlorite service.

To provide both chemical resistance and flexibility, manufacturers of diaphragm valves recommended a two-part unbonded diaphragm material. Most manufacturers recommend a Teflon exterior and an EPDM backing for sodium hypochlorite service, which can be of one-piece or two-piece construction. A one-piece diaphragm is produced by etching the EPDM backing followed by Teflon bonding, and is subject to delamination when the bonds between the Teflon and EPDM layers are broken. One theory claims that chlorine in the sodium hypochlorite permeates through the Teflon and attacks the EPDM backing, causing the delamination.

A two-piece diaphragm consists of two separate diaphragms—one Teflon and one EPDM, which are not bonded allowing the Teflon room to creep and the EPDM room to swell. Typically, in a two-piece diaphragm, the Teflon layer is thicker than in one-piece diaphragms. As a result, the diffusion of chlorine across the Teflon diaphragm is slower.

The shape of the diaphragm can either be close molded or open molded. Looking from the top of the valve, an open-molded diaphragm is convex, while a close-molded diaphragm is concave. A close-molded diaphragm is better for EPDM-backed Teflon diaphragms as it requires the Teflon to flex less, which results in less creep.

Unlike the ball valve, most diaphragm valves have a removable top portion called a bonnet. Removal of the bolts and the bonnet will provide access to the diaphragm. Effectively, nearly all of the valve internals can be removed and replaced by the removal of the bonnet. For this reason, it is not imperative that true union connections be used to facilitate complete valve removal. It is recommended, in thermoplastic piping, to use non-true union socket (solvent)-welded ends on diaphragm valves with removable bonnets because the socket end is much less likely to leak than the true union connection.

Diaphragm valve design provides for effective flow throttling if desired by the service conditions. A valve body configuration effective for throttling service will also introduce more headloss into a piping system than a ball valve even when completely open. Compared with a full port ball valve, a wide-open

diaphragm valve would be considered substantially obstructed. Considerably more headloss will be introduced if the valve is inadvertently left partially closed. The higher headloss through diaphragm valves could reduce the output of existing pumping equipment. Consideration must be given to piping hydraulic calculations when diaphragm valves are used or when ball valves are replaced with diaphragm valves in an existing system.

SODIUM HYPOCHLORITE FACILITY LAYOUTS

Critical to the success of the sodium hypochlorite system is a layout that allows sufficient space for access and maintenance. A properly designed layout can effectively eliminate the off-gassing and vapor locking. Developing the layout of any chemical feed facility should begin with an understanding of the conceptual design and size of the equipment. The layout must be sized to contain all the tanks and equipment so it is critical to understand the quantities of equipment before developing a layout. A designer should determine the number and size of storage tanks (diameter and height for vertical tanks; diameter and overall length for horizontal tanks) in consideration of the typical delivery volume and the anticipated 30-day average usage.

A designer must also determine whether transfer pumps and day tanks are needed. Often, water plants require a day tank to contain an average day's supply. Day tanks are typically filled daily by manually initiated transfer pumps. Metering pumps feed from the day tanks. Day tanks are intended to help monitor chemical usage and prevent overfeed to the water treatment process by limiting the volume of chemical available for feeding. In general, each chemical application point should have a dedicated metering pump.

Space must also be allocated for at least one safety shower/eyewash station in the sodium hypochlorite containment area at least 5 ft from any electrically operated equipment or control panel to prevent electrical shock.

It is highly recommended that all the chemical storage, transfer, and metering equipment be located inside the containment area. It is therefore critical to understand the conceptual design first in order to properly size the containment area. The following diagram is an example of an improper layout where the pumps are located outside the containment area with inadequate containment (Fig. 9.21).

Elevation Differences

In liquid pumping terminology, a design where the transfer or metering pumps are placed at an elevation higher than the bottom of the withdrawing tank is called a suction lift design/arrangement. In some applications with water or other chemicals that do not off-gas, suction lift can be successfully accomplished if careful consideration is given to the design parameters in

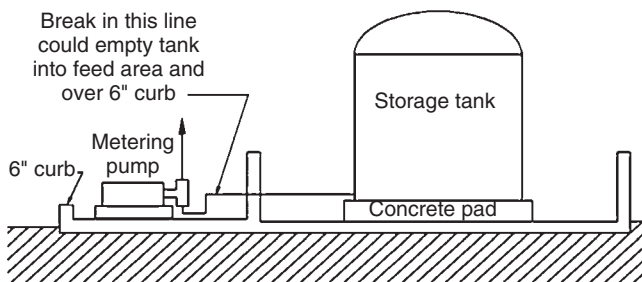


Figure 9.21. Improper layout—pump outside tank containment.

comparison with the equipment's capabilities. However, because sodium hypochlorite has a strong tendency to off-gas, suction lift designs/arrangements should never be attempted. A sodium hypochlorite facility often includes concrete bases for tanks and metering pumps structural bases and a superstructure to cover the installation. Once it is constructed, it cannot easily be modified to correct design errors.

Designs employing such a suction lift arrangement simply will likely be problematic and dissatisfactory to the end user for a number of reasons. Early designs of sodium hypochlorite systems attempted to employ suction lift with sodium hypochlorite only to determine later that the pumps will only draw liquid down in the withdrawing tank to an elevation equal to the pump centerline. Storage capacity in the tank below this elevation remains unused and oftentimes serves only as a repository for aged sodium hypochlorite containing significantly degraded hypochlorite and an excess of undesired chlorate ions. As previously discussed, it is desired to completely empty sodium hypochlorite tanks prior to refilling.

Many facilities have sodium hypochlorite storage tanks sized slightly larger than bulk truck delivery of approximately 4500 gal. If the storage tank cannot be completely emptied because of a suction lift design arrangement, the facility often cannot receive a full shipment of new sodium hypochlorite because the tanks are still partially full. Regardless of their ability to accept a full truckload, end users are charged a full transportation fee for a partial shipment. Chemical delivery services resist delivering partial loads because partially full tanker trucks are difficult to drive, as partially full tanks allow liquid to slosh from one end to another. In addition, some chemical delivery companies impose a secondary partial load fee to the end users to discourage partial truck loads.

In designs where the metering pumps are located at an elevation higher than the tanks, off-gas bubbles can form in the suction piping between the tank and the pumps. Gas bubbles will rise to the highest point possible. If the metering pumps are the highest point, gas bubbles will tend to accumulate at the pump head. For diaphragm pumps, these bubbles are the root cause of

vapor locking problems. In a properly designed system, the tank's bottom is located higher than metering pumps to provide flooded suction to the pumps at all tank levels and the suction piping is sloped to allow developed bubbles to travel back to the storage tank instead of to the metering pumps.

Tank and Pump Bases

Building and fire codes will require secondary containment for tanks with capacity exceeding 500 gallons. Often, this is accomplished by using a concrete containment area surrounding the storage tank and equipment. The depth of the containment area is a function of tank size (plus sprinkler volume or rain-fall) and the lateral area provided for the sodium hypochlorite system. Typically, depth of containment areas ranges from 2 to 5 ft.

A containment area can be built in two basic designs. First, the containment area can be a recessed concrete area below the surrounding grade. This is often done when sodium hypochlorite systems are located indoors. Alternatively, a slab can be poured at grade level and containment walls can be erected around the perimeter of the slab to form a containment area. This is often done when sodium hypochlorite systems are located outdoors.

In both cases, it has been very common for engineers to pour 6-inch concrete housekeeping pads inside the containment area for tanks and equipment. In such an arrangement, a leak event could fill the containment area up to the top of the containment wall with spilled chemical. As a result, complete submergence of the transfer and metering equipment can occur. Complete submergence of electrically powered equipment in a corrosive chemical such as sodium hypochlorite can easily destroy thousands of dollars of equipment. This design is not recommended (Fig. 9.22).

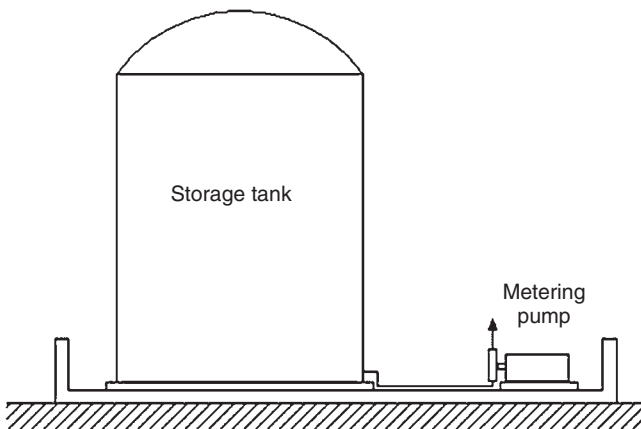


Figure 9.22. Improper layout—pump subject to flooding.

The simplest design to avoid such a catastrophe is to place the tanks and equipment bases at an elevation equal to the containment wall height or depth. This design provides an equal elevation for tanks and pumps to prevent suction lift arrangements. In addition, this design prevents submergence of electronic equipment. The diagrams presented in Figures 9.23 and 9.24 are examples of proper layouts.

For permanent installation and safety, tanks and rotating equipment must be anchored to a suitable base to prevent movement. Tank and equipment bases should be larger than the equipment bolted to the base. It is recommended that vertical tank bases be sized a minimum of 1 ft larger in diameter than the tank itself. The additional 6 inches of concrete is necessary for anchor bolts. Structural engineers often recommend that anchor bolts be

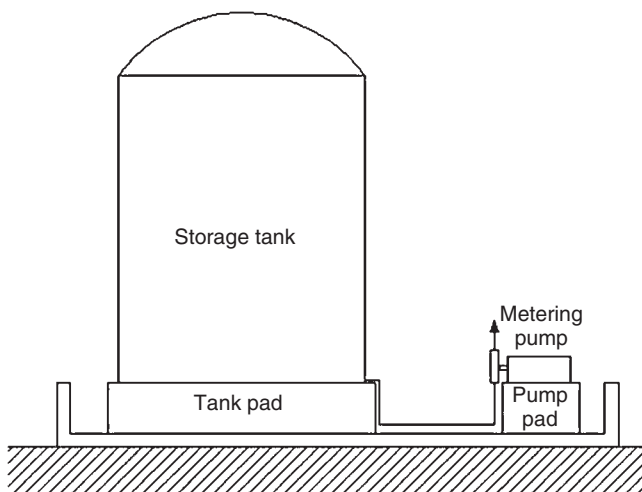


Figure 9.23. Preferred layout—tank and pump out of containment.

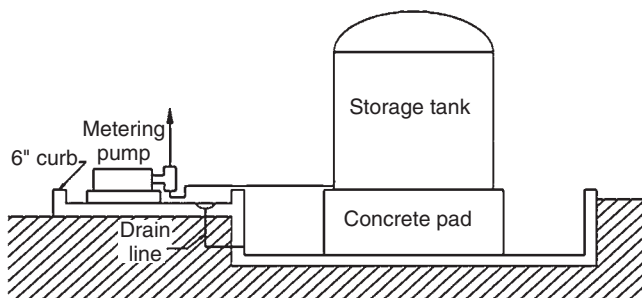


Figure 9.24. Proper layout.

drilled into concrete bases no less than 4 in. from the edge of the concrete. Additionally, anchor bolts should be installed inside the outward run of reinforcing rebar in the concrete base. Adherence to this standard will ensure the bolts do not fracture the concrete at the edges and result in chunks breaking off of the edge of the pad. Loss of concrete around the anchor bolt is a complete loss of the anchoring system. In highly seismic areas, additional anchoring systems may be required, which would require even larger bases of up to 2 ft larger than the tank diameter. A licensed structural engineer should be consulted in that area for tank and equipment base system requirements.

Access and Clearances

In general, there should be 3 ft of clear space around the entire perimeter of the tank base to allow for sufficient ingress and egress in the event of an emergency. Unless unavoidable in retrofit designs, tanks should not be backed into corners or against walls creating dead ends that preclude egress. Other considerations are sumps, sump pumps, platforms, building columns, and safety equipment.

All rotating and mechanical equipment will require periodic maintenance and repair. It is important to provide adequate spacing between and around equipment to allow for operator access and even equipment removal. Tanks and pumps of all types have a finite lifetime and will eventually need to be replaced. It is important to keep in mind that piping and valves must also reside in this area, and access should be clear so that maintenance can be accomplished without removing or damaging the piping. This is especially important for thermoplastic piping which is easily damaged and cannot support the weight of an average human. A layout should allow sufficient room for operator maintenance without the risk of damaging piping, valves, or other equipment during the routine maintenance.

As a rule of thumb, it is recommended to maintain at least 3 ft of centerline-to-centerline distance between each piece of rotating or reciprocating equipment. Additionally, the storage tank (or day tank) should be at least 5 ft from the metering pumps to provide adequate room for tank outlet valves, suction piping, calibration columns, and so on. The area between the storage tank and the metering pumps is often the busiest area in the layout.

Sodium hypochlorite storage over the threshold quantity of 500 gal is considered a hazardous occupancy by IBC and IFC. As such, these containment areas must have multiple means of ingress and egress. Consideration should be given for space to accommodate multiple stairs and doors into sodium hypochlorite storage areas. Architectural standards should be followed for stair height, length, and spacing.

Clearance must be maintained above the tanks as well for access to top-mounted level instruments. Refer to the recommendations provided earlier for top access restrictions and limitations.

Control Panels

In developing the layout, it is important to provide space not only for the transfer and metering pumps but also for the control features necessary to control the equipment. While peristaltic pumps and solenoid driven diaphragm pumps have integral control panels, motor drive diaphragm metering pumps and centrifugal transfer pumps must use external control panels. Control panel should be placed in proximity to the pump for convenience. The National Electric Code (NEC) has requirements for clearances in front of electrically energized panels. Panels using 120V require 36 in. of clearance; panels using 480V require 42 in. of clearance.

CALCIUM HYPOCHLORITE

Another type of hypochlorite is calcium hypochlorite, which is available in a variety of forms, including powder, granules, briquettes, and tablets. All these delivery forms contain solid calcium hypochlorite with 65%–70% available chlorine. These products differ only in their physical delivery form.

There are multiple manufacturers of calcium hypochlorite, briquettes or tablets, and feed equipment. However, the most familiar to water and wastewater operators is the PPG “Accu-Tab Tablet Chlorination Systems,” Arch Chemicals, Inc., with their “Constant ChlorPlus” calcium hypochlorite system, and Hammond Technical Services. These systems use briquettes or tablets. Currently, the PPG systems are applicable to applications up to 650 ppd of available chlorine. The Arch Chemicals system is capable of applications of up to 250 ppd of available chlorine. Hammond is capable of up to 720 ppd available chlorine.

Calcium hypochlorite systems are typically used for small applications of chlorine such as industrial usages, small water treatment plants, or well water sites. In general, these systems require operators to manually handle and load the dry calcium hypochlorite product into tanks or hoppers for feed solution preparation. Large municipal water and wastewater plants normally do not consider the manual handling of large quantities a cost-effective method.

History

Dry calcium hypochlorite is the most commonly used form of dry bleach used in North America. It is marketed at 65%–70% available chlorine content. The first calcium hypochlorite was marketed by German Perchloron, which consisted of hemibasic calcium hypochlorite and impurities. The available chlorine content was about 65%.

In the early years, the Mathieson Chemical Company produced calcium hypochlorite by mixing equal amounts of sodium hypochlorite and calcium

chloride. In this process, a slurry of lime and caustic soda is chlorinated and then cooled to -10°F . The crystals that form are centrifuged to remove the mother liquor and the insoluble impurities, and are then added to the slurry of chlorinated lime that contains calcium chloride in an amount equivalent to the sodium hypochlorite content of the crystals. When this mixture is warmed, a calcium hypochlorite dehydrate precipitate is formed, and the sodium chloride remains in solution. The precipitate is filtered, and the resulting cake is granulated, sized, and dried. The resulting product contains more than 70% available chlorine and less than 3% lime.¹

The Pennwalt Corp. (formerly the Pennsylvania Salt Co.) developed the American version of the Perchloron process, an improvement over the German process, which consists of forming calcium hypochlorite dihydrate crystals while retaining a sufficient amount of the large hemibasic crystals to permit filtration. This product has an available chlorine content more than 70%. This process reduces the lime content of the German method from 12%–16% to 3%–5%.¹

PPG Industries utilizes an approach that consists of bubbling chlorine gas through a solution of calcium hydroxide to produce calcium hypochlorite and a calcium chloride by-product in the form of a liquor. The clear liquor is filtered through a filter press to remove the water, and the product is dried with air to produce granular calcium hypochlorite containing 68% available chlorine as well as some hydrolyzed water, salt, calcium carbonate, and other soluble and insoluble inert inorganic compounds. The insolubles can cause precipitates when dissolved in tap water during application. The amount of precipitates formed depends on the dilution factor and the total hardness of the diluting water.

Briquettes and tablets are made by compressing granular calcium hypochlorite into the desired form. Powdered and granular forms of calcium hypochlorite are also available. However, in bulk form, their use involves complex handling and feed equipment, such as silos with dust collection and level measurement equipment, secondary hoppers, vibrators, delumpers, volumetric feeders, and mixing tanks. Dry chemicals are typically avoided, especially for small feed rate applications because the equipment intensive designs are not cost-effective. Accordingly, few plants use granular calcium hypochlorite.

PPG Industries Inc. and Hammond Services were one of the first to realize the market for providing dry calcium hypochlorite in a form easily handled by the end user without expensive and complex dry chemical handling equipment. As a result, the briquette and tablet forms were developed and introduced for continuous chlorination of small water supplies.

PPG combined its technology with Hammond Services using PPG's 3-in.-diameter-by-1.25-in.-thick tablet of dry calcium hypochlorite. The tablets were sometimes call "pucks" as they resembled a hockey puck. Each tablet is approximately 300 g in weight. The equipment (chlorinators) was designed and

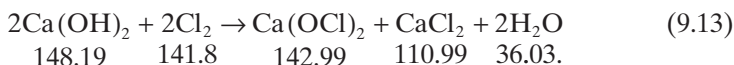
provided by Hammond Services. However, PPG is no longer partnered with Hammond. PPG not only makes the calcium hypochlorite tablets but also has its own equipment line for using the tablets in small chlorination applications.

Of the various sizes of briquettes and tablets, end users should be aware that individual supplier's systems are designed for a specific size or shape of briquette or tablet and the systems may not be interchangeable. Changing to an inappropriately sized briquette or tablet could result in operational problems and, possibly, loss of chlorination control. In addition, this could void the warranties associated with the unit.

Although very rare, some plants have used liquid calcium hypochlorite liquor. It is likely that these plants have a special contract with a calcium hypochlorite manufacturer to receive the calcium hypochlorite liquor before dewatering and drying. The advantages of this practice are not apparent. One disadvantage would be the additional cost of transporting the water content of this product in lieu of transporting dry calcium hypochlorite.

Manufacturing Process

Calcium hypochlorite liquor can be made directly from the reaction of chlorine and hydrated lime in solution. The maximum strength of these liquors is limited to about 35% available chlorine. These solutions are made by passing chlorine into a milk of lime suspension according to the equation¹



The numbers shown below the reaction are the stoichiometric weights (in pounds) of reactants and products derived from the reaction stoichiometry and each compound's MW. Theoretically, 1.045lb of actual $\text{Ca}(\text{OH})_2$ or 0.791lb of actual CaO will react with 1lb of chlorine to produce 1.008lb of calcium hypochlorite and 0.782lb of calcium chloride. In actual practice, it is usually assumed that the hydrated lime contains 95% $\text{Ca}(\text{OH})_2$ and that the quicklime contains 95% CaO .¹

In practice, an excess of 10–20lb of $\text{Ca}(\text{OH})_2$ (hydrated lime) or 7–14lb of CaO (quicklime) should be used per 1000 gal of calcium hypochlorite to ensure proper stability by keeping the pH at 11.2 or above. The following formula calculates the total pounds of hydrated or quicklime required to produce 1000 gal of calcium hypochlorite of various strengths:¹

$$\text{lb Cl}_2 = \text{g/l available chlorine} \times 8.341$$

$$\text{lb Ca}(\text{OH})_2 = \text{lb Cl}_2 \times (1.043 \times 100) / (\% \text{ Ca}(\text{OH})_2 \text{ in lime}) + 10\text{--}20\text{lb}$$

$$\text{lb CaO} = \text{lb Cl}_2 \times (0.791 \times 100) / (\% \text{ CaO in quicklime}) + 7\text{--}14\text{lb}.$$

TABLE 9.6. Pounds Required per 1000 gal of $\text{Ca}(\text{OCl})_2$ ¹

Available Cl_2 (g/l)	Cl_2 (lb)	Hydrated Lime $\text{Ca}(\text{OH})_2$ 95%			Quicklime CaO 95%		
		Theoretical	Minimum	Maximum	Theoretical	Minimum	Maximum
10	83.4	91.7	101.0	110.3	69.4	76.4	83.5
20	166.8	183.5	192.7	202.0	138.8	145.9	152.9
30	250.2	275.2	284.5	193.7	208.2	215.3	222.3
40	333.6	367.0	376.2	385.5	277.7	284.7	291.7
50	417.0	458.7	468.0	477.2	347.1	354.1	361.1
60	500.4	550.4	559.7	568.9	416.5	423.5	430.5
70	583.8	642.2	651.4	660.7	485.9	492.9	499.9

Table 9.6 shows the theoretical minimum and maximum amounts of lime required to make liquid calcium hypochlorite.¹

Properties

Calcium hypochlorite is a dry white chemical that can be refined to approximately 70% available chlorine in dry form. The remainder of the dry product consists of hydrolyzed water and other soluble and insoluble inert materials. Some products even contain a small percentage of scale inhibitor (0.5%–0.9%) to reduce scale formation inside the feeder.

Calcium hypochlorite molecular formula is $\text{Ca}(\text{OCl})_2$ and an MW of 142.9 lb/lbmol (g/mol). The bulk density of various calcium hypochlorite products is as follows:

Form	Density (lb/ft ³)
Powdered	32–50
Granular	68–80
Tablets	70–75

The available chlorine content in calcium hypochlorite can be a confusing concept if one tries to ratio the MWs of calcium hypochlorite and chlorine. Dry calcium hypochlorite of 65%–70% purity (whether powder, granular, or tablet) contains 70% available chlorine.

Disinfection

When dry calcium hypochlorite is dissolved in water, it forms 2 mol of hypochlorous acid per 1 mol of calcium hypochlorite. The hypochlorous acid disassociates into hydrogen ion and the hypochlorite ion (OCl^-).



Because two hypochlorous acid molecules result from one calcium hypochlorite molecule, calcium hypochlorite has a high oxidizing strength, which provides the high available chlorine content. Essentially, each pound of dry calcium hypochlorite has 1 lb of available chlorine.

Solubility

Granular calcium hypochlorite is readily soluble in water at room temperature. However, in tablet form, it is sometimes designed for slower dissolving rates. Table 9.7 includes solubility data for calcium hypochlorite in water.¹²

Additional information regarding the available chlorine content of calcium hypochlorite solutions is presented in Table 9.8. The available chlorine concentration in this table is given in milligrams per liter rather than in grams per liter.

Calcium hypochlorite dissolves in water to form a solution with basic pH value, which is slightly lower than that of commercial sodium hypochlorite. pH values for solutions of calcium hypochlorite are presented in Table 9.9.

TABLE 9.7. Solubility of Calcium Hypochlorite

Temperature (°F)	Maximum Solubility (g/l)	Available Chlorine (g/l)
32	215.2	213.5
68	217.6	215.9
86	222.9	221.1
104	232.1	230.3

TABLE 9.8 Weight of Calcium Hypochlorite to Produce a Solution¹²

Available Cl ₂ (mg/l)	Weight of Calcium Hypochlorite to Make the Solution							
	1 gal		10 gal		50 gal		100 gal	
	lb	oz	lb	oz	lb	oz	lb	oz
5	0	0.001	0	0.01	0	0.05	0	0.10
10	0	0.002	0	0.02	0	0.10	0	0.21
25	0	0.005	0	0.05	0	0.26	0	0.51
50	0	0.01	0	0.10	0	0.51	0	1.03
100	0	0.02	0	0.21	0	1.03	0	2.05
150	0	0.03	0	0.31	0	1.54	0	3.08
200	0	0.04	0	0.41	0	2.05	0	4.11
300	0	0.06	0	0.62	0	3.08	0	6.16
500	0	0.11	0	1.03	0	5.13	0	10.27
600	0	0.12	0	1.23	0	6.16	0	12.32
1,000	0	0.21	0	2.05	0	10.26	1	4.53
2,500 (0.25%)	0	0.51	0	5.13	1	9.66	3	3.32
5,000 (0.5%)	0	1.03	0	10.26	3	3.32	6	6.65
10,000 (1%)	0	2.05	1	4.53	6	6.65	12	13.29

TABLE 9.9. Resulting pH of Calcium Hypochlorite Solutions¹²

Available Chlorine (g/l)	pH
100	9.7
200	10.0
600	10.4
1000	10.7

Hazards and Stability

Because of its strong oxidizing potential, dry calcium hypochlorite is difficult and dangerous to store and use. It is somewhat unstable chemically and should not be dropped or skidded across the floor, as the friction could cause a fire. Heat, shock, and friction are among some of the conditions that can cause it to combust or explode.

Calcium hypochlorite is hygroscopic; that is, it will absorb moisture from the air. It will degrade slowly with time. Absorption of moisture from air is believed to induce the decomposition. Although, its degradation has not been studied to the same extent as sodium hypochlorite degradation, it is widely believed that calcium hypochlorite will lose its available chlorine content at a rate of 3%–5% per year under normal indoor storage conditions.

Calcium hypochlorite is a strong oxidizer and considered a Class III oxidizer by the DOT as well as by most building and fire codes, including National Fire Protection Association (NFPA). It will react vigorously with acids to generate heat and toxic chlorine gas. Dry calcium hypochlorite will react with organics such as fuels, oils, greases, solvents, lotions, cosmetics, food, dead vegetation, cardboard, soap, and many other organics containing materials to spontaneously start a fire. It will chemically decompose at temperatures above 212°F to release chlorine and oxygen gas. Since a calcium hypochlorite fire will generate its own oxygen, attempts to smother it will not be effective, and it must be quenched with water.

Calcium hypochlorite must be stored in a cool, dry, well-ventilated location, free of organics, acids, and combustible materials. It is a corrosive material that can cause severe burns to the skin and eyes and will cause interval burns when inhaled. Persons handling calcium hypochlorite must wear PPE.

Tablet and Briquette Systems

Despite minor differences in size and shape, tablets and briquettes operate in a similar manner. Calcium hypochlorite tablets and/or briquettes are manually loaded into a tank or vessel called a chlorinator, where they are partially submerged or sprayed with a continuous stream of water (30–100 gpm, depending on the size of the unit), which causes them to slowly dissolve to make a solution with high available chlorine content.

PPG produces a solution of 200–400 mg/l of available chlorine. Even though the saturation point of calcium hypochlorite in water is much higher, the tablet chlorinators are designed to work from the surface area of the exposed tablets (or the spray volume) to maintain a more dilute solution concentration, far below the saturation point, to control scaling inside the chlorinator and the downstream piping.

Arch Chemicals makes a much more concentration solution of 1.5% (15,000 mg/L) available chlorine. Arch Chemicals uses an electronically controlled spray system for controlling dissolution of briquettes. Hammond uses a high-energy vortex feeder to prepare a constant concentration of calcium hypochlorite to be fed by integral metering pumps.

For low-pressure application point conditions where gravity feed can be used, chlorine delivery rates are automatically adjustable by modulating the flow rate of incoming water by using a modulated water control valve and a controller. Increasing the water rate will increase the dissolution of calcium hypochlorite and deliver more available chlorine to the process. The PPG units are capable of approximately 10:1 turndown. Arch Chemicals literature indicates a turndown of approximately 6:1. The dry calcium hypochlorite feeders mentioned are capable of receiving an external analog signal for remote flow facing by a 4- to 20-mA signal. The calcium hypochlorite solution is gravity-drained to the application point through PVC piping.

In high-pressure application-point conditions, the chlorinators discharge a constant-concentration calcium hypochlorite solution to a tank, which is equipped with level (or weight) sensors to turn the chlorinator ON or OFF to maintain a constant supply of solution. Metering pumps, often the diaphragm type, are used to withdraw the solution from the tank and feed it to high-pressure application points. Figure 9.25 presents a diagram of a PPG tablet system for high-pressure application.

Each manufacturer has sizing charts for designers and users to select the proper size unit from either the required chlorine pound per day rate or from process water flows and chlorine dosages.

The tablets are available for purchase from PPG in 55-lb pails, 45-kg drums, and 400-lb bulk supersacks. Pails and drums are delivered on pallets.

Applicable Standards

There are a number of standards and certifications applicable to calcium hypochlorite tablets as follows. Some of the key standards for water and wastewater applications are

- NSF Standard 60 and 61 for drinking water,
- AWWA Standard B-300, and
- U.S. Food and Drug Administration (FDA) approval (21 CFR 178.1010).

Calcium hypochlorite used in drinking water must conform to the standards listed above.

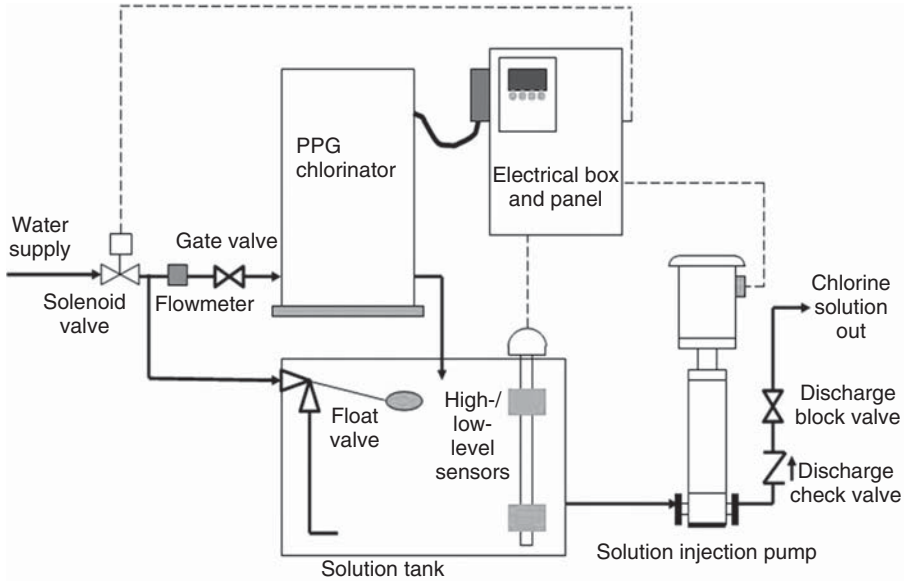


Figure 9.25. Tablet chlorinator.

LITHIUM HYPOCHLORITE

Lithium hypochlorite is a highly unusual and infrequently used type of hypochlorite. In general, water treatment plants do not favor the introduction of lithium into their systems.

Lithium hypochlorite is produced in granular form and is manufactured by mixing a strong solution of lithium chloride with a strong solution of sodium hypochlorite. A large portion of sodium chloride precipitates and the 30%–35% solution of lithium hypochlorite are evaporated and drum-dried. The finished product is white, free flowing, granular, and dust free.¹

Lithium Corporation of America, the manufacturer of this product, lists the following ingredients:¹

	Percent by Weight
Available chlorine	35
LiOCl	30
NaCl	34
Na ₂ SO ₄ and K ₂ SO ₄	20
LiCl	3
LiClO ₃	3
LiOH	1
Li ₂ CO ₃	2
H ₂ O	7

Lithium hypochlorite is readily soluble in water and has the distinct advantage over calcium hypochlorite solutions of being clear when prepared, thereby eliminating the need for settling and discarding of sludge. When stored properly in closed containers at 75 °F and 75% relative humidity for 4 months, it retains more than 90% of its available chlorine.¹

It does not affect the alkalinity or pH of treated water to the extent that other hypochlorite products do. The pH of a 100ppm solution of available chlorine at 25 °C is only 10.0.¹

This product was introduced in 1964 as a laundry bleach and dishwashing compound because of its excellent solubility. Then it was introduced to the swimming pool industry in competition with all the other disinfectants. It has the same disinfecting characteristics as any other chlorine compound that produces HOCl as a hydrolysis product.¹

The same safety precautions must be followed for the storage of granular lithium hypochlorite as those used with granular calcium hypochlorite.¹

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10 On-Site Sodium Hypochlorite Generation System

HISTORICAL BACKGROUND¹

The Beginning

There is currently considerable interest in electrolytically producing chlorine at the point of use, thereby eliminating the hazard of chlorine stored on-site in containers.

One of the first installations of this kind was at Brewster, New York, in 1893. The installation was known as the Woolf process. The Central Electricity Generating Board of London experimented with such systems as an alternative method of chlorinating condenser-cooling water at electricity-generating stations but found that the method was inefficient and beset by a great many operating problems, and terminated the experiment.

On-site generation of chlorine by electrolysis dates back to the 1930s, when Wallace & Tiernan (now part of Siemens Water Technologies) made electrolytic chlorinators for YMCA swimming pools. These systems actually produced dilute sodium hypochlorite.

Electrodes have always been a major source of trouble in electrolytic systems. The most common of these have been platinum coated; others have been made of carbon and iron, of graphite with a lead shield inside a stainless steel sheath, and of titanium coated with rare metals. Manufacturing methods and durability of these electrodes have improved in recent years, but they still have a limited life span.

On-site generation of sodium hypochlorite is an inefficient process in comparison with the generation of bulk chlorine, but it does have interesting possibilities, in particular, the safety factor and the fact that all raw materials might be at the point of application, thereby eliminating a significant portion of storage requirements. The cost of electricity is the Achilles' heel of the process.

White's Handbook of Chlorination and Alternative Disinfectants, 5th edition,
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Early Experience in the United States¹

On-site generation of hypochlorite in the United States was largely inspired by the use of hypochlorite solution during World War I (1914–1918). This solution became known as the Carrell–Dakin solution. Its success as an anti-septic for treatment of open wounds led to on-site generation of it in hospitals. One of the first electrolytic cells for this purpose, developed by Van Peurseem et al., was designed to produce the equivalent of the Carrell–Dakin solution.

Wallace & Tiernan first made electrolytic chlorinators to provide a safe means of chlorinating swimming pools located in buildings where people slept. As early as 1939, Wallace & Tiernan established a policy that chlorine gas equipment should not be installed in such buildings, and developed an electrolytic chlorinator for this purpose.

The chlorinator aroused the interest of Pan American Airways, which, at the time (1936), was establishing refueling sites on its San Francisco-to-Sydney and Orient flights. The use of the electrolytic chlorinator for water supplies at these way stations was ideal. World War II changed all these plans.

Current Interest¹

After World War II, the enthusiasm for on-site generation of chlorine disappeared until the hazard potential of chlorine gas stored in containers was evaluated, owing to the proliferation of chlorine gas installations at wastewater and potable water treatment plants. At about the same time (1950s), small electrolytic generators for use in backyard swimming pools began appearing on the market. The cost of these units and the manufacturer's inability to provide satisfactory service discouraged their use.

In the 1970s, the popularity of on-site generation began to rise once again, largely because of the potential hazards of liquid–gas systems using chlorine stored in containers and the availability of federal funds for research and development of reliable equipment.

Starting in the 1990s, after the advent of the Uniform Fire Code, there has been a great surge in the interest of on-site generation of chlorine. The product is inherently safer because of its lower concentration, but some argue that the greater safety is balanced by the production of flammable hydrogen gas as a major by-product. Moreover, current on-site generation systems produce chlorine solutions containing only 0.8% chlorine, and this concentration is not classified as hazardous. Operating personnel are very favorably disposed toward these systems because their operation does not require special training in the use of hazardous material.

Further interest in the system has been generated in the early years of the twenty-first century as a result of the terrorist attacks of September 11. After the attacks, the risk associated with chlorine gas systems was reevaluated. In addition, with a culture more attuned to risk and safety of operators and surrounding communities, interest in and installation of on-site generation sodium

hypochlorite units have seen a significant increase, with the established players reinvigorating their product lines and with new players entering the market.

RAW MATERIAL QUALITY

Salt and Brine Systems

The quality of the raw material is of great concern in the operation of any electrolytic process. Chlorine manufacturers have long realized that successful cell operation is dependent on the use of pure brine. There are two sources of salt: seawater and mines.

Seawater is composed of salt and many other minerals, as shown in Table 10.1. When heat is applied to seawater, the water evaporates, and the remaining crystals, called solar salt, are collected. Solar salt is unrefined and undesirable in the electrolytic process. For pure salt to be obtained, the other minerals must be removed by recrystallization.

There is also mined salt, or naturally occurring brines, in the earth’s crust. This material, unless of exceptional quality, also requires treatment at the site. Any underground brine should be checked for ammonia nitrogen (NH₃-N) content, as this is an undesirable impurity in the electrolytic production of chlorine.

Impurities in salt or brine seriously affect the operation and maintenance of any type of membrane cell. The impurities will scale and build up on the cell, thus interfering with its ability to transmit electricity. According to Eltech, the maximum allowable calcium ion content in brine is 0.05 mg/l.

The majority of on-site sodium hypochlorite generation systems today use solar or food grade salt that originates from seawater and is 99% pure sodium chloride. This type of salt produces less mineral scale and generally yields fewer unwanted by-products, such as bromate.

Impact of Salt Quality and Bromate Formation²

On-site production of sodium hypochlorite may be a significant source of sodium bromate in treated water. The sodium bromate formation results from

TABLE 10.1. Composition of Standard Seawater (Total Salinity: 36,047 mg/l; Total Alkalinity: 119.8 mg/l)

Cations	mg/l	Anions	mg/l
NW	11,035	Cl ⁻	19,841
Mr ⁻	1,330	SO ₄ ⁻	2,769
Ca ^{''}	418	HCO ₃ ⁻	146
IC	397	Br	68
SR [']	14	F ⁻	1.4

the concentration of bromide in the raw sodium chloride salt. Bromate concentration in potable water is regulated by the Environmental Protection Agency, in accordance to Phase I of the Disinfection Byproducts Rule of the Safe Drinking Water Act. Sodium bromate is a known carcinogen with a maximum contaminant level of 10ppb. Under current American National Standards Institute/National Sanitation Foundation (ANSI/NSF) Standard 60 guidelines, the maximum amount of sodium bromate that can be produced from sodium hypochlorite is 50% of the regulated amount.⁴ This regulated percentage is to be lowered annually since the regulation was established in 2004.

The designer of an on-site generation system must be aware of this regulation and must take appropriate action when specifying the grade of salt (sodium chloride) used for on-site generation. The salt must be at least 99% sodium chloride, solar or food grade, and produced by evaporation.

Seawater Systems

In some instances, seawater may be used rather than a brine made on site. The concentration of the brine is limited to 30,000mg/l, and whatever goes into the onsite sodium hypochlorite generator is discharged into the treated process stream. Therefore, the total dissolved solids concentration in the generator discharge is 30,000mg/l, which limits the application of the “seawater” product in the disinfection of wastewater, chlorination of cooling water, offshore well-drilling installations that use chlorine to control marine growth, and other marine installations. Only under special circumstances can it be used for treatment of potable water and water reuse. It is not suitable for controlling hydrogen sulfide in wastewater collection systems because seawater increases the formation of H_2S in wastewater.

Seawater composition varies from ocean to ocean. The TDS concentration ranges from 30,000 to 36,000mg/l, and the chloride concentration averages about 19,000mg/l.

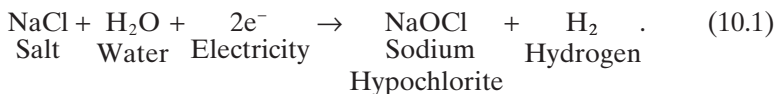
Generator units that use saline waters may not require any pretreatment of the brine, except screening or microstraining. However, in some instances, filtration has proven to be necessary. The electrolytic cells are more susceptible to scaling and need more frequent cleaning when seawater is used rather than solar or food grade salt.

ON-SITE GENERATION OF SODIUM HYPOCHLORITE

Electrolytic Formation of Sodium Hypochlorite

On-site generation of sodium hypochlorite is accomplished by combining salt, water, and electricity in electrolytic cells. The sodium hypochlorite solution produced has a concentration of 0.8% by weight, with approximately 0.067lb of available chlorine per gallon, and a density of approximately 8.44lb per

gallon. The equation below illustrates the electrochemical reaction that takes place:



Unlike the 12%–15% by weight full-strength sodium hypochlorite solution, the final 0.8% solution produces significantly lower off-gassing as a result of degradation, causes minimal scaling and crystallization at the feed point, and has a lesser impact on finished water pH.

In addition to these advantages, the 0.8% solution is typically classified as an irritant health hazard. As such, it may be exempt from regulations stated in fire and building codes. However, state and local regulations must be examined, as more stringent policies may apply.

The feasibility of an on-site sodium hypochlorite generation system is determined by local regulations and performing a life cycle cost analysis for comparison with other methods of disinfection. The life cycle analysis should include the costs of equipment and buildings, operation and maintenance, raw materials, and electric power.

Process Overview

On-site generation of sodium hypochlorite involves a variety of distinct technologies and equipment, as described in more detail below.

The on-site generation process starts with the preparation of a concentrated brine solution by diluting solar or food-grade sodium chloride salt stored in a brine maker/saturator tank with water to make a 26.4% by weight solution. Water enters the brine maker, flows through its saturator ring to absorb salt, exits as brine solution, and is pumped by metering pumps to the electrolytic cell skid. The dilution water is typically softened to reduce scale buildup inside the cells, and the brine may be used for regeneration of the softener. Figure 10.1 is a process flow diagram of the water softener, brine maker, and brine pumps.

Since the temperature of the softened dilution water has a direct effect on electrode efficiency, water chillers and heaters may be used to maintain the water temperature in an acceptable range, as illustrated in Figure 10.2.

At the electrolytic cells, the brine is further diluted to a 2.5%–3% solution, which enters the electrolytic cell where a calculated amount of electricity is delivered by a dedicated rectifier. The reaction occurs in the cell, and the products (sodium hypochlorite solution and hydrogen gas) are transferred to the standpipe. The mixture enters the standpipe at the top so that the liquid sodium hypochlorite falls to the bottom and the hydrogen gas exits through the vent. A hydrogen dilution blower supplies air to lower the hydrogen con-

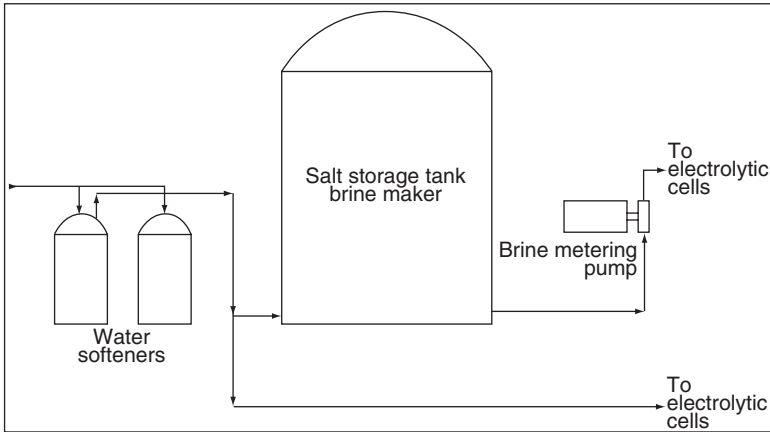


Figure 10.1. Typical brine preparation equipment (courtesy of Black & Veatch).

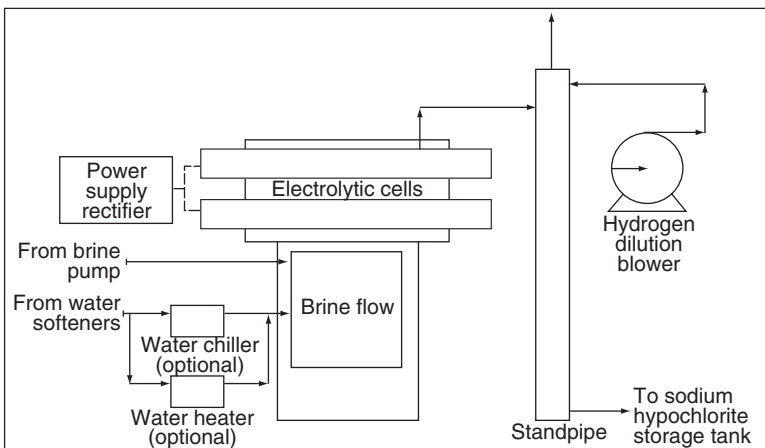


Figure 10.2. Typical electrolytic cell and hydrogen dilution arrangement (courtesy of Black & Veatch).

centration to nonexplosive level. Figure 10.2 is a process flow diagram of the electrolytic cells, standpipe, water chillers, and blowers.

Combining the softened water, salt, and electricity in electrolytic cell results in the formation of chlorine gas (Cl_2) on the anode side, and sodium hydroxide (NaOH) on the cathode side. The chlorine gas and the sodium hydroxide combine to form sodium hypochlorite and hydrogen gas, as shown in Equation (10.1). Hydrogen gas is explosive at certain concentrations in air, which must be considered during design. The sodium hypochlorite and hydrogen gas exit the electrolytic cells into a standpipe or other equipment designed for hydro-

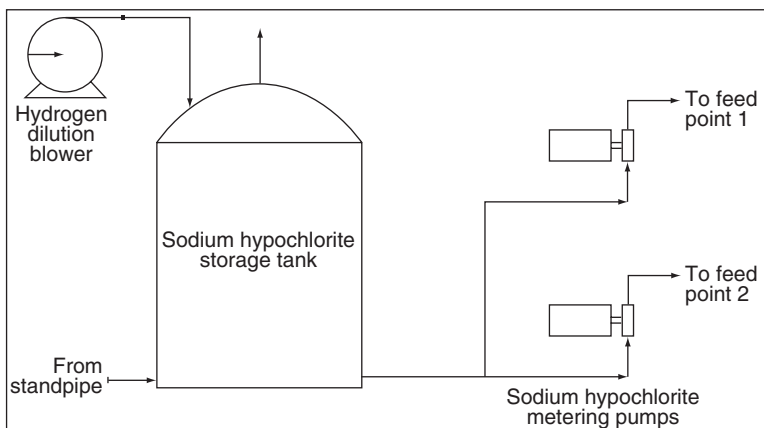


Figure 10.3. Typical sodium hypochlorite bulk storage and metering equipment arrangement (courtesy of Black & Veatch).

gen removal. Since hydrogen gas is lighter than the sodium hypochlorite solution, it rises in the standpipe (where it is vented), while the sodium hypochlorite solution is stored in bulk storage tanks.

The hydrogen gas at the standpipe is diluted by mechanical blowers to a concentration below its lower explosive limit (LEL) before being vented to the atmosphere. Even though the sodium hypochlorite in the storage tanks is essentially free of hydrogen gas, it is recommended that mechanical blowers also be connected to each storage tank to keep the hydrogen gas concentration in the headspace below the LEL. Figure 10.3 is a process flow diagram of the storage tank and metering pumps.

The sodium hypochlorite solution is transferred to points of application by chemical metering pumps that can be of either diaphragm or peristaltic type.

SYSTEM COMPONENTS

The main components of an on-site sodium hypochlorite generation system are described below.

Water Softener

Water-softening systems are used to reduce the hardness caused by high concentrations of naturally occurring ions of calcium, magnesium, bicarbonates, and sulfates in groundwater. Hardness values are typically expressed in milligrams per liter of calcium carbonate (CaCO_3) and vary, depending on the location of the water source. Table 10.2 illustrates the different levels of hardness as described by the U.S. Geological Survey.

TABLE 10.2. Hardness Value Classification by U.S. Geological Survey (USGS)

Classification	Range (mg/l of CaCO_3)
Soft	0–60
Moderately hard	61–120
Hard	121–180
Very hard	>180

Calcium and magnesium ions in the water can develop into a hard scale in piping systems and other equipment. In on-site generation systems, the scale will coat the electrodes in the cells and, over time, reduce their efficiency, thus increasing their electricity demand. It can also inhibit flow through the cell and cause blockage. When the sodium hypochlorite and hydrogen cannot exit the cell, pressure will rise and, if ignored, the cell may burst. Ideally, water hardness for on-site generation systems should not exceed 17 mg/l as CaCO_3 ; using water with cells this level of hardness will need cleaning every 6 months. Water with hardness up to 40 mg/l as CaCO_3 may be used, but cleaning of cells will be required more often. The water quality data should be coordinated with the system supplier early during design; if the water is too hard, a water softener will have to be provided.

Most conventional water softeners operate on the principle of ion exchange. Hard water, rich in calcium and magnesium, is passed through a tank filled with negatively charged porous polystyrene resin beads, which tend to attract positively charged ions to form ion bonding sites. The resin beads are charged with sodium ions in a saturated sodium chloride (brine) bath. The positively charged sodium ions from the brine solution will stay coupled to the resin beads until exposed to other positively charged ions that have a higher density charge, such as calcium and magnesium. The resin beads will preferentially bond to those with higher-density ions. This is how univalent cations such as hydrogen (H^+), potassium (K^+), and sodium (Na^+), which are originally loaded onto the resin beads, can be exchanged at each resin bead surface for higher density bivalent cations, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}), in turn, reducing the water hardness.

The most commonly used ion exchange system is the sodium cycle ion exchanger. The softening system components include two resin tanks, control valves, and appurtenances as required by the system manufacturer. Figure 10.4 illustrates the flow through a duplex softening system.

Once all sodium ions at the resin surface have been exchanged by hardness-causing ions, the resin tank/bed is considered to be exhausted and has to be regenerated. The regeneration usually takes about 90 min and involves a backwash cycle, a concentrated sodium chloride (brine) flush, and a rinse cycle. The backwashing removes accumulated solids and loosens the compacted resin. The concentrated brine flush, which follows, replenishes the sodium

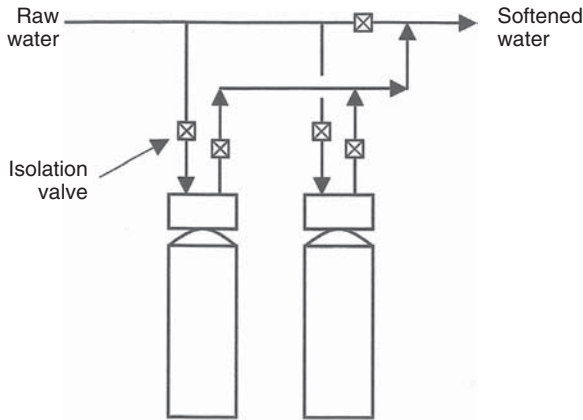


Figure 10.4. Typical duplex softening system (courtesy of Black & Veatch).

charge on the resin beads. The rinse cycle consists of a slow rinse and a fast phase. The slow rinse extends the resin–brine contact time; the fast rinse removes any remaining brine solution from the bottom of the resin tank. The regeneration can be accomplished manually or by using automatic valves and manufacturer controls.

It is recommended that the regeneration cycle be based on time rather than on volume, that is, every so many hours instead of after a certain number of gallons treated. Another way to determine when to regenerate the resin tank is to measure the treated water hardness by using a hardness analyzer. Hardness analyzers can also be used to alarm the control system in the event that the water hardness is above acceptable limit.

For continuous operation, the softening system should remain in operation during regeneration. This can be accomplished by using dual resin tanks with automatic changeover during regeneration cycles shown in Figure 10.4.

Typical duplex water-softening vessel installation is shown in Figure 10.5.

The resin tanks can be constructed of metal or resin wound polyethylene. Metallic tanks are constructed in accordance with Section VIII, Division 1, of the ASME Boiler and Pressure Vessel Code, and resin-wound polyethylene tanks in accordance with Section X of the ASME Boiler and Pressure Vessel Code as a Class I vessel.

Sufficient freeboard should be provided in each resin tank to accommodate expansion of the resin during backwashing. Another consideration is the inclusion of pressure-relief valves for protection against over pressurization.

In addition to space constraints, the water use and the drainage piping used for the regeneration and rinse cycles of the softening system should be considered.

The brine demand will depend on the size of the on-site sodium hypochlorite generation system and the demand for softener regeneration. The brine



Figure 10.5. Typical duplex softening unit (courtesy of Black & Veatch).

demand for water-softener regeneration is approximately 15 lb/ft^3 of resin and may vary, depending on the resin manufacturer. This demand should be considered when estimating the entire system's sodium chloride demand, as discussed in more detail later in this chapter.

Brine Saturator Tank

The brine saturator system consists of a storage tank, a brine saturator assembly, a dust collection filter, a salt level indicator, and a brine level indicator. A typical saturator tank installation is shown in Figure 10.6.

The brine saturator tanks in larger systems (larger than 100lb/day of chlorine) are usually closed-top type, constructed of fiberglass-reinforced plastic (FRP), and are generally filled by bulk truck delivery.

Tanks in smaller systems (100lb/day of chlorine or less) may be open-top type and manufactured of high-density polyethylene. The salt for smaller systems is typically delivered in 55-lb bags. The design and construction of the tanks are discussed in Chapter 9. Typical nozzle connections of brine saturator tanks include dry salt fill, soft-water inlet, level indicator, side and top maintenance manways, tank vent, and brine suction discharge.

Tank sizes vary among manufacturers and are available in capacities based on maximum recommended salt deliveries. Bulk trucks can carry 20–25 tons of salt per delivery. Coarse solar salt has an average bulk density between 65 and 75 lb/ft^3 . Brine saturator tanks are sized for 30 days' storage, based on average plant chlorine use and hydraulic flow rate. It is recommended that the saturator tank be designed with sufficient storage volume to maintain an uninterrupted supply of brine while minimizing partial salt deliveries.

For larger systems, the dry salt is delivered by tanker truck and pneumatically transferred to brine saturator tanks. The salt conveyance pipe should be manufactured of high-grade metal alloy such as stainless steel, with

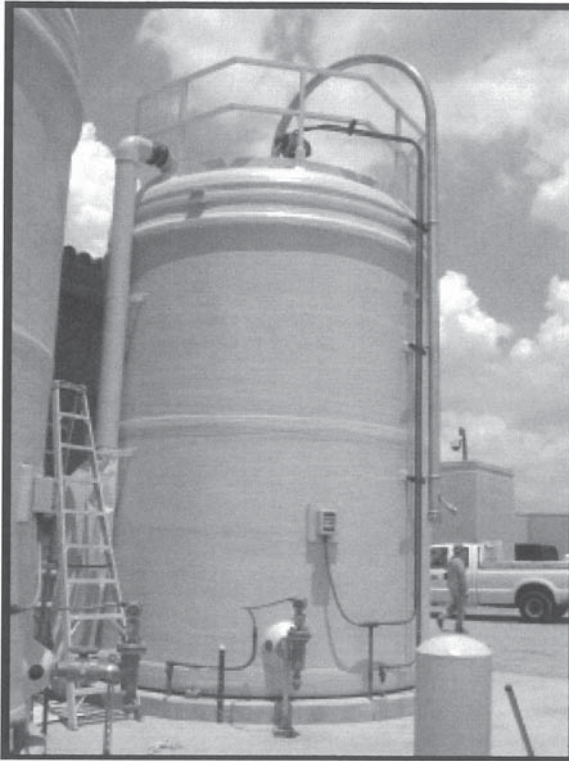


Figure 10.6. Typical brine saturator (courtesy of Black & Veatch).

long-radius elbows that can be lined for additional wear resistance and an air/water flushing connection for clearing line blockages or salt accumulation.

The soft-water inlet connection on the side of the tank is placed in the best location for brine saturation, as recommended by the system manufacturer. Flow of the soft water is controlled by a solenoid valve that is energized, based on brine solution level in the tank. The soft water is delivered through a ring distribution header to spread the water evenly over the dry salt to produce a saturated brine of about 26.4% sodium chloride by weight at standard temperature and pressure.

The brine solution leaves the saturator tank through a plenum, which minimizes transfer of undissolved salts to the electrolytic cells. Saturator tanks for fine-grade salts are equipped with filters that capture undissolved salts ahead of the collection plenum. With coarse salt, the filters may not be needed, so the type of salt should be coordinated with the system supplier.

The dust generated during transfer of dry salt from the delivery truck to the saturator tank is captured in a dust collector bag on the tank's vent. The vent nozzle is oversized to protect the tank against the pressure drop caused by the bag.

The maintenance manways should be at least 24 inches in diameter and should be equipped with overpressurization relief protection for top manways, as discussed in more detail in Chapter 9. Tall tanks are equipped with ladder and safety cage assemblies, as discussed in Chapter 9.

Tank level is monitored by electronic indicators and transmitters. The brine solution level indicator is typically differential pressure type; the salt level indicator is a cable measurement transmitter type. Connections for the brine solution level indicator are on the side at the bottom of the tank; connections for the salt level indicator are on top of the tank.

The differential pressure-sensing elements for brine solution level are isolated from the process fluid by type 316 stainless steel, Hastelloy-C, ceramic, or cobalt–chromium–nickel alloy diaphragm. The transmitter enclosures and parts are manufactured of corrosion-resistant materials. An isolation valve is typically provided for the brine solution differential pressure type transmitter to allow servicing the cell without emptying the tank. The transmitter should be capable of sending a continuous 4- to 20-mA signal to the system control panel. The brine solution level transmitter is used to control the soft-water flow to the saturator tank. The salt level indicator transmitter measurement cable should extend along the entire height of the brine tank to allow the salt to be measured at all levels.

Brine saturator tanks are installed outdoors and, where winter temperatures are lower than (32 °F, or 0 °C), should be provided with heating pads and pipe heat tracing.

Soft-Water Heater

A soft-water heater may be needed in some locations to maintain the water temperature at the proper level, usually above 50 °F to prevent undesirable shifting of the reactions within the electrolytic cell, as discussed in more detail elsewhere in this chapter.

Some on-site generation systems are equipped with heat exchangers to keep the temperature difference between the soft water and the on-site generation temperature from exceeding the limit recommended by the manufacturer. Where the temperature difference between the available soft water and the required electrolytic generation temperature exceeds the manufacturer's recommendations, an electric water heater should be provided. In some cases, the combination of a heat exchanger and supplemental electric heating may be needed.

The heat capacity for the water heater can be determined by considering the system's mass flow rate, the heat capacity of the water, and the temperature difference between the available water and the required temperature by using the following equation:

$$\text{Heater Capacity} = M \times C_p \times \Delta T, \quad (10.2)$$

where M is water mass flow rate, C_p is the heat capacity of the water, and ΔT is the temperature differential between the water and the required water temperature. A 20% safety factor should be applied to the required capacity to account for heat losses. For the heater's actual power draw estimation, the heater's power efficiency is included as a numerical factor on the right side of the equation.

For generator skids that contain multiple cells, the inlet water flow is often split between the first and second cells. The cells are typically piped in series. The heat generated during the electrolysis process makes it unnecessary to heat the part of the water added to the discharge of the first cell upstream from the second cell.

In selecting the water heating equipment, the water should be evaluated for corrosiveness to select appropriate materials of construction.

The water heater is equipped with a thermostat to control the outlet water temperature and to limit heater interior temperatures during low flow. A temperature switch should be on the inlet and discharge sides of the electric heater to signal heater malfunction.

Soft-Water Chiller

A soft-water chiller may be needed where the water temperature exceeds the acceptable range. The chiller is downstream of the water softener. The temperature range varies among manufacturers, but a temperature above 80°F can be detrimental to generation cells. According to Faraday's law (Fig. 10.7), the optimal temperature for sodium chloride electrolysis is 65°F.

Chiller units can be air cooled or water cooled. The air-cooled units are typically single-stage compression type and use a refrigerant to extract the heat, which is then rejected to the environment through condenser coils coupled with fans. Water-cooled chillers operate on the same principle, but instead of condenser coils, the heat is discharged through a cooling tower. Water-cooled chillers are more efficient than air-cooled units, but their initial cost is higher; therefore, they are generally used to meet higher capacity demands where efficiency is a deciding factor.

On-site hypochlorite generation systems are generally served by air-cooled chillers. Their main components include a refrigerant compressor, a chilled water recirculation pump, a refrigerant coil, an evaporator, and condenser coils and fans. The chiller compressor is sealed type, with antislugging devices, shutoff valves, and spring-type vibration isolators. A crankcase heater prevents migration and condensation of refrigerant in the compressor's crankcase. The compressor should also include safety devices for fusible relief and current overloads, a motor winding thermostat, and suction pressure-operated capacity controllers.

The evaporator coils can be of the brazed plate or multirow coil type. Brazed plate evaporators consist of stainless steel plates with copper brazing, which make it less susceptible to damage by freezing. Coil-type evaporators

Impact of Temperature on the Efficiency of the Electrolysis Process
 Impact of Faraday's Law
 Optimal temperature for electrolysis process is 65°F, and, above or below that point, the efficiency of the process deteriorates quickly.
 Eds18NNS 35000 TDS QUAL

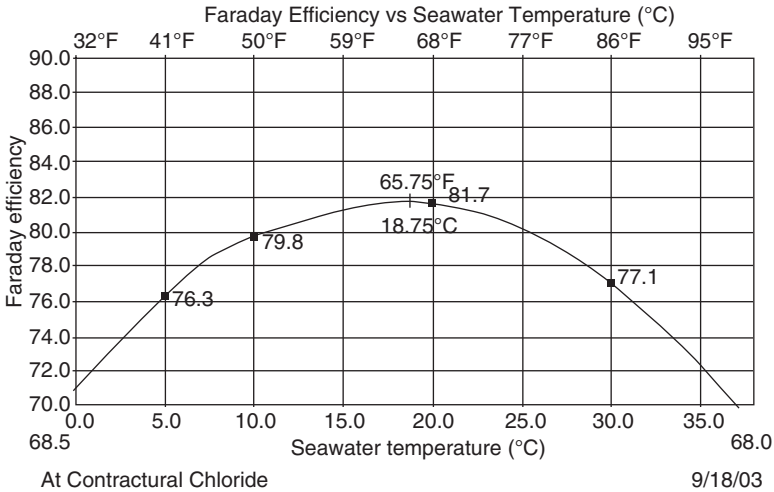


Figure 10.7. Faraday efficiency plot (courtesy of Siemens Water Technologies).

are constructed of seamless copper tubes. Both types of evaporators are usually furnished with a factory charge of refrigerant. Additional components include expansion valves, dryers, solenoid valves, sight glasses, moisture indicators, and insulated drip pans.

Condenser coils are dual circuited and arranged in multiple rows. They are typically constructed of copper and are mechanically bonded to aluminum condenser fins. In areas prone to galvanic action among dissimilar metals (such as coastal regions and industrial zones), condenser fans should be protected by anticorrosion dielectric coating.

The condenser fans are multiblade, up-flow design, direct-driven by permanently lubricated motors, and should be Underwriters Laboratories (UL) listed for outdoor use. They should be equipped with a built-in thermal overload protection and should be statically and dynamically balanced at the factory. The process water is recirculated through the evaporator by a centrifugal pump of sufficient capacity to overcome the associated chiller and the process pressure drops as required for each application.

The chiller system capacity can be determined by considering the flow rate, the heat capacity of the water, and the temperature differential between the available water and the water temperature by using the following equation:

$$\text{Chiller Capacity} = M \times C_p \times \Delta T. \quad (10.3)$$

Here, M is the water mass flow rate, C_p is the heat capacity of water, and ΔT is the temperature differential between the water and the required water temperature. A 20% safety factor should be applied to the capacity to account for heat transfer losses. For the chiller's actual power draw to be calculated, the chiller power efficiency is included as a numerical factor on the right side of the equation.

Chiller units may be provided with dedicated control panels, which should control the condenser fans, the compressor contactors, the transformer, the chilled water pump, and the outlet water temperature. The control panel includes a cycle guard function to prevent the chiller from cycling on overloads. At a minimum, the chiller should be provided with safety controls for high and low pressure, winding thermostats, and compressor overloads.

Brine Metering

The brine solution can be conveyed to generator cells by using an eductor-type system or by the traditional metering pumps.

The optimal sodium chloride concentration for electrolysis is 2.5%–3% by weight. For this concentration to be produced, approximately 26.4% by weight, saturated brine solution is diluted at the electrolytic cell skid.

The concentrated solution is conveyed by metering pumps to the electrolytic cell skid and then is moved by the dilution water through the electrolytic cells and the standpipe to the storage tanks.

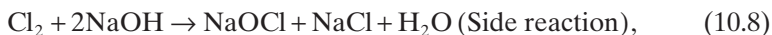
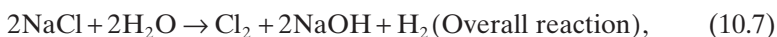
The strainers on the suction side of the brine metering pumps must be sized to capture all undissolved sodium chloride and debris from the saturator tank's gravel bed to prevent them from plugging the suction to the metering pumps. The design criteria for brine metering pumps, appurtenances, and controls are presented in the metering pump design considerations section in Chapter 9.

The brine metering pumps can be used to control generator cell efficiency by supplying excess sodium chloride solution for electrolysis. Some manufacturers vary the feed rate of brine to the cells by adjusting metering pump stroke length or speed. By modulating the feed rate, the electrode input current can be maintained at a constant rate while controlling cell efficiency. Other manufacturers vary the input current to the electrolytic cells and maintain a constant brine feed rate.

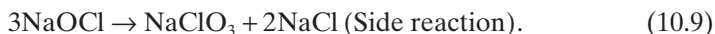
Electrolytic Cell

The electrolytic cell is the principal component of the on-site sodium hypochlorite generation system. It is a continuous-flow, steady-state, plug flow-type reactor where the sodium hypochlorite is produced in accordance to the following reactions:





and



Once in solution, the sodium chloride dissociates into free sodium and chloride ions. The chloride ions are oxidized at the anode to form chlorine gas, while the water molecules are reduced at the cathode to form hydroxyl anions and hydrogen gas. The sodium and hydroxyl ions combine to form sodium hydroxide, which in turn will react with the chlorine gas to produce the desired sodium hypochlorite solution. As shown above, a side reaction forms a sodium chlorate by-product that can contribute to cell inefficiency, and it has the potential to consume the hypochlorite and hypochlorous acid intermediates before sodium hypochlorite formation. Both the brine inlet temperature and the salt inlet concentration can affect the formation of by-products. Therefore, these two variables are closely monitored and controlled by the on-site generation system.

The capacity of generators varies from 6 to 3000 lb of available chlorine per day, and multiple generators may be used to meet higher chlorine demands. Generator systems are often composed of several electrolytic cells, called modules with capacities of 6–50 lb/day. Both single- and multiple-module systems are available. Although most multiple module systems are composed of vertically stacked units, some horizontally stacked skids can also be used.

Each electrolytic cell consists of compartments containing electrode plate pairs (cathode and anode) vertically assembled to form an array of electrodes that serve as the flow path for the dilute brine solution. As the brine solution flows between the electrode plates and is electrolyzed, its concentration decreases, the sodium hypochlorite concentration increases, and hydrogen gas is formed. The parallel bank configuration facilitates hydrogen purge and minimizes scale. The number of electrode plate pairs in the cell compartments can be adjusted to match the desired unit capacity.

The main components of the generator cell skid include a cylindrical clear acrylic or polyvinyl chloride (PVC) electrode-holding chamber, electrode plates, hydrogen gas vent, heat exchanger, and brine dilution (Fig. 10.8).

The electrolyzer cells that house the anodic and cathodic electrodes are cylindrical chambers of clear acrylic with bolted-end flanges. All cell components are joined by solvent welding or mechanical compression. The electrode plates are constructed of titanium. The anode plates are of the dimensionally

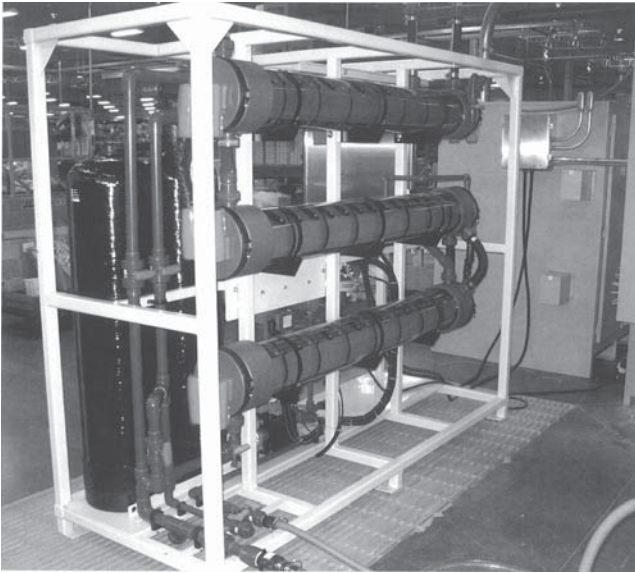


Figure 10.8. Sample multiple cell generator skid installation (courtesy of Siemens Water Technologies).

stable type electrodes coated with a precious metal oxide to minimize deterioration. As the current is applied to each node of the electrodes, a constant direct current (DC) potential is maintained across their cell plates. The electrodes have a maximum alternating current (AC) requirement of 2.0 kW per pound of chlorine output, with a maximum current density of 1.2 A/in.². The energy requirements vary among manufacturers. Electrolytic cells constructed for this service are membraneless, which reduces the potential for fouling and should be factory tested for a pressure of at least 50 psig.

Electrode plates are either monopolar or bipolar. The monopolar plates are segregated inside the cell into anode and cathode plates, which allows replacement of a single deteriorated anode or cathode. The bipolar plates contain both the anode and the cathode, so the entire plate must be replaced.

The generator skid is preassembled at the factory and mounted in a corrosion-resistant and epoxy-coated steel frame. All major system components including brine dilution appurtenances and the soft-water heat exchanger are preplumbed and skid mounted at the factory. The anode and cathode plates are designed to be removable without removing the module from the skid.

The chemical in the electrolytic cell follows a two-phase flow pattern: One phase consists of the newly formed sodium hypochlorite liquid plus some unreacted brine solution, and the other phase consists of hydrogen gas. The flow stream is moved through the cell modules by back pressure created by

the brine dilution water. Each cell module includes an interstage hydrogen vent piped to the hydrogen dilution standpipe. The hydrogen gas is also present as entrained bubbles and in dissolved form in the sodium hypochlorite solution. The hydrogen is not allowed to separate from the solution until the hypochlorite leaves the cell and the hydrogen can diffuse into the air. The additional hydrogen gas is diluted at the standpipe and the storage tanks, (as described in the “Hydrogen Formation, Separation, and Safety” section of this chapter).

The electrolysis of sodium hypochlorite causes the temperature across the generator cell module to rise, which can raise the temperature of the solution to rise by 20°F or more. The temperature is controlled by a heat exchanger or a chiller. Heat exchangers may be skid mounted as an integral part of the generator.

Preparing and diluting the brine with soft water help reduce scale buildup on the electrode plates but does not completely eliminate it. Metal deposits on electrodes will increase the current density, electricity use, and salt consumption, and the efficiency of electrolytic cells will decrease. The generator system logic controller is programmed to alarm when the cell requires maintenance and will also start an automatic shutdown sequence if the operating voltage drops to a dangerous level. The scale on the electrodes is removed by using a weak acid-cleaning solution, applied by pumps mounted on a cleaning cart. The anode plates are coated with a precious metal oxide to reduce their rate of degradation. Most anode manufacturers provide warranties for up to 7 years. Among the factors affecting the life expectancy of electrodes are water and salt quality, frequency of preventive maintenance, and hours of operation.

The generator system skid and a number of its peripheral components are controlled by a control panel that should monitor and control at least the variables such as electrolyzer cell brine solution level, dilution water flow, and rectifier supply current. Because the electrolytic cells are sensitive to UV exposure, they should be located indoors, at room temperatures between 45 and 100°F. Additional details on generator skid layout are discussed in the “System Layout” section of this chapter.

Brine Dilution

Each generator skid is equipped with brine dilution appurtenances. The main components include piping, valves, brine solution rotameter, soft-water rotameter, pressure transmitter, pressure gauge, flow sensors, and/or flow switch. Appurtenances for small capacity generators may also include an eductor.

The rotameter is a glass or acrylic tube and a float or a paddle wheel for flow indication and has sufficient capacity to measure the brine solution and soft-water flows. The electrolytic cell needs at least 50 psi of water pressure at the water line solenoid valve on the rack or skid. If adequate pressure is not available, a booster pump should be provided.

Rectifier

The rectifier converts the AC supplied by the utility to DC used for electrolysis. Each generator rack or skid assembly has a dedicated rectifier sized to produce DC for the associated generator. The rectifier's main components include a built-in voltmeter and ammeter, a cell voltage-monitoring contact with alarm, an air-cooling fan, and the copper bus bars and cables for connecting it to the electrolytic cell(s). The built-in voltmeter and ammeter are used to indicate the output voltage and current of the rectifier. Cell voltage monitoring is important for protecting the generator cell from damage. The rectifier unit may be placed adjacent to the generator skid or rack, or at a remote location, depending on the application.

The rate of electrolysis may be controlled by adjusting the amount of current supplied. Since electricity in the form of electrons is one of the essential reactants for sodium hypochlorite formation, its rate increase translates into a higher rate of reduction at the cathode plate and a higher rate of oxidation at the anode plate. By following this principle, the generator cell can overcome inefficiencies such as scale buildup and competing reactions by modulating the input current. The increase in the supplied current is directly related to an increase in power consumption. It should be noted that some manufacturers experience higher power consumption and lower efficiency when operating in this manner; thus, they use constant current and brine flow for steady-state operation.

The rectifier is designed with a power factor of at least 90%. The power factor is defined by the ratio of real power to apparent power. Thus, a low power factor causes a high current requirement. Since real power translates into the capacity for the system to perform work, higher power factor renders higher efficiency. Utility providers tend to penalize end users who have a power factor lower than the set limit for that provider.

Rectifier units generate a substantial amount of heat, which must be taken into account in HVAC system design. Overheating is typical for large rectifiers. Integral cooling fans and thyristor-type heat sinks in conjunction with internal thermal overload protection are essential for safe and reliable rectifier operation. Some rectifier units are equipped with built-in high-performance cooling fans that discharge outdoors.

Hydrogen Formation, Separation, and Safety

Electrolysis of sodium chloride solution generates hydrogen gas that rises to the top of the electrolytic cell where part of it is vented and the remainder exits the cell with the finished 0.8% by weight sodium hypochlorite solution.

The hydrogen gas is of concern because of its flammability and explosiveness limit. Below the LEL, the concentration of the gas in the air is not high enough for it to ignite. Above the upper explosive limit, the gas has displaced

sufficient air, and there is not enough oxygen available for ignition. The LEL for hydrogen in air is 4% by volume. As a safety measure, the system is designed to maintain the hydrogen gas concentration in air below 25% of the LEL, or 1% by volume.

The hydrogen gas is formed in the electrolytic cells at a stoichiometric rate of approximately 0.03 lb per pound of available chlorine produced. The actual production is 0.04 lb of hydrogen per pound of available chlorine. For example, a 1200-lb/day electrolytic cell unit can produce 48 lb of hydrogen gas per day, which may lead to hazardous conditions. A common method of preventing accumulation of ignitable hydrogen gas is providing hydrogen dilution standpipe, dilution blowers, gas sensors, and an emergency high-rate ventilation system.

The principle governing the design of a hydrogen dilution standpipe is that of mass and concentration differential. As the two-phase flow exits the on-site generation chamber, the hydrogen gas concentration in the solution and at the solution surface is higher than that in the surrounding air. The blowers force air to the surface of the liquid and dilute the hydrogen before it is vented to the atmosphere. In addition, the hydrogen gas is approximately 14.5 times lighter than air and therefore rises rapidly above the air.

The dilution standpipe is an open, vertical, cylindrical FRP pipe that is located between the electrolytic cells and the sodium hypochlorite storage tank (Fig. 10.2). It is used as a wide spot in the line, where the hydrogen gas can be separated from the sodium hypochlorite solution. The standpipe receives the two-phase flow composed of hydrogen gas and sodium hypochlorite solution from the electrolytic cells and allows the hydrogen gas to diffuse out of solution and rise to a vent stack. Other means of separation include a large-diameter pipe to allow hydrogen separation, dilution, and escape before it enters the storage tank.

The size of the hydrogen dilution standpipe is proportional to system capacity. It is also necessary to consider structural support and space availability when the standpipe is designed. For larger systems with capacities of 1500 lb/day of chlorine and more, the standpipe should have a diameter of at least 36 in.

The standpipe is hydraulically balanced with the sodium hypochlorite storage tank(s), which is where the sodium hypochlorite solution is stored. It is recommended that the standpipe be placed within a 6-ft radius from the electrolytic cells to minimize hydraulic back pressure to the electrolytic cells. For indoor installations, layout must be given proper attention, as the height of the standpipe may affect building structure (as discussed in more detail in the on-site generation system layout considerations section of this chapter). A typical outdoor installation of a standpipe is in Figure 10.9.

A dedicated air dilution blower should be used to supply the standpipe with air for hydrogen dilution. The blower must be sized to supply enough dilution air to keep the hydrogen concentration below 25% of the LEL, or 1% by volume. A standby blower should be provided for use in the event of an equipment failure (see the “Hydrogen Dilution Blowers” section of



Figure 10.9. Standpipe installation (courtesy of Black & Veatch).

this chapter). The typical connections to a hydrogen dilution standpipe include the electrolytic cell effluent line, the hydrogen dilution air blower discharge, the standpipe outlet to the bulk storage tank, and the vent stack to the outdoors (Fig. 10.10).

Some manufacturers elect to use an alternative method for hydrogen removal, which include transferring sodium hypochlorite directly from the electrolytic cells to the storage tank. For hydrogen traps to be prevented, nozzles are not located on top of the tank, each tank has its own vent, and two blowers are dedicated to each tank. The tank is filled from the bottom, and a differential pressure level transmitter is used in lieu of an ultrasonic. An orifice plate is required on the tank vent for airflow verification.

The electrolytic cell discharge pipe should have an upward slope of at least $\frac{1}{4}$ in/ft toward the hydrogen dilution standpipe, as illustrated in Figure 10.10. It should contain as few elbows and turns as possible to eliminate locations where the hydrogen gas could accumulate. Piping installation requirements may vary among manufacturers.

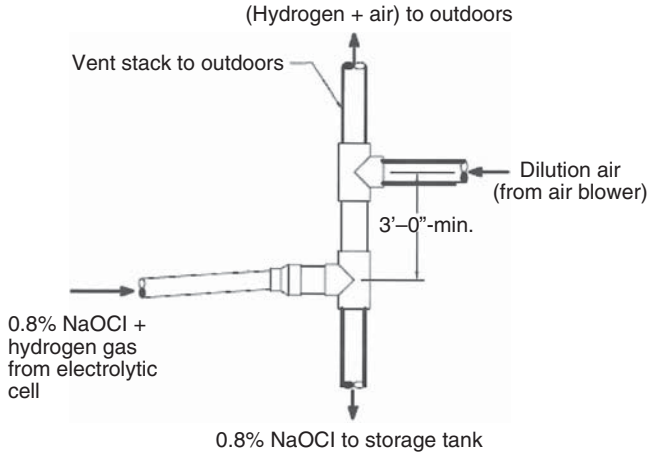


Figure 10.10. Typical standpipe installation (courtesy of Severn Trent Services).

No isolation valves should be located between the electrolytic cells and the standpipe. Any blockage on the discharge pipe could lead to overpressurization of the piping and the electrolytic cells, and the potential for explosive rupture of the pipe, equipment damage, and a hazard to operators. A pressure-relief assembly containing a rupture disk and relief piping should be installed on the discharge line to protect the piping and the system from overpressurization. If isolation valves are required by the manufacturer, limit switches must be provided. The limit switches must be interlocked with the sodium hypochlorite generation control panel so that the system will not start if the valves are in the closed position. A typical rupture disk installation is shown in Figure 10.11.

Although most of the hydrogen gas should escape through the standpipe, some of it may travel in solution with the sodium hypochlorite to the storage tank concentrate in the tank's overhead space. The maintenance manways and nozzles on the bulk storage tanks provide space for the hydrogen gas to accumulate. For the potential for hydrogen gas to accumulate in the tank's overhead space to be minimized, a dilution air line with a dedicated air blower is typically connected to the tank. In installations consisting of multiple storage tanks, the dedicated dilution blowers can be served by a common standby blower. The blowers on multiple tank systems are typically connected in a daisy chain fashion to minimize air balance³ issues. The vent line of each tank is piped into the common vent header, which can be routed outdoors or to the hydrogen dilution standpipe.

The vent stack of the standpipe should extend at least 3 ft above the highest point of the building housing the standpipe, and 2 ft above the highest point in any building within 20 ft from the vent stack. It should terminate at least 20 ft from any building entrances, windows, air inlets, and

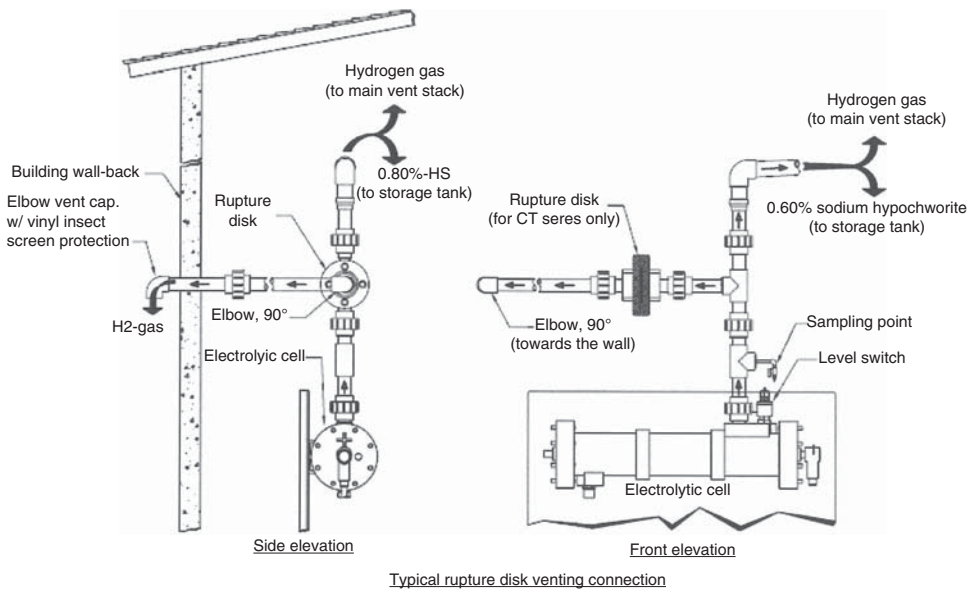


Figure 10.11. Relief/Rupture disk installation (courtesy of Severn Trent Services).

HVAC equipment. Vent piping should not be routed above walkways or occupied spaces.

Vent stacks typically terminate in vent caps, should be equipped with bird or insect screens, and should be designed to prevent frosting and infiltration back to the storage tank. The local lightning protection requirements should be observed. Lightning protection equipment may include lightning conductors and air terminals. Since PVC, the vent stack piping material, is sensitive to extremely low temperatures, high-density polyethylene may be used for a system installed in cold climates.

An alarm system should be installed in the room to monitor the hydrogen concentration. The system should consist of one hydrogen transmitter with at least two independent sensors. The sensors should be installed around areas and equipment where a high concentration of hydrogen gas would be expected in the event of a system failure and in areas that are prone to air stagnation. Upon high hydrogen alarm, the system will shut down, and a high rate ventilation system is energized. Alarm points may vary, but, typically, a hydrogen concentration of 1% should activate the alarm, and a 2% concentration should stop hypochlorite production. The alarm should also be sent to the facility main control system in case the emergency ventilation system fails. The ventilation system failure alarm is typically tripped by an airflow switch in the ventilation system ductwork.

Placement of the standpipe and the storage tank outdoors can make the system safer. However, the electrolytic cells must be installed indoors.

A high-rate emergency ventilation system that is energized by a high hydrogen level alarm and operates for at least 10 min after the hydrogen alarm stops must be provided for the indoor process space. The ventilation system must be linked to the standby or emergency power supply in accordance to Chapter 27 of the 2003 International Fire Code.

High concentrations of hydrogen in the sodium hypochlorite generation room are usually caused by system failure. The generation systems include safety interlocks that are energized by high concentrations of hydrogen in the process space and shut down the system.

The size of the ventilation system should be based on the maximum amount of gas that may be produced by the entire system (including standby generators), and the room's dimensions and normal operating temperature and pressure. The amount of outside ventilation air for the ventilation system can be calculated by the following formulas:

Hydrogen Production Calculations

$$F_{H_2}(\text{lb } H_2/\text{day}) = (0.03 \text{ lb } H_2/\text{lb } Cl_2) \times (\text{lb } Cl_2/\text{day}) \quad (10.10)$$

$$M_{H_2}(\text{lb-mol } H_2/\text{day}) = F_{H_2}(\text{lb } H_2/\text{day}) / (2.01594 \text{ lb } H_2/\text{lb-mol } H_2) \quad (10.11)$$

Air Requirement Calculations

$$\begin{aligned} M_{\text{air}}(\text{lb-mol air/day}) \\ = M_{H_2}(\text{lb-mol } H_2/\text{day}) \times (1 \text{ lb-mol air}/0.01 \text{ lb-mol } H_2) \times SF \end{aligned} \quad (10.12)$$

$$M_{\text{air}}(\text{lb-mol air/min}) = M_{\text{air}}(\text{lb-mol air/day}) \times (1 \text{ day}/24 \text{ h}) \times (1 \text{ h}/60 \text{ min}) \quad (10.13)$$

$$25\% \text{ of LEL of Hydrogen} = 1\% = (1 \text{ part air}/0.01 \text{ part } H_2)$$

$$SF = 4(\text{recommended value})$$

Outside Ventilation Air Induction Rate

$$T_{\text{air,R}} = T_{\text{air,STD}} + 460^\circ\text{F} = 60^\circ\text{F} + 460^\circ\text{F} = 520^\circ\text{F} \quad (10.14)$$

$$P_{\text{air}} = P_{\text{atm}} = 14.7 \text{ psia}$$

$$Q_{\text{air}}(\text{ft}^3 \text{ air/min}) = \frac{M_{\text{air}}(\text{lb-mol air/min}) \times T_{\text{air,R}} \times (10.73 \text{ ft}^3 \times \text{psia}/\text{lb-mol} \times ^\circ\text{R})}{P_{\text{air}}(\text{psia})} \quad (10.15)$$

Room Volume Calculation

$$V_{\text{room}}(\text{ft}^3) = L_{\text{room}}(\text{ft}) \times W_{\text{room}}(\text{ft}) \times H_{\text{room}}(\text{ft}) \quad (10.16)$$

Room Turnover Rate Calculation

$$\text{RTR (TO/h)} = Q_{\text{air}} (\text{ft}^3 \text{ air/min}) \times [\text{TO}/V_{\text{room}} (\text{ft}^3 \text{ air})] \times 60 \text{ min/h} \quad (10.17)$$

Calculation Variables

- V_{room} = room total volume in feet
- L_{room} = room length in feet
- W_{room} = room width in feet
- H_{room} = room height in feet
- F_{H_2} = mass flow rate of hydrogen produced in pounds per day
- F_{air} = mass flow rate of outside air into the room in pounds per day
- M_{H_2} = molar flow rate of hydrogen in lb-mol/day
- M_{air} = molar flow rate of air in lb-mol/day
- Q_{air} = air volumetric flow rate in ft³/min
- $T_{\text{air,STD}}$ = standard temperature of air in degrees Fahrenheit (60°F)
- $T_{\text{air,R}}$ = temperature of air in degrees Rankine
- P = pressure in lb/in² absolute
- MW_{air} = molecular weight of air in lb/lb-mol
- SF = safety factor
- TO = room turnover rate based on room volumetric air space
- RTR = room turnover rate in air changes per hour

The emergency ventilation system does not eliminate the need for normal continuous ventilation. The requirements for continuous ventilation in an occupied space are described in local mechanical and international building codes. Air discharge and exhaust points for the ventilation system should be located to provide cross airflow above the generation system whenever possible. Since hydrogen gas is lighter than air, room ventilation air exhaust vents should be placed near the ceiling. In some cases, outdoor air may be used to maintain room temperature requirements at the appropriate level. If the outside air ventilation system is of sufficient capacity to meet the required room turnover rate, it may be used as the emergency high-rate ventilation system.

On-site hypochlorite generation equipment, such as rectifiers and mechanical blowers, are a significant source of additional heat to the room and should be taken into account when calculating heat loads. Ductwork for heating or cooling units must be routed away from the generation equipment and other possible sources of ignition. The heating and cooling unit inlets should be placed near the finished floor, where hydrogen gas would be present at the lowest concentration.

With respect to regulations, an on-site sodium hypochlorite generation room is not typically subject to a class rating as described by the National Fire

Protection Agency unless it is located next to a room classified as Class I, Division I. In the event that the system must be located next to a Class I, Division I room, proper precautions must be taken to avoid contact with ignitable concentrations of gases. The precautions include positive pressure ventilation from clean air sources and safeguards against ventilation failure. If these precautions cannot be taken, the on-site hypochlorite generation (OSG) room must be rated Class I, Division 2. The National Fire Protection Association (NFPA) Section 70-500.7 requires the equipment within a Class I, Division 2 room to be explosion proof.

Hydrogen Dilution Blowers

The forced air ventilation for hydrogen gas dilution is provided by mechanical air blowers, which run during the generation system operation and for a minimum of 10 min after the generators stop. A typical multiple-blower system is composed of mechanical blowers, blower piping, inlet silencers, inlet filters, sound enclosures, check valves, and differential pressure switches.

The dilution blower is sized, considering the total capacity of all the generator cells and the need to keep the hydrogen gas concentration below 25% of the LEL. The standpipe blower is typically sized to provide 1 scfm of dilution air for every pound of available chlorine capacity. The dilution ratio at the storage tanks is for 0.5 scfm of air per pound of available chlorine capacity. If a standpipe is not provided, the storage tank blowers are sized to provide 1 scfm of air from every pound of chlorine capacity. A total capacity of 3000 lb of chlorine per day would require a dilution blower with a minimum capacity of 3000 scfm to serve the standpipe. For this same example, each storage tank would require a blower with a minimum capacity of only 1500 scfm; however, if a standpipe was not provided, each storage tank blower would require a minimum capacity of 3000 scfm.

The blower horsepower is dependent on the air volumetric flow rate, the static pressure in the discharge pipe, and the velocity pressure exerted by the airflow on the pipe. The designer must first decide on an air velocity, which is determined by the overall required volumetric flow and the discharge pipeline cross-sectional area:

$$V_{\text{air}} = Q_{\text{air}} / \text{OA}, \quad (10.18)$$

where V_{air} is the air velocity in ft/min, Q_{air} is the air volumetric flow rate, and OA is the discharge pipe cross-sectional area.

The air velocity is inversely proportional to the cross-sectional area of the discharge pipe and should not exceed 3500 ft/min. For horsepower to be calculated, the total pressure must be determined. The total pressure is the sum of the velocity pressure and the static pressure. The static pressure is a function of the pipe or duct material and shape, while the velocity pressure is calculated by using the following equation:

$$VP = (V_{\text{air}}/4005)^2. \quad (10.19)$$

where VP is the velocity pressure in inches of water column.

The total pressure is determined by the sum of the static pressure and the velocity pressure. The air horsepower is calculated by using the following equation:

$$AHP = (Q_{\text{air}} \times TP)/6356, \quad (10.20)$$

where AHP is the air horsepower in horsepower and TP is the total pressure in inches of water column.

The mechanical efficiency is calculated by the ratio of air horsepower to the rated break horsepower of the fan:

$$ME = AHP/BHP, \quad (10.21)$$

where ME is the mechanical efficiency and BHP is the break horsepower.

For a known motor input, the electrical efficiency can also be calculated as shown below:

$$EE = (0.746 \times BHP)/kW, \quad (10.22)$$

where EE is the electrical efficiency and MI is the motor input in kW.

The total fan efficiency is multiplicative and can be obtained by multiplying the mechanical and electrical efficiency. It can also be determined directly from a combination of static efficiency (not shown) and mechanical efficiency.

$$TE = ME \times EE \quad (10.23)$$

$$TE = (Q_{\text{air}} \times TP)/(6356 \times BHP), \quad (10.24)$$

where TE is the total efficiency.

The total fan efficiency has a direct impact on operating cost and energy use. Although the initial cost of higher efficiency fans may be higher, their use may result in considerable savings in operating cost. Fan efficiency should also be considered in the economic analysis. Among blower manufacturers are Cincinnati Fan and New York Blower.

The best material for blower air piping is nonmetallic, such as FRP or Schedule 80 PVC. Schedule 80 PVC is not recommend for pressurized gas; therefore, the sizing of the pipe is very critical to ensure that the pressure inside the pipe does not exceed 2 in. of water column above atmospheric pressure. The size of the blower pipe depends on air velocity, as described above, and is directly affected by external static pressure and noise caused by the

forced air movement. Another major factor in determining the diameter of the blower discharge pipe is the pipe routing. The effect of discharge pipe routing with respect to blower size must be considered when establishing the system configuration.

The discharge piping downstream from each blower should include a check valve to prevent short-circuited airflow from another blower. The use of isolation valves for airflow control should also be considered.

Mechanical air dilution blowers are usually located indoors because certain system components and ancillary equipment, such as pressure and flow switches, are temperature sensitive. Blowers located indoors can bring in cold outside air, which could cause the sodium hypochlorite solution to freeze. In temperate climates where the blowers may be located outdoors, they should be shielded with a sunshade. Blowers located indoors may exceed the allowable noise level and can infringe on sound levels for an occupied room. Therefore, the blowers may have to be installed in sound enclosures and may have to be equipped with inlet and outlet silencers.

Formation of condensation in blower discharge piping is a common occurrence, which may lead to equipment corrosion if not controlled. A drip leg assembly can be used to prevent condensation from reaching the blower equipment and to keep the sodium hypochlorite fumes from entering the room through the blower.³ A typical blower drip leg installation is shown in Figure 10.12.

Blowers should be installed at no higher than two-thirds of the sodium hypochlorite storage tank height to avoid bleed-back of hydrogen to the

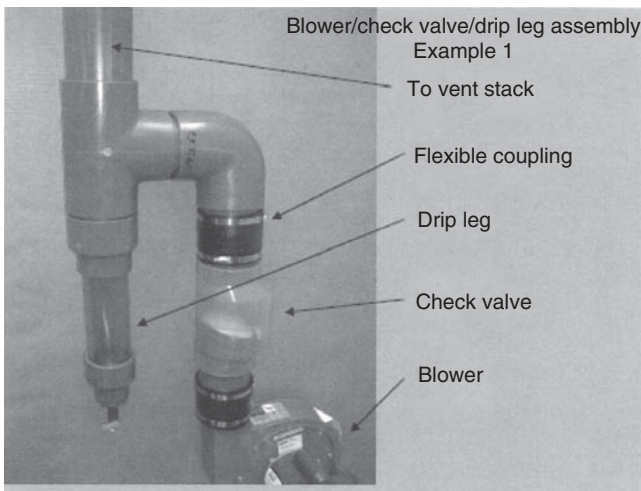


Figure 10.12. Typical blower drip leg installation (courtesy of Severn Trent Services).

blower cage. Each blower should be equipped with a current-sensing device interlocked with system controls to alarm the system in the event of blower failure, and with differential pressure switches in both the standpipe vent piping and the storage tank vent. The discharge piping of each blower, the inlet of each storage tank, and the standpipe ventilation piping are usually equipped with airflow orifices that interface with the local pressure switches to alarm the control system in the event of airflow failure.

It is recommended that the blower be allowed to run for a minimum of 10 min after the on-site generator ceases production to ensure that the system is completely purged of any leftover hydrogen gas. The blower should also be run before the generator starts to ensure that the purge system is operating properly.

Sodium Hypochlorite Storage Tank

The sodium hypochlorite solution is stored in FRP tanks. Design of storage tank systems is covered in Chapter 9 of this manual.

The duration storage of dilute on-site generated sodium hypochlorite will vary depending on demand, but it is typical to provide 3 days of storage at average dosages and flow, or 1 day at maximum dosage and maximum flow.

Each sodium hypochlorite storage tank will be equipped with a level transmitter nozzle, sight gauge nozzles, overflow and drain nozzles, and a pump suction nozzle, as well as a ventilation air nozzle, which should be one size larger than the dilution air inlet nozzle. The tank fill nozzle is typically placed on the side bottom to maintain hydraulic balance with the hydrogen dilution standpipe. The storage tanks may be located outdoors, except in areas of very cold climate. The sodium hypochlorite storage tanks are not designed to be pressurized. Therefore, the hydrogen dilution blowers must be of low-pressure type, and the tank vent must be properly sized, as discussed above.

Sodium Hypochlorite Feed Equipment

The sodium hypochlorite solution is delivered to the treatment process by metering pumps that can be of the diaphragm or peristaltic type. Design of metering pump systems is covered in Chapter 9 of this manual. On-site-generated sodium hypochlorite is of lower concentration (0.8% by weight) than the full-strength sodium product (12%–15% by weight). The lower concentration translates into higher flow rates to provide the same amount of available chlorine as in the full-strength solution. It is customary to use delivered full-strength solution to back up the on-site generation system. Therefore, either the metering pumps will be sized to deliver solution of both strengths or provisions will be made for diluting the full-strength solution, so it can be metered at the same rate as the dilute solution. System redundancy is discussed further in this chapter.

ON-SITE SODIUM HYPOCHLORITE GENERATION SYSTEM DESIGN

Equipment Sizing

Sizing the sodium hypochlorite generation system, from salt storage to electrode capacity, is based on the plant's total chlorine demand. Assuming that a plant's total chlorine demand is 1200 lb of available chlorine per day, the system will be sized as described below. The salt storage requirement is calculated by using a ratio of 3–3.5 lb of sodium chloride salt per pound of chlorine produced. The total amount of salt to be stored is 4200 lb/day, which is calculated as follows:

$$\text{pound of NaCl required} = \frac{3.5 \text{ lb of NaCl}}{1 \text{ lb of Cl}_2} \times 1200 \text{ lb of Cl}_2. \quad (10.25)$$

For a 30-day supply of salt, the storage tank should hold 63 tons of sodium chloride. Several tanks may be needed to store this entire amount. If the site footprint is limited, the dry salt may be stored in a silo or a bulk bag system, which adds complexity to the design but may save space.

For the brine metering pumps to be sized, two variables should be considered: the total capacity of the generator system and the saturation concentration of brine in water. Assuming two 600-lb/day generator modules for the 1200-lb/day unit, a 26.4% saturated solution, and 3.5 lb of sodium chloride per pound of chlorine produced, the brine metering pump will have a capacity of approximately 80 gph, as calculated below:

$$(\text{lb of NaCl/h}) = (50 \text{ lb of Cl}_2/\text{h}) \times (3.5 \text{ lb NaCl}) / (1 \text{ lb of Cl}_2) \quad (10.26)$$

$$\frac{\text{lb of NaCl sat'd solution}}{\text{hr}} = \frac{175 \text{ lb of NaCl}}{\text{hr}} \times \frac{1 \text{ lb of NaCl sat'd solution}}{0.264 \text{ lb of NaCl}} \quad (10.27)$$

$$\frac{\text{total lb of sat'd NaCl sol}}{\text{hr}} = \frac{\text{lb of NaCl}}{\text{hr}} + \frac{\text{lb of water}}{\text{hr}} \quad (10.28)$$

$$\frac{\text{gal of NaCl sat'd solution}}{\text{hr}} = \frac{662 \text{ lb of NaCl sat'd sol.}}{\text{hr}} \times \frac{1 \text{ gal of NaCl sat'd}}{8.5 \text{ lb of NaCl}}. \quad (10.29)$$

By using a ratio of 3% sodium chloride solution and 3.5 lb of sodium chloride per pound of chlorine produced, approximately 690 gal of soft water per hour is needed at maximum plant chlorine demand to dilute the sodium chloride from the 26.4% saturated solution to the 3% solution.

Hydrogen dilution blowers are sized for the maximum amount of sodium hypochlorite to be produced. If the two generators are used, their combined

capacity is used to size the blowers. The standpipe blowers are sized for 1 scfm per lb/day chlorine, and the storage tank blowers are sized for 0.5 scfm per lb/day of chlorine, as shown by the calculations below. If a standpipe is not provided, use Equation (10.30) to size the storage tank blowers.

$$(\text{scfm per standpipe blower}) = (1 \text{ scfm}) \times (\text{lb/day Cl}_2) \quad (10.30)$$

$$(\text{scfm per storage tank blower}) = (0.5 \text{ scfm}) \times (\text{lb/day Cl}_2) \quad (10.31)$$

Thus, the capacity of the standpipe blower in this example should be at least 1200 scfm, and the storage tank blower capacity should be at least 600 scfm.

For the rectifier to be supplied with adequate power, the necessary wattage must be determined. The ratio of power to chlorine is 2.0 kW AC to 1 lb/day Cl₂. Thus, the amount of power required for the plant is 2400 kWh AC.

System Redundancy

The amount of system redundancy will depend on user preference and facility type and location. Redundancy requirements for facilities serving a common distribution system will depend on the chlorine feed capacity of the other systems serving that distribution system. Redundancy in such facilities is often limited to only feed equipment. All major rotating equipment, such as pumps, chillers, heaters, and blowers, should also have redundancy.

For a system backup to be provided by utilizing full-strength (12%–15% by weight) sodium hypochlorite, storage tank design, metering pump capacity, and feed system controls should be considered, as well as the regulations pertaining to handling full-strength sodium hypochlorite solution. The 12%–15% weight solution contains about 15 times as much available chlorine as the same volume of on-site-generated solution. The metering pumps should be suitable for pumping and accurately metering both the dilute 0.8% and the full-strength 12%–15% solutions and should be sized to accommodate the entire range of feed rates. The change in solution strength influence may require adjustment of the metering pump controls for the full-strength solution.

The impact on pump design and regulatory requirements is minimized by diluting the full-strength solution prior to storage. The 12%–15% full-strength solution can be diluted to 0.8% by using a dilution panel installed near the truck unloading station. Storage and handling of the diluted solution are subject to the same rules that apply to on-site-generated solution; therefore, minimal changes would be needed to site layout and pump selections. Since the available storage for the on-site generated system is between 1 and 3 days, the appropriate dilution ratios should be considered and enough storage should be provided. A sodium hypochlorite dilution panel is shown in Figure 10.13.

Maintaining system redundancy by using multiple trains of generators can be costly but does provide full backup in the case of a major failure. The options for providing redundancy range from two 50% capacity generator

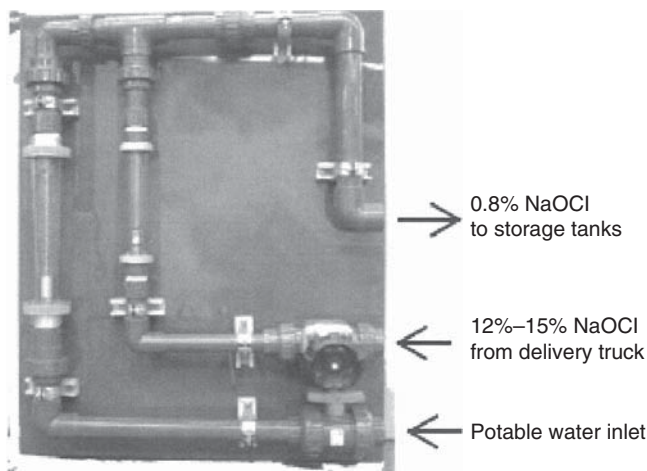


Figure 10.13. Sodium hypochlorite dilution panel (courtesy of Severn Trent Services).

cells to two 100% capacity cells. Two 50% capacity generator cells would provide full system redundancy for the lower half of the feed rate requirements. The disadvantage is that once above the full capacity of one generator cell or at system peak demand, this combination would not provide full backup. Three 50% capacity cells will meet peak demand in the event that one generator fails. The disadvantage of this combination is that it would occupy a larger footprint and would provide full system backup only if just one generator fails. Two 100% capacity generator cells would provide full system redundancy even at peak flow. The disadvantage of this combination is its initial cost, which would be higher than the cost of any other option discussed.

Amount of Sodium Hypochlorite Storage

Since on-site generation of sodium hypochlorite is a continuous process, lead times or uncertainties of bulk chemical delivery are not a concern. Therefore, the decision about the amount of storage to be provided for the on-site-generated hypochlorite solution will depend on the sodium hypochlorite feed point. On-site-generated sodium hypochlorite storage tanks are typically sized for a 3-day supply. They should also have sufficient capacity for 1 day's storage at maximum chlorine dosage and maximum plant flow. The average number of days needed for delivery of a major equipment item to the site.

System Layout

The space requirements of an on-site generation system should include, in addition to the system components, the recommended maintenance clearances for each item of equipment. A sample layout is presented in Figure 10.14.

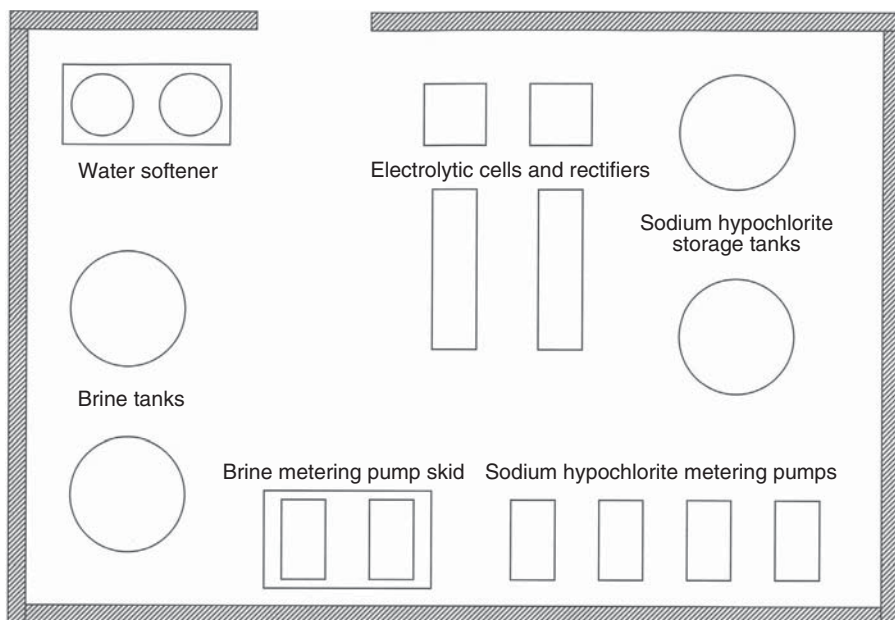


Figure 10.14. Typical layout of on-site generation system (courtesy of Black & Veatch).

The system illustrated above is housed in a closed process building. The hypochlorite storage tanks and the brine tanks are provided with containment. The remaining equipment may be installed inside a curbed area to contain incidental spills.

The brine maker/saturator solution tank is illustrated in Figure 10.14. These tanks should be located near an exterior wall, convenient to the salt truck unloading station to simplify the length and routing of salt delivery piping. While this is a lesser issue for outdoor installations, it should still be considered. An enlarged plan of a brine saturator is shown in Figure 10.15.

For the water or brine solution to be contained in case of a spill, a containment curb of adequate size should be provided. For uncovered outdoor installations, the additional volumes of rainwater must also be included in the containment volume.

Figure 10.15 presents a simplified view of the brine saturator tank. The tank is equipped with level instrumentation, ladder access, and salt fill and brine metering pump suction piping. Thus, adequate clearance must be provided for instrument removal and maintenance, tank maintenance manways, and ladder access (with safety cages for taller tanks). The tank fill piping may be routed low or high, depending on the position of the truck unloading

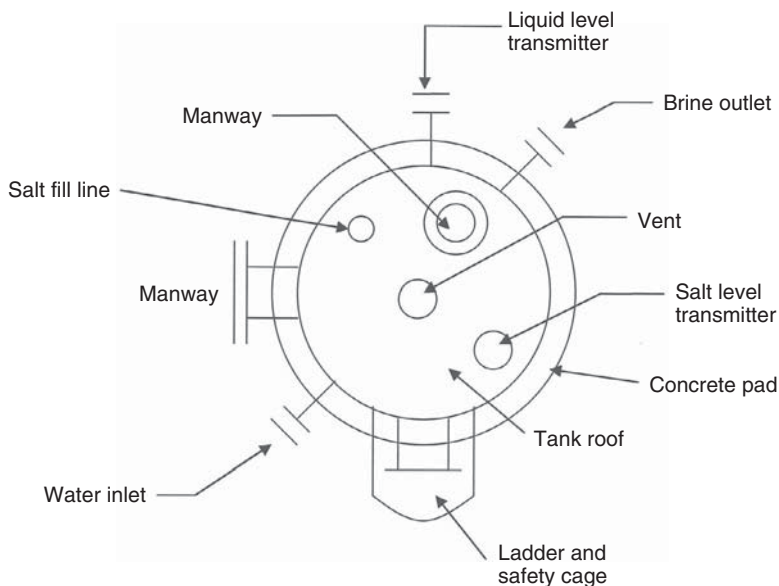


Figure 10.15. Enlarged plan of brine saturator layout.

station; the brine suction piping is typically routed low to maintain flooded suction for the brine metering pumps. Overhead clearances and tripping hazards must also be considered when routing the piping. A detailed section is shown in Figure 10.16.

At least 3 ft of ground-level clearance as well as an overhead clearance of 6.5 ft should be provided around each brine maker tank. The overhead clearance for the brine tank will depend on whether the tank will have top access.

When preparing the system layout, it is necessary to consider how parts of the overall system interact and to place them accordingly. For example, the discharge from the water-softening system will fill the brine storage tanks with soft water, while a bypass stream from the brine maker tank's metering pump suction piping will be used to regenerate the softening system resin. Therefore, the softening system and the brine maker tank should be located near each other to minimize interconnecting piping. This applies also to the chillers and heaters of the soft-water system.

The soft-water system may be designed as a skid or as separate items to be installed in the field. A skidded system may simplify installation but will have a higher initial cost. The clearances for system maintenance and the removal of a resin tank must be considered. A clearance of at least 5.5 ft should be provided between the softening system and other equipment. The softening system inlet and outlet piping will occupy a considerable amount of space, so

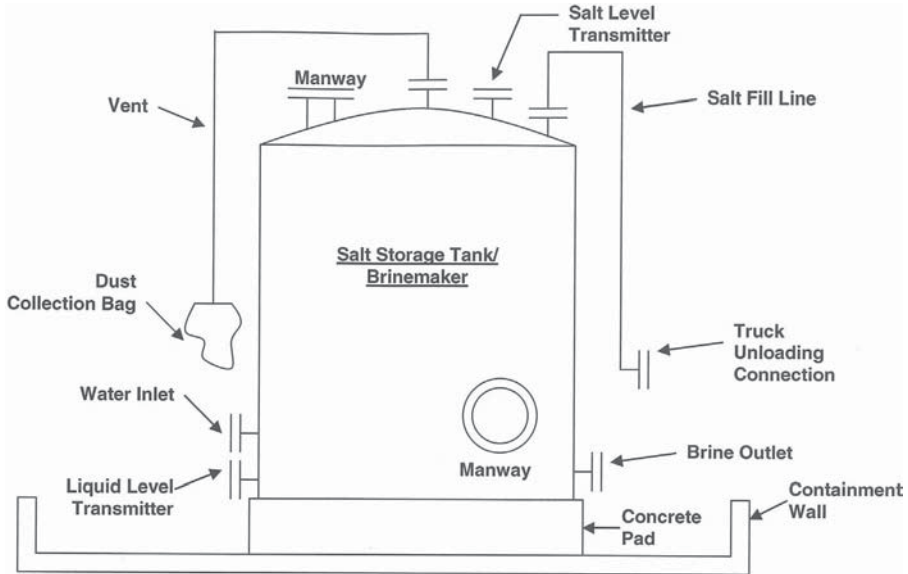


Figure 10.16. Detailed brine saturator tank enlarged section (courtesy of Black & Veatch).

mounting the pipe on a wall is recommended whenever possible. Wall-mounted isolation valves and instrumentation should be mounted at a readily accessible height from the floor.

Soft-water chillers may require a considerable amount of space, depending on system capacity. While small chillers may be part of a skidded package to be located indoors, indoor installation of most chillers is not practical. Because the chiller generates a large amount of heat, it is recommended that it be installed outdoors. In general, chiller units require at least 3 ft of clearance on both sides of the evaporator coil for adequate airflow and heat exchange. Since most air-cooled chillers have an upward vertical fan design, they also require a minimum of 6 ft of clearance above the fan. An additional 4 ft of clearance should be provided for the chiller control panel if it is mounted on the unit (clearances for control panels should meet local and federal regulations for electrical equipment). The chilled-water pump is usually located under the evaporator coils, so enough space must be available for its maintenance and removal. The chiller's water inlet and outlet piping is routed to the brine dilution panel, mounted indoors on the electrolyzer cell skids. The number of chilled water pipes depends on the number of electrolyzer skids. A typical air-cooled chiller installation is illustrated in Figure 10.17.

Soft-water heaters are usually small and can be mounted on the wall. Large heaters should have at least 3 ft of clearance on all sides.

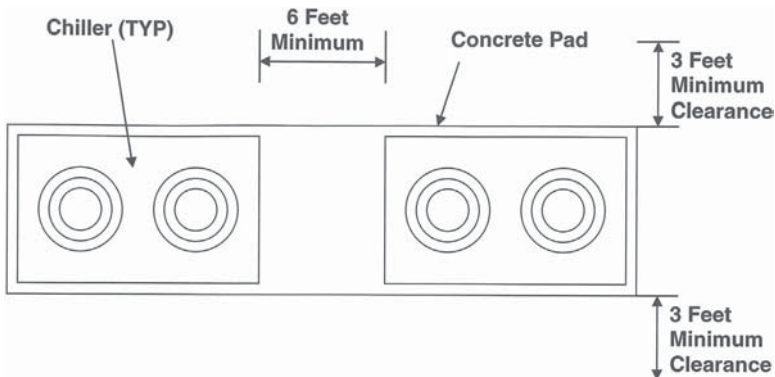


Figure 10.17. Outdoor chiller installation (courtesy of Black & Veatch).

The electrolytic cell skids/trains should be located indoors. The clearances around cell skids depend on how plate racks are removed from their holding chamber. Because the electrode plates must be periodically removed and replaced, enough clearance should be provided for their removal. It is recommended that the full length of a cell chamber plus 3 ft be provided on one side of the skid. Removal clearances vary among manufacturers, so provisions should be made for the worst-case condition. A typical layout of generator cell skids and ancillary equipment is shown in Figure 10.18.

Each generator cell skid includes a rectifier for its power supply, and it generates a significant amount of heat that will have to be taken into account when the room heat loads are calculated. Depending on the application, the rectifier may have to be located inside an electrical room. In such cases, consideration must be given to routing the large-diameter, nonflexible, high-voltage electrolytic cell-rectifier interconnecting cables, and it is recommended that the rectifier be placed as close to the electrolytic cells as possible. However, regardless of the location of the rectifier, a distance of at least 4 ft should be provided between units and at least 6 ft ahead of the control panel.

The hydrogen dilution blowers and associated piping can take up a substantial amount of space. The blowers can be placed indoors or outdoors. Blowers placed outdoors should be sheltered from direct sunlight and, regardless of their location, should be provided with clearance of at least 3 ft on all sides. The discharge piping of duty-standby blowers is typically combined at the blower so that only one air dilution pipe is routed to each tank or standpipe. An additional space of at least 5 ft needs to be provided where the discharge pipes meet.

The blower air piping can be quite large in diameter, making it difficult to route especially for indoor systems. Mounting the pipe can on walls may be possible in some cases. If the piping is routed low within the building, possible

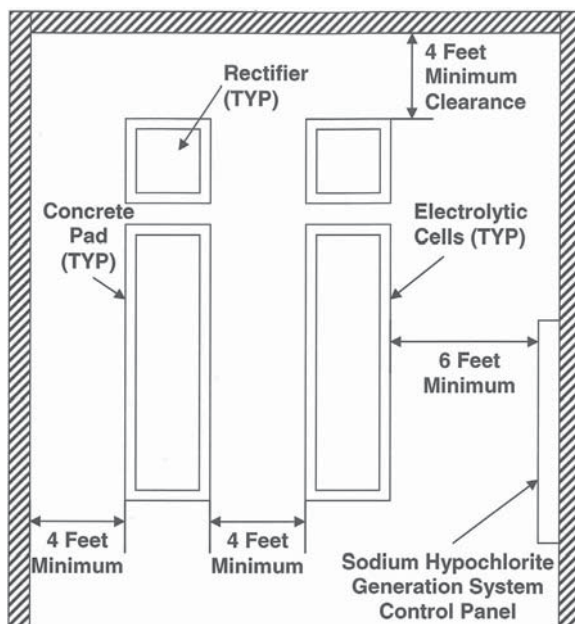


Figure 10.18. Typical layout of generator cell skid and ancillary equipment (courtesy of Black & Veatch).

interference with other equipment and additional clearance requirements should be considered. If the piping is routed high within the building, interferences with HVAC ductwork and building structural members should be considered. Piping support may also be a factor in determining whether to route the piping low or high within the building. A typical blower section is shown in Figure 10.19.

As indicated in the figure, sufficient clearance must be provided for the discharge piping of the hydrogen dilution blowers.

Another component of the hydrogen dilution system is the standpipe, which can be larger than 36 inches in diameter and is typically taller than the sodium hypochlorite storage tank. It must be properly supported and can be installed indoors or outdoors. Indoor placement is challenging because of the height of the standpipe. It must be coordinated with the structural design of the building to avoid interference with supporting beams and height restrictions. At least 3 ft of clearance should be provided around the standpipe and should be located within a 6-ft radius from the electrolytic cells. If the standpipe must be located farther than 6 ft from the cells, the system manufacturer should be consulted.

The sodium hypochlorite storage tanks can be located indoors or outdoors. A clearance of 3 ft should be provided on all sides for each storage tank. The

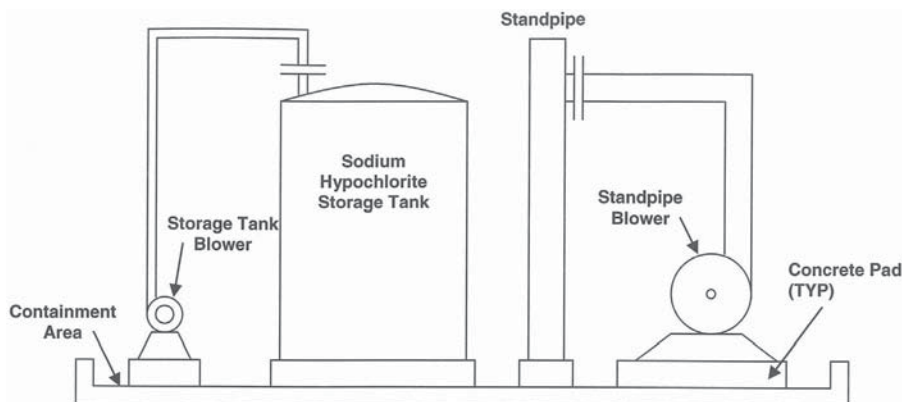


Figure 10.19. Typical blower and associated piping section (courtesy of Black & Veatch).

space requirements of the tank piping should be considered, and the pipe should be routed to minimize interference between this piping and other equipment.

Concrete maintenance pads should be provided for the on-site generation equipment. The clearances recommended here are minimum distances as measured from the maintenance pads. The distance between the outside edges of the maintenance pad and the equipment is assumed to be 6 in.

Because the on-site hypochlorite generation system includes a substantial amount of piping between the various components within the system, it is recommended that the system manufacturer be consulted when preparing the facility layout.

SYSTEM MANUFACTURERS

ClorTec⁴

The ClorTec generators are owned by Severn Trent Services, and the technology was first developed by Gruppo DeNora. The ClorTec products were first manufactured in 1988, and the technology was sold to Severn Trent Services in 1999. Currently, there are more than 3000 ClorTec systems, with capacities of 6–3000 lb/day of free chlorine, operating worldwide.

Severn Trent also owns the SANILEC and SEACHLOR electrochlorination systems, which are used in offshore and marine applications. Severn Trent's OMNIPURE and MARINER OMNIPURE products are marine wastewater systems that generate sodium hypochlorite and oxidize wastewater aboard oceangoing vessels and on offshore production platforms.

Figure 10.20 is a picture of Severn Trent's electrolytic cell.

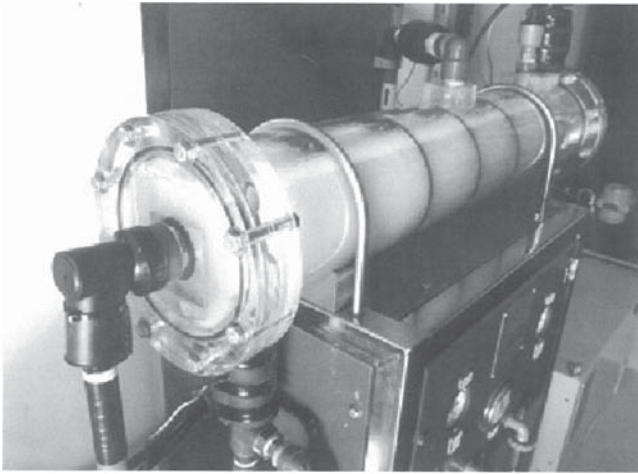


Figure 10.20. ClorTec electrolytic cell (courtesy of Severn Trent Services).

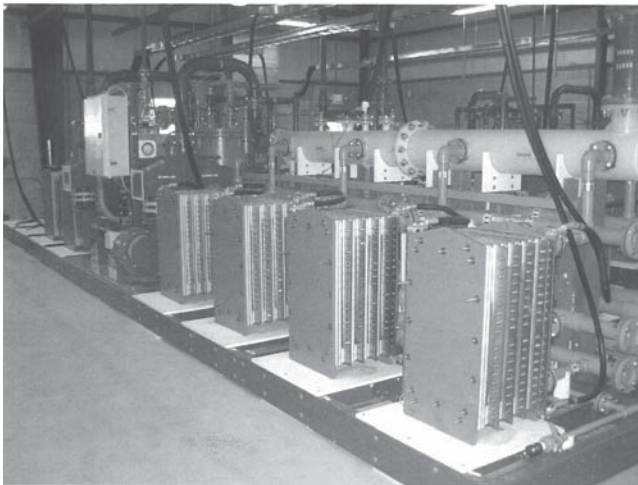
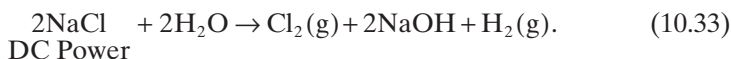
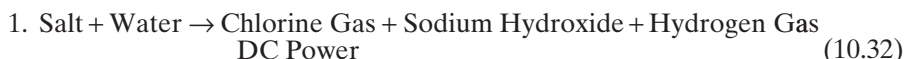


Figure 10.21. Klorigen generation equipment (courtesy of Electrolytic Technologies Corporation).

Klorigen⁵

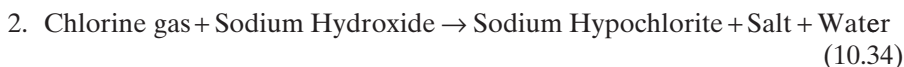
The Klorigen system is manufactured by Electrolytic Technologies Corporation, which was founded in 2001. The Klorigen system's most distinguishing characteristic is that it generates concentrated sodium hypochlorite solution (12.5%–15%). Klorigen manufactures generation systems with capacities ranging from 40 to 40,000 lb/day of chlorine equivalent. Figure 10.21 is a photograph of a Klorigen system.

Process Overview. The Klorigen system can generate either chlorine gas or concentrated sodium hypochlorite (12.5% or 15%). The process is similar to that used to make 0.8% sodium hypochlorite, except that it includes an additional step. The chemical reactions to make chlorine gas are as follows:



At this point, the chlorine gas is delivered to the process, hydrogen gas is diluted and vented to the atmosphere, and sodium hydroxide is disposed of.

If sodium hypochlorite is the final product, the process continues with the following reaction:



The sodium hypochlorite is transferred to a storage tank, while the salt and water by-products are recycled to the beginning of the process.

A process flow diagram of the Klorigen generation process is shown in Figure 10.22.

MIOX⁶

MIOX is a U.S.-based manufacturer that has been providing on-site generation systems since 1994. MIOX currently has more than 1500 installations in 30 countries, with capacities of single generators ranging from 4 to 1550 lb/day.

The MIOX skid integrates most of the major system components (cell, rectifier, controls, brine pump, hydrogen dilution blower) within an ergonomically designed enclosure. MIOX systems come with fully integrated remote monitoring capability, and their electrolytic cells are rectangular instead of cylindrical.

Figure 10.23 is a picture of a MIOX on-site generator.

Figure 10.24 is a flow diagram of the MIOX generation process.

OSEC⁷

The OSEC system was first developed and patented by Wallace & Tiernan in 1981. At the time, the demand for on-site hypochlorite generation systems

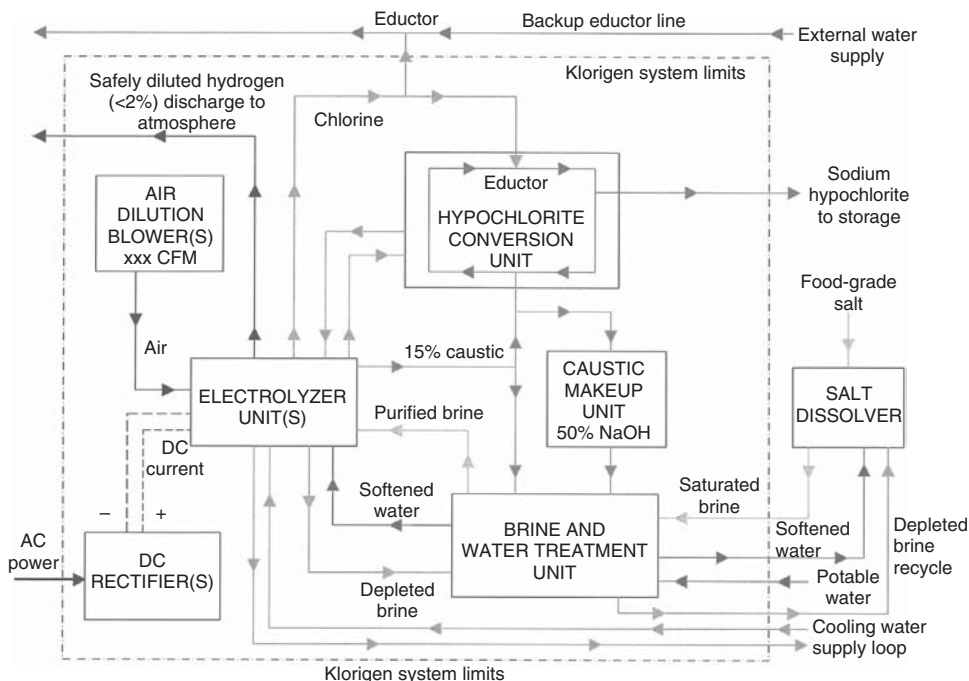


Figure 10.22. Process flow diagram of klorigen system (courtesy of Electrolytic Technologies Corporation).

for water and wastewater chlorination in the United States was limited, but the system was widely used in Europe, particularly in the United Kingdom. In the late 1990s, the OSEC B Series was reintroduced to the North American market, and hundreds have been commissioned in the United States since.

The OSEC system uses solar salt to produce brine for electrolytic cells and produces 0.8% sodium hypochlorite solution. The electrolyzer capacity ranges from 2 to 2000lb of free chlorine per day. Siemens also manufactures the Chloropac, which produces brine from seawater.

Figure 10.25 is a picture of a B-Pak OSEC unit. The OSEC B-Pak skid is a prepiped, prewired, factory-tested package that includes key system components such as water softener, brine feed pumps, control panel, and blowers. Skid capacities range from 250 to 1500lb/day.

Process Solutions, Inc. (PSI)⁸

PSI started in 2003 and is currently located in Campbell, CA. PSI manufactures the Microclor systems that use high-quality salt to produce

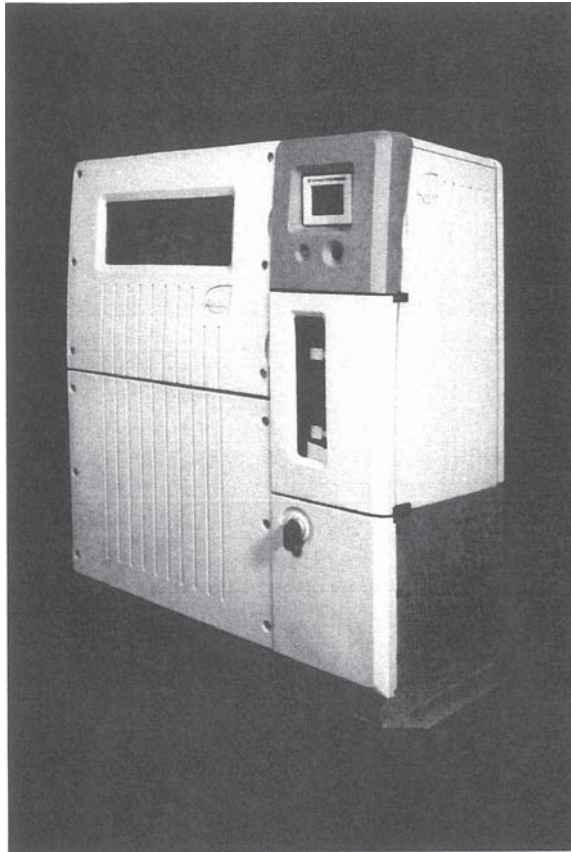


Figure 10.23. MIOX hypochlorite generation equipment (courtesy of MIOX Corporation).

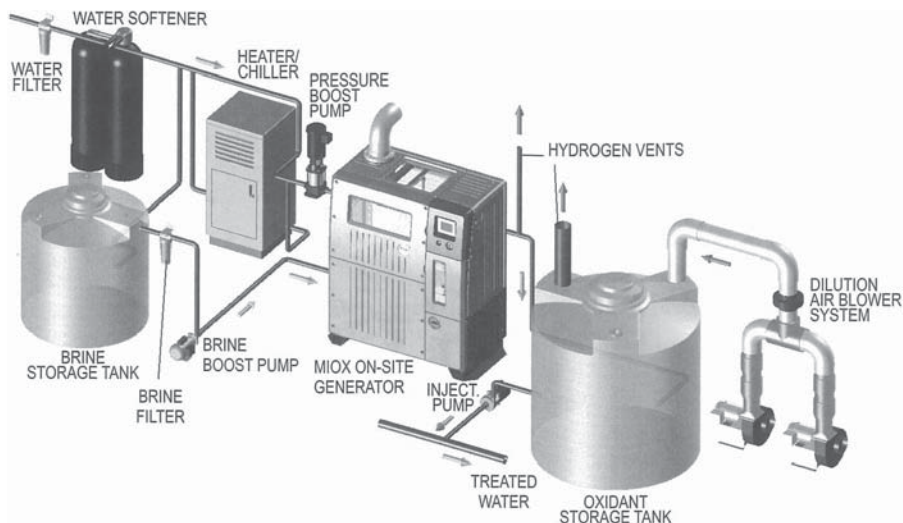


Figure 10.24. MIOX process flow diagram (courtesy of MIOX Corporation).

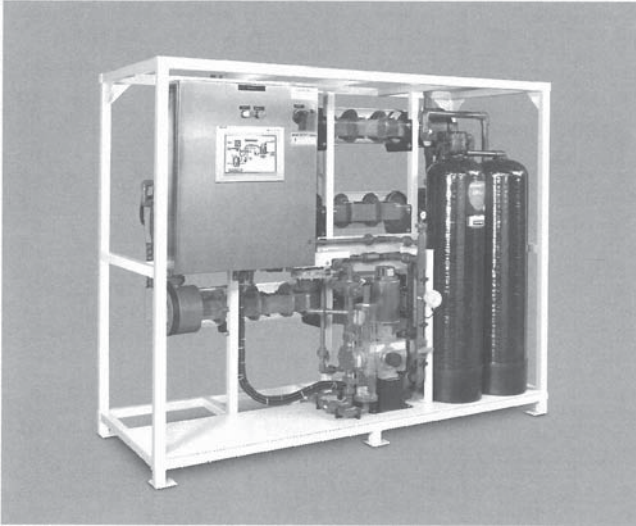


Figure 10.25. OSEC hypochlorite generation system (courtesy of Siemens Water Technologies).

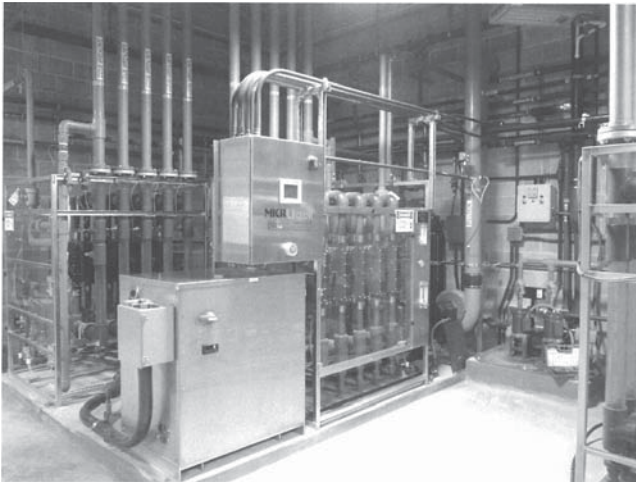


Figure 10.26. MicrOclor hypochlorite generation equipment (courtesy of PSI, Inc.).

0.8% sodium hypochlorite. The most distinguishing characteristic of the MicrOclor generators is that they consist of vertical, rather than horizontal, cells. Available capacities range from 20 to 3000 lb/day of free chlorine. Figure 10.26 is a picture of the MicrOclor equipment.

Figure 10.27 is a process flow diagram of the MicrOclor generation system.

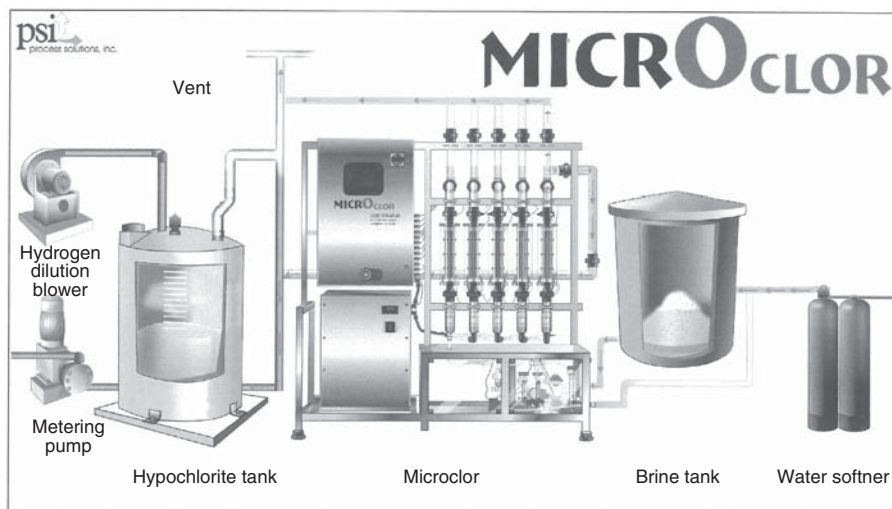


Figure 10.27. MicroOclor process flow diagram (courtesy of PSI, Inc.).

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11 Dechlorination

INTRODUCTION

Dechlorination can be described as the practice of removing all or a specified fraction of the total chlorine residual. In potable water practice, dechlorination is used to reduce the residual to a specified level at the point where the water enters the distribution system. In some cases where taste and odor control is a severe problem, control is achieved by complete dechlorination, followed by rechlorination. This removes the taste-producing nuisance residuals and prevents the formation of NCl_3 in the distribution system. Wastewater and power plant cooling water are dechlorinated to eliminate chlorine residual toxicity, which is harmful to the aquatic life in the receiving waters.

History

Before the discovery of the breakpoint phenomenon in 1939, potable water treatment plants practiced what was commonly called “superchlorination” to destroy tastes and odors caused by ordinary doses of chlorine. The tastes and odors arose from free chlorine residuals that were far in excess of what was thought to be desirable at the consumer’s tap (2–4 mg/l). The superchlorinated water was subsequently dechlorinated with sulfur dioxide to provide an acceptable residual (0.5–0.75 mg/l) in the distribution system. This practice is continued today at a great many locations in the United States and Great Britain. Many water systems around the world use the so-called superchlor–dechlor method to compensate for limited contact time. In fact, some plants dechlorinate the water completely and rechlorinate it to the desired residual as it leaves the plant. This procedure removes all possibility of any off-flavors in the water caused by the chlorination process.

Bottled water is often ordinary tap water that has been subjected to the superchlor–dechlor process. Dechlorination is achieved by using activated carbon filters that are carefully monitored for zero residual. Free chlorine consumes the carbon, and combined chlorine destroys the adsorption power of carbon.

Military vessels also employ the superchlor–dechlor method, so that they can take on practically any raw water supply and still produce palatable water. During World War II, water treatment systems in ships were fitted with special baffled contact tanks that provided 45 min of detention, ensuring destruction of amebic cysts, as the chlorination system was designed to provide a 10 mg/l residual. A safety factor was built into the system by providing a carbon filter bypass, which assured a continuous residual in the ship's distribution system at all times.

Several industrial processes use zeolite softeners along with chlorine-based disinfection. Since residual chlorine in the water can destroy the zeolite, the water must be dechlorinated before it enters the softeners. In such applications, carbon filters are typically used to dechlorinate the water.

Howard and Thompson were among the first to report the earliest dechlorination effort for potable water treatment.¹ Their study focused on the removal of taste and odor from chlorine residuals in Toronto's water supply. Chlorination followed by dechlorination is widely used in Britain. Its principal use is for the disinfection of underground supplies where contact time is short. By using the chlorine residual contact time (*Ct*) concept, the chlorine residual can be elevated to achieve disinfection in contact times as low as 5–10 minutes. The residual concentration at the end of this time may be as high as 3–5 mg/l and is trimmed to the desired distribution system level by dechlorination.

Dechlorination has been found to be beneficial for waters with high concentrations of ammonia N and organic N. When the free residual process is practiced for these waters, terminal dechlorination may be partial or complete, depending on the ratio of free chlorine to total combined chlorine residual immediately ahead of the point of dechlorination. If the free residual concentration at this point is 85% or more of the total, it is usually satisfactory to dechlorinate to the desired free chlorine residual because the amount of nuisance residuals—those made up of other than free chlorine—is so small that it will not be a factor in the palatability of the finished water nor will it cause any problems in the distribution system.

When the ratio of free residual to total residual chlorine drops below 85%, it usually indicates the presence of significant amounts of organic nitrogen in the raw water interfering with the free residual process. At this point, the combined chlorine residual contains what appears to be dichloramine but may actually be some type of organochloramine. These nuisance residuals have no germicidal effect and add an unpalatable taste. Furthermore, they may cause the formation of nitrogen trichloride (NCl_3), which introduces obnoxious odor to the water. If the resulting combined residual is allowed to proceed into the distribution system, the remaining free chlorine continues to react with the combined residual to produce more NCl_3 . Therefore, in such waters, it is desirable to go to complete dechlorination. This removes all of the nuisance residuals and prevents further formation of either dichloramine or nitrogen trichloride. This water, which may contain a slight excess of sulfur dioxide, is then rechlorinated.

Because dechlorination by SO_2 does not remove any of the ammonia, there may be insufficient ammonia remaining after dechlorination to form a predominantly monochloramine residual upon rechlorination. This depends entirely on the amount of ammonia in the raw water that has not been destroyed by the free residual process. Usually, such waters need postammoniation to assure that they contain the proper mono-chloramine residual as they enter the distribution system.

The most common method of dechlorination is by using sulfur dioxide and/or aqueous solutions of sulfite compounds. Other methods involve the use of granular activated carbon and hydrogen peroxide. Ammonia has also been described as a dechlorinating agent, although it is a misnomer. The addition of ammonia converts all free chlorine to monochloramine. When this method of "dechlorination" is used, its sole purpose is to prevent the formation of NCl_3 in the distribution system, which does not form in the absence of HOCl .

Nitrite (NO_2^-) has also been used to dechlorinate the HOCl fraction of total chlorine residual. This is a special case where the combined residual would interfere with the accuracy of an analyzer arranged to record only free chlorine residual. In this case, the analyzer is arranged to measure total residual. At frequent intervals, NO_2^- is automatically injected into the sample. The nitrite consumes the HOCl fraction, which is instantly reflected on the recorder chart. The dip on the chart is a record of the HOCl fraction that the operator needs to know in order to control the free residual process.

The widespread use of chlorine in wastewater discharges and cooling water treatment came under scrutiny when Esvelt et al. reported about the toxicity of wastewater effluents being discharged into San Francisco Bay.² This study proved that chlorinated effluents were more toxic to aquatic life than unchlorinated effluents. The studies also showed that a dechlorinated effluent was less toxic than either the chlorinated or the unchlorinated effluent. Esvelt et al. used continuous-flow online bioassays with golden shiners (*Notemigonus chryssoleucas*) for toxicity evaluation.² The fish were captive in tanks of various chlorine residuals for a minimum of 96 h.

Two years later, Brungs produced a comprehensive report in which the toxicity of chlorine to aquatic life was quantitated.³ This paper reviewed and discussed the uses of chlorine and chlorine chemistry and emphasized toxicity studies in the field and the laboratory. The following two key conclusions were reached in the report:

1. In areas receiving wastes treated continuously with chlorine, total residual chlorine should not exceed 0.01 mg/l for the protection of more resistant organisms only, or 0.002 mg/l for the protection of most aquatic organisms.
2. In areas receiving intermittently chlorinated wastes (power plants), total residual chlorine should not exceed 0.2 mg/l for a period of 2 h/day for more resistant species of fish, or exceed 0.04 mg/l for a period of 2 h/day

for trout or salmon. If free chlorine persists, total residual chlorine should not exceed 0.01 mg/l for a period of 30 min/day for areas with populations of trout and salmon.

To the chlorination-dechlorination practitioner, the above restrictions translated to zero chlorine residual at all times. This was also the interpretation of the California Fish and Game Commission as well as the California Water Quality Resources Board. Zero residual was the consensus among other state regulatory boards, with some exceptions.

Table D of the California Ocean Plan of 1988 indicates a conservative estimate of chronic toxicity by chlorine in surface waters to be 0.01 mg/l. The Ocean Plan therefore sets chlorine residual discharge limits at 0.01 mg/l daily maximum and 0.126 mg/l instantaneous maximum. Discharges to inland surface waters are governed by Basin Plans, which contain generalized narratives to regulate the discharge of toxic chemicals.

Regional Water Quality Board 2, San Francisco Bay Region, has greatly restricted the discharge of chlorine and adopted an effluent limit of 0.00 mg/l in the Basin Plan. As there is no technology that can be used to control chlorine at zero residual, all plants in California dechlorinate to a positive sulfite ion residual, that is, a small excess of sulfur dioxide.

Modern wastewater dechlorination systems are generally designed to produce zero chlorine residual in the effluent before it leaves the plant. In some cases, the outfall may be long enough to consume up to 0.5 mg/l of chlorine residual before it reaches the receiving waters. In such a system, a closed-loop residual control system with a 0.5 mg/l set point can be used. A major challenge with this kind of installation is producing a monitoring system to satisfy the regulatory agency, which often requires a continuous zero residual in the effluent.

In Australia and in the arid states of southwestern United States, where water conservation is important, water must contain chlorine residual to prevent biofouling in the distribution system. Therefore, in these areas, effluent does not require dechlorination unless it is to be discharged into an environment containing aquatic life.

Chen and Gan reported the results of a comprehensive investigation into wastewater dechlorination conducted by the Sanitary Districts of Los Angeles County.⁴ The report included the following important conclusions:

1. The SO_2 method was the most cost-effective of three methods studied. For 5 mg/l total chlorine residual to be completely dechlorinated, the SO_2 method cost \$0.02/1000 gal; with the holding pond method, it cost \$0.045/1000 gal; with carbon adsorption, the cost was \$0.135/1000 gal.
2. The feed-forward control procedure, with flow as the primary signal and residual as the secondary signal, was the most commonly used way to control for the SO_2 method.

3. Overdosing with SO_2 was essential to achieve consistent dechlorination, which provided the SO_2 method with generally good reliability.
4. The chlorine residual analyzers were the weakest link in the SO_2 system because they were unable to maintain calibration for extended periods (~24h) and to remain in calibration at zero residual.
5. No depletion of dissolved oxygen or reduction in pH was observed in the pilot plant studies at a SO_2 -to-residual chlorine dosage ratio of 2:1.
6. No significant physical-chemical degradation was found in the effluent after dechlorination with SO_2 .
7. Postdechlorination bacterial regrowth in the 10-min sample showed an increase of one to two orders of magnitude in all three processes.
8. The regrowth, which occurred predominantly in the total coliform group, seemed to originate from contamination by the existing microorganism communities in the dechlorinated effluent rather than from the reactivation of injured bacteria cells. Fecal streptococci in the effluent remained relatively unchanged after dechlorination.

Significance of Chlorine Species

Chlorine species important in the context of water and wastewater disinfection include free chlorine, combined chlorine, organic chloramines, and nitrogen trichloride.

Free chlorine does not typically appear in wastewater treatment plant effluent, either pre or post chlorination, because of the high concentrations of ammonia N in treated wastewater (10–15 mg/l). Chlorine residuals usually exist as combined species (mono- and dichloramine). The species that titrate as dichloramine can include organochloramine, which is nongermicidal, and are the result of the presence of organic N in the wastewater. Although pure dichloramine is about 60% more germicidal than monochloramine, it rarely occurs in wastewater treatment. Dichloramine is produced when the Cl_2 -to- NH_3 -ratio is 6:1 or when the pH is 7.0 or lower.

Although free chlorine is highly germicidal, it also is naturally highly reactive. Therefore, two side effects tend to consume free chlorine, robbing it of a significant amount of disinfection power: (a) its reaction with organic N: free chlorine (HOCl) reacts quickly with all the organic N present, whereas monochloramine reacts very slowly with organic N, which is why in many cases where total nitrification occurs (complete removal of $\text{NH}_3\text{-N}$), ammonium hydroxide has to be added to meet the disinfection requirements, and (b) the effluent contains organic color up to 10–15 mg/l of free chlorine and is consumed by the natural bleaching effect.

Combined chlorine includes those species that titrate as mono- and dichloramine by the forward amperometric titration procedure. The most important of them is monochloramine. In wastewater disinfection, where contact times

approach 45–50 min, monochloramine can be almost as germicidal as free chlorine.

Organochloramines always occur in wastewater chlorination. The amount that forms is a function of the concentration of organic N and the detention time in the contact chamber. Since this species is not germicidal, its concentration should be regularly monitored, as should the organic N level before chlorination of the final effluent. The only acceptable methods of evaluating the presence of this species are amperometric forward-titration and the DPD-FAS titrimetric procedure. It is believed that most of the organochloramines found in wastewater effluent are not toxic. However, laboratory tests on some specific organic N compounds have demonstrated toxicity.

Nitrogen trichloride (NCl_3) occurs only during breakpoint chlorination. In wastewater practice it is merely a nuisance. Although it is so volatile and unstable that it is difficult to quantitate by analytical methods, it is easily identified. Exposure to this species will result in watering of the eyes immediately upon contact when it off-gasses, and remaining long enough in the off-gas area will lead to difficulty in breathing. While it is a powerful oxidant, it has no relevancy to wastewater disinfection except as an air pollution hazard.

SULFUR DIOXIDE

Chemical Properties

Sulfur dioxide is a colorless gas with a characteristic pungent odor. It may be cooled and compressed to a colorless liquid. Selected properties of the two gases are summarized in Table 11.1.

Although SO_2 is similar in many ways to chlorine, a notable difference is in the vapor pressure. At 70°F , the vapor pressure of SO_2 is ~ 35 psi, while that of chlorine is ~ 90 psi. This low vapor pressure causes problems in the SO_2 supply system. One major effect is on the withdrawal rate. Assuming that 10 psi is the minimum operating pressure for a sulfonator and that the SO_2 ton container is at 70°F , the withdrawal rate can be calculated as

$$\begin{aligned} &\text{maximum withdrawal rate, lb/day} \\ &= (\text{cylinder pressure} - \text{minimum operating pressure}) \times \text{withdrawal factor.} \end{aligned} \quad (11.1)$$

The withdrawal factor for a ton cylinder of $\text{SO}_2 = 6.0$, therefore, is

$$\text{maximum withdrawal rate, lb/day} = (35 - 10) \times 6 = 150 \text{ lb/day.} \quad (11.2)$$

This compares to a chlorine withdrawal rate of 440 lb/day, where the operating pressure at the chlorinator is 35 psi rather than 10 psi for SO_2 .

Another major effect of the low vapor pressure of SO_2 is its reliquefaction. This can be a chronic problem unless the pressure in the cylinder is raised

TABLE 11.1. Selected Properties of Sulfur Dioxide and Chlorine

Chemical Property	SO ₂	Cl ₂
Molecular weight	64.06	70.91
Latent heat of vaporization at 32 °F, Btu/lb	161.8	109.1
Liquid density at 60 °F, lb/ft ³	87.2	88.8
Solubility in water at 60 °F, g/l	120.0	7.0
Specific gravity of liquid 32 °F (water = 1.0)	1.486	1.468
Vapor density at 32 °F and 1 atm, lb/ft ³	0.1827	0.2006
Vapor density compared with dry air at 32 °F and 1 atm, lb/ft ³	2.264	2.482
Specific volume of vapor at 32 °F and 1 atm, ft ³ /lb	5.47	4.98
Critical temperature, °F	314.8	291.2
Critical pressure, psia	1141.5	1118.4

artificially, or the SO₂ is transferred to an evaporator as a liquid. Keeping the cylinder warm and the pressure up can eliminate operational problems.

From Table 11.1, it can be noted that another important difference between SO₂ and Cl₂ is their aqueous solubility. The solubility of SO₂ is 120 g/l, whereas that of Cl₂ is only 7 g/l, at 60 °F. This makes handling SO₂ solutions easier than handling chlorine. For example, negative pressures or excess turbulence at open-channel diffusers must be avoided in the case of chlorine but not so for SO₂. Consider the case of using a weir as a mixing device for a SO₂ solution. In the case of chlorine, the diffuser should be placed downstream from the weir—in the zone of turbulence—to minimize off-gassing. For the SO₂ solution, the diffuser is placed on the upstream side of the weir, and the full benefit of the weir as a mixing device is realized.

Sulfur dioxide is not flammable or explosive in either gaseous or liquid state. Like Cl₂, dry SO₂ is not corrosive to ordinary metals but, in the presence of any moisture, it is extremely corrosive. Therefore, with one known exception, the same materials of construction are used for handling both SO₂ and Cl₂. The exception is the use of type 316 stainless steel for SO₂ diffusers and valve trim for valves in the SO₂ vapor and liquid timers (monel trim is used for Cl₂ valves). The ability of type 316 stainless steel to withstand the corrosivity of aqueous SO₂ solutions is helpful in application for which polyvinyl chloride does not have sufficient rigidity or structural strength. Although chlorinators and sulfonators may seem identical in construction, they should never be used interchangeably. If evaporators used for Cl₂ are to be used for SO₂, they must be thoroughly cleaned. All of the corrosion products from exposure to Cl₂ must be removed from the container vessel before it is used with SO₂.

The vapor densities of SO₂ and chlorine gases are so similar that a chlorine-indicating rotameter can be used to meter SO₂ without appreciable adverse consequences. To convert chlorine feed rate to that of SO₂ multiply it by 0.95.

TABLE 11.2. Physiological Responses to Exposure to Sulfur Dioxide

Effect	SO ₂ in Air (ppm)
Odor threshold	3–5
Least amount causing immediate eye irritation	20
Least amount causing throat irritation	8–12
Least amount causing immediate coughing	20
Max. conc. allowable for prolonged exposure	10
Max. conc. allowable for ½- to 1-h exposure	50–100
Dangerous for short exposure	400–500

For example, a 1000lb/day chlorine rotameter will serve as a 950lb/day sulfur dioxide rotameter. Since the vapor density and the viscosity of SO₂ are so close to those of chlorine, the long vacuum lines for both can be sized by using the same variables and formulas.

Fatal accidents from sulfur dioxide vapor are rare because persons exposed to lethal concentrations of SO₂ are unable to breathe and are compelled to seek the open air. Low concentrations cause a sensation of suffocation, coughing, sneezing, and burning of the eyes. Following low-level exposure, the victim may experience rapid recovery from these symptoms after a few minutes in the open air. Liquid sulfur dioxide may cause severe injury from freezing of the skin and rapid evaporation of the liquid of the eyes. Physiological responses to various concentrations of SO₂ vapor are summarized in Table 11.2.

First aid treatment for victims of SO₂ is generally the same as for chlorine exposure. All clothing should be removed, and the victim should be kept calm and warm with blankets. Inhalation of ammonium carbonate fumes can relieve respiratory irritation, and coughing is relieved by drinking a mixture of three to five drops of chloroform in a full glass of water. If this is not available, the victim should be allowed to sip 80 proof whiskey or vodka from a teaspoon or through a straw. An amount of 2 oz of either should be sufficient for complete relief from coughing. Depending on the severity of the exposure, the patient should use copious amounts of water for flushing it from the eyes, particularly if liquid SO₂ has touched the victim's skin. The Compressed Gas Association should be consulted for the first aid supplies to be kept on hand. For skin burns, a freshly made 5% solution of tannic acid powder should be used to moisten sterile bandages placed over the skin burn area (eight level tablespoonfuls of tannic acid powder in an 8-oz glass of boiled water).

Dechlorination Chemistry

The reactions involved in the sulfur dioxide dechlorination process are shown below. The first reaction is the formation of sulfurous acid in the sulfonator injector:



The sulfurous acid reacts with the chlorine residual species as follows:



These equations illustrate that all of the chlorine species can be dechlorinated with SO_2 , and that acids that can affect the alkalinity, and possibly the pH, of dechlorinated water are produced. For each part of chlorine removed, 2.8 mg/l alkalinity as CaCO_3 is consumed. However, since most potable waters and wastewaters have sufficient alkalinity, there is no cause for concern about lowering the pH with SO_2 addition.

There has been some apprehension about the possibility that excess SO_2 might consume a significant amount of dissolved oxygen in the receiving waters downstream from a dechlorinated wastewater discharge. The reaction between the excess sulfite ion (SO_3^{2-}) from dechlorination and the dissolved oxygen is



Thus, four parts of SO_2 are needed to remove one part of dissolved oxygen. Because of kinetic limitations, there is never sufficient time to complete the reaction at the optimum reactant concentrations. Chen and Gan demonstrated that an excess sulfite concentration of 2.6 mg/l in the plant effluent had no effect upon pH.⁴ Moreover, the dissolved oxygen concentration increased from 4.8 to 6.1 mg/l after dechlorination with sulfite, probably as a result of the turbulence caused by the mechanical mixers. There is no scientific evidence that sulfur compounds used for dechlorination can affect dissolved oxygen consumption or pH in the receiving waters or in the dechlorinated effluent.

Contactor Design

Dechlorination reaction with free or combined chlorine will generally occur within 15–20s. According to the Recommended Standards of Wastewater Facilities, a minimum of 30s of mixing and contact time should provide at design peak hourly flow or maximum pumping rate.⁵ A suitable sampling point should be provided, and consideration should be given to a means of re-aeration to assure maintenance of acceptable dissolved oxygen following

sulfonation. For design of rapid mix systems, see the appropriate chapter in this text.

Chemical Dose Calculations

As described in the previous section, the stoichiometric relationship requires 0.9 part of SO_2 to remove 1.0 part of chlorine residual. In practice, this ratio can be as high as 1.05 or 1.1 parts of SO_2 to each part chlorine, or 1.1.⁶

Here is a sample dose calculation for dechlorination with sulfur dioxide.

Given a peak flow of 10 mgd and a measured chlorine species concentration of 1.5 mg/l, the maximum dosage of SO_2 needed per day, assuming a 1:1 ratio of SO_2 to Cl_2 , can be calculated as follows:

$$\begin{aligned} &(\text{flow rate}) \times (\text{Cl}_2 \text{ residual}) \times (\text{dosage ratio}) \\ &= (10 \text{ mgd}) \times (1.5 \text{ mg/l of Cl}_2) \times (8.34) \times (1 \text{ mg/l of SO}_2 \text{ per mg/l of Cl}_2). \end{aligned} \quad (11.9)$$

The maximum dose of $\text{SO}_2 = 125 \text{ lb SO}_2/\text{day}$.

SULFITE COMPOUNDS

Sulfite compounds are used in solutions, primarily at smaller installations where feed rates for sulfur dioxide (<100 lb/day) are not practical. Sulfites are also used on large installations where storage of SO_2 might be considered a hazard. The solutions are applied with metering pumps. Feed-rate control and process monitoring of such systems need more attention and require more complex instrumentation than those used for SO_2 systems.

Four sulfur compounds may be considered as alternative chemicals to sulfur dioxide for dechlorination: sodium sulfite (Na_2SO_3), sodium bisulfite (NaHSO_3), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). Sodium sulfite is available only as a white powder or as crystals. It is extremely difficult to handle in the dry form because it is hygroscopic. Therefore, it is never used as a dechlorinating agent. Sodium thiosulfate is used in solution but almost exclusively as a laboratory chemical. It is not a satisfactory dechlorinating agent for treatment plant use because its reaction with chlorine is slow and not amenable to metering control situations. Therefore, only sodium bisulfite and sodium metabisulfite are suitable for use as alternative chemicals to sulfur dioxide.

Chemical Properties

Sodium bisulfite is a white, powder or granular material generally purchased as a solution in strengths up to 44%. The solubility of sodium bisulfite in water is 515 g/l at 20°C, and the pH of a 54 g/l solution of NaHSO_3 equilibrates

to between 3.5 and 5.0 at 20°C. It can be handled wet in stainless steel, PVC, or fiberglass tanks. When used as a dechlorinating agent, it is usually metered by diaphragm-type pumps. Sodium metabisulfite, also known as sodium pyrosulfite, is a cream-colored powder that is readily soluble in water (aqueous solubility of 650 g/l at 25°C) and is available in solutions of various strengths.

Dechlorination Chemistry

The reaction between bisulfite and chlorine residual is as follows:



Each part of chlorine residual removed requires 1.46 parts of sodium bisulfite. The usual solution strength is 38%, with a specific gravity of 1.3. The manufacturer's data sheet advises that, at this specific gravity, a 38% solution contains 3.5 lb of sulfite/gal. This calculates to 2.17 lb sulfur dioxide. For each part chlorine removed, 1.38 parts of alkalinity as CaCO_3 will be consumed.

The reaction between sodium metabisulfite and chlorine residual is as follows:



Each part of chlorine residual requires 1.34 parts of sodium metabisulfite, and, for each part of chlorine removed, 1.38 parts of alkalinity as CaCO_3 is consumed.

Sodium thiosulfate is used in the laboratory as a dechlorinating agent prior to routine coliform concentration determinations. However, it is not used on a plant scale to control the dechlorinating process because (a) it reacts with residual chlorine in a stepwise fashion, creating an unacceptable time factor; (b) its reaction is stoichiometric only at pH 2; and (c) its ability to remove chlorine varies significantly with pH. Its reaction with residual chlorine is as follows:



Contacting Design

All dechlorination chemicals form sulfite in water. Dechlorination chemicals should be introduced at a point in the process where the hydraulic turbulence is adequate to assure complete and thorough mixing. The dechlorination reaction with free or combined chlorine will generally occur within 15–20 s. According to the Recommended Standards of Wastewater Facilities, a minimum of 30 s for mixing and contact time should be provided at design peak hourly flow or at the maximum pumping rate.⁵ A suitable sampling point

TABLE 11.3. Theoretical Chemical Dosages for Dechlorination

Dechlorinating Chemical	Theoretical Dose Required to Neutralize 1 mg/l Chlorine (mg/l)
Sodium thiosulfate (solution)	0.56
Sodium sulfite (tablet)	1.78
Sodium metabisulfite (solution)	1.34
Sodium bisulfite (solution)	1.46

should be provided, and consideration should be given to providing a means of re-aeration to maintain acceptable dissolved oxygen concentration following sulfonation.

Chemical Dose Calculation

The dosages of dechlorination chemicals depend on the residual chlorine concentration in the effluent, the final residual chlorine limit, and the form of dechlorination chemical used. Theoretical dosages for different sulfur salts are summarized in Table 11.3.⁵ Under good mixing conditions, 10% excess dechlorinating chemical is required above the theoretical values.⁵

OTHER DECHLORINATION CHEMICALS

Sulfur dioxide is the most commonly used chemical for dechlorination. Sodium bisulfite and metabisulfite are practical alternatives to SO_2 and are mainly used in small facilities because of safety problems associated with the difficulties the storage, handling, and feeding of gaseous sulfur dioxide. Dechlorination can also be achieved with hydrogen peroxide (H_2O_2) and activated carbon. Hydrogen peroxide is rarely used because it is difficult to handle.⁷ Activated carbon is an effective means of dechlorination but is more expensive than other methods. However, it is useful when total dechlorination is necessary and palatability of the drinking water is important.⁶

Activated carbon for use in water and wastewater treatment is packaged in two forms. Powdered activated carbon is metered by weight and conveyed to the point of application as water slurry, which is used as pretreatment to suppress tastes and odors. It is often applied near the point of prechlorination. Operating experience indicates that only about 10% of the applied carbon reacts with chlorine in the dechlorination reaction. Granular activated carbon (GAC) is used as the filter medium in conventional filter basins and in vertical towers for adsorption of organics and other undesirable compounds. Although powdered activated carbon has not been used intentionally as a dechlorinating agent, GAC has been used for this purpose for many years. It is the method of choice in the beverage industry. GAC has also been used extensively as filter medium and as a dechlorination agent in potable water treatment plants.⁸

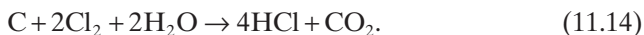
In wastewater treatment, GAC has not been successful as a dechlorinating agent probably for one or more of the following reasons: It may not be able to remove the organochloramines that form in the presence of significant concentrations of organic nitrogen; because with current technology, it may not be possible to design an effective carbon bed; or the time required for completion of the dechlorination reaction in wastewaters may be much too long. Although activated carbon can be an effective means of dechlorination, its cost is almost prohibitive, which is one of the main reasons why sulfur dioxide-containing compounds are commonly used.

The terms *adsorption*, *saturation*, and *absorption* are used frequently in describing the action of GAC. Adsorption is a phenomenon by which molecules in air or water accumulate on surfaces or interfaces of solids that are in contact with the fluid. Absorption or partitioning is a process through which molecules are transferred from one phase (gas or liquid) into another (liquid or solid). A sorbent such as GAC is considered saturated when its capacity to adsorb or absorb contaminants has been exhausted.

GAC reacts with free available chlorine, as shown:

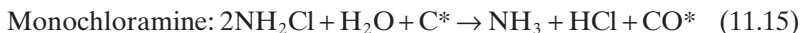


where C^* and CO^* indicate active carbon and a surface oxide on carbon, respectively. If significant amounts of $HOCl$ are allowed to react with the carbon, some of the oxygen attached to the surface may be emitted as CO or CO_2 gas. The stoichiometry of the reaction will be as follows:



In this reaction, 1.0 part of chlorine will destroy 0.00845 part of carbon. As the ultimate reaction consists of conversion of the GAC to carbon dioxide by the chlorine, there is no regeneration of carbon; it must be physically replaced because it has been destroyed.

Studies by Bauer and Snoeyink have demonstrated that pure chloramines can be dechlorinated by GAC, as follows:⁹



The reaction time used in these observations was 20 h. During these reactions the carbon appears to accumulate surface oxides, which partially oxidize the NH_2Cl and $NHCl_2$ nitrogen to N_2 .

Sorption of chloramines by GAC eventually leads to saturation of the sorbent. Therefore, exhaustion of the GAC will result in breakthrough of chloramines, and the carbon will have to be regenerated. Although both free chlorine and chloramines are adsorbed by the carbon, the former chemically

exhausts the sorbent, while the latter physically depletes it. The chemically exhausted GAC has to be replaced, while the physically depleted carbon can be regenerated.

In water treatment, water that passes through a GAC filter bed is considered completely dechlorinated unless the carbon is depleted. Therefore, if chlorine residual is required in the finished water, the filtered water must be rechlorinated. A detailed study of the carbon–chlorine reaction indicates the following relationship between flow rates, bed depths, concentration of influent and effluent chlorine, and the granular carbon itself:¹⁰

$$\log \frac{C_I}{C_E} = \frac{B \times \text{bed depth (ft)}}{\text{filtration rate (gpm/sq ft)}} = \frac{B}{V}, \quad (11.17)$$

where

C_I = concentration of chlorine in influent (mg/l),

C_E = concentration of chlorine in effluent (mg/l),

B = efficiency constant for each carbon, and

V = flow rate (gpm/ft³).

Hager and Flentje reported that a granular carbon medium in a 1 mgd filter at 2.5 gpm/ft² and a 2.5-ft bed can process 700,000,000 gal of 4 mg/l of free chlorine residual, and, with 2 mg/l of chlorine at a 1 mgd rate, a similar bed would last approximately 6 years.⁸ The dechlorination reaction proceeds concurrently with absorption of contaminants. Long-chain organic molecules, such as those of detergents, seem to reduce the dechlorination efficiency somewhat, but many common impurities and phenols have little effect upon the dechlorination reaction. A rise in temperature and a lowering of pH favor the reaction, and it has been found that chlorine–ammonia and other nitrogenous compounds of chlorine tend to react much more slowly than free chlorine. Residual chlorine concentrations in the backwash can be maintained more easily in water when it contains combined chlorine residual, instead of free chlorine.

For a conventional water treatment plant, dechlorination by activated carbon has certain limitations, and it should not be relied upon as the sole means of controlling the chlorine residual in finished water. An exception is the beverage industry, where the raw water is of superior quality, and the dechlorination must be complete.

DECHLORINATION FACILITY DESIGN

Figure 11.1 illustrates a zero-residual dechlorination system with process controls.

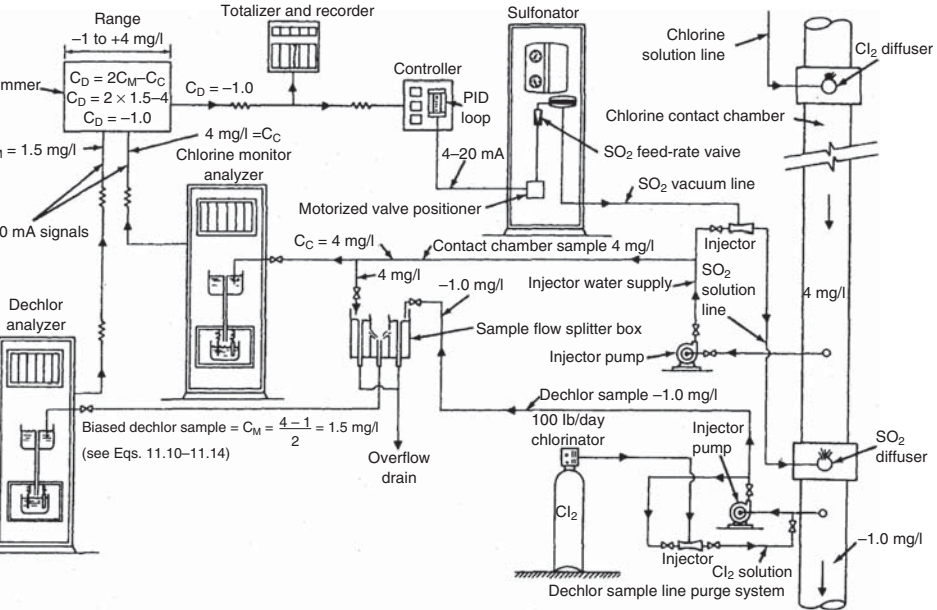


Figure 11.1. Zero-residual dechlorination system with process control. PID, piping and instruction diagram.

Design of Gaseous System Sulfur Dioxide

Sulfur dioxide is available in ton containers, tank trucks, or tank cars. Owing to the low vapor pressure of SO₂, special precautions must be taken to prevent reliquefaction when ton containers are used. Tank cars are designed to be identical to those used for chlorine; therefore, the same guidelines tank car layouts can be used. Users of SO₂ in tank cars must provide a dry-air padding system to raise the tank car pressure to at least 60psi in the lowest ambient temperature. In warmer climates, sunlight has been found to raise tank car pressures by about 10–12 psi.

Owing to its low vapor pressure, SO₂ gas reliquefies quite easily, which causes problems with the control equipment. The low vapor pressure is also a limiting factor in transferring the sulfur dioxide from the supply system to the control equipment. Withdrawing from the gas phase usually requires the application of heat to the cylinders. Gas-phase systems operate best at temperatures around 90–100°F, and it is acceptable practice to apply heat directly to ton cylinders, provided that there are provisions to limit the temperature to 100°F. The maximum gas withdrawal rate from a ton container at 70°F is about 180lb/day without reliquefaction. At 100°F, the rate is about twice as much.

The preferred method of applying heat to ton cylinders is using either an ordinary electric blanket or a nitrogen padding system. If heat for vapor

withdrawal is applied by the blankets, a pressure-reducing valve must be installed immediately downstream from the operating cylinder to reduce the pressure to 40–45 psi to eliminate reliquefaction, which is a common problem with sulfur dioxide.

In earlier years, when liquid withdrawal was used, nitrogen padding was usually suggested. This is no longer necessary, since the electric blanket method has proved to be the most convenient. The nitrogen system has only one advantage: It can be used to purge the piping system. With the availability of the remote vacuum system for both chlorinators and sulfonators, purging is not necessary because, when the systems shut down, the entire piping system is under a vacuum. A pressure-reducing valve should be installed immediately downstream from the evaporator's vapor outlet to prevent reliquefaction at the vacuum regulator check unit.

If required quantities of SO_2 are sufficiently large such that tank car delivery is required, the facility should purchase several tank trucks. One would be kept on site and be fed from, while the other is in transit or being filled. As these tank trucks will under governing standards (in the United States, these are promulgated by the Department of Transportation), but constructing should be identical or nearly so to chlorine tank trucks. Appropriate material modification must be made to the vessels, valves, and appurtenances. Current practice is to use a room that is completely separated from the chlorination equipment. This serves two purposes: The room can be isolated in the event of a leak, and it makes it possible to raise the vapor pressure high enough, to about 65 psi, to prevent reliquefaction by maintaining it at a temperature of about 100°F, using either space heaters or electric blankets.

For a stable withdrawal system that is fully compatible with the metering and control system, the vapor pressure should be reduced to about 40 psi by a manually operated pressure-reducing valve located near to the discharge outlet, whether it is the outlet of the storage tank or the evaporator. This will prevent reliquefaction in the vapor piping and in the sulfonator, which is always the most troublesome part of handling sulfur dioxide. Another problem is the excessive moisture in the liquid SO_2 as a result of faulty manufacturing procedures.

Hydraulic calculations for sulfur dioxide should be performed similarly as to chlorine. On the sulfur dioxide solution side, hydraulic can be treated identically to water using conventional Darcy or Hazen-William methodology. On the gas side, especially the vacuum side, a more rigorous methodology is required. All piping, pipe fittings, pressure gauges, pressure switches, and expansion tanks should be of the same materials as those for chlorine. The only exceptions are the line valves and auxiliary valves that must have type 316 stainless steel trim, rather than monel, which is used for chlorine.

Evaporators for liquid sulfur dioxide are identical to those used for liquid chlorine. However, because of the difference in latent heat of vaporization,

an 8000lb/day chlorine evaporator will vaporize only about 5600lb/day of sulfur dioxide. This is based on latent heat of vaporization, which is 164.5 BTU/lb for sulfur dioxide and 115 BTU/lb for chlorine.

Chlorine gas and sulfur dioxide gas should never be allowed to come in contact with each other, and the supply system piping must be located and arranged to prevent this from happening. This is best accomplished by locating the supply systems in completely separate areas and housing the sulfonators and evaporators in a room separate from the chlorination equipment.

Sulfonator manufacturers use injectors designed for the solubility of chlorine. Since sulfur dioxide is 17 times more soluble than chlorine, all SO₂ injectors are enormously oversized. This practice wastes power and water, unless the water is recycled. As redesigning the injectors for SO₂ installations would be a major project, it is often easier and more practical to use a chemical induction unit like a water champ instead, which eliminates the need for a water supply, a diffuser, and a mechanical mixer. The selection of a chemical induction unit should be based on an understanding of the economics of the given situation and the specific requirements of the system including equipment access and spacing philosophy.

The SO₂ vacuum line and solution line are made from the same materials as those for chlorine, with one exception: the SO₂ solution diffuser can be made of type 316 stainless steel. The diffuser location is less critical for SO₂ solution than for chlorine because SO₂ gas is highly soluble in water. There is no danger of off-gassing to SO₄ as a result of turbulence near the diffuser, whereas with chlorine, it is a serious problem. The SO₂ diffuser can be placed immediately but upstream from a weir, and can utilize the turbulence on the downstream side for immediate mixing without fear of releasing SO₂ vapor.

The application of sulfur dioxide to wastewater differs considerably from the application of chlorine. The SO₃²⁻ ion reacts with the chlorine residual to convert the active chlorine to chloride and the sulfite ion (SO₃²⁻) to sulfate ion (SO₄²⁻). This reaction takes precedence over any side reaction that might be encountered in wastewater. This reaction with chlorine occurs in a matter of seconds, probably 15–20s at the most. Mixing the sulfur dioxide solution to achieve dechlorination is much less demanding than mixing the chlorine to achieve disinfection.

No mechanical mixers are required if the structure is amenable to the diffuser design. It is recommended that SO₂ solution diffusers be designed according to the Egan concept of nozzle counterflow to produce a velocity gradient of 250–300.

Since the reaction time for complete conversion of the total chlorine residual to chloride by the sulfite ion is measurable in seconds, there is no need for a contact chamber between the SO₂ diffuser and the receiving waters. However, common sense dictates that the structure downstream from the diffuser must

be suitable for obtaining a dechlorinated sample about 5 ft downstream from the estimated mixing zone.

The dechlorinated sample line must be kept free from biological slime growths. The lines carrying dechlorinated effluent throughout the transport system will be subject to rapid development of organic debris and slimes, which will introduce errors in the analyzer system, regardless of whether it is used for control or for monitoring.

The growths can be removed or controlled by intermittent purging with either chlorine or caustic. Chlorine should be applied into the sample line collection pipe and should be made available for every chlorine residual analyzer.

Sample lines should be sized to maintain a velocity of 5 ft/s to encourage scouring of the line. In some, higher velocities can be used. At higher velocities, there is a balance between line size, line length, desire for short contact time, and discharge head of the sample pump. The sampling point for measuring coliform bacteria population for proof of disinfection should be 5–10 ft upstream from the SO₂ diffuser. Otherwise, the effects of coliform regrowth after dechlorination will distort the results.

Sulfur Dioxide Leak Detectors

Ambient and source SO₂ leak detectors should be installed at the storage containers and near the sulfonators. Ambient detectors are used for monitoring the pressure of SO₂ in the air, which presents a danger to personnel.

Source detectors for SO₂ leak detection at water and wastewater plants are required to detect concentrations of 5 ppm. Common source detectors include those manufactured by Analytical Technology Inc. (ATI), Interscan Corporation, and Wallace & Tiernan, Inc.

ATI's modular gas detector can be used to detect either sulfur dioxide or chlorine vapors. Its Gas Sens systems consist of individual modules that can be located where desired. Each of these modules includes a digital display of gas concentration, isolated analog output, and four relay outputs (Fig. 11.2). Receivers may be located up to 1000 ft from the sensor/transmitters for remote location or can provide local control functions such as valve shutoff while transmitting a 4- to 20-mA signal to remote displays or data loggers. The range of operation of these units is from 0 to 20 ppm of sulfur dioxide.

Interscan's analyzer-detectors are equipped with a voltammetric sensor, which is an electrochemical gas detector operating under diffusion-controlled conditions. Gas molecules from the sample are adsorbed onto an electrocatalytic-sensing electrode after passing through a diffusion medium (Fig. 11.3). The gas molecules are reacted electrochemically at an appropriate applied voltage to the sensing electrode. This reaction generates an electric current directly proportional to the gas concentration, whose

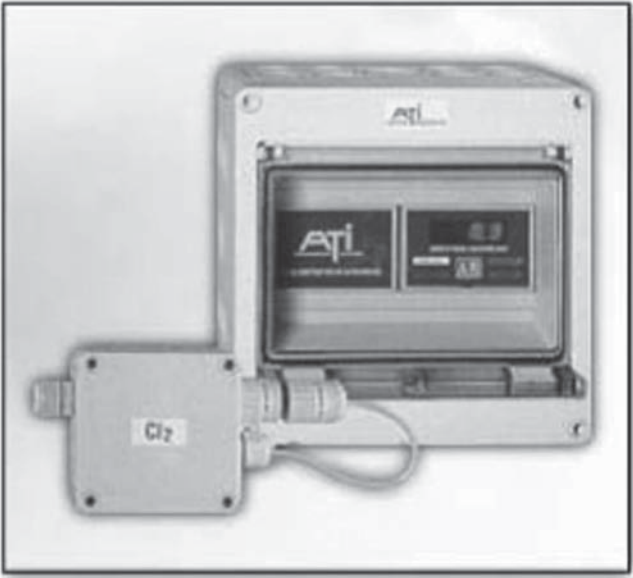


Figure 11.2. ATI modular gas detector (courtesy of Analytical Technologies Inc.).

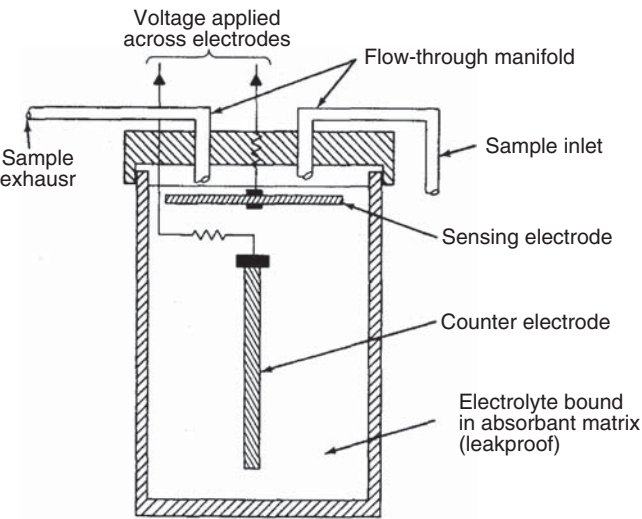


Figure 11.3. Leakproof electrochemical voltammetric sulfur dioxide sensor (courtesy of Interscan).

current is then converted to a voltage for local readout or for a remote recorder.

The diffusion-limited current generated in the voltammeter, I_{LIM} , is directly proportional to the gas concentration:

$$I_{LIM} = \frac{nFADC}{L}, \quad (11.18)$$

where

- I_{LIM} = the limited diffusion current in amperes,
- F = the Faraday constant (96,500 C),
- A = the area of reaction interface (cm^2),
- n = the number of electrons/mole of reactant,
- L = the diffusion path length,
- C = the gas concentration (moles/ cm^3), and
- D = the gas diffusion constant, representing the product of the permeability and solubility coefficient of the gas in the diffusion medium.

An externally applied voltage maintains a constant potential on the sensing electrodes relative to a nonpolarizable reference counterelectrode. This electrode can sustain a current flow without suffering a change in potential. Thus, it acts as a reference electrode. This eliminates the need for a third (reference) electrode and a feedback circuit, as would be required for sensors using a polarizable air counterelectrode.

No chemical reagents are required. The bound electrolyte enables the analyzer to be operated in any position. The sensor has a leakproof reservoir, which extends the sensor's life expectancy and enables it to withstand pressurization, and eliminates the possibility of contamination of the reference electrode in a hostile environment.

Wallace Tiernan's gas detection system utilizes the latest chlorine gas monitoring technology to provide a flexible and reliable self-testing system in a compact modular design (Fig. 11.4). The sensor is ideal for detecting leaks from storage containers, process piping, or gas metering equipment in any type of water, wastewater, or industrial plant environment.

Each point of detection must be equipped with one sensor/transmitter and one receiver module. The sensor/transmitter should be installed in the area to be monitored, and the receiver module can be located up to 1000 ft away. A power supply module sufficient for use with up to two receivers is housed with the receivers in a National Electrical Manufacturers Association (NEMA) type 4X enclosure. All enclosures are provided with knockouts on all four sides to facilitate using the 1/2-inch conduit hubs that are provided. Included with the enclosure is a piezoelectric horn that will provide audible local warning. The detection range for sulfur dioxide is 0–20 ppm.



Figure 11.4. Wallace & Tiernan's Acutec 35 gas detection system.

Liquid System Design for Sulfites

If for any reason sulfur dioxide is not being used, sodium bisulfite solution is the next choice. In large systems, it is usually preferred because of safety concerns associated with SO_2 vapor. In small systems, it would be used because of the difficulty of metering small quantities less than 10 lb/day of SO_2 vapor. Each gallon of 38% sodium bisulfite contains the equivalent of 2.17 lb of sulfur dioxide. As such, sodium bisulfite generally needs to be heated. In interior installations, space heaters are generally sufficient. In exterior installations, tanks and pips should be heat traced and insulated. It should be noted that sodium bisulfite is also available as dry product usually referred to as sodium metabisulfite.

The components and their arrangement and the selection of a sodium bisulfite system are almost precisely the same as those of hypochlorite facilities, as discussed in Chapter 9. In general, there are three types of systems: (a) pumped, (b) gravity, and (c) eductor, each of which incorporates the energy needed to move the solution from storage to the point of application. In practically all cases, the pumped system is preferred. Two types of pumped system are available: (a) the positive displacement-type metering pump system, which is controlled solely by the pump (highly recommended); and (b) the centrifugal pump system, which is controlled by a modulating control valve on the downstream side of the pump.

Regardless of the type of system, a storage vessel will be required. It should be constructed of reinforced fiberglass and should be equipped with a remote type of level-sensing instrumentation, atmospheric vent, drain, pump suction, and sample tap for laboratory monitoring solution strength. Most important is the piping configuration and safety valving used in loading the tank, which should be designed to prevent any other chemical from being inadvertently loaded into this tank. Preferably, the tank should be at a discrete distance from the hypochlorite tank or other chemical tanks. Mixing

bisulfite with hypochlorite produces a violent temperature reaction. Other mixtures may do the same or release a cloud of SO_2 vapor.

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12 Process Controls for Chlorination and Dechlorination

INTRODUCTION

This chapter describes the use of automated process control systems for chlorination and dechlorination. The instruments and control principles presented in this chapter can be applied to both water and wastewater treatment. However, the primary focus of many of the discussions is on wastewater disinfection, which has a wider variation in chlorine demand and more hurdles to overcome in its application. This means that it is more difficult to implement and, at the same time, generally more beneficial than water-treatment applications. The regulatory requirements to maintain microbiological and chemical integrity of surface waters motivated the development and adoption of chlorination and dechlorination processes in modern wastewater treatment. Tightening of regulatory control and the need for water reclamation and reuse have necessitated continuous monitoring and precise control of disinfection processes. Many states require compliance with limits on the concentrations of various pathogenic organisms, residual chlorine, and disinfection by-products (DBPs). Therefore, permit conditions, including organism concentrations and operating data, must be fully identified. DBPs in wastewater effluent are being regulated, and the limits being imposed are much stricter than Safe Drinking Water Act standards. Furthermore, adoption of advanced treatment technologies, such as membrane processes that include control of membrane fouling through disinfection, has created new challenges for engineers and plant operators.

These developments have led to the increasing use of automated chlorination and dechlorination systems in modern wastewater treatment facilities. These systems can help minimize chlorine use while controlling the production and release of DBPs such as trihalomethanes (THMs). Automated systems consist of three critical elements—analyzers, programmable logic controllers

(PLCs), and injectors—that work together to constantly monitor water chemistry and to adjust chemical dosages to produce the desired effluent quality. There are many levels of automation for the control of chlorination systems. For the best control approach to be selected for a facility, both the control strategies and the chlorination chemistry must be understood. However, it is absolutely acceptable and, in some cases, even desirable to maintain a manual chlorination and dechlorination control protocol as a backup in the event of PLC or analyzer failure.

An understanding of breakpoint chlorine chemistry is very important in the selection of online chlorine residual analyzers for control of the disinfection process and the development of a good control strategy. The reader is directed to Chapter 6 for details on the chemistry of breakpoint chlorination.

What is really controlled in a disinfection system? The addition of chlorine to wastewater flowing through a contact chamber is controlled so that the appropriate environmental conditions are created to inactivate sufficient numbers of the regulated organisms to comply with permit limits. In all cases, it is important to remember that the control system *indirectly* controls the final concentration of organisms by managing the environment in which the target organisms are killed.

This chapter begins with the historical background of chlorination/dechlorination control in the water and wastewater industry, describes the principles behind various techniques used to measure the concentrations of chlorine and sulfur dioxide, discusses commonly used online Cl_2 and SO_2 analyzers, and presents the theory and application of online process control for chlorination and dechlorination.

This chapter is not meant to be all-inclusive for designing a complete control system. The control system typically consists of the following:

- Analyzer/Probe
- Transmitter
- PLC
- Transmitter
- Chemical feed device (pump or control valve)
- Chemical flow measurement instruments
- Chemical injector

This chapter is not intended to be a primer for control engineers on how to develop programming code for PLCs or how to develop response signals for valve actuators or variable speed drives, but to provide guidance and information from a process engineer's perspective on how to select the right analyzer and how to devise a control procedure for chlorination and dechlorination that works. It will also include a discussion on chlorine chemistry, as it applies to control procedures. The *Instrument Engineer's Handbook—Process Measurement and Analysis* and *Instrument Engineer's Handbook—Process*

Control and Optimization are two references for detailed design of control systems.^{1,2}

BACKGROUND

Chlorine residuals in water are often monitored by colorimetric or amperometric methods. Wallace & Tiernan Company began investigating the possibilities of automatic control of chlorine residual using orthotolidine (O-T) in about 1927. Units that could continuously record the O-T residual and adjust the chlorinator feed rate were developed. The first such unit was installed in 1929 at Little Falls, New Jersey, and the second in 1930 at Rahway, New Jersey.³ A modified version of these units was installed in about 1930 in Los Angeles and operated for several years.⁴ The latter units differed in that the O-T residual analyzer had a fixed color disk for a given O-T residual of 0.3ppm. If the color in the analyzer did not match that of the disk, the error signal between them drove the control valve on the “trimming chlorinator” until the two colors matched, and the error signal became zero. The residual record then was one of deviation. A few years later, Caldwell⁵ developed an O-T recorder based on the work of Harrington⁶ using neutral O-T.

Colorimetric recorders fell into disuse primarily because the photoelectric cells were not able to differentiate accurately enough between the relatively small changes in the color representing a change in residual. Also, after it was realized how important free chlorine residual was, as compared with total chlorine, another method had to be found, since it was impractical to distinguish between free and combined chlorine by using the O-T method.⁷ Awkward mechanical operation also contributed to making the system impractical.

In about 1955, Fischer and Porter developed an O-T analyzer, which survived for a few years until its amperometric analyzer was developed. Hach Chemical Co. marketed an O-T analyzer about this same time, which was unable to survive competition from the amperometric analyzers. Hach also introduced the first successful diethyl-*p*-phenylenediamine (DPD) colorimetric analyzer in 1980.

The search for a better method of chlorine residual determination resulted in the development of the amperometric titrator, in part inspired by Griffin’s work in 1939–1940 on the breakpoint phenomenon.⁸ The first amperometric chlorine residual recorder was placed on the market by Wallace & Tiernan in about 1948. Among the first installations were those at Wyandotte, Michigan; Allentown, Pennsylvania; and Brantford, Ontario, Canada.^{9,10} Results from these early installations were so impressive that continuous residual recording became popular in the treatment of public water supplies. Operating experience from these installations demonstrated two important characteristics of the amperometric cell: the predictable changes in cell output current due to changes in sample temperature, and in pH. The changes in

pH were corrected by adding pH 4 buffer solutions, and the temperature was corrected either by manual adjustment or by installing a thermistor.

During this period, Wallace & Tiernan manufactured a polarographic cell for the Chicago Water Department that was arranged to measure combined chlorine (chloramines) only. It did not require chemicals to operate but it did need a large sample (1 l/min). Twenty years later, when Chicago built its Central Water Filtration Plant, analyzers were needed only to measure free chlorine. The same type of analyzer was used, except that the applied voltage across the electrodes was different, which made the same cell specific for free chlorine.

Since the 1970s, two notable contributions have been made to online chlorine residual analysis. The first was the development of the Chlor-Trol analyzer by Fischer and Porter, which was capable of measuring free chlorine in a sample containing chloramine at significant concentrations.¹¹ The second was the development of the selective membrane electrode by Johnson et al.¹² By this time, many companies were actively engaged in developing instrumentation for continuous measurement of chlorine residual including Foxboro, Orion, Uniloc (Rosemount), Delta Scientific, Enterra, Chlortect, and IBM. New developments have extended the use of chlorine residual monitoring to wastewater, and finally from monitoring to automatic residual control.

It took nearly 10 years for the step from residual recording to residual control to gain acceptance in the United States, while, in England, residual control was being used for the London water supply as early as 1950 and for controlling superchlorination and dechlorination stations of underground supplies where the only other treatment was microstraining.

The use of continuous residual analyzers for chlorination of wastewater began in about 1960, with the immediate purpose of controlling the chlorination system. Before 1960, analyzers were used to a limited extent on highly polished tertiary effluents. One of the first successful installations on secondary-treated effluents was at the Napa, California, Sanitary District plant in 1961, where the unit installed was identical to that used for potable water, except that a motorized filter was installed on the analyzer cell sampling line. When this unit was tried for operation on primary treated effluent, various problems related to the quality and the characteristics of the wastewater were encountered. The high grease content in the primary effluent coated the electrodes, and the insulation effect of the grease caused a severe distortion of the calibration, resulting in erroneous readings.

The amount of buffer solution required to lower the pH of primary effluent was very high, and an appreciable excess of iodide was necessary to make the reaction with combined residual chlorine proceed as fast as possible. This made the chemical cost a most significant factor in the operating cost. Experience showed that chlorine residual analyzers were not reliable enough to be used on primary effluent, owing to the dirtiness and fouling characteristics of the sample and the inability to maintain a sample flow through the cell. Another factor that operating personnel found discouraging was the

amount of time they had to spend keeping the electrode surfaces clean enough to maintain the system in calibration.

This short review illustrates that there is a long history of automated chlorine-based disinfection systems. Two basic problems have often arisen: the lag time inherent in the feedback control of plug flow systems and the difficulty of interpreting the impacts of chlorine chemistry on process control. Unless the two issues are resolved, the control system will have notable limitations and hinder its use.

Strict effluent nitrogen limits are forcing many chlorine disinfection systems to vacillate between monochloramines and free chlorine. Both will effectively disinfect wastewater, but each has its own characteristics. Along with strict nitrogen limits, authorities in parts of the United States are implementing end-of-pipe limits for THM compounds for control of DBPs discharged to receiving waters. Drinking water standards regulate THMs as an aggregate parameter; however, the National Pollutant Discharge Elimination System (NPDES) water quality standards specify individual limits for each THM compound.

Many states are setting low limits on pathogenic organisms in effluents used in reuse applications and on receiving streams that are used for recreation. Some states are going so far as to set the limits at nondetectable levels. Compliance with such stringent limits requires careful control of chlorine dosages. Overdosing is not a viable alternative because it would lead to THM formation and because of the high costs involved. Effective control of the chlorination process can enable the utility to meet either its permit limits or the target levels for the organisms, while minimizing chlorine use, which lowers chemical costs, reduces the use of dechlorination chemicals, and minimizes THM formation.

ONLINE ANALYTICAL MEASUREMENTS

This section discusses the methods of monitoring disinfection processes in water and wastewater treatment. These analytical techniques include amperometry, voltametry, polarography, membrane cells, potentiometry, and oxidation–reduction potential (ORP). Chapter 3 gives further details of chlorine detection methods used in the laboratory.

Amperometry

Continuous analyzers that use two electrodes for measurement are usually categorized as amperometric. This was the case with the original Fischer and Porter and Wallace & Tiernan analyzers. However, it is no longer true of the array of analyzers currently available.

Electrode reactions are characterized by the transfer of electrons between the electrode and the substances in the sample solution. The reaction that

initiates the transfer of electrons results in flow of current between the electrodes. When the electrode reactions occur spontaneously upon short-circuiting of the two electrodes, the system is described as a galvanic cell. If, however, the reaction is forced to occur by imposing an external electromotive force, the cell is referred to as an electrolysis cell (i.e., with the generation of chlorine). The term “reactions” here refers to the chemical changes of the solution that might occur. When chlorine residuals are being measured, the current flows between the electrodes primarily as a characteristic of the species involved. Dual electrode analyzers such as those made by Capital Controls, Fischer and Porter, and Wallace & Tiernan are galvanic cells—the amperometric type, which respond in a linear fashion only to the elemental halogens (bromine, chlorine, and iodine). They do respond to most chloramines but not in a linear fashion.

Voltametry

When the galvanic cell is subjected to an externally applied voltage to measure a particular chemical species in the presence of other species, the system is described as voltametry. In this case, the voltage applied provides qualitative information on the electroactive substance, and the current measured provides quantitative information on the species selected by the applied voltage. This technique is used to isolate the free chlorine species in the presence of chloramines. This is a variation of the amperometric measurement technique. The term “amperometric” has been used to indicate concentration measure based on the measurement of the current flowing between two electrodes at a constant potential at the indicator electrode.

Polarography

Polarography is used to describe analytical measurement of trace materials in solution, metallic ions, and so on. It is based on the principles of voltametry, that is, current–voltage curves, but with a polarographic cell. A polarographic cell is an electrolytic cell consisting of a nonpolarizable reference electrode, a readily polarizable electrode, and an electrolyte solution containing electro-oxidizable or electroreducible material.

At this point, the difference between a polarized and a depolarized electrode should be understood. An electrode is said to be polarized when it adopts the externally impressed potential (voltage) on it, with little or no change in the rate of the electrode reaction (i.e., no change in current). Therefore, if only one electrode in the cell is polarized, its potential changes in the same amount as the change in applied voltage.

At the other extreme, an ideally depolarized electrode is one that retains a constant potential regardless of the magnitude of the current flowing between the electrodes. Therefore, the nonpolarizable electrode’s potential is not altered by the changes in the externally applied voltage.

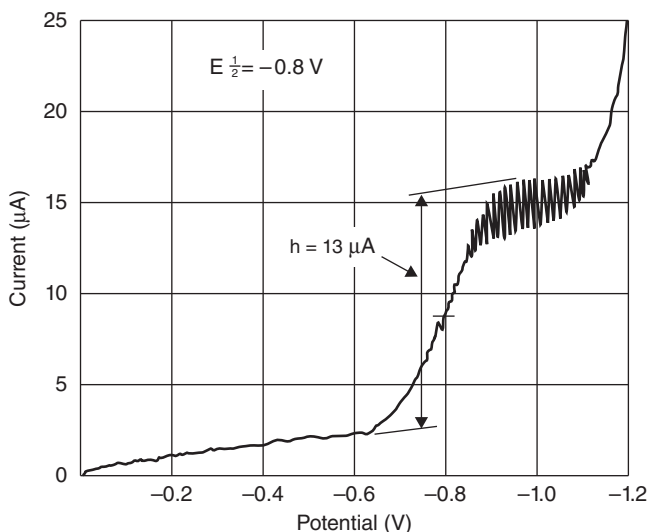


Figure 12.1. Polarographic curve.

When an increasing electromotive force (applied voltage) is impressed across the electrodes of a polarographic cell and if the resulting current is plotted as a function of the applied voltage, a curve is obtained, as shown in Figure 12.1. The extension of the wave curve along the current axis is directly related to the concentration of the material in the sample of solution, and its inflection point (0.8V) is at the applied voltage that is characteristic for this particular species of material.

Membrane Cell

These probe-type chlorine residual monitors are descended from the work of Johnson and others.¹² They operate on the same principle as that of polarographic cells except that they use selective membranes—one for free chlorine and another for total chlorine residual. The exact materials for the membranes are always proprietary items. The cell is designed in such a way that it can monitor chlorine residuals without the need for chemical addition, which is required by the amperometric cells. The sensor consists of two noble metal electrodes immersed in a common electrolyte. The electrodes are isolated from the monitored sample by the chlorine-permeable polymeric membrane (Fig. 12.2). In essence, the sensor is much like a battery, with the chlorine species generating the current flow.

Potentiometry

This method is used for measuring trace materials in solution by means of an electrode containing two sensing elements. The method is based on the

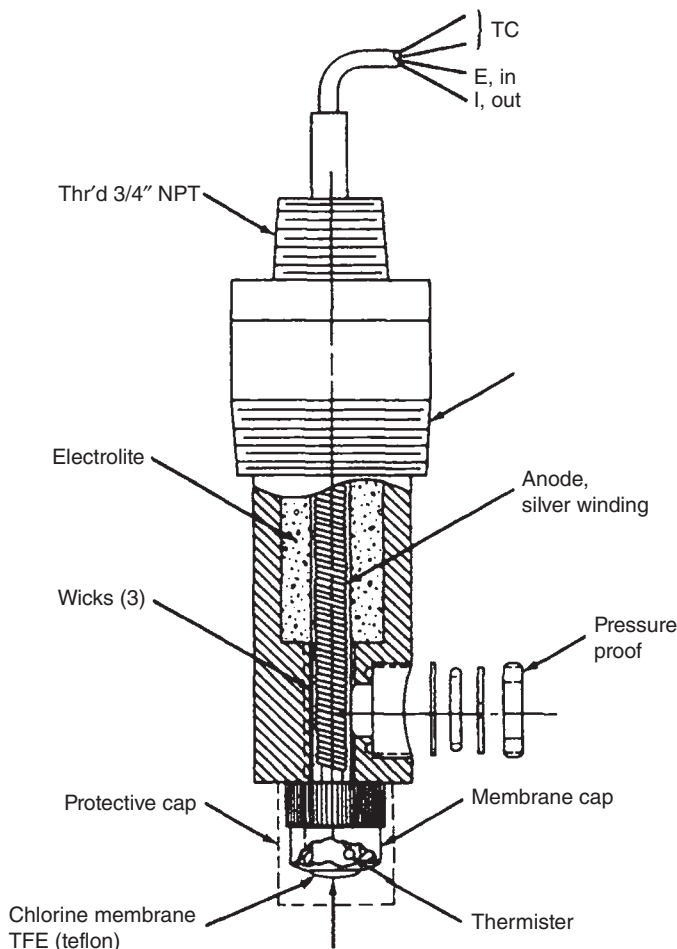


Figure 12.2. Chlorine sensor polarographic membrane cell (courtesy Delta Analytical Div. Xertex Corp.). NPT, normal pipe thread; TC, temperature compensation.

constant current technique of species separation, which measures the potential at each element. It is not widely used in the measurement of chlorine residuals.

The potentiometric method for chlorine residual is only applicable to the measurement of total residual chlorine because it measures the iodine species released from the potassium iodide electrolyte oxidized by total residual chlorine. A platinum electrode develops a potential that depends on the relative concentration of iodine and iodide in the solution:

$$E_1 = E_0 + (S/2) \left(\log [I_2] / [I^-]^2 \right) \quad (12.1)$$

$$E_1 = E_0 + (S/2) \log [I_2] - S \log [I^-], \quad (12.2)$$

where

E_1 = potential developed by the platinum sensing element (mV),

E_0 = a cell constant (mV),

S = monovalent electrode slope (58mV/decade at 20°C),

$[I_2]$ = iodine concentration (mol/l), and

$[I^-]$ = iodide concentration (mol/l).

A second electrode, the iodide element, develops a potential that depends on the iodide ion concentration in solution:

$$E_2 = E'_0 - S \log[I^-], \quad (12.3)$$

where

E_2 = potential developed by the iodide sensing element (mV), and

E'_0 = a cell constant (mV).

The electrode thus measures the difference between potentials developed at the two sensing elements:

$$E = E_1 - E_2 = (E_0 - E'_0) + (S/2) \log[I_2] \quad (12.4)$$

$$= E''_0 + (S/2) \log[I_2], \quad (12.5)$$

where

E''_0 = potential measured by the analyzer (mV), and

$E''_0 = E_0 - E'_0$ = a cell constant (mV).

The net potential measured by the electrode is converted by analog electronics to read directly as residual chlorine in mg/l. The electrode is calibrated with a standard of known equivalent residual chlorine concentration. The preceding equations demonstrate that the output of the electrode is proportional to the log of the iodine concentration and, thus, proportional to the log of the total residual chlorine concentration. This enables the electrodes to measure the residual chlorine concentration over a four-decade range from 0.001 to 10mg/l.

ORP

Every oxidation reaction is accompanied by a reduction reaction, and vice versa; expressed another way; an oxidant is a substance that causes oxidation to occur while being reduced itself. The oxidation state or the oxidation number

(mV) represents a hypothetical charge that an atom would have if the ion or molecule were to dissociate:



Any chemical in solution that is capable of entering into an oxidation or reduction reaction causes a potential difference between a standard half-cell (reference electrode) and a measuring electrode. The measuring electrode (also known as the sensing electrode) for potable water, wastewater, or bio-solids has to be a pure noble metal such as 99.999% platinum. The electrode circuitry for pH is the same as described above, except that the measuring electrode is made of glass and specifically measures the hydrogen ion concentration.

The ORP, also called the redox potential, is a measure of the net potential from an aqueous solution composed of oxidants (chlorine species) or reductants (sulfites). This gives redox potential the unique ability to detect whether the chlorine species present at any given time is sufficient to meet the demand or whether sulfite addition is sufficient to neutralize the chlorine to achieve complete dechlorination. ORP responds logarithmically to concentration (Fig. 12.3a), making the ORP probes most sensitive at extremely low concentrations of chlorine or sulfite.

Figure 12.3b illustrates the redox potential as a function of free chlorine (85% HOCl), chloramine, and sulfite concentrations. This clearly shows the dramatic change on the redox potential when the residual is near zero, which makes detection and control of both chlorine and sulfite in extremely low concentrations (0.10 mg/l) a practical matter. Figure 12.4 shows the ORP versus concentration profiles, that is, the relative oxidizing power of various chlorine residual species.

When sulfite addition is controlled by redox measurement, an ORP probe reports the ORP levels in the source water to the controller. The controller modulates the rate of sulfite feed based on the changing chlorine and sulfite activity. The redox technique differs several ways from the procedure used by chlorine residual analyzers:

1. It measures the actual oxidant and reductant activity, instead of residuals. Residual measurements are vulnerable to compounds in water that cause serious quantitative errors in the measurement of chlorine residuals.
2. Redox can measure the potential (in mV) of both sides of the chlorine and sulfite couple. This means that it can measure both the chlorine and the sulfite activity, which enables the operator to lock in a slight residual of either chlorine or sulfite.

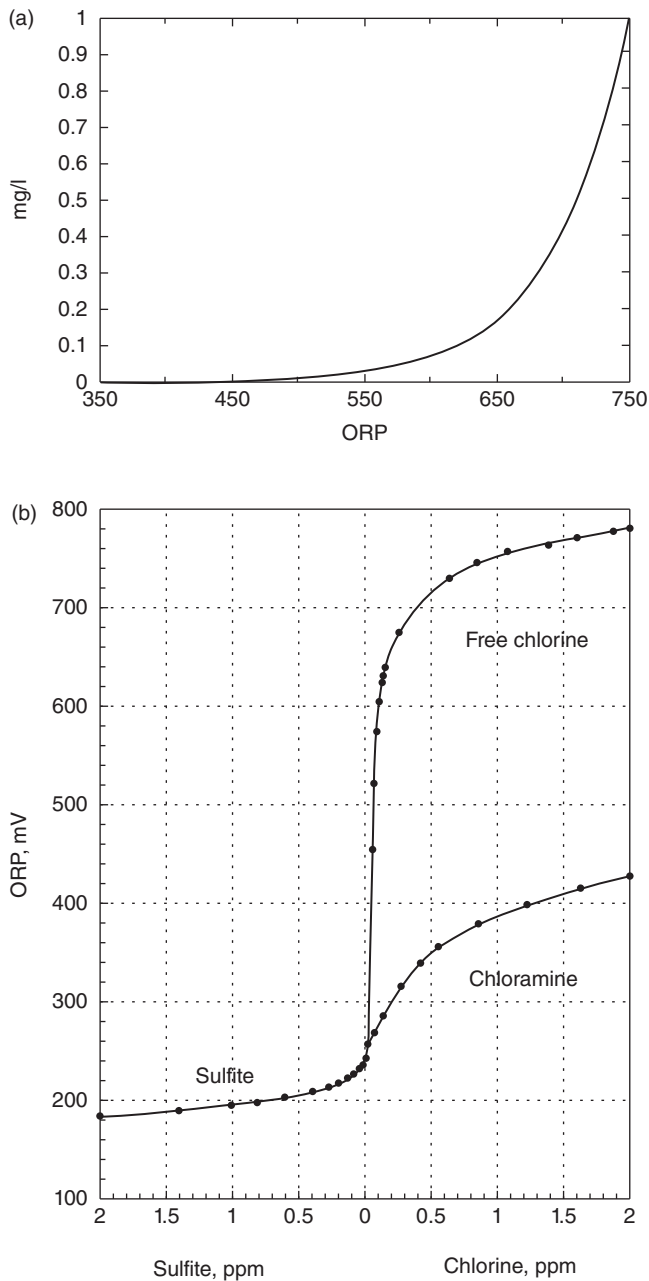


Figure 12.3. ORP (a) versus chlorine and sulfite concentrations (b) (tap water, 21 °C, pH 7.5).

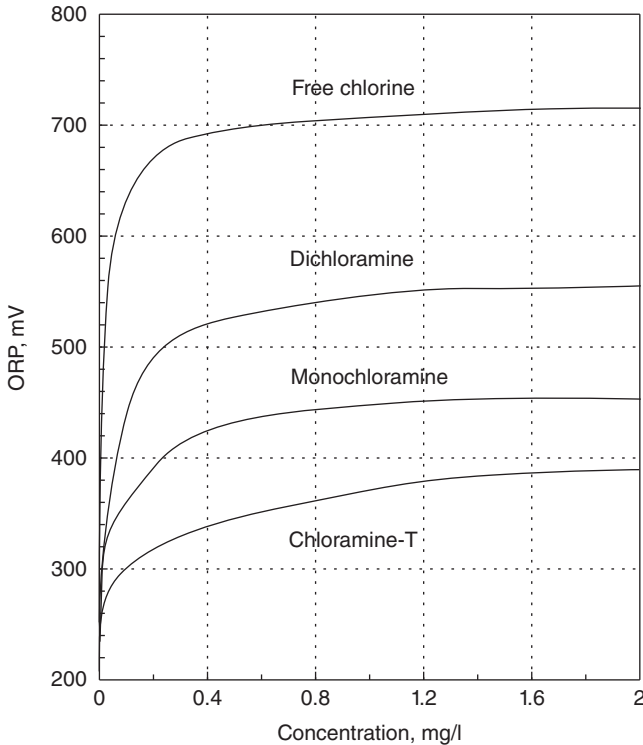


Figure 12.4. ORP of various chlorine compounds.¹⁴

3. Redox responses are logarithmic and allow more precise control of dechlorination where zero residual is the discharge requirement.
4. Properly designed redox electrodes are very forgiving of process contamination because they do not measure current. The electrodes can continue to operate properly even after being partially coated with the contaminants in the source water.

Figure 12.5 illustrates the typical microorganism inactivation rate developed by Ebba Lund from her extensive work on inactivation of the polio virus.¹³ It shows that redox measurement accurately predicts the rate of virus inactivation, regardless of the oxidizers used. Lund found that, once a minimum redox potential has been exceeded, the inactivation rate progresses proportionally with respect to increasing redox potential. Various oxidants, such as chlorine, KMnO_4 , and cystine, were employed in the study and, in all cases, illustrated how unreliable the residual measurement is in predicting the disinfection efficiency. Figure 12.6 illustrates the difference between ORP readings by free residual chlorine and by chloramines.

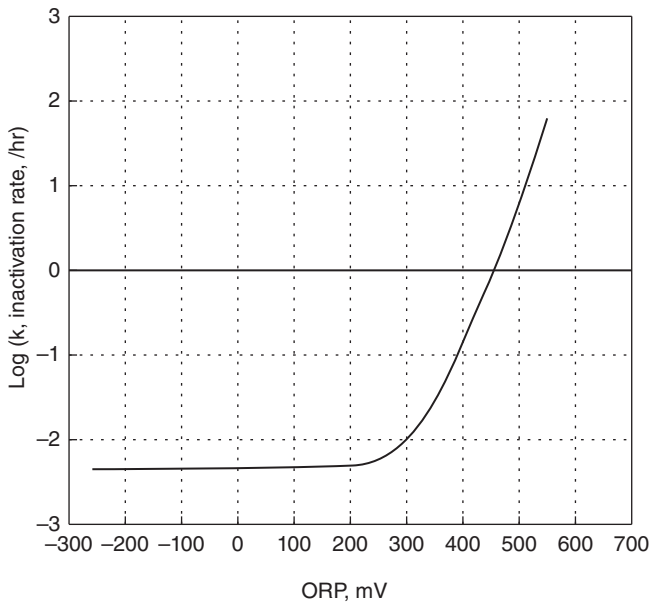


Figure 12.5. Rate of poliovirus inactivation as a function of redox potential.¹³

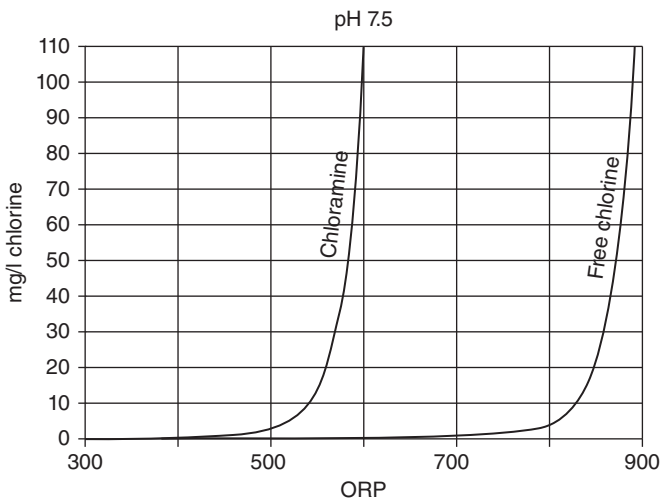


Figure 12.6. ORP of free chlorine versus chloramine.

Colorimetry

Certain chemical reactions produce a color change. The intensity of the color in these reactions can be used to measure the concentration of one of the reactants present using a colorimeter. The colorimeter works by

shining a certain wavelength of light through the sample and measuring how much of that light is absorbed (absorbance) or passes through the sample (transmittance). Different wavelengths of light are used to detect different colors.

ONLINE ANALYZERS FOR CHLORINATION

Online analyzers are perhaps the most critical components of chlorination–dechlorination process control systems. Their use can significantly improve the effectiveness and accuracy of real-time data collection. Quick access to information about plant flow and residual disinfectant enables the operator to adjust chlorine dosages in a timely manner. If the chlorine feed valve can be operated remotely, the operator can monitor and control the chemical feed rate from the plant control room. This approach has the potential of minimizing chemical use while keeping a close watch on chlorine residual to achieve good disinfection.

Automation can be resource intensive. Analyzers are perhaps the most sensitive part of the entire process control system, as they need frequent calibration and maintenance. There are two broad categories of analyzers: (a) those that directly or indirectly measure the free or total residual chlorine, and (b) those that measure the ORP of the water. Instruments based on the former technique quantitate chlorine in water through potentiometric, amperometric, or colorimetric analyses, while those based on the ORP principle measure chlorine or sulfur dioxide indirectly from the sample's redox chemistry.

A large variety of online analyzers are available to monitor and control disinfection processes in water and wastewater treatment. Table 12.1 lists some

TABLE 12.1. Widely Used Online Chlorine Analyzers

Analyzer Code	Analyzer Model Name	Manufacturer	Method of Analysis
ATI	A15/79	Analytical Technology, Inc.	Potentiometric
	Q45H		Polarographic
HACH	CL17	Hach	Colorimetric
CAP	1770	Severn Trent Services	Amperometric
	1870E		
	OXITRACE 1871		
	CL1000		
	CHIORTROL 5000		
GLI	AccuChlor2	GLI International	Amperometric
ORION	1770	Orion Research, Inc.	Potentiometric
WT	Micro/2000	Wallace & Tiernan	Amperometric

widely used online chlorine analyzers and their respective methods of analysis. This section discusses selected online analyzers in greater detail.

Analytical Technology, Inc.

Analytical Technology, Inc. has two widely used chlorine residual analyzers: the ATI A15/79 and the ATIQ45H. The ATI A15/79 is a continuously measuring analyzer (Fig. 12.7). It measures total chlorine electrochemically by allowing the buffered sample to react with potassium iodide (KI) to form iodine (I_2) at a 1:1 molar ratio with total chlorine in the sample. The instrument consists of three separate modules: (a) a chemistry module where the buffer and the KI are delivered to the analyzer, (b) an inlet flow assembly through which the raw sample is pumped into the system, and (c) an electronic display unit that reads out the chlorine concentration and houses the analog outputs and alarm contacts.

The A15/79 houses all components used to measure residual chlorine by the potassium iodide method. Two types of chemistry modules are employed to measure the iodine released when KI reacts with HOCl. In one, the treated sample is allowed to flow directly into a chamber containing the iodine gas sensor. The sensor consists of a membrane that allows iodine to diffuse through. The iodine is reduced to iodide at the active electrode surface, generating a current proportional to the iodine produced. In the other configuration, the reacted sample is air-stripped, and the iodine released into the air stream is directed to the gas sensor located in a separate chamber (Fig. 12.8). This analytical method has a significant advantage over other methods of

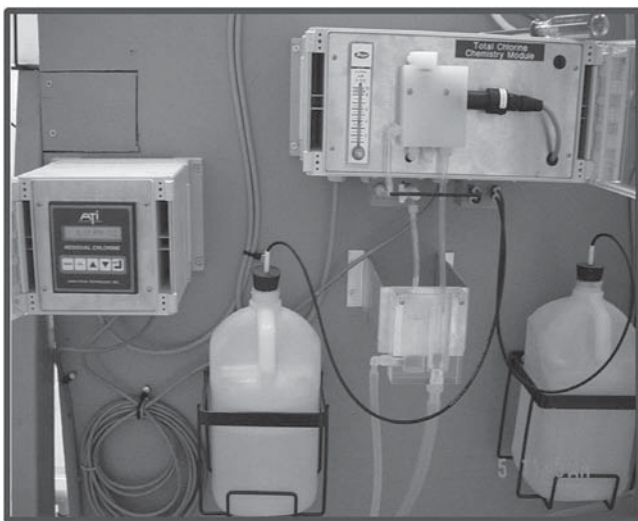


Figure 12.7. The ATI 15/79 online chlorine analyzer.

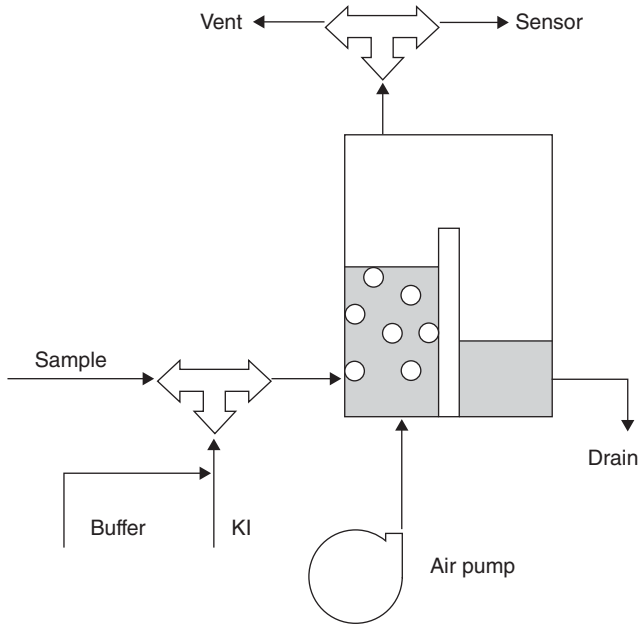


Figure 12.8. Schematic for ATI A15/79 residual chlorine monitor with air-stripper.

detecting residual chlorine in wastewater since the sample does not come in direct contact with the sensor and therefore does not cause fouling. Fouling of the sensor is often the most troublesome aspect of online analyzer maintenance.

The electronic monitor in the A15/79 provides a real-time display of chlorine concentration, control outputs, an isolated analog output, and an external alarm. The monitor is housed in a compact 1/4 DIN panel mounted in an aluminum or corrosion-resistant NEMA 4X Fiberglass enclosure, and is connected to the chemistry module by 20–100 ft of cable. The sample can be introduced into the monitor through 1/4-in. flexible tubing at flow rates of 3–30 gph. At higher flow rates, sample delivery times are shorter. The instrument uses only a small fraction of the sample; the rest overflows into the drainage chamber.

The alphanumeric liquid crystal display (LCD) on the A15/79 displays residual chlorine concentration, alarm status, and configuration information. The relays provide simple on/off control for direct modulation of chemical feed pumps or pulse frequency and pulse width control. They can be programmed for set point, deadband, and time delay. The programmable 4–20 mA output can span to read 0–0.2 or 0–20 ppm.

The ATI Q45H model is available in two versions: (a) a free chlorine monitor for drinking water and cooling water systems, and (b) a combined chlorine monitor for chloraminated drinking water and wastewater containing



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Figure 12.9. ATI Q45H Residual C12 Monitor (courtesy of Analytical Technology Inc.).

sufficient monochloramine residual. It uses membrane-covered polarographic sensors available in the flow cell and submersion configurations. The polarographic membrane sensor measures residual chlorine directly without the need for any kind of treatment of the sample. The result is an operating system that continuously produces dependable measurements in potable water systems. This system is illustrated in Figure 12.9.

The sensor consists of a pair of electrodes immersed in a conductive electrolyte and isolated from the sample by a chlorine-permeable membrane. The chlorine residual diffuses through the membrane and is reduced to chloride on the surface of the working electrode. This process causes a flow of electrons through an external measuring circuit, with the current flow being linearly proportional to the chlorine concentration. The absolute response of the sensor is also temperature dependent, and an RTD in the sensor provides a temperature input to the electronics assembly to allow for automatic temperature compensation.

The combined chlorine sensor can be used in either the flow cell or the submersion configuration. The submersion configuration requires a flow velocity of more than 0.4 ft/s for proper operation. The free chlorine sensor is always used in the flow cell configuration and may require CO₂ buffering if the pH is above 8. A constant-head flow cell is used to maintain constant pressure and flow rate at the face of the sensor.

Residual chlorine sensors have the best sensitivity and stability when the sample flow is controlled. Therefore, a constant-head overflow assembly is provided to control both flow rate and water pressure in the area of the membrane. The sample inlet flow and pressure from the system being monitored

can vary widely without any effect upon the measurement. The only requirement is that the inlet flow rate be kept above the minimum of about 7 gph. A low-volume flow cell can be used at inlet flow rates of 3–6 gph.

The sensor is made of clear acrylic, which makes it possible to easily detect any fouling. Other special features of the sensor include the following:

- Display: 16 character alphanumeric liquid crystal display with backlight
- Sensitivity: 0.001 mg/l above 0.020 mg/l
- Response time: 90% in less than 60s
- Repeatability: +0.05 mg/l
- Control relays: two SPDT, 5A, 239V AC resistive, with programmable set points
- Control relay function: programmable on/off, pulse with modulation, or pulse frequency modulation
- Power: 120/230V AC, 50/60Hz, 5V A max.
- Operating temperature: electronics -20°C to $+50^{\circ}\text{C}$
- Sensor materials: noryl and stainless steel

Hach

The Hach CL17 analyzer employs the potassium iodide reaction with the sample buffered to a pH of 5.1 (Fig. 12.10). The Hach analyzer utilizes the DPD colorimetric method to measure the iodine evolved during the reaction. A sample is pumped into the measuring cell, and the background absorption of light by the sample is measured before the addition of reagents. The buffer,



Figure 12.10. The Hach CL17 online chlorine analyzer.

KI, and an indicator are added to the sample. The I_2 produced oxidizes the indicator and turns the sample to magenta. The intensity of the color is proportional to the I_2 concentration, which, in turn, is proportional to the total chlorine concentration in the water sample. Light absorption of the reacted sample is measured, and the difference between the two absorption measurements is used to determine the total chlorine concentration. The measurement process takes 2.5 min per sample.

The mixing system in CL17 operates without any moving parts—a self-cleaning stirring bar produces vigorous mixing. A transparent gasket that fills the spaces between the light source, the sample chamber, and the detector prevents condensation on the walls of the sample chamber. The CL17 can measure free or residual chlorine over a range of 0–5 mg/l, with a minimum detection limit of 0.035 mg/l, and comes with one 4–20 mA output programmable over any portion of this range.

Figure 12.11 shows the basic mechanical operation and fluid path of sample and reagent through the colorimetric analyzer. The reagent pump and the sample pump pistons are synchronized so that the reagent is added simultaneously with the sample. As the sample piston rises, drawing in the sample, the reagent piston discharges the reagent into the sample stream. A mixing and delay coil provides time for the sample and the reagent to become completely mixed and for the colorimetric reaction to progress to completion before the sample enters the colorimetric cell. After analysis (the other half of the

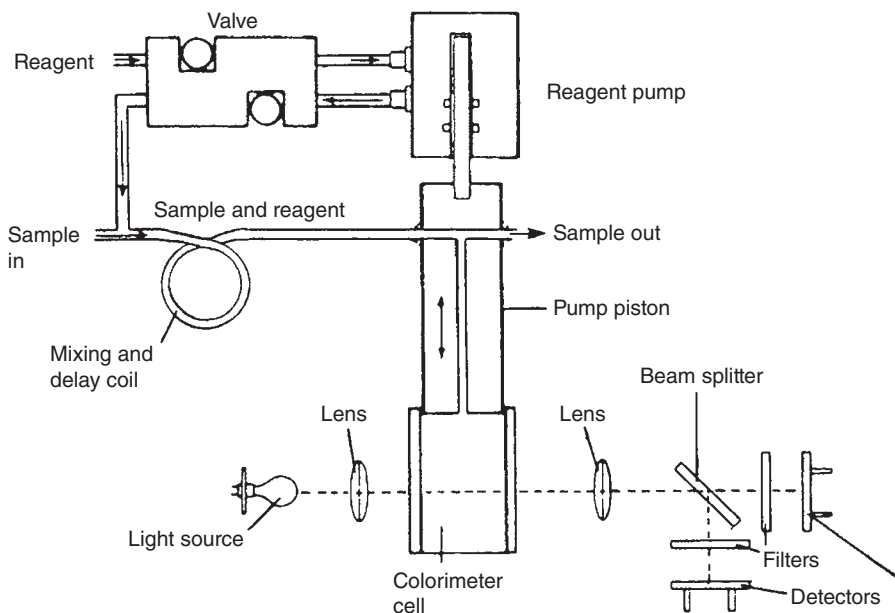


Figure 12.11. Colorimetric analyzer showing fluid path and mechanical operation (courtesy of Hach & Co.).

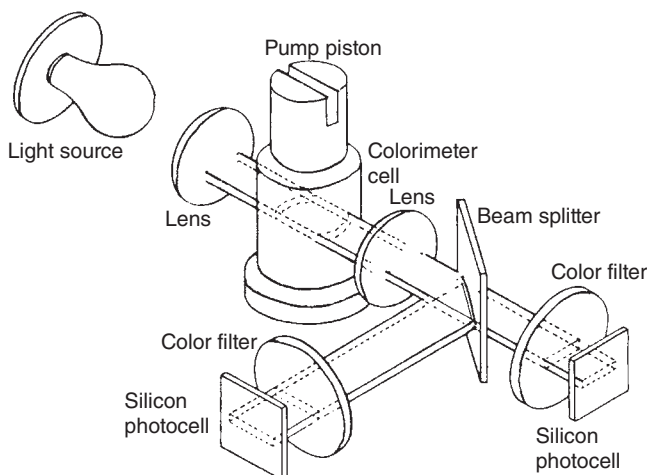


Figure 12.12. DPD colorimetric analyzer, optical design (courtesy of Hach & Co.).

pumping cycle), the sample pump discharges, while the reagent pump draws in the next portion. Valves (not shown in the figure) open and close during the parts of the cycle when the pistons are stationary.

Figure 12.12 shows the optical design of the colorimetric analyzers. The light beam passes through a lens before entering the cylindrical pump/sample cell. After passing through the cell, the light encounters a beam splitter, which directs part of the beam through a filter to a reference detector located at 90° to the light path. The other, the main part of the light beam, passes through a filter to a sample detector. The signals from the two detectors are fed to the electronics package for processing. The single-beam/dual-wavelength capability provides a correction for any changes in light source or sample cell condition, and can compensate for moderate changes in sample turbidity and color by the reference wavelength used in the analyzer. Although these features increase the reliability when the analyzer is used to determine residual chlorine concentrations in wastewaters that may contain suspended solids and other contaminants, sample pretreatment is still required for removal of debris and large solids that may foul or plug the analyzer.

A block diagram of the analyzer electrical system is shown in Figure 12.13. After passing through the sample, the light strikes the reference and sample silicon photocells. This produces a current, which goes to a log-ratio converter. The converter sends out a signal equal to the log of the ratio between the two currents. The log-ratio signal travels to an amplifier with gain and offset controls and then to a sample-and-hold circuit. A microswitch is activated when the sample piston is at the top of the cylinder/sample cell (allowing an unobstructed light path). This advises the sample-and-hold circuit to put the amplifier output into storage. The meter and other external readouts indicate this value, which is stored until the next cycle.

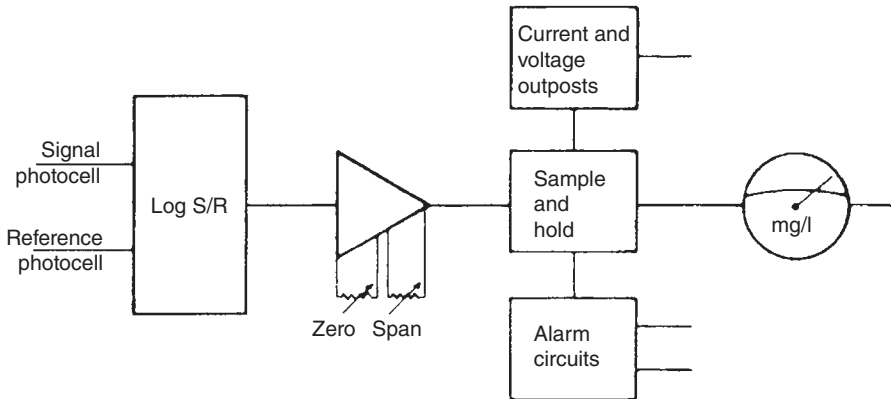


Figure 12.13. DPD colorimetric analyzer, block diagram of electrical system (courtesy of Hach & Co.).

Free available chlorine DPD colorimetric analyzers are available with one of four factory-preset ranges. The widest range is 0–5.0 mg/l. Total residual chlorine DPD colorimetric analyzers are available with one of three factory-preset ranges. The widest range is 0–2.0 mg/l. The analyzers have no automatic temperature compensation. The effect of varying sample temperatures or ambient temperature can be significant. Hach offers an optional sample heater that will maintain the sample temperature within $\pm 1.5^\circ\text{C}$. This should be included as an integral part of these analyzers.

A major limitation of these analyzers is the response time to variations in sample concentrations. Unlike other analyzers, these analyzers determine concentration by using discrete samples. One complete cycle requires time for the sample to enter into the analyzer, for adding the reagent, development of color, and expulsion of the sample from the analyzer. The supplier's specifications state the following response times:

Free available chlorine: initial response in 30 s, 97% in 2 min

Total residual chlorine: initial response in 5 min., 95% response in 7 min

This response time is often unacceptable for either residual control or the dechlorination process. The analyzer is relatively insensitive to drift. The sensitivity claimed by Hach is 0.02 mg/l, precision is $\pm 0.5\%$ of full scale at constant ambient and sample temperatures, and accuracy is $\pm 5\%$ for the same conditions.

Capital Controls

Capital Controls produces a series of chlorine analyzers that all include a central gold and an outer copper electrode assembly, with or without a second

electrode, to measure residual chlorine amperometrically. These analyzers also make use of the iodometric method of combining the KI with the sample buffered to pH 4 to produce free iodine, which is measured amperometrically while it is in solution by using a bare electrode measuring cell, where the electric potential applied across the electrodes produces a current that is proportional to the concentration of iodine in the solution. The electrode surfaces are kept clean by a rotating striker assembly consisting of PVC spheres around the cell. These instruments can continuously monitor residual chlorine in water or wastewater samples, with resolution as low as 0.001 mg/l.

The 1770 Chlorine Analyzer is ideal for continuous measuring of free chlorine in drinking water, swimming pools, and recirculating process waters. The unit can be set to read 0–1, 0–2, and 0–20 mg/l free chlorine. The 1870E model is similar to the 1770 but can measure free or total chlorine, chlorine dioxide, iodine, bromine, and other oxidants in water. Reagents and sample are fed into the analyzer by gravity, eliminating the need for pumps.

The 1870E Chlorine Analyzer has a field-selectable monitoring range, from 0–0.1 to 0–20 mg/l. It also incorporates a constant, direct-drive electrode cleaning system, which eliminates signal drift and the need for frequent recalibration. Internal high and low set points are standard. Extralarge gold and copper electrodes are used to provide maximum signal strength. Sample temperature variations are compensated for by a thermistor to produce consistent residual values.

The sample is delivered to the constant-head weir at about 500 ml/min. The excess overflows to the drain (Fig. 12.14). The sample then passes through the

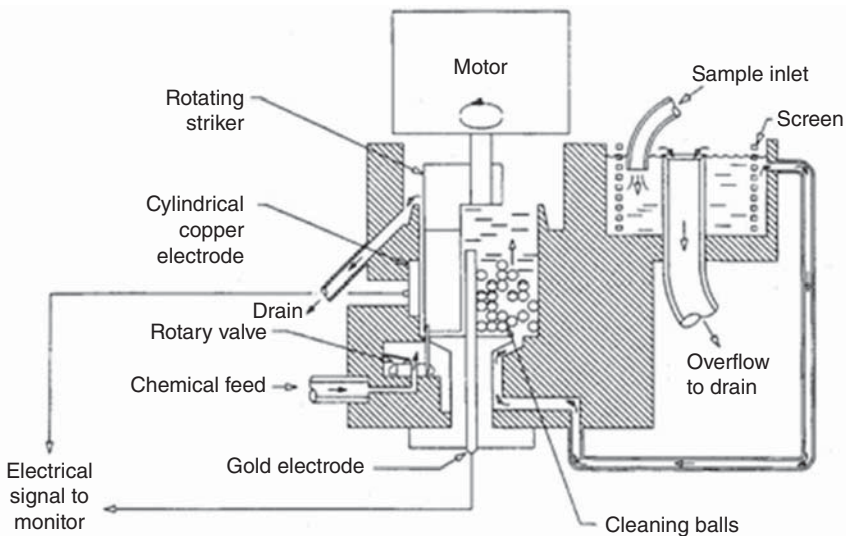


Figure 12.14. Capital control chlorine residual analyzer, series 1870E flow diagram (courtesy of Capital Controls Co.).

annular space between the two fixed electrodes in the “sensing” cell. As it passes through this cell, it generates a small amount of direct current (DC) in direct proportion to the amount of residual chlorine in the sample. This residual value, in mg/l, is displayed on the digital indicator.

The liquid reagent is stored in a single bottle and is fed from a constant head reservoir through a rotary valve, adding the precise amount of solution during each valve rotation. The reagent bottle contains a 7 day’s supply of reagent. An optional reagent feed system may be adopted for pH buffering by using CO₂ gas for certain water treatment applications. The 1870E analyzer is constructed of corrosion-resistant materials. Each unit is prepped and prewired, requiring only field connection to the service points. All components and controls are accessible from the front of the unit for easy observation of the solution level and sample flow, as well as for cleaning the electrodes and making adjustments to the set points.

Capital Controls’ OXITRACE model 1871 represents a significant advancement in residual analysis through microprocessor-based electronics. It offers precise proportional-integral-derivative (PID) control of the critical factors involved in measuring residual chlorine concentration: pH, temperature, and process water flow rate (Fig. 12.15). The 1871 is an amperometry-based instrument designed to continuously analyze free (85% HOCl) chlorine or total chlorine plus chlorine dioxide, potassium permanganate, iodine, bromine, or other oxidants for potable water, wastewater, cooling water, and other process water. All components and controls are accessible from the front for ease of

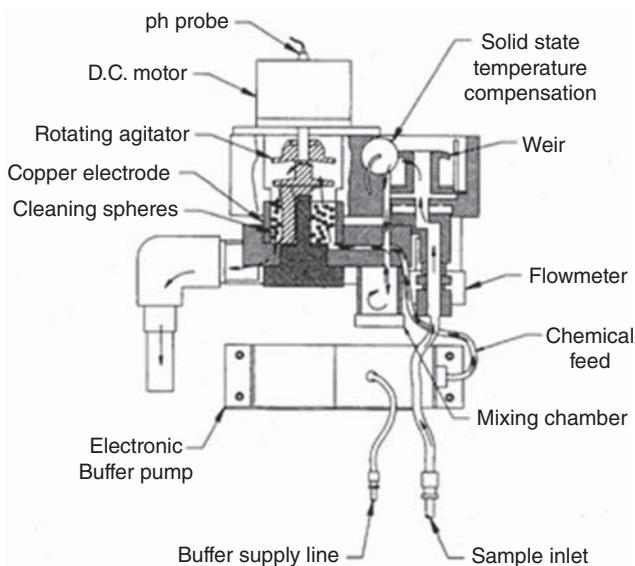


Figure 12.15. Capital Controls on-track analyzer, OXITRACE® model 1871 flow diagram (courtesy of Capital Controls Co.).

set-up and operation. The digital electronics system provides unequaled accuracy and reliability. The entire unit is constructed of corrosion-resistant materials. Each unit is prewired and prepiped, requiring only field connections to service points.

The Oxitrace analyzers incorporate a direct-drive electrode cleaning system that eliminates signal drift and minimizes the need for frequent recalibration. The extralarge gold and copper electrodes provide continuous maximum signal strength. The ability to accurately measure low levels of chlorine residuals is enhanced by a cell pH monitoring and PID control system, plus an infrared flow detector and solid-state temperature compensation.

As the sample flow passes through the dual electrode cell, a small amount of direct current is generated in direct proportion to the amount of residual present in the sample. The surfaces of both electrodes are kept clean by the action of PVC spheres, which are dispersed by a motor-driven agitator. This continuous cleaning of the electrodes maintains an accurate residual measurement. In addition, a solid-state temperature device compensates for sample temperature variations.

A pH probe, with its associated PID function, controls the frequency of reagent feed through an electronic solenoid buffer pump. As the sample pH rises, the control system within this unit increases the reagent pumping frequency to bring the pH back to the correct operating range. This range is between 4.3 and 4.5 pH. The 1-gal reagent bottle provides storage for 14–30 days' operation in most applications.

The model 1871 analyzer has a 10 ppb detection limit. The 1% accuracy of this unit is ideal for precise control of potable water, wastewater, and other process waters. A continuous direct-drive cleaning system maintains a constant level of electrode cleanliness. This maintains system accuracy.

Capital Controls' CL1000 Residual Analyzer uses microprocessor-based electronics to precisely measure residual chlorine (Fig. 12.16). It is capable of continuously analyzing free or total chlorine, chlorine dioxide, iodine, bromine, and other oxidants in water or wastewater. The CL1000 uses a three-electrode measuring cell arrangement that allows it to measure residual chlorine from low parts-per-billion range to as high as 60 mg/l. This instrument comes with six alarm relays and two 4–20 mA output signals. Reagents and sample are gravity-fed into the analyzer eliminating the need for pumps.

Capital Controls' CHLORTROL 5000 (Series 17B5000) is also an amperometric-type residual chlorine analyzer with bare electrodes designed to provide continuous measurement of the chlorine residual content in the process water being used (Fig. 12.17). The analyzer uses a flow-through measurement cell containing two dissimilar metal electrodes. As the water sample flows past these electrodes, an electric current that is directly proportional to the chlorine residual concentration is generated.

One of the electrodes is rotated by an electric motor that imparts a swirling velocity to the water sample. This electrode rotation at a constant speed provides reproducible electrolytic conditions and makes the cell independent of



Figure 12.16. Capital Controls CL1000 online chlorine analyzer.

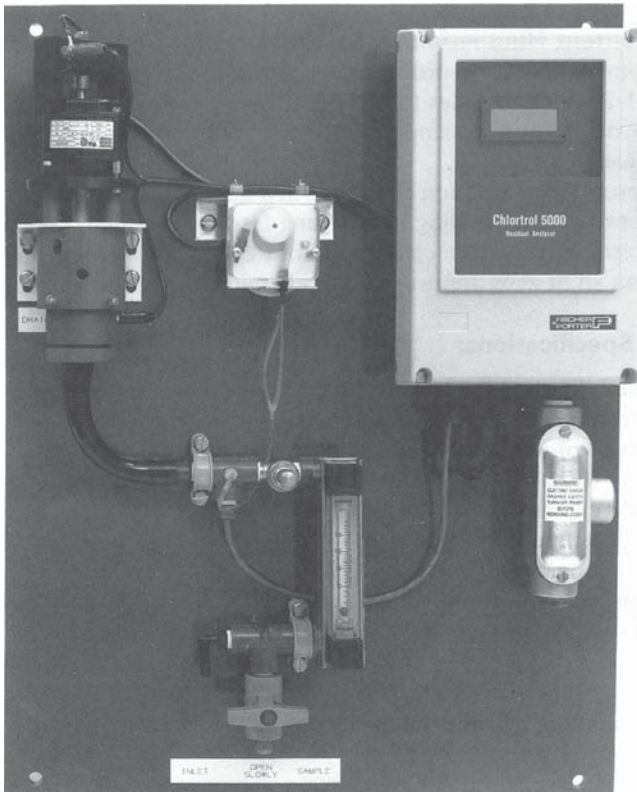


Figure 12.17. Capital Controls' CHLORTROL 5000™ (Series 17B5000) bare electrode cell chlorine residual analyzer (courtesy of Bailey—Fisher and Porter Co.).

sample flow variations. Inert plastic nonabrasive pellets in the cell keep the electrodes in a clean condition by scouring action. By proper reagent selection, either free chlorine (85% HOCl) or total chlorine residual (free chlorine plus combined chlorine) may be measured.

The analyzer is also supplied with a digital indicator to eliminate the need for additional instrumentation at the point of measurement. The indicator is wall mounted for operating and maintenance convenience. The reagent feed pump is a motor-driven peristaltic type, which pumps the necessary chemicals. When acetic acid is used for pH control, an 8-gal-capacity reagent container is provided for free chlorine measurement. When total chlorine is being measured, two 8-gallon containers are provided. These containers represent a 60-day supply in each case. When carbon dioxide is used for pH control, one less container is required.

GLI International

The GLI AccuChlor2 residual chlorine analyzer uses the amperometric method to measure free and total residual chlorine in water and wastewater (Fig. 12.18). The system consists of the menu-operated analyzer and an integrated, prewired measurement cell. The cell consists of a gold cathode and a copper anode. Drift is reduced by using a constant pH buffer feed rate, constant flow rate to sample flow cell, and continuous cleaning of the electrodes by PVC spheres. Flow of the sample to the cell is held constant by an integral overflow weir. Buffer solution, a 5% distilled, white, food-grade vinegar, is delivered by an integrated peristaltic pump and used with the PVC balls as scrubbing solution for electrodes.

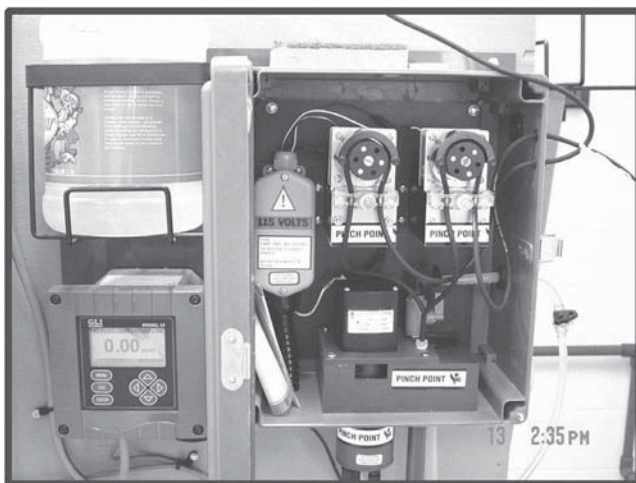


Figure 12.18. GLI's AccuChlor2 online chlorine analyzer.

AccuChlor2 measures residual chlorine continuously. Alternatively, the sample/hold feature can be used to conserve the buffer solution. With this feature turned on, the analyzer measures for 15 min followed by a user-defined (1–60 min) hold period with the buffer pump turned off. The analyzer can operate continuously in this sample/hold configuration until the feature is turned off. The instrument comes with two DC outputs that can be set to 0–20 or 4–20 mA. The three electromechanical relays can be set to function as alarm, timer, status, or control.

Orion Research, Inc.

Orion's Model 1770 chlorine monitor is designed to continuously measure total chlorine residual in water over a concentration range of 0.001–10 mg/l. It uses the potentiometric method to determine total chlorine residual by detecting the concentration of iodine in the sample using a special electrode. A pH buffer is added to the sample to lower its pH to between 3.0 and 4.0, followed by adding potassium iodide to convert all the residual chlorine to iodine. The electrode contains two sensing elements.

The stream enters the inlet block of the Model 1770 and flows directed at high velocity parallel to the inlet screen; less than 1% of it passes through the screen into the monitor. The screen surface is subjected to considerable shear force, which keeps it clean, making it possible to use the analyzer on unfiltered samples. The sample then flows to the flow cell block. The reagent is passed through a purification column to remove any background iodine that might have formed during storage, and is delivered to the block by a separate reagent pump to be combined with the sample reagent. The reagent contains sufficient acid to produce a pH between 3.0 and 4.0 (depending upon the alkalinity of the sample) and iodide. The turbulent mixture is directed out of the flow cell block through a mixing loop. Under these conditions, any total residual chlorine reacts completely to form iodine; the resulting iodine concentration is equal to the sample residual chlorine concentration before the reaction. The sample then returns to the flow cell block and is directed past a sensing electrode. Turbulence in the mixing loop and agitation against the electrode both promote mixing and help minimize fouling of the electrode.

Electrode response is affected by the sample temperature, so automatic temperature compensation circuitry is incorporated in the analyzer. Specifications for the analyzer claim a sensitivity of 0.001 mg/l and an accuracy and a precision of $\pm 10\%$ and $\pm 5\%$, respectively. Note that, for precision and accuracy, the specifications are stated as a percentage of the actual reading, whereas manufacturers of other residual chlorine analyzers state their specifications for precision and accuracy in terms of percentage of the full-scale reading. The time to obtain a full response from a change in residual chlorine concentration in the sample is 2 min. Minimum sample flow is 0.5 gpm, and minimum allowable water pressure is 20 psi; the maximum allowable is 100 psi.

The manufacturer recommends weekly checking of the analyzer for leaks and replenishment of reagent, and monthly calibration. The analyzer is equipped with a sample tap and a valve for calibration of grab samples. There are no operating data on how often this analyzer must be calibrated if it is used in wastewater practice.

Wallace & Tiernan

The Wallace & Tiernan Micro 2000 is an amperometric analyzer capable of continuously measuring free and total residual chlorine (including dichloramine), residual chlorine dioxide, and potassium permanganate in water and wastewater (Fig. 12.19). It can also measure 0–100 $\mu\text{g/l}$ to 0–100 mg/l of residual disinfectant, with a stability of $\pm 1\%$ of full scale over 1 month. Its installation involves only attachment of the sample line, a drain, and a 120V AC power supply. All electronics are housed in a NEMA 4X enclosure. The alphanumeric LCD can read residual concentration, type of residual, and alarm messages. A standard isolated 4–20 mA analog output signal is generated in proportion to the residual concentration in the sample.

The Micro/2000 includes a three-electrode measuring cell for direct measurement of residuals (Fig. 12.20). The cell contains a spiral-wound platinum measuring electrode and a circular platinum counter electrode. The third electrode is a silver–silver chloride reference electrode surrounded by a potassium chloride gel in an upper electrolyte cavity. A replaceable porous reference junction, located behind the measuring electrode, maintains a potential on the measuring electrode and makes possible the grit bombardment to

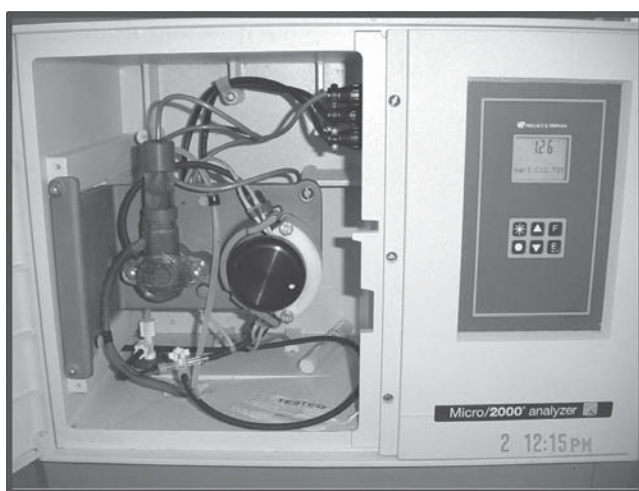


Figure 12.19. Wallace & Tiernan's Micro 2000 online chlorine analyzer.

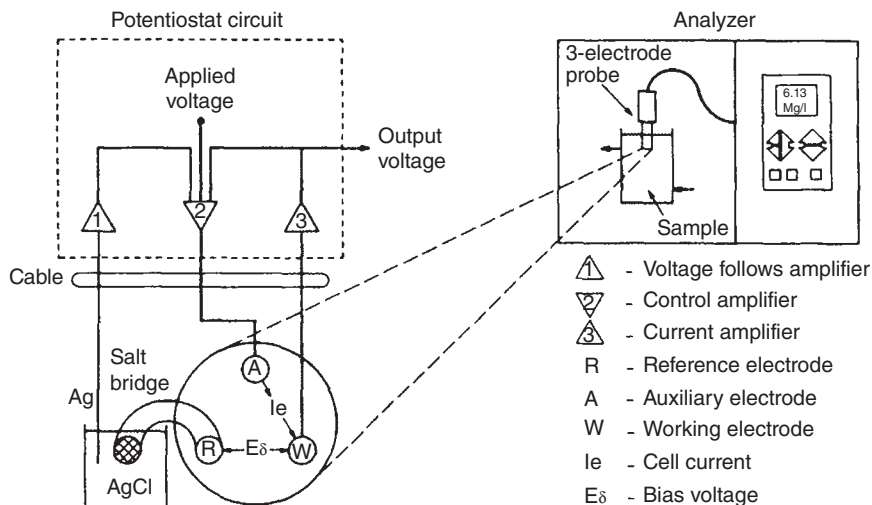


Figure 12.20. Schematic of three-electrode cell (courtesy of Wallace & Tiernan).

keep the electrode clean. A potentiostat circuit serves to eliminate any background noise that might affect the stability of the reference electrode. Its bare electrode design prevents the type of fouling observed in membrane probe analyzers. The three-electrode probe eliminates the need of zero adjustment, and the accuracy of the analyzer is not affected by turbidity or conductivity. Under favorable conditions, the three-electrode system can maintain calibration for up to 1 year.

The sample is pumped into the analyzer at 1–2 gpm in drinking water applications and 3–5 gpm in wastewater applications, and a flushing Y-strainer splits the sample into two streams (Fig. 12.21). The smaller stream flows to the analyzer, while the larger, excess sample stream continuously flushes through the strainer screen. A peristaltic pump delivers the sample and other reagents to the analyzer. A motor-driven impeller in the cell compartment keeps the electrodes clean by constantly bombarding the electrode with grit.

Stranco Products

The Strantrol 890 is an ORP-based analyzer used in the Strantrol Chlor–Dechlor System (Siemens Water Technologies). Figure 12.22 shows the system with the submersible sensor that is dropped in a channel or an open tank. It sends the ORP signal to the controller, to be converted to a 4–20 mA signal that actuates the chemical feed equipment and indicates the process flow. The system also includes an automatic probe cleaning device plus a data logger and a voice modem.

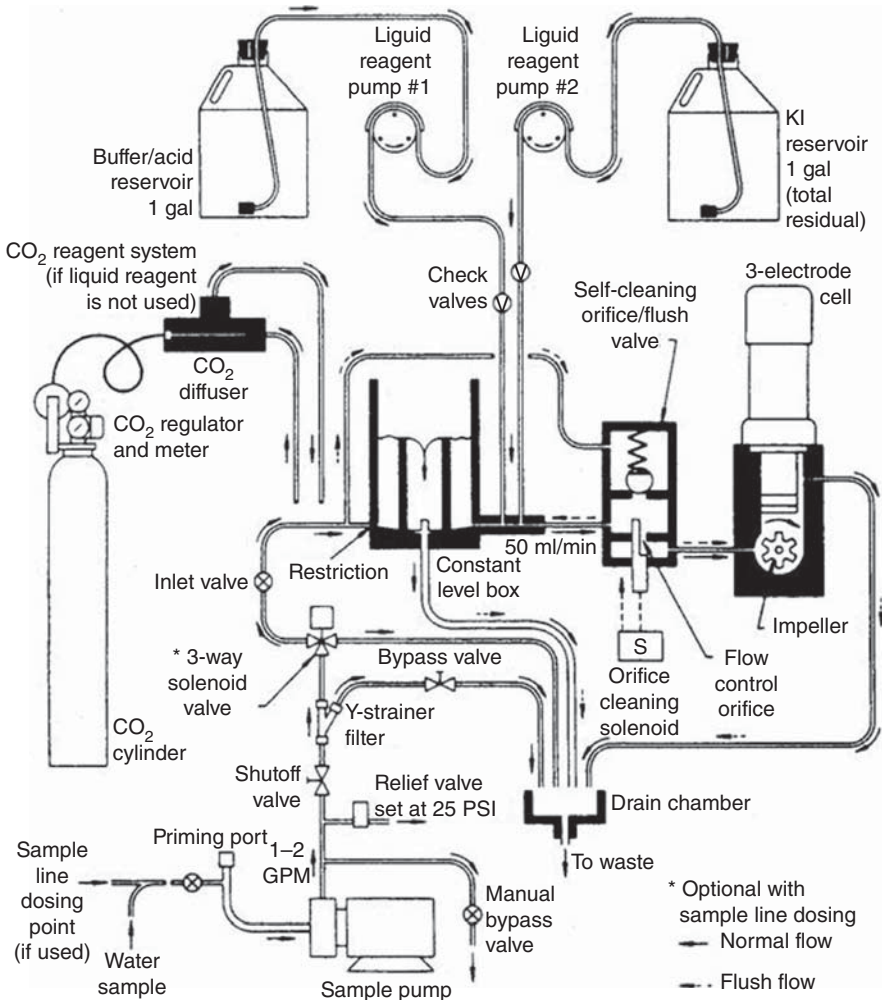


Figure 12.21. Schematic of the Micro 2000 chlorine residual three-electrode cell analyzer (courtesy of Wallace & Tiernan).

Figure 12.23 depicts a typical application of Strantról controllers for a wastewater treatment plant chlorination-dechlorination system. One high-resolution redox (HRR) probe is located in the contact chamber about 5 min downstream from the chlorine diffusers, and a second one is suspended about 20 s downstream from the sulfur dioxide application point.

Figure 12.24 illustrates a compact, low-cost, easy-to-install rechlorination station for potable water distribution systems.

Figure 12.25 shows one of the latest advancements in the features of the Strantról 900 System, which operates and adjusts feed rates of up to three

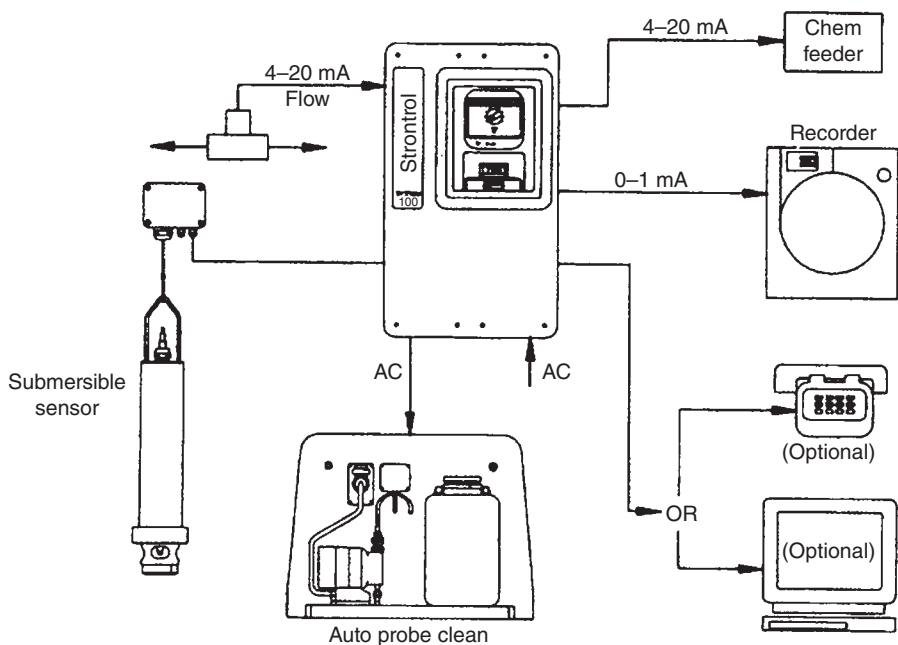


Figure 12.22. Automatic control of the chlor-dechlor systems (courtesy of Stranco Co.).

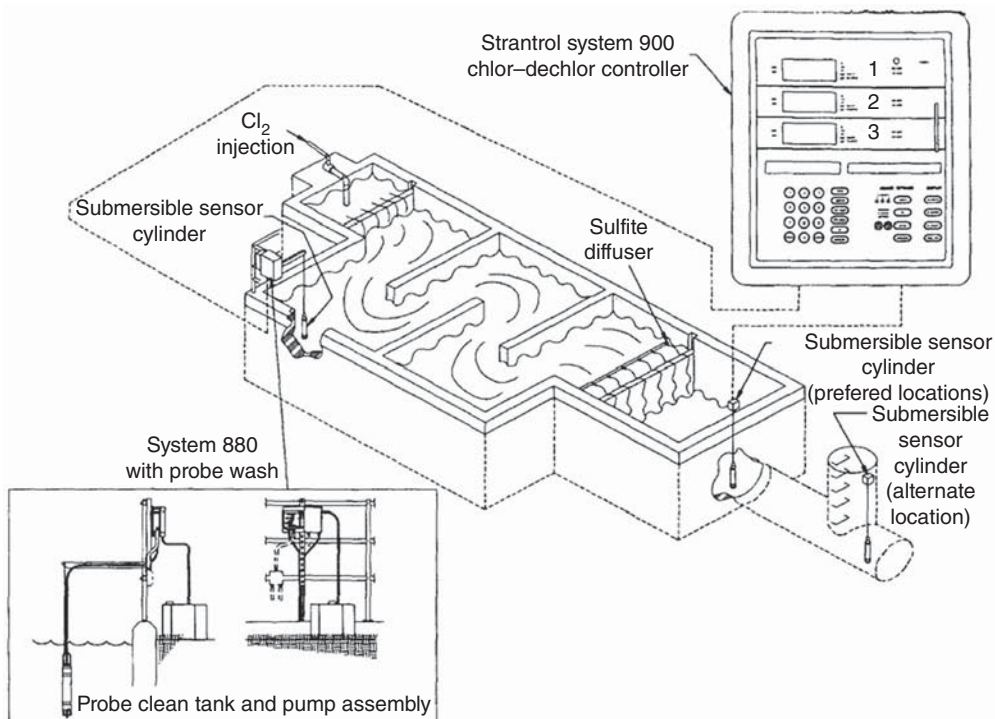


Figure 12.23. Typical contact chamber with Strontrol chlor-dechlor control.

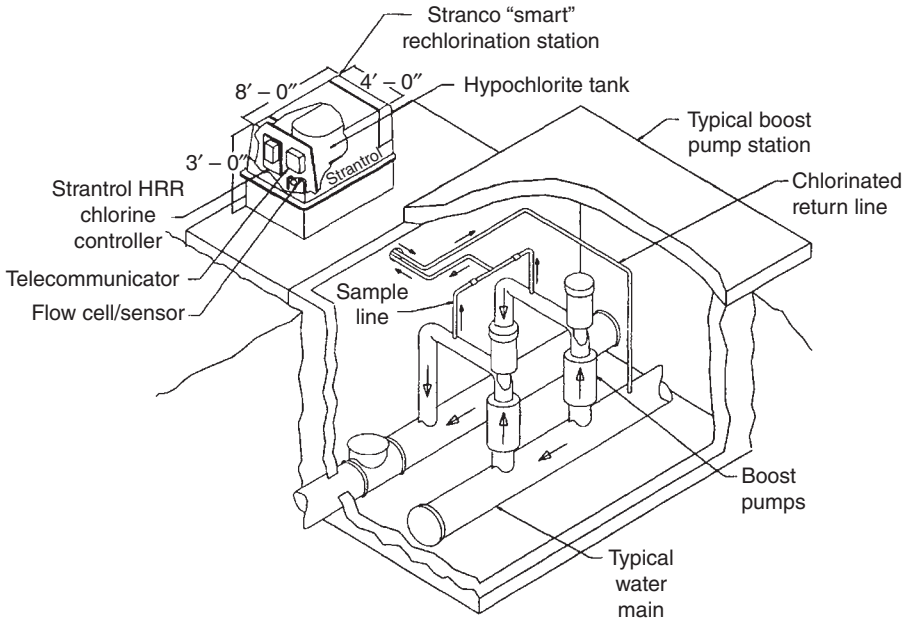


Figure 12.24. Compact, low-cost, Strantrol rechlorination station for water distribution systems.

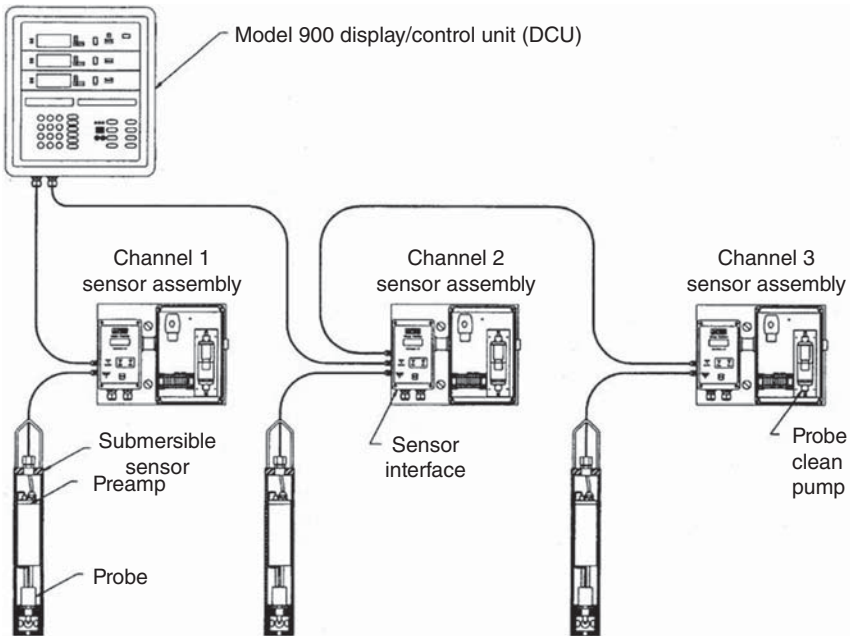


Figure 12.25. Strantrol 900 multiple control system (courtesy of Stranco Products).

processes by using the Sensor Interface, a sensor management unit that converts the probe signal to a usable signal and transmits it to the 900 System.

An important discovery made by Stranco to eliminate electrode measuring errors was to make the reference electrode out of 99.999% pure platinum and for the silver–silver chloride-measuring electrode to be immersed in a gel solution (Figs. 12.26 and 12.27). These improvements eliminated the hydrogen overvoltage phenomenon that had been causing sensing errors owing to the electrolysis of water (separation into H_2 and O_2) commonly encountered at potentials used for chlorinated waters. When these gases enter into redox reactions at the electrodes, they interfere with system operation.

The purpose of the measuring electrode is to act as a pool for the oxidizing species in the water. The potential difference between the oxidation-reduction species and the reference electrode produces the measured voltage. Theoretically, no current needs to flow for the potential to exist. This causes the classic ORP response. Any change of output that occurs as a result of influences other than the oxidant causes errors. Therefore, the redox system must have high-purity electrodes and must remain stable in the presence of potentially interfering ionic species.

The Stranco HRR system electrodes can operate under highly oxidative conditions, such as those in high chlorine residual (15–20mg/l) environments without becoming “poisoned.” The Stranco technology is also distinguished by its ability to remain stable in the presence of potentially interfering ionic species and to repeatedly detect differences as small as 0.1 mg/l.

Many substances in treated wastewater can affect the electrochemical response of pure platinum electrodes. The electrodes can be treated to resist such substances although the treatment affects their stability and sensitivity. The electrode surfaces can be restored by an automated cleaning system using a small timer-actuated pump that periodically rinses the electrode with hydrochloric acid.

The liquid junction (salt bridge) is the pathway for ionic species to travel to and from the reference electrode. Some passage of ions is required to transfer current, which allows a reading to be taken, whereas other ions pass simply to satisfy concentration gradients. As with an artery, the effects of contamination or blockage are disastrous. If the current cannot pass, the system simply will not function. If some ionic species can pass, but others cannot, the result is charge separation, which causes a potential to develop across the liquid junction, resulting in instability. In HRR instruments, the junction is constructed from porous Teflon with large pores to facilitate free ionic movement. Teflon is an inert, chemically resistant material, slippery enough to prevent many contaminants from adhering to it.

The electrolyte in the reference electrode conducts current and enters into ionic changes with the reference element and the process. Owing to the large liquid junction pores in an HRR reference cell, the risk of losing electrolyte is high; therefore, the solution is thickened with a special gelling agent that is impervious to oxidation by chlorine or bromine.

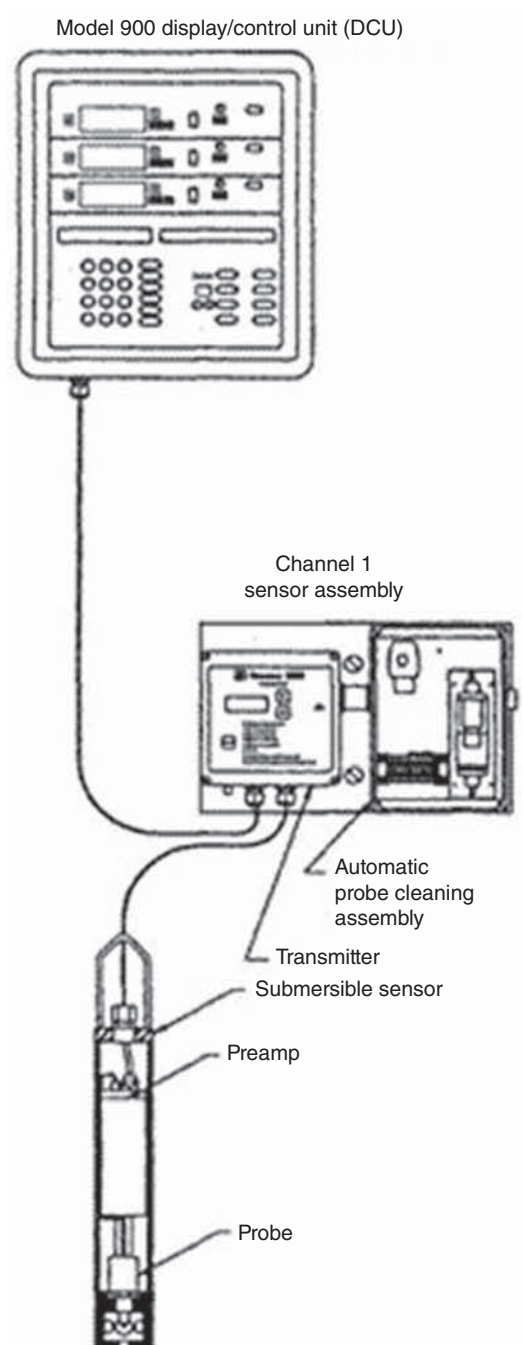


Figure 12.26. Strantrol silver chloride measuring electrode immersed in gel solution (courtesy of Stranco Products).

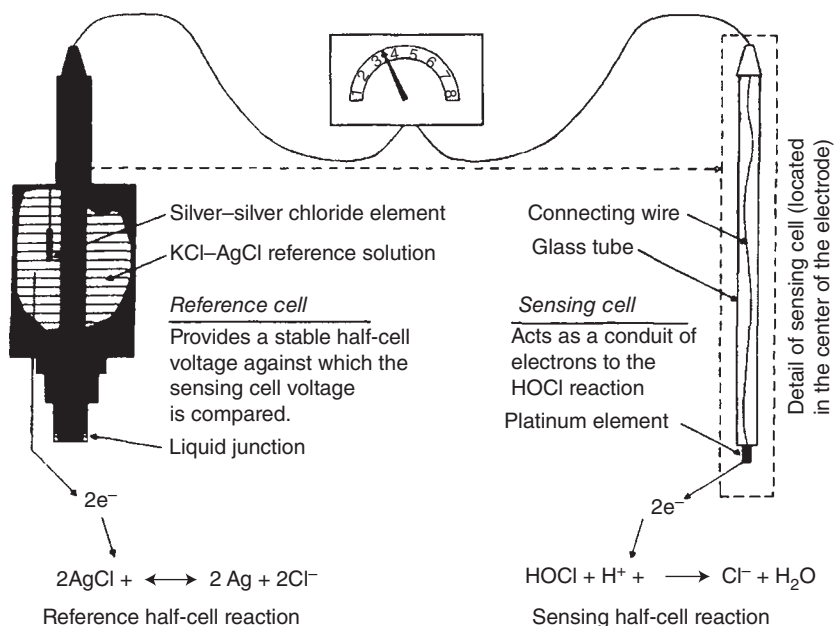


Figure 12.27. ORP reactions at the referencing and sensing cells (courtesy of Stranco Products).

Another vital component of the HRR system is its high-impedance electronics/electrode interface that allows practically no current to be drawn through the electrode. Current draw causes a rush of chemical changes within the reference cell, resulting in polarization, and too much current will cause reduction of some ionic species in the water, masking the measurement of the chlorine residual.

Every wastewater effluent will have a different chemical equilibrium or ORP “poise.” In untreated water, the ORP poise changes as the concentrations of various electroactive contaminants change, ultimately reaching equilibrium. If this reading happens to be 200 mV, the ORP contributed by the chlorine will be added to this value. Stranco has found that, although poise varies from water to water, it affects mainly the zero point of the ORP-mg/l Cl_2 curve and not the span. Therefore, Stranco does a single-point calibration (zero shift). The poise is usually determined after the system has been in operation for at least 24 h under normal operating conditions. When equilibration has occurred, the system is standardized by one of the titrimetric chlorine residual procedures. ORP measurements are much simpler to obtain, and it is hoped that the ORP cell will be easier to maintain than either the membrane or amperometric cells. There is a marked difference in the ORP mV curves between the residuals of free chlorine and of chloramine, typically about 750 mV for free chlorine at 1.0 mg/l versus 550 mV for chloramine at 1.0 mg/l.

Figure 12.3a illustrates the logarithmic relationship between the ORP and concentration of chlorine residual. Starting a system that covers a 1.0-mg/l range requires only a single-point calibration, which involves shifting the entire graph either to the right or the left, depending on the ORP poise of the water. For example, the theoretical ORP at a 0.5 mg/l residual is approximately 710 mV, which assumes that zero residual is 350 mV. Typically, however, when a system is started up, there is rarely an opportunity to observe a zero residual in the sample line, and a residual test has to be made. If the measured residual is 0.5 mg/l, the unit is shifted to read 710 mV and 0.5 mg/l. Once the single calibration point is set correctly, the progression of the ORP readings will match the progression of the residuals. As an example, if 0.5 mg/l shows 710 mV, then at 750 mV, it should be 1.0 mg/l. But if the poise at start-up is such that 0.5 mg/l occurs at 600 mV ORP, then, at 640 mV, the chlorine residual should be reading 1.0 mg/l.

Field Comparison of Analyzers

An analyzer that works for one wastewater may not necessarily be best suited for another. Rapid advances in technology have also made available a large variety of analyzers. It is therefore beneficial for each treatment facility to conduct field tests with loaner analyzers to find the one that is best for it. The testing will also give operators the opportunity to become familiar with the calibration and maintenance procedures of the various models before investing in the programming needed for system automation.

In a recent study, some of the analyzers listed in Table 12.1 were subjected to a performance evaluation under field conditions.¹⁵ The analyzers evaluated using a common sample from a wastewater treatment plant's chlorine contact basin included Capital Controls' Aztec CL000, Wallace & Tiernan's Micro/2000, Analytical Technology, Inc.'s (ATI) A 15/79, GLI International's Accutronic, and Hach's CL17.

The test sample was spiked with additional chlorine, and the responses from the five analyzers were recorded. Figure 12.28 shows the outputs from four of the analyzers. The Capital Controls and Wallace & Tiernan instruments responded almost immediately to the spike in chlorine concentration. The ATI instrument's response was delayed by approximately 1 min, in part because of its long sample piping, which delayed the sample reaching the analyzer, and because the sample had to be pumped from the inlet to the air stripping/chemistry chamber. The response curve for the Hach analyzer illustrated the batch nature of the analyses performed by it. The response time of the Hach instrument can be shortened by increasing the doses of reagent for the colorimetric test.

The maintenance requirements of the analyzers evaluated in this study included calibration, adjustment of sample flow, replenishment of reagent, routine cleaning, nonroutine cleaning and adjustments, and acknowledgment of instrument alarms. The most service-intensive instrument was found to be

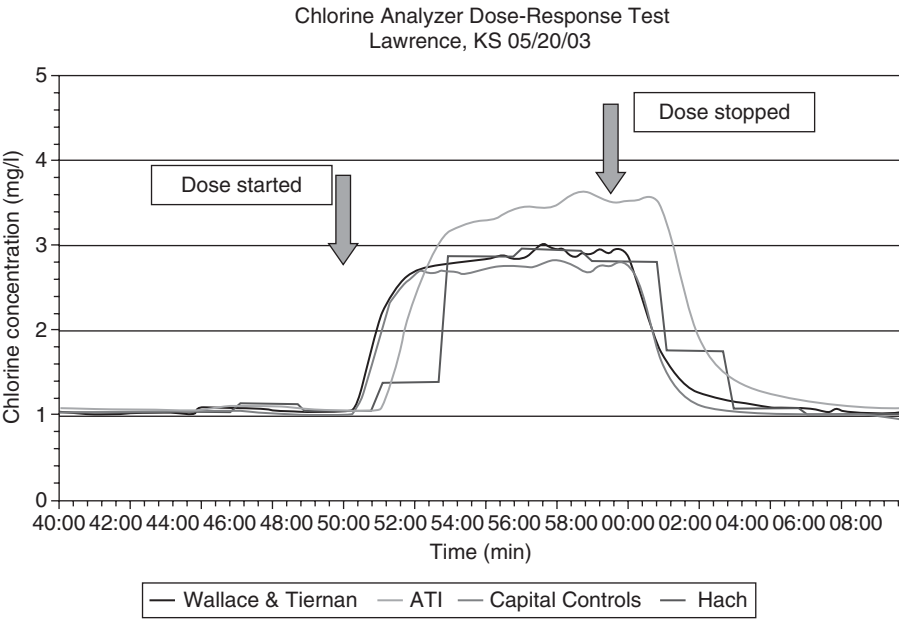


Figure 12.28. Comparison of analyzer responses to a spike in chlorine concentration.

TABLE 12.2. Maintenance Requirements for Chlorine Analyzers under Test Conditions

Analyzer	Number of Maintenance Functions Performed	Average Time per Visit (min)	Total Time Spent ^a (min)
ATI	30	7	197
Capital Controls	50	4	206
GLI International	25	16	399
Hach	20	8	156
Wallace & Tiernan	30	3	78

^aDuring the 75-day field trial.

the GLI International AccuChlor2, which included small PVC pellets in the electrode chamber for cleaning of the electrodes. Difficulties encountered with the GLI International were caused by breakage of some of the pellets, and the need for frequent manual scouring of the copper electrode. The instrument was also difficult to calibrate during the study.

The maintenance requirements of each instrument during the 75-day evaluation period are summarized in Table 12.2. In addition, the initial set-up time for both the Hach and GLI International instruments was 36 min. (The remaining units did not require significant set-up time). The maintenance analysis described above applied solely to the trial site. The maintenance requirements

are expected to vary from site to site, depending on the plant effluent characteristics and other site-specific conditions.

The performance of each analyzer was inferred from the reliability of the response generated by the instrument during the evaluation period. A response was generated by each instrument every second and averaged at 15-min intervals during the 75-day evaluation. The 15-min averages were used to evaluate the reliability of the analyzers. Reliability was defined as the percentage of accurate readings out of the total number of readings for each instrument using two criteria to determine whether a data point was inaccurate: (a) When a 15-min average was within ± 0.005 mg/l of the preceding average and did not change for $2\frac{1}{2}$ h, it was assumed that the instrument was not generating new data, and the reading was counted as a bad reading; and (2) when the instrument indicated a zero value when chlorine was present in a sample. The reliability of each instrument was calculated as follows:

$$\text{reliability (\%)} = 1 - \frac{\text{number of bad data readings}}{\text{number of available data readings}} \times 100. \quad (12.9)$$

Based on this definition, the reliability of the online chlorine analyzers evaluated in this study was determined to be as follows: Wallace & Tiernan (100%) > Capital Control (99.7%) > ATI (97.4%) > Hach (93.2%) > GLI International (36.2%). The lower reliability of the Hach instrument was an experimental artifact caused by reagent consumption. The GLI International instrument appeared to be unsuitable for use in wastewater.

In summary, all online chlorine analyzers require maintenance and calibration. A program must be devised to collect grab samples and check for drift in the instrument readings. Instruments with autocalibration require less maintenance. Key features to be evaluated when selecting analyzers based on site-specific conditions are summarized in Table 12.3.

How to Select an Online Analyzer

Selecting an online analyzer should be more involved than picking a supplier and an analyzer model number. The first question is, "Am I willing to dedicate the time for calibration and maintenance to keep the unit running?" If your facility and staff have no experience with online instrumentation, time and effort must be spent in investigating a suitable analyzer and the training required to maintain it. You cannot believe the sales hype of the local representative. The evaluation described above lists a number of issues that must be addressed for care and upkeep of an online instrument, requiring a larger investment in time than one would expect. Although the online instrument may reduce process control time, it will create the need for an instrumentation specialist whose time must be dedicated, first, to keeping the instrument running and, second, to the maintenance of the electrical and mechanical components that support that instrument and process automation.

TABLE 12.3. Key Features of Online Analyzers for Disinfection Monitoring and Control

Feature	Description
Species measurement	Ability to measure the desired species of chlorine residual without interference from other species in the sample
Accuracy	Agreement between the amount of component measured by the analytical method and the actual amount; usually expressed as percentage of the full scale over a specified range
Precision	Reproducibility of measurement when repeated on a homogeneous sample under controlled conditions; usually expressed as percentage of the full scale over a specified range
Sensitivity	Smallest concentration of a chlorine species detected in a sample
Range	The measurable range of concentrations of a chlorine species
Response time	Time to provide a percentage response to a step change in residual concentration after the sample has entered the analyzer
Temperature compensation	Thermistors to compensate for temperature variations

It is not recommended to jump into automation if you have not already decided to fully support it. Rent or obtain an instrument on loan for at least 60 days. During that time, get the local manufacturer’s representative to set up and get the unit fully functional and have them get the bugs work out for you. Then, with one of your staff, assigned to the project, set up a schedule, and record the time it takes to service the instrument daily. Break down the service functions, so you can analyze where your staff will spend most of their effort. Some items to include in your time assessment include:

- changing out reagents,
- instrument calibration—time to calibrate and time between calibrations,
- replacing/cleaning filters
- replacing/changing tuning in sample/reagent pumps,
- dose response tests,
- sample loop maintenance—cleaning/replacing, unplugging, disinfection of tubing; control algae growth; cleaning/replacing in-line filters,
- servicing the sample loop pump, and
- responding to instrument errors/failures/service alarms.

If possible, test more than one unit at a time. Side-by-side comparisons help to define the desirable features and those to be avoided. Summarize the field data, and take a critical look at the time dedicated to keeping the instrument online to determine whether or not you are willing and able to dedicate the staff time to keep the instrument running. The testing also enables you to compare laboratory data with the field instrument to detect any incompatibilities between your wastewater's chemistry and the instrument's analytical method.

Online instrumentation becomes the heart of any automation scheme. If the instrument does not work, is too expensive to keep on line, is always broken and needs factory service, or fails to produce good data for control, it becomes a liability and may wind up being abandoned in place. Deciding whether to invest the time before investing in the programming to develop a complete control system is a better way of spending your money and proceeding with the project. This approach will require more time before implementing the project, but it does increase the potential for success.

Allow at least 60 days for the trial, as this gives your staff plenty of time to get accustomed to the new equipment and to develop the daily care and upkeep into a routine. Experience indicates that the time investment during the first 2 weeks of the field trial is usually greater than the time investment during the last 2 weeks. Familiarity with the equipment also increases operator comfort.

Ultimately, a decision will be made as to whether the project moves forward or is scrapped. Based on the result of the field test, a competitive bid may be developed, or it may be decided to buy an analyzer sole source. Each state has different rules and requirements for bidding, so carefully review these criteria to determine how to get the equipment that was tested.

One of the more time-consuming activities for operators is instrument calibration. Some instruments include an autocalibration function, which may save a significant amount of servicing time as well as increase the confidence in the data collected. While it sounds ideal, it is another level of programming in the PLC and mechanical complexity in the instrument that should be reviewed during the 60-day on-site field test. If it is not field-tested, a telephone survey of operating installations or a questionnaire review should be conducted to collect information on the time required to service the instrument and its reliability from actual operating installations.

ONLINE PROCESS CONTROL OVERVIEW

Adoption of online process control configurations can significantly improve the performance of chlorination and dechlorination systems. A control system uses measured input variables that then are used, through control logic, to manipulate output or response variables. The controller unit receives the desired information from measurements and takes control actions to adjust

the values of the manipulated variables. Process control is achieved through feedback, inferential, or feed-forward signaling that ensures system stability by responding dynamically to changes in inputs or outputs (Table 12.4).

An effective controller uses information from measurements to produce stable responses around desired set points. Figure 12.29 illustrates how a good feed-forward controller manipulates the increase in an input variable, such as flow, at time t_0 to produce a stable system response, while ineffective or no process control results in an unstable system. Figure 12.29a shows how chlorine dose, the controlled variable, responds by increasing from an initial stable value of x_1 to a higher stable value of x_2 over a short time interval. When appropriate process control is not implemented, the system becomes unstable, and the response fails to stabilize at the increased flow, as illustrated by response curves A, B, and C in Figure 12.29b.

The concept of feedback control is illustrated in Figure 12.30. A unit process receives input i and delivers response r . The response is read by a measuring

TABLE 12.4. Types of Process Control Configurations

Type	Description
Feedback control	Uses direct measurements of response variables to adjust values of manipulated variables in order to maintain the former at desired set points; reacts in a compensatory manner
Inferential control	Uses indirect or secondary measurements of response variables to adjust manipulated variables in order to maintain the former at desired set points
Feed-forward control	Uses direct measurements of input variables to adjust manipulated variables in order to maintain the values of response variables at desired set points; Reacts in an anticipatory manner

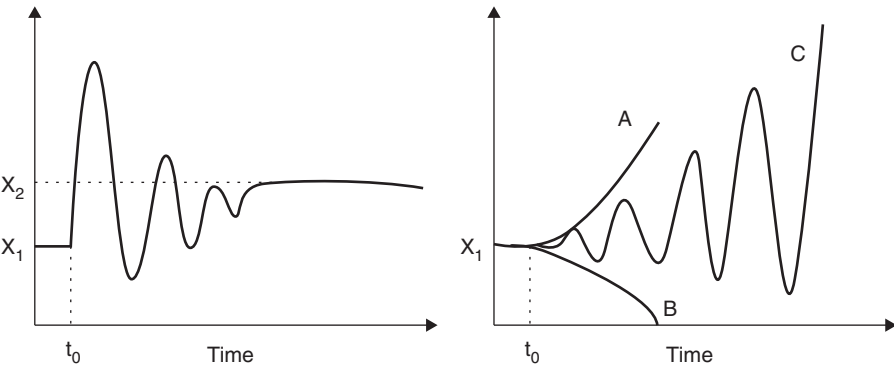


Figure 12.29. Stable and unstable systems.¹⁶

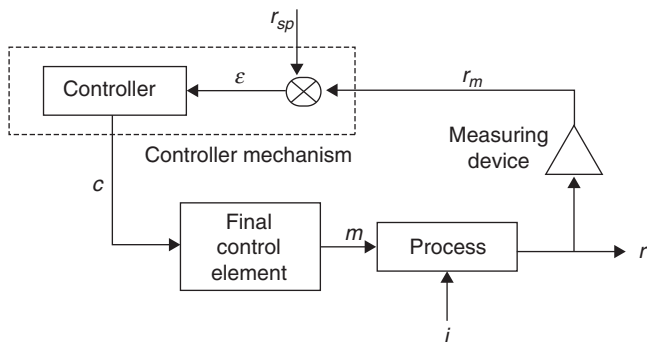


Figure 12.30. Concept of online feedback control systems.

device as r_m and is reported to the logic unit of a controller. The controller compares r_m with the set point response r_{SP} and calculates the deviation ε . This deviation is reported to the controller, which relays a signal c to the final control element. The final control element adjusts the value of the manipulated variable m to reduce the magnitude of the deviation ε .

There are three types of feedback controllers that are commonly used in control systems: (a) proportional; (b) proportional-integral, and (c) PID systems. In a proportional controller, the relay signal c is proportional to the deviation ε . A proportional-integral controller causes the relay signal to change as long as a deviation is observed, while the PID controller is able to anticipate the error in the immediate future and applies an appropriate corrective relay signal that is proportional to the observed rate of change in the deviation ε . Since feedback controllers react only after a deviation between the actual response and set point response has been detected, these instruments are unable to achieve perfect control of the chemical process.

An inferential controller is similar to the feedback instrument, with the exception that it measures the response variable indirectly (Fig. 12.31). These secondary response variables (r') are selected because they are good surrogates or simple functions of the controlled response variable (r) and can be measured relatively easily. The controller logic unit includes an estimator, which uses the values of the measured secondary response (r'_m) to mathematically compute the values of the unmeasured primary response (r_{EST}). The calculated deviation between r_{EST} and r_{SP} values is utilized by the controller to adjust the manipulated variables.

A feed-forward control configuration directly measures the input variable and reacts to minimize the expected deviation between the actual response and set point response before it has occurred. In theory, these control units can achieve perfect control of a chemical process if the response of the system is fully understood and can be defined mathematically.

The concept of feed-forward control is illustrated in Figure 12.32. A unit process measures the input i directly and anticipates its impact on the response

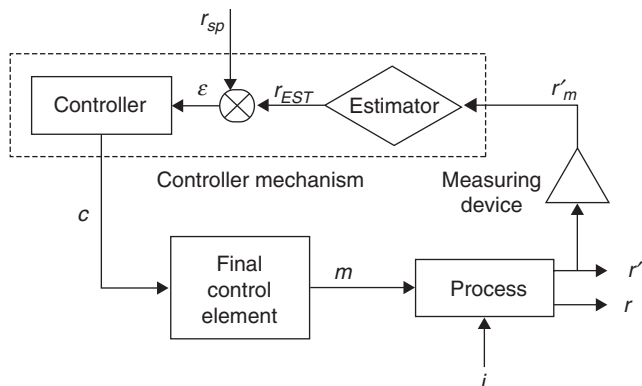


Figure 12.31. Concept of online inferential feedback control systems.

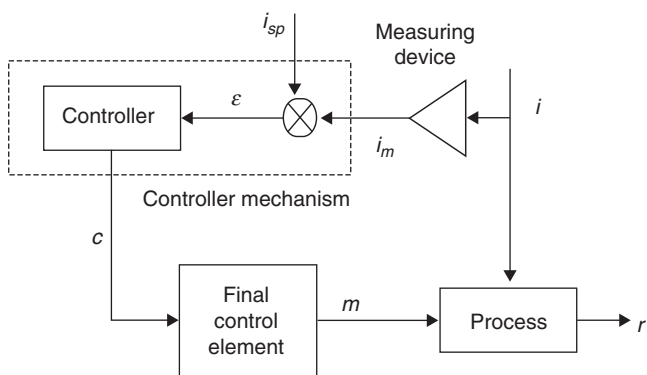


Figure 12.32. Concept of online feed-forward control systems.

variable r . The input is read by a measuring device as i_m and reported to the logic unit of a controller. The controller compares i_m with the set point input i_{sp} that would give the desired response. The controller calculates the deviation ε and relays a signal c to the final control element. The final control element changes the manipulated variable m to adjust process chemistry such that it yields the desired response r . Thus, the feed-forward controller reacts immediately upon detecting a deviation in the input.

In practical terms, feedback control is a quality-control approach while feed-forward control is a predictive approach. Feedback control adds chemical, and the result of that chemical addition is measured and compared with a desired set point. If the right amount of chemical has been added, no change will be made to chemical addition. However, in the case of chlorination, if the residual chlorine concentration is too high, the rate of chemical addition will be reduced. So feedback control always grades and rates its actions to determine what must be carried out next.

Feed-forward control anticipates an outcome based on some measured indicator. Flow pacing is a type of feed-forward control and is a powerful control method for chlorination. In flow pacing, it is assumed that the dose of chlorine necessary to meet disinfection criteria stays the same, and the chemical addition rate is changed as the flow varies to maintain the same chemical dose at all times. With this approach, the diurnal flow variations can be managed with a control system that only requires flow measurement.

Feed-forward control assumes that the chlorine demand never changes. If the chlorine dose requirement does change, the feed-forward control system never checks to see if the targeted goal is ever met. Even if the feed-forward system measures a parameter, it is an add-and-forget control method. The quality-control function of how well the chemical addition worked is left up to the operator to determine.

The combination of feedback and feed-forward control produces a very responsive compound control loop. The feed-forward function allows the control system to rapidly respond to process changes. The feedback control function checks to see how well the feed-forward system anticipated the correct chemical dose. If it is not correct, the feedback system makes a modification to the chemical dose. The two systems work together to rapidly bring the system under control to meet the set point.

Technological advances in PLC software features including fuzzy logic are recently available and will become more widely improved in the future.

The fuzzy logic approach provides a method to establish and maintain control of complex time-varying or nonlinear processes by monitoring sets of associated variables, and determine the required output based on characteristic response rules.

The usual variables for chlorination or dechlorination include flow pacing, water chemistry, temperature, demand curve, permit limitations, and analytical measurements such as ORP. Characteristic control rules and associated logic derived from these operational parameters are programmed into a fuzzy controller function to create a predictive control component. The associated output from a fuzzy logic control function coupled with conventional proportional and flow-pacing techniques offers significant promise for the future improvements of chlorination control. For example, the Wallace & Tiernan MFC analyzer/controller contains an option to use fuzzy logic to correct its control actions.

CHLORINATION PROCESS CONTROL

A chlorination system controls the addition of the disinfectant to water or wastewater flowing through a contact chamber to provide the appropriate environmental conditions to deactivate sufficient numbers of regulated organisms. It should be noted that the chlorination system controls the concentration of organisms indirectly or inferentially by manipulating the water

chemistry to achieve desired residual chlorine concentration in the treated water.

Chlorination systems can be controlled manually or through a variety of automation systems. Automated approaches to control chlorination systems include flow pacing, feed-forward systems, and feedback systems. However, selection of the best control configuration for a facility requires understanding of the site-specific chlorination chemistry, regulatory requirements, and available control strategies. Effective control of the chlorination process can help the WWTP meet the regulatory requirements for target organisms, reduce chemical costs by minimizing chlorine use and the need for dechlorination, and reduce formation of DBPs such as THMs.

Chlorine contact tanks are designed as plug flow reactors to avoid short-circuiting and to exploit the kinetics of chlorine chemistry. The plug flow configuration creates a time lag between the point of chlorine injection and the point when the residual disinfectant is measured. Thus, whether the set point response has been met is not known until the water has passed through the tank and past the sampling location. For example, if the hydraulic retention time of the plug flow reactors is 30 min, the online analyzer should remove a sample from the reactor effluent 30 min after the chlorine dose has been adjusted. Since the online analyzer takes about 5 min to measure chlorine, it will take 35 min before the control system detects the actual response of the adjusted chlorine dose on the residual chlorine concentration. Therefore, it is critical that an appropriate time lag is incorporated in the controller logic to prevent serious overdosing or underdosing of chlorine.

Water plants typically use flow pacing, as the changing flow rate is usually the only variable. Chlorine demand does change but usually according to plan such as when a new or different water supply is brought online or there are changes in the influent blend of water that can change the demand. While the feed-forward method will respond to changes in the plant flow, it makes it necessary for the operator to change the reference or set point chlorine dose for other process changes.

Reuse applications may have an extended retention time, depending on the design chlorine residual $\times$ contact time (CT) criteria or retention time specified by state code. A 90-min contact time is needed in some states, while a 90-min modal contact time is required in others. The modal contact time accounts for short-circuiting, and a 90-min modal contact time may require up to a 180 min theoretical retention time. The time lag in these reuse applications poses unique process control challenges for feedback control.

Manual Control

When a chlorination system is controlled manually, the operator sets the feed rate on the chlorine feed system (Fig. 12.33). This feed rate remains constant until the operator decides to change it. With this method, the operator must

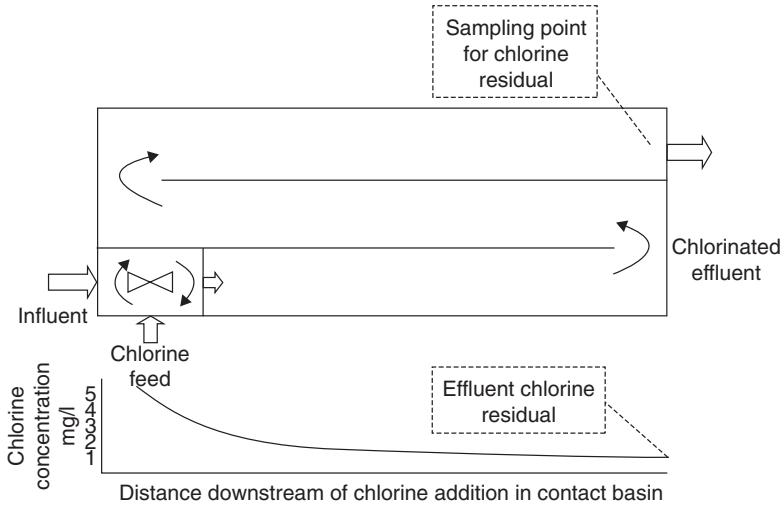


Figure 12.33. Schematic illustrating manual control of chlorination system.¹⁷

sample the chlorine contact chamber effluent for both residual chlorine and the target organism concentration to determine compliance.

Figure 12.33 shows a classic feedback control system. The operator measures the effluent chlorine concentration and makes a decision on what to do. The operator will examine the chlorine demand curve to determine if the demand changes or if he or she only has to adjust the feed rate to respond to a change in flow rate. The requirement for the operator to make all of the decisions makes it a manual control system.

Since the diurnal flow variations are well known, the only drawback associated with the manual control method is its operating cost. As the wastewater influent flow varies throughout the day, the operator is faced with two basic choices: (a) to leave the chlorine feed rate unchanged to use too much or not enough chlorine, or (b) to change the feed rate to match the flow (or at least reduce the high afternoon feed rate for late-night operation) and increase the workload. These choices lead to a number of other factors to be considered; for example, if the operator elects to leave the chlorine feed rate constant throughout the day, not only is more chlorine being added than is necessary, but also the dechlorination system must use more chemical, which further increases the operating cost. There is one other dilemma: The operator must also ensure that the effluent remains in compliance at all times. At a minimum, the operator is gambling with saving a few hundred dollars a day in chemical costs versus a fine of \$20,000–25,000 per day for permit violations. So the default approach is to always ensure that sufficient chlorine has been added to avoid noncompliance.

In order to lower operating costs, it is necessary either to add less chemical or hope that the POTW stays in compliance, or to pay very close attention to

the operation and to adjust the chlorine feed rate periodically throughout the day. Once the correct chlorine dose has been determined, it is a simple matter to develop a delivery chart of chlorine feed rate versus plant flow to enable operators to quickly determine the manually set chlorine feed rate to dispense the correct dose of chlorine for the wastewater being treated. The only question is how many times a day the operator needs to adjust the chlorine delivery rate. More frequent changes in the chemical feed rate equal tighter process control and lower operating costs. The drawback of this approach is the amount of time the operator has to spend controlling the process. The current trend in staffing for both water and wastewater treatment facilities is reducing staff, so assuming that an operator has time to continuously monitor and control chlorine addition is unrealistic.

To make manual control work, the operator must collect and analyze samples of chlorine contact chamber effluent to determine whether the proper chlorine residual is being maintained for adequate disinfection. Additional analyses for the effluent microbial concentrations are usually conducted in the laboratory and take 24 h or longer.

This method of control sounds cumbersome but it has been used as the standard for chlorination systems since Environmental Protection Agency established permit limits for bacteria, and it works even though it is not the most chemical efficient or labor efficient, and has minimal maintenance needs. However, it has the potential to waste chemicals in both chlorination and dechlorination.

Manual control can also be accomplished with online instrumentation. Using an online chlorine residual analyzer to monitor the chlorine contact chamber effluent simplifies the operator's job in controlling the chlorine feed-rate setting (Fig. 12.34). If the chlorine feed valve or pump can be operated

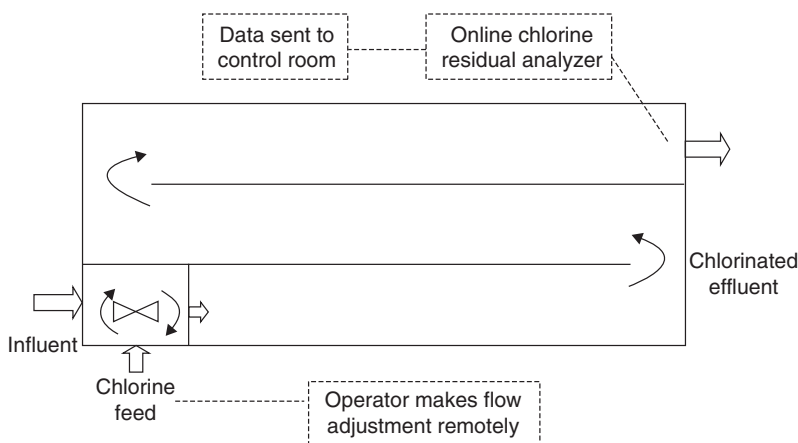


Figure 12.34. Schematic illustrating manual control of chlorination with online monitoring.¹⁷

remotely, the operator can monitor and control the feed rate from the plant control room. The operator would adjust it based on readings of the plant flow rate and the chlorine residual concentrations on the local display. This approach takes only a couple of minutes and can be carried out hourly. It has the potential to closely control chemical use and to keep a close watch on the chlorine residual to achieve good disinfection and comply with any regulatory requirement for maintaining a residual chlorine concentration in the effluent.

While online monitoring significantly improves control of the disinfection process, it adds a new variable to the maintenance equation: The online chlorine residual analyzer will need routine maintenance and frequent calibration, which will entail additional training for selected staff to ensure that the analyzer is maintained properly to produce accurate, reliable readings.

The chief advantage of this control method is that the operator, without leaving the control room, can closely monitor the effluent chlorine residual and adjust the chlorine feed rate and thus minimize chemical costs. The disadvantage is the cost of the online chlorine residual analyzer and its maintenance. Remote operation of the chemical feed system increases mechanical/electrical complexity of the control system but it is more familiar to operating staff, as the mechanical/electrical principles of the system are commonly used with other control systems at the plant.

Flow Pacing

Chlorine dosing must be accurate and keep pace with the amount of water being processed. Too little chemical can make the process inefficient; overdosing adds to operating cost and raises the chlorine concentration in the processed water and can promote THM formation. Flow pacing or flow-proportioning control allows addition of chlorine in direct proportion to the measured flow rate. It works well in situations where the flow rate varies but the chlorine demand of the water remains relatively constant. Chlorine feed for both pre and post chlorination should be flow proportional. The prechlorinator should be controlled from the influent flowmeter and the postchlorinator from an effluent flowmeter.

Flow pacing is a form of feed-forward control that can be used alone or with a feedback control system (Figs. 12.35 and 12.36). It involves the use of a flow rate-monitoring device just ahead of or just after the chlorine contact chamber, and remote control of the chemical feed system by a flow control valve or a variable delivery metering pump. With flow-paced control, the operator can enter the chlorine dose to be maintained under all flow conditions. As flow rate changes, the control system will adjust the rate of chlorine feed to maintain this dose. Flow pacing merely increases the total control signal (metering pump or feed system output) in response to changes in the flow rate. For example, if the flow increases by 20%, flow pacing adjusts the manipulated variable by 20% to keep the chlorine dose constant.

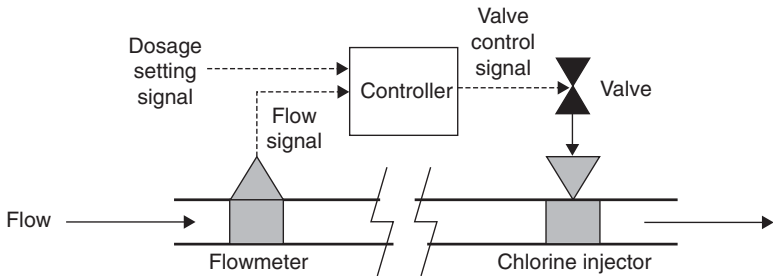


Figure 12.35. Online chlorine control using flow pacing.

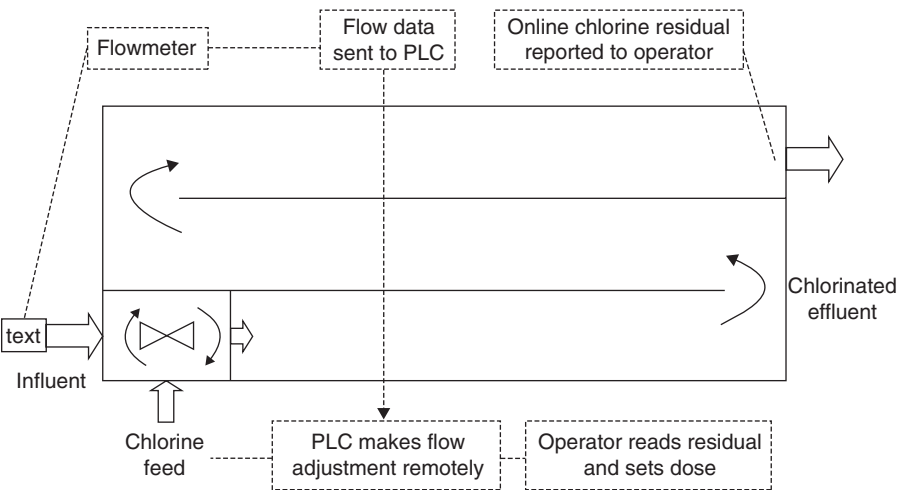


Figure 12.36. Schematic illustrating flow-pacing process control of chlorination.¹⁷ PLC, programmable logic controller.

The advantage of a flow-paced control system is that the chemical delivery rate is automatically adjusted by the control system. However, the operator must monitor the residual chlorine concentration in the contact tank effluent to determine whether altering the dose is warranted. The disadvantage is that the operator has to manually monitor the residual chlorine and effluent bacteria count by periodically checking the chlorine decay curve to ensure proper chlorination. Adding an online monitor to the system simplifies the operator's job. If the chlorine concentration in the chlorine contact chamber effluent is monitored and transmitted to the control room, the operator can determine whether the current dose set point is correct, which reduces the operator's labor by adjusting the chemical feed rate in response to flow changes and eliminating the need for collecting samples and analyzing them in the field.

The residual chlorine concentration can be trended over time, and, if needed, a control algorithm can be developed to change the selected dose. Most of these adjustments can be made from the control room.

The online analyzer must be serviced to keep it in calibration, and a program must be devised to collect grab samples to check for drift in the instrument readings. Units with autocalibrating features would reduce the quality control aspects of the maintenance program. This is true for any online analyzer.

When a chlorinator is used with a flow-pacing system, the metering pump must be able to span the expected flow range of water. For example, if it is between 0 and 30 mgd, and the desired dosage is 16 lb of chlorine per million gallons, the maximum chlorine feed rate will be 480 lb/day, and a 500 lb/day metering pump should be used. If the turndown on the metering pump is only 10:1, and the delivery system must drop below 48 lb/day, an additional, smaller pump may be needed to deliver this flow accurately.

When the chlorine feed rate is paced by a flow signal, the chlorinator must be adjusted for zero and span. However, these adjustments can typically be made properly when there is a flow of chlorine through the machine. A chlorinator is not designed for zero flow conditions while the injector is in operation. Thus, the zero adjustment is contingent upon a mechanical linkage. As long as the injector is operating, and even though the chlorine-metering orifice is adjusted to read zero, some chlorine will be passing through the chlorinator.

An important aid to chlorinator adjustment and calibration is the use of signal simulators to simulate the input signals from flow and dosage measurement devices to the chlorinator over the entire range of the chlorinator.

Special adjustments are required for chlorinators whose feed rate is controlled solely from a variable vacuum signal. This mode is commonly used for straight residual control. The special adjusting procedure is usually outlined in the manufacturer's instruction manual and involves the zero adjustment of the chlorine inlet-reducing valve. The accuracy of this adjustment, as well as the overall accuracy of this method of control, is greatly improved by an external pressure-reducing valve installed in the supply system upstream from the chlorinator inlet. Without that additional valve, the chlorinator inlet pressure-reducing valve would be the primary instrument of control in a variable vacuum system.

Flow pacing is accomplished by an analog signal transmitted from the process flowmeter to the motor drive on the shaft that positions the chlorine-metering orifice. The chlorine orifice valve is designed and characterized so that the flow of chlorine varies directly as the process flow changes. Therefore, the signal transmitted by the process flowmeter must be linear with the process flow. The signal can be either electric (4–20 mA) or pneumatic (3–15 psi). In the Wallace & Tiernan chlorinators, the chlorine orifice valve is commonly referred to as the V-notch plug. Depending on local conditions, an optional item for flow-paced control is the use of a ratio relay, which is desirable when the primary meter is oversized for future conditions.

When flow pacing is being considered by itself, there is a trade-off between range and accuracy. A flow-paced chlorine dosage will be only as accurate as the transmitted flow signal, the accuracy of which depends on the primary metering element. Designers should specify the desired accuracy over a specified range (i.e., 3:1, 5:1, 10:1). Many makers of primary elements are reluctant to claim $\pm 2\%$ accuracy over a range that exceeds 4:1, which is a crucial factor in precise control of the chlorine dosage.

The Regal SmartValve (Series 7000) chlorinator manufactured by Regal Systems International, Inc., can be factory-configured to operate in flow control mode. A linearization program in the valve's controller unit compensates for differences in tolerance of plugs, rotameter, and other parts. A digital display indicates the flow rate, set point, and actual gas feed rates, low flow alarm, and the mode of operation (automatic or manual). A serial to analog converter can produce a 4–20 mA DC output equal to the gas feed rate. Moore Industries' 555 1/4 DIN Chlorination Controller can be set up to handle flow proportional control, and residual control, compound loop control with lag times, and dechlorination with sulfur dioxide.

Feedback Control

Feedback control using residual chlorine measurements allows adjustment of chlorine dose based on the residual chlorine in the contact chamber effluent detected using an online chlorine analyzer (Fig. 12.37). The controller compares the measured residual chlorine with the set point value and sends a compensatory signal to the chlorinator to adjust the dose. This control method is suitable when the flow rate of water is relatively constant, but the chlorine demand varies.

Some online instruments collect a batch of wastewater and analyze it for chlorine residual while others provide a more instantaneous reading. There is

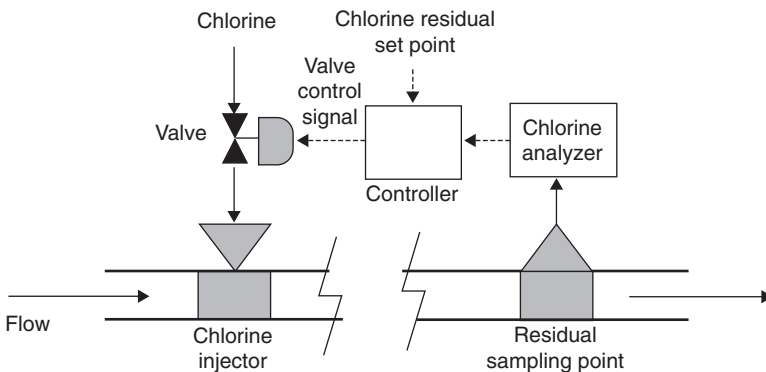


Figure 12.37. Online chlorine control using feedback control from direct residual measurements.

a lag time during the analysis before the concentration is determined. The reading from a given batch is displayed until the next batch of wastewater is analyzed. If the analyzer is placed at the basin effluent, there is also a lag time between chlorine addition at the inlet of the contact basin and the response reading by the analyzer located at the effluent end of the basin. The control loop must wait until the wastewater has passed through the system and the residual chlorine concentration has been measured by the online instrument. The control system must be able to compare the residual chlorine concentration with the set point value and then decide how much to change the target chlorine dose. It must then wait until the wastewater that received the changed dose has had time to flow through the chlorine contact basin so that the analyzer will measure its chlorine residual. Then the PLC can determine whether the chlorine dose should be increased or decreased to meet the chlorine residual set point.

While feedback control is a standard control method for feeding numerous chemicals, it has drawbacks for chlorination. There are two variables that affect the effluent residual chlorine concentration: flow and water chemistry. Flow is more problematic in wastewater applications, as it changes throughout the day. The diurnal flow pattern in domestic wastewater is predictable because it usually changes little from one day to the next. Storms, however, can radically affect the total daily flow for several days. The control system must be able to ride out these events and keep the system under control. The sudden flow changes challenge feedback control systems especially when a minimum 30-min or variable lag time is involved.

The other complicating factor is the presence of other material in the water that the chlorine will react with, defined as the chlorine demand. The chlorine demand in both water and wastewater varies, as different waters contain different concentrations of total organic carbon and wastewaters will contain different concentrations of chemical oxygen demand after secondary treatment. The type of secondary treatment process can also affect the effluent residual chemical oxygen demand concentration. Typical chlorine demand curves are shown in Figure 12.38.

The variations in flow and chlorine demand complicate feedback control systems but do not make their use impossible. They only make it necessary to select a control set point that may be a bit higher than needed to ensure that the downstream chlorine residual is within the permit limits while remaining in compliance with any chlorine residual requirements. Simply put, feedback control alone may result in a higher chemical use because of the lag times inherent in a chlorination process, especially in wastewater applications. Wastewater reuse becomes even more problematic because of the longer retention times required by code or by permit.

Water treatment systems may be able to move the chlorine analyzer up closer to the point of application and shorten the retention time in the control loop. Coupled with a less variable flow regime, chlorination in water plants is a less complicated method of feedback control. Figure 12.39 shows

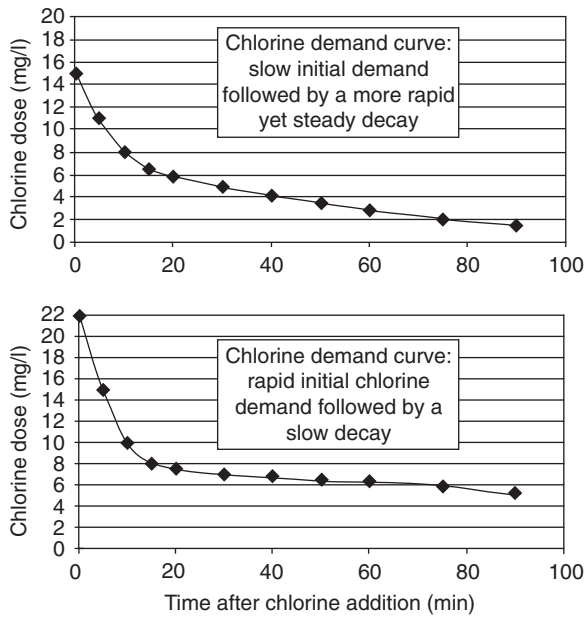


Figure 12.38. Chlorine demand curves illustrating varying demand rates.

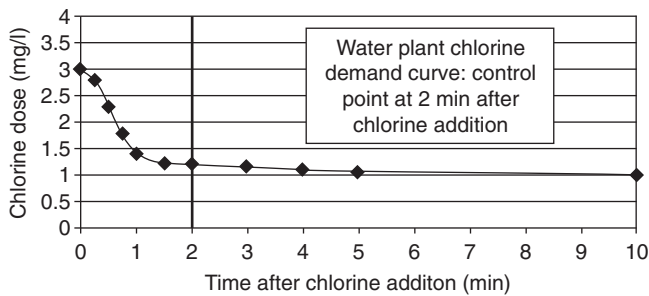


Figure 12.39. Chlorine demand curve for rapid demand uptake and slow decay.

a demand curve and the control point for a short retention time feedback control loop.

For the control method shown in Figure 12.39 to work well, the shape of the demand curve must be well defined. A demand curve can usually be divided into two sections: the initial demand and the long-term demand. The curve represents the multitude of reactions chlorine can have with organic compounds—some of them are very fast reactions; others are slow. The fast reactions reduce the chlorine residual rapidly and limit the concentration of chlorine available for the slower reactions. In this control method, the initial

rapid demand occurs, and a set point is selected after the rapid reaction demand is met. It is assumed that the slow demand section of the curve is predictable enough to control the process at the intermediate point and still produce an acceptable final residual chlorine concentration.

Compound Loop Control

The compound loop control method utilizes both feedback and feed-forward control to adjust chlorine addition. Figures 12.40 and 12.41 illustrate schematics of compound loop control devices for online chlorination. The position of the chlorinator valve is adjusted based on the chlorine residual detected by the analyzer and water flow measured by the metering device. The residual control signal adjusts the valve position signal generated in response to flow.

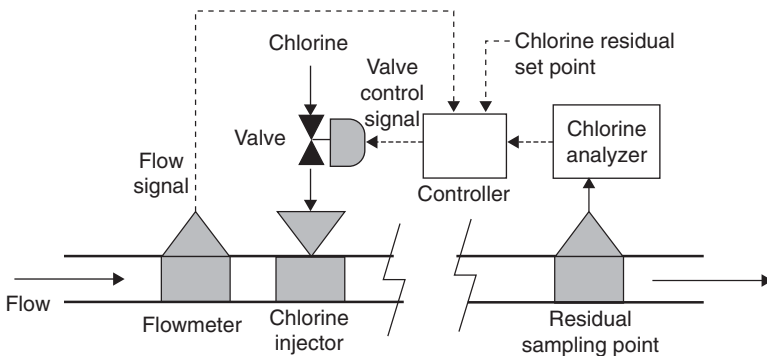


Figure 12.40. Compound loop chlorine control system.

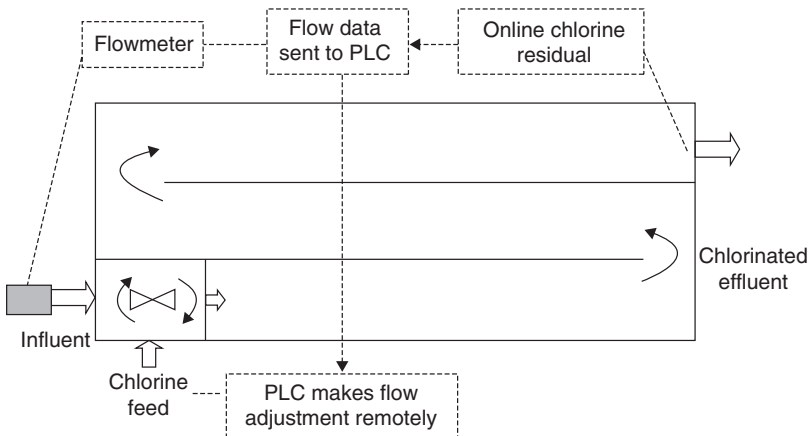


Figure 12.41. Schematic illustrating compound loop control of chlorination.¹⁷

This approach allows fast response to changes in flow and variations in chlorine demand.

There is a time lag between the point of residual chlorine analysis that occurs near the effluent of the contact tank, and the point of chlorination that is in the front of the contact chamber. The control loop must wait until the water has passed through the system and the residual chlorine concentration has been measured by the online instrument. If the flow rate changes during this time, the flow pacing control still adjusts the chlorine feed rate independently of the feedback control, so the chlorine dose remains constant. The controller compares the residual chlorine concentration with the set point value and determines the target chlorine dose. It then waits until the water that received the new dose flows through the contact tank and the residual chlorine in the effluent is detected by the downstream analyzer. The controller once again compares the residual chlorine concentration with the set point value and calculates a new target chlorine dose.

In flow-paced chlorinators, the controller changes the chlorine feed rate based on residual measurement, and the flow paced control loop uses the dose set by the controller to calculate the actual feed rate to be used. Since the flow through the contact tank can vary continuously, the controller should be able to calculate the exact time when the downstream analyzer should take a sample after adjustment of the chlorine dose. This approach is cumbersome and can lengthen the response time when the flow changes rapidly. To compensate for the slow response time, the change made in the target dose when the controller calls for an increase in chlorine dose must be large. This reduces the chances of the residual falling far below the set point. A special increase in chlorine dose can be programmed into the controller to make a large step change in chlorine feed rate in the event the chlorine residual concentration drops close to zero. For the system to be prevented from oscillating, the correction factors (step changes) to decrease the dose should be lower from the correction factors used to increase the dose. These correction factors can be made to be operator adjustable, which will enable the operator to change the response time of the control system without reprogramming by adjusting only the magnitude of the chlorine feed correction factor.

For example, under normal conditions, the system is set to increase the chlorine feed rate by 10 %, if needed. Assuming that the current chlorine dose is 5 mg/l and the set point chlorine residual is 1.0 mg/l, the measured chlorine residual is less than 1 mg/l the chlorine dose would be increased to 5.5 mg/l. If the residual chlorine concentration ever drops to near zero, the PLC can make an emergency correction to the chlorine dose by increasing the chlorine dose by 2 mg/l, so the chlorine dose for flow-paced feeding would increase from 5 to 7 mg/l, which should be adequate to restore the effluent residual chlorine concentration to the desired level. The 10% increase in the chlorine feed concentration and the 2 mg/l increase in the chlorine dose would be operator adjustable, based on system performance as a form of system tuning. If the

dose corrections are too large, they can be reduced or adjusted to fit current conditions.

Conversely, if the chlorine dose needs to be reduced, a similar approach would be used. For the system to be kept from an oscillating sequence, the correction factors to decrease the dose should be different from the correction factors to increase the dose. For example, if the correction factor to increase the dose is 10%, the factor to decrease the dose should not be 10%. If a signal is received, indicating that too much chlorine was added and the dose is reduced by the same factor, the dose would return to the condition that triggered the sequence. If the PLC reduces the dose by 3%, the control system will slowly reduce the chlorine dose to the set point value or until it is reduced too much. Overdosing is acceptable because the permit limit is met but it will waste chlorine. Therefore, it is better to overdose the chlorine to ensure compliance and then to slowly reduce the dose until the desired residual is obtained to minimize chemical use.

Another approach is to use an acceptable range of values rather than a specific set point. For example, a range between 1.0 and 1.2 mg/l can be used instead of attempting to maintain a chlorine residual of 1 mg/l. If the chlorine residual is below 1 mg/l, the dose should be increased. If the chlorine residual is between 1 and 1.2 mg/l, the chlorine dose need not be changed. If the chlorine residual is above 1.2 mg/l, the dose should be decreased.

When programming the PLC, it must be remembered that the lag time in the chlorine contact basin is a physical reality that must be considered in the control logic. If the lag time is not considered, the chlorine will be either overdosed or underdosed, and, in the latter case, the effluent will fail to meet permit limits. A sample-and-hold type lag control function should be programmed to take into account the lag time versus the flow rate. The sample-and-hold function provides a method for freezing the dosage in the PID controller until the next treated batch of flow reaches the effluent chlorine analyzer. The flow is divided by the fixed basin volume to yield the desired lag time. When the calculated lag time has expired, the PID control function will calculate the readjusted dose for a fixed period, and the PID control function will return to the frozen state until the next lag time has expired.

This control approach includes built-in process control redundancy. If the chlorine residual analyzer fails, the control system can revert to flow pacing only. Thus, there is no need for a backup chlorine analyzer.

The biggest drawbacks of this approach, especially in long retention time reuse applications, are the retention time lag and the lack of responsiveness when the chlorine demand changes. A second compound control loop approach is practical and involves moving the residual analyzer closer to the point of chlorine addition, much like the one shown in Figure 12.39. Install a residual chlorine analyzer just downstream of the chlorine rapid mix chamber to measure the residual after the initial high demand has been met. A second analyzer can be installed at the end of the chlorine contact basin to provide overall feedback on system performance.

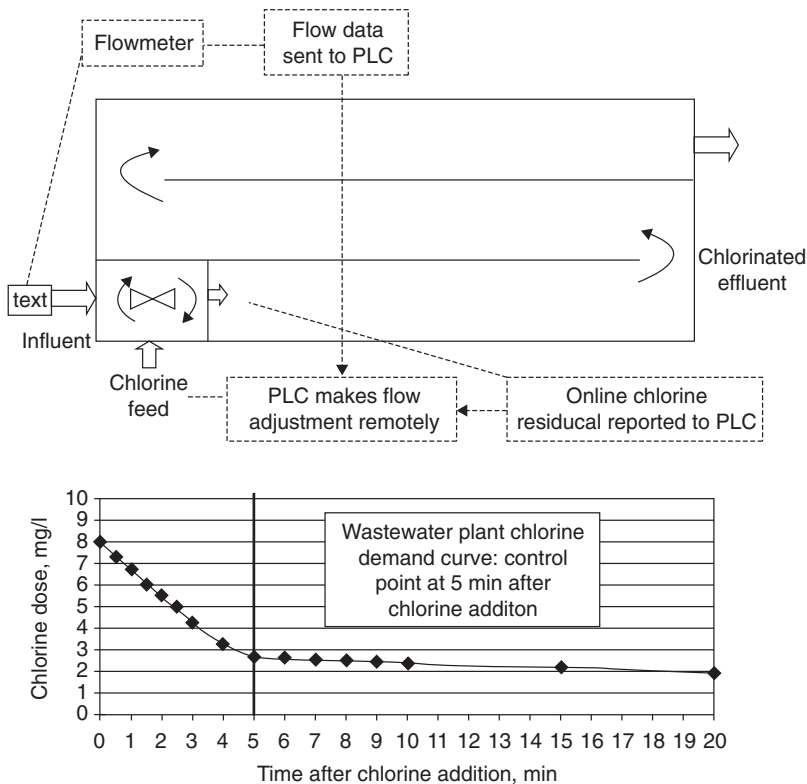


Figure 12.42. Schematic illustrating compound loop control of chlorination with online residual measurement immediately downstream of the chlorinator.¹⁷

Figure 12.42 illustrates an application of compound loop control where the online analyzer determines the residual chlorine in the basin immediately after chlorine addition. The residual analyzer collects a wastewater sample 5–10ft downstream from the chlorine injection point or the rapid mix chamber, at a point where the immediate chlorine demand has been satisfied.

This process control approach assumes that a sufficient chlorine residual concentration can be set to maintain the desired chlorine residual in the contact chamber effluent. The readily oxidized material will be oxidized before the chlorine residual is measured, and it is assumed that the rate of chlorine decay with the remaining materials will be more constant or predictable. This control approach is comparable to assuming a chlorine dose and waiting 30min to check the effluent residual chlorine. The big advantage is that, with the proximity of the sampling point to the chemical addition point, there is a small but manageable lag time that makes it possible to use standard feedback PID control to control the chlorine feed rate.

A second analyzer could be installed to monitor the chlorine concentration in the contact basin effluent to provide trend information or it could be added to the sample-and-hold control function. If used for automatic control, the second analyzer would change the set point used by the upstream chlorine feed control system. However, this approach too is subject to the long lag time issues.

The compound loop control strategy was first introduced in 1960 by Wallace & Tiernan (U.S. Patent No. 2,929,393). The control scheme is based on two separate but independent signals so that each can change the chlorine feed rate separately. One signal represents process flow changes, and the other registers chlorine residual changes. Although Wallace & Tiernan elected to drop this system in favor of the remote vacuum method, the compound loop system continues to be used extensively and can be made available on special order.

The differences between this method and other systems using two signals are as follows: Each signal controls a different component within the chlorinator and each performs an independent chlorine feed-rate change by a different function of gas flow mechanics. Other systems using dual signals integrate the two signals by external instrumentation that transmits a single multiplied signal to the chlorine feed-rate valve.

The process flow signal is transmitted to the motor-operated chlorine feed-rate valve, and the chlorine residual signal goes to the vacuum differential regulating valve. This concept is based on the fundamental law of fluid mechanics: $Q = AV$, where Q is the chlorine flow, A is the area of the chlorine orifice opening, and V is the velocity through the orifice. The velocity through the orifice follows the law of fluid mechanics: $V = (2gh)^{0.5}$, where h is the head loss required to initiate a gas flow change. In this method, h is the vacuum differential across the orifice that is controlled by the vacuum differential-regulating valve.

The chlorine feed-rate valve is controlled by the signal from the primary flowmeter and consists of a motor drive capable of changing the feed rate from 0 to maximum in 15 s. An internal feedback loop controls and verifies valve travel for any signal from 4 to 20 mA. The vacuum differential-regulating valve changes the chlorine feed rate by changing the vacuum differential across the chlorine rate valve orifice. On Wallace & Tiernan equipment, the vacuum range is from 8 to 88 in. of water, 0 to maximum feed rate. This vacuum level can be controlled by a vacuum transmitter capable of changing the vacuum over the complete range in about 5 s. This vacuum level can also be controlled by a motorized vacuum valve, which has a much slower vacuum rate change, approximately 15 min, from 8 to 88 in. of water. This provides floating control by a cycle and duration timer.

Figure 12.43 illustrates a potable water chlorination system that was retrofitted from flow-pacing control to compound loop control by using a programmable controller to perform the intelligence functions. The programmable controller for each chlorinator installation requires the control strategy to be designed for specific field conditions.

Modes of operation:

Primary control circuit (feedback)

PID loop controls residual in a narrow band based on site conditions and requirements.

Secondary control circuit (feed-forward)

PID loop controls chlorine feed-rate valve to achieve a constant dosage in accordance with site flow changes. This circuit is arranged for a wider dead band.

Residual loop achieves chlorine feed-rate adjustment by vacuum transmitter control of chlorinator vacuum regulating valve.

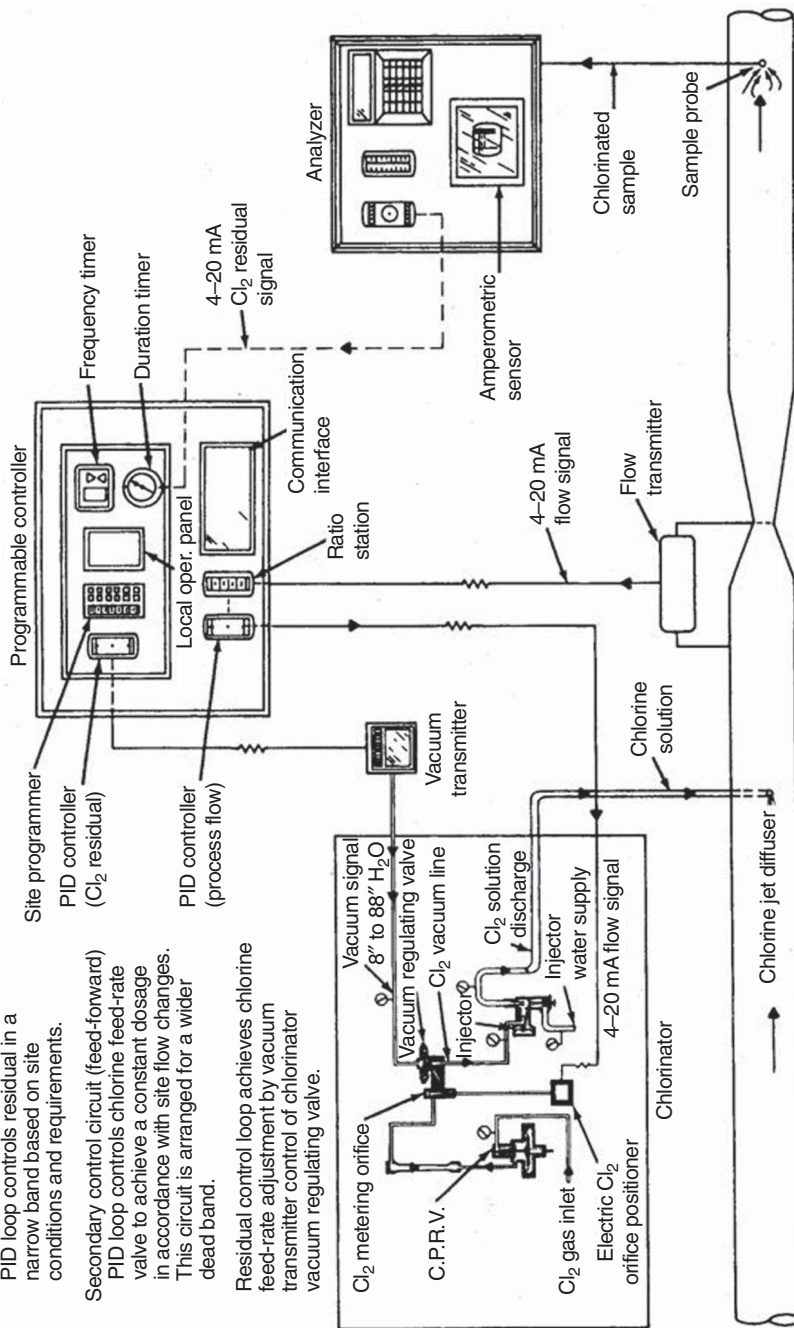


Figure 12.43. Compound-loop residual control system using a programmable controller. CPRV, chlorine pressure-reducing valve.

The system described by Figure 12.43 had the following characteristics:

1. The chlorinator was located at the outlet of a reservoir where reverse flow occurred daily.
2. The flowmeter in a 60-in. concrete pipe had a range far exceeding any practical use, 0–200 cfs. The actual flow range in the high demand season was from 10 to 120 cfs, a 12:1 range.
3. The piping configuration was such that upstream supplies entering this pipeline occasionally contributed some measurable chlorine residual.

DECHLORINATION

Many water treatment plants practice the superchlorine–dechlorination method of disinfection, whereby the water is subjected to a high dose of chlorine over a short contact time. The water is then dechlorinated and subsequently rechlorinated to achieve the desired residual chlorine concentration in the distribution system. Dechlorination is practiced in wastewater treatment, where it is used to reduce or remove the amount of chlorine discharged into receiving streams. This is carried out to attenuate the toxicity from residual chlorine to aquatic species. The concentrations of free and combined residual chlorine in water can be decreased by adding reducing agents such as sulfur dioxide or certain sulfites.

After a study conducted by the U.S. Fish and Game Commission found that fish exposed to heavily chlorinated water died from toxicity caused by the exposure, the federal government limited the total chlorine residuals in wastewater effluents discharging into surface water to between 0.02 and 0.2 mg/l. Shortly thereafter, some graduate students doing ocean research at the Sanitary Engineering Laboratory of the University of California, Berkeley, found that sulfur dioxide residuals at concentrations up to 10–15 mg/l on San Francisco Bay water had no ill effects. This was seen as a solution by many plant operators struggling with toxicity from high residual chlorine concentrations present in plant effluent: Just add excess sulfur dioxide.

Dechlorination in potable water is concerned primarily with obtaining zero chlorine residual. There are three major reasons, however, why the wastewater dechlorination control procedures must be different from those used for potable water: (a) No analytical system has been available to measure the concentration of the sulfite ion (prior to release of the Deox 2000 Analyzer by Wallace & Tiernan); (b2) dechlorination must be complete (zero); and (c) chlorine residual analyzers cannot maintain their calibration in a zero residual environment.

A part of the total chlorine residual in wastewaters will always be nongermicidal because the organic N compounds and nitrites in the wastewater detract from the germicidal efficiency of the chlorine. In simpler terms, measurement of chlorine residuals is not an accurate way to evaluate the germicidal efficiency of chlorine, particularly in wastewater. However, as early as in

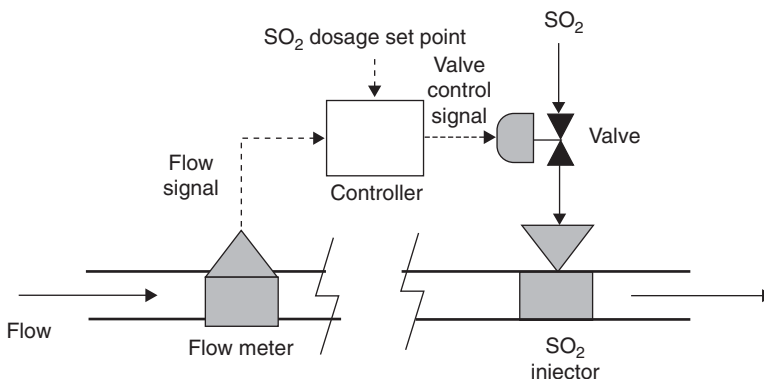


Figure 12.44. Flow pacing control system for dechlorination.

the 1950s, it was suggested that the measurement of ORP of chlorinated water could be used to assess the disinfection efficiency of chlorination, based largely on the wide range of disinfection efficiencies of various chlorine species, as shown in Figure 12.44.

Flow Pacing

Flow proportioning or flow pacing can be used to control a system that is subject to fluctuating flow rates but requires a fairly consistent sulfur dioxide (SO₂) dosage. In such case, the controller allows a linear control of the SO₂ feed rate in direct response to the flow signal from the flowmeter (Fig. 12.44).

Feedback Control

A closed loop feedback or residual control system may be used to maintain effective dechlorination where chlorine demand is variable at relatively constant flows. The dechlorination controller responds to the signal from the residual chlorine analyzer (Fig. 12.45). Long system lag times can reduce the effectiveness of this method; however, lag times can be shortened by locating the dechlorinator close to the point of application and by locating the residual chlorine sampling point close to the chlorine analyzer and the dechlorinator injection point. Such systems where the residual chlorine in the effluent has to remain below 0.1 ppm are not very effective.

The one drawback of using a chlorine residual analyzer in a feedback mode of operation for dechlorination is that the analyzer must be accurate at very low residual chlorine concentrations because, in this range, the analyzer usually is not very accurate. If the permit limit for residual chlorine is less than 0.1 mg/l, there may be some uncertainty in the analytical results.

Compound Loop Control

A compound loop control system involves both flow proportioning and feedback control procedures to accurately control dechlorination of disinfected

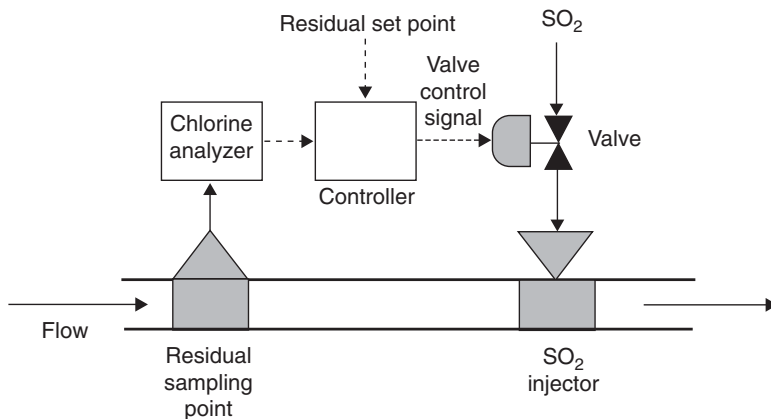


Figure 12.45. Feedback or residual control system for dechlorination.

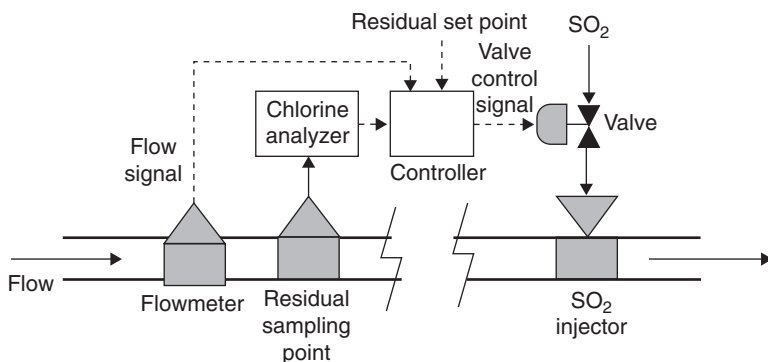


Figure 12.46. Compound loop control system for dechlorination.

wastewater (Fig. 12.46). Signals from the flow-measuring device and the residual chlorine analyzer are used to calculate the amount of SO₂ to be injected in the water, and the residual controller automatically adjusts the dosage to maintain the desired chlorine concentration in the effluent. The controller responds primarily to the signal received from the flowmeter and proportions the feed rate of SO₂ to the amount of residual chlorine to be removed from the wastewater. These systems, however, are not very effective when the residual chlorine has to be below 0.1 ppm.

Zero Residual Control

Wastewater dechlorination systems are designed to produce zero chlorine residual in the effluent before it leaves the plant. Chlorine residual in a wastewater effluent can be composed of free chlorine, monochloramine, dichloramine, and organochloramine. These species have an important relationship to the disinfection process but not to the dechlorination requirements, as the

objective is usually zero residual. However, if a chlorine residual analyzer is used in wastewater treatment, it is calibrated to measure total chlorine residual. Therefore, the operator should occasionally check the overall accuracy of the analyzer readings using the forward-titration procedure, either the amperometric method or the DPD–ferrous ammonium sulfate (FAS) titrimetric method.

Amperometric back titration is the most convenient method of determining sulfur dioxide residuals. It is described in *Standard Methods*, with an equation to calculate the results. The following method is much easier than the iodometric method:

Pour 200 ml of sample into the titrator cup. It is assumed that either (a) the chlorine concentration is less than 5 mg/l, or (b) there is no chlorine and possibly an excess of the sulfite ion in the sample from the application of sulfur dioxide or sodium bisulfite. Add 5 ml of phenylarsine oxide (PAO), and, while stirring, add 4 ml of pH 4.0 buffer solution and 1 ml of KI solution. Then titrate with 0.0282 N iodine solutions. The end point is reached when the needle of the microammeter clearly deflects upward and does not quickly drop back. Record the amount of iodine solution used.

Calculation:

$$\text{mg/l Cl}_2 = (A - 5B) \times 200/C, \quad (12.10)$$

where

A = ml PAO,

B = ml iodine solution, and

C = ml sample.

When there is chlorine in the sample, less than 1 ml of iodine is needed to titrate, and the above calculation will give a positive number. When no chlorine residual is present and there is an excess of the sulfite ion in the sample, caused by the addition of SO_2 , the iodine titrant will react quantitatively, with both the 5 ml of PAO and with the excess sulfite ion, which is also a reducing agent. Therefore, more than 1 ml of iodine will be required to complete the titration procedure. For example, if $B = 2$ ml, then

$$\text{mg/l Cl}_2 = (5 - 10) \times 200/200 = -5. \quad (12.11)$$

This then is the amount of excess sulfite ion. As the mass ratio of sulfur dioxide to chlorine is about 1 is to 1, a reasonable estimation of excess SO_2 concentration can be made. The only suitable method for this in *Standard Methods* is listed as “Sulfite.”

ORP systems are ideal for zero residual control because they can quite easily detect extremely low concentrations of chlorine or sulfite, such as

0.1 mg/l. An ORP system differs from residual analyzers in several important aspects. First, it measures the actual oxidant and reductant activity instead of residuals. Second, redox can measure the potential (voltage) of both sides of the chlorine and sulfite couple. This means that it can measure the activity of both chemicals, allowing the operator to lock in a slight residual of either chlorine or sulfite. Third, redox responses are logarithmic, which means more precise dechlorination control where zero residual is the goal. Fourth, properly designed ORP electrodes can continue to operate properly even after being partially coated with process contaminants.

ONLINE ANALYZERS FOR DECHLORINATION

The microprocessor-based control system has made possible many refinements in the monitoring and control technology. The newest dechlorination control systems discussed in this section include the Stranco HRR Control System, the Wallace & Tiernan Deox/2000R Dechlorination Analyzer, and Capital Controls' Z-CHLOR 3000.

Stranco HRR

The Stranco HRR Control System is described in the section on online chlorine analyzers earlier in this chapter. One of the first systems of this type was installed at the Simi Valley, California, wastewater treatment plant. At the time of this installation, the 12.5 mgd tertiary treatment facility served more than 100,000 residents and 1100 local businesses.

The plant effluent is discharged into the Arroyo Simi Creek, which discharges into the ocean near a very popular bathing beach. Therefore, the NPDES discharge limit was 2.2 most probable number (MPN) of total coliforms, and the total chlorine residual concentration was restricted to less than 0.1 mg/l. The plant operators had to continuously overfeed SO_2 to meet the chlorine residual limit because of the high maintenance requirements of their existing chlorine residual analyzer.

Stranco setup a pilot test system at this facility in 1992, and, after this successful completion of pilot study, the plant operators decided to adopt the Stranco's HRR System for control of both chlorination and dechlorination systems.

The chlorine controller of the HRR System at the Simi Valley plant maintains a 520 mV set point, which meets the limit of less than 2.2 MPN/100 ml of total coliforms. The dechlorination controller is set to 200 mV, which meets the required effluent chlorine residual limit less than 0.1 mg/l. The daily use of both chlorine and sulfur dioxide was significantly reduced after implementing dechlorination control, as indicated in Figure 12.47.

The ORP-based system was far more accurate than the previously used system and reduced the monthly chemical costs significantly. It was also easy

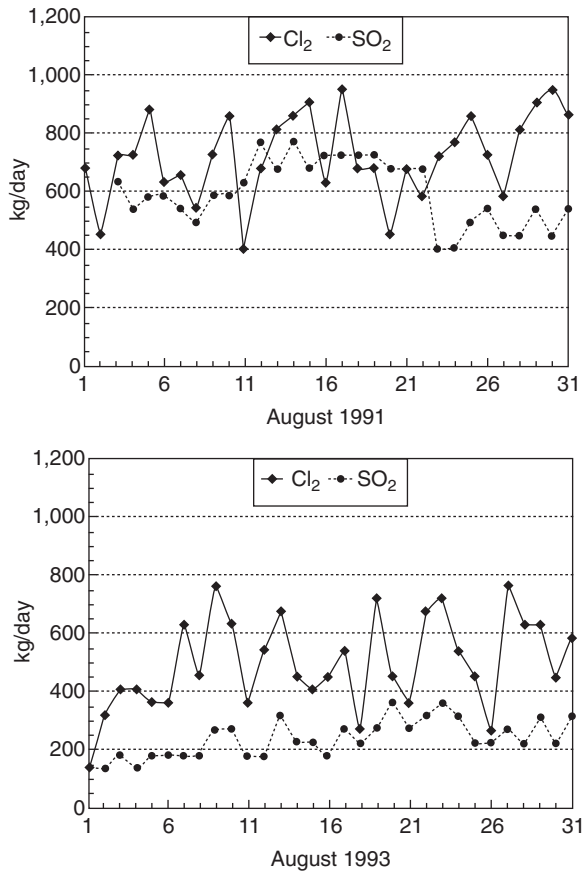


Figure 12.47. Daily use of chlorine and sulfur dioxide at the Simi Valley, California, wastewater treatment facility in August 1991 and August 1993.

to operate and needed only minimal maintenance. The ORP chlorination probe had to be cleaned once a month, and the dechlorination probe had to be cleaned once a week.

Wallace & Tiernan

The Wallace & Tiernan Deox 2000 dechlorination analyzer can measure both SO_2 and total chlorine residuals in disinfected wastewater. Its “center-zero” residual analysis capability makes it possible to achieve complete dechlorination of the treated wastewater while eliminating costly overdosing of SO_2 . The unit employs the amperometric technique and uses a three-electrode measuring cell for direct measurement of residuals.

The process used by Deox 2000 analyzer to measure the SO_2 (sulfite) residuals is based on the principle of biasing the sample with an iodine source,

which is unaffected by the sample quality. With a stable “iodine bias,” the SO_2 or Cl_2 residuals are automatically determined from the measured amount of iodine that has reacted with the sample.

With its bare electrode design, the Deox 2000 is not susceptible to fouling by microorganisms, grease, or turbidity. Because of the stability of its three-electrode measuring cell, daily maintenance for recalibration is virtually eliminated, and the requirement for zero adjustment is entirely eliminated.

This analyzer gives a continuous online determination of SO_2 residuals by metering a predetermined amount of iodine (Fig. 12.48). Since iodine is the measured chemical in total chlorine residual analyzers, the change in iodine residual indicates either chlorine or a sulfur dioxide residual, depending on whether the change is positive or negative. Iodine reacts with sulfur dioxide in the same manner in which chlorine reacts with sulfur dioxide. Therefore, the amount of iodine consumed represents the amount of SO_2 in the water; alternatively, if excess iodine is measured, chlorine residual is present, and the chlorine residual can be accurately determined.

Iodine is less likely to react with oxidative demand in the water, making determination of wastewater residuals more reliable than a hypochlorite-biased measurement. Since iodine is not stable when exposed to air and is very reactive with many materials, it is stored as potassium iodate (KIO_3) to maintain its stability and is converted back to iodine immediately before use. The chemistry of the system is illustrated by the following equations:



The reaction of SO_2 with iodine is



The reaction of free chlorine with iodide is



A continuous sample is delivered to the analyzer. A flushing strainer divides the sample into two streams. The larger bypass stream continuously flushes the filter, and the smaller stream flows to the constant level chamber in the analyzer flow block. The constant level box inlet is designed for a 500- to 1000-ml/min sample flow, but only about 50 ml/min of this sample is used to make the analysis. The sample flows out through the cell block. Here, a rotating impeller maintains a constant sample velocity and entrains grit to scour the electrode, which is the key to maintaining proper operation.

The three-electrode amperometric cell reduces a portion of the iodine to iodide at the working electrode. The resulting current (μA) is proportional to the residual in the cell. The working electrode and the counter electrode are made of the same material (platinum), so there is no current flowing at zero

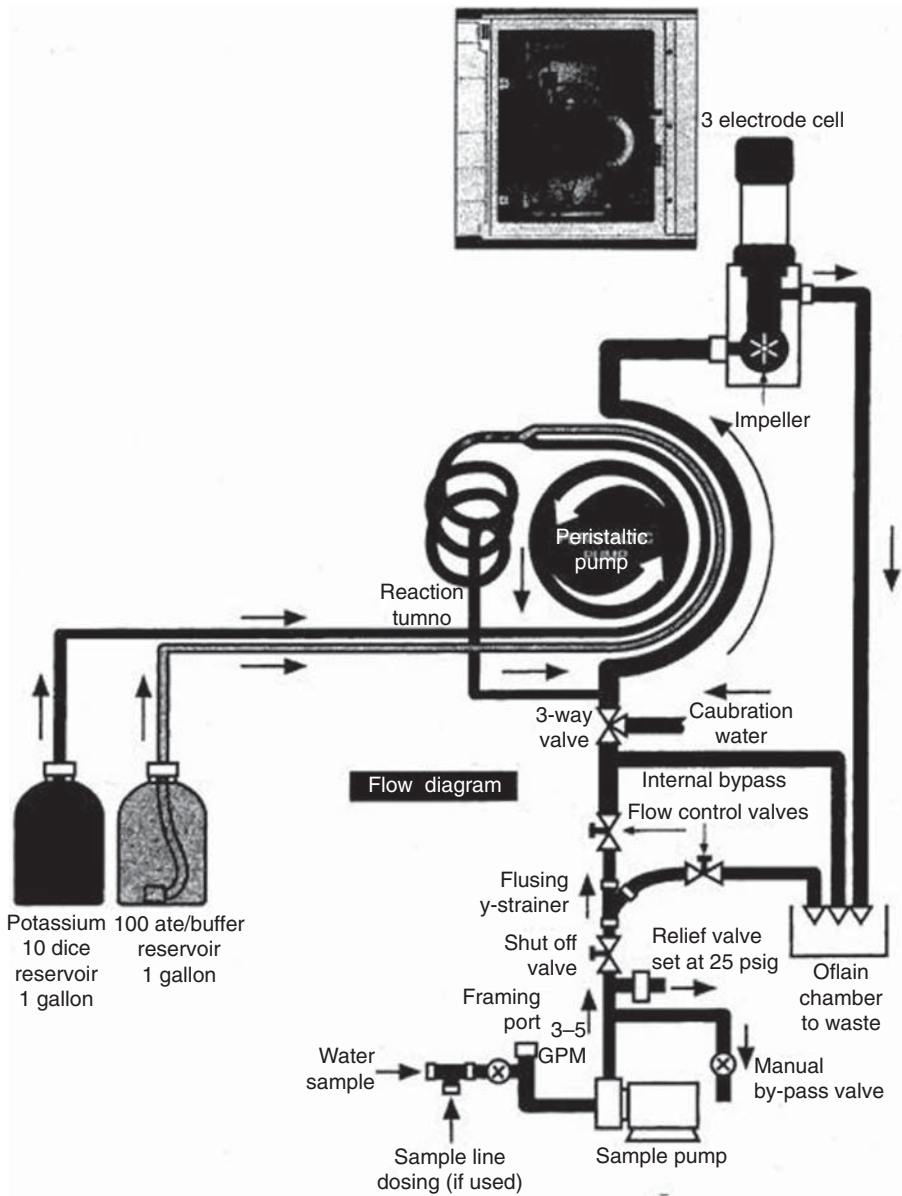


Figure 12.48. Flow diagram for Wallace & Tiernan Deox 2000 Dechlor Analyzer.

residual. This eliminates the need for a zero setting. The selectivity of the probe is set by biasing the working electrode to a standard reference electrode, 0.2V for iodine.

Because of the small sample flow through the unit, buildup of organic matter in the sample line could cause a chlorine residual demand that would affect the system accuracy or completely block the sample flow. To minimize this possibility, the system periodically energizes the solenoid, which raises the orifice plunger, which removes all the unwanted material from the orifice. Directly above the orifice is a gas purge membrane that is used to remove any accumulated gas released from either the sample or the reagents because of the lowered pH. Flushing is not possible, as it would remove the biasing agent and upset the equilibrium of the cell.

Typically, both wastewaters and condenser cooling tower waters must be dechlorinated by using either sulfur dioxide gas or sodium bisulfite solution, both of which produce sulfite as the dechlorinating agent. The chemistry is as follows:



Sulfite reacts with all inorganic chlorine residuals to form sulfate and ammonium chloride. Removing 1 mg/l of chlorine residual requires 0.9 mg/l sulfur dioxide or 1.46 mg/l sodium bisulfite.

The calibration method used by Deox 2000 is both simple and automatic. To calibrate the analyzer, the operator must only scroll to the iodine bias screen (in the main operating mode) and press the change key. This freezes the output signal and initiates automatic calibration of the iodine bias. After a stable iodine bias has been established in the cell (by the use of the demand-free water that has been fed with the calibration pump), the operator is prompted to take a sample for titration and scroll in the value as the iodine bias in mg/l. The analyzer will automatically calculate the process residual level (in mg/l, SO_2 or Cl_2) from the actual measured residual and the iodine bias.

Before this analyzer became available, it was not possible to control chlorine residuals by dechlorination in wastewater discharges with satisfactory consistency or accuracy acceptable to the regulatory agencies in several states. The regulatory limits are usually 0.02 mg/l chlorine, so most dischargers went to at least a 2 mg/l excess of sulfur dioxide. With this analyzer, the bias stability is $\pm 1.0\%$, and the overall analyzer is rated as better than $\pm 5\%$ of full scale.

Because both chlorine and sulfite can be accurately monitored with zero calibration by the third electrode, the bias analyzer can be used in a closed-loop feedback control system for dechlorination by sulfur dioxide with an alarm to signal a chlorine residual violation. After calibration, the analyzer is returned to operation, and residual chlorine and sulfite concentrations are displayed on the alphanumeric display. The 4- to 20-mA analyzer output can

be used to operate a recorder or drive a suitable controller in a feedback control system.

Under laboratory conditions, overall accuracy has been on the order of $\pm 2\%$ of full scale, that is, $\pm 0.2 \text{ mg/l}$ with a 5.0 mg/l bias or $\pm 0.02 \text{ mg/l}$ with a 0.5 mg/l bias. The establishment of the center point (0 mg/l of both chlorine and sulfur dioxide residual) is independent of analytical error. Overall analyzer accuracy will improve as residuals approach zero.

Capital Controls

Capital Controls' Z-CHLOR 3000 continuously measures chlorine or sulfite ion residuals in the wastewater treatment plant effluent and controls the residual at a given preset value, which may be a positive chlorine residual, a zero chlorine residual, or a positive sulfite ion residual value. The flow signal from the plant flowmeter on the effluent line is combined with the residual signal in the controller. The system can measure and control chlorine residuals as low as 0 mg/l through a unique, precisely controlled biasing system, which introduces a small, constant quantity of oxidizing chlorine solution (a dilute NaOCl solution) into the sample immediately before the analysis of residual chlorine. In this way, the Z-CHLOR 3000 is continuously provided with a chlorinated sample.

The addition of dilute NaOCl to make the biased sample results in a signal equal to 50% of full scale on the controller display, or it records it on an optional recorder. The 50% point is equivalent to a zero chlorine or sulfite residual. If any chlorine is present in the sample, it is added to the bias value, and the analyzers will show positive chlorine residual. Conversely, if sulfite is present in the sample, the signal will move below zero (a positive sulfite number) when the instantaneous reaction between the chlorine in the bias solution and sulfite ion reduces the chlorine in the analyzer cell.

The heart of the Z-CHLOR control system is the microprocessor-based controller mounted on the cabinet face. It contains a specifically designed control logic keyed to the dechlorination process. It includes a multistage alarm system to alert operating personnel to residuals above or below the desired concentrations. An override system is activated if the residual reaches the maximum allowable concentration stated in the plant discharge permit.

The Z-CHLOR 3000 sensor does not come into contact with the sample; therefore, it is not affected by sulfur-reducing bacteria that may be in the water and could lead to fouling. The instrument is available with an optional cleaning system and an optional circular chart recorder mounted on the front of the cabinet. The cleaning system is used to keep the sampling line to the Z-CHLOR clean, free of slime and algae, which would reduce the amount of chlorine residual reaching the analyzer. It incorporates an external chemical feed pump in a weatherproof enclosure for feeding sodium hypochlorite if the sample line to the analyzer is longer than 5 ft. A corrosion-resistant solenoid

is included if the hypochlorite is injected into the pump suction. The solenoid and the chemical pump should be located at the beginning of the sample line to maintain the inside of the sample line free from slime and algae.

In operation, the chemical pump and solenoid are automatically activated for several minutes (field-adjustable) during every 8-h period. The cleaning system includes a bottle of 5% sodium hypochlorite (bleach). The controller includes all operating controls for the cleaning system, including a locking feature to freeze the output of the controller during cleaning.

BLENDING CHEMISTRY WITH PROCESS CONTROL

Process control procedures do not control the chemistry of chlorination; they merely control the dose and the effluent chlorine residual concentration. The system operator or designer must consider the chlorine chemistry when designing the control logic in the PLC.¹⁸ For example, in specifying a chlorine residual analyzer, it should be absolutely clear whether free, total, or combined chlorine will be measured. If a free chlorine analyzer is being specified and the water chemistry results in monochloramine formation and disinfection, the analyzer will never measure sufficient free chlorine residual until the breakpoint chlorine demand has been met.

It is easy to blend process control with chemistry when the facility's effluent ammonia concentration is less than 1 mg/l as N. Such facilities will always use free chlorine for disinfection. Any facility that discharges ammonia at concentrations in the 1–5 mg/l range will be faced with operating in Zone 2, 3, or 4 on the breakpoint chlorination curve (Fig. 12.49). As the secondary effluent ammonia concentration varies, the chlorine dose used must change to shift through Zone 3. The controller must decide whether to increase the chlorine dose to move into Zone 4–full breakpoint or to decrease the chlorine dose and move into Zone 2 chloramination.

The designer or the operator must configure the PLC to distinguish between free and combined chlorine and to choose between free and combined chlorine control responses. Both free and total chlorine analyzers must be added to the control system to enable the PLC to interpret the data and to determine which chemistry is in use and which control response should be used.

The success of the control system begins with the selection of the chlorine analyzer. Since chlorine analyzers are continually being improved, the recommendations made in this chapter may be outdated. Therefore, features of the analyzers and other considerations will be discussed only in general terms, and it is up to the reader to find the specific analyzer best suited for a given application.

If a single chlorine analyzer can distinguish between free and combined chlorine, it may be the best choice. Otherwise, two analyzers may be needed: one to measure total chlorine and the other to measure free chlorine concentration. Combined chlorine concentration would then be calculated as total

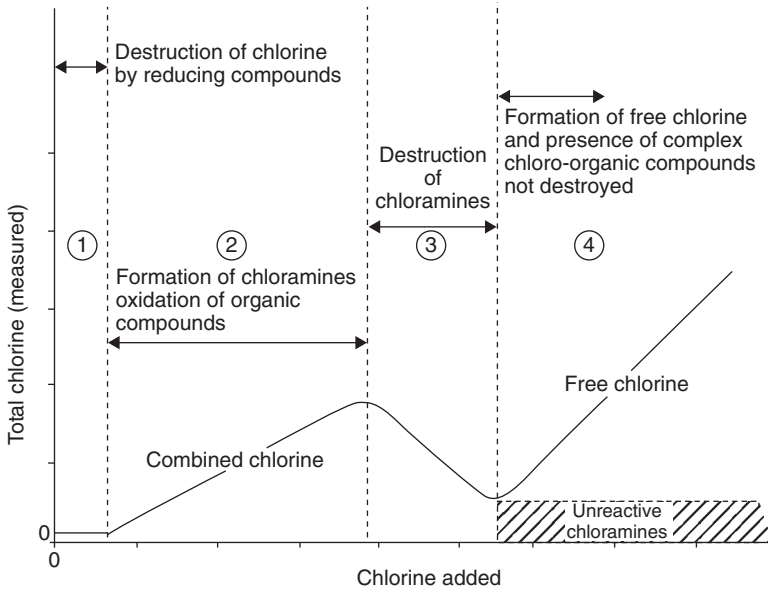


Figure 12.49. Breakpoint chlorination.¹⁷

chlorine minus free chlorine. Or, if total chlorine equals free chlorine, the system is understood to be using free chlorine for disinfection. If the free chlorine concentration is zero, only combined chlorine is present. The PLC must be able to interpret these data to determine the appropriate dose response.

Control systems often become confused during breakpoint chlorination. As shown in Figure 12.49, the chlorine residual increases as chlorine is added (Zone 2) until all ammonia is converted into monochloramine. The response that confuses control systems is Zone 3, where monochloramine is converted to dichloramine. Since the combined chlorine is monochloramine, conversion of monochloramine to dichloramine results in a decrease in the chlorine residual as more chlorine is added. Unless the PLC is programmed to recognize this, the control system will respond by adding more chlorine and will force the system through breakpoint chemistry to the formation of free chlorine. Either free chlorine or monochloramine will kill enough pathogens to maintain compliance with the NPDES permit, however, at significantly different chlorine doses. Operating costs will be higher if the disinfection process proceeds through breakpoint chlorination.

The PLC must be programmed to recognize the Zone 3 response. The proper response should be to first reduce the chlorine dose to move back into Zone 2 to maximize the monochloramine concentration. The control system can be programmed to respond automatically or to sound an alarm to alert the operator.

When dealing with variable concentrations of effluent ammonia, it may be wise to routinely monitor the ammonia concentration data ahead of chlorination by periodic grab sampling or through continuous online monitoring.¹⁸ Using the chlorine contact chambers influent ammonia concentration, the PLC can calculate the chlorine dose that will convert all the ammonia to chloramines and use this value as an alarm point or as part of the PLC control logic to determine when the chemistry is transitioning into Zone 3. For feed-back control systems that monitor the chlorine basin effluent residual, it is a long wait to find out whether the chlorine dose should be increased or decreased to move either into Zone 4 or back into Zone 2. If an online ammonia analyzer is added to the control system, the PLC can be easily programmed to compare the mole ratio of chlorine to ammonia to decide which portion of the breakpoint chemistry predominates.

All these considerations address only effluent residual chlorine concentrations. The control system cannot monitor the effluent organism concentrations. This must be carried out by the operator, who then must determine the proper chlorine dose and decide whether to leave the control system in automatic mode or to return it to flow-paced control. Occasionally during process upsets or peak loads on the upstream biologic process, the ammonia concentration may fluctuate. Under these conditions, it may be preferable to operate the system in flow-paced mode and to concentrate on correcting the biologic system upset.

Some states have placed a 4 of 7-day median limit of 2.2 cfu/100 ml on total coliforms or nondetect on fecal coliforms. In such cases, the chlorine contact chamber will be designed to provide a contact time of 30–120 min, which poses a greater challenge for disinfection process control.¹⁸ Another approach, if allowed, is to operate at a higher chlorine dose.

Prolonged exposure to direct sunlight will cause chlorine to degrade. For systems that use free chlorine for disinfection, the challenge is to maintain chlorine residual through the contact chamber. If the permit allows some ammonia in the effluent, one solution is to add ammonia to convert the disinfection process from free chlorine to combined chlorine.¹⁸ When monochloramine is dechlorinated or fully reacted, it degrades into ammonia, so ammonia addition may be limited, based on the allowable effluent ammonia or total nitrogen concentration. In fact, both monochloramine and dichloramine revert to ammonia when dechlorinated, so it is necessary to understand chlorine chemistry and to know the NPDES permit limits.

One issue that has come to light is how to maintain free chlorine residual when a long retention time is required, such as in reuse applications. The basic hurdle is one of chemistry. Chlorine will react with anything it can, so to maintain a CT value higher than 450 during a 90-min retention time, the chlorine residual must be at least 5 mg/l, which requires a higher chlorine dose to compensate for the chlorine decay over the 90-min retention time. At such a high initial chlorine concentration, unwanted side reactions occur, which may

require an even higher initial chlorine dose to maintain of the desired 5-mg/l residual.

Maintaining a CT value higher than 450 at lower than design flows results in a longer retention time, which should provide some relief if the chlorine decay can be kept under control. So there are two basic issues: first, how to control the retention time and second, how to control the chlorine residual concentration. Both issues should be taken into account in the physical design of the chlorine contact basin.

Control of retention time is only part of the overall issue in managing disinfection in long-retention time systems. Control of chlorine chemistry is the other issue.

For treatment plants that have a relaxed ammonia limit, a numerical limit of over 3 mg/l $\text{NH}_3\text{-N}$, it is possible to use the ammonia limit as an advantage. Chloramine is less reactive than free chlorine and is also a good disinfectant. Adding ammonia to the wastewater treatment plant effluent before adding chlorine will allow the use of chloramine chemistry for disinfection. Chloramine is more stable in sunlight (slower rate of decay) and has fewer competing side reactions and, thus, a lower chlorine demand, which will also produce fewer THMs.

Assuming a CT value of 450 requires a 5-mg/l chlorine residual, which equals 0.07 mmol of Cl_2 . The reaction of chlorine with nitrogen is 1 mol to 1 mol, so 0.07 mmol of ammonia would be needed, which equals 1.2 mg/l of ammonia or 1 mg/l of ammonia as N. Allowing for some decay would mean that 2–3 mg/l of ammonia would be needed to maintain the correct chlorine residual at the end of the chlorine contact chamber.

One drawback of this approach is the need to manage the effluent ammonia concentration. Upon dechlorination, chloramine will revert into ammonia. If the ammonia limit is near 3 mg/l, it will be difficult to manage ammonia addition while avoiding permit violations. Online ammonia analyzers may have to be used to provide the necessary real-time process control.

If ammonia is added for disinfection with chloramine, it is also possible to provide a second point of chlorine addition near the end of the contact basin to oxidize the ammonia by breakpoint chlorination. If parallel treatment trains are used, only part of the flow needs to be treated for breakpoint chlorination to ensure compliance with the ammonia limit by blending. This means that a free chlorine concentration would be maintained in a smaller portion of the basin.

If ammonia addition is not the solution, multiple chlorine addition points should be provided.¹⁸ Simply adding more chlorine at the beginning of the chlorine contact chamber does not ensure that an effluent residual will be maintained in systems with a long retention time: As the chlorine concentration increases, chlorine can participate in more chemical reactions. Thus, adding a higher chlorine dose may increase the chlorine demand without producing a net increase in the effluent residual. Instead, it may result in the formation of more DBPs such as THMs.

Free chlorine reactions are numerous and often depend on the actual chlorine concentration present at the time. Some reactions require a threshold activation energy that is related to the chlorine concentration. So, in essence, as the chlorine concentration is increased, more reactions or more chlorine demand will occur. An example of chlorine demand is shown in Figure 12.50.

Once the chlorine demand has been met, adding more chlorine to raise its concentration to that of the initial dose may not increase the overall demand. This can be determined in the laboratory through jar testing. If the demand curve shows that a second dosing point does not exert a second chlorine demand, then adding chlorine at a second location is feasible. This means that, for disinfection systems with a long retention time, a second or a third chlorine addition point can be used to boost the chlorine residual to meet the CT requirement as shown in Figure 12.51. This is shown graphically in Figure

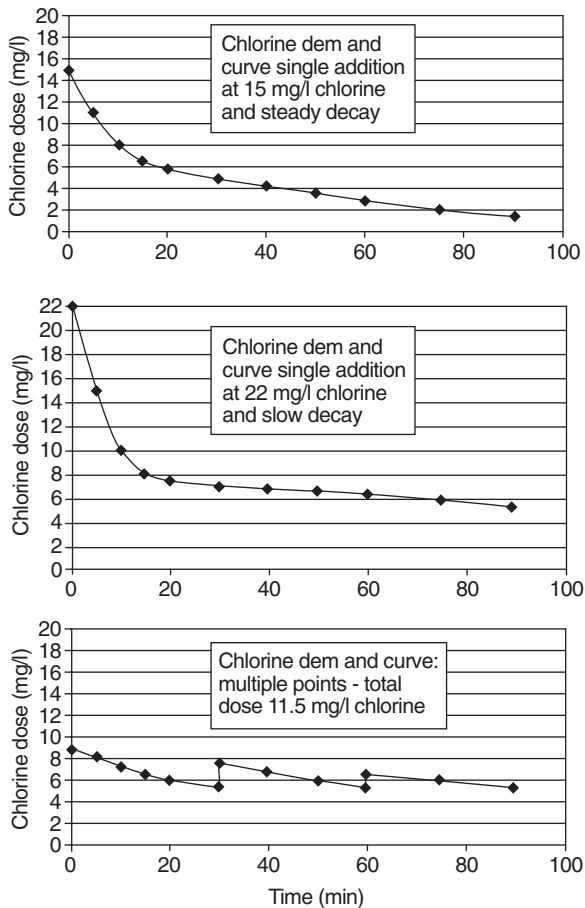


Figure 12.50. Chlorine demand curves.¹⁹

12.50. Jar tests for chlorine demand must be run to simulate expected operating conditions. Figure 12.50 shows possible demand curves. If the demand curve is flat after the first addition of chlorine, then several small doses of chlorine may be preferable to a single large dose. If the high dose produces a curve that is steep over the first few minutes of the reaction and then flattens out, the single dose works well. Several dosing strategies should be evaluated by jar testing to determine the best and most cost-effective approach.

The standard approach to controlling chlorine feed with ORP probes has some limitations. Some ORP systems use a single probe for feedback control to a specific ORP set point. The ORP set point is an arbitrary selection of an ORP value that is believed to result in sufficient chemical addition to meet the disinfection or dechlorination goals. A single ORP probe control system will always require considerable operator attention to properly manage the coliform kill to meet the permit.

The ORP reading is a complex chemical relationship that is a function of a number of variables. Variables that affect ORP readings in a given wastewater include temperature, pH, concentration of total dissolved solids, and concentration of oxidants or reducing agents already present in solution. The wastewater quality, particularly during storm events, will produce a varying ORP concentration at the chlorine contact chamber. This is a problem that a single-probe ORP control cannot handle. Newer models of the Stranco system use a second ORP probe to monitor and adjust for the background ORP of the wastewater.

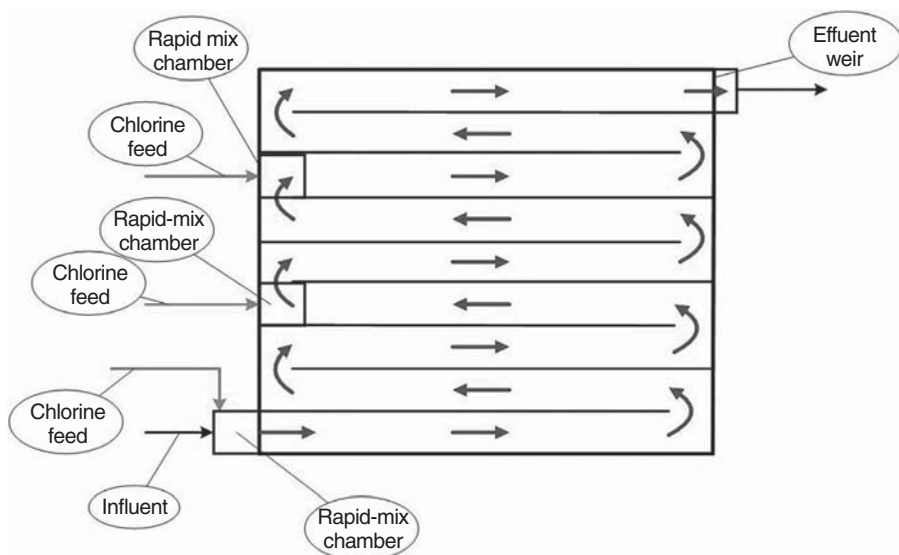


Figure 12.51. Multiple chlorine feed points.¹⁹

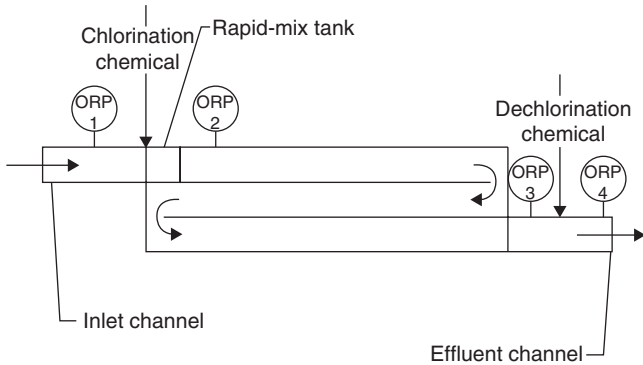


Figure 12.52. Positioning of ORP probes for monitoring chlorine and sulfur dioxide addition.

A good approach for using ORP readings to control chlorine addition is using two ORP probes at the influent end of the chlorine contact chamber. Figure 12.52 shows ORP probe 1 located upstream and ORP probe 2 located 5–10ft downstream from the chlorine rapid mix chamber. The two-probe system would work as follows:

- The upstream probe measures the ORP quality of the wastewater before chlorine addition. It becomes the baseline for comparison.
- The downstream ORP probe measures the chlorine residual after chlorine addition.
- The actual control of chemical addition is based on the ORP rise. Downstream ORP minus upstream ORP equals ORP rise, which should be proportional to the addition of chlorine, or at least the residual chlorine, at that point in time. The relationship between residual chlorine and ORP rise should be established experimentally to produce a site-specific curve.
- The upstream probe can also include an alarm set point to indicate when the wastewater quality drifts outside a given range, indicating that the raw wastewater quality has changed and that a change in set point ORP rise is needed. The downstream ORP reading at ORP probe 2 can be similarly alarmed.

This approach eliminates some of the deficiencies in the Stranco system in that it takes into account changes in wastewater quality as they affect chlorine demand as measured by ORP.

The ORP probe located at the outlet from the chlorine contact basin can be used to track the residual chlorine concentration, or a residual chlorine analyzer can be used. The residual chlorine concentration reading will be used to determine whether the expected chlorine dose used to control chlorine feed

was sufficient to maintain the desired residual through the chlorine contact basin. This reading can be used to sound an alarm when the residual drops too low. It can also be used to increase the initial chlorine dose. Because of the 30-plus-min lag between a change in the initial chlorine dose and obtaining a measurement of the impact on the effluent residual chlorine concentration, this control loop must have a built-in delay in making any subsequent adjustments in the chlorine dose. If a delay is not used in the control loop, this feedback control approach can result in gross overfeeding of chlorine. The time delay must be long enough to ensure that a representative effluent residual chlorine concentration has been measured before a second change to the initial chlorine dose is made.

CONTROL SYSTEM O&M

There is a significant difference between the operation of an analyzer for potable water treatment and the operation of one for wastewater. Chlorine residual analyzers require zero, span, and temperature adjustment. If a thermometer is used, it automatically compensates for temperature changes in the sample. The zero adjustment is simple. The sample flow to the analyzer is shut off, or one lead to the cell is disconnected (depending on the manufacturer). Under these conditions, the indicator or pen on the recorder should go to 0. If not, the potentiometer marked 0 is rotated until the pen reads 0. The span adjustment depends on the calibration.

Advanced wastewater treatment plants that nitrify may have either free residual chlorine or combined chlorine. In these cases, it is desirable to differentiate the free from the combined; therefore, the forward titration procedure must be used. Whenever extensive calibration of the analyzer is required or desired, it is desirable to have a signal simulator available. This instrument provides checkpoints throughout the range of the analyzer cell output.

The amperometric analyzer is generally calibrated by using an amperometric titrator. Other titration methods can also be used such as starch-iodide or DPD-FAS. These methods are outlined in the 19th edition of *Standard Methods*. For wastewater applications, the back titration method using the amperometric titrator is preferred. The DPD-FAS and starch-iodide titrations are equally acceptable in wastewater practice. Colorimetric methods are not reliable for calibration of wastewater analyzers.

Many potable water installations are interested only in free-chlorine measurement. The free chlorine can be measured with or without chemicals. If the pH is constant, as it is in some instances, no buffer solution is required. No KI is required because free chlorine is measured directly by the analyzer. In most of such cases, there is not enough combined chlorine to cause any error in the free reading. If, however, the pH varies (which causes a variation in cell output), then a pH 4 buffer solution or carbon dioxide must be added to the sample to stabilize the pH at 4.

Water systems that add ammonia to produce chloramines or those that treat water with a natural ammonia content are concerned with measuring total chlorine residual. In such instances, it is imperative that the sample pH be lowered to 4 by a buffer solution and that potassium iodide be added to the buffer solution in sufficient quantity to convert the total residual to free iodine. The amount of KI to be added to the buffer solution depends on the sample flow through the analyzer and the magnitude of the residual. The cell flow rates vary from one manufacturer to another.

All wastewater analyzers should have a sample filter such as an inlet-line, disk-type strainer. The drain valve on this strainer should always be wide open for continuous flushing. The sample pump or sample supply should be able to deliver about 12 gpm sample at 25 psi at the inlet to the filter. Under these conditions, there will be about 9–10 gpm of sample discharging to waste through the filter, leaving sufficient capacity to supply the cell with an adequate continuous, filtered sample.

Chlorine residual analyzers for wastewater applications need many more calibration checks than those measuring residuals in potable water. Wastewaters also generally have a significantly higher alkalinity than potable water, so pH control of the sample through the cell is critical. The amount of KI added is critical as well because of the higher residuals required in wastewaters.

The sample pH must be kept at 4.5–5.0, preferably at 4.5. Multicolored pH papers are satisfactory for this determination. Sufficient potassium iodide must be added to the pH 4 buffer solution to allow the chemical reaction between the KI and the chloramine residual to go to completion. The chlorine residual reacts with the potassium iodide to release free iodine in proportion to the total residual. The analyzer cell measures the free iodine. A rule of thumb for KI addition is 15 g/l of buffer solution per 150-ml/min cell flow of undiluted sample per mg/l of total chlorine residual. The Wallace & Tiernan wastewater analyzer is arranged for dilution of the sample with freshwater. Dilution is usually on a ratio of 1:1.

The operator is advised to consult the manufacturer's instruction book to make sure of the proper calibration and operating procedures with respect to the buffer solution, KI addition, and so on. This is extremely important in the operation of a wastewater analyzer. An easy way for the operator to determine whether or not sufficient KI is being added is to add about 1 ml of KI solution (from the amperometric titrator test solutions) to the sample head box or diversion box and to observe the chlorine residual indicator on the analyzer. If it does not move, the KI addition is sufficient. If it deflects upscale, the KI addition is insufficient.

Owing to the importance of the addition of a buffer solution and KI, it is obvious that the operation of the reagent pumps is critical. Therefore, the operator must check the sample pH daily.

Once the analyzer has been put into operation, it is not necessary to respan the instrument each day. It is preferable to plot a graph of the indicated versus the titrated sample readings. The curves of each of these groups of readings

should indicate a span adjustment either upward or downward. Initially, this procedure should be carried out weekly, inasmuch as most wastewater systems require respawning of the analyzer once a week.

Daily inspection of the sample line and pumping system to the cell is necessary to assure a continuous sample. The noble metal electrode in the cell may be either gold or platinum, depending on the manufacturer. It should be kept free of grease deposits by wiping it with a soft cloth. However, the sacrificial copper electrode should never be disturbed.

Zero adjustment of analyzers used to monitor the dechlorinated sample will always identify a calibration problem that is best ignored. These analyzers are used primarily to monitor and control the sulfonation process. However, they are often arranged to monitor the dechlorinated effluent for 5 or 10 min every hour. When the dechlorinated sample reaches the cell, the analyzer indicator or pen will drop below zero even though zero and span have already been adjusted for sample containing chlorine residual. This phenomenon is probably caused by the presence of excess SO_2 being applied. It does not signify a negative residual. It does, however, demonstrate that when a dechlorinated sample passes through the cell, it changes the molecular surface of the electrodes so that they are slightly different (electrochemically) from when the zero calibration check is made with a sample containing chlorine residual. This phenomenon does not necessarily affect the span adjustment of the analyzer.

The typical amperometric continuous analyzer consists of a cell assembly that accepts the sample from the sample piping and/or pumping system, plus electronic circuitry that interprets and records (or indicates) the intelligence from the cell. Wastewater analyzers differ from potable water analyzers in the way the sample is delivered to the cell because wastewater analyzers are equipped with a special filter on the sample line.

The sample line to the analyzer is probably the most neglected component of a chlorine residual measuring system. It is subject to biofouling whether by potable water or by wastewater. This exerts a chlorine demand that gives a false reading at the analyzer. Usually, the sample flow velocity is far below what would be considered a scouring velocity, and, in wastewater systems, where grease and other organics are involved, the problem can be acute. Therefore, it is a good practice to routinely flush the sample line with caustic or chlorine. The frequency of flushing will have to be determined by experience and trial and error.

Some operators at wastewater plants have installed a point of chlorination into the dechlorinated sample line, which is chlorinated heavily for 10 min/day. This is probably the easiest way to keep this line from fouling up the dechlorination process.

The amperometric cell consists of a two-electrode system: one made of platinum or gold and the other, of copper. The copper electrode loses metal ions in accordance with the amount of chlorine residual it is measuring, so it will have to be replaced from time to time. The copper electrode needs to be

replaced according to the amount of chlorine residual passing through the cell. Replacement intervals might vary from 6 months to 3 years. A wastewater analyzer measuring residuals at concentrations around 5 mg/l will use up one copper electrode about every 9 months. The cell is equipped with a type of electrode bombardment system that keeps the electrodes clean and in molecular balance. A common type is grit, which has to be replaced periodically in the cell.

If the output signal is erratic and the cell refuses to remain in calibration, then both electrodes should be cleaned with the recommended abrasives. It is imperative that maintenance personnel become familiar with the manufacturer's instructions before cleaning these electrodes and for returning the analyzer into operation.

If the cell is operating on potable water, little maintenance is required, depending on how clean the water is. For some waters, particularly raw or untreated, it will be necessary to install a manually operated filter on the sample line. If the cell is operating on wastewater, the sample line must be equipped with a motorized filter. This operation requires more maintenance of the sampling system because of the suspended solids, fibrous materials, and grease, which are present in varying amounts, depending on the type of wastewater treatment process. A continuous and adequate flow of sample to the cell is the most important single factor in this type of operation. The maintenance and inspection program will vary widely from plant to plant.

The filter on a wastewater system is so important that it is desirable to have available a complete unit with motor drive for replacement or as a source of spare parts.

Most control devices have a combination of plug-in transistorized components that give long and reliable service. However, the operator should be able to obtain replacements for any of these components in the event of failure. Devices with moving parts, such as potentiometers or safety devices dependent upon mercury switches, are subject to wear and will require eventual replacement. The operator should have spares for these items also. Reversible motors used in these control devices, such as electric chlorine orifice positioners and motorized vacuum valves, are also subject to failure even though they give long and reliable service. The operator should check the source and the availability of these motors. The manufacturers of these special-duty motors may run into production problems, resulting in delivery schedule delays. Most components of electric control and alarm devices are off-the-shelf items and are readily available.

RECORD KEEPING AND REGULATORY ISSUES

Reliable records should be kept as a proof of performance and effectiveness of the control system and to justify decisions, including expenditures, and various recommendations. These records serve as a source of information

for plant operation, modifications, and maintenance. Adequate records of disinfection are also important from the standpoint of regulatory agencies. Records will facilitate public health surveillance and enable the regulatory agencies to assess compliance with state regulations. Always consult the facility operating permit, state code, or other state documents that require data collection for operating water and wastewater systems. Even if the facility always produces a good-quality effluent, failure to maintain the proper records may result in a violation. Two classes of records should be maintained at a wastewater treatment plant using chlorination: (a) descriptive, planning, and inventory records related to the physical plant, and (b) performance records.

Records of the following items at the end of the chlorine contact chamber should be kept on a twice-daily basis, at peak flow and at low flow, if convenient to operating personnel:

1. ORP (mV)
2. Chlorine feed rate (lb/day)
3. Plant treated water effluent (mgd)
4. Chlorine residual (mg/l)

The following record on the chlorination–dechlorination unit should be available for reference:

1. Design engineer's report, including basis of design, equipment capacities, population served, design flow, reliability features, and other data
2. Contract and "as-built" plans and specifications
3. Shop drawings and operating instructions for all equipment
4. Cost of each equipment item
5. Detailed plans of all piping and electrical wiring
6. A complete record of each piece of equipment, including name of manufacturer, identifying number, rated capacity, and dates of purchase and installation
7. Supply of chlorine and dechlorinating agents, including reserves and availability estimate

Daily records of the following should be kept:

1. Continuous ORP mV readings from a chart recorder or a data logger
2. Results of bacteriological analyses: coliform count exiting contact chamber and other required tests
3. If possible, chart of ORP mV versus coliform count
4. On dechlorination applications, daily grab samples verifying the ORP mV set point

5. Chlorine: daily quantities used, including dosage for both pre and post chlorination, method used, and continuous record of chlorine residuals
6. Wastewater flow: preferably continuous recording; total daily flow treated; maximum, minimum, and average daily flow
7. Daily inspection: operating problems, equipment breakdowns, periods of chlorinator outage, diversions to emergency disposal, and all corrective and preventive actions taken

In addition, the following important records and plans should be kept at each facility:

1. Routine equipment maintenance schedule and record
2. Annual equipment inspection and maintenance record
3. Plan for prearranged repair service
4. Emergency plan for chlorinator failure
5. Emergency plan for accidental chlorine or sulfur dioxide release
6. Weekly inspection records for ORP probes. Remove ORP probes from process to inspect and clean weekly
7. Historical ORP mV readings on a month-to-month basis to predict the end of probe life expectancy of 3 years
8. Record fluid levels in automatic probe cleaning systems

Monthly operating reports containing information on chemical use, wastewater flows, laboratory analyses, ORP response, and significant operating problems should be prepared.

Operators should be aware of the potential limitations of online process control as it relates to NPDES permit compliance. The NPDES permit will define the parameters that define compliance and noncompliance. Whenever an online instrument is used and this instrument uses an analytical method that is accepted legally (40 CFR Part 136 defines the legal analytical method to use for NPDES permit reporting), it may be used to determine compliance.

The legal approach to monitoring an effluent for coliform concentrations and chlorine residual concentrations is collecting a grab sample at the defined monitoring point and analyzing this sample immediately. Composite samples are not valid. Online instrumentation is viewed as an acceptable and sometimes desirable means of monitoring to determine compliance. The usual regulatory interpretation is that any reading that exceeds the permit limit constitutes a violation. Usually, on a legal basis, a facility can be cited for only one violation per day for a given pollutant. With online monitoring, all readings must be within the limits established in the permit.

ORP is a surrogate for measuring chlorine residual. It is not yet a legally defined method for measuring chlorine concentrations (must check the

regulations in each state). Therefore, an online ORP reading that strays outside process control boundaries may not be legally interpreted as a permit violation. On the other hand, a chlorine residual measurement that strays outside the permitted range will be counted as a permit violation. The POTW's NPDES permit should be reviewed, and research should be conducted on how the State regulates chlorine residual analyzers and ORP measurements for process control before selecting an effluent dechlorination control system.

Whenever an online instrument is used to monitor the effluent chlorine concentration, the regulatory agency may want to use the data from the chlorine analyzer to verify compliance. This is a very sensitive issue: Regulators often interpret any deviation from the permit limit as a violation. For example, if the supervisory control and data acquisition (SCADA) system records chlorine analyzer output readings every 20s and the State requires a 1-mg/l chlorine residual in the chlorine contact basin effluent, if even one data point (out of the 4320 data points collected/recorded during the day) is lower than 1 mg/l, the facility may be considered out of compliance for that day.

Calibration and maintenance functions may cause the analyzer to produce abnormally low readings during servicing of the instrument. If the regulatory agency is using the data from the analyzer to determine compliance, all maintenance activities must be documented to prove that the out-of-compliance reading was the result of maintenance activities, rather than poor process control.

A continuous analyzer should not be placed at the location defined in the NPDES permit as the point of compliance for sampling. The analyzer should be located upstream from this location, so the analyzer data are process control information and any grab samples collected at the point of compliance are compliance data.

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13 Operation and Maintenance

GENERAL

Proper operation and maintenance of chlorination systems are essential for the safe and effective disinfection processes of the water and wastewater treatment plants. The operators should have available for reference the design engineer's report delineating the system design criteria. This information is vital to the overall operation of the system because it specifies the capabilities of the equipment. Of equal importance are the chlorination equipment manufacturer's instruction books, one for each specific piece of equipment. It is imperative that operators take the time to familiarize themselves with the content of these books. As the manufacturers always provide supervision for installation, the operators should make it a point to have the manufacturers' representatives clarify any specific features of the equipment not adequately described in the instruction books.

If the chlorination system is part of a treatment plant complex, the following items should be available to the operator:

- The plant operation and maintenance manual.
- The project drawings and specifications
- A complete record of on each piece of equipment, including name of manufacturer, manufacturer's representative (if equipment not purchased directly from the manufacturer), identifying number (model), serial number, rated capacity, and dates of purchase, and date of installation.
- A Material Safety Data Sheet (MSDS) for chlorine gas or sodium hypochlorite

Other useful reference material is available through the Chlorine Institute at www.chlorineinstitute.org. Pamphlets on almost every chlorine related topic can be downloaded free of charge. They cover design and engineering information but also have specific industry standards and procedures for operating and maintaining chlorine systems. The institute also offers useful

operations and maintenance (O&M) materials including audiovisual media, drawings, and health and safety information.

Standard Operating Procedures (SOPs)

SOPs should be developed for the gaseous chlorination system. The SOP is essential for safe and consistent operation by plant personnel. It is a “living” document that should be updated whenever plant operating procedures are changed or equipment replacements are made. The SOP document should include the following information:

- Equipment name designation
- Equipment description
- Equipment function
- System controls
- Start-up procedures
- Normal operating valve positions
- Normal operating conditions
- Shutdown procedures
- Emergency operation
- Troubleshooting guide
- Safety procedures

The SOP document should list all major equipment of the system together with a general description of each component and all system controls, including local manual, remote manual, and remote automatic controls. Local manual controls are defined as controls located at local control panels in the field. Remote manual controls are defined as controls the operator can change, located at the human/machine interface. Remote automatic control is defined as the control by the plant control system to adjust for either flow rate through the plant or chlorine residual in the process water.

Start-up and shutdown procedures apply only to normal operation and should include a detailed step-by-step approach to starting or stopping all equipment associated with the gaseous chlorine system. If desired, a separate section on alternative operation can be included in the SOP to address operating scenarios during abnormal operating conditions.

A tabular format is best for describing normal valve operating positions, as it enables the operator to quickly identify the valve numbers in the field and to check the positions of valves throughout the system. It can also identify normal operating conditions, such as normal pressures at various points throughout the system, and normal ranges of flow rate and switch the settings and positions pressure or temperature switches and sensors (pressure or temperature) and sensor settings and positions in the system.

Emergency operating practices procedures that should be identified include emergency response measures and emergency contact information. Basic safety and chemical handling information should be included as well.

Finally, each SOP should also include a troubleshooting guide for typical system problems associated with chlorine systems such as equipment malfunctions, unexplained decrease of water supply, and chlorine. The troubleshooting guide should be comprehensive but not cumbersome to the operator. If a major problem is detected, the operator should switch to an alternative operating scenario and contact the maintenance staff.

Maintenance Plan

A maintenance plan is vital to continued operation and long equipment life. Preventive maintenance should be performed on a regular schedule as recommended by the equipment manufacturer. Unless otherwise indicated by operating experience, seals, gaskets, flexible tubing, and other wearing parts should be replaced according to the schedule established by the equipment manufacturer and/or recommended by the Chlorine Institute.

The preventive maintenance schedule should cover not only the chlorine gas system but also all ancillary components such as the water booster pumps, chlorine gas scrubber, and chlorine gas detectors.

The maintenance plan is a “living” document and/or electronic file system that should be regularly received, reviewed, and updated by the plant personnel. It should include the following:

- Equipment name
- Equipment designation
- Equipment function
- Manufacturers information
- Schedule of preventive maintenance tasks
- Lubricants and materials list
- Lockout/tagout procedures
- Safety information procedures

The equipment name, designation, and function provide the information needed for scheduling preventive maintenance, which is the most important part of the maintenance plan and should be followed strictly to ensure proper operation and long equipment life.

In addition, the maintenance plan should also include a list of the lubricants required to be used for each system component together with the type of lubricant, manufacturer, and the quantity required, as well as the plant lockout/tagout procedures, the appropriate safety and chemical handling information, and emergency procedures and contact information.

Residual Analyzer Maintenance and Calibration of Residual Analyzer

The chlorine residual analyzer may require slope (gain) and the zero (offset) calibration. Calibration is performed by first running deionized water through the unit and setting the zero (offset), followed by calibrating the slope (gain) of the unit using chlorine solution of a known strength and calibrating the slope (gain) of the unit.

The typical continuous amperometric analyzer consists of a cell assembly that receives the sample from the sample piping and/or the pumping system, plus electronic circuitry that interprets and records (or indicates) the information from the cell. Wastewater analyzers differ from potable water analyzers by being equipped with a filter in the sample line.

In potable water systems that add ammonia to produce chloramines or those that treat water with a natural ammonia content, it is necessary to measure the total chlorine residual. The sample pH must be lowered to 4 by adding buffer solution and a sufficient amount of potassium iodide to convert the total residual to free iodine. The amount of potassium iodide depends on the rate of sample flow through the analyzer and the concentration of the residual. Flow rates vary among equipment from different manufacturers.

Chlorine residual analyzers for wastewater systems need many more frequent calibration checks than those used in potable water applications. Also, since wastewaters generally have higher alkalinity than potable water, it is important to control the pH of the sample through the cell, as well as the amount of potassium iodide added, because of the need to maintain a higher residual concentration in wastewaters.

The sample pH must be kept at between 4.5 and 5.0, preferably at 4.5. Sufficient potassium iodide must be added to the pH 4 buffer solutions to allow completion of the chemical reaction between potassium iodide and chloramine residual. The residual reacts with the iodide to release free iodine in proportion to the total residual, and the analyzer cell measures the free iodine. A rule of thumb for potassium iodide addition is 15 g/l of buffer solution per 150 ml/min cell flow of undiluted sample per mg/l of total chlorine residual. The operator should consult the manufacturer's instruction book for proper calibration and operating procedures with respect to the buffer solution and the potassium iodide addition dose.

Once the analyzer has been placed into operation, it is not necessary to zero it each day. A zero calibration should be performed when changing the solution. Daily inspection of the sampling system to the cell is necessary to assure a continuous sample.

The sample line to the analyzer is subject to biofouling regardless of whether it is used in potable water or wastewater. The biofouling exerts a chlorine demand that gives a false reading at the analyzer. Since the sample flow usually does not reach scouring velocity, biofouling is particularly severe in wastewater systems, which contain grease. It is a good practice to routinely flush the

sample line with caustic or chlorine or to regularly replace the flexible tubing. The frequency of flushing will have to be determined by experience. In some cases, a chlorination point has been added to the dechlorination sample line to reduce biofouling.

In potable water systems, little maintenance is required, depending on the purity of the water being sampled. Sample lines in raw or untreated water can be equipped with a manually operated filter if necessary.

CHLORINE GAS SYSTEMS

Operation

Operation of chlorine gas systems can be either manual or automatic.

Manual operation requires manual adjustment of the rotameter located at the chlorine gas feeder. This mode of operation makes it difficult to maintain an appropriate residual and concentration unless the flow rate of chlorine is high enough to maintain the minimum required residual. This is a waste of chemical and could cause problems downstream if too much chlorine is added to the process.

The second control mode is automatic, which makes it easier to maintain the desired residual concentration and to reduce chemical consumption. Flow pacing, or compound control, is the preferred method. Flow pacing control uses a dosage set point and the measured flow of process water to determine the position of the rotameter at the chlorine feeder. Compound control uses flow pacing but will trim the feed rate of chlorine by a feedback signal from the chlorine residual analyzer located downstream from the chlorine injection point.

When chlorine feed rate is flow-paced, the chlorinator must be adjusted for zero and span. These adjustments are outlined in the manufacturer's instruction book. The adjustment is usually a combination of signal input and mechanical linkage, depending on the type of signal—pneumatic or electric.

The important point in attempting to adjust the chlorinator control mechanism is that the adjustment can be made properly only when there is a flow of chlorine through the machine. Since a chlorinator is not designed for zero flow, the zero adjustment is contingent on a mechanical linkage. As long as the injector is operating and even though the chlorine-metering orifice is adjusted to read zero on the rotameter scale, some chlorine will be passing through the chlorinator. This is easily verified by shutting off the inlet gas valve to the chlorinator and observing the chlorine pressure gauge gradually creep toward zero.

The most important aid to chlorinator adjustment and calibration is the signal simulators that simulate input signals from flow and dosage measurement devices to the chlorinator. The simulators used should be capable of providing input signals over the entire operating range of the chlorinator.

Special adjustments are required for chlorinators that operate from a variable vacuum signal, as the sole means of controlling the chlorine feed rate requires special adjustments. This mode is commonly used for straight residual control. The special adjusting procedure is outlined in the manufacturer's instruction manual and has to do with the zero adjustment of the chlorine inlet reducing valve. The accuracy of this adjustment, as well as the overall accuracy of this method of control, is greatly improved by the use of an external chlorine pressure-reducing valve (CPRV) installed in the supply system upstream from the chlorinator inlet, which takes the burden off the CPRV in the chlorinator. Without that additional valve, the chlorinator inlet pressure-reducing valve would be the primary means of controlling the variable vacuum system.

The only satisfactory means of measuring the flow of chlorine gas through a chlorinator is a differential transmitter. For this to be accomplished, an orifice is placed in the chlorinator gas discharge line. The orifice should be sized so that the vacuum differential will be 1 in. of water at maximum chlorine flow. The orifice is specific for a given size of rotameter. The transmitter consists of a spring-loaded diaphragm assembly, which must be mounted on top of the chlorinator to protect it against moist chlorine gas. Since the relationship of the chlorine flow to the vacuum differential is a square root function, the diaphragm movement is converted to a linear function by a characterized spring, making the diaphragm movement directly proportional to gas flow. The diaphragm controls the armature in a differential transformer, which puts out an alternating current (AC) signal. This signal is converted to a 4- to 20-mA direct current (DC) signal in a separate unit identified as a demodulator. Snap-in resistors are available to change the output signal to fit various receivers.

It is necessary to verify first the differential across the orifice at 100% of chlorine flow. This can be carried out by connecting a water manometer across the tubing that leads to the transmitter. This requires disconnecting the leads to the transmitter. The manometer should read between 10 and 14 in. of water differential. If it does not, the flow-measuring orifice should be checked according to manufacturer's instructions.

If the orifice is of the correct size, the zero setting of the demodulator should be adjusted to produce a mA current equal to the receiver zero signal, which will likely be 4 mA. The chlorinator should be turned on and operated at 100% flow. The coarse and fine spans in the demodulator should be adjusted to obtain a milliampere signal equal to the receiver-recorder 100% signal, which will probably be 20 mA. Zero and span should be rechecked and adjusted as required. The demodulator cover should be kept closed to keep out moisture and chlorine fumes.

Most control devices consist of a combination of long-lasting plug-in transistorized components; however, replacements for any of these components in the event of failure should be readily available. Devices with moving parts, such as potentiometers or safety devices that incorporate mercury switches,

are subject to wear, and a supply of replacement parts should be kept on hand. Reversible motors used in the control devices, such as electric chlorine orifice positioners and motorized vacuum valves, are also subject to failure even though they have a long and reliable service life. Information on the source and availability of these motors should also be readily available. Most components for electric control and alarm devices are readily available off-the-shelf items.

Air control devices are more vulnerable to maintenance problems caused by dirty or wet control air than to wear of moving parts. However, the moving parts such as belloframs and other types of diaphragm assemblies will eventually wear, and spares should be kept on hand. Flapper valves and seat assemblies can be cleaned and resealed many times before replacement is required. The various springs in a pneumatic system have a long life, up to 5 or 6 years, because they operate under normal atmospheric pressure.

Chlorine Gas System Maintenance

A typical chlorine gas/liquid system will include the following components:

- Container scale
- Manifold
- Expansion tanks
- Automatic switchover assembly
- Evaporators
- Gas filters
- Vacuum regulators
- Gas feeders
- Injectors
- Various pressure gauges/switches
- Diffusers

Although guidance on general maintenance guide is presented here for each major piece of equipment, it should not be considered a complete maintenance manual, and the manufacturer's operation and maintenance manuals should be consulted for specific maintenance instructions.

Chlorine gas is highly corrosive and will quickly react with atmospheric moisture to form hydrochloric acid. All components of the chlorine gas system can be occasionally subjected to small chlorine leaks and regular detailed inspections for corrosion damage, as necessary. Joints, fittings, and connections are particularly prone to corrosion and should be the focus of inspections. As a general note, chlorine is a powerful oxidant and may react with some organic lubricants. Only approved lubricants listed in the operation manual should be used.

A scale will require little maintenance, but its rollers should be greased quarterly to prevent rusting or damage. The rollers are an important safety feature because a chlorine cylinder leaking liquid from a fusible plug must be rolled upright until the plug vents gas instead of liquid. The container lift bar should be inspected for any cracks or metal fatigue. The bridge crane or monorail should be kept in working order, and all components subject to wear should be inspected quarterly. The cable or wire rope should be inspected for burrs or defects.

The manifold should be inspected quarterly. Wear components subject to wear include the manifold isolation valve gasket, flexible tubing, and the yoke isolation valve. All worn parts should be replaced immediately to prevent a possible leak. It is a sound maintenance practice to regularly replace flexible pigtails regardless of condition. Some utilities replace pigtails every year. Replacement parts such as flexible tubing, connectors, and gaskets should be kept on site.

The chlorine system expansion tanks are an important part of the chlorine gas system. The expansion tanks allow the chlorine liquid to expand ahead of the evaporator. The rupture disk, which will activate if too much pressure builds up in the expansion tank, should be replaced annually on all chlorine expansion tanks.

The automatic switchover assembly should be inspected for proper operation by comparing switchover with the actual weight from the scale. A set point check for all pressure switches or instrumentation devices should be performed quarterly.

The chlorine evaporator should be inspected and cleaned annually or at 90% of the duty cycle. The evaporator should be flushed to remove deposits from the water used to heat the chlorine liquid. The inlet tubes, baffles, and other internal surfaces should be cleaned with steam to remove oily or non-volatile residue and inspected for evidence of corrosion and sitting any pits. If there are any doubts to the integrity of the unit, it should be hydrostatically tested, and all gaskets and seals should be replaced before it is returned to service. The set points of the instrumentation on the evaporator should be checked.

The chlorine filters remove capture debris and particulates in the chlorine gas. The chlorine filter pads should be replaced semiannually to avoid a large pressure drop across the filter, which would cause problems with the downstream equipment such as the vacuum regulator. The vacuum regulator should be inspected annually. The inlet filter to the vacuum regulator should be cleaned, and the gaskets should be inspected and replaced if necessary.

The chlorine feeder should be inspected and cleaned annually. All O-rings should be inspected and replaced if worn or oxidized. Diaphragms showing signs of cracks, cuts, or weak spots should be inspected and replaced. Lubricant should be applied to the diaphragm for reassembling, as recommended by the equipment manufacturer, and only approved lubricants should be used. The ejector should be inspected quarterly to ensure that it is operating at

the appropriate water pressure and flow and that it is producing the vacuum pressure recommended by the manufacturer.

Chlorine Detection Systems and Emergency Scrubber

Most leak detectors for chlorine are amperometric. However, there are others that respond to discoloration of impregnated strips or compounds, and some use a gas diffusion electrode.

The amperometric detector utilizes dual platinum electrodes as a sensor. The sensor is continuously wetted with a high-conductivity electrolyte solution in continuous contact with the air sample. The electrolyte is a glycerine-based potassium iodide solution diluted with distilled water, which keeps the platinum electrodes of the sensor clean. When the air in contact with the sensor contains chlorine, it reacts with the potassium iodide in the electrolyte by releasing free iodine, initiating an electric current across the electrodes, and the detector activates the alarms through an electronic circuit board. The electrolyte tank is equipped with a level indicator and with an activated carbon air filter that protects it against contamination by chlorine. The air sample is conveyed to the detector by a fan or sample pump within the instrument that draws air across the sensor. The sensor detects chlorine in the air sample, which is detected by the sensor in seconds. Most detectors can detect chlorine gas in air from 1 to 5 ppm volume, and alarms are typically adjustable from 0.5 to 3 ppm.

While initial installation is being prepared, the sensor containing the platinum electrode should be handled carefully. Body oil from hands can insulate the electrodes. The sensor should be cleaned with a household detergent by using a soft brush and rinsed with distilled water, making certain that the glass orifice is clean and dry and avoiding air bubbles in the sensor system that would block the flow of the electrolyte to the sensor.

The detector should be equipped with drain tubing for the disposal of spent electrolyte. The electrolyte reservoir has a capacity of about 5–6 qt. It should be filled with the electrolyte furnished with the unit without leaving any air space, to avoid excessive drip rate and unnecessary consumption of electrolyte. The electrolyte flow to the sensor should be checked to verify that the sensor and its electrodes are completely wetted by the electrolyte by using a cotton swab to spread the electrolyte around the sensor or by spraying the sensor with electrolyte or distilled water from a plastic spray bottle.

The electrolyte drip rate should initially be one drop every 5 sec to 1 min and should decrease to one drop every 2–5 min after a few hours. It will vary with changes in temperature and barometric pressure. Testing the response of the detector to chlorine involves turning on the power, mixing 3 or 4 drops of pH 4 buffer solution with an equal amount of household bleach in a small beaker to generate a small amount of chlorine gas, and holding the beaker 1 in. below the suction inlet pipe. The detector should respond in seconds. If it does not, the manufacturer's troubleshooting guide should be consulted for appropriate

corrective measures. After the initial alarm—or any future alarm—the sensor should be flushed with distilled water from the plastic wash bottle supplied with the detector. Leak detectors should be checked at least once a week.

The detector is often equipped with or connected to alarm lights for local indication of a leak and may also have audible claxons or horns. Additional relay contacts for external alarms and other equipment such as ventilating fans and emergency chlorine shutoff valves are provided.

Caustic soda chlorine scrubber systems consist of a packed bed and a caustic storage tank, one or more pumps for the caustic solution that is sprayed across the packed bed, and fans for drawing air from the chlorine storage room to the scrubber system. Dampers in the chlorine storage or feed area may also be used to close the normal HVAC vents or to open supplemental air supply vents. When a chlorine leak is detected, the scrubber sequence automatically begins, starting the caustic chemical pump and the air fans to draw air from the chlorine storage room across the packed bed. As the air passes through the caustic spray in the packed bed, the chlorine is absorbed into the liquid and mixes with the caustic to produce sodium hypochlorite. Once the chlorine leak is contained, the waste sodium hypochlorite should be disposed of in a proper manner, and the caustic storage tank should be refilled.

The scrubber should be inspected monthly to ensure that the nozzles, fans, and pumps are operational. The caustic solution should be tested regularly for the appropriate concentration, as sodium hydroxide reacts with carbon dioxide to form sodium carbonate. Caustic soda will absorb CO_2 from the air each time the scrubber operates, eventually forming carbonate solids. When the level of caustic in the tank drops below the level recommended by the equipment manufacturer or if the sodium carbonate content in the solution reaches 4%–5%, the caustic should be discarded, and the tank should be refilled with a fresh supply of caustic.

SODIUM HYPOCHLORITE SYSTEMS

In order to operate and maintain sodium hypochlorite systems at water and wastewater treatment facilities, the operator should refer to the material suggested at the beginning of the chapter.

Sodium Hypochlorite System Operation

There are essentially two types of sodium hypochlorite feed systems: storage and pumping systems, which purchase bulk sodium hypochlorite, and on-site generation systems, which produce sodium hypochlorite from a salt solution, both of which will be discussed below.

The storage and pumping system consists of a storage tank and a feed pump. The sodium hypochlorite is delivered to the site either in totes or in tanker trucks, and the tanker is transferred to a bulk storage tank, which is

equipped with a level indicator for inventory control and for monitoring the level in the tank level during filling.

A metering pump conveys the chemical from the tank to the application point. It can be operated either manually or automatically. In the manual mode, the pump is started from the local control panel, and the residual chlorine residual is monitored by the operator. In the automatic mode, the operator sets the chlorine dosage at the plant computer system, and the feed rate chemical is flow-paced by the process flowmeter, which regulates the amount of sodium hypochlorite fed to the process. The feed rate can also be trim-adjusted by using the chlorine residual monitor located downstream from the application point. Automatic operation is the preferred method, as it reduces chemical usage and leaves the operator free to perform other tasks.

Sodium hypochlorite is usually delivered at concentrations of 12%–15% by weight. At this strength, it has a tendency to off-gas, which can cause air binding in diaphragm pumps. Several methods are available to minimize the air binding, and most involve bleeding the trapped gas back to the storage tank. For off-gassing to be minimized in diaphragm-type pumps, the stroke length should be maintained at 50% or more, and the stroke speed at 20 per minute. Peristaltic hose pumps are not subject to air binding but are limited by the discharge pressure. Thus, the choice may be limited to diaphragm pumps. More recently, liquid vacuum feed systems similar to gas injectors have been developed and show promise for addressing the off-gas problem. These systems use an injector driven by motive water, but the suction from the venture draws the hypochlorite solution instead of chlorine gas.

Bulk sodium hypochlorite at 12%–15% will also decay, and the solution becomes weaker with time. Chemical deliveries stored for 30 days or longer may decay sufficiently to affect the required feed rate. If so, the metering pump must be adjusted either manually or automatically to account for the weaker solution. The decay rate is faster at higher temperatures and so the problem is more pronounced at plants in warm climates. If a stored volume of hypochlorite has decayed and a fresh load of chemical is delivered to the same tank, the feed rate must be adjusted to prevent a rise in the chlorine residual.

An on-site sodium hypochlorite generation system is considerably more complex than a bulk-delivered sodium hypochlorite feed system because of the amount of equipment involved. The system works by a brine solution (sodium chloride) flowing across an electrolytic cell, producing a weak sodium hypochlorite solution and hydrogen gas as a by-product. The solution is typically 1.0%–1.5% concentration. The hydrogen off-gas is explosive and must be diluted with air before it is vented to the atmosphere. Because the hypochlorite solution is very weak, the feed pumps are much larger for on-site generation systems, up to 10 times larger than commercial hypochlorite systems. However, weak hypochlorite decays much slower than commercial bulk solutions, so decay is not an issue for these systems. An on-site generation system can include the following components:

- Rectifier
- Electrolytic cell
- Brine dissolving tank
- Brine pump
- Sodium hypochlorite storage tank
- Sodium hypochlorite metering pumps
- Hydrogen dilution air blowers
- Water softener
- Water chiller

The water softener and water chiller may or may not be needed, depending on the water quality at the site. All components of the sodium hypochlorite generation system, except the storage tank and the metering pumps, operate in the automatic mode. If the sodium hypochlorite level in the storage tank drops to the predetermined low level, the generation system will start to produce sodium hypochlorite solution and to fill the tank. When the tank is filled, the generation system stops. The hydrogen dilution air blower operates continuously to prevent buildup of hydrogen gas. The exhaust from the tank is vented outdoors, above the sodium hypochlorite storage tank. The storage tank and metering pumps of the on-site generation system operate in the same fashion as those of the storage and feed only system.

Sodium Hypochlorite System Maintenance

The storage and metering pump systems require minimal maintenance compared with that required for an on-site generation system. Daily maintenance tasks for an on-site generation system include the following:

- Inspecting and cleaning strainers or filters in the water system
- Verifying that the inlet water pressure is 40–60 psi
- Checking the generation system for all alarm conditions by scrolling through the alarm history located at the generation system control panel and taking appropriate action
- Checking salt inventory to verify that availability of at least four days' supply is available in the tank
- Inspecting entire system for leaks, including pump, piping, and tanks

The inlet water should be tested weekly for hardness. If water hardness exceeds 10ppm, it can cause scaling or damage to the electrolytic cells. The rectifier should be inspected and cleaned with a vacuum cleaner every 6 months to remove dust and debris, and all connection should be cleaned and tightened. The system cables should be checked for wear and replaced as

necessary. The brine tank, including the associated piping and level control assembly, should be emptied and cleaned every 2 years.

The electrolytic cells may have to be cleaned by washing with muriatic acid to remove the buildup of calcium and magnesium resulting from hard water. The buildup may be caused by a faulty or a poorly functioning water softener. Excessive buildup will reduce the efficiency and shorten the useful life of electrodes. The manufacturer's recommendations should be followed precisely to avoid injury to personnel or damage to the equipment, and the spent muriatic acid should be neutralized prior to disposal.

The sodium hypochlorite tank should be periodically inspected for leaks and for loose connections around flanges and the pumps. Hoses on peristaltic pumps should be replaced every 6 months or more frequently if excessive wear is observed. Diaphragms on metering pumps in the sodium hypochlorite feed system should be replaced every 2 years or as recommended by the pump manufacturer. Other wearing parts, such as O-rings, gaskets, seals, and pressure switches, should be inspected and replaced as needed. Instrumentation set points should be checked periodically.

DECHLORINATION GAS SYSTEMS

Operation and maintenance of dechlorination systems at water and wastewater treatment facilities should be performed according to the same procedures as outlined in the beginning of the chapter, for the chlorination equipment. The same procedures also apply to the use of the safety equipment and start-up of dechlorination systems.

The same amount of superheat is required for using of an SO_2 evaporator as with chlorine: The higher the SO_2 vapor pressure, the better it is for the operation of the facility. Is very unlikely that high SO_2 vapor pressure would cause operating problems.

The only difference between the operating the injector systems for sulfur dioxide and for chlorine is that SO_2 gas is more readily soluble than chlorine in water. The sulfur dioxide injector system is operated in the same manner as a chlorine injector. Limiting the maximum strength of sulfurous acid solution in the injector discharge to 3500 mg/L will prevent breakout of molecular SO_2 at the point of application.

Sulfonator Operation

The same operating procedures as those described for chlorinators, including adjustments and calibration, apply to sulfonators. However, because many sulfonator systems rely on feed-forward control, the operating conditions differ slightly. The difference concerns the function of the ratio station

on the flow-pacing signal, ahead of the flow-residual signal multiplier. The ratio station is a precise dosage control instrument particularly valuable to feed-forward systems.

Sulfonator Maintenance

The characteristics of sulfur dioxide are so similar to those of chlorine that most of the maintenance procedures for chlorine systems are applicable to SO₂ systems as well. However, there are some exceptions. The life of the diaphragm protectors on the vapor and liquid pressure gauges of an SO₂ system is much longer than those of chlorine systems because of the lower vapor pressure of SO₂ (35 psi). The corrosion caused by moisture in the SO₂ system is almost identical to that for chlorine but is different from different metals. For example, in a chlorine system, line valves and header valves have monel trim, whereas those in sulfur dioxide systems have type 316 stainless steel trim.

Sulfur dioxide producers claim that the moisture content of their product does not exceed 40 ppm; however, it can escalate to more than 100 ppm mg/l during transfer from the producer's tank car into the packager's tanker truck. Experience in the San Francisco Bay area indicates that some supplies of sulfur dioxide are more corrosive than chlorine by a factor of 10 to 1, which suggests inadequate moisture control during the SO₂ transfer procedure. Attempts by the user to quantify and monitor the moisture content by the user proved fruitless; however, a preventive measures like that described below are available.

This preventive procedure involves the use of an evaporator to boil off accumulated excess moisture. The evaporator should be shut down once every day or every 3 days, depending upon the SO₂ use, by closing the inlet liquid line; the sulfonator vacuum relief line should be plugged, and the sulfonator should be allowed to operate to create a vacuum in the SO₂ evaporator container vessel. Because any moisture in the supply system will always float on the liquid SO₂, the first step is to withdraw the liquid SO₂ from the evaporator. Next, the moisture in the container vessel should be boiled off by drawing a vacuum through the sulfonator while maintaining the temperature in the SO₂ evaporator water-bath at 160–180°F.

The amount of moisture that collects in the container will depend on the moisture content in the SO₂ and the rate of SO₂ withdrawals of the SO₂. Therefore, the time and frequency of boil-off will differ for each installation. In most cases, moisture will be visible in the sulfonator rotameter tube, and when it disappears, the boil-off procedure can be terminated. The use of this procedure requires redundancy of the SO₂ evaporator equipment to continue operation during evaporator shutdown periods.

Installations not using evaporators will probably not experience corrosion as severe as those with evaporators. This problem is directly related to the increased corrosive activity of the heated SO₂ caused by the elevated

temperature of the moisture in the evaporators. However, those systems not using evaporators suffer a malaise of considerable importance. Owing to its low vapor pressure, SO_2 reliquefies readily in the supply system. This phenomenon interferes severely with the ability to meter the SO_2 with any degree of accuracy.

At installations that do not use evaporators, corrosion problems are less severe, since corrosive corrosion activity is aggravated by the heated SO_2 in the evaporators. However, systems that are not using evaporators are subject to different problems: Owing to its low vapor pressure, SO_2 reliquefies readily in the supply system, which makes it difficult to meter it with any degree of accuracy.

One of the major maintenance differences between chlorine and sulfur dioxide systems is in the leak detection equipment. Although the spot-checking with NH_4OH solution to locate leaks is the same for both SO_2 and chlorine, continuous leak detectors for the two chemicals differ considerably. The equipment for detecting SO_2 in the air is much more complicated than the equipment for detecting a chlorine leaks. Therefore, it is important to adhere to the manufacturer's instructions for its calibration and maintenance.

Although the control and metering systems for sulfonators are similar to those of chlorinators, they should never be used interchangeably for the two chemicals because doing so would result in a violent heat reaction.

DECHLORINATION LIQUID SYSTEMS

Operation and maintenance procedures for liquid dechlorination systems at a water and wastewater treatment facilities are similar to those outlined in the beginning of the chapter for other liquid chemical metering systems including sodium hypochlorite chlorination systems.

Operation of Liquid Dechlorination Systems

The chemical feed systems for typical liquid dechlorination agents such as sodium bisulfite, sodium metasilfite, sodium thiosulfate, and calcium thiosulfate are basically identical. Each system consists of a chemical tote or storage tank followed by one or more metering pumps. The operation is very similar to that of the liquid sodium hypochlorite feed system: The chemical is pumped from the storage tank directly to the application point.

The operator needs to enter only the required dosage, and operation and the pump stroke speed and/or stroke length will be automatically adjusted to the flow rate of the process and will be trimmed by the chlorine residual analyzer. This mode of operation is preferred because it requires minimal operator attention.

Liquid Dechlorination Systems Maintenance

The maintenance of the liquid chemical feed system is the same as for the sodium hypochlorite liquid feed system. O-rings, seals, and diaphragms should be inspected and replaced as recommended by the pump manufacturer. Daily inspections should include looking for leaks, checking pump discharge pressures, and monitoring chemical tank levels.

OPERATOR TRAINING AND SAFETY

Safety in handling chemicals depends largely upon proper operator training. As recommended by the Chlorine Institute, training should include the following:

- Instruction and periodic refresher courses in the operation of chlorination and dechlorination equipment
- Instruction in the properties and effects of all chemicals used at the plant
- Familiarization with all appropriate MSDS
- Procedures of reporting to the proper authorities all equipment failures and chemical leaks
- Instruction and periodic drills on emergency procedures and equipment and in the event of chlorine spills, fires, and other emergencies
- Instruction and periodic drills in the use of emergency kits and personal protection equipment
- Instruction and periodic drills in the location and use of safety showers, eye baths, bubbler fountains, and the nearest source of water for use in emergencies
- Instruction and periodic drills in the location and the use of first aid equipment

STORAGE SYSTEMS

Chlorine and dechlorination gas storage systems consist of 100- and 150-lb cylinders, ton containers, bulk chemical trailers, and rail cars. Sodium hypochlorite and dechlorination liquids are stored in totes or bulk storage tanks.

Small (100- and 150-lb) Gas Cylinders

The most difficult aspect associated with the use of small cylinders is the temperature sensitivity of chlorine gas. A cylinder exposed to the sun for an extended period should never be connected to the feed system without allowing it to cool under the chlorinator room temperature, which may take

several hours. If the cylinder and the chlorinator are connected while hot, the gas between them will cool rapidly, causing liquefaction of the chlorine at the inlet pressure-reducing valve. Impurities in the chlorine gas will precipitate during the liquefaction and the small ports are plugged in the chlorinator.

If a hot cylinder must be connected to the chlorinator, it should be cooled by wrapping the cylinder within a wet blanket or burlap and kept wet with a continuous small stream of water. As a guideline to operators, particularly in hot climates, when the chlorine pressure reaches 120 psi, trouble can be expected. The chlorinator room should be sufficiently insulated, or the cylinder should be cooled to keep the chlorine pressure below 120 psi. The problem is accentuated in areas where ambient temperature fluctuates widely over a 24-h period. The proper solution to this problem is insulation. The problem is aggravated if the chlorine feed rate is well below the maximum withdrawal rate, which for a 150-lb cylinder is 40 lb/day at 68 °F. Higher withdrawal rates will result in cooling of the liquid chlorine in the cylinder, thereby and thus reducing the vapor pressure. At a multicylinder installation where the chlorine feed rate exceeds 40 lb/day, an easy way to cool a hot 150-lb cylinder is to connect it to the chlorination equipment and to withdraw the gas at a considerably higher rate than 40 lb/day. For example, withdrawing chlorine from a 100- or 150-lb cylinder at a rate of 100 lb/day will lower its temperature and consequently the pressure by at least 20 °F in 30 min. The rate will stabilize at ambient temperature when other cylinders are connected so that the withdrawal rate is normal again.

Because of this temperature–pressure property of chlorine, cylinder discharging chlorine in the gas phase should never be exposed to the heat of the sun. There is also the potential hazard of a serious leak if cylinders are exposed to the heat of the sun. All chlorine cylinders are equipped with fusible plugs that melt at 158–165 °F to prevent the cylinder from rupturing in case of fire. Although such instances are rare, there have been cases of fusible plugs melting in the sun's heat.

Ton Containers

Withdrawal of gas from ton containers should be carried out in the same manner as from 100- and 150-lb cylinders. The maximum withdrawal rate is 400 lb/day at 68 °F. These cylinders containers can be cooled with water, as described above, or by exceeding the vapor withdrawal rate. Where multiple cylinders containers are used, a chlorine pressure-reducing valve is installed in the chlorine header adjacent to the containers.

Reducing the chlorine pressure to about 40 psi will eliminate liquefaction in the header and in the chlorinator. Reducing the pressure has the same effect as cooling the gas. Because liquefaction will occur in the pressure-reducing valve, a filter should be installed ahead of it to capture the impurities in the liquid chlorine that could clog the valve preceded by a filter.

Each ton container is equipped with two outlet valves and six fusible plugs, three plugs on each end of the cylinder. One outlet valve is used for withdrawal of gas, and one is used for liquid. These cylinders must be so positioned so that the two outlet valves are lined up in a vertical plane. The top valve is for withdrawal of gas, and the bottom valve is for liquid. Failure to vertically align the two outlet valves can cause serious damage to the chlorination equipment. If a liquid withdrawal system withdraws gas, it will result in severe loss of chlorine supply.

Certain precautions must be taken when manifolding ton containers used for liquid withdrawal. A hot cylinder should never be manifolded with cooler ones. The hot cylinder should be cooled by the procedure described for cooling the 100- and 150-lb cylinders. Failure to cool it may result in the partially cool empty cylinders being filled with chlorine from the hot cylinders, which could lead to hydrostatic rupture of the filled cylinder(s) and consequently to a disastrous accident. Therefore, it is important to make sure that the new cylinder being connected to the manifold is at the same temperature as the cylinders already connected. This will be revealed by comparing the vapor pressure in the new cylinders with those already in use. If there is a significant difference between these pressures, the new cylinders must be allowed to cool to the temperature of the online cylinders.

The best way to operate a system using ton containers is to never add a full cylinder to a group of partly full cylinders already online. The maximum liquid withdrawal rate from a ton cylinder is 12,000 lb/day.

Sulfur dioxide is available in ton containers, tanker trucks, and tank cars. Tanker trucks are used commonly throughout the United States, and suppliers using tanker trucks can usually furnish a storage tank for the user. Sulfur dioxide is prone to reliquefaction, which is undesirable when trying to meter the gas. Unless the container is "padded" with a propellant, its pressure at room temperature will be about 35 psi. If stored outdoors in a carport-type structure, the SO₂ gas in the header between the container and the sulfonator will reliquefy. If the SO₂ is to be used, in its gaseous form, the containers should be heated, since gas-phase systems do not operate well at temperatures below 85°F. They operate best at 100°F with an external pressure-reducing valve in the header adjacent to the cylinders. The best way to apply heat is to use a commercial Teflon-fabric electric blanket, immediately downstream from the container header valve. An alternative method is to install an evaporator and to raise the vapor pressure in the cylinders by using an air-pad system. Although SO₂ manufacturers may claim that gas withdrawal rates from ton containers can be as high as 500 lb/day, it is best to keep the withdrawal rate to 175–200 lb/day to avoid the reliquefaction.

Rail Cars

The most important operating consideration for rail car storage and supply systems is adequate instruction in proper procedures. A representative of

the chlorine supplier should be engaged to demonstrate the use of safety equipment and to outline safety precautions and preventive maintenance procedures. The most critical time for the large systems supplied by rail cars is the initial start-up, or start-up after a prolonged shutdown. The systems should always be started using the chemical in the gas phase first. A vapor leak is less hazardous than a liquid leak. When starting liquid withdrawal, the tank car (or storage tank) liquid valve must be opened very slowly to allow the piping system to be completely filled. If the valve is opened too quickly, the sudden flow of liquid chlorine will cause the emergency ball check valve in the liquid withdrawal tubes in the tank dome assembly to become jammed shut.

Liquid Chemical Storage

The use of storage tanks for SO_2 is popular because of the low vapor pressure of SO_2 (35 psi). The maximum load delivered by road tankers is 20t, which takes about 2–3 h to unload. After the sulfur dioxide gas has been transferred to the storage tank, the tank should be air-padded to about 60 psi, which is a convenient operating pressure. The pressure of the gas leaving the evaporator should be reduced to the sulfonator inlet pressure of about 25 psi. The sulfur dioxide storage tank should be so designed that the suction line on the tanker's compressor can be connected to the gas phase of the storage tank. This to speed up the unloading by utilizing the vapor pressure in SO_2 tank.

The most important maintenance task associated with the storage tanks applies to the valves in the tank's dome. A complete set of spare dome valves, including the safety valve, should always be kept on hand. The safety valve should be replaced every 2 years, but the liquid valve and the two gas valves in the dome should be serviced annually and sent to a company specializing in valve repair. After being cleaned and repaired, the valves should be hydrostatically tested for 500 psi.

The storage tank should be hydrostatically tested every 3 years. For this procedure to be simplified, two additional 3- or 4-in. flanged connections should be provided at either end of the tank and on the crown: One is for filling the tank with water, and the other is for the overflow. If such connections are not available, the safety valve can be temporarily removed and used as the water inlet, and the two gas valves should be manifolded together for the overflow.

The tank should be filled through a fire hose as quickly as possible, adding water until the overflow water is clear. Then the water should be removed by pumping, the interior with air padding or the tank should be inspected, and any remaining scale or debris should be removed by scraping. A storage tank that has not been properly flushed out should never be entered because any remaining chlorine will combine with body perspiration to form strong hydrochloric acid, which can cause painful burning of the skin.

The hydrostatic test is made after the tank has been washed, cleaned, and inspected. It is first evacuated of all gas using the eductor provided for this purpose and is then filled with water again. Tank must provide for this purpose.

Before handling any chemicals, the operator should thoroughly review the hazard information and should wear the appropriate personal protective equipment during filling, transfer, or emptying the tank. Sodium hypochlorite bulk storage tanks and other dechlorination liquid chemical tanks should be inspected frequently for leaks, cracks, and other defects, and tanks should be drained and expected once every 3 years. Flexible connections should be inspected and replaced if they show wear. When chemical is delivered to the site, an operator should be present to ensure that the correct tank is filled and that valves are in the correct operating position.

REGULATORY REQUIREMENTS

Regulatory Regulations requirements vary, depending on the chemicals stored on site and used. The U.S. Environmental Protection Agency (USEPA) regulates programs such as the Clean Air Act (CAA), the Safe Drinking Water Act (SDWA), and the Clean Water Act (CWA), although most states have received the authority from the EPA to administer the programs through state agencies. The three most common EPA programs that facilities are required to adhere to include a Risk Management Plan, SDWA and State Testing Reporting Requirements, and Wastewater Chlorine Use Reporting Requirements.

Chlorine gas is classified by the USEPA as an extremely hazardous substance under the Super Fund Amendments and Reauthorization Act (SARA title III). This piece of legislation, also known as the Emergency Planning and Community Right to Know Act (EPCRA), regulates emergency planning and reporting requirements for the storage and the use of hazardous and toxic chemicals. The extremely hazardous classification of chlorine gas requires to be inventoried and reported annually under the Tier II provisions of the Act.

Risk Management Plan

When congress passed the CAA amendments of 1990, it required the USEPA to publish regulations and guidance for chemical accident prevention at facilities using extremely hazardous substances. Within the regulations written by the USEPA, the Risk Management Program was established. The basics of the Risk Management Program include the following:

- Hazard assessment detailing the potential effects of an accidental release, an accident history for the last 15 years, and an evaluation of worst case and alternative accidental releases

- Prevention program that includes safety precautions and maintenance, monitoring, and employee training measures
- Emergency response program that includes emergency health care, employee training measures, and procedures for informing the public and response agencies should an accident occur at the site

Each facility must revise and resubmit the required information every 5 years. The Risk Management Program reduces chemical risk at the local level by informing local fire, police, and emergency response personnel of the hazards in the community.

Those covered by the Risk Management Program include sites generating, storing, or using hazardous chemicals defined in 40 CFR Part 68 Section 112(r) of the CAA. States that have been authorized by the EPA to administer this program may have additional requirements; therefore, the local authority should be consulted for details.

SDWA and State Testing and Reporting Requirements

The SDWA was originally passed by Congress in 1974 to protect public health by regulating the nation's public drinking water supply. It is the governing piece of legislation that regulates drinking water in the United States over the years and requires many actions to protect drinking water and its sources: rivers, lakes, reservoirs, springs, and ground water wells. The SDWA applies to every public water system. There are currently more than 160,000 public water systems supplying potable water to almost all Americans at some time in their lives. The responsibility for making sure that the water supplied by these public water systems is safe is divided among the USEPA, the states, the tribes, the water systems, and the public. The SDWA provides a framework in which these parties work together to protect this valuable resource.

Regulations under the SDWA stipulate minimum disinfection requirements by establishing appropriate chlorine residuals and contact times needed for sufficient protection against bacteria, viruses, and protozoa. This method of process control, called CT (chlorine residual $\times$ time), is now established as the standard for disinfection monitoring. More recently, the regulation was amended to include maximum chlorine residual levels as a method of controlling potentially dangerous by-products from the chlorination of drinking water.

The SDWA recognizes that, since everyone drinks water, everyone has the right to know what is in it and where it comes from. All water suppliers must promptly notify when there are any serious problems with water quality. Water systems serving the same people year-round must provide annual consumer confidence reports on the source and quality of their tap water including data on chlorine residuals and on disinfection by-products. In addition, all analytical results are to be reported to the regulatory agency within 10 days of receipt.

Wastewater Chlorine Use Reporting Requirements for Wastewater Facilities

The CWA is the cornerstone of surface water quality protection in the United States. The statute employs a variety of regulatory and nonregulatory tools to sharply reduce direct discharges of pollutants into waterways, to finance municipal wastewater treatment facilities, and to manage polluted runoff.

Evolution of CWA programs over the last decade has also included a shift from a program-by-program, source-by-source, pollutant-by-pollutant approach to more holistic watershed-based strategies. Under the watershed approach, equal emphasis is placed on protecting healthy waters and restoring impaired ones. A full array of issues are addressed, not just those subject to CWA regulatory authority. Involvement of stakeholder groups in the development and implementation of strategies for achieving and maintaining state water quality and other environmental goals is another hallmark of this approach.

Wastewater plants may be required to disinfect their effluent, depending on the location and receiving stream. In the not-so-distant future, all wastewater facilities will be required to disinfect their effluent before it is discharged to navigable waters. Adding chlorine used for disinfection can cause consequences downstream from the treatment plant. Chlorine use at wastewater facilities is monitored regularly, as it can be harmful to aquatic life. Therefore, the authorized regulatory agency will require monitoring of the chlorine residual in the process waters leaving the plant. The frequency of monitoring is listed in the discharge permit for the wastewater plant and reported to the regulating agency in the monthly operating report.

14 Chlorine Dioxide

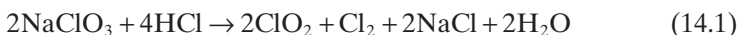
INTRODUCTION

Chlorine dioxide (ClO_2) is an oxidant that is widely used in the pulp and paper industry and has been successfully applied to drinking water supplies for oxidation, disinfection, color reduction, bleaching, and taste/odor control for many decades. There are several commercially available systems for generating ClO_2 on-site, which is typically required because it is highly volatile and not stable in highly concentrated solution. It normally cannot be shipped in the amounts needed for public drinking water plants, nor can it be stored on-site like other common water treatment chemicals at high concentration. ClO_2 does not react with natural organic matter (NOM, containing humic or fulvic acids) to form total trihalomethanes (TTHMs) or haloacetic acids (HAAs) to the same degree as chlorine. However, it does form two other inorganic disinfection by-products (DBPs): chlorite (ClO_2^-) and chlorate (ClO_3^-). It is also effective for iron and manganese oxidation along with controlling nuisance algae growth.

The popularity of ClO_2 for drinking water treatment is evidenced by the large number of publications in the technical literature during the past 50 years, especially since 1979, following the promulgation of U.S. Environmental Protection Agency's (USEPA) final rule for controlling trihalomethanes (THMs).^{1,2} Interest in ClO_2 surged thereafter because it does not form halogenated DBPs.

Historical Background

ClO_2 was discovered by Sir Humphrey Davy in 1811, who prepared ClO_2 gas by pouring a strong solution of sulfuric acid on potassium chlorate. Subsequently, Millon replaced sulfuric acid with hydrochloric acid, and this practice has continued to be used, especially in large-scale production facilities, but with sodium chlorate (NaClO_3) instead of potassium chlorate:



Today, most ClO_2 is used for bleaching paper pulp because it produces a brighter, stronger fiber than chlorine bleach and does not form environmentally harmful chlorinated by-products (e.g., dioxins). Virtually, all ClO_2 used for pulp bleaching is generated on-site from NaClO_3 in large quantities (i.e., tons per day).

The principal use of ClO_2 in North America for drinking water treatment has historically been for the control of tastes and odors that are caused by phenolic compounds. A Wallace & Tiernan survey reported in a paper by Jordan³ in 1981 showed that ClO_2 was being applied in North America for destruction of phenolic tastes and for oxidation of iron and manganese. Another survey found that Canadian installations were using ClO_2 to control tastes and odors caused by industrial-phenolic pollution of the receiving waters.⁴

While the water industry was using ClO_2 to control phenolic taste, it was also learning about the challenge of DBP formation in chlorinated supplies, and researchers began investigating the disinfection capability, and any associated DBP formation, of ClO_2 . In 1972, USEPA⁵ reported that industrial pollution of the Lower Mississippi River in Louisiana resulted in high concentrations of chloroform (a THM) in the chlorinated potable water of New Orleans. This triggered further investigations, which confirmed that chlorination was causing the formation of other undesirable chloro-organics. These findings spurred the industry to search for alternatives to chlorination.

Miltner's⁶ research showed that ClO_2 does not form THMs in drinking water and that it seemed to lower the concentration of precursors to THMs. These findings spurred new interest in the use of ClO_2 for potable water disinfection. Today, many drinking water utilities use ClO_2 for manganese oxidation, for taste and odor control, and for lowering THM levels.⁷ ClO_2 is routinely used in bench and pilot studies, and its use for inactivating chlorine-resistant *Giardia* will continue. ClO_2 is also an excellent disinfectant for inactivating not only *Giardia* but also *Cryptosporidium* and bacteria, and these topics are addressed later in this chapter.

European Practice

In Europe, where many surface water supplies have long suffered from industrial pollution, particularly from phenol spills, a 1977 survey reported chlorine dioxide installations at several thousand water treatment plants.⁸ Chlorine dioxide's popularity resulted from its superior power to oxidize phenols and chlorophenols without imparting off flavors and without adding a chlorinous taste and from its superiority over chlorine for pretreatment to remove iron and manganese.

Prevention of THM formation was a key using ClO_2 in many plants in France and other western European countries. Practically all of these installations were switchovers from chlorine. The following process train, with multiple barriers of treatment, is typical of a French water treatment plant:

- Pretreatment with ClO_2 at raw water pumping station to produce a residual of 0.5–2.0 mg/l
- Flocculation and sedimentation
- Filtration with sand and activated carbon
- Ozonation (1–2 mg/l)
- Clearwell storage for 30 min
- Breakpoint chlorination to remove ammonia N, if any
- Storage in another reservoir
- Postchlorination of finished water for disinfection and protection of distribution system (0.3 to 0.5 mg/l residual).

A variation of this treatment train might include chlorination and dechlorination, followed by for posttreatment with ClO_2 .

Historically, ClO_2 has been used in the United Kingdom for bleaching textiles and paper pulp. In 1948,⁹ however, it was concluded that it is effective against tastes caused by chlorophenols and algae and that it does not react with ammonium compounds.

Large-scale use of ClO_2 was first implemented in 1961, following trials at the Sutton Hall water treatment facility for the control of taste and odor.¹⁰ In the early 1970s, following an industrial dispute by the local government, it was not possible to produce a free chlorine residual at the Huntington water treatment plant as a result of the very high ammonia concentration in the River Dee. ClO_2 was used at the plant to overcome the ammonia problem.

Since about early 1970s, ClO_2 has been used in the United Kingdom primarily as pretreatment to remove algae-derived taste and odor, treatment of water containing phenolic compounds, and oxidation of iron and manganese. It has also been used successfully in the United Kingdom to eliminate water quality problems in distribution systems.^{9,10} However, the reinstallations have been few. The method used to generate ClO_2 has been the reaction between sodium chlorite and gaseous chlorine.

More recently, the use of ClO_2 in the United Kingdom has been limited by the restrictions on residual ClO_2 and its inorganic by-products in the treated water. The UK water quality regulations¹¹ stipulate that the combined concentration of ClO_2 , chlorate, and chlorite should not exceed 0.5 mg/l as ClO_2 . This would limit the dose to about 0.75 mg/l as ClO_2 .

Other Uses

Drinking water treatment is the dominant application of ClO_2 and is the focus of this chapter. However, its potency as a biocide, together with advances in ClO_2 generating methods, has made it attractive for other applications, such as wastewater treatment, industrial process water treatment, mollusk control, food processing, disinfection of food-handling equipment, oxidation of industrial wastes, and sterilization of medical instruments. The

vast majority of ClO_2 produced in North America, however, is used in the pulp and paper industry.¹²

CHEMICAL AND BIOLOGIC PROPERTIES

ClO_2 has unique chemical and biologic properties, which makes it an attractive oxidant and disinfectant for treatment of waters from many sources.

Chemical Properties

ClO_2 , a relatively small, volatile, and highly energetic molecule, is a free radical. Because of its instability, it is almost never used commercially at high concentrations as a gas. For treatment of potable and wastewater, it has been produced and applied as a dissolved gas in an aqueous solution. ClO_2 gas has an intense greenish-yellow color with a distinctive odor similar to that of chlorine. The odor is detectable at 0.1 ppmv in air. The short term exposure limit (STEL) of 0.3 ppmv can cause tears as well as coughing or throat irritation, and at 5 ppmv it can be fatal.¹³

ClO_2 cannot be compressed without detonation; it demonstrates induction periods, even of a few seconds, to detonation at aqueous concentrations above 4%. It is a gas at typical ambient temperatures. It has a boiling point of 11 °C and a melting point of -59 °C.¹³ Compressed liquid ClO_2 is explosive at temperatures higher than 40 °C;^{13,14} therefore, ClO_2 cannot be economically shipped and stored but must be generated at the point of use. The Department of Transportation (DOT) has recently approved shipping of small amounts of ~3 g/l ClO_2 for unique secondary uses.¹⁵

Typically, ClO_2 is generated in aqueous solutions at concentrations of 3 g/l or less, depending on generator design and rated production capacity, but it can safely be generated at about 4 g/l under most conditions. It is the volatilized ClO_2 that results from storing generated solutions without adequate ventilation, rather than the aqueous solutions themselves, that may be of concern. Likewise, accidental acidification of concentrated sodium chlorite solutions can result in rapid and uncontrollable release of ClO_2 at dangerous levels in closed containment such as in plastic shipping drums.

One of the important physical properties of ClO_2 is its high solubility and low hydrolysis rate in water, particularly at lower temperatures. The gas is soluble in water at room temperature: At 25 °C, it is about 23 times more concentrated in an aqueous solution than in the gas phase at atmospheric pressure (i.e., 760 mmHg), under which it is in equilibrium. The water solubility of ClO_2 depends on temperature and pressure: At 20 °C and atmospheric pressure, its solubility limit in water is about 70 g/l, but it is very difficult to achieve such high concentrations. In comparison, the solubility of chlorine is only about 7 g/l at the same conditions.¹⁶ In some patented generation systems, ClO_2 is initially formed (under high vacuum) in “vapor phase” by immediate

and intimate contact at very high concentrations between molecular chlorine and atomized chlorite held under extremely low vapor pressures by constant vacuum on the reactor column. Such transient mixtures of ClO_2 and any related asymmetric intermediates (Cl_2O_2 , Cl_2O_4 , and possibly HClO_2^-) exist in a gaseous phase only very early in the key reaction zone, being completely converted to ClO_2 well before being diluted by the ejector water to final concentrations, typically ranging from 1 to 4 g/l. Side reactions cease when the gaseous-phase ClO_2 is dissolved in dilution water passing through the ejector, about 0.5 ms after the precursors first enter the reaction zone.¹⁷⁻¹⁹

ClO_2 exists in aqueous solution as a dissolved gas but is extremely volatile and can be readily removed by aeration and vigorous agitation. For this reason, the ClO_2 concentration in solution is not stable when the solution is in an open vessel. If it is left in an open container, its strength deteriorates rapidly. Also, aqueous solutions of ClO_2 are subject to photolytic decomposition, the extent of which is a function of both time and the intensity of the ultraviolet component of the light source. Aqueous solutions of ClO_2 will retain their strength for periods ranging from a few days to several months if properly refrigerated in the dark.^{18,20}

Chemistry in Potable Water Treatment

Since the publication of the benchmark treatise by Gordon et al.,¹⁶ the chemistry of ClO_2 in water treatment has become better understood. Although ClO_2 does not belong to the family of “available chlorine” compounds (i.e., those chlorine compounds that contain elemental chlorine or are able to hydrolyze to form hypochlorous acid), the oxidizing power of ClO_2 has previously been referred to as having an “available chlorine” content of 263%, as calculated below.

The chlorine in ClO_2 is 52.6% by weight. The chlorine atom undergoes five valence changes in the process of oxidation to the chloride ion.



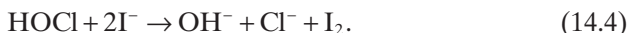
Thus, the equivalent available chlorine content is $52.6 \times 5 = 263\%$, which suggests that ClO_2 , at least theoretically, has 2.63 times the oxidizing power of chlorine.

This can be substantiated by the reactions that occur in the liberation of iodine from iodide in the acid starch–iodide analytical procedure at pH 2:

Chlorine dioxide:



Chlorine:



In drinking water treatments, however, ClO_2 is rarely reduced completely to chloride ion; therefore, its “263% equivalent available chlorine content” is not fully realized. Rather, the oxidizing power of ClO_2 is more likely attributable to its oxidation potential (0.95 eV), and only the one electron shift at pH7 in the following example showing oxidation of NOM:



Its efficacy as both a useful oxidant and a disinfectant is complemented by recycling the chlorite in the presence of free chlorine in drinking water with ClO_2 being reduced to ClO_2^- ion, which is then reoxidized to ClO_2 and so forth.

Selectivity as an Oxidant

ClO_2 functions as a highly selective oxidant, owing to the unique, single-electron transfer mechanisms, wherein it attacks electron-rich centers in organic molecules and, in the process, is reduced to chlorite ion.^{21,22} In contrast to chlorine, ClO_2 does not react by substitution reactions but purely by electrophilic abstraction, nor does it react to any significant degree with ammonia nitrogen or primary amines. It will, however, oxidize nitrite to nitrate.

Oxidation of organics to extinction, that is, formation of CO_2 and H_2O as end products, rarely occurs in redox reactions. Primarily, ClO_2 reactions alter charge ratios on NOM and thereby enhance coagulation during water treatment. ClO_2 also evokes differences in labile/refractile fractions of the NOM while delaying and reducing formation of chlorinated by-products such as THMs and HAAs.

High-purity ClO_2 that is introduced to water produces fewer DBPs than aqueous ClO_2 solutions, which often contain free chlorine and other oxychlorine species.²¹ In contrast to ozone, high-purity ClO_2 does not oxidize bromide ion to bromate ion, unless photolyzed.²¹⁻²⁴

Low molecular-weight organic compounds, such as aldehydes, ketones, and ketoacids, are produced by ClO_2 oxidation of NOM, but their concentrations are not as high as when ozone is the oxidant.^{21,22,25} Production of numerous compounds other than aldehydes, ketones, and ketoacids by ClO_2 oxidation of NOM has been reported.^{21,22} However, these may not persist because they are biologic nutrients, they are produced nonetheless.

Germicidal Efficiency

Since the introduction of ClO_2 for treatment of U.S. water supplies in 1944, many investigations have been conducted to determine its germicidal efficiency. Early investigations were carried out in sterile, chlorine-demand-free systems, and, usually, the biocidal efficiency of ClO_2 was compared with that of free chlorine. Other investigations compared the germicidal effects of ClO_2

and chlorine (as HOCl and OCl⁻) in ammonia-laden wastewater. In general, the germicidal efficiency of ClO₂ is at least equal to chlorine in water and increases as pH increases.²⁶ This is true because ClO₂ is a gas in water and, unlike free chlorine, does not hydrolyze quickly. Free chlorine solutions at pH more than 7.45 become increasingly dominated by the hypochlorite ion (OCl⁻), which is as a germicide, inferior to hypochlorous acid (HOCl), whose germicidal effectiveness increases markedly at pH values less than 7.45. In contrast, Ridenour and Ingols²⁷ reported that the germicidal efficiency of ClO₂ remained relatively unchanged at pH levels between 6 and 10.

Because of its superior germicidal properties over a wide pH range, the regulatory dosages for disinfection using ClO₂ are lower. In general, chlorine residual $\times$ contact time (CT) values for ClO₂ are much lower than those of chlorine or chloramines, although some values are close to those for chlorine in waters at neutral pH. Likewise, higher pH and lower temperatures in drinking water favor the use of ClO₂ over free chlorine because the required CT values for ClO₂ to achieve adequate disinfection are lower.^{18,28}

Inactivation of Viruses and Bacteria

Some of the references cited here discuss the efficacy of ClO₂ for inactivating bacteria alone or both bacteria and viruses in either water or wastewater effluent. In some references, the disinfection efficiency of ClO₂ was compared to that of chlorine and chloramines.²⁸

Ridenour and Armbruster²⁹ found that less than 0.1 mg/l ClO₂ for 5 min successfully inactivated the common water pathogens, *Eberthella typhosa*, *Shigella dysenteriae*, and *Salmonella paratyphi B*, at temperatures between 5°C and 20°C and at pH values above 7. An increase in pH resulted in an increase in germicidal efficiency, but this may be due solely to an elevated pH effect and not the chemical disinfectant itself.

Ridenour et al.³⁰ reported that ClO₂ was clearly superior to chlorine in destroying of bacterial spores when both oxidants were dosed on an equal residual basis. Their results showed that a 99.9% reduction of *Bacillus subtilis* could be achieved in 5 min when the ClO₂ concentration was 1.0 mg/l. A residual free chlorine concentration of 3.5 mg/l was required to achieve the same results. They believed that ClO₂ penetrated the *B. subtilis* spores and, in doing, so was reduced completely to chloride ion, which would equate to a transfer of five electrons. Their results also showed that ClO₂ was more effective against spores than against vegetative cells probably because the ClO₂ was reduced only to chlorite ion (i.e., a one-electron transfer) in those reactions. Malpas³¹ also concluded that the bactericidal efficiency of ClO₂ toward *Escherichia coli*, *Salmonella typhosa*, and *S. paratyphi* was as great as or greater than that of chlorine.

Hettche and Ehlbeck³² investigated the action of ClO₂ on poliomyelitis virus and reported that it is more effective than either ozone or chlorine. This superior effectiveness may be explained by a chemical characteristic of ClO₂,

reported by Ingols and Ridenour in 1948,²⁰ who found that ClO_2 reacted with peptone in amounts that followed the laws of adsorption. As viruses have a protein coating, it is likely that ClO_2 is adsorbed by the virus coating, thus resulting in local ClO_2 concentrations on the viral surface being higher than would be expected from the measured residual. This may explain why ClO_2 was proving to be superior to chlorine for inactivation of viruses. This theory appears to be compatible with the findings of Bernarde et al.,³³ who investigated the mechanism of bacterial kill by ClO_2 . Their work indicated that ClO_2 does not react sufficiently with amino acids to alter their characteristic structures, thus eliminating the possibility of a reaction within the cell. They found, however, that, in some unknown fashion, ClO_2 abruptly inhibits protein synthesis in viruses, which most likely is the mechanism by which it destroys them.

Bernarde et al.³⁴ also found that the ClO_2 molecule remained unaltered and intact at different pH values: specifically at pH 4.0, 6.45, and 8.42. They concluded that ClO_2 must therefore be the bactericidal compound. These results can be explained by the previously mentioned fact that ClO_2 does not hydrolyze in water as does chlorine.

Another important achievement of Bernarde et al.³⁴ was establishing the disinfecting ability of ClO_2 and its relative efficiency as a function of pH. The relative efficiencies of both ClO_2 and chlorine with respect to pH are illustrated in Figure 14.1. At pH 6.5, chlorine appears to be more efficient at the lower dosages. Both compounds are equally efficient at an initial dose of 0.75 mg/l. Increasing the pH to 8.5 results in a dramatic change in efficiency. As would be expected, the chlorine efficiency drops, for only 8.72% of the residual is HOCl at this pH level, whereas the residual is 89.2% HOCl at pH 6.5. As the efficiency of chlorine drops with the increase in pH, the efficiency

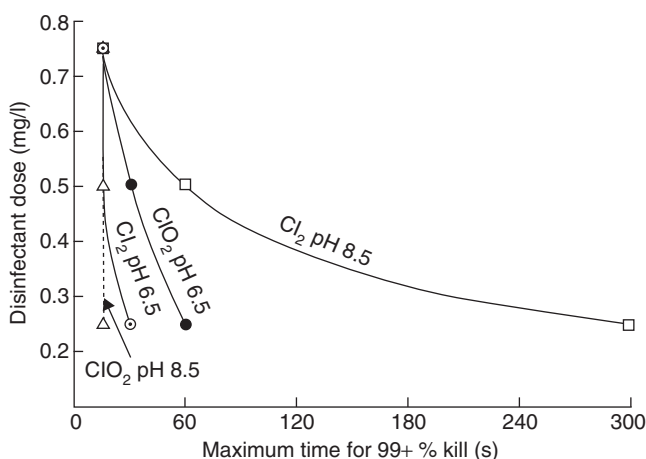


Figure 14.1. Relative germicidal efficiency of chlorine and chlorine dioxide. (dosage in mg/l versus time required for a 99+% destruction of *E. coli* at the pH indicated).³⁴

of ClO_2 increases. Greater than 99% destruction of *E. coli* is achieved in 15 s with a 0.25-mg/l dose of ClO_2 at pH 8.5 than with a 0.75-mg/l dose of chlorine.

Longley et al.^{35,36} compared the disinfection efficiencies of chlorine and ClO_2 in a sidestream from the effluent of a 90 mgd wastewater treatment plant; the flow rate of the sidestream through the contactor was about 0.9 mgd. A 5.0-mg/l ClO_2 dose reduced the fecal coliform population by 5 logs, or 99.999%, which was 1 log greater than that achieved with chlorine at the same dose and 30-min contact time. Moreover, the inactivation of fecal coliforms by ClO_2 in 3 min exceeded the inactivation by chlorine in 30 min at the same dosage.

Even more impressive results were observed for the viricidal efficiency of ClO_2 in comparison with that of chlorine under similar test conditions. The observed inactivation of coliphage after 3 min with ClO_2 was 3 log, or 99.9%, which exceeded the comparable inactivation by chlorine by nearly 2 log, or 99%.

Chlorite ion, the major by-product of ClO_2 in drinking water, has been shown to inhibit nitrifying bacteria that develop in distribution systems where chloramines are used for secondary disinfection. McGuire et al.^{37,38} demonstrated that chlorite ion inhibits nitrification in distribution systems at concentrations as low as 0.1 mg/l. The researchers found the same effect when the water was dosed directly with chlorite ion. In pilot-scale evaluations, intermittent dosing of chlorite ion delayed the onset of nitrification, but continuous feeding at dosages as low as 0.1 mg/l prevented nitrification altogether.

Chlorite ion does not inhibit all microbial growth. McGuire et al.³⁷ reported in 1999 that chlorite ion at concentrations as high as 1.0 mg/l and contact times of up to 24 h did not inhibit growth of either *E. coli* or heterotrophic plate count (HPC) bacteria. Rand et al.³⁹ (also showed that chlorite ion was ineffective for inactivating heterotrophic bacteria in either biofilms or suspended in water samples, but ClO_2 at a concentration of 0.2 mg/l achieved 1.8–2.7 log inactivation of HPC bacteria suspended in water samples and 1.3–3.3 log inactivation of HPC bacteria in biofilms.

Gagnon et al.⁴⁰ investigated the ability of continuous doses of ClO_2 , chlorine, and monochloramines to limit the regrowth of heterotrophic bacteria in bulk suspension and in biofilms. The biofilms were grown on two types of coupons: polycarbonate and cast iron. Each of the three oxidants was applied at two dosages: (a) ClO_2 dosages were 0.23 and 0.45 mg/l; (b) Cl_2 dosages were 0.47 and 0.95 mg/l; and (c) monochloramine dosages were 0.97 and 1.85 mg/l. ClO_2 was the most effective oxidant for limiting regrowth, followed by chlorine and then monochloramine. Test results showed that ClO_3^- was ineffective for inactivating heterotrophs, either in bulk solution or in established biofilms. Results varied with the type of coupon material. The authors reported that biofilm densities on the cast iron coupons were 18–32 times greater than those on the polycarbonate coupons, which affected the disinfection results.

Researchers at Stanford University^{41–45} conducted comprehensive evaluations of the efficiency of ClO_2 for inactivating natural coliform populations in

the effluent from three wastewater treatment plants using the conventional, activated sludge process. Two of the plants filtered in the secondary effluent, but the focus of this investigation was on the nonfiltered secondary effluent. All of the coliform studies were based on the natural population in the secondary effluent, but the virus studies were based on *Poliovirus I*, *LCS* strain grown on Buffalo Green Monkey kidney cell and inoculated into the effluents. Several disinfection experiments were run on different days.

Figure 14.2 compares the bactericidal efficiencies of chlorine and chlorine dioxide applied at three dosages. Three sets of samples were collected for analysis over a period of 30 min. The log survival ratios were then calculated and plotted as functions of contact time.⁴¹

The data in Figure 14.2 show that ClO_2 coliforms were inactivated more rapidly by ClO_2 than by chlorine at the shortest contact time (5 min) and the highest dosage (10 mg/l). However, at dosages of 2 and 5 mg/l, chlorine was marginally more effective. The mean log survival ratio in one set of experiments was -4.40 for ClO_2 , while this ratio was only -3.44 (i.e., 99.99964%) in the experiments for chlorine. Chlorine dioxide, however, proved to be superior to chlorine in other experiments when the activated sludge effluents were both nitrified and filtered. The authors stated that the superior disinfecting capability of ClO_2 in their studies was the result of filtration rather than nitrification because chlorine reacts with ammonia to form chloramines, which are

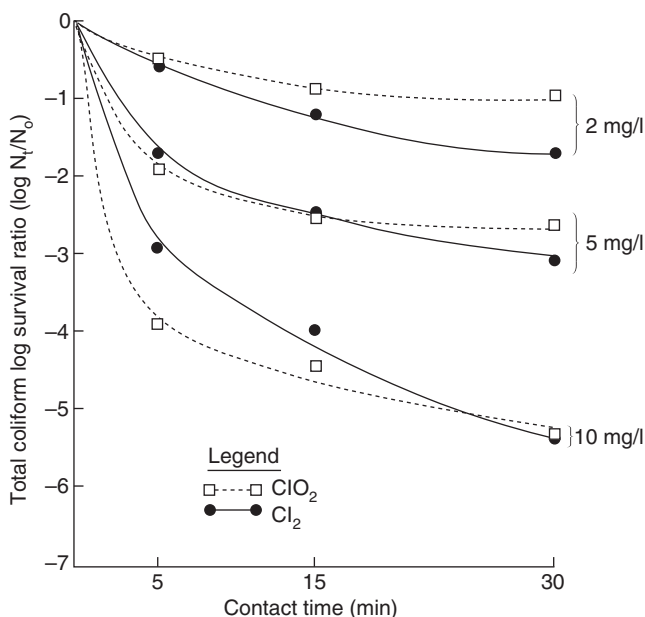


Figure 14.2. Comparison of germicidal efficiency between ClO_2 and chlorine showing coliform survival in nonnitrified secondary effluent.⁴¹

less effective as disinfectants. Chlorine dioxide, on the other hand, does not react with ammonia and, therefore, its germicidal efficiency is not affected by unnitrified effluents.

Roberts et al.⁴¹ compared the viricidal effectiveness of ClO_2 and combined chlorine for disinfecting wastewater effluent. Secondary effluents (nonnitrified) containing natural coliphage and an inoculum of *poliovirus I* were each dosed with 5 mg/l ClO_2 and 5 mg/l chlorine. Aliquots were collected at several intervals and analyzed for coliphage, poliovirus, and fecal coliforms. The results, shown in Figure 14.3, demonstrate that ClO_2 is a far better viricide

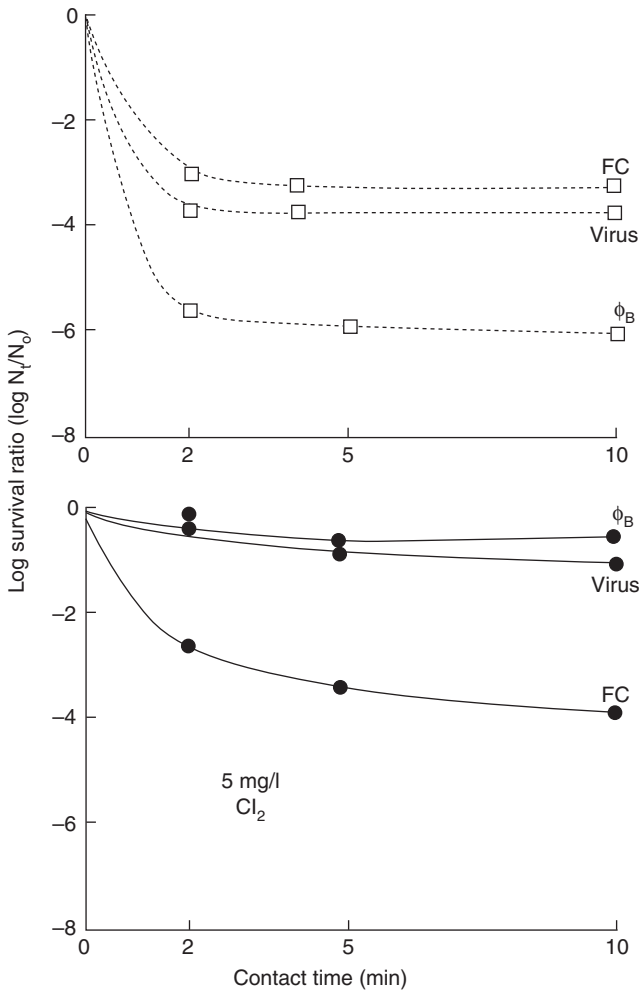


Figure 14.3. Comparison of viricidal efficiency between chlorine dioxide and chlorine using an *in situ* coliphage and an inoculum of poliovirus I in a nonnitrified secondary effluent⁴¹ 5 mg/l ClO_2 . ϕ_B , coliphage, *E. coli* B host; FC, fecal coliform; virus, polio virus.

TABLE 14.1. CT Requirements for Virus Inactivation by ClO₂⁴⁸

Log Credit	Water Temperature (°C)					
	≤1	5	10	15	20	25
2	8.4	5.6	4.2	2.8	2.1	1.4
3	25.6	17.1	12.8	8.6	6.4	4.3
4	50.1	33.4	25.1	16.7	12.5	8.4

than combined chlorine. The disinfection results on coliphage chloramines agree with the work by Snead and Olivieri.⁴⁶

The CT (concentration, mg/l × time [min]) requirements of the Surface Water Treatment Rule (SWTR)^{47,48} for virus inactivation by ClO₂ are listed in Table 14.1.

Encysted Parasites

Outbreaks of cryptosporidiosis and giardiasis due to ingestion of waterborne encysted parasites have been documented in the United States, Canada, and Great Britain.^{49–52} At practical doses, the most common drinking water disinfectants, chlorine and monochloramine, have been shown wholly ineffective against *Giardia* cysts and *Cryptosporidium* oocysts.^{53,54}

Cryptosporidium oocysts are smaller, harder to detect, and more difficult to kill than *Giardia* cysts. Among alternative chemical disinfectants, ClO₂ and ozone are the only promising candidates for controlling encysted parasites. Using comprehensive animal-infectivity studies as a measure of oocyst viability, Finch et al.^{55–57} have shown quantitatively that ClO₂ can achieve substantial levels of *Cryptosporidium* kill at practical dosages in one sensitive strain of the parasite, but other strains were shown in later studies by Chauret et al.²⁸ to be more resistant. These studies were the basis of action by the USEPA to disallow the use of ClO₂ for controlling *Cryptosporidium*. Fortunately, by then, the use of ultraviolet (UV) light irradiation for *Cryptosporidium* control had been investigated, but, for the most part, UV was given only one-half log credit in the Long-Term 2 Enhanced SWTR (LT2ESWTR) microbial toolbox.⁵⁸

Liyanage et al.⁵⁹ showed that the sequential use of oxidants, such as ozone followed by ClO₂, results in remarkable synergetic inactivation levels that exceed those achieved by applying these oxidants either individually or concurrently.

The C × t concept for disinfection is described in Chapter 4, but the principles apply for inactivation of both *Giardia* and *Cryptosporidium* in drinking water treatment plants. ClO₂ is very effective for inactivating *Giardia*, with CT requirements (Table 14.2) being easily achieved in waters where there is a low to moderate ClO₂ demand. The CT requirements for colder waters are higher.

TABLE 14.2. CT Values (mg-min/l) for Inactivation of *Giardia* by Chlorine Dioxide (from the SWTR)⁴⁸

Log Credit	Water Temperature (°C)					
	≤1	5	10	15	20	25
0.5	10	4.3	4	3.2	2.5	2
1.0	21	8.7	7.7	6.3	5	3.7
1.5	32	13	12	10	7.5	5.5
2.0	42	17	15	13	10	7.3
2.5	52	22	19	16	13	9
3.0	63	26	23	19	15	11

TABLE 14.3. CT Values (mg-min/l) for *Cryptosporidium* Inactivation by Chlorine Dioxide⁵⁸

Log Credit	Water Temperature (°C)										
	≤0.5	1	2	3	5	7	10	15	20	25	30
0.25	159	153	140	128	107	90	69	45	29	19	12
0.5	319	305	279	256	214	180	138	89	58	38	24
1.0	637	610	558	511	429	360	277	179	116	75	49
1.5	956	915	838	767	643	539	415	268	174	113	73
2.0	1275	1220	1117	1023	858	719	553	357	232	150	98
2.5	1594	1525	1396	1278	1072	899	691	447	289	188	122
3.0	1912	1830	1675	1534	1286	1079	830	536	347	226	147

Systems may use this equation to determine log credit between the indicated values: Log credit = $(0.001506 \times [1.09116]^{\text{Temp}}) \times \text{CT}$.

The LT2ESWTR⁵⁸ outlined the required CT values for *Cryptosporidium* inactivation. These are shown in Table 14.3. The CT requirements for the higher log removals are very high. Also, as the temperature rises, the CT requirement decreases. When the CT requirements for ClO₂ for *Cryptosporidium* are being calculated, it is important to recognize that the maximum contaminant limit (MCL) for ClO₂ is 1.0 mg/l, which limits the applied ClO₂ dose to about 1.4 mg/l. Thus, the maximum ClO₂ dosage, as well as the resulting residual after the contact time, limits the applicability of ClO₂ to waters, especially where there is a high ClO₂ demand because the low ClO₂ residual will not likely be sufficient to meet the CT requirements for inactivating *Cryptosporidium*.

EQUIPMENT AND GENERATION

The oft-stated goal of on-site ClO₂ generation is to achieve high generator “yield” or “efficiency.” But both of these terms are process oriented; neither

relates directly to the quality (or purity) of the ClO_2 produced and, unfortunately, neither is used consistently or in accordance with any generally accepted or enforceable definition. The lack of clarity with regard to these terms has led to confusion both in the ClO_2 literature and in the marketplace, and the issue is often clouded by the similarity in the rather limited number of feed-stock chemicals (only two or three), along with the lack of distinction among specific reactions that can occur in the many different generator systems.

Purity

The need for a simple, uniform, chemical *product-oriented* standard for ClO_2 has given rise to the use of *purity* as a precisely defined term of art; of necessity, it takes into account all of the following oxychlorine species:

Chlorine dioxide	ClO_2
Free available chlorine (FAC)	Cl_2 ; HOCl ; OCl^-
Chlorite ion	ClO_2^-
Chlorate ion	ClO_3^-

The following equation is a process-independent definition of the purity of ClO_2 solutions, expressed as a percentage:

$$\text{ClO}_2 \text{ purity (solution)} = \frac{[\text{ClO}_2] \times 100}{[\text{ClO}_2] + [\text{FAC}] + [\text{ClO}_2^-] + [\text{ClO}_3^-]} \quad (14.6)$$

Gates,¹⁸ however, stated that “absolutely pure aqueous ClO_2 solutions are difficult to generate” and that “there is no universally acceptable method for determining such purity or for comparing performance characteristics of different generators.” He noted that “the terms *yield*, *conversion*, and *efficiency* are used to describe generator performance and some of these processes.”

For ClO_2 gas, neither the chlorite ion $[\text{ClO}_2^-]$ nor the chlorate ion $[\text{ClO}_3^-]$ terms need be considered, since these ions do not pass from the reactor in the gaseous phase. Similarly, the $[\text{HOCl}]$ and $[\text{OCl}^-]$ terms drop out (unless Cl_2 is carried into the eductor water for injection into process), and the FAC term is thus simplified to $[\text{Cl}_2]$.

Commercial Generation Methods and Chemistry

Gordon,¹⁷ Gates,¹⁸ and Gates et al.¹⁹ have thoroughly addressed the chemistry and commercial generation systems. The key equations associated with reactions taking place in these generation systems are presented in the subsections that follow.

Historically, ClO_2 has been produced in commercial generators from 25% sodium chlorite (NaClO_2) solutions. The most common methods of disinfection for drinking water have been using chlorine gas dissolved in

water and then mixing with a chlorite solution, and allowing molecular chlorine gas to react with the chlorite under vacuum before adding dilution water in a completely separate design. A variety of three-chemical systems using hydrochloric acid, sodium hypochlorite, and the sodium chlorite have also emerged. Another method produces ClO_2 from solid rather than liquid NaClO_2 . Large generators that produce ClO_2 from chlorate salts have long been used by the pulp and paper industry, which produces many tons of ClO_2 each day. Only recently have three-chemical generators based on sodium chlorate (together with concentrated hydrogen peroxide and sulfuric acid) come into use in the drinking water industry, with one such advantage being driven by the fact that they do not need chlorine gas to make ClO_2 .

The USEPA⁶⁰ discusses the seven major classes of ClO_2 generators in its *Alternative Disinfectants and Oxidants Guidance Manual*, as summarized in Table 14.4, which was adapted from the guidance manual.

Acid–Chlorite Solution

Chlorine dioxide can be generated by acidification of sodium chlorite solution, and several stoichiometric reactions have been reported for such processes.^{16–19} When ClO_2 is generated from sodium chlorite by acid activation, the final composition depends on several variables that include sodium chlorite concentration, purity of sodium chlorite, acid concentration, pH of reaction, and the presence of chloride ion.

Sulfuric Acid. The two most widely accepted reactions for sulfuric acid activation of sodium chlorite are



and



The first reaction is catalyzed by the chloride ion, which is also a product of the reaction. It has been reported that the reaction is accelerated by the chloride ion and that the stoichiometry is altered by the presence of chloride ion to that of the second reaction.¹⁶

It is of prime significance that the reaction is only 50% efficient, but equally important is that it is a very exothermic reaction primarily because of the sulfuric acid. This causes a hot solution of ClO_2 to be produced, which leads to more rapid off-gassing of the volatile product. For these reasons, this method of using sulfuric acid to activate sodium chlorite to produce ClO_2 is not a very common practice.

TABLE 14.4. Commercial Chlorine Dioxide Generators⁶⁰

Generator Type	Main Reactions, Reactants, By-Products Key Reactions, and Chemistry Notes	Special Attributes
Acid–chlorite solution (direct acid system)	$4\text{HCl} + 5\text{NaClO}_2 \rightarrow 4\text{ClO}_{2(\text{aq})} + \text{ClO}_3^-$ • Low pH • ClO_3^- possible • Slow reaction rates	Chemical feed pump interlocks required Production limit ~ 25–30 lb/day Maximum yield at ~80% efficiency
Chlorine gas–chlorite solution (Cl_2 gas ejectors with chemical pumps for liquids or booster pump for ejector water)	$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow [\text{HOCl}/\text{HCl}]$ $[\text{HOCl}/\text{HCl}] + \text{NaClO}_2 \rightarrow \text{ClO}_{2(\text{aq})} + \text{H}/\text{OCl}^- + \text{NaOH} + \text{ClO}_3^-$ • Low pH • ClO_3^- possible • Relatively slow reaction rates	Excess Cl_2 or acid to neutralize NaOH used as a stabilizer for chlorite feedstock Production rates limited to about 1,000 lb/day High conversion but yield only 80%–92%. More corrosive effluent due to low pH (2.8–3.5) Concentration of ~3 g/l required for maximum efficiency. Production rate limited to ~1000 lb/day Yield of 92%–98% with about 10% excess Cl_2 reported. Highly corrosive to pumps; draw-down calibration needed. Maturation tank required after mixing.
Recycled aqueous chlorine or “French Loop™” (Saturated Cl_2 solution through a recycling loop before mixing with chlorite solution)	$2\text{HOCl} + \text{NaClO}_{2(\text{aq})} \rightarrow 2\text{ClO}_{2(\text{aq})} + \text{Cl}_2 + 2\text{NaOH}$ Excess Cl_2 or HCl needed due to NaOH formed in feedstock and by the above reaction	

Table 14.4. Continued

Generator Type	Main Reactions, Reactants, By-Products Key Reactions, and Chemistry Notes	Special Attributes
Chlorine gas–chlorite solution (Gaseous Cl ₂ gas is drawn through an atomized chlorite solution under vacuum)	$\text{Cl}_{2(g)} + 2\text{NaClO}_{2(aq)} \rightarrow 2\text{ClO}_2 + 2\text{NaCl}$ • Neutral pH, high purity • Rapid reaction rate under vacuum • Potential sealing in reactor under vacuum due to feedstock hardness	Production rates 5–120,000 lb/day. Ejector based, with no pumps. Motive water is dilution water. Near neutral pH effluent. Turndown rated at 5–10× with yields 90%–95%. Less than 2% excess chlorine. Needs calibrated flowmeters with minimum line pressure 40 psig.
Chlorine gas–solid chlorite (Humidified Cl ₂ gas is drawn or pumped through a stable matrix containing solid sodium chlorite.)	$\text{Cl}_{2(g)} + 2\text{NaClO}_{2(aq)} \rightarrow 2\text{ClO}_2 + 2\text{NaCl}$ • Rapid reaction rate • High purity and turndown	Cl ₂ gas diluted with N ₂ or filtered air to produce about 8% gaseous ClO ₂ stream. High turndown is possible with >99% yield. Maximum rate to about 1200 lb/day per column; more than >10,000 lb/day but needs moving heavy reactors more often than feasible.
Electrochemical (Continuous generation of ClO ₂ from 25% chlorite solution recycled through electrolyte cell)	$\text{NaClO}_{2(aq)} \rightarrow \text{ClO}_{2(g)} + \text{e}^-$ New technology	Countercurrent chilled water stream accepts gaseous ClO ₂ from production cell after it diffuses across the gas-permeable membrane. Small one-pass system requires precise flow for power requirement (Coulomb's law).
Acid/Peroxide/Chlorate	$2\text{NaClO}_3 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_{2(g)} + \text{O}_2 + \text{NaSO}_4 + \text{H}_2\text{O}$	Uses concentrated H ₂ O ₂ and H ₂ SO ₄ . Downscaled version. Foam binding. Low pH.

Hydrochloric Acid. The stoichiometry expected for hydrochloric acid activation of sodium chlorite is



Research has shown HCl activation of chlorite to achieve better results than those reported for sulfuric acid processes, with ClO_2 yielding more than 77%.¹⁶ Because of this relatively better yield and because the presence of chloride ion is helpful, hydrochloric acid is generally the reagent of choice for sodium chlorite acidification processes. When catalyzed by the chloride ion, activation of sodium chlorite by the acid has a maximum possible yield of 80% of the ClO_2 that theoretically could be produced from reaction of the same amount of sodium chlorite with chlorine. Acid chlorite solution processes can achieve production capacities up to about 100 lb/day.⁶¹

Chlorine Solution–Chlorite Solution

Chlorite ion will react in aqueous solution with chlorine or hypochlorous acid (HOCl) to form chlorine dioxide:



Thus, 2 mol of chlorite ions theoretically will react with 1 mol of chlorine (i.e., as hypochlorous acid) to produce 2 mol of ClO_2 . If the chlorine and chlorite ion react under ideal conditions and in a purely stoichiometric ratio, the resulting pH is close to 7. For the sodium chlorite solution to be fully utilized, which is the more expensive of the two precursors, excess chlorine is often used to overcome the alkalinity of the chlorite feedstock, to lower the pH, and to drive the reaction toward completion more rapidly, but at the expense of maximum purity.

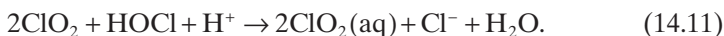
Equation (14.10), however, is a much simplified expression of the multitude of other reactions that occur during this process. Most of the inefficiencies in the reaction exist during the transformation of the stable intermediates in all ClO_2 reactions. Thus, more is involved than simply balancing chloride (Cl^-) in the equation.

Using a laboratory reactor to evaluate the chlorine solution chlorite solution method, researchers⁴¹ were able to achieve ClO_2 yields between 93% and 98% when chlorine was about 4% in excess of the chlorite-based stoichiometric requirement. The reaction time in the laboratory reactor was far longer than that used in continuous commercial generators, and yields were better than those produced in commercial settings. Nonetheless, this then-novel method of generation has the potential of producing a significantly better yield than the acid chlorite solution methods. Some researchers have claimed maximum yield from aqueous generator systems when the pH is on the order of 3.5–4.0.⁶² Others have reported that even lower pH may be desirable.⁶³

Because they are relatively slow, chlorine solution chlorite solution processes are, for all practical purposes, limited to production capacities of up to about 250lb/day.⁶¹

Three-Chemical Systems (D. A. Gates, pers. comm.)

Many conventional generator designs take advantage of using three chemical feedstocks (hydrochloric acid, sodium hypochlorite, and sodium chlorite) to avoid complications or restrictions of storing liquid chlorine on-site. While the chemical reactions are essentially the same as shown in Equation (14.10) above (i.e., some hypochlorous acid can form from the HCl and hypochlorite salt solution, which in turn can react with the chlorite to form ClO₂), the order and manner of mixing can affect the conversion efficiency and other dominant reactions drastically. Conventional and convenient systems that require mixing of all three precursors in a common reactor require the addition of dilution water to avoid exothermia, but this extends the reaction time considerably. These can often take several minutes (large reaction chambers on the generator) or require that the diluted solution be held in a batch tank while ClO₂ formation continues to near completion. These are usually mixed at a reduced pH from more efficient systems with subtle mixing and order changes as described below:



In a few unique systems, instantaneous prereaction of HCl and hypochlorite under vacuum (with no dilution water) allows transient formation of molecular chlorine within the reactor column, which can then react in turn with atomized chlorite in much the same manner as the “vapor-phase” gas chlorine systems described above:



And subsequently, immediately (i.e., approximately 50 μsec) within the reactor zone, the following reaction occurs:

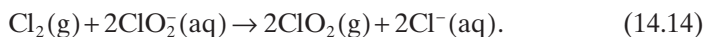


This second reaction, the ideal reaction discussed later to proceed through a stable intermediate dimer [Cl₂O₂] to form mostly ClO₂, has a much shorter half-life than any reaction between molecular chlorine and water that may be present; about 50–80 times faster, in fact. So all of the chlorine reacts with the atomized chlorite before the hypochlorous acid/hydrochloric acid can re-form by hydrolysis. By that time (i.e., 0.5 ms on the column), all the ClO₂ has been removed by the vacuum, and there remains no chlorite to form chlorate.

The key to these systems continuing to demonstrate proper function in the field (for several decades now) is that no substantial vapor pressure develops in the reactor zone. This sustains the formation reaction of ClO_2 under safe conditions in the reactor (by avoiding any potential time spent in solution or a significant partial vapor pressure to develop). These conditions virtually prevent those circumstances of concentration and time needed for induction to conflagration. Conventional systems may allow more concentrated ClO_2 solutions to develop sufficient vapor pressure leading possibly to dangerous gas-phase concentrations under atmospheric conditions, even at ambient temperatures. Ejector water driving the vacuum serves also as the dilution water after the reactor zone, which takes place only about 0.5 ms after the precursors are first allowed to mix. Proper design requires a vertical reaction column to avoid pooling along the sides or bottom of the reactor columns to force the molecular chlorine gas formed transiently to blow through the atomized chlorite and assist the removal of ClO_2 gas by expansion principles endeared through Henry's Law.

Chlorine Gas–Chlorite Solution

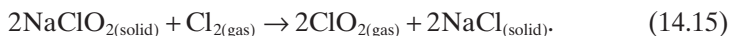
In a method that was, for some time, the industry standard, sodium chlorite solution is atomized in “vapor-phase systems™” and safely reacted under a vacuum with molecular chlorine in a highly efficient mixing ratio that is closer to stoichiometric ratios without the excess water that is usually required due to exothermic considerations. These systems can produce near-neutral pH generated solutions. This process uses undiluted feedstocks (sodium chlorite and the chlorine gas) as reactants and is much more rapid than the chlorine solution:chlorite solution methods. The optimal concentration for the reaction was found to be 25% active chlorite (i.e., 32% sodium chlorite by weight) and molecular chlorine without dilution. Generators employing the chlorine gas:chlorite solution process can reliably supply ClO_2 solutions that approach or exceed 95% purity, assuming that they are well calibrated, properly designed and maintained, and use properly inventoried sodium chlorite solution.²⁶ Benefiting from extremely fast reaction kinetics, the chlorine gas atomized chlorite solution process can produce many thousands of pounds of ClO_2 per day provided that the reaction conditions are favored by such conventional physical attributes as gravity (i.e., to avoid pooling along the reaction zone) and Henry's law (i.e., gases are easier to draw from the chamber than solutions; Trademark™ originally from Rio Linda Chemical Co.). This reaction is described by the classic formation described as



No reaction is required to describe the simple dilution step, which, in effect, stops all reactions effectively unless there is a huge oxidant demand constituent in the motive water.

Chlorine Gas–Solid Chlorite

Another method of generating high-purity, chlorine-free ClO_2 gas is by the reaction of dilute, humidified chlorine gas with specially processed solid sodium chlorite in a sealed proprietary reactor cartridge:



The reaction is rapid and produces high-purity ClO_2 gas free of chlorite and chlorate ions, which do not exist in the gaseous phase. Any unreacted sodium chlorite feedstock or any impurities it contains remain in the sealed reactor cartridge, and any excess chlorine is removed by passing the gas phase through a second reactor cartridge. Because the ClO_2 production rate depends *solely* on the chlorine gas feed rate, generators that employ chlorine gas solid chlorite technology are the only type of ClO_2 generators that are capable of high turndown; that is, the ClO_2 production rate can be adjusted without recalibration between settings.^{64,65} The chlorine gas solid chlorite method, limited only by the chlorine feed rate, can produce many thousands of pounds of high-purity chlorine dioxide gas per day.

The process described here differs from the superficially similar methods explored in the 1940s and 1950s,⁶⁶ which were inefficient at converting sodium chlorite to ClO_2 and were dangerous. It is the modified chemistry of the specially processed solid sodium chlorite that makes possible the efficient, safe, and reliable production of chlorine-free ClO_2 gas, which is usually educted into a carrier stream before it is applied to the water.

Electrochemical^{17,18,19}

The chief advantage of generating ClO_2 electrolytically at water treatment facilities is that there is only one chemical (sodium chlorite solution) and a power source; a disadvantage is that the generators can produce only limited quantities of ClO_2 and therefore are not suitable for larger utilities. The technology is not new in that it has been used for many years by the paper pulp industry for bleaching, but only recently have the generators been scaled down for use at water treatment plants. Currently available generators can produce 50–150 lb (23–68 kg) of ClO_2 per day, although larger units are under development that will be able to produce 300 lb (136 kg)/day.

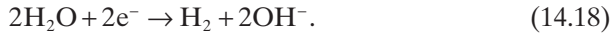
While, in principle, the process appears to be quite simple, it involves many related chemical reactions besides the formation of ClO_2 . The NaClO_2 solution enters the reaction chamber, and ClO_2 gas is produced at the anode by a one-electron transfer:



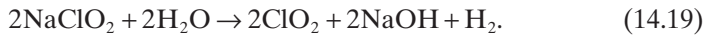
Electrolysis of water also occurs at the anode, producing oxygen:



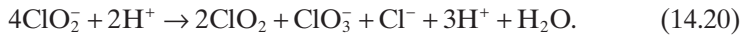
Hydroxyl ions (OH^-) and hydrogen gas (H_2) are produced at the cathode:



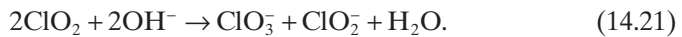
The hydrogen gas produced by this reaction is diluted with air and vented, and the hydroxyl ions react with sodium ions (contributed by sodium chlorite) to form sodium hydroxide at low concentrations. The overall reaction at the anode and cathode is shown below:



The caustic solution generated during the process is dilute but quite pure (i.e., food grade) and can be used for adjusting the pH of the process water. Under acidic conditions created by the electrolysis of water, chlorate ions can be produced from chlorite ion, as shown:



Under alkaline conditions created by the production of hydroxyl ions, ClO_2 can disproportionate to form both chlorate ion and chlorite ion, as shown below:



A small amount of chlorine can be produced from the oxidation of the chloride ion found in the feedstock sodium chlorite solution if the reactor pH is less than 5. Chlorine production will be greater if the pH is 2.5 or less. The equation describing the reaction is



The chlorine produced by this reaction (Eq. 14.22) forms hypochlorous acid and hydrochloric acid in water, as shown in Equation (14.23); both of these products further depress the solution pH:



The relative amounts of Cl_2 and hypochlorous acid (HOCl) shown in Equation (14.23) are dictated by the solution pH, with more Cl_2 being present at lower pH. Both acids can result in lower purity ClO_2 by forming chlorate ion or remaining in solution as free chlorine.

Small amounts of gaseous CO_2 can be produced from carbonate ion in the sodium chlorite feedstock, and it, along with the oxygen produced by the electrolysis of water, will appear in the ClO_2 gas product stream.

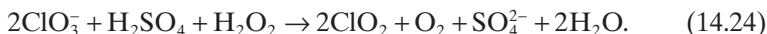
The hydrogen gas produced in the ClO_2 generation is diluted with air to one-fourth the explosion limit and vented to the atmosphere.¹⁸ Chlorine dioxide is removed from the anode portion of the reactor to avoid its oxidation to chlorate ion (ClO_3^-) and possibly perchlorate ion (ClO_4^-).¹⁷⁻¹⁹ Commercial electrochemical ClO_2 generation systems separate the ClO_2 by either airstripping or membrane separation.

Hypochlorite Electrochemical Systems. The second basic class of electrochemical generators utilizes the formation of hypochlorite and hydrochloric acid from brine and then mixes the effluent with sodium chlorite solutions in much the same way as the conventional three-chemical or direct acid reactions. The major limitation is 80% maximal yield, less the thermal and mixing inefficiencies of the physical process. It essentially is a two-chemical (brine and sodium chlorite) process but eliminates the need to store liquid chlorine, sodium hypochlorite, and hydrochloric acid on-site.¹⁹

Chlorate-Based Systems

Technology for the reduction of NaClO_3 has long been used for large-scale, on-site ClO_2 production for bleaching wood pulp to make paper. Chlorate-based ClO_2 generators have employed processes that use a variety of reducing agents, including sulfuric acid (H_2SO_4), methanol, and hydrogen peroxide.

Equation (14.24) shows the overall reaction between chlorate, sulfuric acid, and hydrogen peroxide:



Gordon¹⁷ noted that the optimized production of ClO_2 requires excess acid and peroxide for efficient conversion of ClO_3^- to ClO_2 and that the H_2O_2 -to- H_2SO_4 ratio is very important. He also noted that, because excess reactants are used, side reactions probably occur. Thus, the conditions for maximum ClO_2 production are not necessarily those that minimize by product formation. Equation (14.24) shows that molecular oxygen is a product of the process.

Chemical Feed Design Considerations

The design of a ClO_2 generation system involves many of the same principles as the other chemical feed systems, but the control and mixing of the precursor chemicals are vitally important in generating a ClO_2 solution with high purity. Details on the design of a ClO_2 generation system can be found in the *The Chlorine Dioxide Handbook*¹⁸ and the 2008 book by Gates et al.¹⁹ The

following section provides an overview of some aspects of batch tanks, chemical storage, and purity specifications.

Batch Tank

If the ClO_2 application will require intermittent feeding, multiple feed points, a wide range of generator turndown, or very small use, a ClO_2 batch tank should be considered in the system design. If the generator is started and stopped frequently, considerable operator attention is needed to maintain efficient performance and a batch tank is recommended. The ClO_2 solution can remain stable for several hours or even for several days under the right conditions.^{18,20} A batch tank makes it possible to produce ClO_2 solution in batches so that it can be metered in the process as would any other bulk chemical. The system is typically sized to produce one to four batches per day; thus, the solution is always relatively fresh.

The advantage of the batch system is that the generator can be tuned to produce high strength ClO_2 at a constant rate and at a wide range of dosages and feed points by using metering pumps instead of multiple ClO_2 generators. The disadvantages are the potential for the degradation of the ClO_2 solution, the additional equipment required, and the potential for ClO_2 gas to accumulate and to explode.

Storage

For ClO_2 generation using sodium chlorite solution, any impurities in the feedstock will pass through the generator and into the water being treated.¹² Commercially produced sodium chlorite solution is manufactured under strictly controlled conditions and is very high in purity, but its composition varies within a certain range. Also, if it outlasts its recommended shelf life, is exposed to extreme temperatures, or is otherwise mishandled, it may chemically degrade, which can result in impurities being carried through the generator and make it difficult to maintain the correct chlorine-to-sodium chlorite solution ratios needed for efficient generator operation. Therefore, utilities should follow all proper procedures in handling and analyzing their sodium chlorite solution inventories at least monthly. Measured values should include specific gravity and the concentrations of bulk sodium chlorite and sodium chlorate.

Purity Specification

Consistent with using purity as the standard for evaluating ClO_2 generator performance, the specifications for ClO_2 procurement should include the following language.

Vendor shall provide a means for on-site production of chlorine dioxide (ClO_2), that the ClO_2 produced is consistently at least 95% pure. In this specification, *purity* is defined as the weight ratio of ClO_2 concentration to the sum of the concentrations of ClO_2 , chlorite ion (ClO_2^-), chlorate ion (ClO_3^-), and FAC (FAC being Cl_2 , HOCl , and OCl^-) so that

$$\text{ClO}_2 \text{ Purity} = \frac{[\text{ClO}_2] \times 100}{[\text{ClO}_2] + [\text{FAC}] + [\text{ClO}_2^-] + [\text{ClO}_3^-]}. \quad (14.25)$$

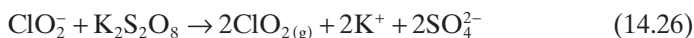
The ClO_2 production method shall be capable of maintaining the specified ClO_2 purity across the specified turndown range (e.g., 5:1, 10:1) without requiring recalibration between production rate set points.⁶⁷

Bench-Scale Generation of ClO_2

In preparing ClO_2 stock solutions for testing in the laboratory, it is important to generate solutions that contain no chlorine. Standard solutions of chlorine dioxide should be prepared on the same day the samples are collected for analysis and should always be shielded from light to prevent decomposition and the formation of ClO_3^- . The samples should be analyzed within 1 h of collection rather than shipped overnight to a laboratory for analysis. Useful guidelines for sampling generator effluent are presented in a 1994 AWWA Research Foundation report⁶⁸ and in the work of Gates et al.¹⁹

Potassium Persulfate–Chlorite Solution

A procedure for preparation of ClO_2 stock solutions in the laboratory consists of the reaction of sodium chlorite solution with potassium persulfate.^{69,70}



The following procedure is suitable for preparation of 300-mg/l ClO_2 solutions, although solutions up to 2 g/l can be prepared by using reagents of higher concentrations. The procedure uses 50 ml of 4% potassium persulfate, 25 ml of 16% sodium chlorite solution, and a generation apparatus with a three bubble-tower arrangement. A nitrogen source is connected to the first tower. The second tower, filled with approximately 50 ml of water, is attached to the first tower. A scrubber containing sodium chlorite solution is positioned between the second and third bubble towers, and the discharge from the third tower is directed to a 500-ml glass reservoir containing 300 ml of water. The sodium chlorite and potassium persulfate solutions are poured into the first tower and swept with nitrogen so that the ClO_2 generated is stripped from the solution and passed through the system to the collection reservoir for 15–30 min. Care must be taken avoid stripping the ClO_2 from the collection reservoir. After ClO_2 generation is completed (the collection reservoir liquid

should have a green-yellow color), the ClO_2 concentration is measured by ultraviolet–visible (UV-VIS) spectrophotometry.

Sulfuric Acid–Chlorite Solution

Another laboratory method for preparation of ClO_2 solutions is described in *Standard Methods*.⁷¹ Used by Hood,⁷² Roberts et al.,⁴¹ and Aieta et al.,⁴³ this method consists of generating ClO_2 by reacting sulfuric acid with sodium chlorite solution. Like in the persulfate method, nitrogen is used to transfer the ClO_2 gas from the reaction vessel to a final flask, which contains the resultant stock solution (Fig. 14.4).

Sodium Hypochlorite–Hydrochloric Acid–Chlorite Solution

When sodium chlorite solution is mixed with stoichiometric amounts of sodium hypochlorite and hydrochloric acid, ClO_2 is generated according to the following reaction:



To prepare 1 l of 1-g/l ClO_2 solution, add in the following order: 9.2 ml of 6% sodium hypochlorite, 1.4 ml of 12 N HCl, and 4.5 ml of 25% sodium chlorite to 985 ml of nanopure or distilled water. Mix for 1 min and allow to react for 10 min.

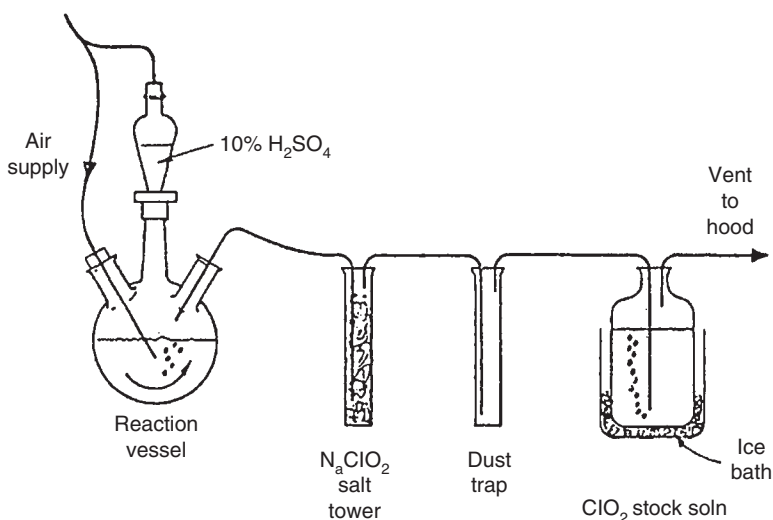


Figure 14.4. Laboratory ClO_2 apparatus using acid activator of sodium chlorite to produce approximately 500 mg/l of ClO_2 .

Gates (pers. comm.) recommends the following procedure for making a solution of approximately 3g/l of ClO_2 . Add 6ml of 12% HCl to 1l of water and mix thoroughly. Next, add 6ml of 15% bleach and mix. Next, add 8ml of 25% commercial sodium chlorite solution. Keep the liter sample jar on ice in an ice bucket for the duration, possibly 20min. Titrate to check purity, and adjust with slightly more sodium chlorite if excess chlorine is detected.

Chlorine Gas–Solid Chlorite

A bench-scale counterpart to the commercial chlorine gas/solid chlorite generation method is used by some leading researchers^{55,73} because of its simplicity. The bench-scale generator, however, may not be readily available. Specific laboratory certifications for handling and storing the cylinders of hazardous chlorine gas may restrict the process for some laboratories in research or public-access buildings. The process (Fig. 14.5) uses a preblended cylinder of 4% Cl_2 in a nitrogen gas carrier (Air Products and Chemicals, Inc., Allentown, PA), a humidification column, and a sealed reactor cartridge of specially processed solid sodium chlorite. The chlorine gas blend is bubbled through the water in the humidification column, and the dilute, humidified chlorine is transferred into the solid sodium chlorite reactor cartridge, where it produces high-purity ClO_2 gas. The gas, whose flow rate is controlled by a rotameter, can be dissolved in water to produce about 7.5g/l of stock solution. The generation process is essentially instantaneous. The concentration of the ClO_2 product gas is a function of solely the chlorine gas feed rate. Because the reaction chemistry is stoichiometric, according to Equation (14.15), each mole of Cl_2 feed gas produces 2mol of ClO_2 gas.

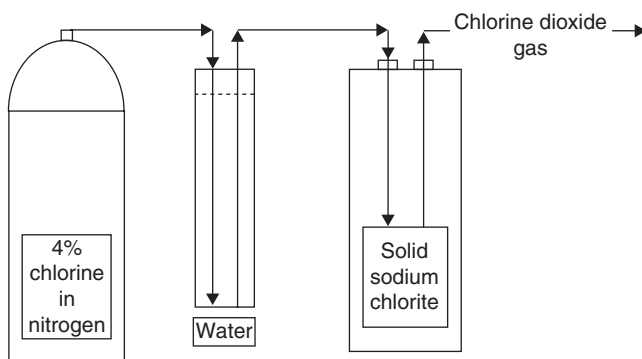


Figure 14.5. Bench-scale chlorine gas/solid chlorite generator (courtesy of CDG Technology, Inc., New York, New York, and Bethlehem, Pennsylvania).

USE IN DRINKING WATER AND WASTEWATER DISINFECTION

ClO_2 is a versatile water treatment chemical; however, each prospective application (taste, odor, and color control; manganese oxidation; or disinfection) may be subject to complex kinetic interrelationships in natural water. For the appropriate ClO_2 application to be determined, each water supply must be studied as a special case. Very often, the dose needed for biologic inactivation is a fraction of the overall oxidant demand of the water, but this demand must be met in order to carry a residual for a sufficient time to ensure adequate disinfection credit earned.

The measurement of oxidant demand, which is the difference between the added oxidant dose and the residual oxidant concentration after a prescribed contact time, is the necessary first step in applying ClO_2 or any other oxidant. ClO_2 demand generally increases nonlinearly with time and must be characterized for a given contact time under particular pH and temperature conditions. Oxidant consumption data generally cannot be extrapolated from one set of conditions to another; rather, studies corresponding to the range of conditions expected at the water treatment plant should be conducted, with samples taken at several time intervals so that proper demand curves can be constructed. Oxidant demand is discussed in Chapter 2, but the same procedures apply for ClO_2 oxidant demand testing. Only a few models for calculating or estimating demand have been developed for specific waters.⁷⁴

Drinking Water Primary Disinfection Application Points

Primary disinfection of groundwater was generally not required until the promulgation of the Ground Water Rule,⁷⁵ and secondary disinfection with chlorine or chloramines is typical. For surface waters, primary disinfection is required by the SWTR^{47,48} and the staged “enhanced” SWTR’s^{76,77} and LT2ESWTR⁵⁸ regulations, and the following feed points are typically used in drinking water treatment.

Raw water can be dosed with ClO_2 , and this is most feasible in clean surface waters containing low concentrations of oxidant-demanding substances such as iron, manganese, and naturally occurring organics. If the surface water contains high concentrations of these substances, a raw water ClO_2 -dosing location might not retain enough residual after the required contact time to meet CT requirements. In other words, ClO_2 will be reacting with constituents and not producing a residual for assessment of disinfection results. When ClO_2 is applied to raw water, it is usually for oxidation of iron and manganese (as discussed later in this chapter) and rarely for primary disinfection.

One commonly used application point for ClO_2 is in clarified water, after coagulation, flocculation, and some form of clarification (such as sedimentation and flotation). Clarified water will have a lower oxidant demand than raw water, and, in most instances, will provide a stable ClO_2 residual for assessing

results. The CT tables of the SWTR^{47,48} show CT requirements for different temperatures.

ClO₂ is not typically applied to the top of filters only because it is a dissolved gas and might cause some gas evolution within the filter bed, which can result in air binding and head loss.

Postfiltration disinfection with ClO₂ is common because the concentrations of oxidant-demanding substances are lower in filtered water, which improves the stability of ClO₂ throughout the required contact time. Because disinfection by ClO₂ is similar in the range of pH from 6 to 9, posttreatment pH adjustment can also be carried out ahead of the ClO₂ contact chamber.

Contactor Design Criteria

The design criteria for ClO₂ contactors are generally similar to chlorine contactors. However, given the higher decay rate and higher relative cost of ClO₂, more importance may be placed on the hydraulic efficiency of the contactor and the baffling factor (i.e., $T_{10}/T_{\text{theoretical}}$) used to maintain compliance with SWTR. The contact time (T) used to calculate CT is never based solely on hydraulic retention time but instead takes into account the various inefficiencies of contactor design. For hydraulic efficiency to be improved, ClO₂ should be added as low in the basin as possible rather than in open pipes. ClO₂ for preoxidation is often added in a raw water pipeline, which eliminates the need for a separate contact basin and has the added benefit of being granted a baffling factor of 1.0 for disinfection credit. Other application points may be at the rapid mix basin, which generally allows the ClO₂ reaction to proceed through the flocculation and sedimentation basins. Where ClO₂ is used for disinfection (i.e., using CT criteria), it may be appropriate to use a covered serpentine contactor similar to a chlorine contactor to maximize the disinfection efficiency.

Diffusers and Injectors

The design of ClO₂ diffusers and injectors is very similar to that of chlorine diffusers and injectors. PVC is acceptable for ClO₂ solutions; however, in high-velocity pipeline feed points, a Teflon®-lined and Teflon®-coated steel should be used to avoid shearing the diffuser pipe. The diffuser should be designed for mixing the ClO₂ solution into the main process flow. Dosing in open pipes or spillways, and injection upstream from aerators, GAC or lime feed points, or rapid mixers is not recommended to avoid ClO₂ escaping into the atmosphere.

Exposure to Sunlight

Studies^{78–80} have shown that ClO₂ will decompose to chloride and ClO₃⁻ when exposed to sunlight. This poses two problems. First, photodecomposition of

ClO_2 will result in lower residual concentration, which makes it more difficult for the system disinfection to meet CT requirements, and, although ClO_3^- in public drinking water is not regulated as a DBP by the USEPA, the California DPH has a notification level of 0.8 mg/l for ClO_3^- , but only as a residual pesticide of interest. As a DBP from both ClO_2 and hypochlorination practices, the potential health impacts of ClO_3^- continue to be researched, and it may be regulated by the USEPA in the future.^{81,82}

There is no regulated practice or requirement to avoid photodecomposition of ClO_2 , nor is there any regulation limiting the level of chlorate in drinking water. For areas where photodecomposition is likely, a covered contact basin is recommended. Some utilities use uncovered basins for ClO_2 contact time, but this practice is becoming less common, as utilities strive to protect disinfection basins from pathogens by installing covers. Clearly, the loss of the ClO_2 residual is a cost consideration, as up to 70% of the residual can be lost within a few seconds at depths of even a few meters in open basins exposed to bright sunlight.⁸³

Griese et al.⁷⁸ have discussed papers by Zika et al.⁸⁴ and Zepp and Cline⁸⁵ and proposed a sequence of reactions in which ClO_2 can be photolytically decomposed to chloride and ClO_3^- . Griese et al. demonstrated in pilot studies at the Evansville, Indiana, water treatment plant that water treated with ClO_2 at concentrations ranging from 3.56 to 3.99 mg/l and exposed to fluorescent lights contained ClO_3^- at concentrations of 0.36- to 0.97-mg/l ClO_3^- . Water treated in control tests in the dark did not contain any ClO_3^- .

These findings suggest that exposure to sunlight lowers the ClO_2 residual and causes an increase in the ClO_3^- concentration. The best practice is to apply ClO_2 in basins that are not exposed to sunlight, or at other locations where the treatment train are shielded from bright sunlight and in-line UV irradiation.

DBPs

ClO_3^- and ClO_2^- are the principal inorganic by-products of ClO_2 . In the pH ranges normally encountered in potable water and wastewater treatment, ClO_2 is reduced principally to ClO_2^- when it reacts with organic compounds.⁸⁶ There are many other considerations relating to these inorganic DBPs in public drinking water distribution systems that incorporate ClO_2 into the treatment process.⁸⁷

Chlorite

There are two principal sources of ClO_2^- :

1. *Generator-originated chlorite.* In generators that use sodium chlorite solution, some ClO_2^- can come from unreacted sodium chlorite feed-stock that passes through the generator and into the water that is treated.

2. *Reduction of ClO_2 .* A major source of ClO_2^- in treated water is the reduction of ClO_2 as it reacts with target compounds.⁶⁸ Up to 70% of the initial ClO_2 dose is converted to ClO_2^- in finished waters, although, theoretically, up to 100% of the ClO_2 dose can form chlorite by the one-electron shift.⁸⁶

When sodium chlorite solutions are used to generate ClO_2 , generator-originated ClO_2^- can be minimized by feedstock control, frequent generator tuning, and operating with a *slightly* chlorine-rich environment in some types of generators. Alternatively, this source of ClO_2^- is minimized by using properly designed and operated vapor-phase or chlorine gas-to-solid chlorite matrix generators, which have been shown to minimize any unreacted sodium chlorite feedstock by complete conversion and high-purity effluent from the various types of reactors. Low pH systems typically minimize chlorite (some even to nondetectable levels), but at the expense of producing some chlorate and excess chlorine in the generator effluent. This is due to a loss in conversion efficiency as well as increased production because of losses of the expensive chlorite feedstock.

The MCL for ClO_2^- is 1 mg/l.⁸⁸ To comply with this regulation, ClO_2 dosages in potable water treatment should be limited to about 1.4 mg/l, unless the excess ClO_2^- is removed by other processes. USEPA's Best Available Technology (BAT) for chlorite control remains limitation of the ClO_2 dosage rather than DBP removal techniques. This BAT can be realized by the selection of application points where oxidant demand has been decreased by treatment techniques such as coagulation (enhanced or otherwise), settling, conventional or biologically active filtration, or lime softening.

ClO_2^- formation is inherent in the use of ClO_2 . For the use of ClO_2 to be expanded, especially in waters with a high oxidant demand, ClO_2^- removal would be required. Two chemical processes are available for ClO_2^- removal; both use typical water treatment chemicals.

Reduced Iron. The use of reduced iron (i.e., ferrous) to remove ClO_2^- by reducing it to chloride ion has been successfully accomplished under laboratory-, pilot-, and full-scale treatment conditions.^{89,90} In the presence of reduced iron (Fe^{2+}), ClO_2^- is reduced to chloride (Cl^-):



This reaction is rapid at pH between 5 and 7 and is essentially complete in 15 s or less for 1 mg/l ClO_2 , and there is no evidence of ClO_3^- formation.^{12,91} The reaction is slower at high pH values (e.g., pH 7–10).⁹²

Sulfite Ion. ClO_2^- can also be reduced to chloride by sulfite ion, and this reaction is efficient when the pH is between 5 and 6.5. The reaction slows markedly at pH of about above 7.0 and is too slow for water treatment at very high pH

TABLE 14.5. The Half-life and Reaction Time for ClO_2^- Removal with Sulfite Addition⁴⁵

pH	ClO_2^- (mg/l)	SO_3^{2-} (mg/l)	Half-Life (sec)	Reaction Time for 99% ClO_2^- Removal
5.0	0.5	5.0	2.9	0.3 min.
5.5	0.5	5.0	38.0	4.4 min.
5.5	1.0	10.0	9.5	1.1 min.
6.5	1.0	10.0	130.0	15.2 min.
6.5	1.0	20.0	32.6	3.8 min.
7.5	1.0	10.0	8,020.0	15.6 min.
7.5	1.0	100.0	80.2	9.4 min.
8.5	1.0	100.0	4×10^4	3.2 days

values.¹² Slootmaekers et al.⁹³ made a comprehensive investigation of the use of sulfur dioxide/sulfite ion to remove ClO_2^- .

The stoichiometry of the sulfur compounds for ClO_2^- reduction is as follows:



This corresponds to 2 mol of sulfite ion (SO_3^{2-}) consumed for every mole of ClO_2^- removed. The reaction is considered to be 95% effective; however, the reaction time is an important factor. With a 10-fold excess of the sulfite ion and a ClO_2^- residual of 0.5–7.0 mg/l, complete removal of the ClO_2^- occurred in less than 1 min at pH values less than 5.0. At pH 6.5, less than 15 min was required. Based on these studies,⁹³ it was concluded that ClO_2^- concentrations could be reduced to less than 0.1 mg/l in drinking water. The reaction times for various concentrations of ClO_2^- with sulfite addition when the pH ranged from pH 5 to 8.5 are listed in Table 14.5.

Chlorate

There are five principal sources of ClO_3^- in drinking water: (a) oxidation of ClO_2 within some generators, (b) sodium chlorite feedstock impurities, (c) photodecomposition, (d) degradation impurity in sodium hypochlorite feedstock solutions, and (e) downstream oxidation of ClO_2^- by residual disinfectants such as FAC.

1. *Oxidation of ClO_2 (generation stage).* This is probably the main source of ClO_3^- in generator effluents, primarily from poorly operated systems or conventional acid–base generators. The ClO_2 generation reactions associated with the chlorine gas-to-chlorite solution, high chlorine water content (e.g., French loop, recirculated chlorine, or acid-enriched one-

pass chlorine ejector-based systems), along with the chlorine gas-to-solid chlorite methods (Eqs. 14.14 and 14.15) form a stable asymmetrical intermediate, Cl_2O_2 , that is very important in potential ClO_3^- formation.^{64,86}



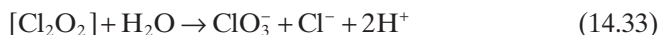
When there are high concentrations of both reactants in intimate contact, the intermediate is formed readily and produces mainly ClO_2 :



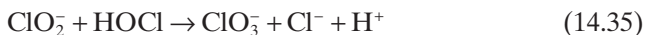
or



However, under conditions of low initial reactant concentrations or in the presence of excess chlorine (or hypochlorous acid), the intermediate forms ClO_3^- :



Thus, high concentrations of ClO_2^- favor the production of ClO_2 . This is another reason why some conventional two- and three-chemical generators can produce high-purity ClO_2 only at their maximum design range but fail when turned down to the 80% or 90% production range. Unwanted ClO_3^- production is favored in the presence of high concentrations of free chlorine, which can react with the Cl_2O_2 intermediate (Eq. 14.34). Some chlorate is also formed in reaction mixtures that are diluted too soon after mixing, as a result of deterioration of the intermediate through direct reaction with water (Eq. 14.33). This is the second way excess water can interfere with efficient generation of ClO_2 in some systems. Erroneous operation can limit efficient generation of ClO_2 in modern systems by incorrect design and misunderstanding of the chemical reactions. In some cases, directions for using the systems are ignored, and overfeeding chlorine to generators continues. Without really understanding the negative implications of the purity and yield in the resulting ClO_2 solutions, the systems are not routinely monitored for chlorate. The common generalization of “overfeeding chlorine” typically remains from the early and archaic methods of generation (some of which required up to 50% excess chlorine) and arises essentially from the widespread lack of understanding of the key formation reactions.¹⁹ The stoichiometry of the chlorate-forming reactions is



Besides being formed by the reaction from excess chlorine in the generator, ClO_3^- can also be formed downstream from its generation by oxidation of ClO_2 when other treatment chemicals, such as ozone, are fed simultaneously. Activated carbon, either as PAC or GAC, also results in the formation of ClO_3^- by the reactions on the activated surface. This is thought to be a result of the interaction with the acid-etched surfaces of the carbon used in its preparation.

2. *Feedstock impurities.* Commercial solutions of sodium chlorite can contain a certain percentage of sodium chlorate as an impurity (e.g., 5% of the total weight of a solution that contains 25%–34% sodium chlorite, according to American Water Works Association (AWWA) Standard⁶⁷ B303 [05]). If sodium chlorite is stored beyond its recommended shelf life or exposed to extreme temperatures (e.g., in dark drums or tote bins unprotected from hot sun), it may degrade so that its ClO_3^- content increases. In ClO_2 generation methods that use chlorite solutions, ClO_3^- in the feedstock is directly passed through the generator into the water being treated. Degraded hypochlorite solutions are the most common cause of poor chemical performance in three-chemical ClO_2 generators. In ClO_2 production methods that react chlorine gas or chlorine solution with ClO_2^- solutions, the amount of ClO_3^- that is a by-product can be minimized by careful handling of the feedstock and by frequent tuning of the generator to avoid the production of excess chlorine. In chlorine gas-to-solid chlorite generators, any sodium chlorate impurity in the sodium chlorite feedstock remains in the reactor cartridge. Thus, there is no possibility of generator-originated ClO_3^- with chlorine gas-to-solid chlorite-type generators other than downstream reactions in aqueous carrier streams.
3. *Photolytic decomposition of ClO_2 .* ClO_2 in solution can undergo a series of complex photochemical reactions that produce ClO_3^- . This issue was discussed in detail earlier in this chapter.
4. *Impurity of sodium hypochlorite solutions.* ClO_3^- has been shown to be an impurity in sodium hypochlorite solutions, (B. Bubnis, pers. comm.),^{17,94–95} with concentrations in aging feedstock sodium hypochlorite solutions above 6000 $\mu\text{g/l}$.⁹⁵

There are no cost-effective chemical methods to remove ClO_3^- . It cannot be removed by sulfur compounds, owing to its very long half-life at mg/l levels. Sloomackers et al.⁹³ reported that the calculated half-life of ClO_3^- treated in solution with excess sulfur dioxide/sulfite ion exceeds many months.

Beyond generator- and feedstock-related considerations, other steps necessary to control ClO_3^- formation are as follows: (a) Do not apply ClO_2 where

other oxidants like chlorine or ozone can reactive with either the ClO_2 or its main DBP chlorite, and (b) protect waters that were dosed with ClO_2 from exposure to light, or install basin covers.

THMs and HAAs

ClO_2 does not react with naturally occurring organic compounds to form TTHMs or HAAs. This was reported by numerous researchers.^{22,86,96}

Secondary Disinfection

Secondary disinfection, or carrying a residual into the distribution system, requires a long-lasting, stable compound so that disinfection occurs throughout the system over a very long contact time, possibly several days. ClO_2 is not effective for secondary disinfection in most North American facilities because the residual dissipates quite rapidly, and the distribution systems are usually not biologically stable. Therefore, free chlorine or chloramines are used for secondary disinfection in North America.

Some special circumstances should be considered when using ClO_2 for secondary disinfection in drinking water treatment. As noted previously, ClO_2^- in chloraminated distribution systems has been found to beneficially minimize the growth of nitrifying bacteria.^{37,38}

With free chlorine as the secondary disinfectant, severe odors have sometimes been reported at customer's taps when the water had been treated with ClO_2 at the water treatment plant.

Objectionable Taste and Odor Formation

A survey of 37 utilities using ClO_2 found that, although relatively rarely, strange odors were detected at customer's taps.⁹⁷⁻⁹⁹ Infrequent and seemingly random complaints of unpleasant odors were reported when ClO_2 was applied to drinking water. The odors were described as being similar to the odor of kerosene or cat urine. On investigation, these odors coincided with the presence of new carpeting in certain homes; the odors were apparently being formed in the atmosphere by a reaction between ClO_2 , which was purged from the water at the tap, and airborne chemicals from new carpet. In a later study, Hoehn et al.⁷⁰ found that ClO_2 concentrations less than 0.1 mg/l at the customer's tap could cause complaints of kerosene and cat urine.

It was also learned that ClO_2 can be regenerated from ClO_2^- , either directly or indirectly, by reactions with hypochlorous acid in the distribution system. This occurred even with very low or nondetected ClO_2 residuals at the consumer's tap. The offensive odors were produced by reactions between regenerated ClO_2 vapor that was escaping from the tap and volatile organic compounds in the household air, such as those released by new carpeting.

The investigation concluded that these odors can be prevented either if free residual chlorine is removed from the water at the entrance to the distribution system (e.g., by using chloramines instead of free chlorine), or if ClO_2^- is removed by using sulfite ion or ferrous salts.

Disinfection of Wastewater Effluent

The first critical study of ClO_2 for wastewater treatment was a laboratory investigation conducted by Bernarde et al.³⁴ in 1965 using sterile solutions seeded with *E. coli*. There is very little information on field experience with using ClO_2 as a disinfectant for either secondary or tertiary wastewater effluent. There are currently no known wastewater installations using ClO_2 (other than pilot plants) in the United States. Evaluation of ClO_2 as a wastewater disinfectant by the Stanford group,⁴¹ which dealt with wastewater effluents and the indigenous organisms populations, found that ClO_2 is only slightly superior to chlorine as a bactericide but is a much superior virucide.

The findings of the Stanford group were confirmed by a lengthy investigation in France.¹⁰⁰ Covering a period of 2–3 years, this study examined the disinfection efficiency of various disinfectants on effluents of varying quality: primary, secondary, and filtered secondary.

Although the disinfection of wastewater treatment effluent with ClO_2 appears feasible, it is not commonly applied in the United States. Some municipalities are evaluating ClO_2 for disinfection at reclamation facilities, and some of the research shows how ClO_2 can be used for disinfection while not forming TTHMs.¹⁰¹

Combined Sewer Overflow (CSO)

Many U.S. cities have combined sanitary and storm sewer systems.¹⁰² During heavy wet-weather events, the substantially increased water volume, a mixture of runoff and raw sewage, may greatly exceed the sewer capacity. This excess water is discharged, generally into local waterways, and is often the cause for closure of beach, riverbank, and lakeshore recreational areas. This is generally referred to a CSO. There is increasing regulatory and political pressure to treat this sewage–runoff mixture before discharge. However, this poses a number of technical hurdles: The runoff flows intermittently in huge volumes at wildly variable rates, its pH is subject to great excursions, and it can contain high concentrations of ammonia. Because of its high pH and ammonia content, this water can exert a chlorine demand as high as 100 mg/l. Another problem is that the high volumes and rapid flow rates make the available contact time very brief.

Because ClO_2 is unreactive with ammonia, is effective across a broad range of pH, is more soluble in water than chlorine, has a front-end-weighted bacterial kill curve, and is a stronger virucide than chlorine, it is a good candidate for treatment of CSO. The main drawbacks of its use for treating CSO are the

cost and maintenance of the system for intermittent use; therefore, there are currently no known installations using ClO_2 for treatment of CSO.

OTHER DISINFECTION APPLICATIONS

Medical Devices

ClO_2 gas is effective for sterilizing of packaged medical products.^{103–106} This use of ClO_2 , developed by Rosenblatt et al., begun as an alternative to gas sterilization using ethylene oxide. It was also the application for which the chlorine gas-to-solid chlorite generation process was originally developed.

Food Processing

Chlorination of food processing water in the United States, which began at potato dehydration plants, spread rapidly to fruit and vegetable canneries and frozen food packaging plants and became an established practice in the 1940s.

Originally, cannery water was supplied from a once-through system. However, after about 10 years of breakpoint chlorination, canneries began attempting to conserve water, primarily to cut down on the cost of treating the wastewater. A recycling system for food processing plants was developed. It was soon discovered, though, that the recycled water contained high concentrations of ammonia, which made it difficult to achieve breakpoint chlorination unless multiple points of application were used. It was eventually found impractical to pursue breakpoint chlorination because of the excessive chlorine consumption combined with the generation of large amounts of nitrogen trichloride, which spread throughout the working areas.

In 1975, the Green Giant Co. decided to try using ClO_2 .¹⁰⁷ Its Blue Earth, Minnesota, plant's chlorination system was retrofitted to generate ClO_2 . The prime objective was to evaluate the feasibility of water conservation through recycling while maintaining acceptably low bacteria counts. The experiment was highly effective in controlling bacteria growth and biofouling in pea and corn canneries. The persistent residuals and the lack of reaction with ammonia made possible one-point application, which was less cumbersome than the previous practice of using multiple chlorination points. The ClO_2 residuals in the recycled water did not produce offensive odors in the plant, nor were there any off flavors in the product.

This success spread rapidly to other food processing plants. Since 1975, a majority of processing plants have retrofitted their chlorination systems or purchased new ClO_2 systems. These plants include all types of food processing. In most cases, the ClO_2 dosages range from 2 to 8 mg/l.

ClO_2 has been proved effective for disinfection of poultry chiller water, which is known for its high content of organic matter,¹⁰⁸ and its use has been

approved by the U.S. Food and Drug Administration (FDA) for disinfection of some fruits and vegetables.¹⁰⁹

ClO_2 is particularly well suited for use in systems with high organic loading because, compared with chlorine, it is relatively nonreactive. A common perception of ClO_2 is that it is a stronger oxidizer than chlorine, that is, bleach or hypochlorous acid. This fallacy has been perpetuated because when a molecule of ClO_2 is fully reduced to a chloride ion, a total of 5 electrons are gained versus only one when hypochlorous acid is reduced. Furthermore, the oxidative potential for hypochlorous acid and ClO_2 is 1.36 and 0.95V respectively. However, what is not often recognized is that it is only the single electron gained when ClO_2 is reduced to ClO_2^- that provides the antimicrobial activity of ClO_2 . This one electron transfer results in a redox potential of 0.95V, which is insufficient to oxidize most polysaccharides, lipids, and most amino acids. Only the most labile compounds such as the tertiary amines in nucleic acids and disulfide bonds found in proteins are readily amenable to oxidation by ClO_2 . Thus, in an environment rich in organic substances (e.g., poultry chillers and flume waters for transporting fruits and vegetables), ClO_2 is an ideal candidate for water disinfection.

ClO_2 is commonly viewed as a compound that is able to traverse biofilms because unlike chlorine, it is a nonionic molecule. Unfortunately, there is no evidence to support the recalcitrant nature of ClO_2 vis-a-vis biofilms. In fact, a recent publication¹¹⁰ clearly shows that ClO_2 is consumed by biofilms. What might be the source of confusion is that hypochlorous acid is capable of oxidizing the polysaccharides that constitute biofilms, whereas ClO_2 cannot. The chlorine demand exerted by a biofilm may explain its weakened ability to kill the bacteria within the biofilm.

In addition to ClO_2 being relatively nonreactive to many organic compounds, ClO_2 will not oxidize ammonia as does chlorine when it forms chloramines. Chloramines are themselves biocidal but can generate odor issues that can be more offensive than hypochlorous acid itself. In a similar manner, ClO_2 can become troublesome because of its gaseous properties. For it to be used effectively, water containing ClO_2 must not be atomized, as this will result in off-gassing of the ClO_2 .

Aside from its disinfection properties, ClO_2 offers an advantage to chlorination in that it does not produce the number of toxic by-products of disinfection as does chlorine. This phenomenon is also related to its comparatively weaker oxidative capability such that it cannot transfer its chlorine atom to substances undergoing oxidation. Therefore, effluents that have been previously treated with ClO_2 are deemed less toxic to the environment than had it been treated with chlorine.

Other Pathogens

In 2001, bioterrorism attacks with *Bacillus anthracis* spores (the causative agent of the disease anthrax) were carried out in several locations in the

eastern United States. ClO_2 , along with bleach and hydrogen peroxide, was used as the decontamination agent.^{111,112}

OTHER USES FOR CHLORINE DIOXIDE IN WATER TREATMENT

In addition to disinfection, ClO_2 has several other beneficial uses in drinking water treatment, which include taste and odor control (for some compounds), iron and manganese oxidation, and zebra mussel control.

Taste and Odor Control

Historically, ClO_2 has been successfully used to remove tastes and odors arising from phenolic compounds.¹⁹ The success is attributed to the following factors:

1. ClO_2 reacts completely to destroy the taste-producing phenolic compounds many times faster than FAC does.
2. In all cases studied so far, it has been reported that ClO_2 will always destroy any chlorophenol taste caused by prechlorination.
3. The efficiency of ClO_2 is improved, not impaired (as is the efficiency of HOCl), by a high-pH environment.
4. ClO_2 also oxidizes other compounds that cause off tastes and odors, such as mercaptans and disubstituted organic sulfides. Krasner et al.¹¹³ evaluated the effectiveness of ClO_2 for removing compounds that cause fishy/swampy/grassy odors. They spiked a variety of odor-causing compounds into Colorado River water and State Project water, dosed the samples with 1.5-mg/l ClO_2 , and analyzed them after 1 h of contact. Only dimethyl trisulfide, dimethyl disulfide, and 2,3-benzopyrrole (indole), which produce swampy or septic odors, were oxidized. Several aldehydes, such as trans, 2-cis, 6-nonadienal, which causes cucumber odors, and cis, 3-hexen-1-ol, which causes grassy odors, were reduced to levels more than 50% of the original concentrations. Glaze et al. (1990)¹¹⁴ also reported that ClO_2 at treatment-plant dosages was only marginally effective in oxidizing dimethyl sulfide (swampy odor) in Colorado River water.

ClO_2 is generally ineffective at concentrations normally used in water treatment for eliminating most tastes and odors produced by algae and, in fact, may be responsible for either producing odorous compounds by oxidizing algal metabolites or unmasking odorous compounds already present in the water.^{115–118} The researchers used flavor profile analysis (FPA) and gas chromatography/mass spectroscopy. Dietrich et al.¹¹⁹ summarized the results from these studies, which were conducted with model organic compounds and compounds produced by algae in laboratory cultures. ClO_2 was ineffective for

removing the odors of β -cyclocitral (tobacco/grape) or phenethyl alcohol (floral/rose) but did eliminate the odor of linolenic acid (watermelon). Grassy odors were generated after ClO_2 treatment of linoleic acid and linolenic acid, both of which are nonodorous.

ClO_2 is also relatively ineffective for removing the earthy and musty odors caused by geosmin and 2-methylisoborneol (MIB), which are produced by blue-green algae (cyanobacteria) and actinomycetes. Glaze et al.¹¹⁴ reported that 3 mg/l of ClO_2 after 120 min removed only 17% of geosmin and 2% of MIB that was added to Colorado River water during pilot-scale evaluations.

Iron and Manganese Oxidation

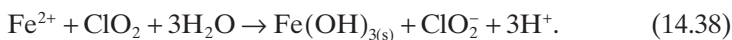
ClO_2 is very effective for oxidation of iron and manganese. Even in the presence of organic matter, ClO_2 , in excess of the stoichiometric requirement, can oxidize the metals to facilitate their removal by water treatment.

There are two possible reactions for oxidizing ferrous iron (Fe^{2+}) by ClO_2 . If ClO_2 is reduced to chloride, the following equation applies:



At a pH of 7, five electrons are transferred in the reduction of Cl_2 to Cl^- . Only 0.24 mg of ClO_2 is required to oxidize 1.0 mg of Fe^{2+} .

If ClO_2 is reduced to ClO_2^- , the following reaction applies:



In this reaction, only one electron is transferred, thus requiring 1.2 mg of ClO_2 to oxidize 1.0 mg of Fe^{2+} .

The oxidation of iron by ClO_2 occurs within seconds¹²⁰ at pH values greater than 5.5. ClO_2 oxidizes iron from the moderately soluble ferrous state to the ferric ion, which forms ferric hydroxide as a heavy gelatinous brown floc that can be removed by sedimentation followed by filtration. Note that chlorine is often preferred to ClO_2 for oxidation of iron, unless the water has a high THM formation potential or if it contains high concentrations of ammonia or other nitrogenous compounds that would exert a high chlorine demand or phenols or other compounds that react with chlorine to produce off-tastes and odors.

Manganese (Mn^{2+}) is also readily oxidized by ClO_2 . The oxidation reaction is as follows:



The stoichiometric requirement for oxidation is 2.45-mg ClO_2 /mg Mn. ClO_2 is oxidizing manganese at pH values higher than 5.0.¹²¹ If organic matter is present and exhibits a ClO_2 demand, excess ClO_2 must be applied to effectively oxidize the manganese.

ClO_2 is used by many utilities for oxidation of iron and or manganese. Research at Fort Collins, Colorado,¹²² has shown ClO_2 to be superior not only to chlorine but also to ozone and potassium permanganate for oxidation of manganese.

Usually, the amounts of iron and manganese involved in the removal processes are so small that the consumption of alkalinity caused by the above reactions will be insignificant. Manganese removals are usually less than 1.0 mg/l, and those for iron are less than 5.0 mg/l. However, if there is a significant reduction in alkalinity, it can be restored by the adding of commercially available chemicals, such as hydrated lime ($\text{Ca}(\text{OH})_2$), soda ash (Na_2CO_3), or caustic (NaOH).

Algae Growth Control

Stolarik and Liu reported on controlling of algae in the open reservoirs of the Los Angeles Department of Water and Power's distribution system.¹²³ In many cases, the higher cost of ClO_2 instead of chlorine to control the algae can offset the cost of the activated carbon needed to remove tastes and odors caused by the algae.⁷⁴

Zebra Mussels

Chlorine dioxide has been proved effective in controlling mollusks, such as zebra mussels (*Dreissena polymorpha*), which can clog the intake pipes of water treatment plants.⁹¹

DBP Control

Preoxidation with ClO_2 has been highly effective for decreasing THMs by altering the precursors and has been reported anecdotally to improve coagulation and settling properties, resulting in longer filter-run times.⁷⁴ It does not "destroy" THM's or their precursors by "oxidation to extinction" (i.e., oxidation to CO_2 and H_2O). It can alter charge distribution and produce different molecular weight fractions from NOM, avoiding substitution reactions while doing so.²² Mostly, ClO_2 suppresses THM formation in the water treatment plant by avoiding chlorine or other halo-substitution disinfection reactions long enough to lower TTHM precursor concentrations by physical methods, such as coagulation and filtration.

ANALYTIC METHODS FOR CHLORINE DIOXIDE AND ITS OXYCHLORINE BY-PRODUCTS

In 1998, the USEPA⁸⁸ established monitoring requirements for disinfectants and disinfection by-products, including ClO_2 and ClO_2^- , in public drinking

water supplies. ClO_3^- was not included in either the proposed rule or the final rule because no MCL had been established for it. However, ClO_3^- was included under the Information Collection Rule (ICR) promulgated in 1996.¹²⁴ The objective of the ICR was to provide the USEPA with information on DBPs and disease-causing microorganisms in drinking water, primarily at large treatment facilities.

USEPA regulations⁸⁸ require that the ClO_2 and ClO_2^- concentrations be determined daily at the entrance to the distribution system and that ClO_2^- concentrations be determined monthly at multiple points in the distribution system. If ClO_2 is used for inactivation of *Cryptosporidium*, the LT2ESWTR⁵⁸ requires that the CT be calculated at least once per day, during the peak hourly flow.

The Stage 1 DBP Rule approves three methods of daily monitoring of ClO_2 and ClO_2^- at the entrance to the distribution system in and only one method is approved for monthly determination of ClO_2^- concentration throughout the distribution system. The frequency of monitoring for ClO_2^- can be reduced to quarterly if its concentration in the distribution system is consistently less than the MCL.

Analytical methods that were originally approved by the USEPA⁸⁸ for daily monitoring of ClO_2 and ClO_2^- included amperometric titration (*Standard Methods* 4500- ClO_2 -E, Amperometric Method II⁷¹) and N,N-diethyl-p-phenylenediamine (DPD) method (*Standard Methods* 4500- ClO_2 D⁷¹). Since 1998, Lissamine Green B (LGB) has been added to the list of methods approved for monitoring both ClO_2 and ClO_2^- (USEPA Method 327.0 version 1.1). In the future, the DPD method may no longer be approved by the USEPA for drinking water measurement of ClO_2 and related by-products (P. Fair, pers. comm.). The only method approved for monthly ClO_2^- analysis at multiple points in the distribution system is the ion chromatographic method (USEPA Method 300.1). While there is no MCL for ClO_3^- , which is the other major ClO_2 by-product, it can be measured with the one remaining USEPA-approved method for ClO_2 and ClO_2^- ; however, this method is tedious and subject to considerable error. A more reliable method for determining ClO_3^- determination is ion chromatography (IC) by USEPA Method 300.1.

Analyzing ClO_2 , especially in solution, is complicated by its volatility, its sensitivity to light, instability over time, and interference from other redox species such as free chlorine, chloramines, nitrates, and sulfates. Also, some of the techniques are labor intensive, involve the use expensive equipment, and require a high degree of technical skill. Different methods are required for analyzing ClO_2 generator effluent and samples of drinking water from the system distribution, and many other constituents of potable water can interfere with measuring the of target compounds.

Gordon et al.^{125,126} critiqued the procedures listed in the 16th and 17th editions of *Standard Methods*^{127,128} for analyzing oxidants commonly used for disinfection and oxidation. These methods were virtually unchanged in

subsequent editions.^{71,129–131} In 1988, Gordon et al.¹³² summarized the oxidant-analysis methods in the first edition of their AwwRF report and presented an easy-to-reference table that listed detection limits, expected accuracy and precision of each method, and the overall operator skill level required for using these methods. The two most significant methods for have evolved in the ClO_2 field since then are Standard Method 4500- ClO_2 -E Amperometric method II and LGB (USEPA Method 327.0 version 1.1). USEPA-approved methods that use IC for chlorite and chlorate have significantly improved detection levels for monitoring inorganic DBPs associated with ClO_2 use since the drafting of the Stage 1 DBP Rule.

The LGB method is not included in the 21st edition of *Standard Methods* but is approved by the USEPA. All methods approved for compliance monitoring of ClO_2 and ClO_2^- are discussed in the following subsections of this chapter. All of the USEPA-approved methods for analysis of ClO_2 , except the LGB method, are “difference methods,” which means that concentrations are calculated as the difference between two other concentration measurements, which, according to Gordon et al., is a major disadvantage. On the other hand, the LGB method for ClO_2^- is a difference method and suffers the same disadvantage as the other differential methods for the analytes, with the exception of the ion chromatographic method, USEPA 300.1, for chlorite, chlorate, and bromate concentrations.

Several colorimetric methods other than DPD have been used for ClO_2 analysis, and three of them are discussed briefly in this chapter. The detection limit of each is less than 0.1 mg/l, but all are susceptible to false-positives because of high chlorine concentrations.

Iodometry

Iodometric titration of ClO_2 , Cl_2 , ClO_2^- , and, theoretically, ClO_3^- is based on the oxidation of the iodide ion at various pH values to distinguish these oxy-chlorine species from each other. The titration can be performed manually by using a starch indicator for end point analysis, as described in *Standard Methods* 4500- ClO_2 -B, Iodometric Method.⁷¹ However, iodometry is not readily practicable for ClO_2 analysis because it is subject to severe interferences, even with careful pH buffering and selective chemical masking. More accurate methods such as amperometric titration that is based on the same iodometry principles are available.

The introduction to the methods for analyzing ClO_2 , ClO_2^- , and ClO_3^- in the 21st edition of *Standard Methods*⁷¹ (Method 4500-A.) states that the iodometric method (4500- ClO_2 -B) gives a “very precise measure of the total available strength in terms of its ability to liberate iodine from iodide” but notes that “it is designed primarily, and best used, for standardizing ClO_2 solutions needed for preparation of temporary standards.” The iodometric method is also not appropriate for determining the various regulated oxy-chlorine fractions in water samples.

Amperometric Titration Methods

Concentrations of ClO_2 , Cl_2 , and ClO_2^- in water and wastewater samples can be readily determined by amperometric titration at concentrations in mg/l. At concentrations below 1 mg/l, the accuracy of the results depends primarily on the skill of the technician. Although techniques are available for using amperometric titration to measure ClO_3^- , they rely on the calculation of a small number by the difference between two large numbers. The results, especially for ClO_3^- at levels less than 1 mg/l, are subject to large errors.

*Standard Methods*⁷¹ includes two amperometric titration methods for ClO_2 , ClO_2^- , and ClO_3^- , but only the second (4500- ClO_2 -E. Amperometric Method II) was specified later by the USEPA⁸⁸ for daily compliance monitoring and generator performance evaluations. Only steps A, B, C, and D in Method II are used routinely, whereas step E, which is for ClO_3^- , is seldom included because it is a complicated procedure, and ClO_3^- concentrations are best determined by ion chromatography. Both amperometric methods are discussed below, but Amperometric Method I (*Standard Methods* 4500- ClO_2 -C) is no longer recommended by the USEPA for drinking water, as explained below.

Standard Methods 4500- ClO_2 -C, Amperometric Method I

This method is described on pages 4-78 and 4-79 in the 21st edition of *Standard Methods*.⁷¹ It is an extension of the amperometric procedure for measuring chlorine (*Standard Methods* 4500-Cl-D. Amperometric Titration Method, pages 4-62 through 4-65). A dual-platinum electrode assembly is used to measure the concentrations of the residual oxychlorine species in mg/l when ClO_2 is applied during the treatment of drinking water or wastewater. Due to inherent errors resulting from both underestimation of dichloramines (there is no pH 4 titration) and directly contributing to false high-positives (by organic chloramines appearing as apparent ClO_2 residuals), this method is no longer recommended by the USEPA for monitoring ClO_2 concentration in drinking water.

Amperometric titration is an electrochemical technique that measures current, in amperes, at a constant voltage. As a titrant is added to the titration cell, the current will change, based on the reaction of phenylarsine oxide (PAO) with the oxyhalogen. When the reaction is complete, a constant current is recorded, and the end point is reached:



This method is a sequential titration procedure that measures the various oxyhalogen species. The sample pH is first raised to 12 to decompose the ClO_2 to ClO_2^- and ClO_3^- . Upon the lowering of the pH to 7, the sample is titrated for Cl_2 . In the second sample, the pH also is first raised to 12 and then lowered

to 7, and potassium iodide (KI) is added to the titration flask to react with monochloramine to produce iodine, which is then titrated. To the third sample buffered at pH 7, KI is added, and the solution is titrated for free chlorine, monochloramine, and one-fifth the ClO_2 ($\text{ClO}_2 \rightarrow \text{ClO}_2^-$, one e^- or one-fifth the total). Potassium iodide is added to a fourth sample, and the pH is lowered to 2, where free chlorine, monochloramine, ClO_2 , and ClO_2^- ($\text{ClO}_2^- \rightarrow \text{Cl}^-$, $4e^-$ or four-fifths) react to produce iodine, which is then titrated with 0.000564 N PAO. Sodium thiosulfate (0.1 N) is typically used as the titrant for analyzing of samples such as generator effluent that contain higher concentrations of ClO_2 .

Standard Methods 4500- ClO_2 -E, Amperometric Method II

This method is described on pages 4–79 through 4–81 in the 21st edition of *Standard Methods*.⁷¹ Much like Amperometric Method I, the procedure consists of successive titrations of combinations of chlorine and oxychlorine species whose concentrations can be calculated but without the complications of indeterminate disproportionation at elevated pH along with the inconvenience of restoring the pH of the solutions to neutrality before titrating. Either PAO or sodium thiosulfate (NTS) can be used as the titrant. The total mass of the oxidant species should not exceed 15 mg. Sample volumes should be in the range of 200–300 ml.

Free and combined chlorine and one-fifth of the ClO_2 are determined at pH 7, then the pH is lowered to 2 and the remaining four-fifths of the ClO_2 and all of the ClO_2^- . Under even more highly acidic conditions (<pH 1), all the oxidized chlorine species, including ClO_3^- , are determined.

Amperometric Titration Equivalence Point

According to *Standard Methods*,⁷¹ amperometric titration should be carried out to the end point without presenting any information regarding what constitutes the end point. Many water and wastewater treatment plant operators and laboratory technicians believe the end point to be the point at which no deflection of the ammeter needle is observed. Actually, however, according to Lasagna et al.¹³³ it is “the point at which a stoichiometric amount of titrant has been added and the titration reaction is complete.” It is further described as “the volume of titrant where there is a maximum change in signal per unit time.” The authors also note that “for accurate results, the equivalence point and the endpoint should coincide.”

Gates (pers. comm.) clarified the definition of equivalence point as “the midpoint or inflection at the steepest slope” of the line in a plot of titrant volume along the x -axis of a graph versus milliamperes as meter deflection along the y -axis of a graph. This point is readily identified if either an autotitrator (if so programmed) or an electromechanical autopipette with sufficiently precise delivery increments (about 10 μl) is used. It can be more difficult

when manual titrations are performed by using conventional titration equipment, where visible movement of the needle in the built-in meter is the only indicator. The advantages to using the equivalence point rather than a null or zero “end point” are higher sensitivity and better reproducibility of the method. This approach is vastly superior to the convention of zero deflection as the indicator of the titration end point. Operators and most analysts have generally been trained to keep adding titrant until the meter reaches the lowest level, or the null deflection position, on the built-in ammeter of most instruments.

The first indication that the equivalence point is near is a sudden downward deflection of the ammeter needle. The titrant volume at which this occurs should be noted by the analyst, then the titration should be continued quickly until the needle stops moving downward the first time. This can usually be achieved in a properly working titrator equipped with a Pt/Pt or Pt/Ag electrode by adding a single drop or two of titrant such as 0.1 mol sodium thiosulfate.

A practical (but less accurate) end point is defined as the “final volume” added, although many analysts overshoot this point in the titration and do not stop adding titrant until a confirmed null-meter deflection is observed. Additionally, commercial autotitrators primarily used for Method 4500-ClO₂-E (steps A through D) have not typically been programmed to calculate this inflection point, but rather are preprogrammed to calculate the slope intercepting a null deflection value, which again leads to overestimation of the first-step volumes used in calculating the various species.

Iodine will re-form quickly at low pH from the excess iodide in the sample in the presence of light, and the ammeter needle will then rebound slowly, and iodine continues to be re-formed by current flux across the electrodes from iodide in amperometric methods (although this is not a widely known feature) and contributes inherently to a slightly higher amount of iodine than the original iodine formed from the oxidant species in the sample if the titrations are not carried out quickly and efficiently.

It is not appropriate to continue adding titrant until absolutely no needle movement (or zero deflection) is observed. This approach can lead to serious false positive and negative errors in calculating the concentration of the species based on methods-by-difference. This is of concern in the two-stage methods-by-difference specifically in Standard Method 4500-ClO₂-E.

The major impact of using an unclear end point or equivalence point at null meter deflection settings is the likelihood of having significantly overshoot the volume of titrant to indicate the end point. While this may not appear to be a problem in free or combined chlorine amperometry, it causes a tremendous error in methods-by-difference for ClO₂, as the extra titrant volume is then excluded in the second step of the titration. This further complicates the additive errors inherent in such methods-by-difference by unknowingly eliminating or underestimating the actual titrant volumes that would be needed for accurate “B” or “D” steps in method 4500-ClO₂-E. This results in a lower

TABLE 14.6. Example Amperometric Titration Data

Titrant Volume (ml)	Output (mA)	Δ Output/ Δ Titrant (mA/ml)
1.0	1.5	
2.0	1.5	0
3.0	1.5	0
3.1	1.48	0.2
3.2	1.42	0.6
3.25	0.35	21.4 ←
3.3	0.32	0.6
3.4	0.31	0.1
3.5	0.30	0.1
3.6	0.30	0
4.0	0.30	0

←, equivalence point from Bubnis (pers. comm.).

calculation for the ClO_2^- concentrations directly. In the case of generator solutions, this can be significant in overestimating the percent purity, yield, or conversion values, both from overestimation of ClO_2 and underestimation of the unconverted ClO_2^- . It is also significant when using dilute PAO for finished water ClO_2^- levels due to the less clear end points observed at such low levels caused by instrumentation limitations. This is one of the reasons that practical quantitation limits (PQLs) for ClO_2^- by amperometric methods are often cited as more than 1 mg/l.

Bubnis (pers. comm.) provided additional comments regarding the equivalence point and gave an example (Table 14.6), as follows:

The fundamental basis of a titration is founded on the concept of equivalence. For example when one titrates an acid unknown with a standardized base (the titrant), the point at which the added base neutralizes the acid is called the equivalence point. At the equivalence point, the solution is neither acidic nor basic. The solution is pH neutral or pH 7. Calculations can be made to determine the original concentration of the acid by using the amount of the standardized base:

$$\text{acid volume} \times \text{acid concentration} = \text{base volume} \times \text{base concentration}.$$

The same concept of equivalence can be applied to titrations developed to measure the concentration of chlorine dioxide. A typical chlorine dioxide titration might use a standard sodium thiosulfate titrant to react with iodine liberated from the reaction of chlorine dioxide and iodide ion. When the appropriate stoichiometry is applied, the concentration of chlorine dioxide can be calculated from the titration data. Sample titration data and the titration curve are shown by the following:

When titration data are being reviewed, it is important to determine the equivalence point carefully. The titration curve below (Fig. 14.6) shows a smooth curve

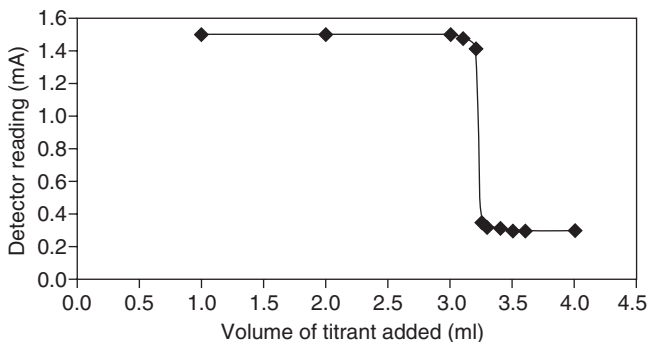


Figure 14.6. Titration curve from amperometric titration data.

with a large decrease in detector output in the 3.2 to 3.3 mL of titrant region. The single most important thing to understand in amperometric titrations is that it is the change in electromotive force (*emf*) versus titrant that is important in determining the equivalence point and not the absolute value of the *emf*. Thus, from the table above one can easily see that the maximum change in output is observed at 3.25 mL of titrant added. This means that the equivalence point is 3.25 mL of added titrant and not along the curved portion of the curve beyond 3.25 mL or the flat portion of that same curve.

Some analysts add starch to the sample when the end point is near, as in iodimetric analyses, and the titration is continued until the blue color disappears. Gates (pers. comm.) stated that a disadvantage of that technique is that “some of the iodine in the sample is trapped within the helical structure of the starch forming the colored complex, and is thus removed from the amperometric reaction going on at the electrode. Thus, it cannot contribute to the flux.” He also pointed out that “this starch–iodine complex slowly releases the iodine, which then becomes available to react with reducing agent after the fact, so it masks a true inflection point.”

DPD Method

The DPD method, which is widely used for measuring chlorine and chloramine, is subject to severe interferences (especially ClO_2^- and chlorine) when used for the analysis of ClO_2 and ClO_2^- . According to Gordon et al.,^{125,126} the presence of ClO_2^- causes a positive interference and a drifting end point in the low-pH step of the analysis. The authors also pointed out that oxidized manganese in drinking water and chromate ions in wastewater can interfere, as can the presence of FAC, even when glycine is added as a masking agent. Gordon et al.¹³⁴ reviewed the chemistry involved in the DPD method for ClO_2 analysis and elaborated further on the positive interference caused by ClO_2^- , which is a major problem because ClO_2^- is formed when ClO_2 oxidizes the

DPD molecule by a nonreversible reaction. The authors presented data showing the steady loss of color over a 600-s interval in a solution containing 1.00-mg/l ClO_2 and 1.00-mg/l ClO_2^- . Color declined steadily throughout the 600-s period and decreased by 24% in the first minute.

A later study by Witte,¹³⁵ however, determined that ClO_2^- at concentrations as high as 25 mg/l did not interfere significantly with the analysis of ClO_2 at concentrations higher than 0.4 mg/l, provided that the detailed steps in the DPD method were rigorously followed. A comparison of the results obtained by an experienced analyst with those of one who was not well trained clearly demonstrated that reliable results could be obtained only after the analyst had received considerable training. Hood⁷⁵ also evaluated the effects of time on color development when DPD is used for the analysis of ClO_2 and concluded that “close control of reaction time and pH are essential ...” for consistent results.

The DPD method for ClO_2 analysis is further complicated in that the concentration is determined by the difference method, which, as noted earlier, is a major source of error. Due to these weaknesses, the DPD method is no longer approved by the USEPA for compliance monitoring of finished-water ClO_2 concentrations yet may still be in use by many water treatment facilities not aware of this change. Commenting on the use of DPD for ClO_2^- analyses, Gordon et al.¹²⁵ stated that “...it [the DPD method] cannot be recommended. It is unreliable.” The DPD method for both ClO_2 and ClO_2^- has been removed from the 21st edition of *Standard Methods*.⁷¹

LGB

ClO_2 concentrations can be determined by using a spectrophotometric procedure based on ClO_2 decolorizing LGB dye. The method is described by Chiswell and O'Halloran,¹³⁶ who listed the detection limit as 0.03 mg/l $\pm$ 0.01 mg/l. In contrast to some other methods, LGB is not subject to interference from chlorine—LGB reacts selectively with ClO_2 in the presence of FAC and is unreactive with combined forms of chlorine as well.^{136–138} The minimum detection level of ClO_2 by USEPA Method 327.1 is 0.1 mg/l.

The LGB method when used for analyzing only ClO_2 is a direct analysis. However, when it is used for determining ClO_2^- concentrations, two analyses are required: the first for ClO_2 and the second following the addition of horseradish peroxidase (HRP) in a citric acid buffer containing glycine. HRP converts ClO_2^- to ClO_2 . Therefore, the second analysis includes both the original concentration of ClO_2 and the ClO_2 produced by oxidation of the ClO_2^- with HRP. The ClO_2^- concentration is then determined by calculating the difference between the two values. This method for ClO_2^- analysis, therefore, suffers from the same drawback as other approved methods, namely, that it is a difference method. It also suffers from the same assumption as methods 4500- ClO_2 -D and 4500- ClO_2 -C that glycine will essentially mask chlorine from appearing as ClO_2 in the analysis.

IC Methods

IC is the method of choice for measuring low concentrations of ClO_2^- , ClO_3^- , bromide, and bromate ions and is required by the USEPA¹³⁹ for monthly (or quarterly) analysis of ClO_2^- in distribution systems. It is based on USEPA Method 300.0 using a sodium carbonate eluent. Samples to be analyzed for ClO_2^- and ClO_3^- are purged with nitrogen to displace ClO_2 and further treated with ethylenediamine (EDA).

The IC method is also in the 21st edition of *Standard Methods*, Method 4110-D.⁷¹ Method detection limits (MDLs) for the ClO_2^- and ClO_3^- in a high ionic strength medium used to simulate drinking water are reported in table 1B of USEPA's Method 300.1 as 0.45 and 0.78 $\mu\text{g/l}$, respectively, and in the 21st edition of *Standard Methods*, table 4110:VI as 1.44 and 2.55 $\mu\text{g/l}$ for ClO_2^- and ClO_3^- , respectively. The MDLs in other references vary with analytical conditions and chemical makeup of the sample water.

Other Analytic Methods

Researchers continue to develop new methods for measuring ClO_2 . Although not USEPA approved for compliance, they can be useful in process monitoring, optimization, and research.

Spectrophotometry

ClO_2 can be measured spectrophotometrically either in solution or in the gas phase. The molar absorptivity ($\epsilon = 1250/\text{mol/cm}$) of ClO_2 at its maximum absorbance wavelength ($\lambda_{\text{max}} = 360\text{nm}$) can be used directly to calculate the concentration of "pure" ClO_2 , given the absorbance of the sample in a spectrophotometric cell of known path length. Commercially available UV-VIS spectrophotometers can be used to measure changes in light intensity through a sample cell. Typically, transmittance or absorbance is measured. The transmittance of a sample is the amount of light passing through a sample as compared with the amount of light passing through a "blank" reference sample. The reference sample is normally just the pure solvent.

The concentration of ClO_2 that is dissolved in water is calculated by using the Beer-Lambert law:

$$I = I_0 \exp(-\epsilon l C), \quad (14.41)$$

where

I = intensity of the light transmitted through the sample

I_0 = intensity of the light transmitted through the reference blank

ϵ = molar absorptivity of the species of interest (e.g., ClO_2)

l = path length of the spectrophotometer cell (typically 2.0cm)

C = concentration of the species of interest (e.g., ClO_2)

Most spectrophotometers can reliably measure absorbance values over the 0.1–1.0 range. However, some spectrophotometers can reliably measure up to 2.0 absorbance units. When a 2-cm measuring cell is used, the maximum ClO_2 concentration that can be reliably measured is about 50 mg/l. When a 0.1-cm cell is used, about 1 g/l of ClO_2 can be measured. The measurement of absorbance values above 2.0 is usually not reliable. Thus, for higher concentrations of ClO_2 , measurements should be made with shorter-path length cells. If different path length cells are not available, measurements can be made at a wavelength away from the wavelength of maximum absorbance (359 nm), but concentrations should be confirmed by amperometric titration using Standard Method 4500- ClO_2 -E.

In solutions containing ClO_2 and ClO_2^- , absorbance measurements are subject to interference by intermediate oxychlorine species. At wavelengths longer than 360 nm, such interference can become dominant, and the calculated ClO_2 concentration may differ from the true value by as much as a factor of two.¹² This absorbance technique is best used for strong ClO_2 solutions with relatively low ClO_2^- and chlorine concentrations, for stock solutions prepared by using demand-free water, or for gas-phase ClO_2 .¹⁸

A potential problem associated with the analysis of concentrated ClO_2 solutions (such as ClO_2 generator effluents) by spectrophotometry is the potential formation of a complex ion $[\text{Cl}_2\text{O}_4]^-$ that is produced by reaction between ClO_2 and ClO_2^- :



This complex is evident when the solution is rust-color rather than light yellow to green. The complex will cause higher absorbance readings at wavelengths longer than the λ_{max} of 360 nm, such as 410 or 465 nm, which will result in a higher calculated ClO_2 concentration than is actually present. More details regarding this problem are presented by Lasagna et al.¹³³

Flow Injection Analysis (FIA)

FIA designates a group of iodometry-related analytical methods that can measure reliably and with great precision ClO_2 and chlorine at concentrations below 1-mg/l. FIA can also be used to measure ClO_2^- and ClO_3^- but with somewhat less precision. Monochloramine can interfere with the FIA redox method. Also, FIA requires a highly skilled technician and specialized, relatively expensive instrumentation.¹⁴⁰ Hollowell et al.¹⁴¹ described the method as “showing excellent selectivity for chlorine dioxide over iron and manganese compounds, as well as other oxy-chlorine compounds such as chlorite and perchlorate ions.” The method is not listed as an analytical method for ClO_2 in the 21st edition of *Standard Methods*.⁷¹

Other Colorimetric Methods for Chlorine Dioxide Analysis

Three colorimetric methods in addition to DPD and LGB have been used for ClO_2 analysis: (a) the amaranth method, (b) the chlorophenol red (CPR) method, and (c) the acid chrome violet potassium (ACVK) method. None of them is approved for compliance monitoring, but they can be used as research methods.

Amaranth.^{18,142} Amaranth is a colorimetric indicator that is selectively decolorized by mg/l concentrations of ClO_2 . It requires minimal technical skill and relatively inexpensive equipment.¹² At the concentrations normally encountered in drinking water, ClO_2^- , ClO_3^- , and monochloramine do not interfere with ClO_2 measurements by this method. Free chlorine will react with amaranth, but the reaction is slower than with ClO_2 . The reaction between ClO_2 and amaranth is linear over the range of 0.25–5.5 mg/l; the product of the reaction is relatively stable and does not require temperature control. These measurements in the presence of free chlorine made within 1 min of mixing the reagents can successfully avoid interference by free chlorine. Alternatively, the free chlorine can be effectively masked by using reagents such as EDA.

Emmert et al.¹⁴² evaluated amaranth for ClO_2 analysis in the presence of FAC, monochloramine, ClO_2^- , ClO_3^- , ferric iron, and manganese dioxide. In addition to the batch method, the authors described a gas-diffusion-flow injection method in which ClO_2 gas is separated from the interfering substances by having it pass through a membrane where it is analyzed spectrophotometrically. This method measures ClO_2 concentrations in the range of 0.2–0.3 mg/l and yields good results in the presence of 300- to 400-mg/l FAC. These methods were superior to the LGB method before it was developed by the USEPA for use under Method 300.0, version 1.1.

Hofman et al.¹⁴³ compared three methods (LGB, amaranth, and ACVK) for analyzing ClO_2 . The minimum detection level for the amaranth method was 0.02 mg/l; the upper limit was 1.1 mg/l. The authors stated that the amaranth method was superior to the ACVK method but not to the LGB method.

CPR. ClO_2 can be measured by its reaction with CPR over the concentration range of 0.2–2 mg/l, with a detection limit of 0.1 mg/l. The CPR method measures a decrease in color, owing to bleaching by ClO_2 . Neither monochloramine nor ClO_3^- interferes with CPR to any meaningful extent, nor does ClO_2^- at concentrations below 1.5 mg/l, as long as its concentration does not exceed the ClO_2 concentration. In the latter case, an interfering intermediate-complex species may be formed. Free chlorine does interfere with CPR measurement of ClO_2 , but the interference can be successfully avoided by treating the sample with masking reagents that reduce free chlorine, such as oxalic acid. Using the CPR method requires minimal technical skill and relatively

inexpensive equipment.¹⁴⁴ It is a convenient, easy way to determine residual ClO_2 concentration in treated water.

ACVK. ACVK is a dye that, like LGB and amaranth, is decolorized by ClO_2 . The results of the ACVK method are not influenced by chlorine, monochloramine, ClO_2^- , or ClO_3^- .¹⁴³ Hofman et al. compared the ACVK method with the LGB and amaranth methods and reported a MDL of 0.08mg/l and an upper limit of 1.8mg/l.

HEALTH AND SAFETY

Many of the chemicals used in the on-site production of ClO_2 are subject to health and safety requirements for their handling and storage. There are also health-based requirements on exposure to some of these chemicals. General information about each is provided herein, and additional information can be obtained from the chemical suppliers or publications.^{18,19}

Chlorine Dioxide

Chlorine dioxide has a significant vapor pressure, which increases as a function of dissolved ClO_2 and time. Care should be taken in handling concentrated aqueous solutions of ClO_2 , especially in buildings or other enclosed areas, such as the headspace of a ClO_2 solution storage tank. Generally, vapor concentrations of ClO_2 in excess of 75–80mmHg are considered dangerous and should be avoided. This corresponds to the vapor pressure over 7.5g/l ClO_2 solution at 25°C. A thorough review of ClO_2 vapor pressure, partial pressure, and stability is presented by Gates et al.¹⁹

Of significance is the induction time to reach equilibrium and subsequent detonation; at levels above 3g/l in closed containment, these are achieved in a matter of seconds at room temperatures. Even at lower aqueous concentrations, these induction times can be reached in minutes to hours, so venting of the batch chemical holding tanks is a prerequisite to proper design of such generating systems.

Sodium Chlorite

Sodium chlorite is a strong Class V oxidizer. If sodium chlorite solution dries in contact with combustibles, it can ignite spontaneously at any time. For example, sodium chlorite solutions spilled on wood or natural fibers (such as coveralls) can dry and then burst into flames, the wood or clothes serving as a fuel source. Similarly, contact with oil or grease, paper products, textiles, leather, and the like can cause dried sodium chlorite to conflagrate. Ignition sources can be as simple as a spark, pressure contact with a forklift driving over a dried chlorite spill, or incidental contact with a burning cigarette butt.

Chlorite solutions can ignite fuels such as gasoline. Dried chlorite crystals on concrete should not be removed with a metal shovel.

Sodium chlorite is also reactive with a number of chemicals, such as acids and hypochlorites, contact with which can cause the uncontrolled release of ClO_2 gas. Pure, dry sodium chlorite is shock sensitive. Dry sodium chlorite should be kept away from open flames, sparks, or excessive heat; it will decompose at temperatures above about 175°C (347°F). Commercial sodium chlorite formulations contain additives (such as sodium chloride) that reduce sensitivity to shock and heat and improve sodium chlorite's safety profile. As long as the manufacturers' precautions are followed, especially those concerning storage and avoidance of contamination with organics, commercial grades of sodium chlorite are relatively safe to handle.¹⁹

Chlorine

Some methods of ClO_2 generation use chlorine gas or sodium hypochlorite solutions. The health and safety, as well as chemical storage considerations for these chemicals, are presented in Chapters 8, 9, and 10 of this handbook.

Toxicity

ClO_2 is a mucosal irritant and lacrimator: Exposure can cause eye, nose, throat, and lung irritation; prolonged exposure at low levels can cause bronchitis, reactive airways disease, and pulmonary edema. Exposure at significant levels (5 ppmV) can lead to confusion and death. The health effects of low-level exposure to ClO_2 are not cumulative, and considerable evidence shows that ClO_2 is unlikely to be carcinogenic at drinking water levels.

Toxicological information on chlorite and chlorate ion can be obtained from the National Toxicology Program (NTP) of 2005.^{81,82}

Workplace Monitoring

ClO_2 vapor has a U.S. Occupational Health and Safety Administration (OSHA) permissible exposure limit (PEL) of 0.1 ppm, 8-h time-weighted average (TWA), and a short-term exposure limit (STEL) of 0.3 ppm, 15-min TWA.

To comply with OSHA limits on allowable levels of exposure to ClO_2 in the workplace, it is necessary to monitor the air where ClO_2 is being generated and used. Various methods are available. Dräger tubes and collector badges, based on colorimetric matrix technology, serve well for average and accumulated exposure. Badges and tubes can be either placed around the worksite or worn by individuals. Tubes require highly accurate air pumps for proper quantitation but are adequate for low-level exposure. Early designs (while relatively inexpensive) of electrochemical sensor technology, for example, can detect ClO_2 but also may respond to Cl_2 without distinguishing between species. Other techniques, such as ion mobility spectroscopy (a

time-of-flight technique), are highly sensitive and expensive but can selectively detect and quantitate small amounts of airborne ClO_2 even in the presence of chlorine.

REGULATORY ISSUES

Compliance with quality and treatment regulations and rules for drinking water and wastewater treatment facilities can be accomplished, in part, with the use of ClO_2 .

Drinking Water Regulations for Disinfection

Regulatory agencies allow ClO_2 for disinfection of potable water.

SWTR

The SWTR requires a certain level of removal or inactivation, the combination of which is “disinfection,” for viruses, bacteria, and *Giardia*. The germicidal efficiency of ClO_2 for these pathogens has been discussed earlier in this chapter.

ClO_2 is a versatile disinfectant for meeting the requirements of the SWTR. It does not react with TOC to form TTHMs or HAAs, although some indication of formation of DXAA (albeit at a lower level than by chlorination) has been reported. It is effective against *Giardia* cysts, which require a high CT if chlorine is used. The main limitation to ClO_2 use has been the ClO_2^- limit (i.e., 1.0 mg/l) set by the Stage 1 D/DBP Rule. Because nearly 75% of the ClO_2 applied to raw or process water is converted to ClO_2^- , ClO_2 dosages have been limited to about 1.3 mg/l. For waters that have a high ClO_2 demand and cannot achieve satisfactory residuals for disinfection compliance, ClO_2 can still be applied at dosages that maintain ClO_2^- concentrations below the MCL of 1.0 mg/l. These waters still benefit from the application of ClO_2 because it lowers the demand for other disinfectants or oxidants, such as chlorine and ozone.

LT2ESWTR

As shown previously, ClO_2 does inactivate *Cryptosporidium*. However, the CT requirements are high, especially at low temperatures. It is unlikely that ClO_2 will be applied at many water treatment plants for inactivation of *Cryptosporidium* in an effort to comply with the LT2ESWTR.

Chlorine Dioxide Residual Limits

The Stage 1 Disinfectants/Disinfection Byproducts Rule (DBPR) has a maximum residual disinfectant level goal (MRDLG) concentration of 0.8 mg/l for ClO_2 to be monitored daily in the water leaving the plant daily. Rarely

does the finished water from a water treatment plant contain a ClO_2 concentration higher than 0.1 mg/l when it enters the distribution system, so this goal is fairly conservative.

Related Disinfection By-Products

The two inorganic DBPs of ClO_2 are ClO_2^- and ClO_3^- . Chlorite must be monitored daily at the inlet to the distribution system, and monthly at three representative sites within the distribution system at the nearest, midway, and farthest points from the plant. Chlorate may also be a product of thermally degraded hypochlorite salts, either directly from hypochlorination or from the feedstock of three-chemical-based ClO_2 generation systems.

Chlorite

The USEPA established a maximum contaminant level goal (MCLG) of 0.8 mg/l and an MCL of 1.0 mg/l for the ClO_2^- ion in Stage 1 D/DBPR in 1998. Because about 75% of ClO_2 applied to water is converted to ClO_2^- , the dosage of ClO_2 is limited to about 1.3 mg/l, unless a ClO_2^- removal process is used (see previous discussion in this chapter).

Chlorate

When the USEPA published the Stage 1 D/DBPR in 1998, it concluded that available health effects were insufficient to establish an MCL for ClO_3^- . In 2005, the NTP⁸¹ released the report on a cancer study that points to chlorate as a potential health problem in drinking water, but no enforceable limit for it has been discussed. Additional research into health effects is in progress, and the USEPA has expressed its intention to set allowable limits for ClO_3^- in the future. The California Department of Public Health (DPH) has set a notification level of 0.8 mg/l for ClO_3^- . In the meantime, its concentration in drinking water should be kept as low as possible.

ClO_2 Use to Meet Wastewater Treatment Plant Regulatory Requirements

Because ClO_2 systems are more costly and more complex than chlorine systems, ClO_2 is not commonly used as a disinfectant in wastewater treatment facilities. Because ClO_2 provides satisfactory disinfection without the formation of organic DBPs, more utility staff will be investigating ClO_2 for disinfection of wastewater effluents.

SUMMARY

ClO_2 is a versatile oxidant and disinfectant used by drinking water, wastewater utilities, and various industries, such as food and beverage producers and

paper/pulp manufacturers. The advantages and disadvantages of ClO_2 are discussed below.

Advantages of Chlorine Dioxide

- Chlorine dioxide is an effective, fast-acting, broad-spectrum bactericide.
- It is a more effective viricide than chlorine, which makes it a promising disinfectant for reuse water.
- It kills chlorine-resistant pathogens, for example, encysted parasites like *Giardia*.
- It does not react with ammonia nitrogen or with primary amines.
- It does not react with oxidizable organic material to form THMs or HAAs.
- It helps to minimize THM formation upon subsequent chlorination and enhances coagulation.
- It is excellent for destruction of phenols, which cause taste and odor in some potable water supplies.
- It has a long track record in oxidizing iron and manganese. It is superior to chlorine, particularly in the presence oxidant-demanding organics.

Disadvantages of Chlorine Dioxide

- ClO_2 is several times more expensive than chlorine, which prevents its use for certain applications.
- ClO_2 inactivates *Cryptosporidium*, but the required CT is very high in cold water.
- ClO_2 cannot be transported as a compressed gas; it must be generated on-site.
- The ClO_2 prepared by some processes may contain significant amounts of free chlorine, which could defeat its use to avoid the formation of THMs.
- The by-products of ClO_2 are ClO_2^- and ClO_3^- . Chlorite is currently regulated, and ClO_3^- may be regulated in the future. Regulatory limits on ClO_2^- and ClO_3^- prohibit the use high doses of ClO_2 for disinfection of drinking water, although there are some promising processes for removing ClO_2^- from drinking water once it is formed.

ACKNOWLEDGMENTS

The author acknowledges the valuable contributions to the revision of this chapter by Drs. Don Gates, Bernard Bubnis, Gilbert Gordon, and David Rosenblatt, as well as the information and suggestions provided by Drew

Industrial Division of Ashland Chemical Company. Don Ratnayaka and Michael Coughlin also contributed valuable information to this chapter.

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15 Ozone

INTRODUCTION

Ozone is one of the strongest oxidants and disinfectants used in treating water and wastewater. It is used internationally for the treatment of synthetic organic compounds (SOCs), oxidation of reduced metals, and removal of taste- and odor-causing compounds, color, turbidity, total organic carbon (TOC), and chlorine disinfection by-product (DBP) precursors. In addition, ozone is a powerful disinfectant that can be used to inactivate viruses, bacteria such as coliforms, *Escherichia coli*, *Giardia lamblia*, and even *Cryptosporidium* oocysts, under certain circumstances.

HISTORY AND APPLICATION

Ozone (O₃) was first identified by its odor by Martinus Van Marum in 1785¹ in the vicinity of an electrical machine, but he failed to identify the odor as a unique form of oxygen. The name “ozone” is derived from the Greek word *ozein*, meaning, “to smell.” It was not until 1840 that Schönbein reported the pungent odor as a new substance he called ozone. The formula for ozone was not determined until 1865 by Jacques-Louis Soret and confirmed by Schönbein in 1867.

In 1886, the first experimental use of ozone in water for disinfection was in de Meritence, France.² As early as 1892, several experimental plants were in operation in European towns. In 1906, the first full-scale plant to disinfect water was the Bon Voyage Plant in France on the Vesubie River. In the United States, ozone was first used in 1908.

Ozone has been utilized for more than a century for water treatment. Currently, several thousand municipal water treatment plants (WTPs) use ozone as part of their chemical treatment.³ In the United States, more than 300 large-scale facilities with a combined treatment capacity of more than 14 billion gal/day are using ozone to treat water and wastewater.⁴

CHEMICAL PROPERTIES

Ozone may be classified as both an oxidant and a germicidal compound. The physical properties of ozone as a gas and in the dissolved form are discussed within in this section. Ozone demand and decay kinetics are also described.

Physical Properties

Ozone is an allotropic form of oxygen. It is produced commercially from dry air or oxygen and is formed by corona discharge of electricity or through photochemical reactions. It is colorless at room temperature and condenses to a dark blue liquid. It is generally encountered in dilute form in a mixture of oxygen or air. Concentrations in excess of 30% in gas can be very unstable and explosive. Explosions may be caused by trace catalysts, organic materials, shocks, electric sparks, or sudden changes in temperature or pressure.

Ozone weighs 0.124 lb/ft³ (2.0 g/l) at 1 atm and 20°C. It is a powerful oxidizing agent as its oxidation potential is -2.07 V, at 25°C and pH 7.0. Only fluoride, elemental oxygen, and hydroxyl radicals have larger standard potential. Standard potential values for oxidants used in water treatment are listed in Chapter 2.

Ozone absorbs light in the infrared, visible, and ultraviolet (UV) wavelengths. It has an absorption maximum at 253.7 nm, which leads to its photodecomposition to atomic oxygen and molecular oxygen. It is this property that allows ozone, in the upper atmosphere, to shield the earth from damaging UV rays. In addition, ozone can be produced from molecular oxygen in the presence of UV light at 185 nm.⁵

Ozone is extremely corrosive. Therefore, materials of construction must be carefully chosen. It attacks most metals except type 316 stainless steel, gold, and platinum. Porcelain and glass do not react with ozone. Polyvinyl chloride (PVC) and other plastics are generally not compatible with ozone gas, although fluoropolymers such as Goretex, Hypalon, Kalrez, Kynar, Teflon, or Viton are resistant to oxidation by ozone. Restructured polytetrafluoroethylene (PTFE), specifically Garlock Style 3500, is used often as gasket material in high concentration ozone applications.

Select physical properties of ozone are listed in Table 15.1.

Solubility of Ozone

Ozone is a gas; therefore, its solubility in a liquid is governed by Henry's law: The weight of any gas that dissolves in a given volume of a liquid at constant temperature is directly proportional to the pressure that the gas exerts above the liquid.

In equation form,

$$Y = H \times X, \quad (15.1)$$

TABLE 15.1. Selected Physical Properties of Ozone^{6,7}

	U.S. Units	SI Units
Molecular weight	48.00	48.00
Specific gravity of gas (air 1.0)	1.66	1.66
Boiling point at 1 atm	-169.4 °F	-111.9 °C
Latent heat of gas at boiling point and 1 atm	127 Btu/lb	297 kJ/kg
Specific heat of gas at 32 °F (0 °C) and 1 atm	0.183 Btu/(lb °F)	0.767 kJ/(kg °C)
Solubility in water, vol/vol at 32 °F (0 °C)	0.64	0.64
Weight of liquid at boiling point	84.4 lb/ft ³	1352 kg/m ³
Weight of gas at normal temperature and pressure (0 °C and 1 atm)	0.1337 lb/ft ³	2.142 g/l
Weight of gas at standard temperature and pressure (20 °C and 1 atm)	0.1246 lb/ft ³	1.996 g/l

where

Y = partial pressure of the gas above the liquid (mmHg),

X = concentration of the gas in the liquid at equilibrium with the gas above the liquid (mol gas/total mol of gas plus liquid), and

H = Henry's law constant (varies with temperature) (mmHg/mol fraction).

Henry's law simply expresses the concentration of gas above the liquid that must exist in order for a given concentration of gas to be dissolved in the liquid. These terms can be converted into units of concentration, such that

Y = concentration of the gas above the liquid in equilibrium with the gas dissolved in the liquid (mg/l),

X = concentration of the gas in the liquid at equilibrium with the gas above the liquid (mg/l), and

H = Henry's law constant (mg gas/l air per mg gas/l water).

The lower the Henry's constant, the more soluble the gas. At 20 °C, ozone is 11.5 times as soluble as oxygen, but, because ozone has a much lower available partial pressure, it is difficult to obtain a concentration of more than 100 mg/l under normal conditions of temperature and pressure.

The equilibrium concentrations of oxygen and ozone in solution at 1 atm are listed in Tables 15.2 and 15.3.

Ozone Reaction Pathways

In aqueous solution, primary reactions with ozone can be described through two mechanisms: direct reaction with molecular ozone or indirect reaction with the radical species formed when ozone decomposes in water.

TABLE 15.2. Solubility of Oxygen in Water

	Temp °C	H	Y	X
		mg O ₂ gas/mg Carrier Gas	mg O ₂	mg O ₂
		mg O ₂ /l Water	L Carrier Gas	L Water
Air (21 % by volume O ₂)	0	20.4	299	14.7
	10	25.4	289	11.4
	20	29.9	279	9.3
	30	34.2	270	7.9
100% O ₂	0	20.4	1428	70.0
	10	25.4	1359	53.5
	20	29.9	1319	44.1
	30	34.2	1274	37.2

TABLE 15.3. Solubility of Ozone in Water

	Temp. °C	H	Y	X
		mg O ₃ Gas/mg Carrier Gas	mg O ₃	mg O ₃
		mg O ₃ /l Water	L Carrier Gas	L Water
Ozone 10% by weight in oxygen	0	1.56	150	96.1
	10	1.89	143	75.7
	20	2.59	139	53.5
	30	3.80	134	35.2

These indirect reactions and the radicals formed are described by the Hoigne, Staehelin, and Bader mechanism and the Bordon, Tomiyasu, and Fukutomi mechanism.

These mechanisms can be divided into three reactions. The first is an initiation step that consists of the reaction between hydroxide ions and ozone to form a superoxide anion (O₂⁻) and hydroperoxyl radical (HO₂). The formation of the superoxide ion is predominant at pH higher than 4.8:



The second series of reactions consists of propagation steps in which ozone and the superoxide anion react to form an ozonide radical (O₃⁻). That ozonide radical can then begin a series of reactions that form several hydroxide and hydroperoxide radicals: OH, HO₂, HO₃, and HO₄. In addition, some organic molecules, R, can contain functional groups that react with hydroxide radicals to form organic peroxy radicals (ROO).

The third series of reactions are termination steps in which the formation of radicals are inhibited through the reaction of the hydroxide radical with carbonate or bicarbonate or the reaction of two radicals.

The free radicals that form when ozone decomposes in aqueous solutions have great oxidizing power and react within a few microseconds with impurities.

Ozone Demand

When ozone is added to water, organic and inorganic compounds react with ozone, and radical species that nonselectively react with contaminants in the water are formed. Most of these reactions go to completion within a few microseconds.

Ozone demand can be expressed in several ways: the difference between the transferred ozone dose and the initial residual, or the transferred ozone dose that results in a measurable dissolved ozone residual. The difficulty with using the first expression in calculating ozone demand is that many ozone demands would be calculated for the same water, as the initial residual is a function of the transferred ozone dosage. Because of that problem, ozone demand is defined as the ozone dosage that results in a barely measurable residual. That value can be determined by adding various dosages of ozone to water and measuring resultant dissolved ozone residual. The ozone demand may then be determined based on a linear regression of the transferred ozone dosages and residuals (Fig. 15.1). The x-intercept value corresponds to the ozone dosage required to satisfy the ozone demand.

Variations in ozone demand are the result of differences in water quality, particularly inorganic and organic content and makeup. Increases in TOC concentration and waters with higher ultraviolet adsorbance at 254 nm (UVA_{254}) are known to increase ozone demand.

The slopes of the regression lines are not unity as is the case with incremental increases in chlorine dosage. Therefore, for each incremental increase in ozone dosage, only a portion is observed as dissolved ozone. Commonly,

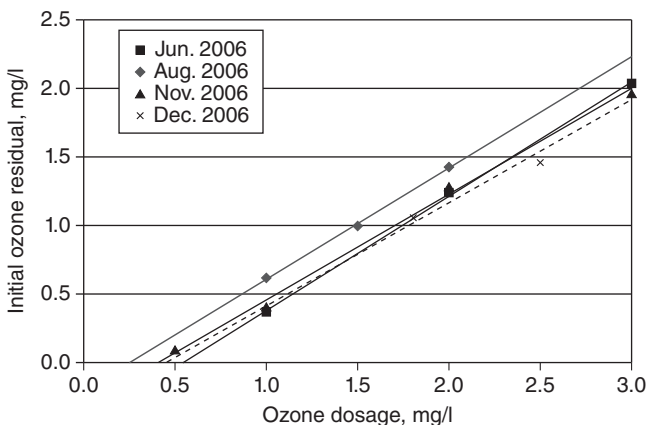


Figure 15.1. Ozone demand.

the slope of dissolved ozone per mg of transferred ozone ranges from 0.5 to 0.8 mg per mg for surface waters.

Dissolved Ozone Decay

When the ozone dosage exceeds the ozone demand, a dissolved ozone concentration will persist. The dissolved ozone residual concentration follows first-order decay kinetics. The first-order equation used to predict ozone residuals at various times is Equation (15.3):

$$C_t = C_o \times e^{(kt)}, \quad (15.3)$$

where

C_t = concentration at time t (mg/l),

C_o = Initial concentration (mg/l),

e = exponent, 2.7183,

k = decay constant, time^{-1} (usually min^{-1} and infrequently s^{-1}), and

t = time (usually min and infrequently s).

The dissolved ozone decay rate can be determined through measurement of dissolved ozone residuals after known periods. That information may then be manipulated as described in *Ozone in Drinking Water Treatment: Process Design, Operation, and Optimization* to determine the decay constant. Decomposition of dissolved ozone is accelerated at higher temperatures, pH, or concentrations of TOC. The dissolved ozone decay rate is also a function of the initial dissolved ozone residual and the amount and type of organic matter present.

Decay rate is often discussed in terms of half-life, which can be calculated by using Equation (15.4):

$$t_{1/2} = \ln(0.5)/k, \quad (15.4)$$

where

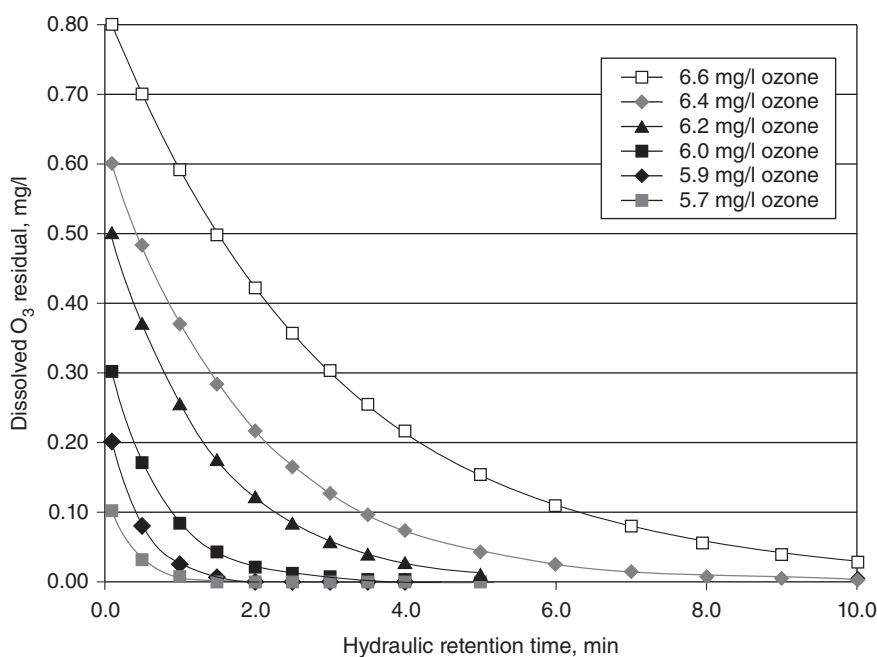
$t_{1/2}$ = half-life, time (usually min and infrequently s), and

$\ln$ = natural log.

Dissolved ozone half-life may be on the order of a few seconds to as long as 20 minutes for waters low in TOC and pH. Usually, it is on the order of a few minutes in water and a few seconds in wastewater. This information is important to correctly size the ozone contactor to ensure that the dissolved ozone residual is sufficiently low at the exit of the contactor to prevent hazardous conditions in subsequent processes. Ozone decay rate data for one water source are listed in Table 15.4 and presented in Figure 15.2.

TABLE 15.4. Ozone Decay Rate Data in Floridian Aquifer

Average ozone dosage (mg/l)	5.7	5.9	6.0	6.2	6.4	6.6
Initial ozone residual (mg/l)	0.10	0.20	0.30	0.50	0.60	0.8
Dissolved ozone decay rate (min^{-1})	-3.00	-2.30	-1.40	-0.75	-0.54	-0.34
Ozone half-life (min)	0.2	0.3	0.5	0.9	1.3	2.1

**Figure 15.2.** Predicted ozone residual data in floridian aquifer.

INORGANIC COMPOUND TREATMENT

Ozone reacts rapidly to oxidize several important ions commonly present in water and wastewater: bromide, chlorite, cyanide, iron (II), manganese (II and IV), nitrite, and sulfide. The reaction and the stoichiometric quantity of ozone required for the reaction are listed in Table 15.5.

Iron and Manganese

Iron and manganese represent an esthetic issue rather than a specific health problem. Their secondary maximum contaminant levels (SMCLs) are 0.30 and 0.05 mg/l, respectively. In practice, though, most utilities try to achieve levels less than 0.05 and 0.02 mg/l, respectively, to ensure continuous control of the two compounds.

TABLE 15.5. Inorganic Ion Oxidation Using Ozone^{8,9,10}

Contaminant	Reaction	Stoichiometric Quantity
Ammonia	$\text{NH}_4^+ + 4\text{O}_3 \rightarrow \text{NH}_3^+ + 4\text{O}_2 + \text{H}_2\text{O} + 2\text{H}^+$	11 mg O ₃ /mg NH ₄ ⁺
Bromide	$\text{Br}^- + \text{O}_3 \rightarrow \text{OBr}^- + \text{O}_2$	1.8 mg O ₃ /mg Br ⁻
Hypobromite	$\text{OBr}^- + \text{O}_3 \rightarrow \text{BrO}_2^- + \text{O}_2$	
Bromite	$\text{BrO}_2^- + \text{O}_3 \rightarrow \text{BrO}_3^- + \text{O}_2$	
Chlorite	$\text{ClO}_2^- + \text{O}_3 \rightarrow \text{ClO}_3^- + \text{O}_2$	0.71 mg O ₃ /mg ClO ₂ ⁻
Cyanide	$\text{CN}^- + \text{O}_3 \rightarrow \text{CNO}^- + \text{O}_2$	4.6 mg O ₃ /mg cyanide
Cyanate	$2\text{CNO}^- + 3\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{N}_2 + 2\text{HCO}_3^- + 3\text{O}_2$	as CN ⁻
Iron	$2\text{Fe}^{+2} + \text{O}_3 + 5\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_{3(s)} + \text{O}_2 + 4\text{H}^+$	0.43 mg O ₃ /mg Fe ²⁺
Manganese	$\text{Mn}^{+2} + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{MnO}_{2(s)} + \text{O}_2 + 2\text{H}^+$	0.88 mg O ₃ /mg Mn ²⁺
Nitrite	$\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$	1.0 mg O ₃ /mg NO ₂ ⁻
Sulfide	$\text{S}^{2-} + 4\text{O}_3 \rightarrow \text{SO}_4^{2-} + 4\text{O}_2$	6.0 mg O ₃ /mg S ²⁻

The predominant treatment method is to oxidize the reduced, soluble forms of iron, Fe (II), and manganese, Mn (II), to their oxidized, much less soluble, forms: Fe (III) and Mn (IV). Once oxidized and precipitated, they are removed by sedimentation and filtration. Oxidation of Fe and Mn with ozone is not highly pH dependent, much less so than oxidation by oxygen or chlorine. Ozone is capable of breaking down organic complexes of both iron and manganese, which usually defy the traditional procedures of iron and manganese removal from potable waters.

Oxidation of Fe by ozone is preferential to oxidation of Mn. Therefore, very little Mn oxidation will occur before the oxidation of all the reduced Fe species. The presence of organic matter may complex with Fe and Mn and reduces their susceptibility to oxidation with ozone. In addition, natural organic matter (NOM) will compete against and inhibit the oxidation of Mn, thereby requiring higher dosages of ozone.

Ozone, when added in sufficient quantities, can actually oxidize Mn (II and IV) to permanganate, Mn (VII), in extreme cases, producing a measurable permanganate residual and discoloring the water pink. The permanganate will slowly revert to the sparingly soluble Mn (IV) species, which may take several minutes. Since permanganate will pass through conventional treatment processes, it is important to monitor for the formation of permanganate during ozonation.

Oxidation of Mn (II) by ozone produces colloidal particles that can pass through multimedia filters. It is therefore essential to stabilize the colloidal particles ahead of the filters. If ozone is added at the head of the plant, upstream from coagulant addition, the Mn (IV) colloids aggregate into large particles that are removed by sedimentation and filtration. If ozone is added between sedimentation and filtration, the Mn (IV) colloids must be destabilized before filtration. A small dose of coagulant or filter aid is generally added

to enhance removal. At the Lincoln Water Services, Lincoln NE, Ashland WTP, a filter aid polymer has been used to capture manganese since the 1980s. The raw-water-soluble manganese concentration is generally 0.10 mg/l, and, following oxidation with ozone, it is approximately 0.020–0.050 mg/l (E. Lee, pers. comm.).

Biologic filtration can also be used to achieve Mn removal downstream intermediate ozonation, although the process can be problematic, as micro-environments may develop where Mn (IV) can be reduced back to Mn (II) and returned to solution. Biologic reduction of Mn (IV) to Mn (II) has been observed in filters with DO present in the effluent (W. Knocke, pers. comm.).

Ozone followed by filtration can typically result in an effluent with total Fe and Mn concentrations less than 0.010 and 0.030 mg/l, respectively. Ozonation followed by chlorination and filtration will produce an effluent with a lower total Mn concentration, <0.010 mg/l. Ozone, although a good oxidant for Mn, is not effective in consistently producing very low (less than 0.010 mg/l) concentrations of soluble Mn.

Sulfides

Sulfide (S^{2-}) is a gas dissolved in water that emits a foul odor at concentrations as low as 0.05 mg/l as S^{2-} . Sulfide can be stripped from the water or oxidized by chlorine, oxygen, ozone, or hydrogen peroxide.

Ozone is an effective means of oxidizing sulfide to the dissolved sulfate ion (SO_4^{2-}). Treatment with chlorine (at dosages of 2 mg of Cl_2 per mg of S^{2-}) or with oxygen results in the formation of elemental sulfur (S^0), which will increase turbidity and impart a bluish color to the water. Although elemental sulfur should not form during ozonation, sulfur species have been documented to foul diffuser stones, and their presence has been observed downstream from ozone treatment. The foulant has been difficult to remove, and many utilities have chosen to replace diffuser stones rather than attempting to clean them. The formation of S^0 is small in comparison to the formation of sulfate, but it occurs nonetheless. The formation of elemental sulfur may be the result of polymeric sulfide molecules not available to immediate treatment by ozone. These compounds may react over several minutes with the dissolved oxygen in the water following ozone treatment and may form sulfur.

Orlando Utilities Commission has five WTPs that use ozone for the oxidation of sulfide. These five facilities have conventional contact basins with large transfer cells and diffusers. At the water's surface, hydrogen sulfide may be released into the gaseous phase, since it is a volatile compound. At the Southwest WTP, in Orlando, Florida, sulfide attack on the catalyst resulted in the replacement of the catalyst, every 3–6 months. The pH of the raw water was increased, which lowered the volatility of sulfide and extended the replacement interval to 18 months. Designing the transfer cell of the ozone basin to be cocurrent to lower the amount of sulfide stripped at the water's surface

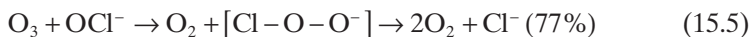
also seemed to increase the period between replacements. Finally, raising the temperature of the destruction unit has extended the periods between catalyst replacements.

Early results indicate that sidestream injection with degas separation in the sidestream may result in less frequent need to replace the catalyst. The Toho WTP in Kissimmee, FL, operated for more than 18 months without having to replace the catalyst (B. Benner, pers. comm.). The concentration of ozone in the sidestream usually exceeds the ozone demand of the water, and a slight ozone residual is maintained, thereby ensuring that all sulfide is oxidized to sulfate. This observation must be confirmed through extended operating experience.

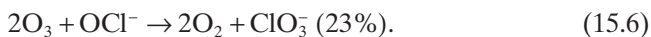
Chlorine, Chlorine Dioxide, and Monochloramine

The usual practice for the addition of chlorine or chlorine dioxide in the treatment train along with ozone is applying the chlorine compounds where there is no ozone residual. This is carried out because ozone reacts to reduce both Cl_2 and ClO_2 . Moreover, radicals formed during ozonation will also act to dechlorinate both Cl_2 and ClO_2 .

Haag and Hoigne¹¹ have shown that ozone reacts with sodium hypochlorite by the following reactions:

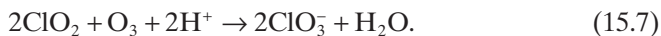


and



That is, when a solution of hypochlorite is exhaustively ozonated, 77% of the chlorine is found as chloride ion, and 23% is found as the chlorate ion. Only the hypochlorite ion reacts with ozone.

Ozone reacts with residual ClO_2 very quickly and the resultant product is chlorate, and no perchlorate is formed at conditions typically found in water treatment.¹² Alternatively, when chlorine dioxide is added to a solution containing dissolved ozone, the following reaction occurs:



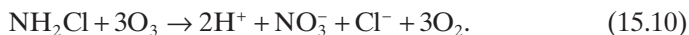
Chlorine dioxide requires only half the ozone required for the oxidation of chlorite to chlorate, as illustrated in Equation (15.8):



Ozone may also react with chlorite to form chlorine dioxide and an ozonide radical:



Ozone will also react with monochloramine according to the following equation:



Chlorine and ammonia are commonly used in strategies to control bromate formation and, in some cases, lower the operating cost of the ozone system. The Lincoln Water Services, Lincoln, Nebraska, applies a small dose of chlorine to maintain a less than 0.2 mg/l residual upstream from the ozone contactor. The chlorine is used to oxidize iron, which in turn lowers ozone demand and operating costs (E. Lee, pers. comm.). Other utilities have evaluated prechlorination to reduce operating costs, although adding another chemical feed location usually adds to the complexity of the treatment process and may lead to the formation of undesirable chlorine DBPs. Chlorine at concentrations higher than 0.2 mg/l may also be stripped from the water and will poison the destruction catalyst, requiring more frequent replacement of the media.

ORGANIC COMPOUNDS

Oxidation of organic materials, both by direct reaction and through radical pathways, is rather selective and incomplete at the concentrations and pH values typical in water and wastewater treatment. Unsaturated and aromatic compounds are oxidized and split at double bonds, producing carboxylic acids and ketones as products.¹³ Because of the high reactivity of ozone, oxidation of organic matter in the aqueous environment, whether it be potable water or wastewater, will consume ozone in varying amounts.

Taste- and Odor-Causing Compounds

Taste- and odor-causing compounds affect the palatability of water supplied by 16% of the utilities in the United States and Canada.¹⁴ Control of musty or earthy odors is of greatest concern. These odors are caused most often by 2-methylisoborneol (MIB) and trans-1,10-dimethyl-trans-9-decalol (geosmin). These compounds are produced by actinomycetes and cyanobacteria, also known as blue-green algae, at concentrations of parts per trillion (ng/l). Concentrations as low as 5–10 ng/l may lead to consumer complaints.

Ozonation is effective for removal of taste- and odor-causing compounds, specifically MIB and geosmin. They are oxidized by hydroxyl radicals formed during ozonation. MIB is generally more difficult than geosmin to remove with ozone.

For the necessary ozone dosage for the removal of MIB and geosmin to be determined, an oxidation dose–response relationship is developed for the

water source. Several researchers have demonstrated that, at a fixed ozone dosage, the percentage of micropollutants such as MIB and geosmin removed is independent of the initial concentration of the contaminant. Therefore, the dose–response curves developed can be used to predict the efficiency of the removal under similar conditions (i.e., pH, TOC, temperature) at any naturally occurring influent micropollutant concentration. Typical ozone dosages to achieve a 1.0 log reduction in MIB or geosmin range from as little as 1.5 mg/l to more than 5 mg/l, depending on the ozone demand, organic matter, and competing species in the water.

The dose–response curve developed for Lake Cheney Reservoir water, near Wichita, Kansas, is presented in Figure 15.3. Testing occurred over a period of 2 months, TOC during this period ranged from 4.2 to 4.7 mg/l, and temperature varied from 15 to 28 °C. The pH remained relatively constant throughout the study, at 7.95–8.20. Despite these ranges in raw water quality, the dose response remained relatively close in terms of geosmin oxidation, regardless of its initial concentration (95–540 ng/l).

Ozone dosages consistent with disinfection for inactivation of *Giardia* and viruses have been capable of eliminating taste- and odor-causing compounds in surface WTPs throughout the United States. The influent concentration of taste- and odor-causing compounds at these plants was generally less than 50 ng/l.⁶

In bench-scale ozonation tests of Detroit River water, an ozone dose of 2 mg/l removed over 95% of the geosmin and 80% of the MIB. Combining

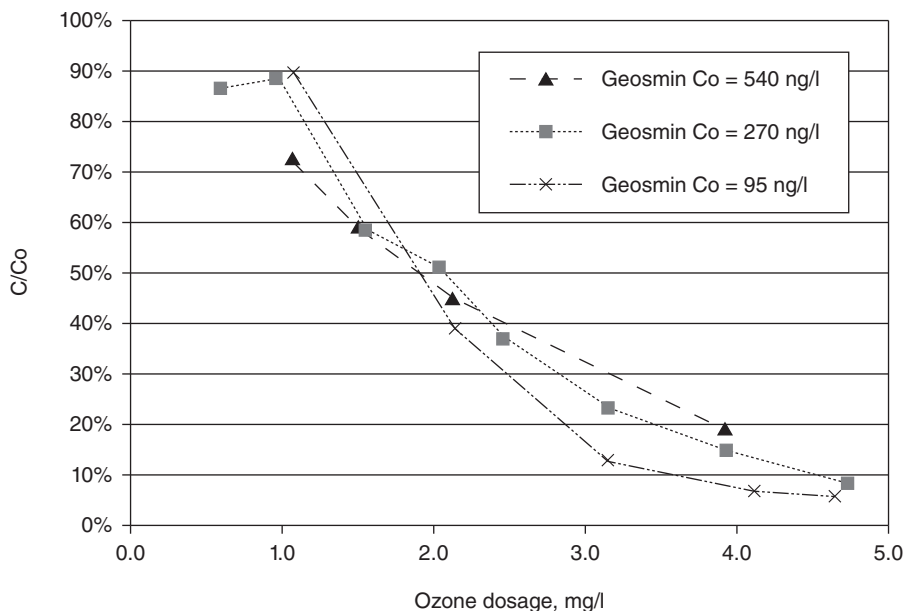


Figure 15.3. Geosmin dose–response curve in Lake Cheney Reservoir.

the ozone with hydrogen peroxide enhanced removal but was deemed unnecessary for achieving the desired removal.¹⁵ In Medford, Oregon, a dosage of 1.0 mg/l achieved an average geosmin removal of 92% and reduced the geosmin concentration in raw water from 88 ng/l to less than 7.0 ng/l. An ozone dosage of 1.5 mg/l removed geosmin to nondetectable levels.¹⁶

Typically, ozone is applied before filtration, and ozone coupled with biofiltration has been found to have a synergistic effect on MIB and geosmin removal.¹⁷ Ozonation followed by biological filtration is an effective method of removing taste- and odor-causing compounds. Ozonation alone can at least partially remove MIB and geosmin but it also increases the biological activity in the filters. Increased biological activity has been shown to remove higher concentrations of MIB and geosmin.¹⁸ The increased biomass in the filter enhances the biological filter's ability to degrade micropollutants such as taste- and odor-causing compounds.

Control of Chlorination By-Products

Ozone will cause a change in the concentration of the by-products generated by disinfection with chlorine as a result of the following mechanisms:

1. Ozone forms or destroys DBP precursors.
2. Ozone alters TOC in such a way that subsequent processes are more or less effective in removing DBP precursors.
3. Ozone makes it possible to use lower dosages of chlorine by oxidizing compounds that exert a chlorine demand.
4. Ozone reduces the rate of DBP formation.
5. Ozone provides primary disinfection (within the treatment plant), which eliminates the need to use free chlorine at the plant. Combined chlorine may be used as the secondary disinfectant (in the distribution system).

In practice, ozone and coagulation or biofiltration usually result in lower concentrations of DBP precursors. Ozone also reacts with some of the inorganic and organic compounds that would have exerted a chlorine demand. Through lowering the chlorine dosage, and often the chlorine decay rate, less chlorine is dosed to react with organic matter and to form the DBPs.

Pretreatment with ozone commonly results in lower concentrations of DBPs, but under certain conditions, ozone may increase DBP precursors, which will result in higher concentrations of total trihalomethanes (TTHMs) and haloacetic acids (HAAs). Typical reduction in TTHM formation potential is 3%–20%.⁸

The key variables that control the effectiveness of operation in treating chlorination DBP precursors are ozone dose, nature of the organic matter, and subsequent treatment processes. Higher ratios of ozone to TOC generally result in lower concentrations of chlorination DBP precursors. Water with

high concentrations of hydrophobic and phenolic organic carbon usually undergoes a reduction in chlorinated DBPs. Waters with low phenolic organic carbon concentration tend to observe higher concentrations of chlorinated DBPs.¹⁹

At locations where even short periods of free chlorine contact time result in substantial quantities of TTHMs and HAAs, ozone may be considered as the primary disinfectant followed by combined chlorine to maintain a residual in the distribution system. This combination has been demonstrated to reduce TTHM and HAA concentrations to less than 0.010 mg/l.

TOC Oxidation

Natural waters contain numerous organic compounds in varying concentrations. When dissolved, these compounds are considered the dissolved organic carbon (DOC) fraction of TOC. The main DOC component in surface waters consists of polymerized organic acids, called humic and fulvic acids.

DOC may be mineralized to carbon dioxide if the ozone dosage is high enough and adequate quantities of hydroxide radicals are formed. As much as 10% mineralization of TOC at ozone dosages of 1 mg O₃ per mg of carbon has been reported.²⁰ To achieve high levels of TOC mineralization, it may require very high dosages of ozone, such as, 10 mg O₃/mg TOC.²¹

Ozone severs some of the bonds within large molecular weight organic compounds, which are semi- or nonbiodegradable, to smaller, more readily biodegradable organic compounds assimilable organic carbon (AOC) and biodegradable dissolved organic carbon (BDOC). These compounds contribute to biological instability in the distribution system, one of the consequences of ozonation. Ketones, aldehydes, and carboxylic acids can be produced by oxidation of naturally occurring organic matter with ozone. The compounds create biological instability that can lead to biological regrowth in the distribution system and the need to increase the disinfectant residual concentration. BDOC and AOC can be removed by coagulation or biologic filtration.

Biological Filtration

Because AOC concentrations increase following ozonation, many facilities choose to apply chlorine downstream from filtration, which allows the filters to develop a biological layer that is effective in removing AOC, BDOC, aldehydes, ketones, and carboxylic acids. Biological filters consist of spent granular activated carbon (GAC) or anthracite/sand dual media filters operated without chlorine in the feed or backwash waters. In some situations, biological filtration is not possible (e.g. removal of Mn to less than 0.010 mg/l), and the utility must instead rely on maintaining a chlorine residual in the distribution system to control biogrowth. If combined chlorine is used as a secondary disinfectant, maintaining free chlorine for a short period prior to the addition of ammonia

may result in more persistent combined chlorine residuals in the distribution system.

The amount of AOC and BDOC following ozonation and the concentrations that may result in growth in the distribution system are site specific. Therefore, monitoring AOC and BDOC is essential for evaluating plant performance. One study found that the AOC would not increase bacterial regrowth in the distribution system as long as the water is filtered after ozonation or a disinfectant residual is maintained in the distribution system. The study evaluated empty bed contact times between 4.5 and 22.5 min and demonstrated that AOC is effectively removed, but the concentration of AOC in the water may not be restored to the same level as it was before ozonation.²² Another study found that AOC could be completely removed if sufficient contact time is provided in the biological activated carbon (BAC) filtration system.²³

Removal of Particulates

It has been well documented that ozonation may enhance the removal of particles during sedimentation and filtration. This phenomenon, commonly referred to as microflocculation, is not well understood; therefore, the benefit cannot be predicted, as it is observed only at some locations. It appears most often in waters with turbidity-to-DOC ratios of 0.5–2.0 NTU/mg C, those containing high molecular-weight organic compounds, or with a calcium-to-DOC ratio higher than 10 mg Ca/mg C, and in those treated with a cationic polymer.^{24,25}

Most particles in surface waters are negatively charged, partly as a result of organic compounds adsorbed within the particle. Preoxidation with ozone makes these organic compounds more polar, causing them to become more soluble and desorbed from the particle. The particle becomes destabilized and more amenable to aggregate, which can result in savings in the use of coagulation chemicals.

Other mechanisms⁸ responsible for enhanced particle removal may include the following:

1. Modification of the organic structure, enabling it to bind coagulants more effectively
2. Oxidization of TOC to form carboxyl groups that may bind with calcium, resulting in precipitation of organic matter
3. Oxidation of organic compounds containing metal complexes, resulting in their release and contributing to particle destabilization
4. Polymerization of organic matter into compounds that assist with enmeshment of floc
5. Lysis of algae cells, which results in the release of biopolymers that may be equivalent to natural organic coagulants

Taking advantage of these mechanisms may result in significant savings in capital and operating costs, as was the case at the Los Angeles Aqueduct Filtration Plant.²⁴ Application of ozone ahead of all other processes resulted in the following advantages over conventional treatment methods:

1. Increased filtration rates by 50% (from 9 to 13.5 gpm/sq ft), which reduced the number of filters required by one-third
2. Shortened flocculation time by 50% (from 20 to 10 min), which reduced the number of flocculation compartments required by half
3. Extended filter run times between backwashing cycles, making it possible to use smaller backwashing facilities
4. Reduced demand for chemical coagulant by 33%
5. Reduced chlorine demand by 50%, which in turn, reduces the generation of chlorinated DBPs and chlorine used at the plant by 1600 t/year
6. Reduces the volume of filter backwash sludge in proportion to the reduction in coagulant use

Color Removal

Ozone is a powerful and effective bleaching agent for the color-causing organic compounds in wastewater and potable water. Ozone oxidizes the humic and fulvic acids, the primary cause for color in natural waters, and can remove large amounts of color at low dosages. However, removing color beyond a certain threshold requires increasingly larger ozone dosages.

In 1987, the City of Long Beach, California, conducted a study of color removal on its 50-mgd underground water supply. When ozone was used for color removal, raw water color was reduced from 32–57 color units to 1–4 color units by using ozone dosages of 4–5 mg/l and residuals of 0.4–0.5 mg/l after about 5 min of contact time. The substances that impart color to water vary between sources; therefore, ozonation must be tested at bench- or pilot-scale to assess its effectiveness for color removal.²⁶

Increase in UV Transmittance at 254 nm (UVT₂₅₄)

Ozone reacts with organic matter and breaks double bonds that absorb light at 254 nm. This wavelength is important for UV disinfection, as intense UV light in the 245 nm range disrupts the replication of the pathogen's genetic material. This is the process used in UV disinfection processes for inactivation of pathogenic organisms. Ozone treatment can increase the UVT₂₅₄, allowing the UV light to penetrate deeper into the water column. The ability of ozone to increase UVT₂₅₄ has made its use upstream from UV an attractive treatment method for locations with low UVT₂₅₄.

Adding ozone upstream from UV treatment may result in large savings in capital cost in the UV system, as demonstrated at the Massachusetts Water Resources Authority's and other large plants' unfiltered supplies, where

capital costs were reduced by about 20% when ozone was applied in addition to the UV treatment.²⁷ The improvements in UVT_{254} afforded by ozone make it possible to use fewer UV units that consist of fewer lamps, and have approximately 30% lower operating costs at the same target level of *Cryptosporidium* inactivation.

The increase in UVT_{254} following ozone treatment has been modeled by using logarithmic functions whereby the majority of the increase in UVT_{254} occurs at low dosages of ozone, and incremental increases in UVT_{254} require progressively more ozone. Bench- and full-scale evaluations for the Greater Vancouver Regional District, Coquitlam source, demonstrated that 60% of the total increase in UVT_{254} occurred when an ozone dose of 1 mg/l was used. Adding another 1 mg/l of ozone, for a total of 2.0 mg/l, accounted for 26% of the improvement, and the third 1-mg/l dose accounted for only 14% of the total improvement.²⁸

The synergistic effects of ozone and UV have been of particular interest to wastewater utilities struggling to meet increasingly strict limits for pathogens and the growing concerns related to endocrine-disrupting compounds (EDCs), pharmaceutical and personal care products (PPCPs), and the estrogenic activity in municipal effluent. These concerns have led some utilities to closely evaluate the use of ozone and UV.

A study to evaluate the primary effluent of the Springfield, Missouri, Southwest Wastewater Treatment Plant demonstrated large increases in UVT_{254} following treatment with ozone (Fig. 15.4). This outcome is largely the result of rupturing the double bonds within these compounds.

SOCs

Ozone reacts with many SOC, commonly referred to as micropollutants or microcontaminants. Commonly, oxidation of micropollutants has not been the

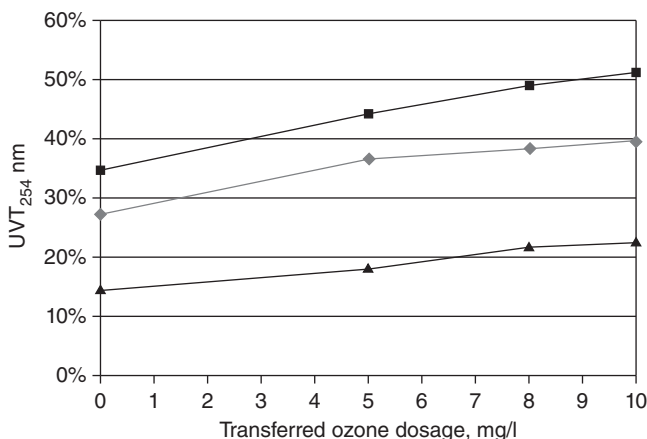


Figure 15.4. UVT_{254} values following ozonation of primary effluent.

primary task but a positive side effect of ozonation. In situations where air stripping or other oxidants were not effective, ozone has been used for oxidation of pollutants.

Ozone is a highly effective oxidant for the treatment of SOC_s that contain double or triple bonds ($C=C$, $C=C-O-R$, $R-C=C-R$, $N=N$), aromatic rings with $-OH$ or $-NH_2$ functional groups, or those with functional groups that contain atoms with a negative charge (N, P, O, S). Rupture at the position of the double bond ($R-C=C-R$) results in the formation of aldehydes ($O=CH-$), ketones (R_1-CO-R_2), and carboxylic acids ($R-COOH$).

Ozone rarely mineralizes the micropollutant but breaks it down into a metabolite that is typically more polar in nature and smaller in molecular weight.²⁹ The ozonated by-products are usually not well understood in terms of their toxicity or measured concentrations. Therefore, it is important before selecting an ozonation process that the ozonation by-products are well understood for the target SOC. Occasionally, an ozonation by-product may be more toxic to humans than the target SOC, as is the case for ozonation by-products of parathion.³⁰ In addition, the ozonated compound may become more stable and less biodegradable and persists in the environment longer than the target contaminant.

There are hundreds of studies dealing with the ozonation of various SOC_s. However, ozonation was commonly performed on volatile compounds via transfer into solution by diffusion. The volatile compounds may have been removed by stripping during diffusion, although that mechanism was commonly either dismissed or not evaluated. Studies were also conducted on the target compound in deionized water, and, when tests were repeated on water with NOM, the results led to different conclusions due to competing reactions. Ideally, bench- or pilot-scale evaluations should be performed to develop design criteria for the treatment of SOC_s.

EDC and PPCP Treatment

There is growing interest in EDCs in both potable water and wastewater. EDCs are a class of chemicals that interfere with the natural action of hormones in the body and are thought to interfere with the reproductive systems of both wildlife and humans. EDCs can include a wide range of chemicals that are used in pesticides and in a number of products for residential, commercial, and industrial applications. Some PPCPs such as antibiotics, prescription drugs, shampoos, and cleansers have also been implicated as potential sources of EDCs.

Ozonation has been used in advanced wastewater treatment for water reuse, for high level wastewater disinfection, and for destruction of EDCs and PPCPs. The majority of EDC and PPCP research has been carried out on the treatment of secondary or tertiary effluent from wastewater treatment plants. Results have demonstrated that ozone is highly effective in removing many EDC and PPCPs. Moreover, compounds that have an effect on *in vitro* cells

similar to that of estrogen, defined as the estrogenicity, were destroyed by ozone and advanced oxidation processes (AOPs) by using ozone. Destruction of EDC and PPCP by AOPs was not significantly greater than by ozone alone. A few microcontaminants that were found to be resistant to oxidation by ozone include tris(2-chloroethyl) phosphate (TCEP, a flame-retardant), meprobamate (an antianxiety pharmaceutical), musk ketone (a synthetic fragrance), and iopromide (an x-ray contrast medium). Pharmaceutical compounds and their removal in treated wastewater are presented in Figure 15.5.

Cyanotoxins

Toxic blue-green algal blooming in drinking water sources are increasing worldwide, killing aquatic species, causing liver damage and gastrointestinal upsets, affecting respiration and muscle activity, and being potentially carcinogenic to humans. The three toxin families of greatest interest are two neurotoxins (anatoxin-a and saxitoxin) and the hepatotoxin (microcystin). None of these compounds can be removed through conventional treatment, although

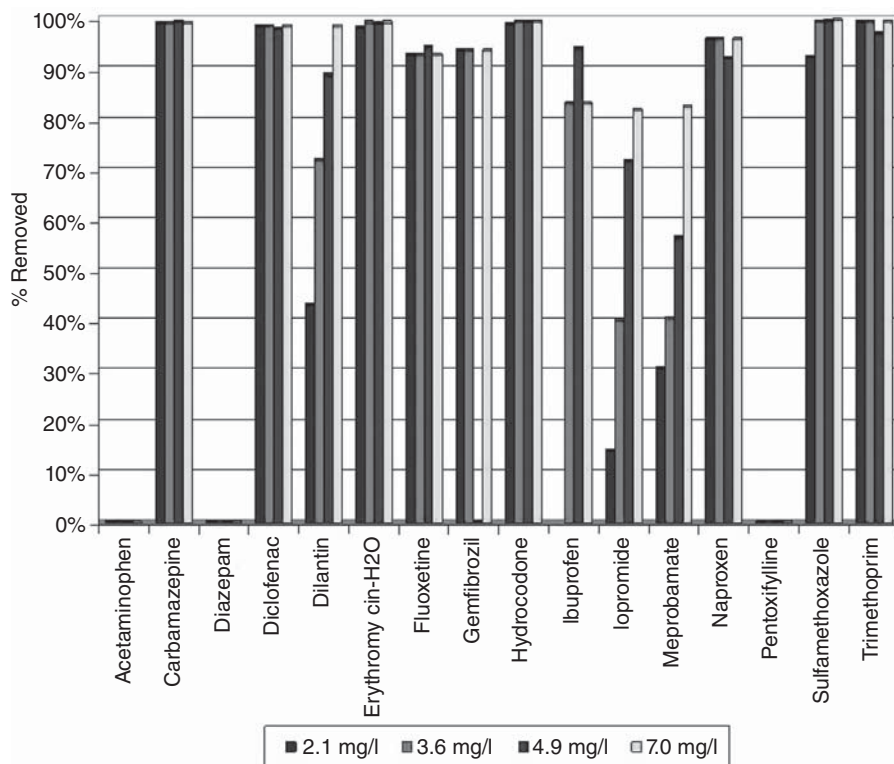


Figure 15.5. Oxidation of PPCPs in secondary effluent by ozone.³¹

anatoxin-a and microcystin can be treated by ozonation. One study found that, when ozone was applied at a sufficient dosage to maintain a residual for several minutes, microcystins and anatoxin-a were destroyed to below the lower detection limit, and toxicity, as measured by mouse bioassays or phosphate inhibition assay, was also removed. Saxitoxins were not well removed with ozone treatment.³²

Treatment of Biological Solids in Wastewater

Three emerging ozonation processes that result in the production of lower quantities of solids during wastewater treatment are available. These processes are patented, have had limited application, and are being used by only a handful of facilities. Their use should be carefully evaluated before implementation by extended pilot testing to document their treatment benefits.

The first of the three processes involves the addition of ozone to return activated sludge (RAS). A small portion of the RAS stream is diverted to a sidestream process where ozone is injected. The ozone acts to lyse the cells and releases the cellular content (proteins, lipids, polysaccharides, and other sugars), which can then be consumed by bacteria in the treatment basin and mineralized to carbon dioxide. A portion of the biological matter is then diverted from the solids that would require further treatment in the waste activated sludge line. The sidestream is returned to the RAS line and conveyed to the aeration tank. Where the RAS is returned to anoxic basins, the ozonated and oxygenated sidestream may be conveyed to an aerobic basin.

The system is operated to supply enough ozone to lyse cells but not so much as to oxidize the cell contents. The ozone dose necessary for sludge reduction is reportedly 1–10 g of ozone per day per kg of sludge. The process is also claimed to control foaming and bulking. The ozone dose necessary to control filamentous organisms with minimal impact on other microbiologic population is 0.1–1.5 g of ozone per day per kg of sludge.³³

The second process includes the use of ozone as a pretreatment to anaerobic digestion. By lyse of the cells and oxidation of the organic content, methane production may increase. One study documented that preozonation at a dose of 0.1 g ozone per g of chemical oxygen demand (COD) enhanced anaerobic sludge digestion by altering up to 67% of the organic matter: 29% was returned to soluble form and 39% was removed. In addition, the methane production was increased by a factor of 1.8.³⁴

The third process is the treatment of sludge to Class A biosolids. One study demonstrated that solids treated with 0.3 g of ozone per g of dried solids resulted in a Class A product. Higher ozone dosages, 0.5 g of ozone per g of dried solids, resulted in biosolids that produced no hydrogen sulfide for a month at 29°C. The ozone-treated biosolids had a low pH, which had to be corrected with quicklime.³⁵

DISINFECTION

Ozone is a powerful disinfectant: It can inactivate coliforms, *Cryptosporidium*, *E. coli*, *G. lamblia*, and viruses. Based on the U.S. Environmental Protection Agency (USEPA) disinfection criteria, ozone is the strongest chemical disinfectant for the inactivation of *Cryptosporidium* and *Giardia*. UV is also a highly effective nonchemical process for the inactivation of those pathogens as well. Ozone is 100–300 times more effective than chlorine for activating *Giardia* cysts.

Ozone inactivates pathogens through lyses of the cell wall or by breakdown of their genetic material. Like other chemical disinfectants, ozone chlorine residual $\times$ contact time (CT) values decrease as the temperature rises; thus, it is more effective at higher temperatures. However, unlike chlorine that dissociates between hypochlorous acid and hypochlorite, disinfection with ozone is not pH dependent between pH 6.0 and 10.0.³⁶

Use in Drinking Water

The USEPA has promulgated treatment techniques for the removal and/or inactivation of pathogens. The USEPA requires WTPs using surface water supplies or waters that are under the influence of surface water to achieve minimum inactivation or removal of 3.0log for *Giardia* and 4.0log for viruses. For well-operated utilities that achieve a combined filter effluent value of 0.3 nephelometric turbidity unit (NTU), 0.5-log inactivation of *Giardia* and 2.0-log inactivation of viruses are required.

The USEPA uses CT values to assess the degree of disinfection achieved. CT values are the product of the disinfectant concentration, C (in mg/l), and the contact time, T (in minutes), at the point of disinfectant residual measurement. Contact time is defined as the T_{10} detention time, or the period during which 10% of the water that enters a contactor has passed through. This definition of time ensures that at least 90% of the water has been exposed to the disinfectant during the reported period.

The T_{10} value is determined by computational fluid dynamic (CFD) modeling or by a tracer study. Most often, a tracer is added at the head of the contactor, and the residual is measured in the contactor effluent and is used to determine the short-circuiting or baffling factor for the basin. A multi-chamber ozone contactor usually is designed to achieve a baffling factor of 0.50–0.65:

$$\text{SCF} = \text{BF} = T_{10}/T \quad (15.11)$$

where

SCF = short circuiting factor (unitless),

BF = baffling factor (unitless),

T_{10} = period during which 10% of the water entering a contactor has passed through (min), and
T = hydraulic retention time of the basin (min).

The CT values for disinfection of *Giardia*, viruses, and *Cryptosporidium* with ozone are listed in Tables 15.6 through 15.8.

Disinfection CT requirements with ozone differ from those for chlorine. Because ozone decays much more rapidly, the residual is commonly measured at multiple locations, and the CT for the contact time upstream from the monitoring location is calculated. The sum of the CT values for the contactor is used to determine the disinfection credit.

Since transfer in a conventional contactor with diffusers may take several minutes, USEPA provides a direct log credit for the transfer cell under certain conditions. These conditions include that the transfer cell must be countercur-

TABLE 15.6. CT Values for Inactivation of *Giardia* Cysts by Ozone³⁷

Log Inactivation Credit	Temperature (°C)					
	1	5	10	15	20	25
0.5	0.48	0.32	0.23	0.16	0.12	0.08
1.0	0.97	0.63	0.48	0.32	0.24	0.16
1.5	1.5	0.95	0.72	0.48	0.36	0.24
2.0	1.9	1.3	0.95	0.63	0.48	0.32
2.5	2.4	1.6	1.2	0.79	0.60	0.40
3.0	2.9	1.9	1.4	0.95	0.72	0.48

TABLE 15.7. CT Values for Viruses Inactivation by Ozone³⁷

Log Inactivation Credit	Temperature (°C)					
	1	5	10	15	20	25
2.0	0.90	0.60	0.50	0.30	0.25	0.15
3.0	1.4	0.90	0.80	0.50	0.40	0.25
4.0	1.8	1.2	1.0	0.60	0.50	0.30

TABLE 15.8. CT Values for *Cryptosporidium* Inactivation by Ozone³⁸

Log Inactivation Credit	Water Temperature (°C)					
	1	5	10	15	20	25
0.5	12	7.9	4.9	3.1	2	1.2
1.0	23	16	9.9	6.2	3.9	2.5
1.5	35	24	15	9.3	5.9	3.7
2.0	46	32	20	12	7.8	4.9
2.5	58	40	25	16	9.8	6.2
3.0	69	47	30	19	12	7.4

TABLE 15.9. Direct Inactivation Credits for Countercurrent Transfer Cells with Diffusers

Ozone Residual at Outlet of Cell 1 (mg/l)	Inactivation Credit
<0.10	None
≥0.10 but <0.30	1.0log viruses
≥0.30	1.0log viruses and 0.5log <i>Giardia</i>

rent and the same as or larger than the subsequent cells. Those values are listed in Table 15.9.

The CT credit for ozone can be calculated by multiplying the residual at the end of a cell by the time in the contactor, as described in Equation (15.12), or by determining the decay rate of ozone by using first-order reaction kinetics and the log-integration method, as described in Equation (15.13). The first method is commonly referred to as the conservative method. The log integration method is discussed as the extended continuously stirred tank reactor (CSTR) method in the *Long Term 2 Enhanced Surface Water Treatment Rule Toolbox Guidance Manual—Draft*.³⁸

$$CT = SCF \times [(C_{\text{cell}2} \times T_{\text{cell}2}) + (C_{\text{cell}2} \times T_{\text{cell}3}) + \dots + (C_{\text{celli}} \times T_{\text{celli}})], \quad (15.12)$$

where

SCF = short-circuiting factor or baffling factor (unitless),

$T_{\text{cell}x}$ = theoretical detention time for cell x (min), and

$C_{\text{cell}x}$ = effluent dissolved ozone concentration in cell x (mg/l),

and

$$CT = (C_o) \times (e^{kt} - 1)/k, \quad (15.13)$$

where

C_o = initial dissolved ozone concentration (mg/l),

e = exponent (2.7183),

k = decay coefficient (min^{-1}), and

t = theoretical contact time of contactor (min).

The integrated method results in the highest CT values, as much as 10%–60% higher than by using the conservative method and does not use a SCF and does not require a tracer test.^{6,27,39} Commonly though, three or more monitors are used to determine the decay coefficient to verify that all monitors are within calibration. As more dissolved ozone monitors are used, the result of the conservative method begins to approach the value derived by the integration method.

Use in Wastewater

The first reported testing of ozone as a wastewater disinfectant was by the U.S. Army in 1955.⁴⁰ The laboratory results demonstrated that ozone could be used successfully for sterilization of sewage seeded with *Bacillus anthracis*, *Bacillus subtilis*, and influenza virus, and for the inactivation of *Clostridium botulinum* toxin. Ozone and the radicals formed during ozone decay attack and lyse cell walls, damage nucleic acids (purines and pyrimidines), and break carbon–nitrogen bonds, leading to depolymerization.⁴¹ Ozone has been applied to wastewater, albeit to a much more limited extent than to potable water. It is highly effective for controlling nuisance odors, for reducing the volume of solids produced in secondary treatment and in digestion of wastewater, and as a disinfectant. The advantages of using ozone in wastewater treatment include the following:

1. Ozone reacts with ammonia to a limited extent at pH less than 9.3. Therefore, unlike with chlorine, wastes high in ammonia do not require excessive amounts of ozone to reach breakpoint.⁴²
2. Ozone is highly effective in removing color and odor from municipal wastewater effluent.
3. Ozone treatment results in an oxygenated effluent that may not require re-aeration before discharge.
4. Ozone decay rate is usually high enough to not require a quench chemical system.
5. The disinfection efficiency of ozone is not dependent on the water pH.
6. The log inactivation of a target pathogen is a function of the ozone demand, residual, and time.

Applying potable water methodologies of CT may underestimate some of the actual disinfection action that occurs in wastewater treatment during the establishment of an ozone residual. Inactivation of fecal coliforms and *E. coli* has been demonstrated at ozone dosages below the ozone demand of the water. Conducting testing to empirically determine inactivation during the establishment of an ozone residual is recommended.

Typical treatment goals in wastewater are not based on achieving a level of inactivation credit. Instead, they are based on achieving a concentration less than the permitted value of a target organism measured daily or weekly in the treated effluent. Disinfection requirements vary among states, types of effluent receiving bodies, and season. Discharge limits for pathogens range from ≤ 2.2 to 5000 most probable number (MPN) of fecal coliform (FC)/100 ml or ≤ 2.2 –10,000 MPN total coliform (TC)/100 ml. The most common standard for receiving waters is 200 MPN FC/100 ml.

Treatment of wastewater with ozone generally requires much larger ozone doses than those observed in potable water, owing to the high reactivity of

ozone, the organic content of municipal effluent, and the unpredictability of wastewater constituents over any 24-h period.

Typical ozone doses for treatment of various wastewaters and based on a contact time of 15 min are listed in Table 15.10. In all cases, bench- and pilot-scale studies must be performed to establish the actual dosages for a given facility.

The information in Table 15.10 is based in part on the equations developed by Venosa and Meckes, who demonstrated that total and fecal coliform levels in a given effluent can be predicted if the demand properties of the effluent (COD, NO_2^- , total suspended solids [TSS], and TOC) and the absorbed ozone doses are known.^{43,44,45} Venosa et al.⁴⁶ developed mathematical models that can be used to predict either the total or fecal coliform concentrations in filtered secondary effluent. The R^2 for the equations are 0.59 and 0.67 (144 data points), respectively.

$$\log(\text{TC}) = 3.95 + 0.030 \times \text{COD} + 0.50 \times \text{NO}_2^- - 3.05 \log(T) \quad (15.14)$$

$$\log(\text{FC}) = 3.34 + 0.029 \times \text{COD} + 0.48 \times \text{NO}_2^- - 3.4 \log(T), \quad (15.15)$$

where

TC = total coliforms/100 ml,

FC = fecal coliforms/100 ml,

T = transferred ozone dose (mg/l),

COD = chemical oxygen demand (mg/l), and

NO_2^- = nitrite nitrogen (mg/l as N).

TABLE 15.10. Typical Ozone Dosages in Wastewater Treatment⁴⁴

Type of wastewater	Initial Coliform Count	Ozone Dosage (mg/l)			
		Effluent Standard, MPN/100 ml			
	MPN/100 ml	1000	200	23	<2.2
Raw wastewater	10^7 – 10^9	15–40	—	—	—
Primary effluent	10^7 – 10^9	10–40	—	—	—
Trickling filter effluent	10^5 – 10^6	4–0	—	—	—
Activated sludge effluent	10^5 – 10^6	4–10	4–8	16–30	30–40
Filtered activated sludge effluent	10^4 – 10^6	6–10	4–8	16–25	30–40
Nitrified effluent	10^4 – 10^6	3–6	4–6	8–20	18–24
Filtered nitrified effluent	10^4 – 10^6	3–6	3–5	4–15	15–20
Microfiltration effluent	10^1 – 10^3	2–6	2–6	3–8	4–8
Reverse osmosis permeate	NA	—	—	—	1–2
Septic tank effluent	10^7 – 10^9	15–40	—	—	—
Intermittent sand filter effluent	10^2 – 10^4	4–8	10–15	12–20	16–25

The following equations can be used to predict the concentration of pathogenic indicator organisms in unfiltered secondary effluent. The concentration of suspended solids can affect the disinfection efficiency of ozone, although to a much lesser extent than nitrite concentration. A stronger correlation was developed as the R^2 for each of the following two equations was 0.83:

$$\begin{aligned} \text{Log}(\text{TC}) = & 0.96 \log(\text{TC}_i) - 0.89 + 0.012 \times \text{COD} + 0.60 \times \text{NO}_2^- + 0.013 \\ & \times \text{TSS} - 4.024 \log(T) - 0.57 \times C^{1/2} \end{aligned} \quad (15.16)$$

$$\begin{aligned} \text{Log}(\text{FC}) = & 4.06 + 0.020 \times \text{COD} - 0.37 \times \text{NO}_2^- + 0.012 \\ & \times \text{TSS} + 3.94 \log(T) - 0.59 \times C^{1/2}, \end{aligned} \quad (15.17)$$

where

TSS = total suspended solids (mg/l),

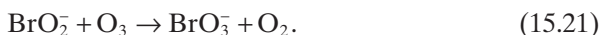
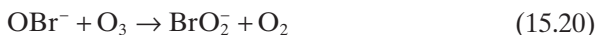
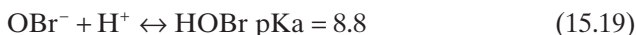
TC_i = initial total coliforms/100 ml, and

C = dissolved ozone concentration (mg/l).

Increases in suspended solids concentration may provide a shielding effect to the pathogens, making treatment difficult. Ozone will inactivate the free-swimming bacteria and those in small clumps, but the dose required to attack the organisms attached to particles becomes a function of the particle size distribution. With particles larger than 20 μm in diameter, disinfection will begin to diverge from the log-linear form that may be developed by using the CT concept.⁴¹

OZONE DBPS

The only regulated by-product of ozone disinfection is bromate, which is formed through the reaction of bromide and ozone:



Bromide will react with chlorine, chlorine dioxide, or ozone to form hypobromous acid and hypobromite. These two species are similar to the disassociated form of chlorine: hypochlorite and hypochlorous acid. Hypobromous acid and hypobromite are in equilibrium with one another at pH 8.8. Ozone is the only oxidant used in water treatment that will further oxidize the hypobromite ion to bromate. Ozone does not react with hypobromous acid. The current drinking water standard for bromate agreed to by the European Union, the

United States, and the World Health Organization is 0.010 mg/l. Samples are taken each month, and the limit is based on a running annual average.

Bromate Control

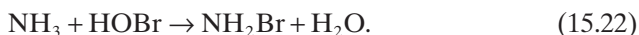
There are several bromate control methods. Their effectiveness for treatment of any water supply cannot be predicted. Therefore, they are usually evaluated at bench- or pilot-scale to determine the most cost-effective bromate mitigation strategy.

Control of Ozone Dosage. Bromate formation will be lower at lower ozone dosages and lower residuals. By tightly controlling the dosage and not adding excess ozone, some utilities have found that they can lower the overall concentration of bromate. This is typically the most cost-effective approach to mitigating bromate formation.

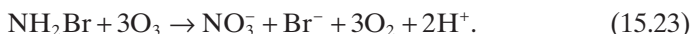
pH Adjustment. Bromate is formed through the reaction of ozone with hypobromite. Hypobromous acid does not react with ozone. Therefore, one control procedure is to limit the concentration of hypobromite by reducing the pH. An acid is used to reduce the pH to a target value, commonly 7.0 or slightly less. At pH 7.0, less than 2% of the bromide is in the hypobromite form available for further oxidation to bromate.

Reducing bromate formation by pH adjustment has been shown to be very effective. The reduction of bromate per unit decrease in pH is generally between 30% and 50%.⁴⁷ The drawback of this control method is that reduction of pH can be very costly for water supplies with high pH and alkalinity. Alternatively, if enhanced coagulation is practiced, the treatment method may involve adding the acid farther upstream in the treatment process.

Ammonia Addition. Ammonia reacts with hypobromous acid to form monobromoamine (NH_2Br), which decreases the concentration of hypobromite available for oxidation to bromate:



The first challenge of this control process is that the bromide ion must first be oxidized to hypobromous acid by adding ozone or chlorine so that it will react with the ammonia. A second complication is that ammonia at pH above 9.3 will be oxidized to nitrate within several minutes, freeing up the hypobromite for oxidation by ozone to bromate. The rate of ammonia oxidation is very slow at pH lower than 9.3, and the reaction between ammonia and ozone is not as large a factor in the overall ability of the strategy to control bromate formation:



Free ammonia concentrations of 0.1–0.5 mg/l as N tend to result in 20%–50% reductions in bromate formation.⁴⁷

Chlorine–Ammonia Process. Chlorine is added upstream from ozone to oxidize the bromide to hypobromous acid, and then ammonia is added to form monobromoamine:



The chlorine dosage is usually just adequate to meet the demand in the water or to produce a very small residual, less than 0.50 mg/l. The reaction between hypochlorite and bromide is slow, and typically as much as 5 min may be provided for hypobromous acid formation.⁴⁸ The reaction between hypochlorous acid and bromide is 10^6 times faster; therefore, depressing the pH can greatly increase the rate of hypobromous acid formation.

Monochloramine and monobromamine are formed following the addition of ammonia, and ammonia is added in excess of the quantity required to react with all the chlorine and bromine. Chlorine and bromine will compete for the ammonia. However, the rate of monobromamine formation is 20 times that of monochloramine formation, and the reaction between ammonia and monobromamine takes only a few microseconds. A trace of free ammonia is usually used as a control point to ensure monobromamine formation.

The chlorine–ammonia process has several advantages over the ammonia procedure. However, the depression of pH and addition of chlorine and ammonia were demonstrated to have a synergistic effect, and the overall formation of bromate was lowest when they were used.⁹ The chlorine–ammonia procedure may be cost-effective for utilities with high-alkalinity water. The process is more complicated, though, as it involves multiple chemical feed locations and online monitoring of chlorine and ammonia concentrations. Control is critical, as overfeeding of chlorine may result in higher concentrations of bromate than would be the case without any mitigation. A second disadvantage to this mitigation procedure is that contact time with free chlorine may result in higher concentrations of chlorinated disinfection by-products.

Chlorine Dioxide. The use of chlorine dioxide upstream from ozone can significantly reduce bromate formation. The reduction can occur in part through substituting the ozone dose with chlorine dioxide; however, chlorine dioxide preoxidation reduces the bromate formation potential even at the same ozone dosage.¹²

Chlorine dioxide reacts with phenolic functional groups in NOM, which otherwise would have reacted with dissolved ozone to form hydroxyl radicals. The yield of hydroxyl radicals by phenolic groups is very large, and hydroxyl radicals are one of two pathways through which bromate is formed. Hence, preoxidation of phenolic compounds results in the formation of less hydroxyl

radicals during ozonation as well as lower bromate formation.¹⁰ This is a different mechanism for the control of bromate from all others discussed. This control method is not targeted so much at the hypobromite ion as the radical products formed during ozonation. In addition, the mechanisms are not well understood and more complex than described above.

Chlorine dioxide used to mitigate bromate formation appears to be more effective on waters with higher TOC and, thus, higher hydroxyl radical formation. Reductions in bromate may be as much as 30%, although the results are highly site specific and a function of the quantity of phenolic functional groups and the TOC. Like the chlorine–ammonia mitigation procedure, combining the chlorine dioxide with pH adjustment has a synergistic effect, resulting in a lower concentration of bromate.

The advantage of the chlorine dioxide mitigation process is that no TTHMs or HAAs are formed; however, chlorine dioxide has its own DBP, chlorite (ClO_2^-). Chlorite exerts an ozone demand and will be oxidized to chlorate (ClO_3^-), which is unregulated in the United States, with the exception of California, where the action level is 0.8mg/l. The chlorite ion is believed to play an important role in the bromate mitigation strategy.¹²

Aldehydes, Carboxylic Acids, and Ketones

Aldehydes and carboxylic acids appear following ozonation. These products are formed through the breakdown of double bonds within an organic molecule. These compounds are biodegradable and can be removed through biologic filtration. The rate of removal is a function of the media type, water temperature, biologic density, and activity.⁴⁹ These compounds, though, can rereform following the addition of chlorine.

USE IN WATER AND WASTEWATER TREATMENT

Ozone has a wide range of applications in water and wastewater treatment, including the following:

1. Inactivation of pathogenic viruses, bacteria, and protozoa
2. Oxidation of inorganic compounds, particularly iron, manganese, and sulfide
3. Oxidation of SOC's
4. Enhanced TOC removal through coagulation or biological filtration
5. Elimination of taste- and odor-causing compounds
6. Color removal
7. Oxidation of EDCs and PPCPs
8. Enhanced turbidity removal through microflocculation and filtration

- 9. Elimination of chlorinated DBPs
- 10. Synergistic effects with UV by increasing UVT₂₅₄

The use of ozone in industry is primarily for color removal and bleaching by the pulp and paper industry, which makes up as much as 20%–25% of the ozone business. Uses of ozone in industry are listed below:

- 1. Bleaching and color removal
- 2. Wafer etching in semiconductor industry
- 3. Treatment of cooling waters for prevention of biogrowths
- 4. Disinfection of air-conditioning systems
- 5. Disinfection of washing water in hospitals for patients, nurses, and doctors
- 6. AOP
- 7. Treatment of heat exchangers to prevent microbially induced corrosion
- 8. Treatment of food products to prevent spoilage
- 9. Mineralization of organic material in ultrapure water systems
- 10. Odor control

Potable Water Installations

In the United States, more than 300 large-scale facilities with a combined treatment capacity of more than 14 billion gal/day are using ozone to treat water and wastewater.⁴ The installation of ozone is typically used to meet multiple treatment objectives, but the most common uses involve primary disinfection, control of taste- and odor-causing compounds, and disinfection by-product control. The ozonation process treatment objectives for potable water installations are summarized in Table 15.11. Because multiple treatment objectives at each location are listed, the percent reporting does not add up to 100%.

TABLE 15.11. Reported Ozonation Process Treatment Objectives for Potable Water⁴

Treatment Objective	Percent (%) Reporting
Primary disinfection	72
Control of taste- and odor-causing compounds	57
Disinfection by-product control	52
Removal of color	20
<i>Cryptosporidium</i> inactivation	9
Oxidation of hydrogen sulfide	9
Iron and manganese oxidation	6

Wastewater Installations

From 1975 through 1983, ozone was used at 41 wastewater treatment plants (WWTP) in the United States.⁴ However, by 2008, only nine of them were still using ozone. Many facilities had installed systems that were undersized, and others found disinfection difficult to achieve as the quality of the treated effluent was inconsistent.

Ozone has since seen a renaissance, as 10 facilities have either upgraded their ozone systems or have installed new systems. Currently operating ozone systems at wastewater treatment plants are listed in Table 15.12, and several larger wastewater systems are considering ozone treatment listed in Table 15.13.

TABLE 15.12. Wastewater Utilities Using Ozone for Disinfection⁴

Start-Up (Year)	Facility	Capacity (mgd)	Installed Ozone Capacity (ppd)	Firm Dosage (mg/l)
1978	Meander Creek WWTP Mahoning County, OH	8	500	7.5
1978	Southwest WWTP Springfield, MO	64	3,200	4.5
1980	Frankfort WWTP, Frankfort, KY	40	1,000	3.0
1982	Belmont WWTP, Indianapolis, IN	150	12,000	3.2
1982	Hagerstown WPCP Hagerstown, MD	12	1,400	4.7
1982	Southport WWTP, Indianapolis, IN	150	12,000	3.2
1985	Fred Hervey WWTP, El Paso, TX	12.5	900	8.6
1997	WWTP, Trion, GA	8	1,800	13.5
2003	F Wayne Hill Water Reclamation Plant, Gwinnett County, GA	60	2,000	4.0

TABLE 15.13. New Facilities Currently in Preliminary or Detailed Design

Facility	Capacity (mgd)
91st Avenue Demonstration Plant, Phoenix, AZ Capacity of full-scale system if pilot successful	5 600
Clark County, NV	30
Eastern Wastewater Treatment Plant, Melbourne, AU	216
Montreal Urban Community WWTP, Montreal, Canada	700

EQUIPMENT AND GENERATION

Ozone must be generated at the point of use because it is subject to rapid decomposition, reverting to oxygen. The source gas may be atmospheric air or enriched oxygen. Ozone can be generated by electrical discharge or by photochemical action by using UV light. The latter produces the ozone layer in the upper atmosphere and may be used in small ozone generators, typically less than 1 ppd. The most practical method for producing larger quantities of ozone is by electrical discharge.

Ozone is produced through electrical discharge when a gas stream containing oxygen is subjected to a high-voltage/high-density electrical current, which provides the energy to drive the reaction. An electrical field develops in a gap between two electrodes, one of which is coated with a dielectric material. Ozone is formed by splitting molecular oxygen into two atoms, which recombine with other oxygen molecules to produce ozone.

There are four basic components to the ozonation process: (a) gas preparation or feed source, (b) the ozone generator, (c) the contactor where ozone is transferred into water, and (d) the exhaust gas destruction system (Fig. 15.6).

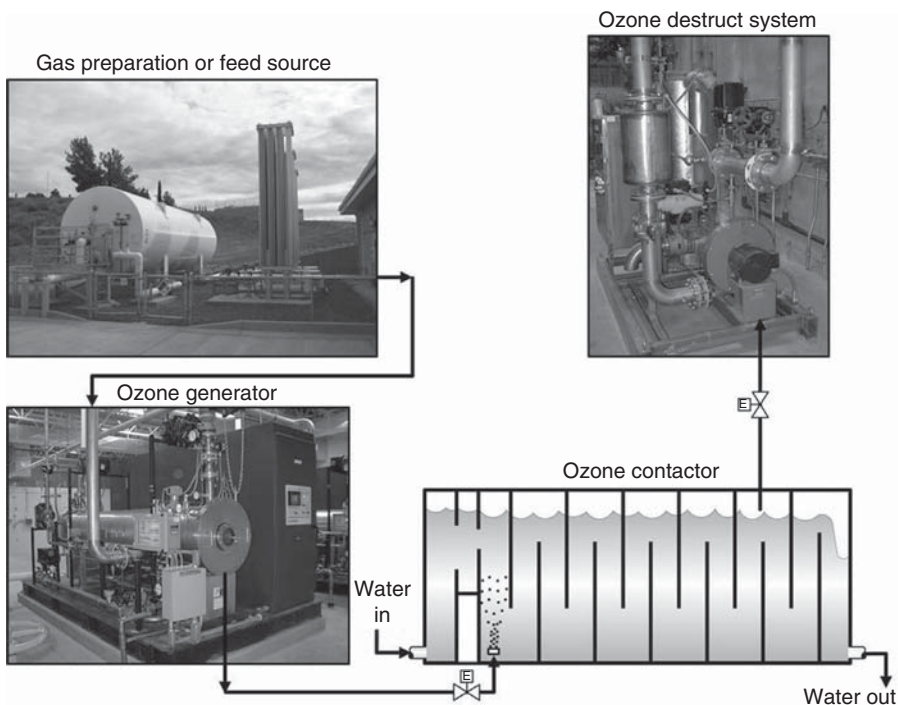


Figure 15.6. Ozone process schematic.

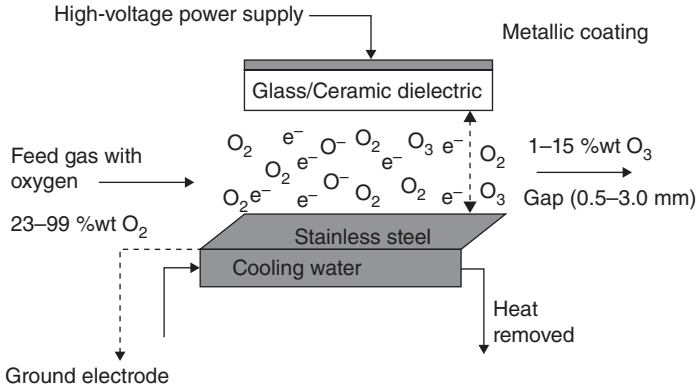


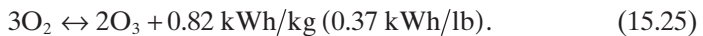
Figure 15.7. Ozone generator cross-sectional schematic.

In addition to these major components, there are many ancillary systems critical to the economical production of ozone.

Theory of O₃ Generation

Ozone is produced when high-voltage alternating current is imposed between two electrodes in the presence of oxygen (Fig. 15.7). The visible effect of the incomplete breakdown of the oxygen molecule in the space between the highly charged electrodes is known as the corona glow.

Ozone is generated from either air or oxygen in proportion to the energy applied to the ozone generator, as demonstrated by the following equation:⁵⁰



The ozone-generating reaction is initiated when free energetic electrons in the corona dissociate oxygen molecules:



This is followed by ozone formation from a three-body collision reaction:



where M is any other molecule in the gas.

At the same time, atomic oxygen and the available electrons react with ozone to form oxygen:⁵⁰



and



Commercially available corona discharge generators produce ozone at concentrations varying from 0.5% to 16% by weight of the carrier gas. All discussion within this chapter refers to ozone concentration as percent by weight unless otherwise noted. It is listed as percent only throughout the remainder of the chapter.

Only about 5%–10% of the applied energy is used to produce ozone. Most of the energy is dissipated in the form of heat. The remainder of the loss is through light. The decomposition of ozone back to oxygen is greatly accelerated with rising temperature, so generators must include means to remove heat.

Gas Source

Ozone can be generated from dry air, oxygen-enriched air, or high-purity oxygen. Nearly all municipal systems today use liquid oxygen (LOX) delivered to the site, which increases the system operating costs by adding the LOX transport and storage costs, but the LOX system is relatively simple and inexpensive to control, maintain, and operate. Other sources of gas are generally found to be more economical for very small ozone systems, less than 10ppd, or for very large ones with capacities more than 10,000ppd. A summary of the gas sources for North American municipal treatment facilities commissioned in 1997 through those planned for 2008 is shown in Table 15.14. LOX was the source gas for 89% of the installations during that period.

Air-Based Systems. The ozone industry has seen a large shift from air-based ozone systems to those that use high-purity oxygen as the source gas. Very few new municipal air-based ozonation systems have been installed since the mid-1990s. When the feed gas is ambient air, the ozone generator’s performance is typically optimized at a concentration of 2% when using low-frequency equipment and 4% when using medium-frequency equipment.

TABLE 15.14. Gas Source for Municipal Ozone Facilities, 1997 through 2008⁴

Gas Source	Number of Installations	Percent (%) of Total
LOX	152	89
Air	10	6
Pressure swing adsorption	4	2
Vacuum swing adsorption	4	2
Cryogenic air separation	1	1
Total	171	100

However, when the feed gas is oxygen, the optimum concentration is about 10%–12%.

Lincoln Water Services, Lincoln, Nebraska, evaluated changing its gas source from air (original installation) to high-concentration oxygen in 2008. The utility anticipated an increase in ozone generating capacity from 350–600ppd while continuing to use the same generator shell, dielectrics, and low-frequency power supplies. However, it ultimately chose to replace the ozone generators, as a present worth evaluation indicated that operating at 4%, affected largely by the cost of LOX, was more costly than new generating equipment that would operate at 12% and use one-third the amount of LOX.

Enriched and High-Purity Oxygen Systems. Oxygen may be purchased and delivered to the site as LOX or produced on-site by oxygen production systems, which separate and concentrate oxygen from air and remove impurities and nonessential gases. Cryogenic air separation will produce a gas that is 95% to more than 99.9% oxygen and pressure swing adsorption (PSA) or vacuum swing adsorption (VSA) units will produce a gas that is 90%–95% oxygen. Ozone generators operating at 6%–12% require between 8 and 17lb of high-purity oxygen gas per pound of ozone generated.

Gas Quality. A high-quality feed gas is essential to the long-term operability of the ozone generator. The feed gas must be extremely dry, free of particulates and hydrocarbons, relatively cool, and at the appropriate pressure and flow for treatment.

Particulate. If dust is allowed to collect on the dielectrics, it will decrease generator efficiency, increase dielectric stress, and cause breakage of the dielectrics. Since the tolerances between the conductors may be as small as 0.3mm, a particle could span that gap, causing an arc within the generator that would result in failure of the dielectric and/or fuse. Therefore, filters must be installed in the piping upstream from the ozone generator.

Hydrocarbons. Hydrocarbons in the feed gas are vulnerable to oxidation by ozone, which would produce a black coating on the dielectrics that would lead to lowering of the generator efficiency. This coating may be flammable in an oxygen-enriched environment and will also increase the potential for failure of the dielectric.

Relative Humidity. Gas with a high humidity, greater than -70°F , not only decreases the ozone production rate but also escalates the contamination of the dielectrics, regardless of whether the feed gas is high-purity oxygen or air. If high-purity oxygen is the feed gas, it leads to the formation of hydrogen peroxide in the presence of water vapor and to deposits on the dielectrics. If air is the feed gas, about 1 mol of nitrogen pentoxide (N_2O_5) will develop for every 100mol of ozone produced.⁵¹ The N_2O_5 can decompose into nitrogen

dioxide (NO_2), which will interfere directly with ozone production. Nitrogen pentoxide in the presence of water vapor will produce nitric acid (HNO_3), which will cause severe corrosion in the generator and downstream piping, and create a heat sink, which will have a detrimental effect on the dielectrics and increase the potential for their failure.

Maintenance should be based on visual inspection of the interior of the generator and evaluation of operating data and generator efficiency. High moisture content in the feed gas not only damages the dielectrics but also will increase generator maintenance requirements.

Ambient Temperature. Gaseous ozone decays rapidly at elevated temperatures, therefore affecting the efficiency of the ozone generator. Tempering the gas is not necessary except for locations where the inlet gas temperature is below 5°C or above 30°C . Water-cooled aftercoolers may be used downstream from blowers and compressors and at facilities in exceptionally hot climates.

Gas Pressure Suitable for Ozone Generator. The gas preparation system supplies the pressure to convey the gas through the generator and into the dissolution system. The gas must be regulated to deliver a constant pressure. Large ozone generators are typically operated at less than 25 psig, although units that operate at higher pressure are available.

Gas Quality. General feed gas quality requirements for ozone generators are listed in Table 15.15. The requirements vary with system manufacturer; therefore, the manufacturer should be consulted before purchasing an ozone-generating system. The LOX supplied must conform to American National Standards Institute (ANSI)/American Water Works Association (AWWA) B304-05 Liquid Oxygen for Ozone Generation with the exception of the hydrocarbon content to which the ozone system supplier may have more stringent requirements.

Select physical properties of air and oxygen are listed in Tables 15.16 and 15.17.

LOX. LOX may be delivered, stored, and vaporized into gaseous oxygen (GOX) on-site. The LOX system consists of one or more large storage tanks, vaporizers, and pressure-regulating valves (Figs. 15.8 and 15.9). In addition, filters and a supplemental nitrogen source are commonly used.

The LOX storage tank is designed to store and deliver LOX to the vaporizers. It is double-walled and jacketed, with the space between the walls maintained under vacuum and filled with perlite media or a composite material to insulate the inner tank. The tank includes both liquid and gas connections and valves to receive LOX deliveries as well as pressure-relief valves and rupture disks to prevent overpressurization of the tank.

A pressure-building coil maintains the pressure within the tank by allowing a small volume of LOX to pass through a vaporizer located on the bottom of

TABLE 15.15. Minimum Requirements for Oxygen and Air⁵²

Quality Parameter	Composition of Feed Gas
Oxygen	
Air systems	23.1% by wt
Enriched air	>90% by wt
LOX	>99.0% by wt
Nitrogen	
Air systems	75.6% by wt
Enriched air	200 ppm up to 10% wt
Moisture	
Dew point	-62 °C (-80 °F)
Concentration	<7.8 ppm _v
Total hydrocarbons (expressed as CH ₄)	<15 ppm _v on average <25 ppm _v 80% of the time <50 ppm _v 100% of the time
Halogenated hydrocarbons	<1 ppm
Nitrogen oxides	<1 ppm
Freons or similar	To be vented totally before startup
Solvents	To be vented totally before startup
Particle size	<2 μm and particle buildup to be avoided
Temperature	>5 °C (>41 °F) and <90 °C (<194 °F)

TABLE 15.16. Selected Physical Properties of Air⁶

	U.S. Units	SI Units
Molecular weight	28.96	28.96
Composition		
Nitrogen (percent by wt)	75.6	75.6
Oxygen (percent by wt)	23.1	23.1
Argon (percent by wt)	1.3	1.3
All others (percent by wt)	<0.01	<0.01
Specific gravity of gas	1.0	1.0
Specific heat of dry air at 32 °F (0 °C) and 1 atm	0.240 Btu/(lb °F)	1.00 kJ/(kg °C)
Weight of gas at NTP (0 °C and 1 atm)	0.08067 lb/ft ³	1.292 g/l
Weight of gas at STP (20 °C and 1 atm)	0.07516 lb/ft ³	1.204 g/l

NTP, normal temperature and air pressure; STP, standard temperature and pressure.

the tank. The LOX is vaporized to GOX (which is more than 800 times larger in volume), which, in turn, is fed back into the tank to maintain the tank pressure at 50–125 psig. The pressure in the LOX tank is used to drive the gas through the rest of the ozone system.

For systems where LOX is not the primary source of oxygen, the tank may sit idle and LOX may vaporize to GOX, which will result in the pressure within the tank building. Usually, boil-off is less than 0.25% of the weight of the LOX in the tank per day. To protect the tank from over pressurizing,

TABLE 15.17. Selected Physical Properties of Oxygen^{6,53}

	U.S. Units	SI Units
Molecular weight	32	32
Specific gravity of gas (air 1.0)	1.10	1.10
Boiling point at 1 atm	-297.3 °F	-182.9 °C
Critical temperature	-181.4 °F	-118.6 °C
Critical pressure	731.4 psia	5043 kPa (abs)
Critical density	27.23 lb/ft ³	436.1 kg/m ³
Latent heat of gas at boiling point and 1 atm	91.7 Btu/lb	213 kJ/kg
Specific heat of gas at 70 °F (21.1 °C) and 1 atm	0.220 Btu/(lb °F)	0.917 kJ/(kg °C)
Solubility in water, vol/vol at 32 °F (0 °C)	0.64	0.64
Weight of liquid at boiling point	9.52 lb/gal	1352 kg/m ³
Weight of gas at NTP (0 °C and 1 atm)	0.0891 lb/ft ³	1.428 g/l
Weight of gas at STP (20 °C and 1 atm)	0.0829 lb/ft ³	1.328 g/l

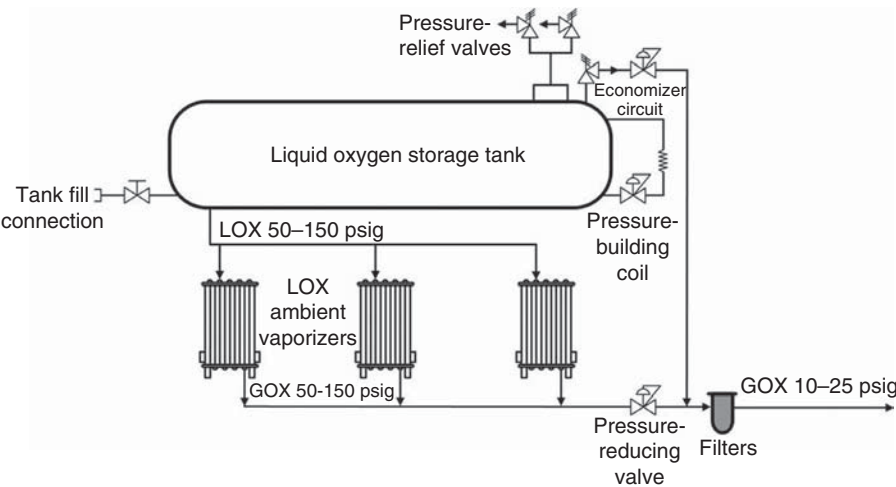


Figure 15.8. LOX system process schematic.

pressure relief valves would actuate to relieve the pressure and the GOX would be wasted to the atmosphere. Some LOX systems include an economizer that allows the boiled off LOX to be used in the ozone system. The economizer pressure-relief valves open at a lower pressure than the tank pressure-relief valves and discharge some of the gas to the GOX pipeline feeding the ozone generators. This prevents the LOX from being wasted.

Vaporizers are heat exchangers that supply the energy to evaporate the LOX into GOX. Ambient vaporizers are most commonly used and consist of a series of looped aluminum pipes with fins. They draw the energy needed to vaporize the LOX from ambient air. Vaporizers are installed outdoors with



Figure 15.9. LOX storage tank and ambient LOX vaporizer.

no obstructions limiting ambient airflow. During the vaporization process, a large amount of moisture is drawn from the atmosphere and deposited on the fins as ice. Vaporizer capacity is controlled by ambient temperature, relative humidity, and, to a lesser extent, elevation. Capacity is reduced at low temperatures, high relative humidity, and high elevation. The historical average number of days when the ambient temperature is continuously below freezing is critical for sizing. In addition, ice will accumulate on the vaporizer and must be considered during the design process, as it can be up to 10 times the vaporizer shipping weight.

The vaporizers operate on a freeze–thaw cycle, with one unit operating until the GOX temperature drops to a preset minimum. It is then allowed to thaw, and the second vaporizer is brought online to repeat the cycle. Often, a third vaporizer is provided as a standby unit. The vaporizers may be rotated based on a set point time, temperature, or production.

A second type of vaporizer is a shell and tube heat exchanger in which the heat is transferred from one fluid to another. Most commonly, water is used to vaporize the LOX. Another variation of these units is the use of the heat from a closed-loop ozone-generator cooling system for GOX vaporization.

GOX pressure-regulating stations regulate the GOX pressure to an adjustable lower level, usually to 15–25 psig, the generator operating pressure.

Oxygen filters capture dust and other debris from the GOX stream and keep particulate contaminants from entering the ozone generators. By proper maintenance of the filters, the frequency of cleaning and maintenance of the generators can be reduced.

In the late 1990s, it was discovered that a small amount of nitrogen (0.01%–4% by weight) added to LOX fed ozone generators resulted in lower specific energy required to produce ozone. In some cases, the presence of nitrogen may increase the operating range of each generator, allowing it to run at

lower capacities. For the nitrogen to be supplied, cylinders of nitrogen or supplemental air systems are installed with LOX systems to add nitrogen. Supplemental air systems are consistent with the air preparation systems described earlier.

Special precautions must be taken to ensure safe storage and handling of LOX. Of most critical importance is prevention of open flames, sparks, or other ignition sources in areas where oxygen may be present at elevated concentrations. Local codes commonly require that the LOX storage tanks be offset from the building, that the area be posted for “no smoking,” and that all electrical components be housed in explosion proof boxes. In addition, pressure relief valves must be located wherever LOX could be trapped between two isolation points to prevent development of overpressure situations due to vaporization.

VSA. VSA technology has been used since the mid-1980s to produce high-purity oxygen. They consist of an air compressor, adsorber vessels, enriched GOX tank, and oxygen-booster compressor (Figs. 15.10 and 15.11). Capacities of VSA systems range from less than 5 t/day to up to 225 t/day and may consist of one or more adsorber vessels.

The VSA units operate by drawing air through a screen and filter into one or more adsorber vessels. The adsorber vessels contain synthetic zeolite media, which preferentially adsorb nitrogen from air, to produce oxygen with more than 90% purity. The remaining 10% consists of approximately 4% argon and 6% nitrogen. The zeolite media also adsorb moisture, hydrocarbons, and

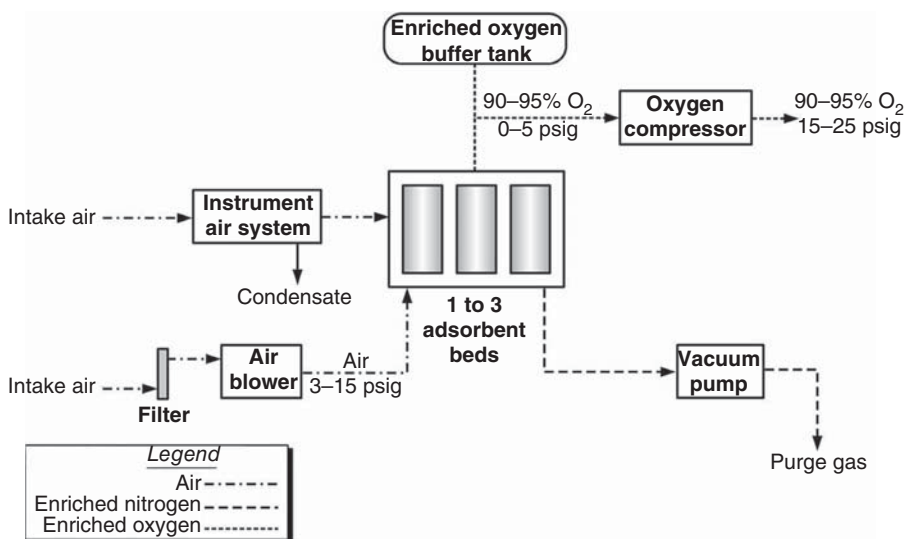


Figure 15.10. VSA process schematic.



Figure 15.11. VPSA Plant; 180t/day; Amarillo, TX (photo courtesy of Praxair) Praxair is a registered trademark of Praxair, Inc.

carbon dioxide. Approximately 40%–45% of the oxygen in the inlet air remains in the high-purity oxygen stream. The remaining 60%–55% is adsorbed by the zeolite and is lost when it is regenerated to remove nitrogen.

The adsorber vessels operate in alternating production and regeneration cycles. VSA units operate at pressures between 0.2 and 1 atm during the production cycle, and the adsorbent bed is regenerated under vacuum. During the production cycle, the nitrogen and moisture are removed from air through molecular sieve media, and oxygen is allowed to pass to an enriched GOX tank. The media are regenerated by reducing the pressure, causing the nitrogen and other constituents to be desorbed. The media are regenerated when it becomes saturated with gas and can no longer produce high-quality oxygen. The duration of the production cycle is usually based on preventing the oxygen concentration in the product gas from falling below 90%.

The air compressors are typically rotary, positive-displacement, oil-free units. Rotary lobe compressors are used most frequently, and multistage centrifugal units are also used. In some systems, the same machine is used to pressurize the air and to draw a vacuum. In other systems, a separate compressor and vacuum pump are provided but are sometimes both driven from the same, dual-shaft motor. For the large, rotary lobe air compressors and vacuum pumps, silencers dampen pulsations in the air stream. Large, multichambered reactive or combination reactive-absorptive silencers are required.

The enriched GOX tank provides very short-term storage between production and regeneration cycles and buffers the pressure swings that occur with the continuous drawing off of GOX by the oxygen booster compressor and intermittent flow from the VSA.

An oxygen booster compressor increases the pressure to 1–2 atm, and the GOX is then conveyed to the ozone generators. Oil-free reciprocating units

constructed for compression of oxygen are generally provided. Recirculation of product oxygen is used as a means of capacity reduction. Both the air and oxygen compressors are provided with atmospheric blow-off lines and after-cooler to reduce the heat of compression. The aftercoolers are usually water cooled.

Since pneumatic switching valves are utilized in the system, an instrument air system is often provided. The instrument air system typically consists of an oil-flooded rotary screw compressor, air receiver, refrigeration dryer, and a coalescing oil-removal filter. The necessity for entirely oil-free air is not as great for the instrument air system since the instrument air does not enter the process stream.

VSA and PSA systems are more maintenance intensive in comparison with a LOX system. The most common maintenance item is the fast-moving pneumatic switching valves, which may move several times per minute as beds switch from adsorption to regeneration. A LOX system is often installed as a backup for regularly scheduled maintenance, which may be as much as 1 week/year.

PSA. The PSA is similar to the VSA process, with nitrogen and other constituents being adsorbed by synthetic zeolite media to produce an oxygen stream, which is 90%–95% pure oxygen. Major differences consist of size of enriched GOX tank, operating pressures, and replacement of the oxygen-booster compressor with pressure-regulating valves (Fig. 15.12).

High-purity oxygen has been produced by PSA commercially since the early 1970s. Approximately 70 PSA systems are operating in water and

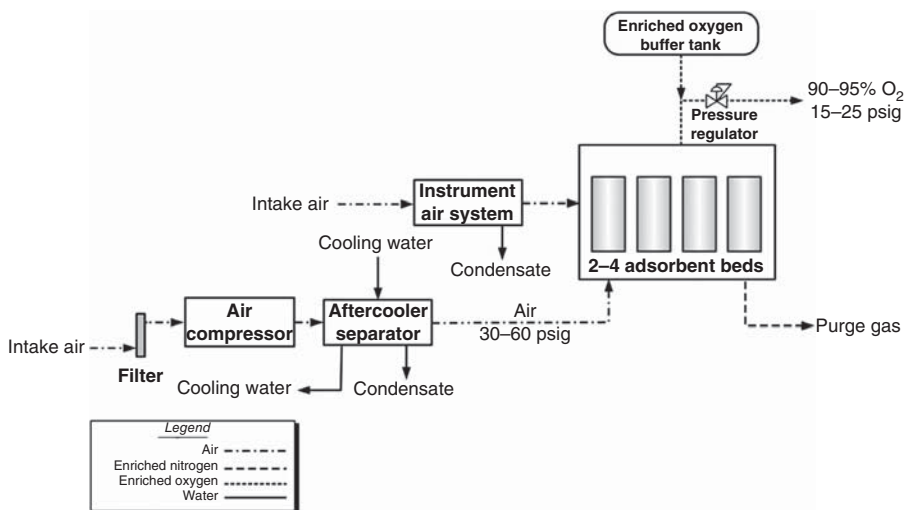


Figure 15.12. PSA process schematic.

wastewater treatment plants in the United States. The capacity of PSA plants for oxygen production ranges from small (50ppd) single units to large, multiple train plants (up to 150t/day). The largest single PSA train is 32 t/day.

Cryogenic Air Separation. Cryogenic air separation is the oldest oxygen preparation technology. It was introduced in 1902 and is used widely in industrial and, to a much lesser extent, in municipal applications. More than 2000 systems have been installed worldwide, with capacities ranging from 20t/day to more than 1000t/day. Cryogenic systems are complex, so the equipment is marketed only in pre-engineered packages, which are tailored to the specific installation. The cryogenic air separation process is based on the principles of gas liquefaction followed by fractional distillation to separate air into oxygen and nitrogen. Air liquefies at or below -184°C and at a pressure of 1 atm. Liquefaction is achieved by rapidly expanding compressed air from a high-pressure stage to a low-pressure stage. The sudden expansion causes the temperature to drop drastically. Nitrogen and oxygen are then separated from the liquefied air by distillation at the different boiling pressures and temperatures. Oxygen concentrations in the product gas are 95%–99.9%. Cryogenic air separation is the only process that can simultaneously produce high-purity streams of LOX, liquid nitrogen, GOX, and gaseous nitrogen.

Major components include an air filter, air compressor, aftercooler, moisture separator, air purification unit, expander, distillation column, LOX storage tank, and LOX vaporizers (Figs. 15.13 and 15.14).

Air Preparation Systems. Many types of air preparation systems are on the market, most of which are distinguished by their operating pressure: ambient (less than 10psig), low (10–20psig), medium (30–50psig), and high (70–100psig). Regardless of the discharge pressure, they all consist of the same components.

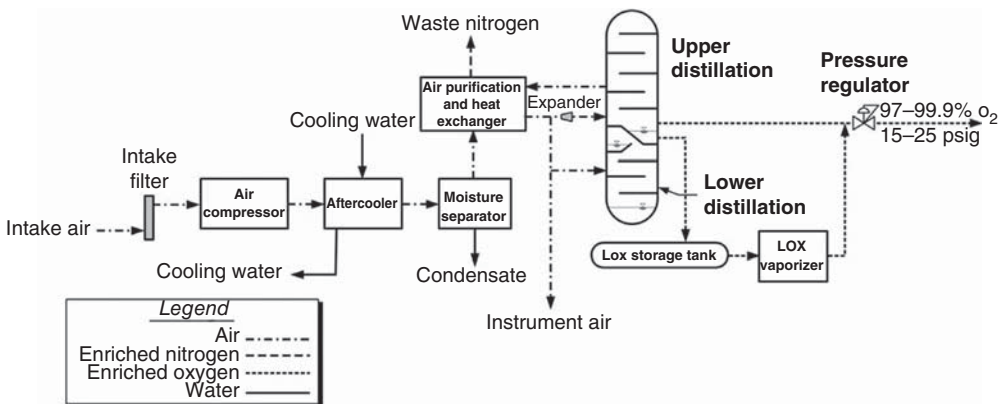


Figure 15.13. Cryogenic air separation process schematic.



Figure 15.14. Cryogenic air separation facility; 6500t/day, East Chicago, IN (photo courtesy of Praxair) PRAXAIR is a registered trademark of Praxair, Inc.

Although a limited number of air systems have been installed since 1997, nearly all LOX systems include supplemental nitrogen feed systems to improve generator efficiency. Those systems add a very high-quality compressed air to the GOX stream to increase the nitrogen content. Systems typically include similar components to the air preparation system described below.

Precompressor Filters. These filters trap the largest particles to protect the compressors from damage.

Compressor. The compressors are typically rotary, positive displacement, oil-free units. The positive-displacement feature provides a constant airflow at variable operating pressures. Oil-free compressors are used to keep the desiccant dryer medium from being contaminated by oil and prevent hydrocarbons from fouling the ozone-generator dielectrics. Rotary lobe and liquid ring

compressors are used most frequently, and oil-free rotary screw compressors are also used to a lesser extent. Oil-free reciprocating or rotary scroll compressors are most commonly used for supplemental nitrogen feed equipment.

Aftercooler or Refrigerant Dryer. An aftercooler is a heat exchanger that removes a portion of the heat generated by compression and reduces the compressed air moisture level. The moisture is removed through a separator.

A refrigerant dryer may alternatively be installed to remove heat and moisture in the gas stream. The dryers cool the incoming air to a lower dew point, and the condensate is collected in a separator. A refrigerant drier commonly includes an air-to-air heat exchanger that precools the incoming wet air and warms up the exhausting dry air.

Pre-desiccant Filter. This filter is used to remove dust and dirt particles larger than 3–5 μm in diameter to help prevent plugging the media in the desiccant.

Desiccant Dryer. The desiccant dryer is the most important component of the air treatment process. It consists of two towers containing moisture-absorbing media, one of which operates while the other is regenerating. In one type of regeneration process, the desiccant is reactivated by heat. An alternative regeneration method is to use a portion of the dry compressed outlet air of the online desiccant. This second method is more common for smaller air preparation systems, particularly supplemental air or instrument air systems.

Postdesiccant Filter. The postdesiccant filter serves to remove particulates smaller than 0.3–0.4 μm in diameter. Two-stage filtration is preferred at this point in the airflow system. The first stage removes particulates larger than 1.0 μm , and the second stage removes particulates less than 0.3–0.4 μm in diameter. The fine particles typically originate from the desiccant.

Pressure-Reducing Valve. In some air preparation systems, the pressure must be reduced as it exceeds the maximum pressure rating of the ozone generator or that may be needed to transfer ozone into solution. A secondary advantage is that it ensures a constant downstream pressure. Pilot-actuated pressure regulators are preferred.

Selection of Gas Source. The ozone system gas source is usually selected by conducting a present worth evaluation that includes capital costs, as well as the cost of power, maintenance, LOX, and any necessary redundant equipment, such as a LOX system, even if a PSA or VSA is installed. The power use and maintenance costs associated with the four types of enriched oxygen equipment are listed in Table 15.18. Capital and operating costs for a system of the exact size being considered should be provided by the manufacturer.

TABLE 15.18. Gas Production Equipment

Gas Source	Typical Ozone Facility, (ppd ozone)	Power Input, (kWh/lb O ₂)	Maintenance Cost (\$/lb)	Energy Efficient Turndown Capabilities
LOX (delivered)	100–20,000	0	Limited	Unlimited
VSA	10,000–30,000	0.15–0.20	Extensive	50%
PSA	0.5–200	0.20–0.25	Extensive	30%
Cryogenic	>20,000	0.15–0.20	Extensive	50%

In addition, the three on-site generation methods evaluated may be capable of being turned down to less than 50%, although their efficiency would be reduced. Therefore, it is important to understand the cost of operating the equipment at minimum, average, and maximum production capacities.

Generation

The principal components of the ozone generating system are (a) an electrical energy source, (b) a discharge gap containing the feed gas, (c) a dielectric material to evenly distribute the power and to prevent arcing, and (d) a means to dissipate waste heat. Three types of ozone generators are commercially available: plate, tube, and photochemical. The horizontal tube-type generators are most common for capacities larger than 100ppd.

The capacity of an ozone generator is determined by:

- Oxygen concentration, dewpoint, temperature, and gas flow.
- Foulants on the dielectric surfaces.
- Frequency and voltage of electricity applied to the electrodes.
- Discharge gap between the electrodes.
- Properties of the dielectric material.
- Surface area of the dielectric material.
- Cooling water temperature and removal of heat from the generator.

In general, the production capacity is higher at higher oxygen concentrations, lower dewpoint, higher frequency of the current applied to the dielectric, and narrower discharge gap. Efficiency improves at lower gas and cooling water temperatures.

Plate Type Generators. Ozone is produced as the gas passes between two conductors, one of which is coated with a dielectric material, and a current is applied. The plates are commonly referred to as floating, and may be limited to pressures less than 12psig. The generator type is therefore limited to low or negative pressure applications. Most plate type generators are capable of

3%–4% in oxygen (1%–2% in air) and are air cooled. A limited number of manufacturers offer generators capable of generating ozone at concentration of 12% in oxygen; these generators are water-cooled. Numerous suppliers offer plate type ozone generators, most of which have capacities less than 10lb/day (Fig. 15.15).

Horizontal Tube Type Generators. Horizontal tube generators dominate the domestic water and wastewater markets in the United States. The generators are capable of producing 1%–4% ozone with air, and 12% with enriched oxygen, although some manufacturers now claim having equipment capable of producing ozone at capacities as high as 16%. There are no large installations operating at capacities as high as 16% in municipal water treatment applications at this time. An individual generator is typically capable of producing 100- to 4000-ppd ozone although larger generators have been provided to the pulp and paper industry or when supplied with chillers (Fig. 15.16). Turndown ratio for horizontal-tube type generators is 10:1 because a minimum threshold must be achieved to form the corona, which is typically somewhere below 10% of the generator capacity.

Horizontal tube-type ozone generators consist of two major components: the power supply unit (PSU) and the generator. The power supply transforms the current from three-phase, low voltage (480V) to single-phase high voltage (3000–20,000V). Most suppliers use medium-frequency equipment (>1000 Hz).

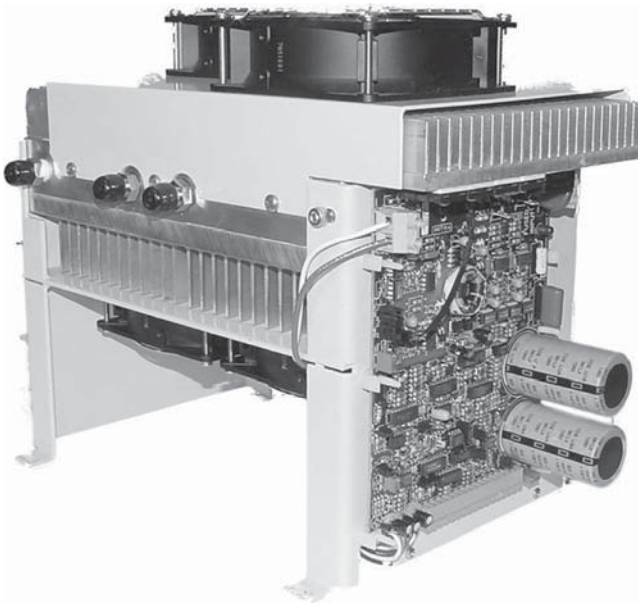


Figure 15.15. Air-cooled plate-type generator (photo courtesy of Guardian Manufacturing Inc.).

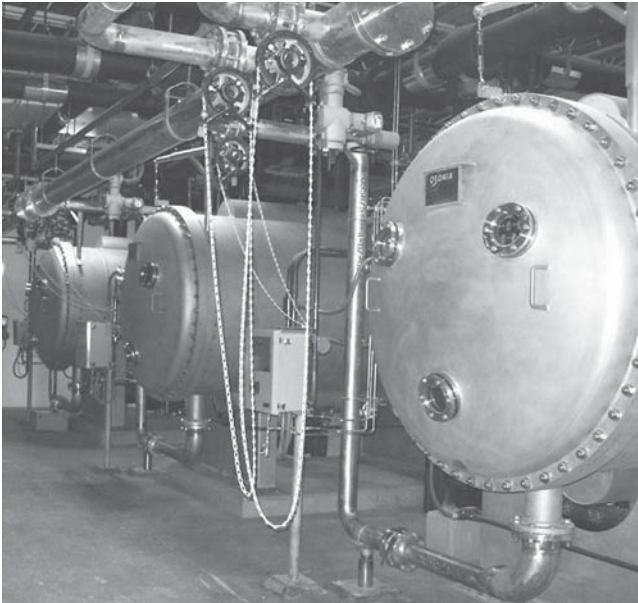


Figure 15.16. Three 3,000-ppd horizontal tube-type ozone generators.

The PSU includes the transformers and the converter switches. Two rectifier technologies are currently used: silicon-controlled rectifiers (SCRs) and insulated-gate bipolar transistors (IGBTs). The IGBT technology reduces electrical harmonics and voltage distortion and increases the power factor. Both types are used and produce reliable and energy-efficient operations.

Horizontal tube-type generators are based on the Welsbach original element design: a conductor surrounded with a material that distributes the charge uniformly (dielectric material), which is connected to the power supply and centered precisely inside a grounded metallic tube. Feed gas flows through the gap between the grounded tube and the dielectric-coated conductor.

The dielectric material is a nonconducting substance that prevents arcing across the two electrodes within the ozone generator. The dielectric-coated conductor is commonly referred to as a dielectric. The two most commonly used dielectric materials are glass and ceramic; both are used by major ozone-generator manufacturers. The number of dielectrics is a function of the generator capacity and the power applied per unit of dielectric area. Each tube within a generator may contain as few as one or as many as seven dielectrics, depending on the manufacturer.

Power is supplied to each dielectric through an axial bus bar containing electrode brushes (Fig. 15.17). The conductors can be fused individually to allow the generator to continue operating in the event of the failure of a single

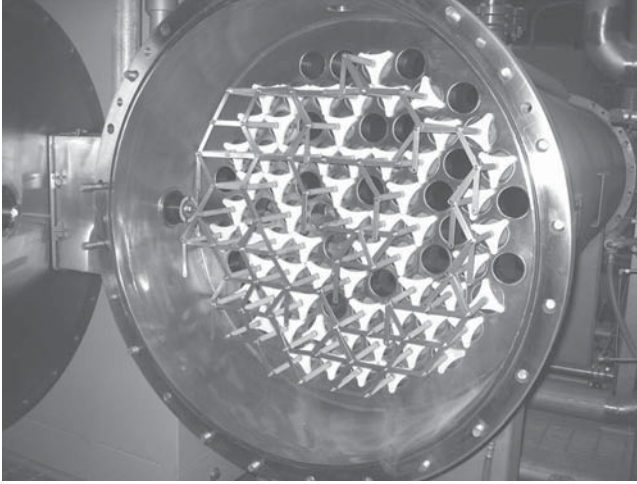


Figure 15.17. Horizontal tube-type generator shell, 690 ppd.

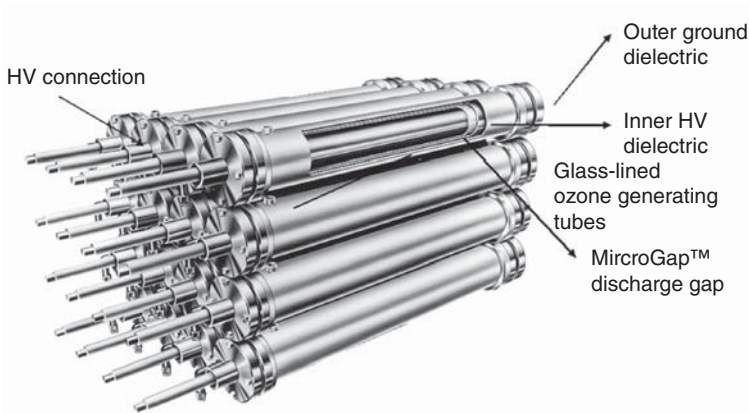


Figure 15.18. Ozone generator tube and dielectric cross section (courtesy of Fuji Electric). HV, high voltage.

dielectric. The failure rate of dielectrics is commonly less than one per year per 1000. Therefore, many generator suppliers do not include fuses.

The heat generated in the process is removed through a cooling system. Ozone generators are manufactured under exacting conditions, as the tubes into which the dielectrics are inserted have uniform, precise gaps. On one side of the tube wall is cooling water, on the other side are the gas and dielectric. In addition to the water on the outside of the tube, one manufacturer also includes deionized cooling water within the dielectric to enhance heat removal (Fig. 15.18), as discussed at greater length under “Ancillary Equipment.”

Transfer

Ozone must be transferred from the gas phase into the liquid phase. Factors affecting transfer of ozone into the water to be treated include contactor geometry, feed gas characteristics, gas-to-water ratio, gas bubble diameter, and ozone demand in the water.

The means to transfer ozone from the gaseous phase into the treated water include the following:

- Fine-bubble diffusers
- Sidestream injectors
- Other means of transfer
 - Packed columns
 - Spray chambers
 - U-tubes
 - Aspirating turbine mixers

The transfer method should be determined by evaluating the application goals, the percentage of ozone gas by weight, and the conditions specific to the site and the application.

Fine-Bubble Diffusers. Fine-bubble diffusers are the most widely used means of ozone transfer in both the United States and Europe primarily because their use requires no input of energy beyond that used initially for compressing the gas.

The most commonly used diffuser is a 7-in.-diameter ceramic dome (Fig. 15.19). A flow rate through a dome diffuser that is adequate to provide proper mixing but not high enough to cause damage to equipment is between 0.5 and 2 ft³/min. A 0.1- μ m pore diffuser will produce bubbles 2–3 mm in diameter. Each diffuser is secured to a stainless steel holder plate held in place with two gaskets, one around the base and on the top and fastened with a bolt and nut through the center of the dome.

Diffusers submerged by 20 ft or more of water can achieve transfer efficiencies of 90%–95% at 10% ozone concentration. Transfer efficiency is somewhat lower in air-fed systems, where the ozone concentration is only 2%–4%. As the diffuser surfaces are fouled and gasket material deteriorates, larger coarse bubbles will form, and transfer efficiency will decrease. The diffusers and gaskets must be regularly inspected and cleaned by taking the contactors off-line to be drained and vented with air. Gaskets may need replacement as often as annually, although they usually last for several years. The frequency of gasket replacement depends on the ozone gas weight percentage and the type of gasket material. The frequency of replacement and cleaning of diffuser stones depends on the rate of accumulation of dissolved inorganic contaminants, particularly sulfur, iron, and manganese.

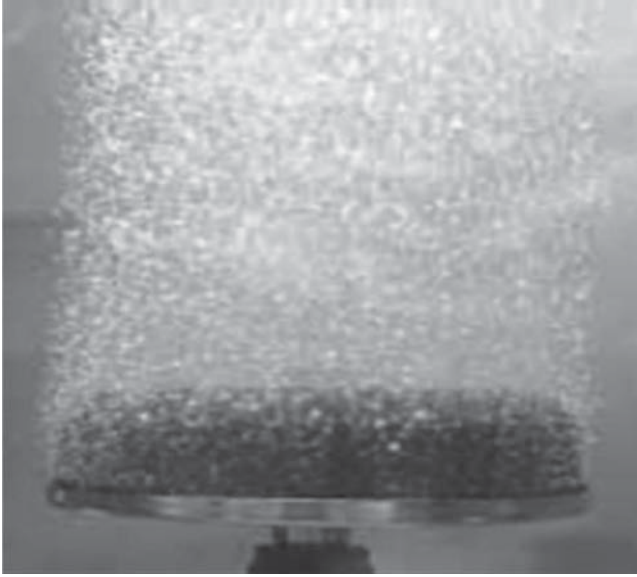


Figure 15.19. Ceramic dome diffuser.

Ozone-resistant gasket materials include Teflon and derivatives, Hypalon, Viton, and Goretex. One-piece, porous alumina diffusers that are completely fused to a ceramic holder are also available. The design eliminates the gaskets, although the porous portion of the diffuser remains subject to fouling.

Sidestream Injectors. Sidestream injection is practiced commonly in the United States, and is becoming increasingly economical because ozone may be generated at higher ozone weight percents. This results in lower pumping requirements to achieve the same gas-to-water ratio and transfer efficiency. Sidestream injection is quickly becoming the most common transfer method for new systems.

Sidestream systems include a pump to boost the water pressure in the sidestream pipeline, a venturi (injector) to draw the ozone gas into the water, and either nozzles, static mixers, or both to mix the sidestream into the main flow (Fig. 15.20). Static mixers may be added downstream from the injector to mix the ozone gas with the sidestream.

One of the critical design values is the gas-to-water ratio, which is expressed in units of volume per unit of time for both the numerator and denominator (l/min, ft/hr, etc.), and the gas should be expressed in units of standard temperature and pressure, 20°C and 1 atm. The gas-to-water ratio selected determines the percentage of the main flow that must be pumped through the sidestream. The number of trains, sidestream pressure, ozone demand, the percentage of ozone transferred from the gas phase to the liquid phase within

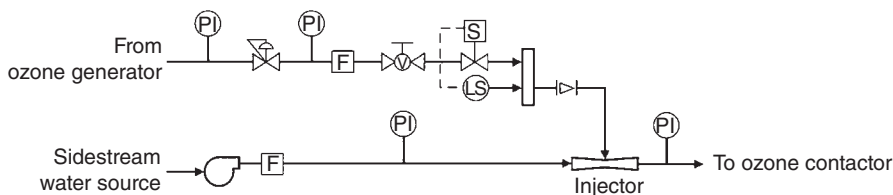


Figure 15.20. Sidestream injection process schematic.

the sidestream, and the percentage of transfer where the sidestream is mixed into the main flow all influence the sidestream flow calculation. A gas-to-water ratio of 0.3–0.5 is commonly used, although the range is highly dependent on the application. Some facilities have gas-to-water ratios as high as 1.0 and rely on a significant amount of transfer occurring where the sidestream is mixed with the main flow. Once blended with the main flow, the gas-to-water ratio is then a fraction of what it was in the sidestream.

For facilities that use sidestream injections with degas separation, the gas-to-water ratio is much lower because the transfer must occur completely within the sidestream and none can occur where the sidestream is mixed with the main flow. A gas-to-water ratio of 0.1–0.2 is typical with degas separation equipment. Higher gas-to-water ratios can be used but require much higher pressures to achieve the same transfer efficiency (J. Jackson, pers. comm.).

There are four major advantages associated with sidestream injection:

Transfer Efficiency. Sidestream injection has been demonstrated to effectively transfer ozone into the water. At the Earl Schmidt Filtration Plant in Castaic, CA, transfer efficiency was found to be more than 99%. It is usually higher than 95% and, unlike diffusers, does not decline significantly over time.

Contactors with diffusers commonly consist of several transfer cells in series, each with a hydraulic retention time (HRT) of 2–5 min. Ozone demand is satisfied in the first cell, and subsequent cells deliver sufficient ozone to maintain an ozone residual. Within these cells, ozone is transferred, but decay of the dissolved residual occurs resulting in lower residuals at the monitoring locations. With sidestream injection, the entire ozone dose can be transferred at one location, which reduces the amount of ozone lost to decay and results in higher dissolved ozone residual.³⁹

Maintenance. Sidestream injection does not require any mechanical equipment within the ozone contactor. Therefore, there is no need to drain the ozone basins and to enter confined spaces to check and service the transfer equipment. Motors, pumps, injectors, and all instrumentation are outside the basin and can be serviced while the ozone contactor remains in service (Fig. 15.21).



Figure 15.21. Ozone injector.

Contactor Layout. Transfer efficiency is controlled within the sidestream system and is largely independent of the ozone contactor. Deep basins are not necessary to achieve high transfer efficiency. Therefore, a contactor may be pipelines, shallow basins, box flumes, or any other structure or vessel that provides contact time and is resistant to attack by ozone. The raw water pipelines formerly used to convey water between the source and the plant may serve as preozone contactors, eliminating the need to construct basins.

Degas Separation. Off-gas can be removed in the sidestream and only a high concentration of dissolved ozone is mixed with the main flow (Fig. 15.22). Degas separation will also result in a lower dissolved oxygen concentration than direct injection, which may be advantageous in some locations where corrosion as a result of high dissolved oxygen concentration may be a concern. A second advantage is that corrosion of contactor materials is of less concern since the ozone gas, which is more corrosive than dissolved ozone, is removed prior to the addition to the contactor. In the case of a pipeline contactor, alternative pipe material other than stainless steel may be used, such as a cement mortar-lined steel pipe. However, the thickness and specific qualities of the mortar must be carefully reviewed to eliminate corrosion as a result of exposure to dissolved ozone.

The largest disadvantage of the sidestream system is the capital and operating cost. The cost of the control system, gas pressure and flow monitoring equipment, the sidestream pump, and injection nozzles is several times higher than the cost of diffusers installed in a basin. Some of those costs may be offset by alternative contactor designs and the elimination of diffuser maintenance.



Figure 15.22. Degas separation column (courtesy of Mazzei Injector Corporation).

The sidestream pumps are typically constant speed type with a fixed power draw regardless of whether the minimum or the maximum ozone dosage is applied. Variable frequency drives have been used at some locations but require additional automation to ensure that the pump continues to deliver the necessary flow and pressure at variable gas flow rates to maintain transfer efficiency and proper operation of the system. If constant speed pumps are selected, the system may include multiple trains, and the number of trains in operation is determined by ozone production. Removing sidestream trains from service at times of low ozone production is used in reducing operating costs. The specific amount of power required to transfer ozone into solution using sidestream injection may be 0.5- to 1.5-kWh/lb ozone, depending on the operating conditions.

A major design concern associated with the use of sidestream injection equipment is providing adequate protection against backflow of water into the ozone generators. With diffuser-based systems, the generators are almost always located above the hydraulic profile of the ozone contactor. This may not be the case with sidestream injection, particularly since the pressure in the sidestream may be over 50 psig. Backflow protection devices must be installed on the ozone supply lines and may consist of check valves and a liquid trap with float switch that detects water and closes a solenoid or other quick-closing valve, preventing further migration of water upstream. A barometric piping loop may be used with lower pressure systems.

Other Means of Transfer. Four alternative transfer methods are discussed although their use is limited. Nearly all municipal systems rely on diffusers or sidestream injection for the transfer of ozone into the solution.

Packed Columns. Ozone can also be added at the bottom of a basin with ceramic media. As the ozone gas bubbles up through the media, water flows down. This method has been used only at a limited number of facilities with flow less than 1 mgd. The advantages of this type of system are that it has no moving parts, it requires little maintenance, and it can achieve high transfer efficiency. In addition, the flow regime within the packing material is nearly plug flow. Its disadvantages are that contaminants can accumulate on the media and the size of the contactor, owing to the large volume of the packing material in the basin.

Spray Chambers. A spray chamber is equipped with nozzles that spray the water into an ozone-rich headspace. This transfer method has been used for only oxidation of inorganic compounds with rapid reaction rates and in areas where topography provides adequate pressure to convey water through the nozzles.

U-tubes. The U-tube is a patented device that consists of two long, concentric, vertical tubes through which ozone is transferred into solution. The ozone is injected into the water at the top of the inner tube and is conveyed down this tube by water for 40ft or more and then up through the outer tube. The travel distance provides contact time between ozone and water, aided by the increase in pressure near the bottom of the U-tube and the turbulence of the flow.

Transfer efficiency can exceed 90%, and the system needs little maintenance because it includes no mechanical equipment. The main disadvantage is the head loss produced by the high flow velocities required to convey ozone bubbles down through the inner reaction tube, and, when flow decreases, the contactors must be taken off-line because the system requires a minimum velocity to convey the gas to the bottom of the inner tube.

Aspirating Turbine Mixers. Aspiration turbine mixers create a vacuum that draws the ozone gas directly into the process stream. The mixers can produce small bubbles and high transfer efficiency because of the high shear and turbulence at the tip of the mixer impeller. Sidewater depth is less important to transfer efficiency. Therefore, contactors can be shallower than those equipped with diffusers to achieve the same transfer efficiency. Turbine mixers are not commonly used in the United States because of their relatively high power use and maintenance requirements. The power use of the mixer motor is constant, regardless of the ozone dosage or water flow, as is the gas flow to the turbine, regardless of the water flow rate.

Contactors

The ozone contactor is one of the most critical design elements. Its purpose is to provide a location for treatment with ozone to take place. A contactor will fit within the hydraulic profile of the plant, enhance ozone transfer

efficiency, provide detention time for oxidation and disinfection, include baffles walls to increase the baffling factor, and allow the ozone residual to decay to a nondetectable level before it leaves the contactor. An ozone quench chemical may be added at the end of the contactor, and mixing must occur at the last baffle wall.

The contactor must be designed carefully to meet these goals. For slow reactions, such as for disinfection, contact time and proper monitoring of dissolved ozone residual are critical. Contactors used for this purpose are designed with extended detention times and multiple monitoring points.

Conventional baffled basins are the most widely used contactor, although pipeline contactors may be advantageous at some locations. The selection of the contactor configuration depends on the transfer method. Therefore, the advantages and disadvantages of various transfer methods and contactor types must be evaluated simultaneously.

Selection of corrosion resistant construction materials is critical. Additional cover over rebar of an appropriate concrete admixture is common on conventional concrete contactors. Pipeline contactors are generally constructed of a welded 316 stainless steel or special mortar-lined steel pipe.

Conventional Baffled Basins. The conventional baffled contactor with diffusers is the most widely used means of transfer and contacting worldwide. Several contactor configurations, baffle wall arrangements, and flow patterns can be used. Contactors with diffusers are equipped with vertical baffle walls that force the water to flow over and under the walls to increase the baffling factor. If sidestream injection is used, baffle walls may be vertical or horizontal.

Diffusers are located in transfer cells, and cells that do not include diffusers are reaction cells. The flow in the first transfer cell is typically countercurrent: The bubbles of ozone gas rise, and the water flows down; this flow pattern minimizes short-circuiting and maximizes contact between the liquid and the ozonated gas. Flow in subsequent transfer cells may be countercurrent or cocurrent. Contactors may include one or more transfer cells, depending on the ozone gas concentration and the design dosage. Usually, if the ozone concentration is low or the dosage is high, the contactor includes more transfer cells. Figure 15.23 illustrates a three-stage bubble diffuser contact basin, and Figure 15.24 illustrates the bubble diffuser contactor basin at the 600-mgd Los Angeles Aqueduct Filter Plant.

When sidestream injection is used with conventionally baffled contactors, the sidestream may be introduced, utilizing nozzles or static mixers into the contactor influent pipe or first cell. Unlike diffusers, sidestream injection transfer occurs typically at one location. The advantage of this approach is that the maximum ozone residual is produced at the end of that transfer cell and is allowed to decay through the entire length of the basin.

The Surface Water Treatment Rule uses the CT method to monitor inactivation of viruses, *Giardia*, and *Cryptosporidium*. For the target level of

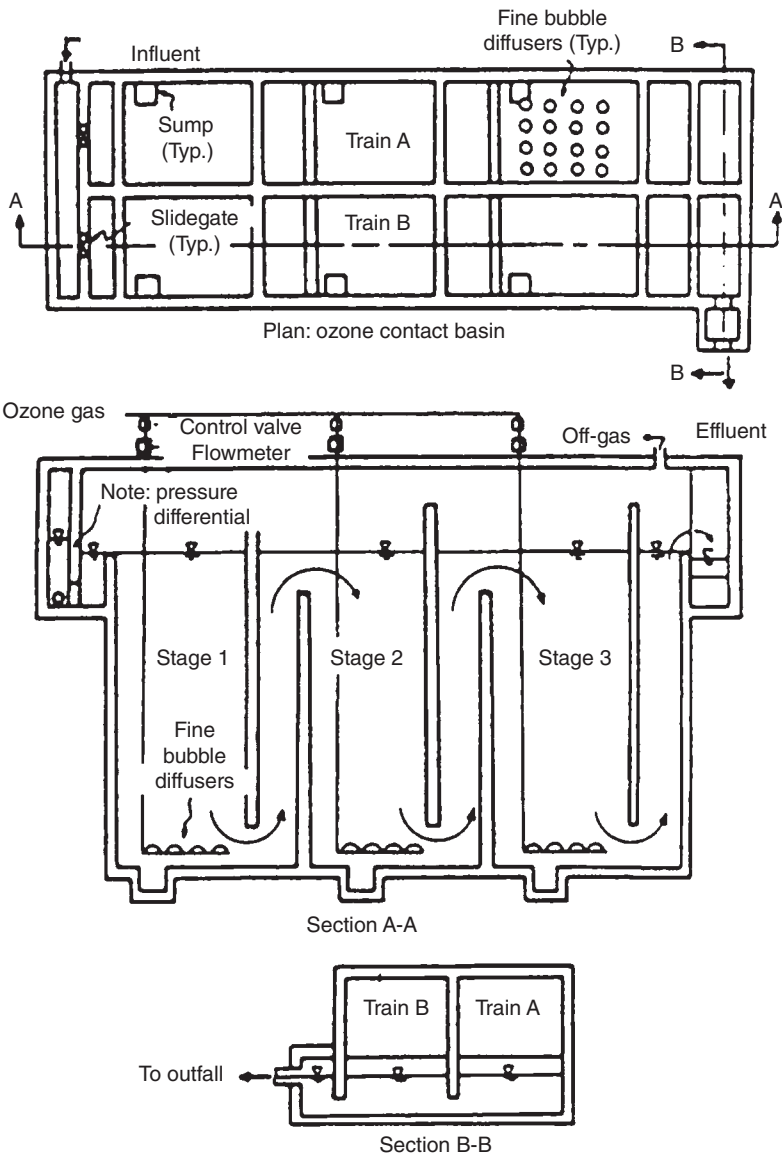


Figure 15.23. Schematic of a three-stage bubble diffuser ozone contact basin (courtesy of Los Angeles Department of Water and Power).

inactivation to be achieved, the contactor must be sized considering the time needed to achieve the targeted initial residual, the ozone decay rate, and the targeted disinfection credit or performance ratio at design conditions. For the size of the contactors to be minimized, basins are baffled in an effort to approach plug-flow conditions and minimize short-circuiting.

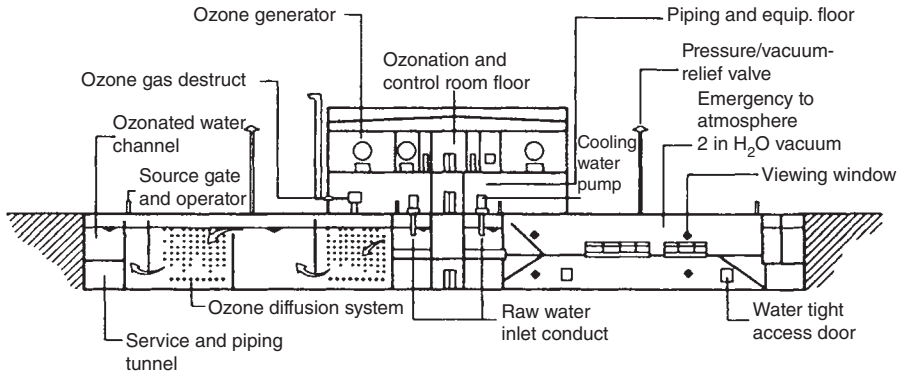


Figure 15.24. Ozone contactor at the 600 mgd Los Angeles Aqueduct Filtration Plant, California (courtesy of Los Angeles Department of Water and Power).

Conventional contactors are usually set up in pairs with a common gallery that contains locations for maintenance access and for dissolved ozone sampling taps. The taps extend into the flow along the entire length of the contactor. The sampling locations for disinfection may change seasonally with changes in water temperature. Therefore, providing multiple sampling locations for each monitor is advantageous.

An ozone contactor usually has 5 ft of headspace to allow for the accumulation of ozone off-gas, although as little as 18 in. may be adequate in some cases. The headspace is maintained under a slight vacuum to prevent ozone leaks by automated valves and suction provided by the off-gas blowers on the ozone destruct equipment. In the event these valves fail, pressure-vacuum relief valves protect the structural integrity of the contactor. The set points of the relief valves are based on the structural design of the contactor. Typical pressure set points range up to +12 in. water column and vacuum set points to -10 in. water column. The contactor is operated at a slight vacuum, typically -3- to -5 in. water column. If the pressure is outside the set points, the relief valve opens and relieves the pressure or vacuum. The locations of these valves should be carefully selected, as release of the gases from the basin may create hazardous conditions near the outlet of the relief valve.

Pipeline Contactors and Other Alternative Designs. Pipeline contactors are commonly coupled with sidestream injection equipment. The ozone is transferred into solution, and the pipeline is sized for adequate contact time to achieve the process goals. Greater Vancouver Water District installed one of the first large pipeline ozone contactors with sidestream injection at the Coquitlam Reservoir. The 3-m-diameter (9.8 ft), 1-k-long (0.62 mile) stainless steel pipeline contactor provides 8.5 min of contact time at a flow of 1200 million liters per day (MLD) (317 mgd). The system was designed to provide *Giardia* and viruses inactivation credit for this unfiltered water source.

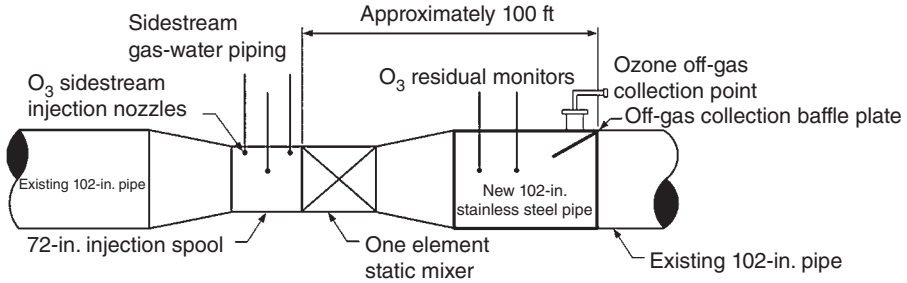


Figure 15.25. Pipeline contactor injection section (Earl Schmidt Filtration Plant, Castaic Lake Water Agency).

Pipeline contactors are usually installed where water must be conveyed from one location to another through a pipe. Often, the pipeline diameter is larger than would typically be provided for conveyance to minimize the length of the contactor and to provide adequate contact time. At the ozone injection point, though, it may narrow to enhance mixing. At the Santa Clarita, California, Rio Vista Water Treatment Plant, an existing raw water pipeline was retrofitted into an ozone contactor by removing a 30-ft section and replacing it with a narrower injection spool piece to provide adequate mixing at flow rates of 10–150 mgd. Between the injection spool and the off-gas collection point, the mortar-lined steel pipe was replaced with a 316 L stainless steel pipe (Fig. 15.25).

One of the advantages of pipeline contactors is that the flow approaches plug flows, as there are no dead spaces except the thin layer at the pipe surface. Pipeline contactors commonly have baffling factors higher than 0.8.

Modesto Irrigation District, during its 2007 expansion of the Modesto Regional WTP, selected a concrete box flume contactor and sized it to provide the same T_{10} value as the conventional contact basins at the original plant. The conventional basins had an HRT of 20 min but had a T_{10} value of only 7.5 min. Because of the enhanced baffling factor of the box flume contactor, the HRT was only 9 min, resulting in significant savings in capital costs.

The design and operation of pipeline ozone contactors present several challenges. The first is collection of off-gas. In a conventional contactor, the off-gas accumulates in the headspace. In a pipeline, this would decrease the cross-sectional area of the pipe, which in severe cases could restrict flow. Therefore, pipeline contactors are equipped with chimneys, which are low-velocity locations downstream from the injection location, may include a free water surface, and are intended for the removal of ozone off-gas. The contactor may be sloped to the chimney location to ensure that off-gas does not exit the contactor. If a free water surface is not possible, gas relief valves may be installed to prevent water from entering the off-gas piping.

Another challenge is the location of dissolved ozone monitoring stations. Pipeline contactors may be several hundred feet long and do not include

galleries. The ozone monitoring locations are fixed, unlike those of conventional contactors on which one analyzer may be piped to sample several locations. Selection of monitoring locations is based on anticipated operating conditions, flow patterns, water quality, and ozone decay rates. Sampling stations are selected along the pipeline, and the sample is pumped back into the pipeline unless other provisions are made.

Destruction Equipment

Not all ozone is transferred into solution. A small concentration remains in the gaseous phase. Because ozone is a hazardous, corrosive gas, it must be treated before discharged to the environment. The maximum allowable ambient ozone concentration for an 8-h working period is 0.1 ppm_v. This concentration is significantly less than the concentration in the off-gas, which may be as high as 3400 ppm_v, or 0.5%.

Current methods of eliminating off-gas from the ozone contactors are thermal destruction, thermal/catalytic destruction, and catalytic destruction. Granular activated carbon (GAC) has been used in the past with disastrous consequences. Ozone, particularly in the presence of elevated concentrations of oxygen, reacts exothermically with GAC, which has resulted in fires and even explosions. Nearly all municipal ozone systems use thermal-catalytic ozone destruction equipment with a manganese dioxide catalyst.

Alternative materials used to destruct ozone include silver, platinum, sodium hydroxide, soda ash, lime, bromine, chlorine, and nitrogen pentoxide. Ozone may also be decomposed photochemically.

Prior to treatment, the off-gas passes through a demister, which consists of a stainless steel wire or ozone-resistant plastic mesh that removes entrained water particles from the gas stream. At the base of the demister, water nozzles are sometimes installed and used to eliminate any foam that may develop. Vacuum in the contactor headspace is controlled by pressure control and pressure-vacuum safety relief valves. Pressure control typically consists of a pressure indicating transmitter and electric modulating control valve. The off-gas ozone concentration is commonly measured to determine transfer efficiency. Following removal of entrained water, the gas is conveyed to an ozone destruction unit. Ozone gas is drawn from the contactor basin by a fan located downstream from the destruction unit catalyst chamber, with its discharge vented to the atmosphere. The vent-gas ozone concentration is also measured to monitor the performance of the destruct units and to verify that the discharged gas has low ozone concentration.

Thermal Catalytic Destruction. Thermal-catalytic ozone destruction unit consists of electrical resistance type heater elements that increase the gas temperature to lower the relative humidity of the gas, which protects the downstream catalyst, a catalytic bed that destroys the remaining ozone, and a gas blower driven by an electric motor (Figs. 15.26 and 15.27). The blower

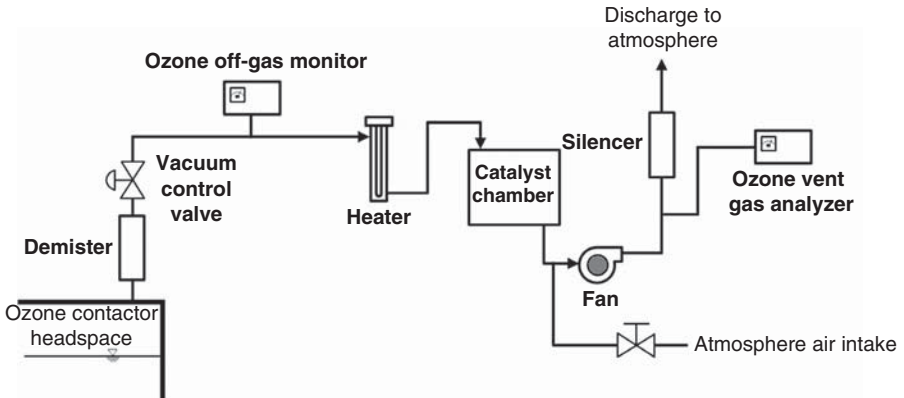


Figure 15.26. Diagram of a thermal-catalyst ozone destruction unit.



Figure 15.27. Ozone destruction unit.

discharges the gas to the atmosphere, and a vent gas monitor measures the ozone concentration in the vent gas. The blower is often stainless steel with an aluminum impeller to reduce the possibility of a spark in the event of a bearing failure. While aluminum is less corrosion-resistant to ozone, ozone should be present at levels less than 0.10 ppm_v by the time the gas stream reaches the blower.

A flow rate per volume of catalyst of 20 standard cubic feet per minute (scfm)/ft³ has been successfully used, and flows as high as 50 scfm/ft³ have been reported.⁵⁴ As catalytic systems are proprietary, the size of the metal catalyst chamber varies with the manufacturer.

Chlorine and sulfide can foul the manganese dioxide destruction catalyst. Therefore, their presence in the feed water and off-gas may require more regular catalyst replacement or the consideration of thermal type ozone destructs. Sulfide foulants are discussed in the section on treatment of sulfide by ozone. The thermal catalytic method is widely used in the United States and is generally most economical, provided that the catalyst lasts longer than 2 years. Disadvantages are that the catalysts are expensive and proprietary (there is only one supplier) and that the service life of the media is difficult to predict.

Thermal Destruction. Thermal destruction of ozone involves heating the off-gas to a high temperature for a predetermined period, for example, to a temperature of 570–660 °F (299–349 °C), held for 3–5 s. Because of the high temperature involved, all thermal destruction systems include heat recovery units. The outlet gas temperatures for a heat recovery unit range from 160 to 230 °F.^{54,55}

The types of heat exchangers include cross-flow, shell and tube, and plate, all of which include a fan to move gas through the system. The heat exchanger uses the heat from the gas stream leaving the system to preheat the gas that is about to enter the heating coils. The head loss for thermal systems with heat exchangers can be as high as 3 ft of water column.

The disadvantages of thermal destruction with heat recovery are its high energy cost and the lengthy (up to 30-min) warm-up period required when starting up a unit. Thus, for uninterrupted ozone destruction to be maintained in the event of the duty unit failure, a “hot” standby unit must be available. Because of these two disadvantages, thermal destruction is not favored in the United States.

Off-Gas Reuse. In certain applications, the off-gas is recycled to an upstream cell with an aspirating turbine mixer, which minimizes but does not normally eliminate the need for off-gas destruction. The concentration of ozone in the recycled off-gas is generally low, so the potential benefits are small compared with the cost of the reuse system. It then becomes an economical evaluation between cost of the reuse system and cost of the destruct system.

The Southwest Wastewater Treatment Plant in Springfield, Missouri, has used ozone for disinfection since the 1970s. The low-concentration (2%) ozone in oxygen is transferred by surface mixers into the wastewater for disinfection. The oxygen-rich off-gas from the process is drawn from the tank headspace by compressors and used in the activated sludge process as an oxygen source. The gas from the basins is discharged to the atmosphere through a chimney to ensure adequate mixing that lowers the ozone concentration. Despite operating in this manner for 30 years, the city has elected to install a thermal-catalytic destruct system upstream from the compressors for safety reasons.

Because of the moisture and potential contaminants in the off-gas, there have been no economical treatment systems that recycle the gas back to the inlet of the ozone generators.

Ancillary Equipment

In addition to the major components, the ozone system includes several sub-systems that are needed to ensure that it operates efficiently. These include the supplemental air system for nitrogen addition and the cooling water system.

Supplemental Air. Ozone systems that use LOX as the gas source are typically fed a small quantity, 0.01%–4%, of nitrogen that may make them operate as much as 10%–20% more efficiently.⁶ Because air is nearly 78% by volume nitrogen, the desired nitrogen concentration is usually achieved by adding air to the generator feed gas.

Supplemental air systems are usually skid mounted and consist of the equipment described in the section on “Air Preparation Systems”. The air dew point is lowered, and particles are removed to protect the ozone generators against fouling. Some systems have used cylinders of liquefied nitrogen and ambient vaporizers to supply the nitrogen.

The efficiency of the ozone equipment is unchanged for a wide range of nitrogen concentrations. Therefore, the flow rate may not be flow paced, and a manual control valve and a rotameter may be used to set the flow. This setup minimizes both capital costs and the complexity of the system. A built-together flow meter and control valve are available for larger systems requiring more variation in the nitrogen supply.

Cooling Water. Ozone generators and their PSUs must be cooled to remove the heat produced during ozone generation. Only 5%–10% of the electrical energy supplied to the generator is used to convert oxygen to ozone; the remaining energy, 90%–95%, is dissipated as heat, light, and sound. The heat must be conveyed away from the ozone generator to prevent autodecomposition of the ozone. The selection of the type of cooling water system is based on technical and economic analyses.

The specific energy for the production of ozone is greatly affected by cooling water temperature, and the use of power-intensive chillers may be cost-effective if large quantities of ozone will be produced where the cooling water temperature exceeds 95°F (35°C). The specific energy required to generate ozone increases greatly as temperatures rise above 85°F (29°C).

Several types of heat exchangers are available, but plate and frame types are most commonly used for ease of maintenance (Fig. 15.28). The type of cooling water system selected often depends on cooling water quality including its solids concentration, chloride content, potential for corrosion, and temperature. Corrosive waters and those with higher fouling potential typically utilize a closed-loop cooling system. Wastewater utilities commonly use treated effluent and a plate-and-frame heat exchanger to prevent fouling on the water side of the generator tubes. Although generator shells are manufactured of type 316L stainless steel, they are vulnerable to corrosion in the

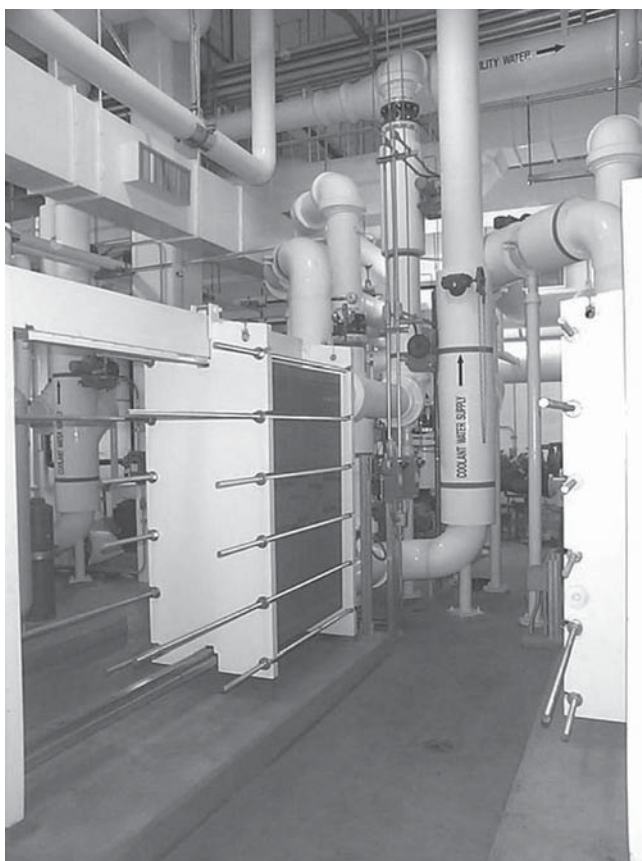


Figure 15.28. Plate and frame heat exchanger.

presence of high chloride concentration or through microbially induced corrosion in anoxic microenvironments. Manufacturers are commonly involved in the selection of the cooling system, as they must warrantee the equipment from corrosion.

Closed-loop cooling water systems are sometimes slightly pressurized to eliminate air from the system. However, there is also an advantage of keeping water pressure below the gas pressure so that if a leak occurs, the water does not enter the gas side of the generator. Corrosion inhibitors and other treatment chemicals may be added to the closed-loop side, allowing less expensive piping materials. However, one-ozone generator manufacturers require deionized water.

The cooling water flow rate is a function of the cooling water temperature and the allowable temperature rise across the ozone generator. The systems are commonly designed for a cooling water temperature rise of less than a 5 °F (2.8 °C). Cooling water flows may vary from as little as 200 to as much as 400-gal/lb ozone as a result of the maximum approach temperature, temperature of the cooling water, and the target-specific energy required to produce ozone.

The water flow rate required by the PSU is typically much smaller than that required by the ozone generator. When water cooling is utilized, the water-cooling system is isolated in a separate section of the cabinet. Often, a separate internal cooling loop is used.

Most small ozone generators, with capacity less than 10ppd, are equipped with fans that blow air across a heat sink to cool the dielectric cell.

Cost Studies

An ozone system will have a higher capital cost than chlorine (gas or sodium hypochlorite) or UV system. However, the other treatment systems may neither meet the treatment goals nor provide other ancillary benefits. When evaluated on a present worth basis, disinfection with ozone is almost always more expensive than with chlorine (gas or sodium hypochlorite), although it may be cost-competitive with UV for waters with low UVT₂₅₄. It has been cost-competitive with UV for disinfection of secondary and tertiary treated wastewaters and is generally cost-competitive with AOP processes that include UV and powdered or GAC for removal of taste- and odor-causing compounds.

Because the capital cost of an ozone system depends on the scope of the project, the degree of automation, the number of instruments, and local construction costs, it is difficult to develop even remotely representative capital cost values for a specific project.

Likewise, operating costs are a function of the cooling water temperature, ozone concentration and transfer method, and the unit costs of power and oxygen. At a concentration of 12%, generation of each pound of ozone requires 8.3lb of oxygen. At 6%, the amount of oxygen required is 17lb. Ozone generators are typically capable of operating at specific energy less than

4.5-kWh/lb ozone, with 4.0kWh/lb regularly reported at 10% weight and 75 degree cooling water temperature.

If sidestream injection is used, the operating conditions within the sidestream such as pressure and flow must be determined to accurately predict the power used in the sidestream system. The specific power for ozone systems that include sidestream injection can vary greatly since the pumps are commonly fixed-speed type requiring a fixed amount of power. This power input does not change except when sidestream trains are bought on- or off-line.

The energy used for converting the ozone in off-gas back to oxygen, and any cooling water pumping/chilling would need to be added onto these values to arrive at an overall specific energy. In addition, operating conditions during turndown will need to be considered when arriving at projected operating costs.

Contact ozone system suppliers or manufacturers of the equipment and develop a detailed scope from which they can provide a budgetary cost number. In addition, work with engineers or contractors to determine the cost for installation, facilities, and other capital improvements necessary for the construction of a fully functional ozone treatment system. Capital cost information is also available in *Ozone in Water Treatment: Application and Engineering* and *Ozone in Drinking Water Treatment: Process Design, Operation, and Optimization*.

PROCESS CALCULATIONS

At most municipal facilities, ozone system calculations are performed automatically within the ozone control system. These equations are used to calculate ozone system set points and maintain operations.

Gas Flow

One of the most critical, and difficult, calculations that must be performed pertains to gas flow rate and the mass of gas at the temperature and pressure within the ozone system. Because oxygen is a compressible fluid, the mass of gas in a given unit volume will vary with temperature and pressure. A method of comparing gases uniformly is standardizing the flow. Standard flow is referred to in units of scfm and non-standardized gas flow in cubic feet per minute (cfm). Standard conditions, 68 °F and 1 atm pressure, are usually used with English units. A normalized flow, 0 °C and 1 atm pressure, is generally used with metric units, normalized meters cubed per hour (Nm³/h).

For flow to be adjusted when measured through an orifice or a rotameter, it is necessary to take the square root of the temperature, pressure, and density in a ratio to their absolute values:

$$TCF = (T_{ref}/T_a)^{0.5}, \quad (15.30)$$

where

TCF = temperature correction factor (unitless),

T_{ref} = reference temperature (K or R) and

T_a = actual temperature (K or R).

$$\text{PCF} = (P_a/P_{\text{ref}})^{0.5}, \quad (15.31)$$

where

PCF = pressure correction factor (unitless),

P_{ref} = reference pressure, absolute, and

P_a = actual pressure, absolute.

$$\text{DCF} = (D_{\text{ref}}/D_a)^{0.5}, \quad (15.32)$$

where

DCF = density correction factor (unitless),

D_{ref} = reference density, and

D_a = actual density.

Once these correction factors are known, Equation (15.33) can be used to calculate the corrected gas flow rate:

$$G = (\text{TCF})(\text{PCF})(\text{DCF})\text{GOX}, \quad (15.33)$$

where

G = corrected gas flow rate, Nm^3/h or scfm and

GOX = gas flow rate, m^3/h or cfm

Once the gas flow rate is known, the density of gas at standard or normal conditions can be located in Table 15.16 or 15.17. That information is used to calculate the total mass of gas used in one day:

$$\text{O}_2 = 1440 \times G_s \times \rho \quad (15.34)$$

and

$$\text{O}_2 = 24 \times G_N \times \rho, \quad (15.35)$$

where

G_s = corrected gas flow rate (scfm),

G_N = corrected gas flow rate (Nm^3/h),

O_2 = mass of gas used in a day (ppd or kg/day), and
 ρ = density of gas (lb/scf or kg/Nm³).

Ozone Production

The quantity of ozone generated can be calculated as follows:

$$P = O_2 \times Y, \quad (15.36)$$

where

P = Ozone generated (ppd or kg/day),
 O_2 = Oxygen used (ppd or kg/day), and
 Y = Ozone concentration (percent by weight).

The mass of the gas following ozonation does not need to be adjusted because the same amount of mass is in the generator influent and effluent. However, the flow from the ozone generator will be slightly less because the average molecular weight of the gas has increased.

Ozone Transfer Efficiency

Transfer efficiency is the fraction of ozone in the gas that has been transferred to the liquid expressed as a percentage. While the mass of the ozone in the feed gas is typically well established, the mass flow of the off gas is different from the feed gas due to the transfer of ozone and oxygen and partial stripping of dissolved nitrogen. As an approximation (not taking into account differences in feed gas and off-gas flow), transfer efficiency can be calculated as follows:

$$TE = \frac{100(Y_1 - Y_2)}{Y_1}, \quad (15.37)$$

where

TE = transfer efficiency (percent),
 Y_1 = ozone concentration in inlet gas (percent or g/Nm³), and
 Y_2 = ozone concentration in exhaust gas (percent or g/Nm³).

Ozone transfer can be best described by the two-film theory.^{56,57} According to this theory, the mass transfer of ozone per unit of time is a function of the two-film exchange area, the exchange potential, and a transfer coefficient. The exchange area is the surface area of a bubble. The exchange potential is known as the driving force and is dependent upon the difference between the saturation concentration and the dissolved ozone residual concentration.

Below is a summary of water quality factors affecting ozone transfer efficiency:

1. Ozone transfer efficiency will decrease as the applied ozone dosage increases.
2. Ozone transfer efficiency will increase as ozone demand increases.
3. Ozone transfer efficiency will increase as the chemical quality of the water favors the presence of hydroxyl radicals (i.e., high pH).
4. Ozone transfer efficiency will decrease as the gas-to-liquid ratio increases.

Applied Ozone Dose

Not all ozone that is added to the water is transferred into the liquid phase. The applied dosage is the quantity of ozone added but not necessarily transferred to the water. Applied ozone dosage is calculated as follows:

$$D = \frac{P}{L}, \quad (15.38)$$

where

D = applied ozone dose (mg/l),
 P = quantity of ozone generated (mg), and
 L = volume of water (l).

Transferred Ozone Dose

The applied dose multiplied by the fraction transferred to the liquid is the transferred dose, the quantity of ozone transferred into the liquid phase. The transferred ozone dose is calculated as follows:

$$T = D \times TE \times 100\%, \quad (15.39)$$

where

T = transferred ozone dose (mg/l),
 D = applied ozone dose (mg/l), and
 TE = transfer efficiency (percent).

Specific Energy

Specific energy is a measure of the efficiency of the ozone generator. It is also applied to the efficiency of the entire system, although it must be clear which convention is used. The specific energy is calculated as follows:

$$SE = \frac{P_w}{P} \times 24,$$

(15.40)

where

- SE = specific energy (kWh/lb or kWh/kg),
- P_w = power demand (kW), and
- P = ozone production (lb/day or kg/day).

QUENCH CHEMICALS

Dissolved ozone residual can be hazardous, as it is a volatile gas that will come out of solution and may produce hazardous conditions, particularly at weirs or in enclosed filter galleries. The off-gas from dissolved ozone residual may increase the corrosion of noncompatible materials and, if concentrations are high enough, may present a health hazard.

Quenching ozone residual is necessary if the ozone contactor does not provide adequate contact time to allow the dissolved ozone residual to decay to very low levels, less than approximately 0.05 mg/l. There are multiple products that may be used to quench dissolved ozone, and these are listed in Table 15.19. These chemicals disassociate in water into anions that react with ozone. In the case of hydrogen peroxide, radicals (hydroxide radical and superoxide ion) that may participate in additional ozone decomposition reactions are formed. For complete reduction of ozone to be achieved, quench chemicals are commonly overfed 10%–50%.

ANALYTICAL METHODS

Ozone concentration must be accurately measured in the gas and liquid phase to evaluate system performance and, in many cases, ensure that the treatment

TABLE 15.19. Ozone Quench Chemicals

Chemical	Equation	Stoichiometric Ratio mg Chemical/mg Ozone
Calcium thiosulfate	$CaS_2O_3 \rightarrow Ca^{2+} + S_2O_3^{2-}$	0.79
	$S_2O_3^{2-} + 4O_3 + H_2O \rightarrow 2SO_4^{2-} + 4O_2$	
Hydrogen peroxide	$H_2O_2 \rightarrow HO_2^- + H^+$	0.71 ^a
	$HO_2^- + O_3 \rightarrow OH + O_2^- + O_2$	
Sodium bisulfite	$NaHSO_3 \rightarrow Na^+ + H^+ + SO_3^{2-}$	2.17
	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	

^aThe ratio assumes no further reduction of dissolved ozone by reaction products.

goals are being met. In addition to process control measurements, ozone in gas is measured for safety reasons as well.

Ozone Concentration in Gas

There are several methods through which ozone in the gas phase can be measured. The most common online method utilizes the absorptive properties of ozone at 253.7 nm. The concentration of ozone is a function of the absorbance of light at that wavelength. A second online method is electrochemical and is used for some safety devices and locations where low concentrations of ozone may be present. The third method is not online and is a wet-chemical method that uses potassium iodine.

Beer–Lambert UV Type Monitors. Ozone absorbs UV light at 253.7 nm. When UV light passes through a gas containing ozone, the loss in intensity in comparison to the reference gas that is free of ozone can be used to calculate the concentration of ozone in the sample. The measurement is a function of the cell length and ozone concentration in the sample. This phenomenon of UV absorbance is expressed by the Beer–Lambert law.

The sample flow rate has no effect on the ozone concentration readings. Also the light intensity is not affected by other substances as long as those substances do not change during adjacent reference and sample cycles. Ambient temperature and pressure variations can be determined and corrected for by using the ideal gas laws and by following the manufacturer's recommended procedures for calibration. All available photometers should have an electronic system that provides automatic ambient temperature and pressure compensation.

For a photometer to be considered accurate and reliable, it must incorporate the following requirements:

1. A sample with a known ozone concentration, usually zero
2. A sample identical to the first in its light-absorbing properties, except for an unknown ozone concentration
3. A UV light source of known wavelength and fixed intensity
4. A stable detector
5. A known and fixed light path length
6. The UV absorption coefficient at the wavelength being used

With good instrumentation, an absolute accuracy of about $\pm 0.5\%$ can be attained. There is no interference from other species that may possibly be found in the output of ozone generators, such as nitrogen oxides, hydrogen peroxide, and nitric acid. However, ambient analyzers may be affected by particulate matter and solvents that may be present in the air. Some cleaning

supplies and paint fumes have resulted in ambient analyzers detecting ozone when none was present.

The photometer can be used to measure high concentration (0.5%–16%), ozone off-gas (0.1%–2%), and ambient ozone concentrations (0.01–1.0 ppm_v). At lower concentrations, many manufacturers increase the path length to improve sensitivity. The detector, lamp and all other components are the same regardless the intended location for installation.

Ozone off-gas requires additional sample preparation to prevent fouling of the analyzer. Water traps, filters, and even dehumidification equipment are used to minimize fouling on the optical cell surfaces.

Ozone analyzers are not maintenance-intensive equipment, but their accuracy is critical to the control, operations, and performance of the ozone system. They should be calibrated or calibration-checked annually. Lamps are routinely replaced annually and the optical cell will require periodic cleaning. The high-concentration ozone analyzers usually require the least amount of maintenance because the feed gas is nearly free of particles and moisture. Other maintenance items are the pumps for the off-gas analyzers, solenoid valves that switch between the sample gas and reference gas, and ozone destruct canisters.

Electrochemical Monitors. A second type of online ozone sensor uses an electrochemical process. The monitor consists of the output interface and a replaceable sensor module. Ozone diffuses through a porous membrane into a cell containing liquid or gel electrolyte and electrodes. Ozone produces a change in the electrochemical potential between the electrodes proportional to the ozone partial pressure.

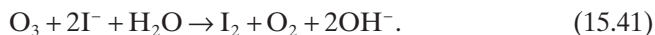
These types of online ozone monitors are limited to use in low concentration applications, generally less than 10 ppm_v although sensors that can detect concentrations as high as 150 ppm_v are available. At higher concentrations, the life span of the sensor module is greatly diminished because the rate of electrode oxidation increases with increases in ozone concentration. The sensors are typically replaced every 1–2 years, and calibration needs to be carried out every 6 months. Volatile organic compounds and changes in temperature and humidity interfere with the measurement (J. Leusink, pers. comm.).

Heated Metal Oxide Semiconductor. A third online monitoring technology uses a heated metal oxide semiconductor (HMOS) sensor to detect ozone in the gas phase. The sensor consists of a small platinum substrate that is heated to 300 °F and sensitive to ozone. Gas molecules adsorb onto the heated surface where an oxidation–reduction reaction occurs, causing a change in the electrical conductivity of the metal oxide. This change is proportional to the concentration of ozone in gas.

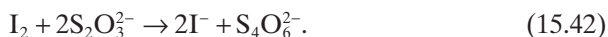
These sensors are more sensitive than electrochemical monitors, capable of monitoring concentrations less than 0.01 ppm_v. However, they are also less selective and may have false-positives caused by particle deposition, smoke,

or any volatile organic carbon/compounds (VOCs). These monitors require up to 24 h for startup during which the element is heated and the contaminants present on the surface of the sensor are burnt off. The instrument also has a delayed response of 1–2 minutes. The sensor is superior to the electrochemical monitors in terms of longevity, and many include small fans to move the sample gas across the sensor, whereas electrochemical are generally passive sensors (J. Leusink, pers. comm.).

Wet-Chemistry Method. The potassium iodide wet-chemistry method relies on the principal that iodide reacts with ozone to iodine and the iodine can be back titrated with sodium thiosulfate to a starch end point. The mass of ozone is then calculated based on a theoretical ozone/iodine stoichiometry of 1.0, as described in Equation (15.41):



Iodine is back titrated with sodium thiosulfate in the following reaction:



The unbuffered potassium–iodide method and the neutral-buffered potassium iodide Europe method that includes a weakly buffered KI solution are the two most commonly used wet-chemistry tests. The methodology for performing the wet test is included in *Ozone in Drinking Water Treatment: Process Design, Operation, and Optimization*.

Beer–Lambert UV type monitors may be calibrated through one of the following two procedures: direct determination by wet-chemistry method or comparison with a reference UV meter verified by wet-chemistry method. Calibration through direct determination by wet-chemistry test should be repeated a minimum of five times and achieve a standard deviation of $\pm 2\%$. The reference UV meters must be validated by performing a minimum of nine wet-chemistry comparative tests and achieving a standard deviation of $\pm 2\%$.⁵⁸

Measuring Dissolved Ozone Residual in Water

The problem encountered in measuring ozone residuals in aqueous solution is strictly a consequence of the nature of ozone: It is a powerful oxidant suffering from continuous self-destruction, off-gassing from solution, and instantaneous reaction with many organic and inorganic contaminants usually found in water. Reliably measuring the ozone residual after a given contact time is crucial to the successful performance and reliability of an ozone facility. Furthermore, the Surface Water Treatment Rule requires that a dissolved residual be accurately measured at a specified contact time to calculate CT and disinfection performance.

Dissolved ozone residual may be monitored through gravity or pumped sampling systems. Gravity sampling systems use the hydraulic head in the ozone contactor to drive the flow of water to the analyzer, whereas pumped systems use the pump to provide the head to return the sample back into the ozone contactor. A well-designed sampling system must consist of the following:

1. A design to minimize the detention time in the sample piping. Ideally, the HRT of the piping should be less than 10s. If long pipe runs are necessary, high flow rates may be used to limit the HRT and the residual monitored in a sidestream;
2. Piping of sufficient size to prevent clogging. Stainless steel pipe, $\frac{3}{4}$ -inch, is typically supplied for large ozone contactors with amperimetric analyzers that require up to 5 gpm flow. Flushing connections may also be provided;
3. A location through which a grab sample may be taken for calibration and verification purposes. The sample isolation valve and piping diameter should be smaller, perhaps $\frac{1}{8}$ in. to control the grab sample flow rate;
4. A rotameter to verify flow rate;
5. Flow control valve to adjust flow to the probe;
6. A location and means through which the sample can be sent to drain or returned to the contactor. If the sample is gravity fed, the hydraulic head must be sufficient to overcome the head loss in the piping, and the drain must be constructed of ozone-resistant materials or the residual decayed to a level low enough to not cause corrosion of the drain materials; and
7. Water with dissolved residual should not be conveyed through floor drains or other open headspace environments, as the dissolved residual will off-gas, which could create hazardous ozone levels.

Indigo Trisulfonate. The indigo trisulfonate method is recognized within the *Standard Methods for the Examination of Water and Wastewater*, 4500-O₃ B. Indigo Colorimetric Method is the method for determination of dissolved ozone concentration. This colorimetric method is quantitative, selective, simple, and applicable to all water matrices: lake water, river infiltrate, groundwater, extremely hard water, and biologically treated wastewater.⁵⁹ The method has not been modified to commercial online dissolved ozone monitors. Some chemical reagent supply companies have modified the procedure and enclosed all the reagents within vacuum ampuls. When the ampul tip is broken, a known volume of sample is drawn into the vial and mixed with the reagents. These vials are commonly used to spot-check online ozone analyzers.

The method works on the principle that ozone reacts with the indigo reagent and that the decrease in absorbance is linear with increasing dissolved ozone concentration. Ozone residual is determined through comparison

between a sample and a blank at 600 nm. The calculation to determine dissolved ozone residual, volumetric method is listed in Equation (15.43).⁵⁹

$$C = \frac{100 \times \Delta A}{f \times b \times V}, \quad (15.43)$$

where

- C = dissolved ozone concentration (mg/l),
- ΔA = difference in absorbance between sample and blank,
- b = path length of cell (cm),
- V = volume of sample (mL, normally is 90 ml), and
- f = 0.421.

The calculation to determine dissolved ozone residual, gravimetric method is shown in Equation (15.44):⁵⁹

$$C = \frac{(A_B \times 100) - (A_s \times V_T)}{f \times V_s \times b}, \quad (15.44)$$

where

- A_B, A_s = absorbance of blank and sample, respectively,
- V_s = volume of sample [ml = ([final weight – tare weight] g $\times$ 1.0 ml/g) – 10 ml],
- V_T = total volume of sample plus indigo (ml = [final weight – tare weight] g $\times$ 1.0 ml/g),
- b = path length of cell (cm), and
- f = 0.421.

Hydrogen peroxide and organic peroxides decolorize the indigo reagent very slowly. If measurement is made less than 6 h after the reagent is added, there will be no interference. Organic peroxides may react more swiftly. Fe III does not interfere, but Mn IV and VII form compounds that decolorize the indigo reagent. This interference can be corrected by making a measurement relative to a blank in which the ozone has been destroyed selectively. Without the corrective step, 0.1 mg/l of ozonated manganese gives a response of about 0.08 mg/l of apparent ozone. Chlorine also interferes, but it can be masked by the addition of malonic acid. When bromide ion is present, ozone oxidizes it to bromine, which interferes at a ratio of 1-mol HOBr to 0.04-mol ozone.⁵⁹

Amperimetric Probes. Amperimetric ozone analyzers use semipermeable membranes that selectively allow ozone to pass through and prevent foulants and other interfering compounds to access the probe. These polymeric

membranes show less than 2% interference, in terms of current response, from the presence of bromine, hypobromous acid, hypochlorous acid, nitrogen trichloride, and chlorine dioxide.^{60,61}

Accurate and reliable online dissolved ozone measurement is possible only when the following occur:

1. The sensor is correctly installed.
2. The sensor is correctly calibrated, and calibration is regularly verified.
3. The probe membrane is periodically cleaned and foulants are removed.
4. The contact time between the sample location and the monitor is minimized to only a few seconds.
5. The flow rate through the sample piping is maintained, and plugging of strainers or accumulation of debris is prevented or eliminated.
6. The piping arrangement eliminates off-gassing and gas binding.
7. A grab sample can be taken downstream from the sensor to verify the accuracy of the online instrument.
8. The sampling piping provides some level of flexibility to monitor ozone residual at various locations, as flow and decay rates vary over time.

HEALTH AND SAFETY

Ozone, like chlorine, is a toxic gas. However, unlike chlorine gas delivered in large cylinders or rail cars, ozone is generated on-site, and there is usually less than 1 lb of ozone on-site at any given time. Ozone also has a distinct advantage in that it can be smelled at concentrations of approximately 0.01–0.04 ppm_v, well below harmful levels. Ozone does cause olfactory fatigue, and extended periods of exposure will result in desensitization to the gas.

The biological effects of slight overexposure to ozone include headache, coughing, and dryness of nose, mouth, throat, and eyes. Extreme exposures may result in shortness of breath and other breathing disorders. Concentrations in excess of 0.5 ppm_v may result in lung irritation, fatigue, chest pain, and dry cough. The Occupational Safety and Health Administration (OSHA) has established safe exposure limits to ozone gas in the workplace, which include a threshold limit value on a time-weighted average (TLV-TWA) of 0.1 ppm_v during an 8-h workday and a threshold limit value-short term exposure limit (TLV-STEL) of 0.3 ppm_v in a 15-min period. In contrast, 10% ozone in oxygen is equivalent to 68,800 ppm_v. Therefore, even small leaks can result in high concentrations of ozone.

Ambient ozone analyzers should be installed in any space where ozone gas is present or may accumulate. The sample should be taken from near the floor, as ozone gas is denser than air. The sensors are commonly connected to the plant control system and will alert the operator to the situation at a high ambient level. While ozone rooms are typically ventilated continuously, a secondary high-rate ventilation system is often provided and will start at high-ambient ozone levels. If the ambient level increases to a high-high set point,

the alarm may trigger the ozone system to shut down, while the high rate ventilation system continues to operate.

Ozone is one of the hazardous elements of smog, and its concentration in the atmosphere is an indicator of smog intensity. Ozone alerts occur at concentrations that exceed 0.10 ppm_v, and communities recommend that people remain indoors and limit outdoor physical activity. Many utilities find that ambient ozone alarms may occur during hot summer days as a result of naturally occurring ozone rather than an ozone leak at the facility.

Enriched oxygen concentrations, higher than 23%, are also hazardous. Oxygen is nonflammable but it does support combustion. Materials and activities that are normally not prone to combustion may become so in oxygen-enriched environments because their combustion limit is lowered. It is of critical importance that clothing worn in oxygen-enriched spaces be changed promptly after leaving the space, and allowed to “air out” for several hours. Smoking in areas where enriched oxygen may accumulate should be strictly prohibited.

Safety monitoring equipment are used to detect elevated oxygen concentrations. Oxygen is denser than air. Therefore, the sampling point should be located near the floor. The monitors are usually connected to the control system and will stop the flow of oxygen if they detect an elevated concentration.

LOX is a cryogenic liquid, -297°F at 1 atm, which will immediately freeze skin on contact. LOX piping should be insulated to protect plant personnel. Because pressure will build when LOX is vaporized, keeping pressure relief valves in good operating condition is of critical importance.

In addition to the hazards posed by ozone and oxygen, their generation and the equipment used also pose electrical and mechanical hazards. Contact basins and oxygen storage tanks are confined spaces.

REGULATORY ISSUES

Ozone can react with naturally occurring bromide in the water and form hypobromous acid that can react with organic matter to form brominated THMs and HAAs. Its use can significantly decrease some chlorinated DBPs but can also cause an increase in the formation of brominated DBPs. The formation of DBPs is influenced by many factors such as bromide, ozone dose, dissolved residual, contact time, pH, DOC, temperature, and alkalinity.

Ozone can oxidize iodine ions, forming hypoiodous acid. The iodine-containing species are seldom monitored but are known to cause medicinal or pharmaceutical tastes and odors in drinking water at very low concentrations. For example, the threshold odor concentration of iodoform is 20 ng/l.⁶²

Although brominated THMs and HAAs can be formed, the formation of bromate is the primary concern because of its MCL of 0.010 mg/l. Several methods for bromate mitigation have been identified, researched, and applied.

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16 Bromine, Bromine Chloride, BCDMH, and Iodine

BROMINE (Br₂)

Physical and Chemical Properties

Bromine is a dark, brownish red, heavy, mobile liquid. It gives off, even at ordinary temperatures, a heavy, brownish red vapor with a sharp, penetrating, suffocating odor. The vapor is extremely irritating to the mucous membranes of the eyes, nasal passages, and throat and is extremely corrosive to most metals. Liquid bromine is likewise corrosive and destructive to organic tissues. In contact with the skin, it produces painful burns, which are slow to heal.

Bromine (Br₂; atomic number: 35; molecular weight: 159.832; specific gravity: 3.12) weighs 26.0lb/gal and has a boiling point of 58.78°C. Of the metals used in handling bromine, lead is the most versatile.¹ Bromine reacts with lead to form a dense, superficial coating of lead bromide, which, if not disturbed, prevents further attack. This is similar to the reaction of chlorine and silver. Tantalum is completely resistant to bromine, wet or dry, at temperatures up to 300°F.

Nickel and its alloy, Monel, resist dry bromine and are especially useful as a material for shipping containers. Other nickel alloys, including the hastelloys, are less suitable. Iron, steel, cast iron, stainless steel, and copper are attacked by bromines, either wet or dry. Silver withstands dry bromine.

Bromine handled in lead, nickel, or Monel containers should be dry (less than 0.003% moisture)¹ and should be protected from ordinary air, from which it can readily absorb enough moisture to make it severely corrosive to these materials.

Bromine is three times as soluble as chlorine (i.e., 3.13g/100ml water at 30°C). This is an important characteristic when one is considering the physical aspects of applying bromine to a process stream. Dispersion and diffusion is made “easier,” and diffuser design to prevent off-gassing is a lesser problem than with chlorine.

White's Handbook of Chlorination and Alternative Disinfectants, 5th edition,
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Occurrence

Bromine was discovered in seawater in 1826, by Antoine J. Balard. It derives its name from its offensive odor: the Greek word *bromos* meaning “stench”. It does not occur in nature as a free element. It exists primarily in the bromide form and is found widely distributed in relatively small proportions. Bromides available for extracting bromine occur in the ocean, salt lakes, brines, or salt deposits left after the waters evaporated during earlier geological periods, and from the mineral bromyrite. The bromide content of seawater is about 70 mg/l. The total bromine content in the earth’s crust is estimated to be 10^{15} – 10^{16} t.²

The Dead Sea in Israel is one of the richest sources of bromine in the world, containing nearly 0.4% at the surface and up to 0.6% at lower depths. In Western Europe, the most significant sources of bromine are the salt deposits at Strassfurt, Germany. Principal sources in the United States are the brine wells in Arkansas (Arkansas produces about three-fourths of the United States’ bromine output), Ohio, Michigan, and West Virginia, with a bromide content ranging from 0.2% to 0.4%. Those in Michigan underlie a large area around the Great Lakes region and occur in various sandstone strata at depths of 700–8000 ft, where the bromide content varies from 0.05% to 0.3%, being generally higher at the deeper levels.

Bromine Production

Bromine was first recovered from seawater on a commercial scale in 1924 by the Ethyl Corporation.³ This process involved treatment of the seawater with chlorine and aniline. The first successful bromine plant was placed into operation at Kure Beach, North Carolina, in 1933, and was capable of extracting 3000 t of bromine per year, a process that consisted of adjusting the pH of seawater to 3.5 with sulfuric acid, followed by the application of chlorine. The bromine, liberated by the chlorine, was removed as a dilute bromine gas with a current of air and absorbed in a sodium carbonate solution, from which it was recovered by acidification and stripping with steam. The critical part of this process is maintaining the pH at 3.5.

The extraction of bromine from bromide compounds consists of four steps: (a) oxidation of bromide to elemental bromine (Br₂), (b) separation of the bromine from solution, (c) condensation and isolation of the bromine vapor, and (d) purification.

Oxidation of bromide to bromine can be accomplished either chemically or electrochemically. Electrolysis instead of chlorine to oxidize bromides was used in early production in Germany. Two electrolysis processes were commonly used: the Wunsche electrochemical process and the Kossuth process.⁴ However, these methods are no longer in commercial production today. Current methods are based on the modified Kubierschky process or steaming out processes and H. H. Dow blowing out process.⁴

Kubierschky Process.⁴ In this process, the raw brine is preheated to about 90°C, treated with chlorine in a packed tower, and then placed in a steaming out tower into which steam and additional chlorine are injected. The outgoing brine is neutralized with caustic and used to preheat the raw brine. From the top of the steaming out tower, the halogen and steam vapor passes into a condenser and then into a gravity separator. Vent gases from the separator return to the chlorination system, the upper water layer containing Br₂ and Cl₂ is returned to the steaming out tower, and the lower layer containing crude bromine passes to a stripping tower. From the stripping column, bromine is purified in a fractionating column to 99.8% pure liquid bromine as the final product.

The H. H. Dow Process.⁴ This process uses air instead of steam for the “blowing-out” step, since it is more economical, especially when the bromine source is as dilute as seawater. In the blowing out process, the halogens are absorbed from the air in a sodium carbonate solution or by sulfur dioxide reduction:²



Bromine can then be separated by chlorinating the mixed acids in the blowing out tower. The theoretical yield is 2.2t of bromine per ton of chlorine.¹ From 1973 to 1975, the estimated total annual bromine production in the United States was about 220,000t.⁵ In 2006, it was about 243,000t.⁶

In the years following World War I, bromine was used in the pharmaceutical and organic chemical industries and in photography. The biggest boon to the bromine industry was the discovery of tetraethyl lead as an antiknock ingredient in gasoline used in the powerful high-compression automobile engines. However, there it posed a serious problem: deposits of lead in the engine. It was found that a mixture of ethylene dibromide and ethylene dichloride added to tetraethyl lead prevented the lead deposits from accumulating in the engines. These lead halides were sufficiently volatile to be expelled in the engine exhausts. It is estimated that about 79% of the 1969–1970 production of bromine was used to make ethylene dibromide for gasoline.⁷ However, air pollution controls later led to a ban on the use of tetraethyl lead in gasoline, thereby wiping out the major market for bromine.⁸ However, the use of bromine as a water treatment chemical was expected to show modest growth during the next several years. Bromine was used in both residential and commercial swimming pools, hot tubs, and whirlpools. It was also used to treat industrial cooling water. The use of bromine compounds was expected to continue increasing in hot tubs, spas, and swimming pools as a gentler disinfectant than chlorine.⁶

Chemistry of Bromine in Water and Wastewater Treatment

Bromine is unique in being the only nonmetallic element that is liquid at ambient temperatures. It reacts with ammonia compounds in solution to form bromamines and displays the breakpoint phenomenon similar to chlorine.

Bromine in water hydrolyzes:



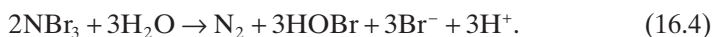
for which reaction the equilibrium constant is 5.8×10^{-9} .

Depending upon the pH, the proportion of dissociation of hypobromous acid (HOBr) and hypobromite is

$$\frac{[\text{OBr}^-][\text{H}^+]}{[\text{HOBr}]} = K = 2 \times 10^{-9}. \quad (16.3)$$

Like chlorine, bromine reacts with ammonia, in forming bromamine. Both Galal-Gorchev and Morris⁹ and Johnson and Overby¹⁰ have identified and studied the rate reactions of the compounds NH₂Br, NHBr₂, and NBr₃ using the ultraviolet absorption spectrophotometry technique. They reported rapid formation of all bromamine species. However, once the bromamines have formed, a series of decomposition reactions take place. The major chemical difference between the bromamine species and the chloramine species is that the formation of the bromamine species is reversible from monobromamine through dibromamine to tribromamine and back again by fast reactions, simply by changing the pH of the solution.

Bromine, like chlorine, displays a break point, and the basis for this reaction is the decomposition of the dibromamine. Tribromamine is the major species of combined residual bromine present beyond the break point. In pH range of 7–8, it decomposes in accordance with the following equation:



La Pointe, Inman, and Johnson have shown that the break point occurs when the bromine-to-ammonia nitrogen molar ratio is 1.5.¹¹ This is precisely the stoichiometric amount of bromine required to oxidize all of the ammonia to nitrogen gas.

For wastewater disinfection, it is of considerable practical significance that the predominant species of bromine compounds is dibromamine over a pH range of 7–8.5 because dibromamine has a germicidal efficiency almost equal to that of free chlorine. Dibromamine is very active and usually displays a rapid decomposition, reverting to the bromide ion. At this point, the bromine residual is extinguished.

Free bromine residuals (hypobromous acid, HOBr), which would occur in highly nitrified effluents, do not decompose nearly as rapidly as the bromamines. Their persistence increases as the halogen demand of the water being treated decreases.

Reactions with Chlorine

The reactions with chlorine and the bromide ion are the only ones of particular interest. It is important to realize that free chlorine (HOCl) has the ability to oxidize bromide ions to form hypobromous acid (HOBr) in the pH range of 7–9. This phenomenon was the basis of a patent issued to Marks and Strandkov¹² and was put to use in the application of chlorine to recirculate condenser-cooling water at gasoline refineries in the 1950s.* Bromide salts were added to the cooling water in the atmospheric tower basin, followed by intermittent chlorination. The only chemical consumed was chlorine. The chlorine added converted the bromides to hypobromous acid. When the bromine residuals disappeared, they reverted to the bromide ion. Thus, the intermittent chlorination kept repeating the process to control algae in the towers and tower basins and slime in the condenser tubes.¹²

Chloramine residuals will not oxidize the bromide ion at pH 4, but free chlorine will. This was the basis for development of the free chlorine residual analyzer by Fischer and Porter in 1968.¹³ This analyzer is not susceptible to any significant chloramine interference when high concentrations of combined residual are present with free chlorine. A bromide salt is added to the sample along with a pH 4 buffer. The free chlorine oxidizes the bromide ion to free bromine (Br_2), which is measured by the analyzer cell. Other applications of this phenomenon are described below.

USE OF BROMINE IN WATER TREATMENT PROCESSES

Potable Water

The use of free bromine (Br_2) in treatment potable water is probably nonexistent to date.

The only known use of free bromine in a municipal potable water treatment system was at Irvington, California, in about 1938. It was discontinued after a reasonable trial period because it did not solve the problem of water quality degradation in the distribution system. The bromine applied reacted so quickly and so completely with the zoological slimes on the pipes walls that it was impossible to obtain a residual downstream from the point of application. It also imparted a strong medicinal taste to the water.³

As early as 1955, significant efforts were being made to produce solid or dry granular disinfectants by using the best attributes of bromine. U.S. Patent 781,730 was issued to the Diversey Corporation of Chicago, Illinois, for the invention of a stable dry product composed of hypochlorite and alkali

*It was thought at the time that combined chlorine could oxidize bromide ions, which it cannot do. This was discovered during the investigations of trihalomethane (THM) formation by chlorination.

metal bromide. This product was claimed to have extraordinary disinfectant properties due to the formation of the hypochlorite–hypobromite mixture when placed in an aqueous solution.

In 1967 and 1969, patents were issued to Jack F. Mills et al. of the Dow Chemical Co.^{14,15} The invention described in these patents represents a process for treating water with elemental bromine obtained from the polybromide form of an anion exchange resin. An effective method for the preparation of this resin is passing an essentially saturated solution of bromine in aqueous sodium bromide slowly up through a bed of quaternary ammonium anion exchange resin. The resulting polybromide resin in wet form contains about 48% bromine. Development of the polybromide resin system as a practical means for disinfection has been concentrated on units capable of treating small quantities of water—potable water for household use and swimming pools.¹⁶ The Everpure Co. of Chicago has developed disposable cartridges containing bromine-impregnated resin to feed predetermined amounts of bromine into the water for disinfection.¹⁷ The polybromide resin is sealed permanently into the cartridge to prevent its escape into the water system. Polybromide resins with bromine loadings of 25% have a very low acute oral toxicity. Direct contact with undiluted 25% resin is only moderately irritating to the skin but is capable of producing uncomfortable irritation upon direct contact with the eyes.

The disposable cartridge-type brominator has been installed and operated aboard offshore oil well-drilling rigs, at some remote land stations, and on oceangoing vessels that use seawater distilling systems for their potable water supply.

Wastewater

The only acceptable use of bromine in commercial wastewater or water reuse in the United States or Canada would be in a wastewater discharging into seawater. In the early 1980s, Dow Chemical Co. made a test project of bromine for disinfection of the East Bay Municipal Utility District Waste Water Treatment Plant effluent that discharges into the San Francisco Bay on the left-hand side of the highway entrance to the San Francisco Bay Bridge en route to San Francisco. The project failed because of the high oxidative power of the bromine. In other words, the bromine demand was “out of site.” The required dosages were cost-prohibitive.

However, when a wastewater plant is near enough to a seawater supply, such as the California coast, if it is convenient, the seawater can be used to operate the chlorine injectors. The 60–80 mg/l of bromides in the seawater will be converted to bromamines in the chlorine solution. As the oxidative power of bromamines is equivalent to that of free chlorine (HOCl), the total effect by a comparative test at the Santa Cruz, California, wastewater treatment plant was an increase of about 15% in disinfection efficiency.

Cooling Water

About 1983, the electric power industry began to investigate using bromine in condenser-cooling water treatment. The objective was to determine whether or not dechlorination could be avoided by using bromine, owing to the expected rapid decay of bromine residuals. The method adopted by some of the steam-generating plants amounted to pumping a bromide salt solution into the chlorine solution being discharged by existing conventional chlorination equipment. The chlorine oxidizes the bromide ion in the salt solution to free bromine, which goes into solution as hypobromous acid, the active ingredient.

Swimming Pools

The most widespread use of bromine as a disinfectant began in Illinois during World War II. The Illinois State Department of Health, under the direction of C. W. Klassen, began an investigation into the use of liquid bromine in the elemental form as a substitute for chlorine when the latter became scarce during the war years. After a trial run in a few swimming pools for a couple of years, it was concluded by bacteriological evidence that the bromine was doing an efficient job as a disinfectant. In 1947, permission to use elemental bromine was granted to a number of additional pools, and, before the end of that year, there were about 25 outdoor and 30 indoor pools being disinfected with bromine instead of the difficult-to-obtain chlorine. However, for the hazards of handling liquid bromine to be avoided, bromine in stick form was introduced about 1958.

The stick is a compound of both bromine and chlorine known as bromochloro-dimethyl hydantoin (Dihalo). The use of this chemical was documented by Brown et al.¹⁸ It is thought that this compound, which hydrolyzes to form hypobromous acid, has the additional capability of releasing some HOCl by hydrolysis, which reacts with the reduced bromides to form more hypobromous acid. This form of bromine can produce satisfactory results for indoor and very small outdoor swimming pools. The high cost of the bromine sticks makes their use in large outdoor pools decidedly uneconomical.

Br₂ Facility Design

Current practice is limited to the use of bromine in stick form or resin impregnation systems described above for treatment of swimming pools and potable water. Neither of these methods is practical for wastewater or reuse water. The hazards of handling and the difficulties associated with metering molecular bromine (liquid or vapor) make its use impractical. The difficulties stem from the unique characteristic of bromine that enables it to remain in the liquid form at room temperature and atmospheric pressure. This is also one of the major reasons why the use of BrCl is being pursued as a practical means

of brominating of wastewater. BrCl has a vapor pressure of 30psi at room temperature (20°C), which simplifies its packaging and handling.

Owing to the undesirable handling characteristics of molecular bromine, there can be no valid recommendations for a facility to handle molecular bromine.

BROMIDES: ON-SITE GENERATION OF Br₂

System Description

On-site oxidation of bromide salts in an aqueous solution to form free bromine (Br₂) is an old concept. In 1948, a patent was issued to Marks and Strandkov of Wallace & Tiernan Co. that involved on-site production of either iodine or bromine by oxidation of the respective salts by either free or combined chlorine at pH 7–8.¹² Chemically, the iodine release was predictable and quantitative, but the bromine release was neither quantitative nor predictable at this pH. The iodine system failed because control was difficult. However, since then, there has been a renewed interest in the on-site generation of bromine from bromide for disinfection of reclaimed water. A patent for such a system was issued in 1973 to A. Derreumaux (France).¹⁹ This system is different from the one proposed by Marks in that the bromide salt solution is oxidized by a chlorine solution at a carefully controlled pH of 1–2. It conforms to all the established kinetics of bromine chemistry. Free bromine is produced in the Derreumaux process by injecting a bromide salt solution of known concentration into the injector discharge of a conventional chlorinator. The reaction between the chlorine and bromide ion to convert the bromide to hypobromous acid takes place in a reactor where the pH for the reaction is kept below 2. The reaction proceeds as follows:



Thus, 2.90lb of pure sodium bromide (NaBr) will react with 1.0lb of chlorine to produce 2.25lb of bromine (Br₂).

The patented Derreumaux system is illustrated in Figure 16.1. It consists of conventional chlorination equipment, a reaction vessel, and a metering pump for the addition of the bromide salt. The success of this system is in its ability to consistently produce an almost pure solution of hypobromous acid at a controlled pH lower than 2. This ensures maximum quantitative conversion of the bromide ion in accordance with Equation (16.5). In cases where the chlorinator injector water is plant effluent (i.e., has a high NH₃ concentration), there will not be any chlorine lost in side reactions with ammonia nitrogen at this low pH and with the reaction time involved. After the bromide is oxidized to free bromine, it will remain as Br₂. Therefore, at this controlled low pH in the reactor zone, the free bromine will not be wasted on side reactions with the ammonia nitrogen present.

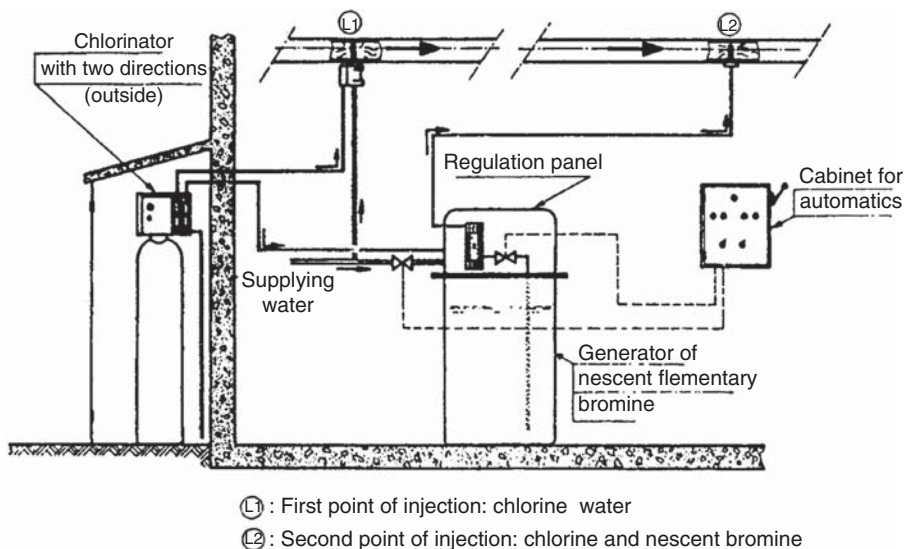


Figure 16.1. The Derreumaux bromine generating system (courtesy of CIFEC Co.).

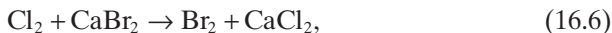
This procedure serves three purposes: (a) It reduces significantly the amount of bromine required, (b) it improves the disinfection efficiency,²⁰ and (c) it solves the problem of coping with the changes in bromine demand usually experienced with wastewater effluent. Field experience has shown that, owing to the rapid die-away of bromamine residuals, it is not practical to control the dosage by residual control.²¹ In a comparable situation, it was shown that chlorine is far more adaptable than bromine to the diurnal variations in halogen demand, particularly those caused by unpredictable and uncontrollable plant upsets. This is to be expected because of the much greater reactivity of bromine with the various constituents in wastewater.

The presumed advantages of bromine in wastewater treatment are considered to be as follows: (a) The presence of ammonia N in wastewater converts the bromine applied to the dibromamine, which is nearly as germicidal as free chlorine, (b) dibromamine, the dominant species, is so highly reactive with seawater constituents that the residual should die away rapidly[†], and (c) owing to these two characteristics, contact times may be reduced from current chlorination practice of 45–60 min to perhaps 20–30 min, thus reducing debromination requirements if necessary.

However, the process must be cost-effective. The average unit value of bromine sold or used in 2006 was about \$0.64/lb, or almost 90% higher than the price in 2005.⁶

[†]Owing to the presence of significant concentrations of organic N (3–10 mg/l) in wastewaters, organic bromamines will form as their chlorine counterparts always do. This species persists as a measurable residual for extended periods of time (several hours).

Dow Chemical Co. produces a low-grade calcium bromide solution (specific gravity of 1.7–1.72 g/ml),² an 80% calcium bromide flake. The bromide ion content is about 42%–43% in the solution and about 64% in the solid form. Assuming the following reaction,



it would take approximately 2.82 lb of pure calcium bromide plus 1 lb of chlorine to make 2.25 lb of bromine.

Current U.S. Practices

The only known installations are those used by the electric power industry. Several power plants are experimenting with this method of on-site generation of bromine in the hope that they can escape the need for dechlorinating the cooling water discharge. These discharges usually contain 0.5- to 2.0-mg/l total residual chlorine. The hope is based on the rapid die-away phenomenon of bromine residuals. The success or failure will depend upon site-specific conditions, which will vary with the water quality at each location. The two most significant water characteristics in addition to halogen demand are (a) ammonia N and (b) organic N concentration. If sufficient ammonia N is present to convert all of the residual to bromamine and if there is insufficient organic N (and contact time) to form organobromamines, the residuals should die away in a few minutes.

From the power industry's point of view, it is much more appealing to retrofit an existing chlorination system to on-site generation of bromine than to install a dechlorination facility. From an environmental point of view, it would be more appropriate to relax the intermittent chlorine residual discharge requirements than to an alternative that will contribute more bromides to the environment.

Comparison with Other Methods

On-site generated of free bromine has the following advantages and disadvantages when compared with the use of molecular bromine and bromine chloride:

Advantages

1. It can be adapted to conventional chlorination equipment and controls.
2. The bromine salt solution conventional metering equipment (diaphragm pumps).
3. It is readily adaptable to conventional compound loop control by using existing chlorine residual analyzers.

4. The equipment specific for this process has been proved satisfactory by sufficient field experience.
5. It eliminates the hazards associated with handling liquid molecular bromine or bromine chloride.
6. It eliminates the problems of equipment corrosion and the chemical problem of dissociation encountered when using bromine chloride and molecular bromine.

Disadvantages

1. The chemical cost is high. The average cost of bromine in 2006 was about \$0.64/lb, or almost double that of chlorine.
2. The availability of bromine compounds is limited. However, the mandatory elimination of leaded gasoline for automobile engines in the United States eliminated the production of bromine compounds for use as lead scavengers in gasoline. (In 1970, 90% of the total U.S. bromine production was for this purpose.)
3. There is potential hazard created by the reaction of bromamines in wastewater effluents with organics and the subsequent formation of undesirable bromoorganics.
4. The end product of bromination, bromide ion, is a potential hazard to the environment.
5. There is insufficient field experience for proper evaluation.

BROMINE CHLORIDE (BrCl)

Physical and Chemical Properties

Bromine chloride is classified as an interhalogen compound because it is formed from two different halogens. These compounds resemble the halogens themselves in their physical and chemical properties except where differences in electronegativity are noted. Bromine chloride at equilibrium is a fuming, dark red liquid at temperatures below 5 °C. It can be withdrawn as a liquid from storage vessels equipped with dip tubes under its own pressure (30 psig at 25 °C). Liquid BrCl can be vaporized and metered as a vapor in equipment similar to that used for handling chlorine.

Bromine chloride is extremely corrosive in the presence of low concentrations of moisture. Although it is less corrosive than bromine,²² great care must be exercised in the selection of materials for metering equipment. Like chlorine and bromine, it may be stored in steel containers, assuming that the BrCl or Br₂ is packaged in dry environment (i.e., a dew point not higher than 40 °F).

Liquid BrCl, like Br₂, causes severe burns to the skin and other tissues. The vapor is extremely irritating to the eyes and the respiratory tract even at low

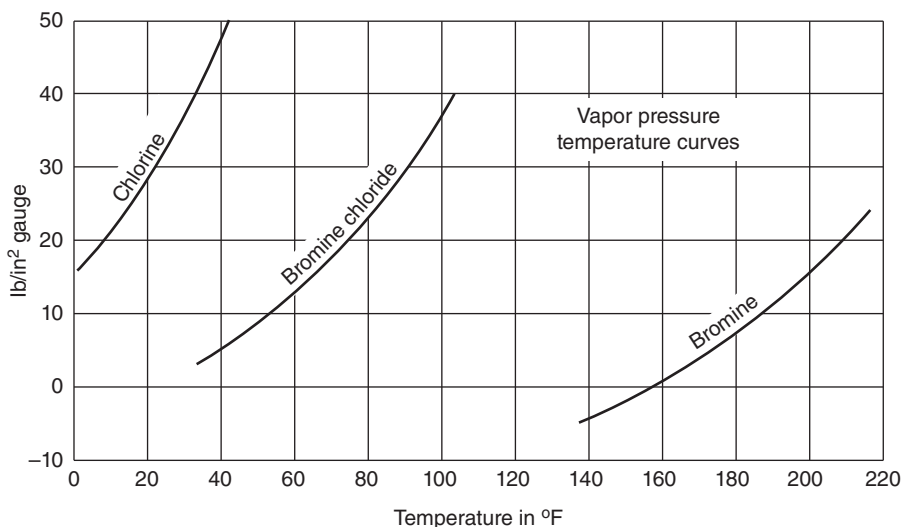


Figure 16.2. Vapor pressure versus temperature curves from bromine, bromine chloride, and chlorine (courtesy of Capital Controls Co.).

concentrations. Bromine chloride exists in equilibrium with bromine and chlorine in both gaseous and liquid phases, as follows:¹⁰



There is little information about equilibrium in the liquid state. A study by Mills²³ and an earlier investigation by Cole and Elverum²⁴ indicate less dissociation in the liquid (20%) than in the vapor state. The equilibrium constant for the vapor phase dissociation of BrCl is close to 0.34, which corresponds to a degree of dissociation of 40.3% at 25 °C.^{2,24}

The density of BrCl is 2.34 g/cc at 20 °C.

A comparison of the vapor pressure–temperature curves for bromine chloride, bromine, and chlorine is presented in Figure 16.2.

The solubility of BrCl in water is 8.5 g/100 cc at 20 °C, which is 2.5 times the solubility of bromine and 11 times that of chlorine.²

Bromine chloride forms a yellow crystalline hydrate, $\text{BrCl} \cdot 7.34\text{H}_2\text{O}$ at 18 °C and 1 atm, which is comparable to the formation of chlorine hydrate ($\text{Cl}_2 \cdot 8\text{H}_2\text{O}$), which takes place at 9.6 °C. This characteristic causes operating problems in metering equipment.

Preparation of Bromine Chloride

Bromine chloride is prepared by adding an equivalent amount of chlorine (as a gas or a liquid) to bromine until the mixture has increased in weight by 44.3%:



Bromine chloride may also be prepared by the reaction of bromine in an aqueous hydrochloric acid solution. In the laboratory, it can be prepared by oxidizing a bromide salt in a solution containing hydrochloric acid, which produces the following reaction:



Chemistry of Bromine Chloride in Water

Bromine chloride vapor appears to hydrolyze exclusively to hypobromous acid and hydrochloric acid:



whereas bromine vapor (or liquid) hydrolyzes to hypobromous acid and hydrogen bromide:



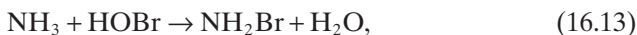
The formation of HBr represents a significant loss in the disinfecting potential of the expensive bromine molecules. In the hydrolysis reaction of BrCl, any HBr formed by the dissociation of elemental bromine is presumed to be oxidized quickly to HOBr by the HOCl remaining in solution:

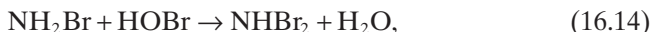


However, in the case of wastewaters, the ammonia nitrogen would immediately convert any HOCl in solution to chloramines in a near-neutral pH environment. Chloramines cannot oxidize any HBr formed by hypobromous acid (HOBr) at these pH levels.²⁵ Therefore, the problem of dissociation of bromine chloride is significant in the presence of ammonium ions.

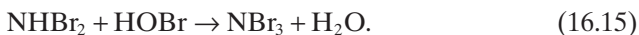
It is of practical significance that the hydrolysis constant for BrCl in water is 2.94×10^{-5} at 0°C, compared with the same constant for chlorine, which is 1.45×10^{-4} at 0°C. It is paradoxical that BrCl is several times more soluble in water than chlorine, yet it hydrolyzes 10 times more slowly. The hydrolysis constant of molecular bromine is 0.7×10^{-9} at 0°C, which differs significantly from that of bromine chloride.

Bromine chloride combines with ammonia in the same manner as molecular bromine to form bromamines. At the usual pH encountered in wastewaters (7–8.5), the dominant species will be dibromamine.²⁶ Typical reactions are as follows:





and



Bromine chloride is presumed to have a higher speed of reactivity than bromine. In wastewater, the formation of bromamines is probably much faster than the formation of chloramines. Of greater practical significance is the rapid die-away of the bromamine residuals. The half-life of bromamine residuals in secondary effluents is about 10 min. If organobromamines are formed, the half-life is much longer. In highly nitrified effluents, the predominant species would be HOBr, which persists for a significant period in a low-halogen-demand environment.**

Design of Bromine Chloride Facilities

Current Practice. The first attempt at plant-scale use of BrCl was a U.S. Environmental Protection Agency (USEPA)-sponsored project intended to evaluate several wastewater disinfectants at Grandville, Michigan²⁷ in 1974 and 1975. It was not strictly an exercise in disinfection because the coliform reduction ratio was too low. The most probable number (MPN) of total coliforms before disinfection ranged between $8 \times 10^4/100$ and $3 \times 10^6/100\text{ml}$. The disinfection goal was to $10^3/100\text{ml}$ MPN.^{††} According to the model developed by Collins et al.,²⁸ the chlorine residual contact time for the destruction is 7 min for the lower range of coliform (8×10^4) and 23.5 min for the higher range (3×10^6). Therefore, if mixing at the point of application is adequate and if 30 min of contact time is available, assuming 80%–90% plug-flow conditions in the contact chamber, the predicted chlorine residual requirement would range from 0.23 to 0.8 mg/l to meet the 1000/100 ml goal of total coliform disinfection. For effluents of comparable quality, this chlorine residual is considered very low.

The chlorine dosage at the beginning of this project was 2.9 mg/l, which resulted in a 2.0 mg/l residual at the end of 30 min. This demonstrates a chlorine demand of 0.9 mg/l in 30 min, which appears to be unreasonably low for an effluent of this quality.

At the middle of the project, the chlorine dosage was lowered to 2.3 mg/l, which produced a 1.0 g/l residual at the end of 30 min. This residual is comparable to the mathematical model prediction of 0.8 mg/l for a total coliform

** An example of this is the practice of power plant condenser-cooling water chlorination, where seawater is used. If the ammonia nitrogen content is less than 0.2 mg/l and the chlorine dose is 1–2 mg/l, the chlorine applied immediately converts (stoichiometrically) an equivalent amount of the bromide ions present into HOBr. The resulting bromine residual persists in the condenser discharge plume nearly as long as comparable chlorine residuals would.

†† Good disinfection is usually considered as a 5-log reduction of initial total coliform content.

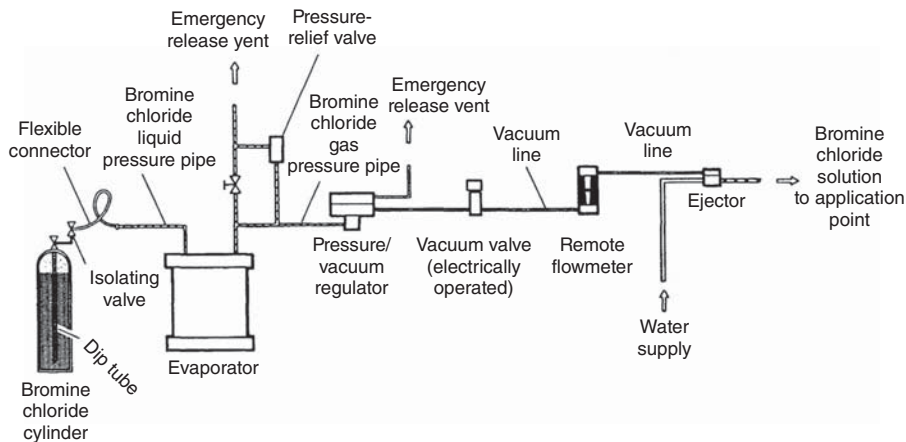


Figure 16.3. Bromine chloride metering and control equipment (courtesy of Capital Controls Co.).

concentration before chlorination (y_o) of $3 \times 10^6/100\text{ml}$, which is the high range of y_o for this above project.

The BrCl dosage was lowered from 3.6 mg/l to 3.0 mg/l early in the project and was lowered to 2.0 mg/l about the middle of the project, where it remained for the rest of the project. Because of the rapid die-away of the BrCl residual, this process could only be controlled by dosage, whereas the chlorination process was controlled by residual.

The performance of BrCl was disappointing. Chlorine succeeded in meeting the requirements on the Grandville project 90% of the time, but BrCl met the requirements only 80% of the time largely because of equipment failures. The reasons are described later in this chapter.

BrCl System Evaluation. The Potomac Electric Power Company studied and compared two parallel systems at the Morgantown Steam Electric Station.²⁹ This is an 1100-MWe, fossil-fuel, two-unit generating facility using low-salinity (7000 mg/l) estuarine water for once-through condenser cooling. One system used chlorine, and the other used bromine chloride. Both disinfectants were applied at levels of 0.5 mg/l or less. Two properties of bromine chloride were examined: decay rate of bromine residuals and biofouling control effectiveness. The BrCl meeting and control unit is shown in Figure 16.3.

On an equal weight basis, the continuous low-level application of BrCl resulted in equally good control of biofouling in the condensers. On an equimolar basis, therefore, BrCl would be nearly twice as effective but would cost about 2.5 times as much as chlorine at current market prices.

The flaw in this investigation stems from the fact that the chlorine applied converted the bromide ion to $\text{HOBr}^\ddagger$ which reacted with the ammonia N

[‡]There were sufficient bromide ions in the estuarine water to affect this conversion.

(0.25–0.50 mg/l) to produce bromamine. This would explain the nearly equal effectiveness of the two halogens on an equal-weight basis.

The BrCl and chlorine residuals dissipated in three decay phases. A very rapid loss of residual occurred in the first phase, which lasted less than 1 min. Quasi first-order decay kinetics characterized the second phase, which lasted about 10 min. In the third phase, the decay was relatively slow, longer than 45 min. The BrCl-induced oxidants dissipated faster than chlorine-induced oxidants. The effluent of the chlorobrominated cooling water contained only two-thirds to one-half the amount of oxidant present in the chlorinated cooling water, even though the BrCl and chlorine were applied at equimolar concentrations.²⁹

The report on this parallel study of BrCl and chlorine recommended the consideration of BrCl as an alternative to chlorine for biofouling control. This recommendation was based on the ability of BrCl to control biofouling at low-level concentrations (less than 1 mg/l) and its more rapid residual dissipation than that of chlorine. Whether or not the use of BrCl will eliminate the need for debromination to meet National Pollutant Discharge Elimination System (NPDES) discharge requirements has not yet been determined.

Metering and Control Equipment. Limited field experience has revealed that a new type of equipment would have to be designed of construction materials that tolerate the corrosivity of bromine chloride. The equipment chosen for the Grandville, Michigan project was a modified Wallace & Tiernan pressure gas feed chlorinator fitted with an injector,²⁷ Model 20-055, that was chosen because it was constructed of materials thought to be resistant to bromine chloride. Many corrosion and vapor dissociation problems were encountered, requiring modifications to the equipment.

At about the same time, the Public Service Electric and Gas Co. of New Jersey launched a project at one of its power stations to evaluate the difference between chlorine and bromine chloride using conventional chlorination equipment for both gases on a side-by-side installation. It took only a few hours' operation to observe that conventional chlorination equipment is not suitable for use with bromine chloride.³⁰ Most of the plastic and rubber components were found to be entirely unsuitable because of susceptibility to permeation and/or direct chemical attack. A successful experimental model was constructed on the direct gas-fed approach of slightly modified current production components such as a stainless steel indicating rotameter, chlorine line valves, and chlorine pressure-reducing valves. Kynar pipe and valves were used adjacent to the injector where moist BrCl vapor might be encountered. The "suck-back" phenomenon was dealt with by using a modified chlorine check valve adjacent to but not part of the injector assembly.

Figure 16.3 illustrates a system subsequently developed by Capitol Controls, Colmar, Pennsylvania, based on essentially the same concept as the Public

Service Co. experimental model described by Cole.³⁰ Figure 16.3 represents the system provided by Capital Controls Co. for the Potomac Electric Power Co. investigation.

Injectors. The injectors used with BrCl may require modifications. The one used on the project described by Cole³⁰ was a 3-in. Wallace & Tiernan Model A452. This unit was about 10 years old and required no modification. The model used on the Grandville project did require some modification, but that used by Capital Controls on the Potomac project was a standard chlorine injector.

Automatic Controls. The system shown in Figure 16.3 is readily adaptable to automatic control by simply automating the control valve.

Conventional amperometric analyzers may be calibrated to record bromine residuals, but, because of the evanescent characteristics of bromine residuals, automatic residual control might not be practical. Field experience is too limited to permit a judgment on this facet.

Solution Lines and Diffusers. The materials and design for these components of the system can be the same as those used in chlorine systems.

Storage and Handling. As in all chemical liquid-vapor exchange systems, the problem of reliquefaction must be considered. The problem increases with decreasing vapor pressure equilibrium of the liquefied gas. Sulfur dioxide reliquefies much more easily than chlorine because of its low vapor pressure (35 psi at 68°F), which is comparable with vapor pressure of 30 psi at 68°F for BrCl. In the case of BrCl, it is more significant because dissociation occurs during reliquefaction, and all chemical advantages of bromine chloride are lost. Reliquefaction can be prevented either by raising the temperature of the liquid vapor container (bromine cylinder) or by external pressure padding with compressed air or nitrogen. Padding the container pressure to about 50 psi and withdrawing the liquid to an evaporator, which is similar to the practice of handling sulfur dioxide, is the preferred procedure. It involves fitting the bromine chloride containers with dip tubes and outlet valves similar to those or ton containers of chlorine or sulfur dioxide. One connection would be for pressurizing the vapor, and the other would be for liquid withdrawal. In such cases, the container storage and handling system would be the same as for chlorine or SO₂.

Evaporators. It is generally conceded that the most practical way to handle bromine chloride is to withdraw the liquid and vaporize it under controlled conditions.

Evaporators used for chlorine and sulfur dioxide can be used without modification for bromine chloride. The piping arrangement and accessories would be the same as for chlorine. The downstream-reducing valve would be set at

25psi, and the containers would be pressurized to 50psi. The evaporator should be large enough to provide 30°F superheat.

Materials of Construction. Although bromine chloride is much less corrosive than bromine,²² great care must be taken in selecting the materials for the design of this facility. The material for handling the liquid and/or the vapor under pressure is the same as that for chlorine. Therefore, schedule 80 seamless steel pipes can be used between the containers and the evaporators, and between the evaporators and the metering system.³⁰

Containers or piping of polyvinyl chloride (PVC) or acrylonitrile butadiene styrene (ABS) plastics are not suitable for storage or handling of bromine chloride vapor or liquid even at very low pressures, unlike chlorine and sulfur dioxide. The preferred piping material for moist BrCl vapor is Kynar, a vinylidene fluoride resin, and Kynar valves should be used with this piping material.

Safety Equipment. Chlorine leak detectors can be readily adapted to detecting BrCl in the atmosphere.

Chlorine container kits can be used on BrCl containers if the BrCl is packaged in containers of similar design.

Comparison with Advantages of Other Methods

1. The use of BrCl eliminates the hazards of handling Br₂.
2. BrCl is presumed to have greater germicidal efficiency than Br₂ and chloramines.
3. At the 1976 price of 20¢/lb, it is less expensive than on-site-generated bromine.
4. Contact time should be less than for chlorine; so contact chambers would be smaller.

Disadvantages

1. Field experience is limited.
2. If BrCl is used alone, residual control will be difficult, owing to rapid die-away of bromine residuals.
3. It is subject to reliquefaction, which causes dissociation of the vapor, which defeats the purpose of using bromine chloride.

Costs. The following is the estimated cost (as of 1976) for wastewater disinfection using bromine chloride as determined by the 1976 USEPA Task Force Report:³¹

Plant size (mgd)	1	10	100
Capital cost (\$)	47,000	129,000	414,000
Disinfection cost (¢/1000 gal)	4.52	3.04	2.65

BCDMH

Physical and Chemical Properties

1-Bromo-3-chloro-5, 5-dimethylhydantoin (BCDMH) is a white crystalline compound with a slight bromine and acetone odor. BCDMH is an excellent source of both chlorine and bromine, as it reacts slowly with water, releasing hypochlorous and hypobromous acid. It is used as a chemical disinfectant for recreational water and for purification of drinking water.

The chemical formula of BCDMH is $C_5H_6BrClN_2O_2$. The density of pure BCDMH solid is 1.9 g/cm^3 , and the melting point is $158\text{--}165^\circ\text{C}$. The solubility of BCDMH in water is about 0.25 g/100 ml water at 25°C .

Application and Production

BCDMH is used mainly for disinfection of swimming pools and spas, for slime control of white liquor for paper manufacturing, and for slime removal in domestic kitchens. During the 1996 Olympic Games in Atlanta, BCDMH was used as a disinfectant in pools for swimming races and was certified by the United States Food and Drug Administration. To date, there are several full-scale installations of BCDMH in municipal wastewater treatment plants in Japan.³² There are also reports of several pilot-scale experimental studies in the United States and Japan.^{32,33}

As of the end of 1997, the annual production of BCDMH was about 10,000 t in Europe and the United States and about 300 t in Japan.³²

Chemistry of BCDMH in Water and Wastewater

BCDMH contains two units of halogen and is used as a disinfectant with strong oxidation characteristics to deal with various kinds of bacteria. The hydrolysis of BCDMH forms monochlorodimethylhydantoin (MCDMH) first and then dimethylhydantoin (DMH), hypobromic acid (HOBr), and hypochloric acid (HOCl). (Eqs. 16.16 and 16.17). The hypochloric acid formed in the reaction contributes to the oxidation of bromic ion (Eq. 16.18), and the hypobromic acid formed in both processes contributes mainly to disinfection. The chemical reactions are shown as follows (R = Dimethylhydantoin):



and



Application of BCDMH in Wastewater

Current Practice. As of 2007, there were no reports of BCDMH being used as the primary disinfectant in municipal water treatment plant, and the only reported full-scale application of BCDMH in municipal wastewater treatment facilities for disinfection is at the wastewater treatment plants of Tokyo.³² However, detailed information was not available to at the time when this manuscript was written. There are reports of several experimental studies of using BCDMH as the emergency disinfectant during wet-weather events at municipal wastewater treatment plants in Japan and the United States.^{32,33}

Yamamoto et al. conducted a pilot study in the Narihirabashi pumping station of the Tokyo Metropolitan Wastewater Treatment Plant.³² BCDMH was used as the disinfectant to control the coliform counts in the overflow, and the results showed that BCDMH was effective in reducing the coliform colony to below 3000 cfu/ml at a dosage of 2 mg/l within 6 min of contact time when the coliform count in the influent wastewater was less than 10^4 cfu/ml. A dosage of 4–7.5 mg/l of BCDMH was sufficient to reduce the coliform colony to less than 3000 cfu/ml when the coliform count plant in the influent was in the range of 10^4 – 10^6 cfu/ml. The success of the pilot studies led to the installation of full-scale disinfection facilities in the Tokyo wastewater plants in 2001.³² The full-scale facilities have been in operation ever since, and more installations were in progress as of 2005.³²

It was also reported by Moffa et al. that Water Environmental Research Foundation conducted a BCDMH pilot study at Columbus, Georgia, in 2003.³³ The study proved that BCDMH was much more effective than sodium hypochlorite in terms of disinfection.

BCDMH Feed and Injection System. BCDMH is normally applied to the wastewater in solid form. The BCDMH feed system used in the Narihirabashi pump station pilot study is shown in Figure 16.4.³² During normal operation, the BCDMH was fed from the disinfectant storage tank at the designated dosage, depending on the rotational speed of the screw feeder mounted in the lower part of the system. The disinfectant was mixed with solution water in the dissolving cone and then mixed with the solution water again in the ejector installed in the injection pipe. The BCDMH feeder was equipped with a load cell to measure weight variations and an electromagnetic vibrator to feed BCDMH at a consistent rate.

Figure 16.5 is a general view of the BCDMH feed and injection system used in a municipal wastewater plant in Tokyo (EBARA Corporation, pers. comm.).

Comparison with Chlorination

Hypobromic acid formed at the dissolution of BCDMH is responsible for the disinfection mechanism of BCDMH. Therefore, the difference between the

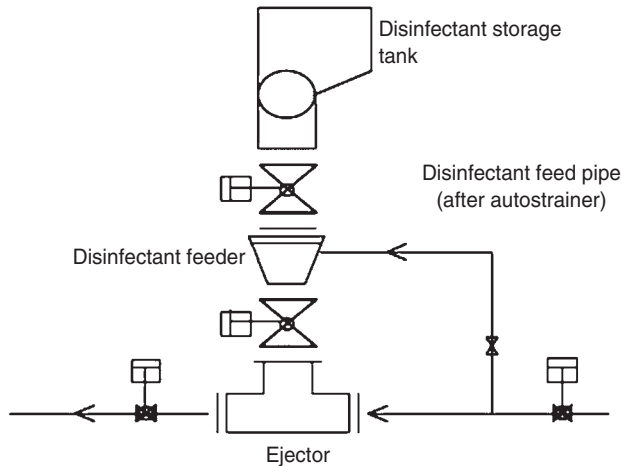


Figure 16.4. A typical BCDMH feed and injection system (courtesy of Yamamoto et al.).³²

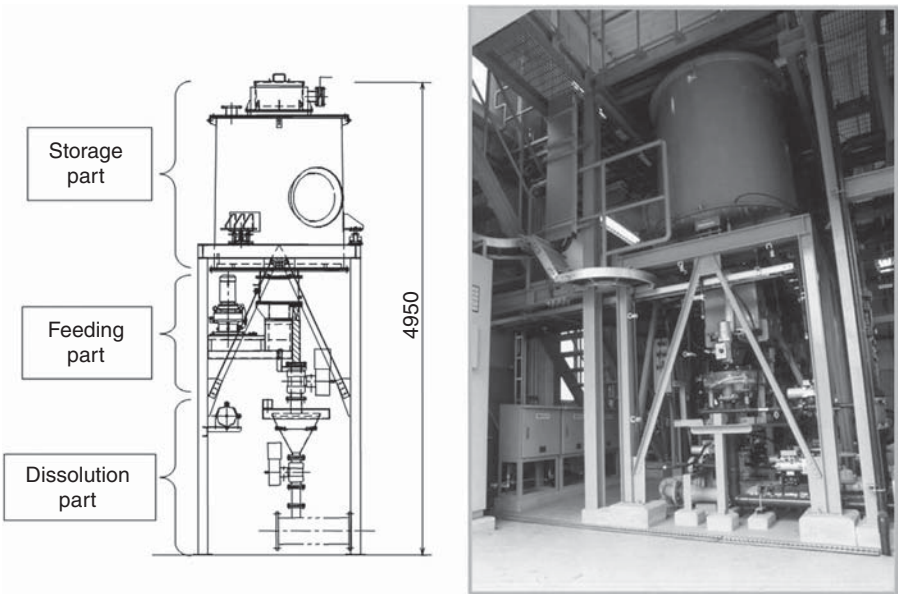


Figure 16.5. View of typical BCDMH feed and injection system (courtesy of EBARA Corporation).

disinfection capabilities of chlorine and BCDMH is actually the difference between hypochloric acid and hypobromic acid. Below is a comparison between the characteristics of hypobromic acid and hypochloric acid:

1. Hypochloric acid hydrolyzes into hypochlorite ions when the pH value exceeds 7, and its disinfection power decreases. Hypobromic acid, on the other hand, does not readily hydrolyze into hypobromite ions, and, even after hydrolysis, hypobromic acid ions maintain the disinfection power of hypobromic acid.
2. Hypochloric acid forms chloramine in the presence of ammonium, and its disinfection power decreases by more than 90%. Hypobromic acid, on the other hand, does not readily form chloramine, and the bromoamine itself is comparable with hypochloric acid in terms of disinfection power.

Compared with chlorine, which is often available in bulk liquid or in gaseous form, BCDMH is available in solid form, which has significant advantages with respect to shelf life. In its bulk liquid form, hypochloric acid decays rapidly and poses a major concern in view of the sporadic nature of combined sewer overflows. Overflows can occur as frequently as every day or as infrequently as once in several months. Bulk liquid 15% hypochloric acid could lose almost half of its strength after 120 days' storage under normal conditions, while, in its solid form, BCDMH does not pose a similar concern over an even longer storage period.³³

BCDMH also requires a short contact time, and the associated equipments are often relatively compact and start up rapidly.

Germicidal Efficiency (Br₂ and BrCl)

A review of the literature for the period of 1945–1976 revealed a considerable lack of agreement on the germicidal efficiency of bromine compounds, that is, free bromine (Br₂), hypobromous acid (HOBr), monobromamine (NH₂Br), and dibromamine (NHBr₂). The chief difficulty in sorting out the literature was in determining which species was actually being investigated. This has to do with bromine chemistry. The publication edited by Johnson³⁴ is the most informative on the germicidal chemistry of bromine. The most informative investigations of the germicidal efficiency of bromine are those by Wyss and Stockton,³⁵ Marks and Strandkov,³⁶ Johannesson,³⁷ McKee et al.,³⁸ Koski and Stuart,³⁹ Schaffer and Mills,⁴⁰ Sollo et al.,⁴¹ and Johnson and Sun.²⁶

Although this work was carried out in the laboratory under ideal conditions, the following pertinent conclusions can be drawn with respect to wastewater disinfection: In a wastewater effluent with an ammonia nitrogen content of 10–30 mg/l and a pH of 7–8, the dominant species of bromine will be dibromamine.²⁶ Dibromamine appears to be almost as germicidal as hypobromous acid (HOBr) but not as germicidal as free bromine (Br₂), which

exists only at pH below 7. Therefore, the germicidal efficiency of dibromamine is almost comparable to that of free chlorine (HOG), as it has been demonstrated that hypobromous acid and hypochlorous acid have about the same germicidal efficiency.^{10,26,34} This is significant in wastewater treatment because the application of bromine to wastewater will result in the formation of dibromamine, which is *theoretically* many times more germicidal than chloramines. The difficulty in resolving these comparisons is the total lack of field experience. As described above, the Grandville, Michigan, work²⁷ revealed disappointment in the germicidal efficiency of bromine. This is probably due to the fact that bromine is such a powerful oxidant that much of it is lost in side reactions with organic matter in the wastewater.

Koski and Stuart,³⁹ using the Association of Official Agricultural Chemists (AOAC) method for evaluating disinfectants, reported that liquid bromine at a concentration of 1.0ppm is as effective as the 0.6ppm of available chlorine control, with *Escherichia coli* as the test organism, but that 2.0ppm liquid bromine is needed to provide activity equivalent to the 0.6ppm available chlorine control when *Streptococcus faecalis* is the test organism. McKee et al.³⁸ found that bromine in settled wastewater at 15min contact times was less effective than either chlorine or iodine. It is to be presumed that this phenomenon is the result of bromine becoming irretrievably bound up with the organic matter in the wastewater, or forming bromamines that decompose rapidly into components that do not have any disinfecting power. The interesting point here is that the residual bromine, which is a combination of HOBr and bromamine, appears to be as colicidal as chlorine, but the difficulty is that not much of the bromine becomes a stable residual. This is based on milliequivalents per liter of the halogen. On a dosage basis, however, chlorine is far superior to either bromine or iodine because much of the bromine or iodine is consumed in satisfying the halogen demand. Consequently, they are the least effective of the halogens where sewage is to be disinfected.³⁸ A dose of 8mg/l of chlorine will achieve disinfection comparable to 45mg/l of bromine or iodine. This is why the literature on this subject stresses the necessity of first satisfying the halogen demand of the wastewater with the old reliable and less expensive chlorine. Kott in 1969⁴² and subsequent investigators have demonstrated the superior germicidal efficiency of the combination of chlorine and bromine. First, chlorine is applied to satisfy the immediate halogen demand, followed by the application of bromine.

This corresponds to the work of Sollo et al.^{20,41} and to the field experience of CIFEC (A. Derreumaux, pers. comm.), who reports that a 3mg/l dose of chlorine in a wastewater effluent at Bormes, France, containing 90mg/l ammonia nitrogen followed by an 8mg/l dose of bromine resulted in a 100% reduction of 10⁶ coliforms with only 10min of contact.

According to Mills, bromine chloride is superior in germicidal efficiency to molecular bromine because the chemical reactivity of BrCl is much faster than that of molecular bromine.

Bromo-Organic Compounds

There is continuing concern over the use of halogens for disinfection of potable water, wastewater, and water for reuse because of some so-called potentially harmful disinfection by-products (DBPs).

In addition to the chloro-organic compounds, a variety of bromo-organic compounds have also been detected. These include bromodichloromethane, dibromo-chloromethane, and bromoform. The sources of these compounds, generally referred to as precursors, are uncertain but they appear to be as a natural phenomenon. The precursors of these compounds have been found in soil and in the chlorophyll of blue-green algae. It has been suggested that the source of halogenated bromine compounds is the fallout from automobile exhausts. It has been postulated that, because bromine was used as a lead scavenger in leaded gasoline, these bromine compounds were deposited as a residue on paved roads and therefore reached water supplies by natural runoff.⁸ This assumption is probably overemphasized because bromides are found almost everywhere in nature. However, the elimination of leaded gasoline certainly must have curtailed this source as a precursor.

An example of how the ubiquitous bromide ion in the environment can affect a potable water supply is in the experience of the Contra Costa County Water District.⁴³ As of 1978, this water utility has been serving the cities of Concord, Clayton, Port Costa, Walnut Creek, Pleasant Hill, and Martinez, California. The principal source of water supply is the Sacramento–San Joaquin delta. During 2 consecutive drought years, saltwater intrusion from the San Francisco Bay increased the bromide concentration in the water/supply to the treatment plant. The chlorine applied to this water converted the bromides to bromine species, which reacted with the chlorine demand of the water to form trihalomethanes (THMs) in concentrations that exceeded the USEPA maximum contaminant level (MCL) of 0.10 mg/l. (In the 1990s, any sane person could hardly become worried about 0.10 mg/l of one of nature's compounds in drinking water, let alone in wastewater!) Nevertheless, this forced the water district to take corrective measures. After evaluating several treatment changes in an effort to reduce the chlorine demand ("THM precursors"), none of which was entirely successful, the district had to switch its chlorination practice to using chloramines.⁴³ Owing to the lower oxidative power of chloramines, this reduced the total THM (TTHM) well below the MCL for THMs.[†]

It is important to recognize that all bromine species are better oxidizing agents than their analogous chlorine species. For example, the oxidation of cellulose by hypobromous acid is much faster than by hypochlorous acid, and the oxidation of glucose to gluconic acid by hypobromite is 1300 times faster

[†]This problem of seawater intrusion is cyclical, owing to the drought years. Adding ammonia N to any water supply for no good reason, such as THM trivia, can produce far more water quality degradation than 0.1 or 0.90 mg/L of THMs simply because the added ammonia N will upset the microbiological life in the distribution system when the chlorine residual disappears.

than by hypochlorite. It is not surprising that bromine is a lesser halogenating agent than chlorine simply because it is a more potent oxidizing agent.

There are many organic-reducing agents in wastewaters, including organic alcohols, aldehydes, amines, and mercaptans, that are completely oxidized by bromine chloride, resulting in the formation of inorganic chloride and bromide salts as the major by-products.

The carbon–bromine bond is less stable than the carbon–chlorine bond, and there is a possibility that, in addition to metabolism by hydroxylation, well-established for chlorobiphenyls, a reductive debromination may be a degradation pathway of brominated aromatics. In general, compounds that are more readily brominated are also more susceptible to either hydrolytic or photochemical degradation. This reduces the incidence of bromo-organic compound formation. Moreover, the chemical bond strengths show that bromine bonds are weaker than chlorine bonds. Thus, bromine compounds are generally more unstable than those of chlorine and are therefore easier to chemically degrade to innocuous inorganic compounds. The fact that bromine residuals die away after a few minutes' contact time in potable water does not mean that a similar die-away pattern will occur in highly polluted water or wastewater effluent. There is evidence that certain species of organic N compounds react with the bromine species to form organo-bromamines that have a very slow decay rate similar to that of organochloramines. Therefore, much more investigative work would have to be carried out to enable us to predict with reasonable accuracy the characteristics of bromine residual die-away in various situations.

Measurement of Bromine Residuals

Regardless of the method of bromine application, whether it is generated on-site or injected as molecular bromine, or is an aqueous solution of either bromine or bromine chloride, the resulting residuals respond in the same way to all analytical procedures.

At the Grandville, Michigan, project²⁷ the bromine residuals were determined by a spectrophotometric procedure developed by Mills of Dow Chemical Co.⁴⁴ Other researchers used the diethyl-*p*-phenylenediamine–ferrous ammonium sulfate (DPD–FAS) titrimetric method,⁴¹ and Johnson et al. used a thiosulfate–iodine amperometric titration that measured the oxidation of iodide to iodine at pH 7 by the bromine residuals.^{10,26,34} Larson and Sollo⁴⁵ used the bromocresol purple colorimetric procedure.

As of 2007, there are no known analytical methods available to an operator or a laboratory technician to distinguish the three bromine species: hypobromous acid (HOBr), monobromamine (NH₂Br), and dibromamine (NHBr₂). Therefore, the only measurement available is total bromine residual.

The 21st edition of *Standard Methods*⁴⁶ offers no methods for determining bromine residual in water and wastewater. Hach Company has adopted the DPD method to which is identical to the method it uses for measuring total

chlorine residual measure total bromine residual in water and wastewater.⁴⁷ This method therefore suffers interference from chlorine and other halogen oxidants residual in the water sample.

When chlorine and bromine are used sequentially, as in water reclamation, there may be a mixture of chloramine and bromamine, owing to the presence of ammonia N in the wastewater. Total residual, measured as either bromine or chlorine, is the preferred choice because, in most instances, it would involve the use of a continuous residual analyzer when dealing with a mixture of chlorine and bromine residuals. This instrument can be calibrated only for the total residual. This can be carried out by using either the amperometric forward-titration method or the DPD–FAS titrimetric method.

Differentiating between total chlorine and total bromine in the same sample can be carried out by Palin's DPD method described below.⁴⁸

Amperometric Method

The amperometric method is well suited to bromine residuals measurement. As the amperometric cell has a linear sensitivity to all the free halogens, and free and combined bromine compounds will release iodine quantitatively at pH 4, the procedure for total available bromine is determined on the titrator by using the procedure given for total residual chlorine: using buffer solution at pH 4 and potassium iodide solution. Then, when titrating for bromine, the pipette reading in milliliters must be multiplied by 2.25 to express the answer in ppm of bromine.

DPD Differentiation Method⁴⁸

The reagents required for the DPD method are (a) standard FAS solution (1ml = 0.100mg available chlorine), (b) DPD No. 1 powder (a combined buffer–indicator reagent), and (c) potassium iodide crystals. The term “residual bromine” is taken to mean free bromine plus bromamines.

Free Chlorine. To a 100ml sample, add 0.5g DPD No. 1 powder, mix rapidly to dissolve, and titrate immediately with the FAS solution. This is reading A. (If free chlorine is not present, this step may be omitted.)

Combined Available Chlorine. Add to the previous sample several crystals (approximately 1.0g) of potassium iodide, mix to dissolve, and, after letting it stand for 2 min, continue titration with FAS solution. This is reading C.

Residual Bromine. To a *second* 100ml sample, add 2ml of 10% wt/v glycine solution and mix.[§] Then add approximately 0.5g DPD No. 1 powder, mix, and titrate with the standard FAS solution. This is reading Br.

[§]If it has already been determined that free chlorine is absent, this step may be omitted.

Calculations. For a 100-ml sample, 1 ml FAS solution = 1 mg/l available chlorine.

Residual bromine = Br

Free available chlorine = A – Br Combined Chlorine = C – A

If it is desired to report the residual bromine concentrations in terms of bromine, multiply the Br reading by 2.25. (This is the ratio of the molecular weight of bromine to chlorine.)

Effect of Seawater Chlorination

Chlorination of seawater and estuarine saline waters reacts to convert the excess bromides into the bromine species. If ammonia N is not present, the species will be hypobromous acid. If ammonia N is present, mono- and dibromamine will be present. Therefore, all of the remaining residual after chlorination will be bromine residual. This chemistry is explained in Chapter 4. Measuring these residuals is usually carried out for total residual and is reported as chlorine residuals.

Toxicity of Bromine Residuals

The acute toxicity tests with chlorobrominated wastewater effluent reported by Ward et al.²⁷ on the Grandville, Michigan, project indicate that bromine residuals are less lethal to fish than the residuals of chlorine compounds. This supports the finding of Mills,⁴⁴ who concluded that chlorobromination produced a less toxic effluent than chlorine did because bromamines are less stable than chloramines and thus do not persist as long as chloramines. This would be true regardless of how the active bromine compounds were applied. The active ingredient would be mostly dibromamine at the pH normally encountered in wastewater treatment. However, if organobromamines are formed because of the presence of certain organic N compounds, the total bromine residual may persist in the wastewater effluent for several hours.

Health and Safety Aspects of Bromine Compounds

Bromine vapor is highly irritating to the human respiratory tract, mucous membranes, and eyes, causing coughing and smarting of the eyes. The maximum allowable concentration of bromine vapor for exposed without harmful effects is 0.1–1 ppm for prolonged exposure (several hours) and 4 ppm for short exposure (0.5–1 h).⁴ Exposure to high concentrations of bromine vapor leads to inflammation and congestion of the respiratory system and edema of the lungs, which, in severe cases, can be fatal.

Liquid bromine presents a serious hazard in handling. It rapidly attacks the skin and other tissues to produce irritation and necrosis; the burns are not

only painful but also slow to heal. Liquid bromine can also cause severe damage to the eyes.

Table salt has been implicated as a major source of dietary bromine: It may contain as much as 0.1% bromide. The World Health Organization in 1967 set the maximum acceptable daily intake of bromide ion at 1.0 mg/kg.⁴

Acute bromide intoxication is rare because amounts sufficient to elevate the serum bromide to a toxic level can hardly be ingested and retained without vomiting. Chronic bromide intoxication from the continued use of large doses (>3–5 g/day) is known as bromism.⁴ The symptoms are skin rash, glandular excretions, gastrointestinal disturbances, and neurological disturbances. Bromide compounds at doses of 3–5 g/day⁴ have been used in the treatment of neurological disturbances as a sedative and in controlling of epilepsy.

Regulatory Issues

As of 2007, there are no regulatory limits applicable to bromine and its derivatives in the water industry other than the rules governing DBPs imposed by the USEPA for bromated THMs and bromated haloacetic acids.⁴⁹ As the use of bromine compounds in water treatment, especially for hot tubs, spas, and swimming pools, increases, additional regulations may be passed place in the foreseeable future; the local regulatory authorities should be consulted before using bromine compounds in any water treatment applications.

IODINE (I₂)

Physical and Chemical Characteristics

Iodine, a nonmetallic element with an atomic weight of 126.92—the heaviest of the halogen group—was discovered by Curtois in 1811. It is the only halogen that is solid at room temperature and can change spontaneously into the vapor state without first passing through a liquid phase. It is isolated as a shining blackish gray crystalline solid with a specific gravity of 4.93 that has a peculiar chlorine-like odor. It melts at 113.6°C to a black mobile liquid and boils at 184°C under atmospheric pressure to produce a characteristic violet vapor.⁵⁰

The principal oxidation states of iodine are −1, +1, +3, +5, +4, and +7. Thermodynamically stable compounds are formed in all these oxidation states except for the +4 state. Iodine is the least electronegative of the halogens and is usually less violent in its reaction than fluorine, chlorine, or bromine. It exhibits mild oxidizing properties in acid solution and is a stronger oxidizing agent than astatine, the fifth halogen. Iodine reacts slowly with metals to form nonvolatile iodides. It forms compounds with all the elements except the noble gas, sulfur, and selenium but reacts only indirectly with carbon, nitrogen, oxygen, and some of the noble metals. Ferric and cupric salts, and compounds of vanadium, chromium, and manganese in their highest oxidation states are reduced in acid solution by iodide ion, with the liberation of free iodine.⁵¹

Occurrence and Production

The world's largest sources of iodine are the underground brines in Japan and the nitrate deposits of northern Chile.⁵² Iodine is always found combined, as in the iodides. It is prepared from kelp, from brine, and from crude Chile saltpeter (NaNO_3), which contains about 0.2% sodium iodate (NaIO_3). Historically, the United States has depended almost entirely on imported iodine. In 2005, about 70% of the iodine used in the United States was imported, and almost 100% of it was from either Chile or Japan.⁵³

Chile is the predominant iodine supplier worldwide, followed by Japan. From 2002 to 2006, the Chile's annual iodine production ranged from 25.7 to 34.3 million lb, while Japan produced about 14.4–17.8 million lb. During the same period, the world's total iodine production was about 46.3–58.4 million lb;⁵³ that is, Chile produced about 55%–63%, and Japan produced about 26%–32% of the world's total iodine.

In 2005, the United States produced about 30% of the iodine it used, more than 95% of the total that came from two companies: Iochem Corp., with a plant near Vici, Oklahoma, and Woodward Iodine Corp. in Woodward County, Oklahoma, operated nine production wells and four injection wells, with a total production capacity of 3 million lb/year. Woodward Iodine operated 22 brine wells. North American Brine Resources operated a miniplant at an oil field-injection-disposal site near Dover, Oklahoma.

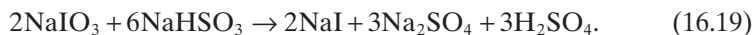
There have been three phases in the history of iodine production:⁵¹

1. Production from seaweed began in 1817 and continued until 1959.
2. Production as a by-product of sodium nitrate production began in 1852.
3. Production from brines began in 1854.

Currently, iodine is produced from three source materials: Chile saltpeter,⁵¹ brine⁵¹, and gas field⁵¹ brines.

Production from Chile Saltpeter

Chile is the only location in the world where an iodine-containing deposit is commercially mined and processed. Iodine is present in the deposits as calcium iodate. Processing of the deposits began before the 1800s. Commercial production began in about 1868 and continues today. Iodine is obtained as a by-product of sodium nitrate production⁵¹ by leaching crushed ore to give a solution containing sodium nitrate and calcium iodate. After the sodium nitrate is removed by precipitation, the iodate-rich mother liquor is treated with aqueous sodium bisulfate to reduce the iodate to iodide as follows:



Free iodine is liberated by adding an equivalent volume of the mother liquor:



Production from Brine

In Oklahoma, iodine is produced by two brine processes: blowing out and adsorption.⁵¹ The brines contain about 300 ppm of iodine. In the blowing out process, brine is pumped from the production well into a surge tank and is fed into a column where it is acidified with hydrochloric acid and treated with chlorine to oxidize the iodide to iodine. The iodine is stripped from the brine by steam and sent to a second column where it is reduced and absorbed in an aqueous solution of hydriodic acid and sulfuric acid. The iodine is reduced to iodide and absorbed into solution. The iodide solution is continuously fed to a storage tank where chlorine gas precipitates crystals of elemental iodine. The iodine is filtered from the solution, and the acid stream is returned to the absorption column. The adsorption process is used with brines from oil field disposal plants. In this process, the brines are skimmed in holding tanks to remove suspended oil and other suspended matters that are removed by filtration through sand. Hydrochloric acid is added to the brine, and chlorine gas is added to oxidize the iodide to iodine. The brine is then passed through the absorber, where iodine is absorbed. The absorbent is treated with sodium hydroxide solution that elutes the iodine as sodium iodide. The iodide-rich eluate is sent to a refinery that uses a process similar to the blowing out process.

In Japan, iodine is produced from underground brines associated with gas fields by a blowing out process and by two adsorption processes (the ion-exchange and the sloping fluidized-bed processes).⁵¹ The blowing out process is similar to that used in the United States.

In the ion-exchange process, the resin bed is fixed, and the brine is filtered first to remove any solids before being passed through the resin bed. The brine is then acidified and treated with chlorine to liberate iodine, which is adsorbed on an ion-exchange resin (amberlite) as polyiodides. The iodine is released from the resin in two stages: by elution with sodium hydroxide and then with sodium chloride. After elution, the resulting iodate-iodide solution is acidified with sulfuric acid to form iodine.

In the sloping fluidized-bed process, sodium iodide is also adsorbed on an ion-exchange resin, but, in this case, the resin is mobile, and filtration of the brine is not necessary. The resin is transferred to a recovery plant, and the sodium iodide is removed as hydrogen iodide by elution with sulfuric acid. Iodine is precipitated by adding chlorine.

Applications

Iodine was first used in medical practice for the treatment of goiter by Prout in 1816.⁵⁴ The first specific reference to the use of iodine on wounds was in 1839. Iodine was officially recognized by the *Pharmacopoeia* of the United

States in 1830 as tincture of iodine. The first official U.S. tincture was a 5% solution of iodine in diluted alcohol.

Iodine and its derivatives are used as industrial and household disinfectants, catalysts in the chemical industry (production of synthetic rubber), and in food products, pharmaceutical preparations, stabilizers (as nylon precursors), antiseptics, medicine (treatment of cretinism and goiter), and inks and colorants, and so on. As of 2000, the estimated percentages of end uses for iodine were as follows: sanitation, 45%; animal feed, 27%; pharmaceuticals, 10%; catalysts, 8%; heat stabilizers, 5%; and other smaller uses that included inks and colorants, photographic chemicals, laboratory reagents, production of batteries, high-purity metals, motor fuels, and lubricants, 5%.⁵⁵

Uses in Water Treatment

The first known field use for iodine in water treatment was during World War I by Vergnoux,⁵⁶ who reported rapid sterilization of water by it for French troops. Investigations into the use of iodine as an alternative method of disinfecting water supplies for U.S. troops were made in the years following World War I. Hitchens⁵⁷ recommended the use of 5 ml of a 7% tincture of iodine for a Lyster bag (about 140 l or 37 gal) and stated that such treatment rendered even raw Potomac River water safe for drinking in 30 min. This investigation was followed in 1930 by Dunham's⁵⁷ recommendation that the dosage increased to 10 ml of a 7% tincture of iodine per Lyster bag, or two to three drops per canteen. Pond and Willard⁵⁸ verified in 1937 that two drops per liter of a 7% tincture of iodine is sufficient to render any water innocuous within 15 min, and that three drops per liter did not yield any better results.

During World War II, a series of studies at Harvard University by Chang and Morris⁵⁹ and Morris et al.⁶⁰ led to the development of globaline tablets for disinfecting small or individual water supplies for the U.S. Army. Each tablet contained 20 mg tetraglycine hydropyridide, which is 40% I_2 and 20% iodide, combined with 85 mg acid pyrophosphate. One tablet imparts 8 mg of I_2 to a liter of water. Chang and Morris⁵⁹ list the following advantages of the globaline tablet over the tincture: (a) iodide is present in half the amount of I_2 , (b) there is a definite dosage, (c) the loss of I_2 is insignificant, (d) the presence of an acid salt counteracts the high pH, (e) the treated water is more palatable (less taste and odor), and (f) the tablets are convenient for field use. The globaline tablets superseded the Halazone tablets for use by troops because one globaline tablet per quart or liter of water destroys the cysts of *Entamoeba histolytica* in 10 min, whereas six Halazone tablets are required to accomplish the same kill.⁵⁷ Likewise, the human enteric pathogens (bacterial, viral, and protozoan) are satisfactorily destroyed in the same time frame^{59,61} under ordinary conditions. If the water is very cold, deeply colored, or highly turbid, the dosage should be increased to two tablets per liter, and the contact time extended to 20 min.

The most popular application is in tablet form or as tincture of iodine solution for emergency treatment of small amounts of water on a batch basis such

as water supplies for troops on bivouac or for travelers in countries where “traveler’s diarrhea” is a common occurrence. This type of emergency treatment has proved to be reliable and effective.⁵⁷

The U.S. Public Health Service lists the iodine dosage for emergency water treatment as five drops of a 2% tincture for 30 min *per quart* (or liter) for clear water and 10 drops for turbid water.⁵⁷ The potential for an unpleasant taste with iodine is about the same as with chlorine. Iodine does not react with nitrogenous compounds as chlorine does, so the taste in polluted waters will be different.

Chemistry of Iodination

There are two methods of dosing a water supply with iodine. The more practical of these methods is the use of iodine crystals. The other possible method is the use of the “iodine bank” scheme, which requires an excess of iodide. Elemental iodine is released from the iodide quantitatively by the application of an oxidant such as chlorine. This procedure is used in swimming pools and has no apparent practical application in drinking-water treatment. It utilizes the only advantage of iodine over chlorine; that is, it will not react with nitrogenous compounds to form iodamines as chlorine does to form the objectionable chloramines.

The following chemistry of weak solutions of elemental iodine is based on the use of iodine crystals without the added iodine. The work by Chang is the basis of this chemistry.⁶¹

Four substances must be considered in the reactions of elemental iodine with water:

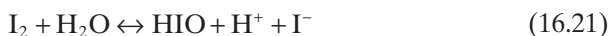
Elemental iodine: I₂

Hypoiodous acid: HI

Periodide or tri-iodide ion: I₃⁻

Iodate ion: IO₃⁻

First is the hydrolysis of I₂ to form hypoiodous acid:



$$\frac{[\text{HIO}][\text{H}^+][\text{I}^-]}{\text{I}_2} = K_h \quad (16.22)$$

$$K_h = 3 \times 10^{-13} \text{ at } 25^\circ\text{C}.$$

Figure 16.6 shows the I₂ hydrolysis data for concentrations of iodine in the 0.1–5 mg/l range at 18 °C and pH 6.0–8.0, the probable range of use for small water supplies. The effect of pH on the hydrolysis of iodine with a total iodine residual of 0.5 ppm is presented in Table 16.1.

Second is the possible dissociation of hypoiodous acid with variations in pH to form hypoiodite ion. It is of interest to compare this phenomenon with

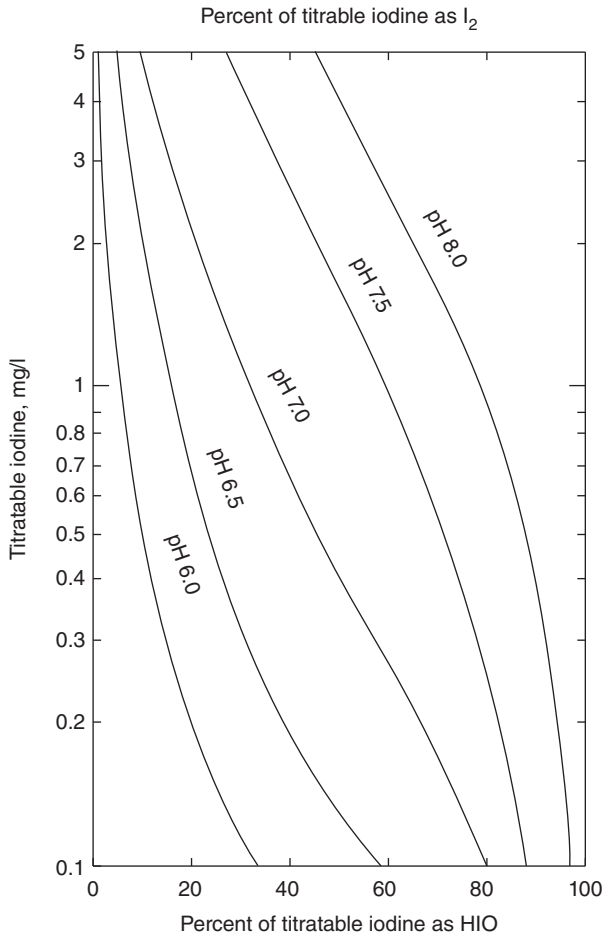


Figure 16.6. Percentage of titratable iodine as I₂, and HIO in water at 18°C and pH as indicated.⁶¹

TABLE 16.1. Content of Residual (%)

pH	I ₂	HIO	IO ⁻
5	99	1	0
6	90	10	0
7	52	48	0
8	12	88	0.005

TABLE 16.2. Content of Residual Percent at 20°C

pH	Cl ₂	HOCl	OCI ⁻
5	0	99.74	0.26
6	0	97.45	2.55
7	0	79.29	20.71
8	0	27.69	72.31

that of hypochlorous acid in the case of chlorine and how it affects the germicidal efficiency of that compound.



$$\frac{[\text{H}^+][\text{IO}^-]}{\text{HIO}} = K_a = 4.5 \times 10^{-13} \quad (16.24)$$

$$\frac{[\text{HIO}]}{[\text{IO}^-]} = \frac{[\text{H}^+]}{K_a}. \quad (16.25)$$

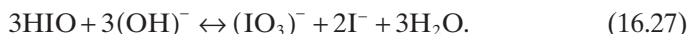
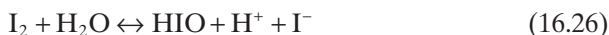
From Equation (16.25), it is possible to calculate the ratio of undissociated acid to hypoiodite ion at any pH. The dissociation constant of hypoiodous acid reveals that it is only slightly stronger as an acid than pure water. The formation of hypoiodite ion (IO⁻) is insignificant, as can be seen in Table 16.1.

Compare the formation of hypoiodite ion with that of the hypochlorite ion for chlorine in Table 16.2.

Both elemental iodine and hypoiodous acid are effective germicides. At pH 8, the effective germicide HOCl is present at 21.5%, whereas the ineffective hypochlorite ion is present at 78.5%. With iodine, however, the ineffective hypoiodite ion is present only at 0.005%, with elemental iodine at 12% and hypoiodous acid at 88%. Therefore, the formation of the ineffective hypoiodite ion can be ignored.

Third is the possibility of the formation of the bactericidally ineffective tri-iodine ion I₃⁻. Chang reports that, when using iodine crystals, iodine tablets, or tincture of iodine, the formation of tri-iodine ion can be ignored. The amount of iodine formed by hydrolysis of I₂ at 1–2 ppm and at pH value of 6.5–8.0 would be so small that the tri-iodide ion I₃⁻ formed in the water should not be much more than 1% of the total titrable iodide.

Fourth is the formation of the iodate ion, which has no apparent cysticidal or virucidal activity. Iodate formation in solutions of elemental iodine (without added iodide) proceeds as follows:



These equations show that alkaline pH values shift the reactions to the right, and acidic pH values shift them to the left. Iodate formation is not likely to be a problem interfering with the disinfection efficiency of iodine until the pH rises above 8.0 and the contact time exceeds 30 min. Since most of the disinfection by iodination is accomplished in the first 15–20 min, the small losses of titrable iodine to iodate need not be a problem in treating waters at pH levels below 8.4.

Germicidal Efficiency

It is the consensus of many investigators^{36,57,58,62–66} that elemental iodine I_2 and hypiodous acid HIO are the two most powerful disinfecting agents among the titrable iodine species.

The relative amounts of titrable iodine existing as I_2 and HIO in an aqueous solution of elemental iodine depend primarily on the strength and pH of the solution and, to a much lesser extent, on the temperature. The comparative disinfection efficiency of I_2 and HIO varies considerably, depending on the type of organism. Wyss and Strandkov⁶³ reported that, against *B. metiens* spores, I_2 is three to six times greater than HIO, but Chang⁵⁷ reported that, in the destruction of cysts of *E. histolytica*, I_2 is two to three times more effective than HIO. On the other hand, Clark et al.⁶⁵ found that hypiodous acid destroys viruses considerably faster than I_2 ; HIO has also been claimed to be three to four times more effective than I_2 in destroying *E. coli*.⁵⁷ The difference in effectiveness of hypiodous acid and elemental iodine on the type of organism suggests a different mode of action, depending on whether or not the organism is protected by a membrane such as a spore or a cyst. The superiority of I_2 to HIO in the destruction of spores and cysts is apparently attributable to the greater penetrating power of I_2 . In the case of vegetative bacteria, which have a physiologically active cell membrane, the oxidizing power of the compound becomes the important factor. This is supported by the fact that the normal redox potential (E_0 at 25 °C) of HIO is 990 mV, whereas that of I_2 is 536 mV.⁵⁷ In virus destruction, which probably proceeds as a function of the oxidizing power of the compound, this can be supported further when comparing the virucidal efficiency of hypiodous acid with that of hypochlorous acid.⁵⁷ HOCl has a normal redox potential of 1490 mV. Its virucidal efficiency is five times greater than that of HIO,⁶⁵ whereas that of HIO is at least 40 times greater than that of I_2 .⁵⁷ These differences support the belief that virus destruction is a result of the reaction of the disinfectant with the protein shell and not with the nucleic acid core; if the latter were involved, the protein shell would act as a protective shield, and the destructive process would not be much different from that of spores and cysts.

In order to relate these differences in the germicidal efficiency of both I_2 and HIO, Chang⁵⁷ prepared Figure 16.7, which shows the relation to titrable iodine and contact time for the 99.9% destruction of cysts, a virus, and bacteria

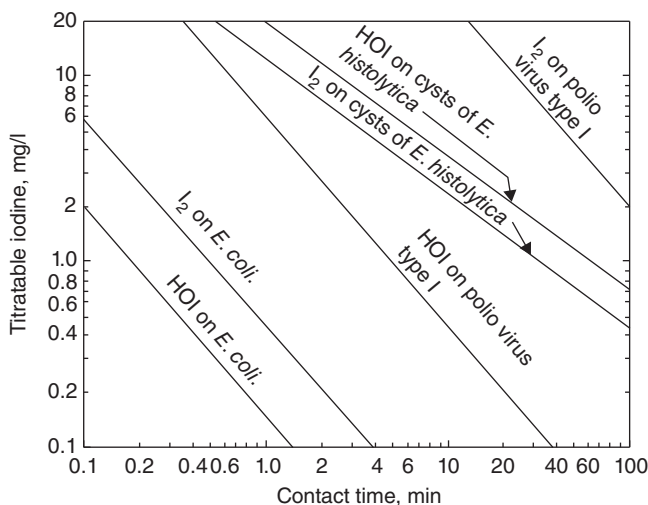


Figure 16.7. Time versus concentration relationship in the destruction (99.0) of cysts, viruses, and bacteria by I_2 and HIO at 18°C.⁵⁷

by I_2 and HIO at 18°C. In practice, these parameters allow a good margin of safety. Satisfactory results on bacteria can be obtained with 0.1–0.2 ppm in less than 4 min. Virus destruction by I_2 lies beyond the practical limit of 1–2 ppm, but, for HIO, it is well within these limits. The I_2 cysticidal curve lies close to the upper limit of practical range: 1.0 ppm in 30 min to 2 ppm in 13 min.

Compared with free chlorine residuals, iodine is definitely inferior. Free chlorine is four times more cysticidal than HIO and is 200 times more virucidal and two times more cysticidal than I_2 .

The 1960 report by McKee et al.³⁸ demonstrates that iodine is an effective disinfectant in wastewater. However, wasted side reactions due to the halogen demand of wastewater and its heavier molecular weight require 45 mg/l of iodine to achieve the same level of disinfection as 8 mg/l of chlorine.

Limitations of Iodination

Iodination can be used where chlorination or more complete treatment of water either is not possible or is impractical. Such use suggests that this process would probably be limited to remote rural areas or undeveloped countries where little or no adequate supervision and expertise are available. Further, it is the consensus that, on a prolonged treatment basis because of possible undesirable physiological effects, dosages of 1–2 mg/l, with occasional dosages of 4–5 mg/l, are the practical limits. This would require an investigative procedure to determine the desirability of iodination.

Comparison with Chlorination

The cost of iodination is an important factor against its use. Iodine was sold by the Defense National Stockpile Center at approximately \$9.66/lb in 2006.⁵³ However, in a remote location, the transportation of the iodine crystals and the installation of an electrically driven pump are about the only considerations for applying iodine. The apparatus for a hypochlorite installation is not too much different from this.

Free chlorine (HOCl) is *five times more virucidal* and *four times more cysticidal* than HIO and is 200 times more virucidal and two times more cysticidal than I_2 . This obvious superiority of chlorination in disinfecting power, together with its low cost, abundance of availability, and pharmacological inertness, makes chlorination the method of choice over iodination in water treatment. The emphasis here is on free rather than combined chlorine.

Iodination Facility

Iodine is the least soluble halogen in water, and its solubility is highly dependent on temperature, as shown in Figure 16.8.⁶² Its use for treatment of water is best accomplished by using a saturator, a device for preparing saturated iodine solution by passing water through a bed of iodine crystal.⁶² The saturated iodine solution is fed to the water to be treated. The saturator used in the study by Black et al. is constructed of a 5-ft-long section of vitrified clay pipe with a reinforced concrete plug (covered by a glass plate, a paraffin seal, and epoxy coating) at the bottom (Fig. 16.9).⁶² Above the plug is a 9-in. column of glass marble, a 1-in. layer of 6-mm glass beads, a 1.5-in. layer of 6-mm glass beads, and 24-in. technical grade elemental-iodine crystals.⁶² Water passes through a small, constant-level tank mounted on the side of the saturator, into the saturator about 2 in. below the top and then flows downward through the

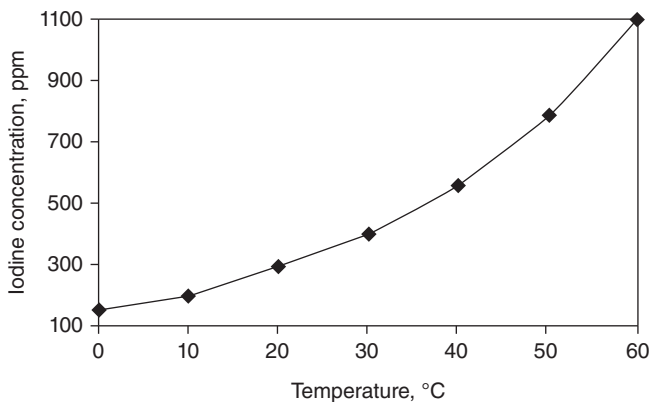


Figure 16.8. Solubility of iodine in water (concentration as a function of temperature).

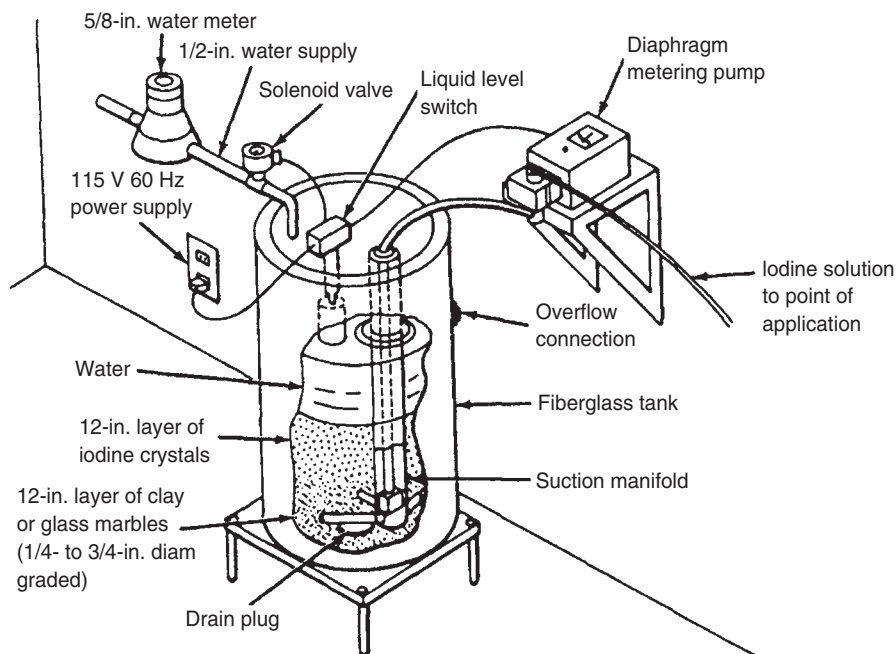


Figure 16.9. Iodination installation.

iodine crystals. The stainless steel pipe that passes through the pipe wall into the glass marble section at the bottom of the saturator carries the saturated iodine solution to the metering pump, as shown in Figure 16.9.⁶²

For the usual water supply, the strength of the saturated iodine feed solution will be in the range of 200–300 ppm.⁶² At these concentrations, Type 316 stainless steel is a satisfactory material for piping and metering pumps. Not all plastics are suitable: Nearly all clear plastic tubing will discolor rather quickly, and some will disintegrate in a matter of months. The temperature of the water will determine the strength of the solution to be injected by the metering pumps. As the accuracy of dosage is critical, it is strongly recommended that only metering pumps be used instead of injection devices that use water pressure to produce a vacuum. The latter devices cannot provide as dependable and accurate feed rates as a positive displacement metering pump does. The metering pumps should be paced from a flow-measuring device through either an automatic stroke positioner or a variable speed silicon-controlled rectifier (SCR) drive if the water flow is variable.⁶²

Cost. The 2006 price for imported crude iodine crystals was \$7.73/lb,⁵³ compared with chlorine at \$0.30–0.50/lb. However, this does not mean that the use of iodine instead of chlorine as a disinfectant is more costly in any given situation. As reported by Black et al., since iodide ion could be reoxidized and

consequently reused in the disinfection process by oxidizing agents such as monochloramine, the cost of iodine to disinfect a swimming pool was only half of the cost of chlorine to achieve the same level of disinfection.⁶²

Determination of Iodine Residuals

The Standard Methods Committee approved the methods of measuring both iodine and iodide in 2005.⁴⁶ These measurements of iodine residuals were obtained by the leukocrystal violet and the amperometric titration methods. The amperometric titration method is the more practical of the two; it is also more precise because the electrodes can be sensitized in a few minutes with a dilute solution of iodine, which gives a sharp end point.

The DPD–FAS titrimetric method has been found to be equally satisfactory for precise measurements.

Toxicity of Iodine Residuals

Iodination of water supplies has been limited largely to emergency treatment by the military. The use of iodine as a disinfectant for water has been recognized for a long time but has never generated enough interest to displace the popular use of chlorine. The much higher cost of iodine and its possible physiological effects are the main reasons for its limited use. The military gave its unqualified approval of the use of iodine as a disinfectant for water a 6-month study at a naval installation in the Marshall Islands in 1949–1950. The use of iodine in drinking water produced no untoward effects in a large group of servicemen,⁶⁷ whose average intake was 12mg/day for 16 weeks and 19.2mg/day for 10 weeks.

In 1965, Black et al.^{62,68} completed a demonstration project, with a grant from the U.S. Public Health Service, to study the effects of prolonged use of iodine at three correctional institutions in Florida. Iodination of these water supplies was carried out over a period of 19 months, serving approximately 700 persons under carefully planned chemical, medical, and bacteriological controls. Iodine proved to be a satisfactory disinfectant and, in doses up to 1.0ppm, did not produce any discernible color, taste, or odor in the water. There was no evidence from the medical investigation that this level of iodine has any adverse effect upon the general health or thyroid function.

Health and Safety Aspects of Iodine

Iodine is essential to animal and humans. A normal person requires about 75mg of iodine/year, which is usually consumed as iodized salt that contains 10 parts of sodium or potassium iodide to 1,000,000 parts of sodium chloride. Iodine deficiency is a major cause of goiter. Overconsumption of iodine,

however, must also be avoided. Studies on chickens link autoimmune thyroiditis directly with consumption of large amounts of iodine.⁵¹

Iodine is safer to handle at ambient temperature than chlorine or bromine because it is a solid with a lower vapor pressure. The maximum safe concentration for short-term exposure of up to 1 h is 1.0 ppm. Exposure of lungs and eyes can be irritating at concentrations of 0.1 ppm and should be avoided. Exposure in concentrations higher than 0.1 ppm for extended periods causes severe irritation to the eyes and the respiratory tract and may lead to pulmonary edema.⁶⁹ The mean lethal oral dose for an adult is 2–4 g.⁶⁹

In the United States, the Occupational Safety and Health Administration (OSHA) has set the maximum concentration of iodine vapor permitted in the working atmosphere as 0.1 ppm. The American Conference of Government and Industrial Hygienists (ACGIH) established 0.1 ppm as the threshold limit value (TLV)/time weighted average for iodine. The TLV/Maximale Arbeitsplatz Konzentrationen (MAK) value is also 0.1 ppm.⁵¹

In general, iodides are acutely toxic only when ingested in large amounts. Chronic ingestion or absorption through the skin may produce iodism, which is manifested by a rash, nasal drip, or headache. In severe cases, weakness, anemia, and general depression may occur. Care should be taken in handling organic iodine compounds.

Regulatory Issues

As of 2007, there were no applications of iodine for in conventional water and wastewater treatment disinfection processes. As a result, the USEPA has no outstanding regulatory requirements for iodine in water. Local regulatory agencies should be consulted when planning to use iodine for disinfection for prolonged periods.

SUMMARY

Bromine

Bromine is considered the most reactive oxidant of all the halogens, except fluorine, which is not considered here because of its desirable chemical characteristics. The hydrolysis of bromine in an aqueous solution is almost identical to that of chlorine. Bromine added to water reacts to form hypobromous acid, and, in the presence of ammonia nitrogen in the quantities usually found in wastewater, bromamines are formed. The germicidal efficiency of these bromamines at a pH similar to that of wastewater is practically equal to that of free chlorine.

Bromine is highly reactive; therefore, its halogen demand is greatly distorted beyond its usefulness. So any wastewater treatment system attempting to exploit the features of bromine should be arranged to use chlorine to minimize the “bromine demand.”

Bromine as Br_2 is difficult and hazardous to handle because it is in liquid form at room temperature. This has led to the development of bromine chloride, which has the same vapor pressure characteristics as sulfur dioxide. BrCl is much more desirable than elemental bromine from the standpoint of its handling characteristics.

Bromine Chloride

Bromine chloride has been investigated thoroughly as a practical substitute for elemental bromine and liquid–gaseous chlorine. The investigations have shown conclusively that new types of equipment will be required for the metering and control of BrCl . Factors such as the greater corrosivity of BrCl and the problem of BrCl dissociation have established the need for major changes in equipment design.

On-site generation of bromine from bromide salts using chlorine as the oxidizer has interesting possibilities. Injecting a bromide salt into a chlorinator's solution discharge line (similar to the generation of chlorine dioxide) causes formation of elemental bromine, which hydrolyzes immediately to hypobromous acid. This concept can be used to great advantage at existing chlorination installations for the following reasons: The existing chlorination system can be arranged to produce in 2–5 min a controlled chlorine residual of 0.3–0.5 mg/l (instead of the usual 5–7 mg/l). This sequesters the halogen demand. Following this is the formation of elemental bromine from the combination of the chlorine solution discharge with the bromide salt injection from the second chlorinator application. This becomes the second point of “chlorine” application downstream from the original point of chlorination.

This system has many desirable features: It can be implemented by using existing chlorination facilities, eliminates the hazards associated with handling bromine, and can utilize the superior germicidal properties of bromine without sacrificing other design considerations. Moreover, the bromamine residual die-away phenomenon may be so rapid that debromination by using SO_2 may not be required, and the contact time for the “hot” bromine residuals can be as short as 5 min and not longer than 15 min. This would bring contact chamber requirements to the lowest recommended for ozone, which is the lowest for all disinfectants.

BCDMH

BCDMH has been used in Japan as the emergency disinfectant for the combined sewer overflows of municipal wastewater treatment plants during wet weather events since 2001. It had been studied for this purpose in the United States, but, currently, there are no known full-scale applications of BCDMH yet. BCDMH is popular as an emergency disinfectant for the wet-weather events because it requires a short contact time and has a prolonged shelf life.

Iodine

Iodine has been used as a temporary expedient for disinfection of small water supplies and as an alternative disinfectant to chlorine for swimming pools.

It has never been tried, even at a pilot-plant scale for disinfection of wastewater. The cost and the reliability of iodine supply make its choice as a disinfectant for wastewaters or reused waters impractical.

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17 Ultraviolet Light

INTRODUCTION

Ultraviolet (UV) systems have been designed to disinfect drinking water, wastewater effluent, wastewater effluent for water reuse, stormwater, and combined sewer overflows.^{1,2} During its history, the implementation of UV disinfection systems has been impacted by numerous advancements in the technology as well as changes in regulations, the public desire for a green technology, and upgrading treatment processes and methods used for design and operation of UV facilities. These changes have made it possible to apply UV disinfection over a wide range of conditions and resulted in rapid growth in the use of UV systems in the United States and throughout the world.

In 1878, the germicidal effects of radiant energy from the sun were first documented by Downs and Blunt. Although the mercury vapor lamp was first invented by Wheatstone in 1835, it was prone to stability and deterioration issues.^{3,4} The practical application of UV light for disinfection did not occur until the first commercially viable mercury vapor lamp was produced by Cooper-Hewitt in 1901⁴ and the discovery of quartz as the ideal material for the lamp envelope in 1905.⁵ The first UV disinfection system was installed in Marseilles, France, in 1910 but was unreliable and complicated to operate.²

The earliest documented UV installation for drinking water disinfection in the United States was in 1916 in Henderson, Kentucky,⁶ with four known UV installations in operation by 1928.⁷ Due to advances in the production and application of chlorine gas coupled with reliability issues of these early UV systems, all of these installations were no longer operational by the late 1930s, and the development of UV disinfection was hampered for several decades.^{3,7}

Wastewater Applications in Europe

In the mid-1950s, interest in UV disinfection of drinking water supplies in Europe began to grow due to advances in the technology and growing concerns regarding taste and odor. In 1955, the first UV disinfection systems were

installed in Switzerland and Austria.⁸ In the 1970s, the growth of UV in drinking water applications was additionally fueled by the discovery of chlorinated disinfection by-products and the first wave of European Union (EU) legislation that included the 1975 Surface Water Directive (75/160/EEC).⁹ Additionally fueled by the discovery of chlorinated disinfection by-products, UV became an accepted process for the disinfection of drinking water in Europe, with the number of UV installations in these as well as other European countries, such as Norway, Germany and the Netherlands growing extensively over the later part of the 20th century, and is expected to continue in the coming years.

The application of UV for the purposes of wastewater disinfection in Europe has gained momentum in recent years. Although general wastewater disinfection is not required by law in Europe, wastewater treatment plants that discharge effluent into certain receiving bodies must meet microbiological criteria per the European Community (EC) Bathing Waters Directive (76/160/EEC and revised version 2006/7/EC)¹⁰ as well as the Urban Waste Water Treatment Directive (91/271/EEC). Pressure for compliance with these directives has prompted the investigation and application of disinfection technologies for wastewater discharges,¹¹ including the use of UV disinfection. Of the member states of the EU, Great Britain is the leader in the application of UV for disinfection of wastewater effluent, with UV disinfection primarily used on coastal areas as an alternative to long sea outfalls.^{9,11}

UV Applications in North America

Wastewater Applications. Chlorine disinfection of water and wastewater continued to dominate the market in the United States, and interest in the application of UV disinfection continued to be nonexistent until the late 1970s, when the United States Environmental Protection Agency (USEPA) began to discourage the use of chlorine for the disinfection of wastewater.¹² During the early part of the 1980s, UV disinfection gained popularity in the United States as a result of the funding of innovative and alternative (I/A) technologies by the USEPA. I/A funding allowed new technologies such as UV light to be implemented at wastewater treatment facilities with the option for complete replacement if the technology failed to achieve compliance with National Pollutant Discharge Elimination System (NPDES) permit requirements. UV technology in the wastewater industry gained limited State regulatory acceptance during the 1980s. In 1984, there were only a handful of UV systems being used in the United States to disinfect wastewater.¹³ Very few of these systems had a design capacity greater than 5 mgd. In some cases, early UV system failures resulted in many State agencies delaying acceptance of UV disinfection until the mid- to late 1990s. Although many problems existed with these early UV systems, the experiences gained during this period demonstrated the effectiveness of UV disinfection of wastewater and supported further advancements in the technology.

Several changes have occurred since the 1980 vintage UV systems were installed at wastewater treatment facilities. The most notable of these changes has been the preference for open-channel systems. Most UV systems installed in the 1980s were pressurized enclosed vessel systems adapted from the drinking water industry. The incorporation of wastewater-specific concerns, including hydraulic (head loss) and water quality (lower UV transmittance [UVT] and increased solids) implications, led to the development of open channel, gravity flow, modular UV system designs for wastewater applications. Coupled with improvements in the quality of UV lamp, ballast, and cleaning system technologies, the new generation of wastewater UV systems began to gain operator and regulator approval and soon dominated the wastewater disinfection market.¹²

In California, testing for compliance with Title 22 requirements was conducted during the early 1990s. Results of this testing^{14,15} indicated that UV disinfection systems can achieve the coliform limits established by Title 22. Other regulatory requirements that have impacted the growth of UV systems in the United States include the Aquatic Toxicity, Uniform Fire Code,¹⁶ and Occupational Safety and Health Administration (OSHA) risk management plans (RMP).¹⁷ The incorporation of aquatic toxicity limits into NPDES permits made it necessary for many communities to dechlorinate their wastewater effluent before it was discharged into the receiving stream. In 1988,¹⁶ the Uniform Fire Code began to impact facilities that were undergoing expansion by requiring the installation of chlorine scrubbers as protection against the accidental release of chlorine gas. In 1999, facilities using more than 1000lb of chlorine were required by OSHA to develop and implement an RMP¹⁷ for use in the event of the accidental release of chlorine. Both the Uniform Fire Code and the RMP requirements have increased the interest in the use of UV light for disinfecting wastewater.

In 1995, approximately 98% of all UV systems being used to disinfect wastewater used low-pressure (LP) mercury vapor lamps.¹⁸ In the mid-1990s, UV disinfection systems with medium-pressure lamps were introduced into the UV disinfection market and were shortly followed by LP, high-intensity and pulsed UV technologies in the late 1990s.¹⁹ These advances in lamp technologies continued to fuel the growth of UV for wastewater applications. Additional advances in the methodologies utilized to design and operate UV systems over the last decade have continued to improve the reliability and efficiency of modern UV disinfection systems, including the incorporation of computational fluid dynamic modeling and the use of biosimetry-based validation testing techniques to determine UV disinfection performance. These methods are discussed in further detail in the “UV System Validation” and “Nonbiological, Mathematical-Based Modeling” sections.

At the end of 1999, the total number of installed UV systems treating wastewater exceeded 500 in the United States. The average design capacity of these systems exceeded 20mgd. Two of the largest systems, both exceeding 100mgd, are located in Canada.²⁰ As of 2003, approximately 15%–20% of the

municipal wastewater market in the United States employed UV disinfection, with the number steadily increasing over the past 5 years.²¹

Drinking Water Applications in the United States

UV disinfection systems for drinking water applications were mostly limited to small groundwater treatment plants until the late 1990s. Initial research conducted in the early and mid-1990s on the efficacy of UV light for the inactivation of *Cryptosporidium parvum* oocysts indicated that extremely high UV doses ($>8000 \text{ mJ/cm}^2$) were required for its disinfection in a water matrix.²² These initial studies utilized *in vitro* surrogate assays, including vital dye assays and *in vitro* excystation methods, to predict the loss of oocyst viability. In 1999, research conducted by Bukhari et al.²³ found that these *in vitro* methodologies demonstrated a poor correlation to inactivation results determined from *in vivo* mouse infectivity studies. This research was the first to demonstrate that *Cryptosporidium* required a much lower UV dose using medium-pressure (MP) UV lamps in bench and demonstration scale testing, with approximately a 4-log inactivation at UV doses as low as 19 mJ/cm^2 . Similar research conducted by Craik et al.²⁴ also concluded that the *in vitro* assays greatly underestimated the UV inactivation of *Giardia muris* compared with the *in vivo* animal infectivity assays.

Further research conducted by Clancy et al.²⁵ concluded that no significant differences were found in the *Cryptosporidium* inactivation efficacy of LP and MP UV lamps, with both technologies demonstrating that extremely low UV doses were highly effective for inactivating oocysts. Studies conducted by Campbell et al.,²⁶ Linden et al.,²⁷ and Mofidi et al.²⁸ concluded that UV inactivation of *Giardia lamblia* cysts occurred at extremely low UV doses, similar to those required by *Cryptosporidium*.

These studies resulted in a new era of interest in the application of UV in drinking water for the inactivation of *Cryptosporidium* and *Giardia* at relatively low doses. In addition, the continued growth of UV in the U.S. drinking market has been fueled by two recently promulgated regulations by the USEPA. The *Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR)*²⁹ sets *Cryptosporidium* inactivation requirements for public water systems (PWSs) (those using surface water or groundwater under the direct influence of surface water [GWUDI]) and states the required UV doses needed for inactivation of *Cryptosporidium*, *Giardia*, and viruses. The Stage 2 Disinfectants and Disinfection By-Products Rule (DBPR) sets stricter monitoring requirements to minimize the concentrations of disinfection by-products in distribution systems. *Cryptosporidium*'s susceptibility to UV disinfection, coupled with a lack of regulated disinfection by-product formation and relatively low cost, has made UV a very attractive option as part of a multiple barrier disinfection approach for many PWSs.

The USEPA's *UV Disinfection Guidance Manual (UVDGM)*,³⁰ was released in draft form in 2003 resulting in the availability of pre-validated UV systems

with treatment capacities up to 2629 lps (60 mgd). The final version of the *UVDGM* was released in November of 2006³¹ and has become the primary document used in the United States for the validation, design, and operation of UV systems and has gained increasing interest and application worldwide. The *UVDGM* is reviewed in greater detail in the “Guidelines” section and in the “UV System Sizing Tools” section.

As of 2000, more than 400 UV installations were used for the disinfection of drinking water throughout the world. Currently, over 410 UV installations have been constructed or are currently in the design phase across North America alone, including the 20,911 lps (475 mgd) UV disinfection facility at the Seymour-Capilano Filtration Plant in Vancouver, BC, and the 96,388 lps (2200 mgd) Catskill/Delaware UV Disinfection Facility in Mount Pleasant, New York.

CHEMICAL AND BIOLOGICAL PROPERTIES

UV Light

UV light is a form of electromagnetic radiation that is located between X-rays and visible light in the electromagnetic spectrum at wavelengths of 100–400 nm. A schematic of the electromagnetic spectrum is presented in Figure 17.1.

UV radiation consists of four classes: (a) UV-A, ranging between 400 and 315 nm; (b) UV-B, ranging between 315 and 280 nm; (c) UV-C, ranging between 280 and 200 nm; and (d) vacuum UV (VUV), ranging between 200 and 100 nm.

Disinfection with UV light occurs at wavelengths ranging between 200 and 300 nm, falling largely within the wavelengths of the UV-B and UV-C regions of the electromagnetic spectrum. The germicidal action of UV-A is much less than that of UV-B and UV-C, requiring extensive exposure times for microbial disinfection.³¹ VUV has been demonstrated to be effective in the disinfection of microorganisms.³² However, it is rapidly attenuated in water and has thus been found to be impractical for water and wastewater disinfection applications.³¹

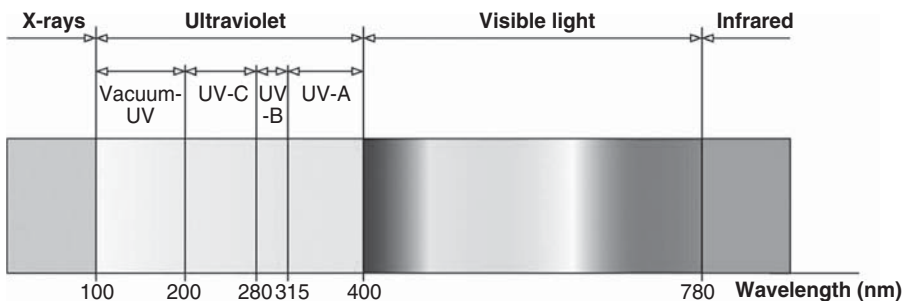
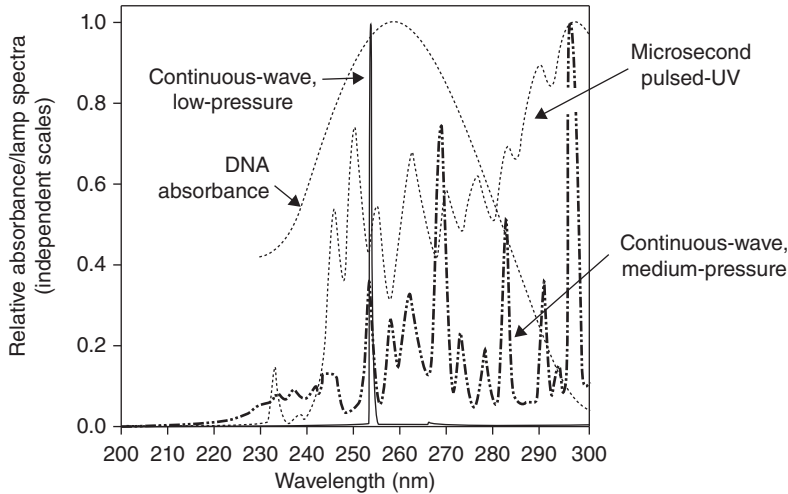


Figure 17.1. Electromagnetic spectrum.⁹



Source: Linden & Mofidi 2000, unpublished data

Figure 17.2. Comparison of wavelength regions of optimal disinfection to DNA absorbance and wavelengths of emission from UV lamps.

Microbial Inactivation Mechanisms

UV disinfection is a physical process that achieves disinfection by inducing photobiochemical changes within microorganisms. For UV light to effectively inactivate a microorganism, the DNA must absorb energy from an appropriate range of the electromagnetic spectrum. At a minimum, two conditions must be met for a photochemical reaction to take place: (a) Light of sufficient energy to alter chemical bonds must be available, and (b) such light must be absorbed by the target molecule in an organism.³³

Figure 17.2 shows the absorption spectrum of deoxyribonucleic acid (DNA) in comparison to the relative output of various types of UV lamps. To be most effective for disinfection, the spectral output of a germicidal UV lamp should match the absorption spectrum of the target organism's genome.

The main mechanism of disinfection by UV light involves the absorption of UV radiation by cellular nucleic acids, resulting in photochemical changes to DNA or ribonucleic acid (RNA) within the target organism. As UV light penetrates bacteria, viruses, protistian cysts, and other microorganisms, the energy is absorbed by the organism's nucleic acids, causing structural damage. DNA and RNA are made up of a series of monomeric units called nucleotides. Nucleotides consist of a sugar–phosphate backbone and a nitrogenous base. Two classes of nitrogenous bases exist: (a) purine bases: adenine and guanine; and (b) pyrimidine bases: thymine, cytosine, and uracil. The nitrogenous bases of DNA consist of adenine, guanine, thymine, and cytosine, with thymine being replaced with uracil in RNA genomes.

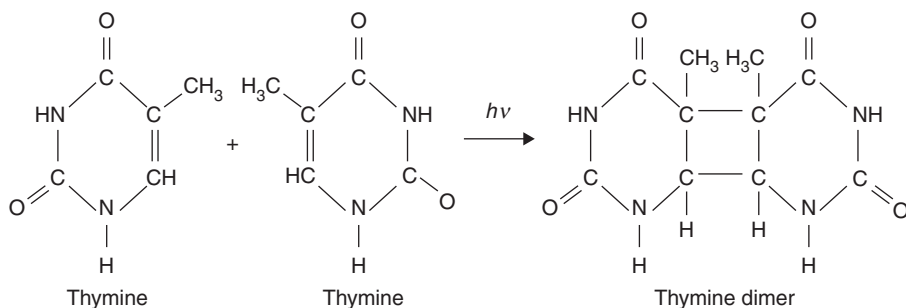


Figure 17.3. Photochemical dimerization of two thymine bases.

The absorption of UV light by DNA or RNA promotes the formation of covalent bonds between adjacent pyrimidine residues, resulting in the formation of cyclobutane-type pyrimidine dimers. With microorganisms having DNA genomes, UV exposure predominantly results in the formation of thymine–thymine dimers with smaller percentages of thymine–cytosine and cytosine–cytosine dimers.³⁴ The formation of a thymine–thymine dimer is presented in Figure 17.3.

UV exposure of microorganisms having RNA genomes predominantly results in uracil–uracil dimers, with smaller percentages of uracil–cytosine and cytosine–cytosine dimers.³⁵

The genetic information of a microorganism is mapped in the specific order of the nitrogenous bases of the DNA or RNA genome. The dimers formed by adjacent pyrimidine bases physically inhibit enzymes used for nucleic acid synthesis and block the copying of the damaged strand during replication, thus rendering the microbe inactive, as presented in Figure 17.4.

Microbial UV Sensitivity

Table 17.1 presents the UV sensitivity of various pathogenic microorganisms of concern in both water and wastewater applications. Of these pathogens, viruses are typically the most resistant to UV disinfection, followed by spore-forming bacteria, non-spore-forming bacteria, and protistian cysts (*Cryptosporidium* oocysts and *Giardia* cysts). The most UV-resistant pathogenic virus currently of concern in water and wastewater is adenovirus type 40 and 41, requiring UV doses many times higher than those required for other pathogens.

Microbial Repair

Under some circumstances, the photobiochemical damage to an organism caused by UV light can be repaired. These repair mechanisms allow

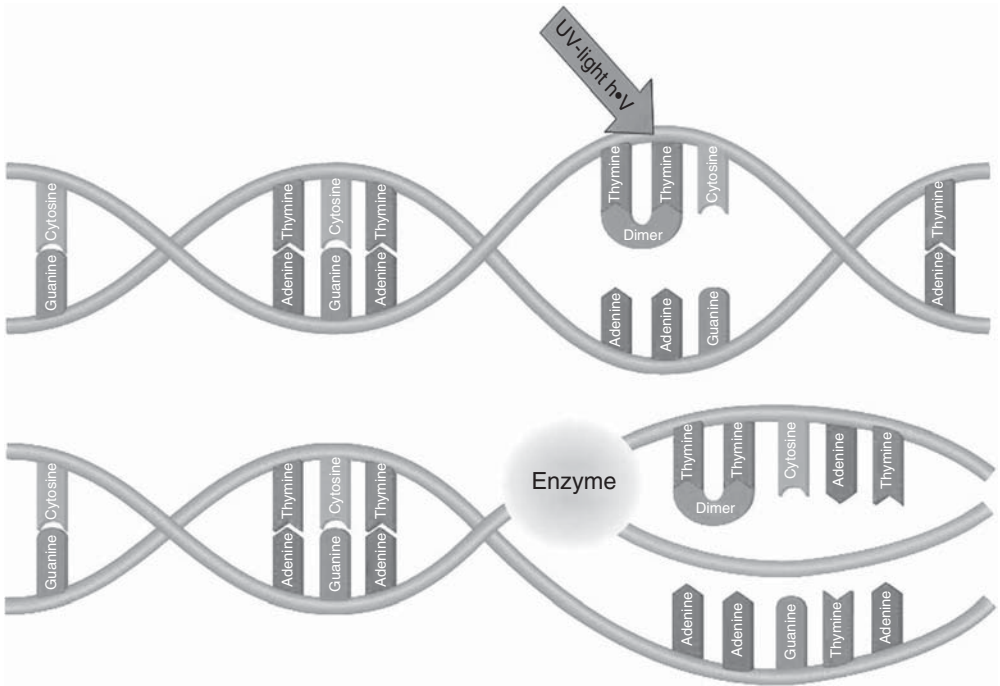


Figure 17.4. Inhibition of DNA replication due to formation of thymine dimer.⁹

UV-inactivated microorganisms to regain viability following the disinfection process.³³ Two types of reactivation mechanisms have been defined. The first type, known as photoreactivation, is a process whereby dimers within microbial nucleic acids are catalytically repaired to their original monomeric forms by a light-activated enzyme. Observations of photoreactivation can be explained by using a two-step reaction mechanism. In the first step, a photoreactivating enzyme (PRE) combines with a pyrimidine dimer to form a PRE-dimer complex. The kinetics of this reversible reaction is such that the forward reaction (complex formation) is favored over the reverse reaction. Step 1 is a strict chemical reaction and, as such, requires no light to take place. In step 2, the PRE-dimer complex absorbs light near and in the visible light range (310nm to 490nm), resulting in a photolytic reformation of the pyrimidine monomers and the release of PRE. Reformation of the monomers results in the reversal of photochemical damage. Once released from the PRE-dimer complex, PRE is available for further complex formation and photolytic repair.³³

The significance of photoreactivation will depend in large part on the initial dose of inactivating (UV) light, the dose of photoreactivating light, and the microorganism. The probability of repair and survival of the microorganism decreases as the UV dose increases and the microorganism accumulates more

TABLE 17.1. UV Sensitivity of Pathogenic Microorganisms³⁰

Microorganism	Type	UV Dose (mJ/cm ²) at Indicated Inactivation			
		1-log	2-log	3-log	4-log
<i>Aeromonas hydrophila</i>	Bacteria	1.1	2.6	3.9	5
<i>Campylobacter jejuni</i>	Bacteria	1.6	3.4	4	4.6
<i>Escherichia coli</i> O157:H7	Bacteria	1.5	2.8	4.1	5.6
<i>Legionella pneumophila</i>	Bacteria	3.1	5	6.9	9.4
<i>Salmonella anatum</i>	Bacteria	7.5	12	15	—
<i>Salmonella enteritidis</i>	Bacteria	5	7	9	10
<i>Salmonella typhi</i>	Bacteria	1.8	4.8	6.4	8.2
<i>Salmonella typhimurium</i>	Bacteria	2	3.5	5	9
<i>Shigella dysenteriae</i>	Bacteria	0.5	1.2	2	3
<i>Shigella sonnei</i>	Bacteria	3.2	4.9	6.5	8.2
<i>Staphylococcus aureus</i>	Bacteria	3.9	5.4	6.5	10.4
<i>Vibrio cholerae</i>	Bacteria	0.8	1.4	2.2	2.9
<i>Yersinia enterocolitica</i>	Bacteria	1.7	2.8	3.7	4.6
Adenovirus Type 40	Virus	30	59	90	120
Adenovirus Type 41	Virus	22	50	80	—
Coxsackievirus B5	Virus	6.9	14	21	—
Hepatitis A HM175	Virus	5.1	14	22	30
		4.1	8.2	12	16
Hepatitis A	Virus	5.5	9.8	15	21
Poliovirus Type 1	Virus	4	8.7	14	21
		6	14	23	30
		5.6	11	16	22
		5.7	11	18	13
Rotavirus SA11	Virus	7.6	15	23	
		7.1	15	25	
		9.1	19	26	36
<i>Cryptosporidium parvum</i>	Protozoa	<2	<3	<5	—
			<3	<6	
<i>Giardia lamblia</i>	Protozoa	<1			<2
		<1	<3	<6	

damage in the form of pyrimidine dimers. Therefore, reversal of that damage (sufficient to allow reactivation) will depend on the availability of photoreactivating light.³³ Photoreactivation and regrowth can be of concern for systems that discharge to surface waters exposed to sunlight if the UV design dose is too low. Although most commonly associated with bacteria, photoreactivation has been observed in other organisms such as viruses. Although viruses themselves do not have the necessary enzymes for photoreactivation, some viruses (such as adenovirus) are able to use the enzymes of their host cell for DNA repair. Research by Rauth³⁵ demonstrated that viruses having RNA genomes were incapable of conducting photorepair in a host cell.

Another form of reactivation, known as dark repair, allows damaged organisms to repair themselves by multienzymatic clipping of the damaged regions of the DNA in one strand and to undergo repair using the undamaged complementary second strand. It is thought that dark repair processes have the ability to repair photoreactive and nonphotoreactive damages.³³ This mechanism is of concern where reactivation might occur in a dark distribution system or a discharge pipe.

The existence of repair mechanisms for UV-induced damage opens several ongoing questions, the primary one being to what extent these mechanisms should be taken into consideration during design. From an operational perspective, the availability of repair mechanisms would indicate a larger UV dose than would be required if no repair were possible. Similarly, the inclusion of reactivation mechanisms in the design process requires more UV hardware. Lindenauer and Darby³⁶ suggest in their analysis that the effect of photoreactivation is relatively insignificant at the dose levels used (i.e., reuse applications at doses greater than 60–80 mW·s/cm²). However, much of the design work for secondary wastewater treatment plants (WWTPs) has been at dose levels of less than 40 mW·s/cm², at which point significant increases in residual densities have been measured (via the static light/dark bottle technique).³³

A consensus does not exist within the engineering or regulatory communities regarding the inclusion of repair in UV disinfection system design. Although repair and recovery mechanisms are known to exist for other disinfectants, including chlorine, little attention is generally given to the subject. Although many operating WWTPs have been designed and are operating successfully with and without consideration of repair, one should be cautioned that this does not mean that photorepair is not occurring, but that it may be masked by overdesign, underuse (WWTPs that are well below their design capacity), and sampling/analysis techniques. Overall, the reader is cautioned about the effects of repair and should be cognizant of the potential impacts of designing a system with or without its consideration.³³ The most widely used method of minimizing reactivation and regrowth is increasing the dose of UV light to ensure that sufficient germicidal effects (number of thymine dimers) are achieved. The safety factor applied to account for reactivation is dependent on a number of factors including target organism, upstream unit processes, and the use of the treated water. Manufacturers should be consulted on the appropriate safety factor to be used to minimize reactivation and regrowth. However, to date, the reactivation mechanism has not been shown to be counterproductive to wastewater UV disinfection.

UV Dose

In theory, dose is the product of the UV intensity (*I*) and the exposure time (*t*) that a microorganism is exposed to UV light:

$$D = It, \quad (17.1)$$

where

D = UV dose (mW-s/cm² or W-s/m² or mJ/cm²),

I = UV intensity (mW/cm² or W/m²), and

T = exposure time (s).

Typically, UV dose is expressed in units of mJ/cm² or in units of J/m², which are equivalent to mW-s/cm² or W-s/m², respectively.

The application of Equation (17.1) for the determination of a dose within a UV reactor assumes that the UV light within the reactor is equally distributed and that the velocity profile throughout the reactor is uniform. However, in practice, these assumptions are not valid, as both the intensity distribution and velocity profile are not uniform. The light intensity distribution (LID) and residence time distribution (RTD) thus result in a distribution of UV doses that are delivered within a UV reactor.

Figure 17.5 presents the dose distribution occurring within an ideal UV reactor having plug flow characteristics and uniform intensity distribution profile as well as examples of potential dose distributions occurring in real-world UV reactors demonstrating nonideal velocity and intensity distributions.

As a result of the actual dose distribution occurring in UV reactors, the UV dose that a microorganism is exposed to as it travels through the UV reactor is a function of the flow path of that microorganism through the reactor, which will dictate the UV intensity experienced by the organism and the UV exposure time.

The LID within a UV reactor is a function of direct and indirect water matrix effects. Direct water matrix effects are water quality parameters that physically inhibit the ability of UV light to come in contact with a microorganism once it is emitted from a UV lamp. These water quality parameters consist of UV transmittance and suspended solids, which are discussed in further

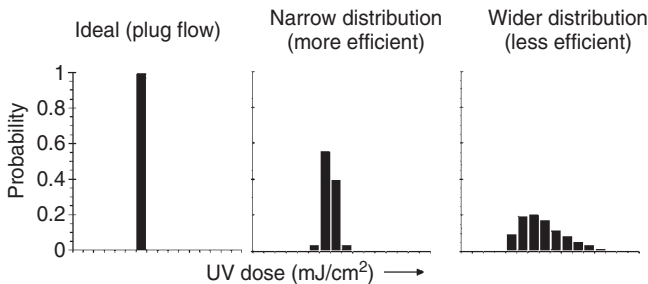


Figure 17.5. Dose distribution examples of ideal and real-world UV reactors.⁸⁵

detail in the “UV System Validation” and the “Nonbiological, Mathematical-Based Modeling” sections, respectively. Indirect water matrix effects primarily consist of those related to the fouling of the UV system. Fouling of quartz sleeves hampers the ability of the UV light to pass from the lamp and into water due to a reduction in the UV transmittance of the sleeve and this is discussed in further detail in the “Fouling” section.

The RTD within a UV reactor results from a distribution of velocity profiles occurring in a UV reactor, as opposed to a single, uniform velocity that would occur within an ideal, plug flow scenario. The velocity profile within a UV reactor is impacted not only by the flow rate and the wetted geometry with the reactor (including baffle plates, structural components, wiper system components, and UV lamp array) but also by the inlet piping arrangement and potentially the outlet piping arrangement to and from the UV reactor (including valves, elbows, expansions, reductions as well as any other obstacles in the flow path).

The combined impact of the LID and RTD within a reactor results in the inability to use Equation (17.1) directly to accurately calculate the UV dose delivered within a reactor. Although the impacts of LID and RTD on UV dose can be incorporated into complex models to mathematically estimate the average UV dose within a reactor, the most accurate methodology currently utilized for determining the disinfection performance of UV systems is biosimetry-based validation testing. The various methods used for the sizing and operation of UV systems are reviewed in further detail in the “UV System Sizing Tools” section.

GUIDELINES

Several formal guidelines have been published in North America for the design, selection, operation, and maintenance of UV systems for the disinfection of various water qualities. These include the USEPA *Ultraviolet Disinfection Guidance Manual*,³¹ National Water Research Institute/American Water Works Association Research Foundation (NWRI/AwwaRF) *Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse*,^{37,38} and the USEPA *Design Manual for Municipal Wastewater Disinfection*.³⁹ A review of the application of these guidelines and their associated components are presented in the following sections.

USEPA's *Ultraviolet Disinfection Guidance Manual*

The USEPA first released a draft version of the *UVDGM* in June 2003.³⁰ A second draft was released in January 2005. The final version, *Ultraviolet Disinfection Guidance Manual (UVDGM)* for the Final *LT2ESWTR*, was released in November 2006.³¹ This document is not a regulation itself but

provides guidance and technical information that can be utilized for the planning, selection, designing, validation, and operation of UV systems for compliance with the UV disinfection requirements as set forth in the *LT2ESWTR*. The *LT2ESWTR* and thus the *UVDGM* are applicable to drinking water treatment for PWSs treating surface water or GWUDI. These guidelines are expected to be adopted (partially or in whole) by states in the United States selecting UV disinfection for the treatment of drinking water. Many state regulators have required *UVDGM*-compliant validated UV system designs since the release of the first draft of the guidelines in 2003. The *UVDGM* is also being used in Canada for the planning and design of drinking water UV disinfection systems.

The *UVDGM* contains six main chapters, which include the following:³¹

- Chapter 1, “Introduction,” reviews the guidance manual objectives, document organization, summary of regulations for PWSs, UV disinfection requirements for PWSs, regulatory timelines, and alternative UV disinfection technologies.
- Chapter 2, “Overview of UV Disinfection,” provides an overview of the history of UV disinfection of drinking water, generation of UV light, microbial inactivation via UV light and microbial repair mechanisms, UV disinfection system components, water quality impacts on disinfection and fouling, and by-product formation.
- Chapter 3, “Planning Analyses for UV Facilities,” includes guidance on determining UV disinfection goals for PWSs; an evaluation of the impact of UV disinfection on the overall treatment process at a facility; a review of potential installation locations; an outline of design parameters for UV systems, data collection guidance, and testing approaches for evaluation of lamp aging and fouling factors; a review of acceptable UV system control philosophies and monitoring strategies; assistance on choosing validation locations, hydraulic recommendations, and influent/effluent piping configuration options; solutions for head loss limitations; guidance on estimation of UV facility footprint; preliminary cost evaluation; and recommendations regarding interaction with state regulatory agencies during the planning phase.
- Chapter 4, “Design Considerations for UV Facilities,” reviews hydraulic considerations including piping configuration, flow distribution and control, water level control, air relief and pressure control, valves, pumps and hydraulic issues associated with groundwater and uncovered finished water reservoirs; selection of the operational approach for the UV system; reactor instrumentation and controls, including reactor start-up procedures, operational automation, alarms, and control signals from monitoring equipment; electrical power configuration and backup power options; recommendations for the layout of UV facilities; review of components

to be included in design specifications and information requested from UV manufacturers; development of the final UV system design; and recommendations regarding interaction with state regulatory agencies during the design stage.

- Chapter 5, “Validation of UV Reactors,” includes the minimum requirements for the validation of UV reactors; the summary of the recommended validation testing protocol; the guidance on selection of the challenge organism(s); validation equipment requirements for the UV system components, validation layout, additives, and water source; required accuracy and calibration of monitoring equipment; the identification of test conditions based on UV system control philosophy, associated quantity of samples, and quality-control sampling; guidelines on conducting testing, including the preparation of the challenge organism, reactor biodosimetry challenges, and collimated beam testing; analysis of data, determination of reduction equivalent dose (RED) and associated disinfection performance models; the calculation of uncertainty factors, RED bias factor, and validation factor; the determination of the validated dose and validated operational conditions for a UV system; UV reactor documentation, test plan, and validation report components; assistance on the review of validation reports; and guidelines for evaluating situations requiring additional validation testing or “re-validation.”
- Chapter 6, “Start-Up and Operation of UV Facilities,” provides guidance on the start-up of UV facilities, functional testing, performance testing, final inspection, and state coordination; operational requirements, recommended operational procedures, and start-up and shut-down procedures; recommended maintenance procedures and general guidelines for maintenance of UV reactors; monitoring and recording of data for compliance and noncompliance purposes; reporting to the state; review of potential operational challenges associated with UV systems; and guidance regarding staffing, training, and safety.

In addition to the above chapters, the *UVDGM* also includes seven appendixes:³¹

- Appendix A: “Preparing and Assaying Challenge Microorganisms”
- Appendix B: “UV Reactor Testing Examples”
- Appendix C: “Collimated Beam Testing to Develop a UV Dose–Response Curve”
- Appendix D: “Background to the UV Reactor Validation Protocol”
- Appendix E: “UV Lamp Break Issues”
- Appendix F: “Case Studies”
- Appendix G: “Reduction Equivalent Dose Bias Tables”

NWRI/AwwaRF's *Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse*

The *Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse*³⁸ is published by the NWRI in collaboration with the AwwaRF. The first edition was published in December 2000, with a second edition released in May 2003. The current version of this document establishes UV system design, validation testing, and field commissioning testing guidelines for UV disinfection systems in drinking water and water reuse applications. These guidelines have been adopted (partially or in whole) by several states in the United States (most notably California) as a requirement for UV disinfection systems in water reuse applications.

The NWRI guidelines are separated into three chapters: (a) “Drinking Water,” (b) “Water Reuse,” and (c) “Protocols.” The first and second chapters establish the UV system design guidelines for drinking water and water reuse, respectively, and include the following sections:³⁸

- Section 1, “Introduction,” includes a general introduction of the guidelines and review of the sections in the associated chapters.
- Section 2, “UV Dose,” reviews the factors impacting dose requirements, such as the target microorganism and water quality, and the establishment of design factors including lamp aging and fouling factors.
- Section 3, “Reactor Design,” includes hydraulic constraints/impacts of system plumbing upstream and downstream of the UV reactor; reactor train layout constraints; and cleaning system constraints.
- Section 4, “Reliability Design,” includes required standby equipment, actions required to address feed water quality variability, operation and maintenance procedures, power supply reliability, electrical safety design, and seismic design.
- Section 5, “Monitoring and Alarm Design,” includes requirements for continuous monitoring and monitoring of UV system operational parameters, calibration of monitoring equipment, high- and low-priority alarm conditions, and historical alarm log.
- Section 6, “Field Commissioning Test,” includes testing requirements prior to a system treating water for distribution.
- Section 7, “Performance Monitoring,” includes microbial sampling and UV dose-monitoring requirements.
- Section 8. Engineering Report,” includes the contents and requirements.

The third chapter, “Protocols,” reviews the requirements and procedures associated with the validation of UV disinfection equipment for water and water reuse applications, including the following sections:³⁸

- Section 1, “Introduction,” includes the purpose of protocol and a review of the sections in the chapter.

- Section 2, “Test Facilities Requirements and Set-Up,” includes the requirements for the collimated beam apparatus; testing requirements for the water supply, mixing of additives, sampling and monitoring locations and configuration of influent and effluent piping; UV reactor equipment and documentation; and qualification requirements for the validation facility and personnel.
- Section 3, “Microbiological Testing,” includes quality assurance/quality control (QA/QC) protocols for the challenge organism (MS2 bacteriophage) and stock dose response, and a review of existing procedures for the propagation and enumeration of MS2.
- Section 4, “Testing and Sampling Requirements,” includes collimated beam UV dose determination; development of the collimated beam-derived dose–response curve for MS2; calibration of collimated beam equipment; establishment of the minimum sensor reading to be used during reactor validation; requirements for the validation water quality matrix; reactor validation testing approach, sample collection, and handling; lamp aging factor testing; fouling factor (i.e., cleaning system efficiency factor) testing; velocity profiling; and calibration of reactor validation instrumentation.
- Section 5, “Data Analysis and Reporting,” includes determination of the MS2 log inactivation and associated UV dose occurring from reactor validation test conditions; data reporting requirements; and limitations regarding the scale-up of the validated UV system size to that of an installed system.

USEPA’s *Design Manual for Municipal Wastewater Disinfection*

Due to the concerns associated with the adverse impacts of chlorination of wastewater effluents (toxic impacts on aquatic life and by-product formation), the USEPA released the *Design Manual for Municipal Wastewater Disinfection* in October 1986.³⁹ The manual reviews the history, process, and design of halogen (chlorine, chlorine dioxide, and bromine chloride) as well as available disinfection alternatives, including ozone and UV. The manual includes a total of seven chapters, with the first four chapters containing an introduction, review of the need for disinfection technologies; disinfection alternatives and options, and kinetics and hydraulic considerations for wastewater effluent disinfection associated with all disinfectant alternatives. The fifth, sixth, and seventh chapters of the manual specifically address halogen, ozone, and UV disinfection, respectively, in detail.

The guidelines associated with UV disinfection within this manual were based on the UV technologies, design procedures, operation and maintenance experience that were available in the mid-1980s, much of which has greatly evolved over the past two decades. Although this manual is

significantly out of date regarding available UV technologies, exiting installations, design/validation procedures, and associated operational and maintenance experience, it remains the only standardized guidance manual for the application of UV in the disinfection of nonreuse wastewater effluent. Chapter 7, “Ultraviolet Radiation,” contains five main sections, as reviewed below:³⁹

- Section 7.1, “Introduction,” reviews chapter contents, general outline of UV process, available UV system design configurations, and current status of wastewater UV disinfection, including advantages/disadvantages of UV and status of existing UV system installations as well as those systems in construction and under design.
- Section 7.2, “Disinfection of Wastewaters by Ultraviolet Radiation,” includes an overview of the nature of UV light and UV light generation by lamps, inactivation process of UV and microbial repair mechanisms, and summary of current studies and evaluations of the application of UV in wastewater disinfection.
- Section 7.3, “Process Design of the UV Wastewater Disinfection System,” reviews microbial inactivation kinetics, impacts of particles, UV system performance process models and associated data requirements for proper modeling; hydraulic characterization of UV reactors via RTD analysis, dispersion characterization, turbulence, and head loss analysis and determination of the effective volume; average intensity estimation techniques, including the point source summation technique, considerations for existing lamp configurations, lamp aging/fouling factors and a bioassay procedure for intensity and dose determination; wastewater quality design considerations, including wastewater quality parameters, performance model parameters; performance data from existing plants and studies, microbial photoreactivation and sampling guidelines for gathering of design data.
- Section 7.4, “UV Disinfection System Design Example,” reviews the steps for establishing design conditions and parameters for UV equipment sizing, including model parameters, pilot-/bench-scale testing requirements; required assumptions; design sequence; and detailed example.
- Section 7.5, “System Design and Operational and Maintenance (O&M) Considerations for the UV Process,” includes an overview of factors impacting UV intensity, including temperature, voltage, and lamp aging impacts on the output of lamps, and fouling impacts on quartz sleeves; reactor cleaning and additional design considerations regarding maintenance procedures; UV system components; Monitoring and control of UV systems; safety; equipment and physical plant requirements for UV installations; and estimation of O&M requirements, including labor, spare parts, and power consumption.

The validation testing protocols associated with these guidelines will be reviewed in greater detail and compared with other existing validation approaches in the “Operation and Maintenance Activities” section.

UV EQUIPMENT

The UV equipment utilized for water and wastewater disinfection consist of the following key components: UV lamps, reactor, ballasts, lamp sleeves, UV sensors, and cleaning systems. In addition, UV equipment may include additional monitors such as on-line UVT monitors, temperature sensors and water level probes. Each of these components is reviewed in the following sections.

UV Lamps

The artificial generation of UV light is typically conducted by applying a voltage across a gas mixture contained within a lamp envelope. The gas is temporarily excited by the discharge and then returns to a lower energy state, resulting in the discharge of photons. The wavelengths of light that are emitted from the photons are specific to the elemental composition of the gas and the power level of the lamp.³¹

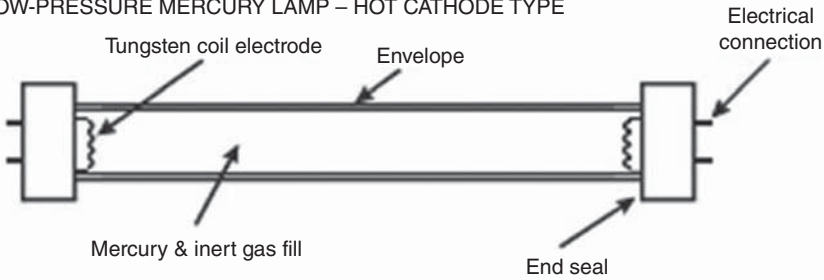
Currently, the most widely utilized UV lamp technologies employed for the disinfection of wastewater and drinking water throughout the world are LP, low-pressure–high-output (LPHO), and MP mercury vapor lamps. In addition to these lamps, several recently emerging UV technologies have also demonstrated promise for the inactivation of microorganisms, including electrodeless mercury vapor lamps, metal halide lamps, pulsed UV lamps, , excimer lamps, and UV light-emitting diodes (LEDs).

Mercury Vapor Lamps. LP, LPHO, and MP lamps consist of several components including (a) lamp envelope, (b) electrodes, (c) mercury fill, and (d) inert gas fill, as presented in Figure 17.6.

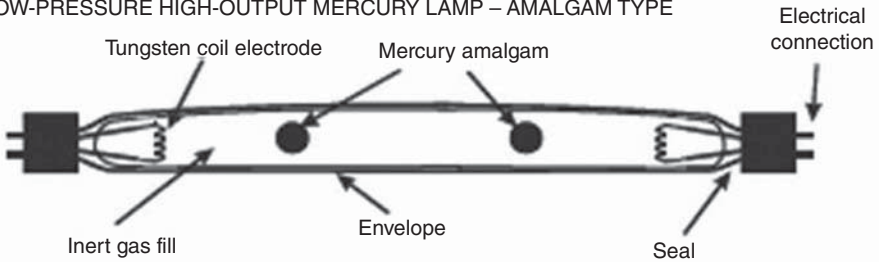
The lamp envelope is a hermetically sealed tube of UV-transmitting material that acts as an electrical insulator. Vitreous silica, a noncrystalline form of quartz, is typically used as the lamp envelope due to its high UV transmittance, temperature resistance, and stability with the lamps fill gasses. Lamp envelopes can also be constructed from quartz that has been “doped” or altered to absorb specific wavelengths emitted from the photons to prevent the emission of nongermicidal wavelengths that may result in unwanted photochemical reactions.³¹

Two electrodes are positioned on each end of the lamp envelope. When current is provided to the electrodes, it results in the generation of an electrical arc, which is passed through the fill gas from one end of the lamp to the other. During the operation of a lamp, the applied current results in the heating of the electrodes, which is required to maintain proper lamp temperatures.

LOW-PRESSURE MERCURY LAMP – HOT CATHODE TYPE



LOW-PRESSURE HIGH-OUTPUT MERCURY LAMP – AMALGAM TYPE



MEDIUM-PRESSURE MERCURY LAMP

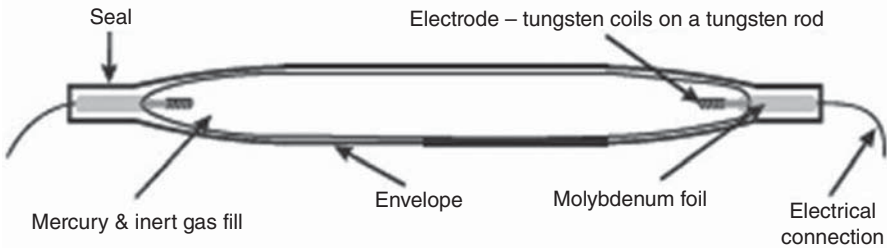


Figure 17.6. Components of mercury vapor lamps.³¹

Additional factors that impact temperature include the power applied to the lamp and the lamp diameter. Due to the heat generated by the electrodes, their thermal design is a critical issue for long-term operation and prevention of early lamp failure.

The mercury fill of a mercury vapor lamp can be in the liquid, solid, or gaseous phase, depending on the type of lamp and operational state. As the lamp heats up, the mercury vapor pressure increases as more mercury enters the gaseous phase. In addition to mercury, an inert gas fill, typically argon, is also added to the lamp envelope at a typical vapor pressure of 0.02–1 psi. The inert gas fill is utilized as a mercury gas discharge aid during lamp start-up and reduces electrode deterioration.³¹

LP and LPHO UV Lamps. Historically, the most commonly used UV lamp technology is the conventional LP mercury vapor continuous-wave lamp. The “low” pressure of these lamps refers to the mercury vapor within the lamp. The electrodes of LP lamps are made of a tungsten wire coil that is embedded with calcium, barium, or strontium oxides. LP lamps contain liquid mercury within the lamp envelope. The generation of UV light is achieved by passing an electrical arc through mercury vapor contained inside a hermetically sealed tube at a vapor pressure of approximately 1.35×10^{-4} psi.³¹ The mercury vapor, excited by the discharge, returns to a lower energy state, resulting in the emission of UV light¹ having an essentially monochromatic UV output at a wavelength of 254 nm, as presented in Figure 17.7. The output power of conventional LP lamps is rather low, having a specific radiant power at a wavelength of 254 nm of approximately 0.2–0.3 W/cm.⁴⁰

During the 1990s, the UV output of conventional LP lamps was dramatically increased via the development of the LPHO continuous-wave lamps. The mercury within these lamps, also referred to as “amalgam” lamps, is in the solid phase, doped with additional elements such as bismuth, indium, and gallium.^{40,40A} LPHO lamps utilize similar electrodes as the conventional LP lamps but have higher operating temperatures and vapor pressures ranging from 2.6×10^{-5} to 2.3×10^{-4} psi.³¹ The result of the mercury amalgam is an increase in output per unit length as compared with the LP counterpart. In addition to the amalgam lamps, some lamp manufacturers have also increased the UV output of the conventional LP lamps via the use of reinforced filaments, allowing for an increased current capacity.³¹

Additional operational parameters for LP and LPHO lamps are presented in Table 17.2. Figure 17.7 presents the typical UV output associated with these mercury vapor lamp technologies. Lamp characteristics vary between lamps; thus, manufacturers typically conduct independent testing to validate the operational parameters of specific UV equipment. Therefore, it is recom-

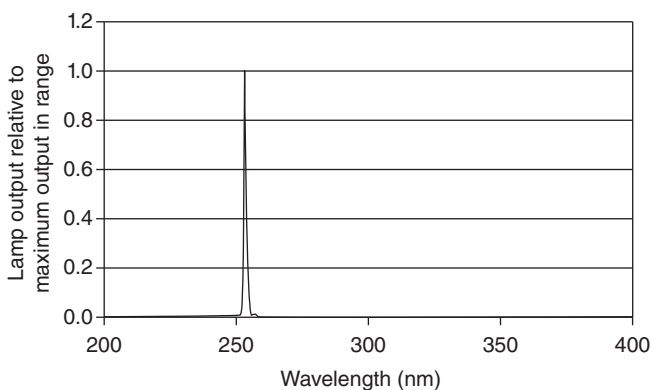


Figure 17.7. Typical UV output of LP lamps.

TABLE 17.2. Operational Characteristics of LP and LPHO Lamps^{31,42,43}

Parameter	LP	LPHO
Germicidal UV light	Monochromatic (254 nm)	Monochromatic (254 nm)
Mercury vapor pressure (psi)	1.35×10^{-4} (0.93 Pa)	2.6×10^{-5} – 2.3×10^{-4} (0.18–1.6 Pa)
Operating temperature (°C)	35–45	130–200
Electrical input (W/cm)	0.5	1.5–10
Germicidal UV output (W/cm)	0.2	0.5–3.5
Electrical to germicidal UV conversion efficiency (%)	35–38	30–40
Arc length (cm)	10–150	10–150
Relative number of lamps needed for a given dose	High	Intermediate
Lifetime (h)	8,000–10,000	8,000–12,000

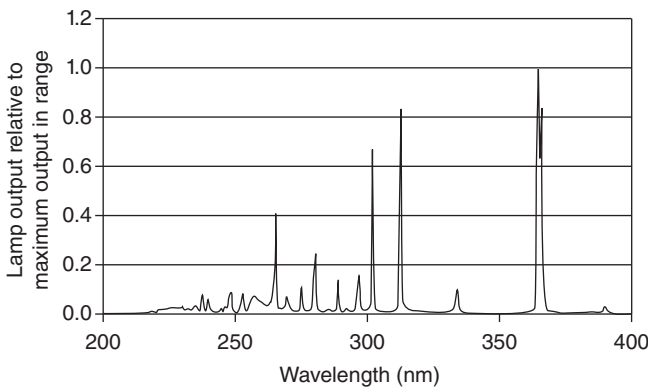


Figure 17.8. Typical UV output of MP lamps.³¹

mended that the reader consult both the UV manufacture and well as various lamp manufactures to verify the current operational characteristics of lamps.

MP UV Lamps. MP mercury vapor, continuous-wave lamps operate at higher mercury vapor pressures, between 5.80 and 10psi, than and highly elevated operational temperatures as compared with those of LP and LPHO lamps.⁴³ The electrodes of MP lamps are made of a tungsten rod wrapped in a coil of tungsten wire.³¹ MP lamps contain liquid mercury within the lamp envelope. The increased vapor pressure and associated power demand of MP lamps result in a broadening of the emission lines and, thus, a change from the monochromatic emission of LP and LPHO lamps to a polychromatic UV spectrum,^{40A} as presented in Figure 17.8. The UV output per unit length for

TABLE 17.3. Operational Characteristics of Mercury Vapor Lamps^{31,42,43}

Parameter	MP
Germicidal UV light	Polychromatic (including 200–300 nm germicidal range)
Mercury vapor pressure (psi)	5.80–10 (40,000–4.0 × 10 ⁶ Pa)
Operating temperature (°C)	600–900
Electrical input (W/cm)	50–250
Germicidal UV output (W/cm)	5–30
Electrical to germicidal UV conversion efficiency (%)	10–20
Arc length (cm)	5–120
Relative number of lamps needed for a given dose	Low
Lifetime (h)	4000–8000

MP lamps can range up to 30 W/cm. This is a substantial increase compared with LP and LPHO lamps. However, MP lamps are less efficient in the conversion efficiency of electrical to germicidal UV since all wavelengths produced by these lamps are not effective in disinfection. Approximately 44% of the light emitted from a MP lamp is within the UV-B and UV-C germicidal range.¹ This covers the entire germicidal spectrum of 200–300 nm. Although MP lamps are not as energy efficient as LP and LPHO lamp technologies, they have become widely used due to the increased UV output per lamp, which has resulted in reduced lamp numbers, smaller reactors and footprint, and reduced capital costs for both wastewater and drinking water installations.

Additional operational parameters for MP lamps are presented in Table 17.3.

Electrodeless Mercury Vapor Lamps. The traditional LP, LPHO, and MP mercury vapor lamps that were previously discussed all contain electrodes for the generation of an electrical arc and production of UV light. The deterioration of the electrodes is the primary source of lamp failure and limits the operational lifetime of these lamp technologies. An alternative to the traditional mercury vapor lamps are the electrodeless mercury vapor lamps. These lamps are similar to LP, LPHO, and MP lamps in that they consist of a lamp envelope, mercury fill gas, and argon inert fill gas, with the exception that the excitation of the mercury vapor is achieved by either microwaves or a magnetic field. The UV output of these lamps is essentially monochromatic at a wavelength of 254 nm. Figure 17.9 shows a figure of this type of lamp type.

Microwave-powered electrodeless UV lamp systems have been successfully applied in the industrial curing market since the 1970s and consist of a large percentage of the installed systems in this industry.⁴⁴ However, their application in the water and wastewater disinfection market has been limited, with



Figure 17.9. Comparison of electrode and electrodeless UV lamps.⁴⁷

only a few full-scale installations existing throughout the world as of the end of 2007.⁴⁵ In these systems, microwave energy is generated by a magnetron. The microwaves are directed through a mesh (Waveguide) surrounding the lamp or cluster of lamp envelopes.⁴⁶ The waveguide is surrounded by a quartz sleeve, and a cooling fan removes excess heat accumulation and maintains proper operating temperature. A schematic of a microwave UV assembly is presented in Figure 17.10.⁴⁷

As occurs within the traditional mercury vapor lamps, the microwave energy excites the mercury–argon fill gas, which then results in the discharge of photons as they return to a lower energy state. Microwave UV lamps have an electrical power to germicidal UV conversion efficiency of approximately 24% (S. Shima, pers. comm.) and operate at pressures of 9.7×10^{-3} – 4.8×10^{-2} psi and temperatures of 40–60°C.⁴⁶

An alternative method of generating UV light is via RF-energized electrodeless lamps. These lamps have been utilized as calibration sources for many years due to their long life and stable UV output over time.⁴⁴ This technology has not yet been successfully applied to the drinking water and wastewater disinfection market. This technology generates UV light via induction coils that are wrapped around the electrodeless lamp envelope, as presented in Figure 17.11.⁴⁸

RF-frequency power is delivered from a power supply to the induction coils, and the electric current in the coils results in the generation of a magnetic field. The mercury–argon fill gas is excited and ionized by the magnetic field, and UV light is discharged in an identical manner as occurs with traditional

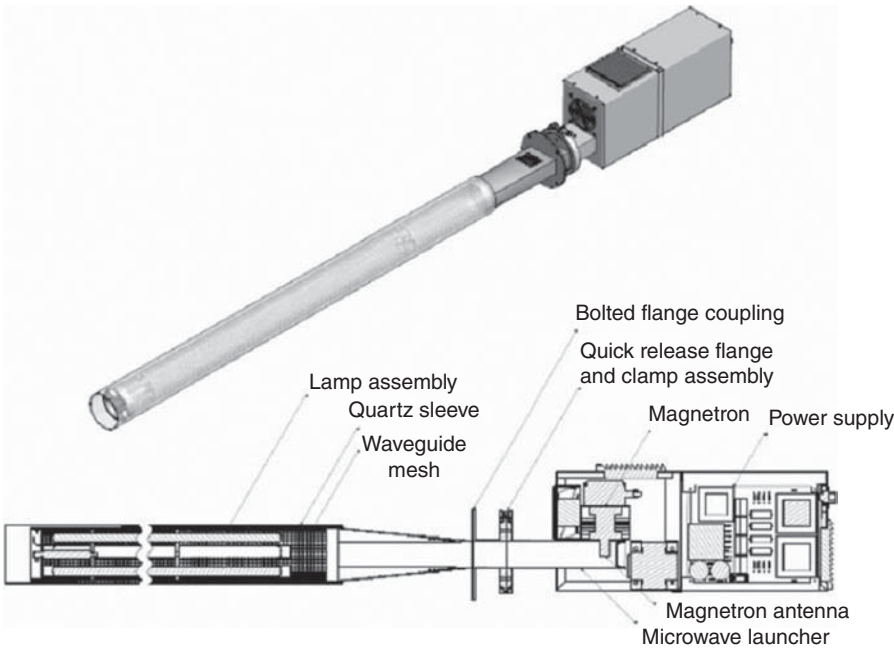


Figure 17.10. Example of microwave UV assembly.⁴⁷

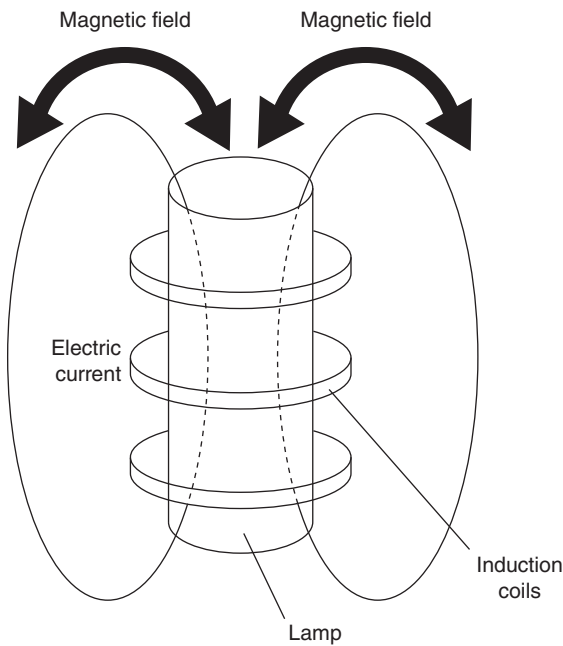


Figure 17.11. Generation of UV light with RF energized electrodeless lamp.⁴⁸

mercury vapor lamps. Based on manufacturer testing, germicidal UV conversion efficiencies of approximately 30% have been observed.⁴⁸

Metal Halide Lamps. The doping of the mercury with small amounts of antimony, colbalt, iron, gallium, magnesium, lead, thallium,⁶ or indium as metal iodides or bromides in medium-high pressure lamps results in a shift in the emission spectrum within the UV-A, UV-B, and UV-C regions.⁴⁰ The output remains polychromatic, and the dominant ranges for several examples of metal halide lamps are presented in Table 17.4.

Metal halide lamps are currently utilized for specialty/effects lighting in the stage-studio-TV field and in headlights as well as in reprographic machines, photochemistry, medical applications, and by the tanning industry.⁴⁹ For the purposes of water and wastewater disinfection, the metal halide lamps doped with antimony iodide hold the greatest promise due to their emission in the germicidal range of the UV spectrum. These lamps are operated at gas pressures of approximately 14.5 psi (1×10^5 Pa). These lamps have an electrical power to germicidal UV conversion efficiency of approximately 12%–15% and germicidal UV output of 3.5–4.5 W/cm. The UV output of these lamps has been noted to be stable over temperature ranges of -20 to 70°C , with an approximate 4000-h lamp lifetime.⁶

Pulsed UV Lamps. Several types of pulsed UV technologies have been investigated for their potential application in the disinfection of water and wastewater, including flashlamps, surface discharge lamps, and sparker pulsed discharges in liquids. Of these technologies, flashlamps represent the only commercially available technology, which have seen a very limited application in the disinfection market.

Flashlamps are similar to LP, LPHO, and MP lamps in that they consist of a lamp envelope with electrodes and a fill gas. However, the fill gas of flashlamps is typically xenon and not mercury. A high-voltage pulse of approximately 10–30 kV,^{40A} is fed by a power supply to the xenon gas, resulting in

TABLE 17.4. Metal Halide Lamps and Associated Wavelength Range^{6,40}

Metal Halide	Wavelength Range (nm)
Antimony iodide (SbI_3)	207–327
Colbalt (II) iodide (CoI_2)	345–353
Iron iodide (FeI_2)	358–440
Gallium iodide (GaI_3)	403–417
Magnesium iodide (MgI_2)	285–384
Lead iodide (PbI_2)	368–406
Thallium iodide (TlI)	535
Indium iodide (InI)	410–451

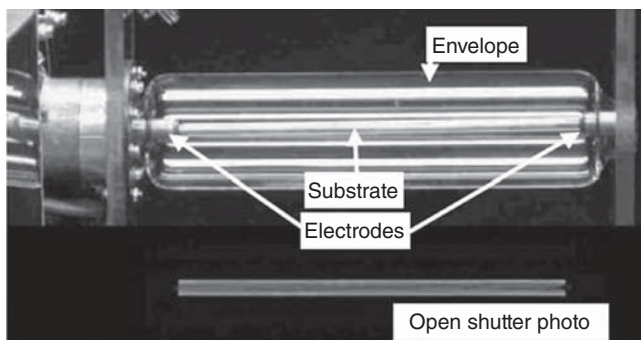


Figure 17.12. Surface discharge lamp.⁵²

strong collisions between electrons and the xenon molecules. The xenon is elevated to an excited state, which then emits an intense, short pulse of broad-band spectrum that includes UV, visible, and infrared wavelengths. The temperature of the plasma generated in these lamps ranges from 10,000 to 15,000 K,⁵⁰ with each pulse typically lasting between 1 μ s and 0.1 s.^{51,52} Pulsed UV flashlamps have been available since the late 1990s; however, their application in the disinfection of water and wastewater disinfection market has been limited due to a lower electrical power to germicidal UV conversion efficiency of approximately 9%⁵³ than the conventional LP, LPHO (30%), and MP (12%) mercury vapor lamps.

New pulsed UV lamp technologies currently under development include surface discharge lamps and sparkers, as shown in Figure 17.12. They are not yet commercially available. Surface discharge lamps generate a polychromatic UV light-emitting plasma discharge along the surface of a tubular substrate between two annular electrodes. The substrate is surrounded by a rare gas (typically xenon) within a lamp envelope.⁵³ Recent research has indicated that the UV efficiency of surface discharge lamps is higher than that of flashlamps. Surface discharge lamps have demonstrated UV efficiencies of 12%–17%.⁵³

A sparker consists of two electrodes within a liquid, between which a high-voltage, high-power electrical pulse is discharged, resulting in the formation of a hot vapor plasma channel. Pulses of light emitted by the plasma are polychromatic, including wavelengths within the germicidal UV spectrum. During this process, a pressure pulse is created in the hot vapor plasma channel, resulting in a pressure wave of the vaporized water. The high-pressure vaporized water cavity continues to expand until it reaches a maximum diameter and then contracts, resulting in a second light and pressure pulse. This cycle continues until all of the energy within the vapor cavity is dissipated, as shown in Figure 17.13.⁵³

Excimer Lamps. Research on excimer lamps that emit a near-monochromatic emission in the UV or vacuum-UV range of the electromagnetic spectrum is

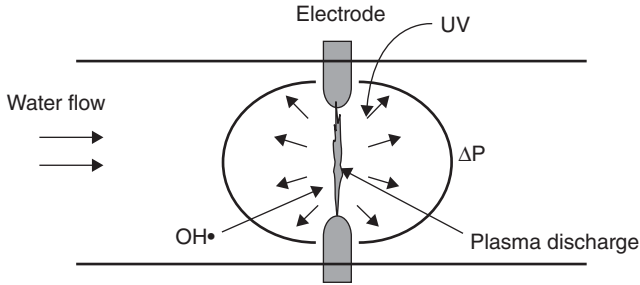


Figure 17.13. Sparker discharge lamp.⁵²

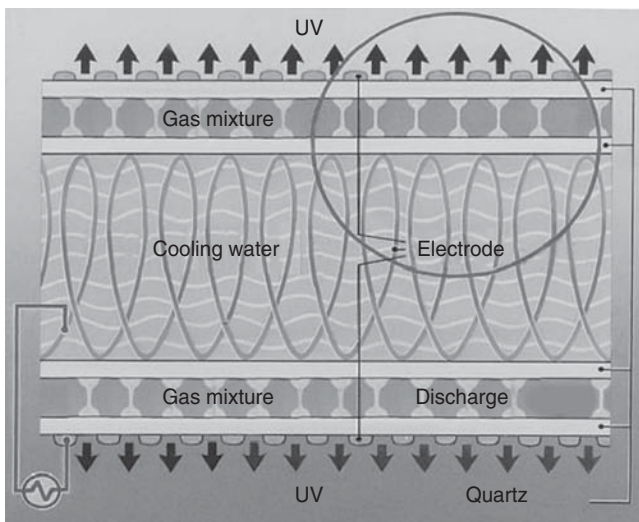


Figure 17.14. Process of excimer formation.⁵¹

currently underway. The fill gas or gas mixture is contained within an enclosed space between two sealed coaxial mounted quartz envelopes.⁵⁴ The electrodes of these lamps are not positioned in the gas space as they are with conventional mercury vapor lamps but are separated by the dielectric barrier (quartz) from the gas.⁴⁰ When the plasma is excited by the current flow, it produces a multitude of microdischarges within a few nanoseconds that results in collisions between electrons and gas molecules. These collisions form excited dimers or excimers, which are unstable, and release photons as they collapse and return to their normal state.⁵⁰ A schematic of excimer formation is presented in Figure 17.14.⁵¹

The wavelength of the photons emitted from these lamps is a function of the type of fill gas or gas mixture, with common examples and their associated wavelengths presented in Table 17.5.

TABLE 17.5. Emission Wavelengths of Excimer Lamps^{40A,49,55}

Excimer	Wavelength (nm)
Xe ₂	172
KrBr	207
KrCl	222
XeJ	253
Cl ₂	259
XeBr	282
XeCl	308
I ₂	342

Of the excimer lamps presented in Table 17.5, five of the fill gases result in wavelengths that reside in the germicidal spectrum of UV between 200 and 300 nm: KrBr, KrCl, XeJ, Cl₂, and XeBr. KrBr, XeJ, and Cl₂ have excessively low conversion efficiencies and/or require extensive burn-in times. The electrical power to germicidal UV conversion efficiency of the remaining two excimer lamps, KrCl and XeBr, are approximately 5%–10%. However, the application of KrCl excimer lamps will likely be limited to the high-quality waters due to the rapid attenuation of UV light at a wavelength of 222 nm in water.⁴⁹ Therefore, XeBr lamps represent the most promising excimer lamp technology for water and wastewater disinfection. These lamps do not require a warm-up period, are mercury free, operate with surface temperatures of approximately 100°C, and have a germicidal UV output of approximately 3%⁵⁵ and lifetimes of several thousand hours.⁴⁹

LEDs. LEDs for the generation of visible light are extremely common in many devices used in home applications, traffic lights, flashlights, and automobile headlights. These LEDs are inexpensive, small, lightweight, and durable. They have efficiencies of approximately 80% and lifetimes up to 100,000 h.⁵⁶

An LED is a device that consists of a chip of semiconducting material that is doped with impurities in order to create a p–n junction. The p–n junction consists of a p-region, which is dominated by positive electric charges (anode), an n-region, which is dominated by negative electrical charges (cathode), which are separated by a junction that acts as a barrier to the flow of electrons between these two regions. As current flows from the p-region to the n-region, charged carriers, electrons and holes, flow into the junction between the p- and n-regions. When an electron combines with a hole, the energy level is reduced and results in the emission of a photon. The wavelength of light emitted by the photon is a function of the band gap energy of the materials forming the p–n junction. LEDs are formed upon an n-type substrate, and an electrode is attached to the p-type layer which is deposited on its surface.

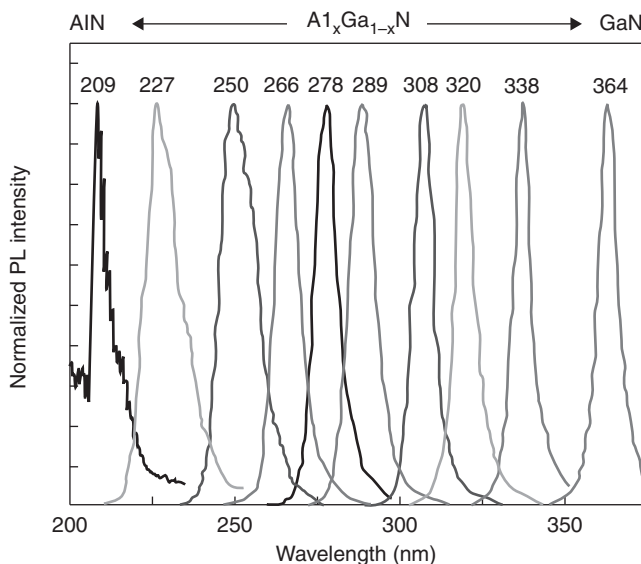


Figure 17.15. Spectral output of AlGaIn structures with different compositions.⁵²

UV LEDs that emit wavelengths between 210 and 340 nm have been developed and consist of aluminum nitride (AlN), gallium nitride (GaN), and intermediate alloys. The use of this technology in the generation of UV light for disinfection applications has many potential advantages over current technologies including power savings, long lamp life, mercury free, and lack of required warm-up times. In addition, depending on the composition of the AlGaIn structure, it is possible to select discrete emission wavelengths within the germicidal range,⁵⁶ as presented in Figure 17.15.

These UV LEDs are only currently available in limited quantities and are still in a developmental stage, having limited lifetimes of several hundred hours and an electrical power to germicidal UV conversion efficiency of less than 1%. The main reason for the reduced lifetime and low efficiency compared with visible light LEDs has been linked to a lack of an appropriate substrate, which historically has been sapphire or silicon carbide. Over the past 5 years, the development of an alternative to the aluminum nitride substrate has demonstrated promise in advancing this technology in the hope that LEDs emitting germicidal UV light will represent a viable disinfection technology for water and wastewater in the next 5 years.⁵⁶

UV Reactors

Two general classes of UV reactors exist: (a) open channels, and (b) closed vessels.

Open-channel reactors are typically utilized in wastewater disinfection applications. In open-channel reactors, water flows via gravity through a basin with the upper surface of the water open to the environment. Lamps are placed into the channel in racks or modules, either vertically or horizontally, as presented in Figures 17.16⁵⁷ and 17.17.⁵⁸

In open-channel reactors utilizing a horizontal lamp arrangement, the lamps are installed parallel to the flow of water. The modules that house these lamps must be removed from the channel to access the lamps, which are completely submerged within the water. In vertical lamp systems, lamps are oriented perpendicular to the water flow, with each lamp covering the entire water depth. This arrangement allows the lamps to be replaced individually from the top of the channel without removing the entire module.

Closed vessels are mainly applied in drinking water disinfection and, in some circumstances, are also utilized in wastewater and water reuse treatment. In these reactors, water flows through the vessel under pressurized conditions (i.e., no free water surface). There are four general closed vessel configurations: (a) in-line (Figure 17.18), (b) L-shaped, (c) Z-shaped, and (d) U-shaped.

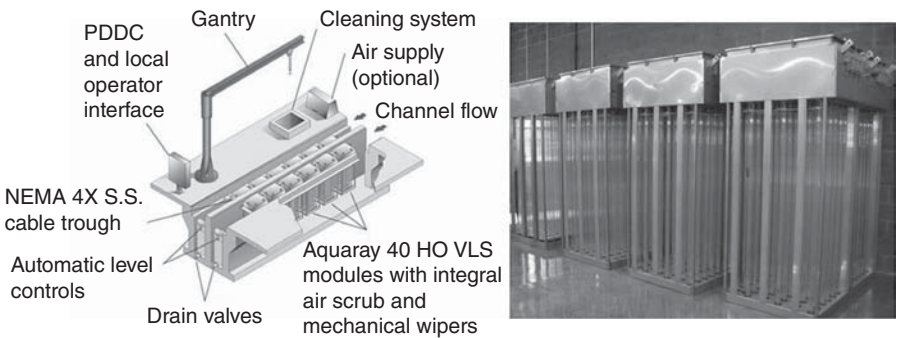


Figure 17.16. Vertical lamp arrangement of open-channel reactors.⁵⁷

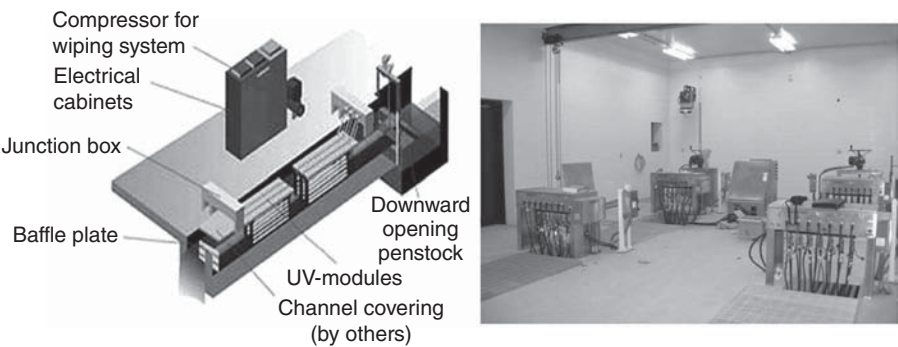


Figure 17.17. Horizontal lamp arrangement of open-channel reactors.⁵⁸

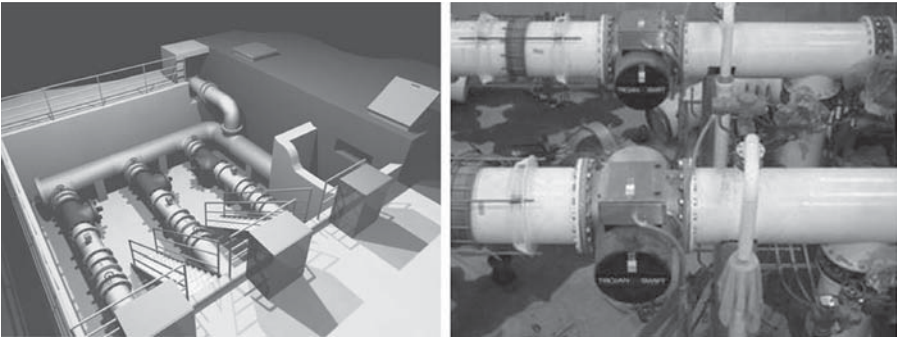


Figure 17.18. In-line enclosed vessel reactor configuration.

In-line reactors include those in which water flows straight through the reactor, with the flow path not requiring any bends or turns to enter or exit the vessel. These reactors may have a circular cross section or a rectangular cross section with expansion inlet and reduction outlet sections to connect to the plumbing of the system.

In L-, Z-, and U-shaped reactors, the lamps are oriented parallel to the water flow, with the lamps installed through the cross section of the vessel. As a result, one or both ends of the reactor are required for lamp access. Thus, the water flow cannot enter and exit the vessel at these locations. In L-shaped reactors, the flow path typically enters the reactor in a straight path but then must exit the reactor via a header that is located perpendicular to the reactor body, thus forcing the water to turn 90 degrees at the end of the vessel to exit. In Z- and U-shaped reactors, water enters the reactor via a header that is perpendicular to the reactor body, flows through the reactor, and then exits through another header that is perpendicular to the body of the reactor at the effluent end of the vessel. The difference between these two reactor configurations is that in a U-shaped reactor, the influent and effluent headers are located on the same side of the reactor, while in a Z-shaped reactor, the influent and effluent headers are located on opposite sides of the reactor.

Open-channel and closed-vessel reactors may also include baffle plates, guides, or mixers to improve the hydraulics through the UV reactor. Baffle plates are designed to straighten the flow through a UV reactor. Additional baffles or guides on channel or vessel walls are designed to direct flow closer to the lamps or to promote cross-sectional mixing of the water within the UV reactor. The purpose of these is to move water from low-intensity zones to high-intensity zones and thus minimize the dose distribution within a reactor. However, with increased baffling and mixing elements, the associated head loss through the reactor also increases.

An alternative but currently less popular design of UV reactors consists of using UV lamps that are not submerged in the water within the reactor.

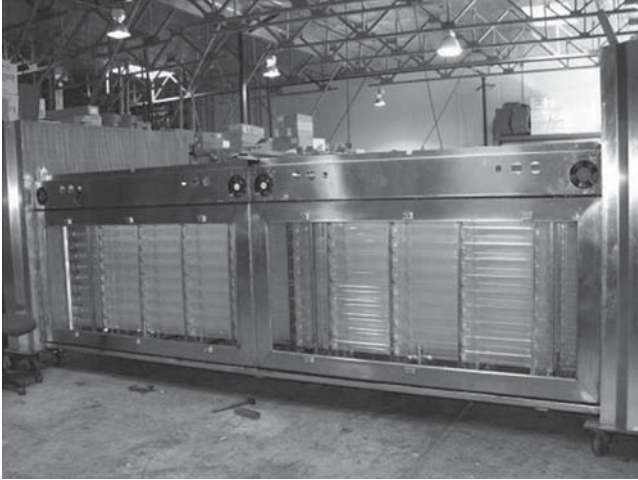


Figure 17.19. UV system with tubes.

In these “noncontact” systems, water flows through the reactor in a tube constructed of Teflon or alternative UV transmissive material. The UV lamps are placed outside the tube, and UV light emitted from the lamps passed through the tube and into the water, as shown in Figure 17.19. The goal of this design approach is to minimize the velocity distribution and create a more uniform dose distribution profile within the reactor, which is greatly impacted by the presence of the lamp/sleeve assemblies and associated support structures required in submerged lamp designs. Although this design approach has existed for some time, their application has been limited to smaller flow rates due to limitations in the tube diameter (in order to limit the intensity distribution in the cross section of the UV reactor) and head loss restrictions. However, this design approach has recently experienced a resurgence, with several UV manufacturers developing innovative approaches to combat the design issues associated with larger flow rates.

Ballasts

Ballasts are used to regulate the incoming power to the lamps for proper lamp ignition and operation. Two general types of ballasts are typically utilized in commercial UV applications: (a) electronic ballasts, and (b) magnetic ballasts. Magnetic ballasts can further be broken down into two types: (a) inductor-based magnetic ballasts, and (b) transformer-based magnetic ballasts.

Electronic ballasts and inductor-based magnetic ballasts allow for continuous adjustment of lamp output (i.e., intensity), thus allowing for greater dose control and increased operational power efficiency of the total UV system.

TABLE 17.6. Comparison of Magnetic and Electronic Ballasts³¹

Magnetic Ballasts	Electronic Ballasts
Less expensive	Continuous power adjustment and ability to adjust to lower power levels (e.g., 30%)
Continuous power adjustment occurs with inductor-based magnetic ballast (but not with transformer-based magnetic ballast)	More power efficient
More resistant to power surges	Lighter weight and smaller size
Proven technology (in use for nearly 70 years)	Allows for longer lamp operating life and less lamp end-darkening
Greater separation distance allowed between the UV reactor and the panel	

Transformer-based magnetic ballasts only allow step adjustment or fixed lamp output, and thus allow a reduced ability for system control and potentially higher operating costs due to overdosing. Transformer-based magnetic ballasts are typically more electrically efficient than inductor-based ballasts but are less electrically efficient than electronic ballasts.³¹ A comparison of electronic and magnetic ballasts is presented in Table 17.6.

Lamp Sleeves

Within the UV reactor of submerged lamp systems, the lamps are encased in sleeves, which serve to isolate the electrical components of the lamp from the water, help maintain optimal lamp operating temperatures, and serve to protect the lamps from liquid-generated forces and thermal shock. The lamp sleeves are typically constructed of high-purity quartz (vitreous silica). The diameter of the sleeves and the distance between the lamp and the sleeve vary between manufacturers. However, typically, sleeve diameters range between 2.5 and 5.0 cm for LP and LPHO lamps and 3.5 and 10.0 cm for MP lamps, with an approximate distance of 1 cm between the exterior lamp surface and the interior surface of the sleeve.⁴¹ Lamp placement within the length of the sleeve varies between UV system manufacturers and reactor designs. Sleeves can be open at both ends, or only open at a single end and domed on the other end. Open ends of the sleeves are sealed to prevent the ingress of water/moisture into the lamp assembly and to prevent the escape of any ozone that is formed within the lamp sleeve.⁴¹

Lamp sleeves are designed to withstand continuous pressures of up to 120 psi during normal operation in a UV reactor.⁴¹ They are most typically damaged during servicing due to improper installation and removal practices. During operation of the UV system, sleeves may also be damaged via water hammers, resonant vibrations, impacts by objects, and wiper system malfunctions, resulting in cracks or fractures.³¹ For the potential for sleeve

and lamp breakage to be minimized in an operating reactor, any sleeves observed as having defects or fractures should be immediately removed from the system.

UV Sensors

The UV sensor is the heart of the monitoring system for UV reactors. UV sensors monitor the intensity of UV light at a fixed point within a UV reactor. Depending on the UV system design, a reactor may have a sensor monitoring each individual lamp, as is typically the case for MP reactors, due to the relatively small number of lamps in these reactors. Alternatively, a UV reactor may employ a single sensor for a row, module, or rack of lamps, as is typically utilized for LP and LPHO reactors due to the larger number of lamps used in these reactors than in MP reactors. When a single sensor is being used to monitor a group of lamps, the sensor is typically monitoring a single lamp or a few lamps within that group, with the assumption that the intensity associated with the monitored lamp(s) is representative of that of the other lamps in that group. The intensity as measured by a UV sensor is a function of the lamp output, which is impacted by the power setting of the lamp, lamp age, sleeve age, and fouling of the quartz sleeve. Depending on the positioning of the UV sensor relative to the lamp(s), sensors may also measure changes in the UV intensity due to variations in the UVT of the water.

Sensors consist of four major components: (a) sensor housing, (b) optics, (c) photodetector, and (d) electronics/amplifier. The sensor housing is the physical body in which the sensor components are enclosed. The optics may include a sensor window (typically constructed of quartz), light pipes, diffusers, apertures, and filters. Sensor windows and light pipes deliver the light to the photodetector. However, diffusers and apertures may be used prior to the photodetector to reduce the amount of delivered light to reduce sensor degradation associated with UV exposure and thus extend the sensor lifetime.⁴¹ Filters may also be used to select the wavelengths of light measured by the sensor. Upon exposure to UV light, the photodetector generates a current, which is then converted into a signal (typically a 4- to 20-mA signal) by the electronics/amplifier, which is then sent to the UV systems programmable logic controller (PLC) for control purposes and/or sent to a display for general monitoring purposes.

Two general types of sensors are employed in water and wastewater UV disinfection systems: (a) wet sensors, and (b) dry sensors. Wet sensors are directly submerged in the water or have some portion of the sensor in direct contact with the internal wetted environment of a UV reactor. Dry sensors have a barrier between the water or wetted interior of a UV reactor. This barrier is typically constructed of housing with a quartz window allowing for the passage of UV light to the UV sensor. The major advantage of a dry sensor over that of a wet sensor is the ability to remove the sensor for replacement,

maintenance, or calibration without shutting down and/or draining the UV reactor.

Cleaning Systems

Several different approaches have been developed for the cleaning of lamp sleeves and UV sensors for the removal of system fouling. These methods can typically be divided into three general groups: (a) off-line chemical cleaning, (b) online mechanical cleaning, and (c) online mechanical–chemical cleaning. The frequency of both online and off-line cleaning is highly variable and can range from weekly to monthly to annually, depending on the site-specific water quality and associated fouling rate.

For closed-vessel reactors, off-line chemical cleaning systems consist of flushing or spraying the internals of a drained UV reactor with a cleaning agent, typically a citric or phosphoric acid-based solution. The cleaning solution is allowed a sufficient contact time with the reactor, after which it is drained, rinsed, and placed back into service. Off-line cleaning systems are typically associated with LP and LPHO drinking water disinfection systems, but these systems may also employ online cleaning systems, depending on the water quality and associated fouling rate.

For open-channel reactors, off-line chemical cleaning may be required even if the UV system employs some type of online wiping system. Off-line chemical cleaning of open-channel UV systems consists of a separate chamber or tub that is filled with an acid cleaning solution. The lamp modules or racks are removed from the channel and placed in the tub where the acid is allowed to dissolve the fouling from the sleeve. The module is removed from the tub, rinsed down, and placed back into the channel. In wastewater systems, regular cleaning is also required of the channel itself, including the baffle plate, walls, floor, and weir.

Online mechanical cleaning systems typically consist of Teflon rings or stainless steel brushes that wipe the sleeves and UV sensor and physically remove fouling. These wipers are driven up and down the quartz sleeves via electric motors or pneumatic piston drives. Online chemical and mechanical cleaning systems utilize a collar filled with a cleaning solution to remove fouling via the combination of physical contact and chemical cleaning. The cleaning agents utilized in systems are similar to that of off-line cleaning systems, typically consisting of a citric or phosphoric acid-based solution. An alternative online cleaning approach is using ultrasonic cleaning devices. This approach is not used in a majority of UV systems due to limited successful application³¹ and is typically limited to “noncontact” UV reactors where lamps are not placed in the path of the water flow, as reviewed in the “UV Reactors” section.

Online cleaning systems are typically utilized in wastewater applications due to the increased fouling tendency associated with a wastewater matrix and MP drinking water systems due to the increased fouling rate associated with

the higher temperatures of these lamps. LP and LPHO drinking water reactors may also require online cleaning. However, this is highly dependent on the water matrix and fouling potential of the source water.

Online UVT Monitors

Online UVT monitors allow for continuous, real-time measurement of the UVT. Depending on the operational strategy employed by the UV reactor, the online UVT measurement may be used for system control or solely as a monitoring parameter. Several types of on-line UVT monitors are commercially available and can be categorized into two general groups: (a) submerged monitors, and (b) flow-through monitors.

Submerged online UVT monitors are typically utilized in wastewater applications, where the monitor is partially submerged into the wastewater stream at a location that is representative of the water quality flowing through the UV system. These systems typically employ two sensors measuring intensity from a light source at a defined path length. One sensor measures the intensity through air, and the second measures the intensity through the wastewater. The difference between these two measurements is then used to calculate the amount of UV absorption at 254nm occurring in the wastewater and the associated UVT. Since these monitors are submerged into the wastewater, they are typically equipped with online cleaning systems to avoid fouling of the light source and UV sensor window.

Flow-through online UVT monitors are used in both drinking water and wastewater applications. Two types of flow-through monitors are commercially available. The first is a flow-through spectrophotometer that is first calibrated with a zero absorbance solution prior to it being placed into service. Once placed into service, the monitor measures the absorbance of UV light at a wavelength of 254nm through a defined path length, which is then converted into a UVT value. The second flow-through system is a device that measures the intensity at various distances from a LP lamp. The difference in the sensor readings coupled with the individual path lengths is used to calculate the UVT.⁴¹

Temperature Sensors/Water Level Probes

Approximately 60%–90% of the energy input to UV lamps is not converted to light but is wasted as heat.⁴¹ As water passes through the reactor, the heat generated by the lamps is constantly removed, preventing lamp overheating. Overheating of lamps may result in premature lamp aging, loss of UV intensity, and/or lamp failure. Overheating may be caused by excessively low flow rates or stagnant flow conditions, as well as low water levels in open channels or partially flooded closed vessels, resulting in lamp exposure to air. Thus, UV

systems typically employ water level probes to ensure that closed vessels are completely flooded and water levels are maintained to proper depths, so lamps are completely submerged in open-channel systems.

Due to their increased operating temperatures, MP UV systems typically install temperature sensors to ensure that the system is operating within a defined temperature zone. LP and LPHO UV systems may or may not employ temperature sensors due to their lower operating temperature. Depending on the operational strategy, a high water temperature or inadequate water level may result in the automatic shutting down of a reactor and/or triggering of an alarm to indicate corrective action by an operator.

WATER QUALITY ISSUES

UV Transmittance

As UV light passes through water, a fraction of that light is absorbed by constituents in the water matrix. UV transmittance is a water quality measurement that quantitates the amount of UV radiation at a particular wavelength that is able to pass through a defined path length of water (typically 1–10 cm). The UV transmittance of water at a wavelength of 254 nm (UVT_{254}) is the primary water quality parameter used as the basis of UV system design and is a function of the physical (suspended solids, turbidity) and chemical (humic/fulvic acids, dissolved organics and inorganics) properties of the water matrix. Typical UVT_{254} values range from 70% to 98% for filtered drinking water, from 55% to 75% for tertiary filtered wastewater effluent, from 45% to 65% for unfiltered secondary effluent, and 45% and below for raw wet-weather flows lacking upstream treatment using primary clarifier, high rate clarification, or biological treatment.

The attenuation of UV light as it passes through a water matrix can also be expressed in terms of UV absorbance at 254 nm (A_{254}). The relationship between UVT_{254} and A_{254} is presented in Equation (17.2).

$$UVT_{254} = 100 \times 10^{-A_{254}}, \quad (17.2)$$

where

UVT_{254} = UV transmittance at wavelength of 254 nm (%), and
 A_{254} = UV absorbance at wavelength of 254 nm.

Particles/Suspended Solids

Suspended solids not only impact the UVT of water but also decrease the efficacy of UV disinfection through their ability to shield microorganisms and scatter UV light within a reactor. The presence of suspended solids in a water

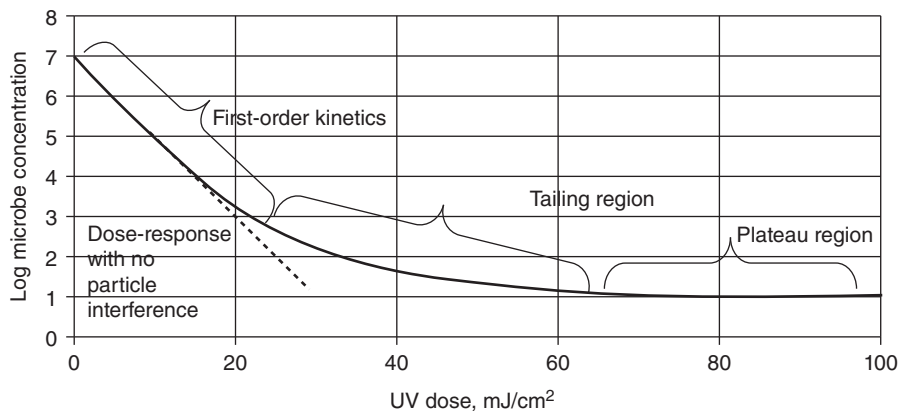


Figure 17.20. Impact of suspended solids on microbial dose response.⁵⁹

matrix can result and/or an inability to inactivate microorganisms to low levels, resulting in a microbial “residual concentration” that cannot be further reduced with continued exposure to UV light, resulting in a higher UV dose to achieve the required compliance level. The potential impact of suspended solids on the efficacy of UV disinfection is best described by the example of a microbial UV dose–response curve presented in Figure 17.20.⁵⁹

Figure 17.20 presents an example of UV dose–response curve for a microorganism resulting from a collimated beam analysis. The UV dose is on the x -axis of the graph, and the corresponding log concentration of a target microorganism is on the y -axis. There exist three regions of the dose–response curve: (a) Linear inactivation region: The reduction of the microorganism with an increasing dose follows first-order kinetics. The majority of microorganisms that are inactivated in this region are not associated with particles and are easily exposed to UV light. (2) Tailing region: This occurs as the dose response begins to deviate from first-order kinetics due to an increasing relative population of particle-associated microorganisms and, thus, a reduction in the efficacy of inactivation with an increasing UV dose. As the relative population of the particle-associated microorganisms continues to increase, UV dose has less and less of an impact on the inactivation rate. (3) Plateau region: With increasing UV doses, the microbial population consists mainly of particle-associated microorganisms that are embedded in and/or shielded from UV light. The presence of particles and their associated microbial populations prevent any additional measurable inactivation from taking place, resulting in a microbial “residual concentration.”

It is important to consider not only the concentration of suspended solids in a water matrix but also the particle size distribution, as larger particles will more effectively shield microorganisms from UV light. Studies have demonstrated that waters having similar total suspended solids (TSS) and turbidity levels required very different UV doses to attain similar levels of microbial

inactivation, which were attributed to differences in the particle size distribution.⁶⁰ Particles larger than 8–10 μm have been demonstrated to adversely impact the efficacy of UV disinfection.⁶¹

Several studies have found that the impacts of turbidity levels up to 10 nephelometric turbidity unit (NTU) do not have any additional impact on the efficacy of UV disinfection other than an impact on the UVT of the water.^{62,63}

Fouling

Fouling within UV reactors occurs when substances are deposited on the quartz sleeves, UV sensors, and walls of a UV reactor. The rate of fouling in a UV reactor is highly variable between water sources with the time required for significant fouling to occur in a UV reactor ranging from a few hours to several months. The fouling rate is impacted by hardness (as CaCO_3), alkalinity, temperature, ion concentration, oxidation–reduction potential (ORP), and pH. Fouling may result from the following:

- Precipitation of compounds resulting from decreased solubility at increased temperatures, including CaCO_3 , CaSO_4 , MgCO_3 , MgSO_4 , FePO_4 , FeCO_3 , and $\text{Al}_2(\text{SO}_4)_3$ ⁴¹
- Photochemical reactions with water constituents not related to temperature⁶⁴
- Precipitation of compounds with low solubility, including $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ ⁴¹
- Deposition of particles due to gravity settling and turbulence-induced collisions⁶⁵
- Precipitation of oxidized inorganic constituents⁶⁶

Fouling of quartz sleeves reduces the ability of the sleeves to transmit UV light from the lamp into the water, thus reducing the power efficiency of the UV system. With increased sleeve fouling, more power needs to be supplied to the lamps to deliver the appropriate intensity to the UV sensors to maintain the required dose.

UV sensors can also foul, which impacts their ability to accurately measure the intensity of the UV light within a reactor, thus also reducing the power efficiency of the UV system. As the fouling on the wetted sensor window increases, the transmittance of the sensor window decreases as well as the intensity measured by the sensor. In the absence of proper cleaning, the sensor will continue to foul, causing the power of the lamps to slowly increase over time to compensate for the decreased sensor measurement.

In addition to inorganic deposits, fouling may also occur in the form of biofilms and algae growth. Biological growth in UV reactors typically occurs when a reactor is not in operation and remains flooded with water. Biofilms may coat the sleeves and sensors as well as the walls of closed-vessel

and open-channel systems. Algae growth, typically associated with open-channel wastewater system, presents fouling issues when upstream processes or channel sections are exposed to sunlight. As the algae flow through the UV channel, they can attach to the sleeves and support structure UV modules. As algae continuously build up in the channel, they can begin to impact the disinfection process by reducing the amount of UV light penetrating into the surrounding water. The visible light from MP UV systems may also promote the growth of algae, and this must be controlled by cleaning. In addition, settled solids or debris present at the bottom of a UV channel may act as a protective environment, shielding microorganisms from the UV light, thus impacting the disinfection efficacy of the UV system.

Algae and biofilms present on the channel walls downstream of the UV reactor may also act as a protective environment for surviving microorganisms in the UV reactor effluent. In situations where extensive growth occurs on channel walls, microbial sampling conducted downstream from such areas may result in counts that are falsely high compared with the UV reactor effluent due to the reintroduction of these populations into the water stream.

It is important to note, however, that the cleaning systems employed in open-channel UV systems do not address the fouling associated with channel walls or the buildup of deposits on the channel floor, and cleaning of these areas must be conducted manually by plant personnel.

UV SYSTEM SIZING TOOLS

Several methodologies are currently used to size and design UV disinfection systems for water and wastewater applications. These approaches can be separated into two general groups: (a) UV system validation, and (b) nonbiological, mathematical-based modeling.

UV System Validation

Because the UV dose delivered is a complex function of many variables, UV reactor validation is used to demonstrate the disinfection efficacy of a system. In essence, the disinfection performance of a UV system is determined based on a series of microbial challenges that are conducted either on full- or pilot-scale UV reactors. During a validation, a UV system is evaluated under various operational conditions, which may include flow rate, UVT, lamp power (or relative lamp output), water level, and number of operational lamps. During each test condition, samples are collected from the influent and effluent of the UV reactor to quantitate the level of inactivation of a target challenge organism that is associated with the specific operational conditions.

Additional samples are collected from the influent of the UV reactor for collimated beam analysis. During the collimated beam analysis, the influent sample is split into a series of subsamples, with each subsample exposed to a different discrete UV dose. Following UV exposure, the concentration of the challenge organism is determined and then compared with the concentration of a subsample that was not exposed to UV (zero dose) to determine the level of inactivation of the challenge organism occurring at each collimated beam UV dose. These data are utilized to construct a dose–response curve of the challenge organism, demonstrating the level of inactivation as a function of UV dose. The level of inactivation occurring for a particular test condition is then compared with the dose–response curve to determine the UV dose associated with the specific operational conditions of the UV system for that individual test condition.

The challenge organism utilized for the UV system validation may be an ambient microbial population of the tested water source or may also be an alternate challenge organism that is injected upstream of the reactor and completely mixed into the source water prior to being exposed to UV disinfection. Typical challenge organisms utilized for validation of UV systems and their reported UV dose requirements based on collimated beam tests are presented in Table 17.7.

Additives may also be added to adjust the UVT of the water and, if necessary, quench any existing chemical disinfectants present in the source water so that any inactivation of the challenge organism is limited to that associated with UV. Typical UV absorbers include instant coffee, lignin sulfonic acid (LSA), and humic acids and are used in either water or wastewater for adjustment of the transmittance.

To ensure that the UV absorber, challenge organism, and any other additives are well mixed in the influent water entering the UV reactor, the

TABLE 17.7. UV Dose Requirements for Commonly Used Challenge Organisms^{67–72}

Microorganism	Reported UV Dose Requirements (mJ/cm ²) for Stated Log Inactivation			
	1-log	2-log	3-log	4-log
<i>E. coli</i> ¹	3.0	4.8	6.7	8.4
<i>Bacillus subtilis</i> spores ²	28	39	50	62
MS2 phage ³	16	34	52	71
Q β phage ⁴	10.9	22.5	34.6	47.6
T7 phage ⁴	3.6	7.5	11.8	16.6
T1 phage ⁵	~5	~10	~15	~20
PRD-1 phage ⁶	9.9	17	24	30
B40-8 phage ²	12	18	23	28
$\Phi \times 174$ phage ²	2.2	5.3	7.3	11

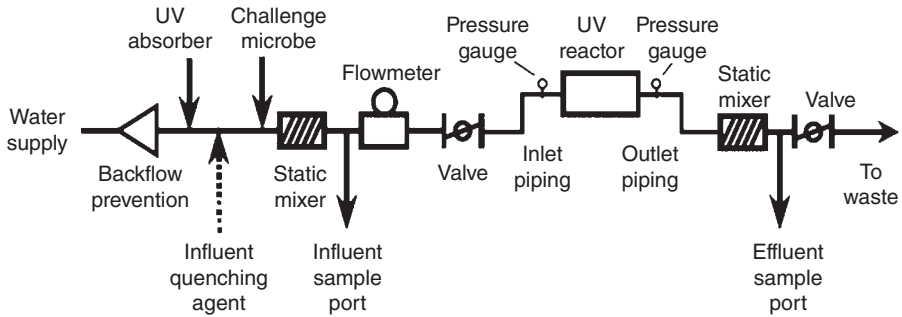


Figure 17.21. Typical validation test stand arrangement.³¹

validation test stand typically includes a static mixer located after additive injection and prior to the influent sample port. An effluent static mixer is also typically installed to ensure that the microbial concentration in the reactor effluent is well mixed prior to the effluent sampling port. In addition to static mixers, the validation test stand typically includes additional equipment, such as piping, backflow prevention, flowmeter, pressure gauges (for closed vessels), and flow control/isolation valves, as presented in Figure 17.21.⁴¹

Since the UV system disinfection performance derived from the validation process is based on the measurement of inactivation associated with challenge organisms, this process has also been termed a bioassay or biodosimetry. Several different formal protocols for UV system validation exist for both water and wastewater applications, which are reviewed in detail in the following sections.

Drinking Water Validation. Formal UV system validation protocols for drinking water applications in the United States consist of the USEPA *UV Disinfection Guidance Manual*³¹ and the NWRI/AwwaRF *UV Disinfection Guidelines for Drinking Water and Water Reuse*.³⁸ The following sections provide a detailed review of the *UVDGM* and NWRI protocols and a general summary of the Central European validation procedures, including those developed by the Austrian Standards Institute (ÖNORM: Österreichisches Normungsinstitut):^{73,74} and the German Technical and Scientific Association for Gas and Water (DVGW: Deutsche Vereinigung des Gas- und Wasserfaches e.V.—Technisch-wissenschaftlicher Verein).⁷⁵

USEPA's UV Disinfection Guidance Manual.³¹ Chapter 5 of the *UVDGM* reviews the validation procedures for UV systems for the disinfection of surface water or groundwater under the direct influence of surface water. Several appendixes of the *UVDGM* provide additional details on the validation procedure including Appendix A, “Preparing and Assaying Challenge Microorganisms”; Appendix B, “UV Reactor Testing Examples”; and

Appendix C, “Collimated Beam Testing to Develop a Dose–Response Curve.” The following sections review the challenge microorganisms utilized in the biodosimetry testing and UV dose requirements for disinfection at PWSs, validation location and test stand considerations, dose-monitoring approaches and associated validation test conditions, sampling and data-recording requirements, collimated beam analysis, and biodosimetry data analysis.

Challenge Microorganisms and UV Dose Requirements. The *UVDGM* allows for the use of a variety of challenge organisms to validate UV disinfection performance. The approach recommended by the *UVDGM* is to validate a UV system using a challenge organism having a similar dose response to the target pathogen of a full-scale installation or two challenge organisms with UV sensitivities that bracket that of the target pathogen of a full-scale installation. The target pathogens of concern to PWSs in the United States, as established by the *LT2ESWTR*, include (in order of increasing UV resistance) *Giardia*, *Cryptosporidium*, and viruses. The dose requirements associated with 0.5–4log inactivation of these target pathogens are presented in Table 17.8.

Validation Location and Test Stand Considerations. The USEPA recommends that the validation testing and associated data analysis be overseen by an independent third party to ensure that the evaluation is conducted in a technically sound manner and without bias. Validation can be conducted on-site at a water treatment plant or off-site at a third-party validation test center or at a UV manufacturer’s facility. If conducted off-site, the *UVDGM* recommends that the validation utilize a potable water source with high UVT. Validation testing must be conducted on a full-scale unit, with identical wetted dimensions, as the reactors to be installed at a water treatment facility in which the validation results are applied (i.e., scaling or extrapolation of results from systems of different size *is not* allowed).

The hydraulic impact of the piping arrangement on the UV dose associated with the validation test stand as compared to that utilized at the water treatment facility is addressed by the *UVDGM*. The *UVDGM* states that the influent and effluent piping arrangement used in the test stand should result in UV doses that are greater than or equal to those resulting from the setup used at

TABLE 17.8. *LT2ESWTR* UV Dose Requirements (in mJ/cm²)³¹

Target Pathogens	Log Inactivation							
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
<i>Cryptosporidium</i>	1.6	2.5	3.9	5.8	8.5	12	15	22
<i>Giardia</i>	1.5	2.1	3.0	5.2	7.7	11	15	22
Virus	39	58	79	100	121	143	163	186

a water treatment facility. If off-site validation is utilized for validation of a UV system, the *UVDGM* recommends the following preferred options to meet this requirement:

- **Minimum five pipe diameters of straight pipe upstream of UV reactor.** The length of straight pipe installed at the water treatment facility should be equal to the straight length of pipe installed immediately upstream of a reactor during validation plus a minimum pipe length of five pipe diameters.
- **Identical inlet and outlet conditions.** Identical inlet and outlet pipe configurations utilized in both the validation test stand and the water treatment facility should be identical for at least ten and five pipe diameters, respectively.
- **Velocity profile measurement.** Velocity profile measured upstream and downstream of the reactor at both the validation test stand and the water treatment facility is within 20% of the theoretical velocity.

In addition, the *UVDGM* recommends that the influent piping should not contain any expansions for a minimum of 10 pipe diameters and that all valves located in this length of pipe should be fully open during normal operation of the UV system to avoid jetting flow through the reactor.

Dose-Monitoring Approaches and Validation Test Conditions. The test conditions that need to be evaluated during validation are highly dependant on the dose-monitoring strategy that is employed by the UV reactor. The *UVDGM* recognizes two general types of monitoring approaches: (a) the UV intensity set point approach, and (b) the calculated dose approach.

The UV Intensity Set point Approach. During operation, delivery of the required dose by the UV system is ensured by maintaining the UV intensity at or above preestablished intensity set point(s). Reactors must also be operated with a flow rate equal to or less than the validated flow rate, and the operational lamp status (on/off setting) must be equivalent to the settings used during validation testing. UVT monitoring is not required since the validation approach accounts for the impact of UVT on sensor readings. A single-set point approach as well as a multiple-set point approach that varies as a function of flow rate can be utilized.

The intensity set point is typically established by the UV manufacturer. This intensity value is based on the minimum design UVT and the expected intensity of the lamp at the end of its operational lifetime with a further reduction applied to account for a fouling factor. This approach requires a minimum of two validation test conditions. The first of these conditions consists of evaluating the maximum design flow rate with the lamps operating at 100% power and the UVT decreasing until the UV intensity set point is reached. For the second test condition, the flow is maintained at the same rate, the

UVT is adjusted to a maximum attainable value, and the lamp power is decreased until the UV intensity set point is attained.

Testing in this manner allows for the determination of the minimum dose that can be attained at the UV intensity set point regardless of whether the decrease in intensity is due to a decrease in UVT, lamp output, or a combination of both factors. Additional test conditions at alternative flow rates can also be conducted if multiple UV intensity set points are utilized in the UV system monitoring approach.

Calculated Dose Approach. A dose-monitoring equation is used by the UV system to determine a calculated UV dose based on the operational conditions of the reactor. The calculated UV dose must then be divided by a validation factor to calculate a validated dose, which is then compared with the required dose for the desired level of inactivation of the target pathogen. Reactors must operate with a UVT that is equal to or greater than the minimum validated UVT, and the flow rate must not exceed the flow range evaluated during validation testing. All other operational conditions of the UV reactor that are part of the dose-monitoring equation must be maintained within the validated range.

For the calculated dose approach, the required validation conditions depend on the operating variables that must be accounted for in the dose-monitoring equation to accurately estimate the UV dose. Operational parameters that are typically included in this equation consist of flow rate, intensity, and UVT and may also include the number of operational lamps. For each operational parameter included in the dose-monitoring equation, the *UVDGM* recommends that a minimum of three conditions be evaluated during validation to allow for interpolation between test points. Many validations consist of the evaluation of three operational parameters (flow, intensity, and UVT), resulting in a test matrix having a minimum of 27 test conditions ($3 \times 3 \times 3 = 27$). More or less test conditions may be required, depending on the quantity of operational parameters included in the dose-monitoring equation. The range of the individual operational parameters should be the minimum and maximum design parameters and operational limits of the UV disinfection system.

Sampling and Data Recording. For both the UV intensity set point and calculated dose approach, a minimum of three replicate influent and effluent samples should be collected for each test condition for microbial analysis. The UVT of the influent water should be measured with a spectrophotometer for each individual influent replicate. During each test condition, operational parameters should be recorded, including flow rate, UV intensity, power setting, number of operational lamps (if applicable), online UVT measurement (if applicable), head loss, and power consumption.

At least one influent sample should be collected per day of validation testing for collimated beam analysis. In addition, a minimum of two collimated beam samples should be collected throughout validation testing at the

maximum and minimum evaluated UVT. The *UVDGM* also recommends that samples, including reactor controls, reactor blanks, trip controls, method blanks, and stability samples, be collected during validation for quality control purposes.

Collimated Beam Analysis. The *UVDGM* recommends that the collimated beam test should incorporate a minimum of five dose points in addition to the zero dose control. The selected doses should cover the range of the targeted doses evaluated in the reactor test conditions, with the maximum dose resulting in a 0.5- to 1.0-log inactivation greater than that of the highest achieved by the UV reactor. The *UVDGM* provides detailed test procedures and criteria regarding the uncertainty associated with the UV spectrophotometer, radiometer, and measurement of components included in the dose calculation for the collimated beam procedure.

The UV dose delivered to a sample during the collimated beam analysis is calculated via Equation (17.3):

$$D_{CB} = E_S P_f (1 - R) \frac{L}{(d + L)} \frac{(1 - 10^{-A_{254}d})}{A_{254}d \ln(10)} t, \quad (17.3)$$

where

- D_{CB} = UV dose (mJ/cm²),
- E_S = average UV intensity (mW/cm²) from measurements conducted before and after sample exposure at center of sample surface,
- P_f = petri factor (unitless),
- R = reflectance at the air–water interface (unitless),
- L = distance from lamp centerline to suspension surface (cm),
- d = depth of sample,
- A_{254} = UV absorbance at 254 nm (unitless), and
- t = exposure time (s).

Alternatively, Equation (17.3) can be rearranged to solve for the required exposure time for a desired UV dose. The *UVDGM* recommends that each dose exposure be conducted in duplicate as a minimum, with three replicates suggested to improve the quality of the fit of the dose–response curve.

To construct the dose–response curve for the challenge organism, the *UVDGM* recommends to first conduct a regression analysis on the microbial log concentration as a function of UV dose. An example of this regression is presented in Figure 17.22.

The log inactivation of the challenge organism for each individual collimated beam dose (including the zero dose) is calculated via Equation (17.4):

$$LI = \text{Log}N_0 - \text{Log}N, \quad (17.4)$$

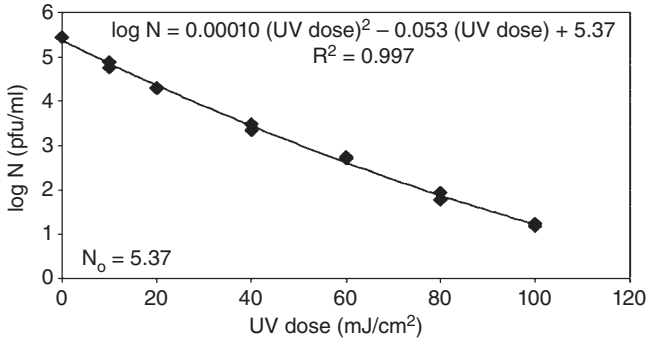


Figure 17.22. Microbial log concentration as a function of UV dose.³¹

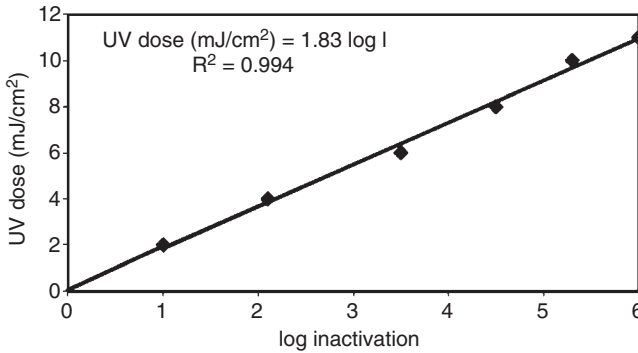


Figure 17.23. Typical *E. coli* linear dose-response curve.³¹

where

LI = log inactivation of the challenge organism,

$\log N_0$ = the common, initial log concentration of Figure 17.22 (y-intercept), and

$\log N$ = concentration of the challenge organism in petri dish after UV exposure.

A regression analysis is then conducted on the collimated beam UV dose as a function of the log inactivation of the challenge organism, resulting in the generation of the dose-response equation. The shape of the dose-response curve depends on the inactivation kinetics of the challenge organism, with both linear and quadratic equations accepted by the *UVDGM*, depending on the relationship that best fits the data. Examples of a linear dose-response curve typical for *Escherichia coli* and quadratic dose-response equation typical for MS2 are presented in Figures 17.23 and 17.24, respectively.

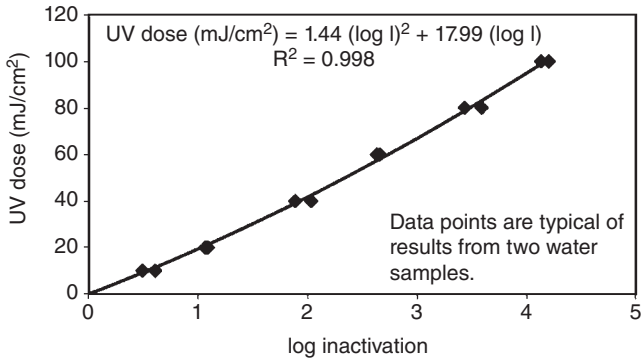


Figure 17.24. Typical MS2 quadratic dose-response curve.³¹

The uncertainty associated with the collimated beam analysis (U_{DR}) is determined from the 95% confidence interval, which can be calculated via standard statistical methods or conservatively estimated via the following equation provided in the *UVDGM*:

$$U_{DR} = t \frac{SD}{UV Dose_{CB}} \times 100\%, \quad (17.5)$$

where

U_{DR} = uncertainty of the UV dose-response fit at a 95% confidence interval,

$UV Dose_{CB}$ = UV dose calculated from the UV dose-response curve for the challenge organism,

SD = standard deviation of the difference between the calculated and the measured UV dose response, and

t = t-statistic at a 95% confidence interval.

Biodosimetry Data Analysis. The log inactivation occurring in the reactor for each test condition replicate is calculated via Equation (17.6):

$$\text{Log } I = \log \left[\frac{N_0}{N} \right], \quad (17.6)$$

where

N_0 = concentration of challenge organism in influent sample (pfu/ml or cfu/ml), and

N = concentration of challenge organism in effluent sample (pfu/ml or cfu/ml).

The RED for each test condition replicate is calculated with the associated dose–response curve generated by the collimated beam analysis and the measured log inactivation determined via Equation (17.6).

For UV systems utilizing the UV intensity set point monitoring approach, the replicate RED values should be averaged for each test condition. The minimum RED of the two test conditions for a single intensity set point should be selected as the validated RED.

For UV systems utilizing the calculated UV monitoring approach, the UVDGM recommends using a multivariate linear regression to fit an equation to the validation test data. Typical variables that are included in the dose-monitoring equation include UVT or UV absorbance, flow rate, UV intensity, and possibly the number of operating lamps or banks of lamps. An example of a dose-monitoring equation is presented as Equation (17.7):

$$\text{RED} = 10^A \times A_{254}^B \times (S/S_0)^C \times (1/Q)^D \times B^E, \quad (17.7)$$

where

- RED = calculated RED, also referred to as the “calculated dose,”
- A_{254} = UV absorbance at 254 nm,
- S = measured UV intensity by UV sensors,
- S_0 = UV intensity of new lamps at 100% power in clean (no fouling) conditions, typically expressed as a function of UVT,
- Q = flow rate,
- B = number of operating lamps or banks of lamps, and
- A, B, C, D, E = model coefficients.

Due to the uncertainties and biases associated with the biodisimetry-based validation approach, the UVDGM utilizes a safety factor that is applied to the RED for the determination of the “validated dose.” This safety factor is referred to as the validation factor and is derived via Equation (17.8):

$$VF = B_{RED} \times \left[\frac{U_{Val}}{100} \right], \quad (17.8)$$

where

- VF = validation factor,
- B_{RED} = RED bias factor, and
- U_{Val} = uncertainty of validation (%).

The RED bias factor is a correction factor to account for the difference between the RED measured by the challenge organism and the dose delivered

to the target pathogen as a result of the difference between the inactivation kinetics of the two organisms and the dose distribution occurring throughout a UV reactor. Appendix G of the *UVDGM* provides values for the RED bias factor based on the sensitivity of the challenge organism, level of log inactivation of a specific target pathogen, and UVT.

The uncertainty of validation (U_{Val}) accounts for the experimental uncertainty of the validation process and is comprised of between one and three input variables. The equations used to determine U_{Val} for UV systems utilizing the UV intensity set point and calculated dose-monitoring approaches are presented as Equations (17.9) and (17.10), respectively:

$$U_{Val} = (U_{SP}^2 + U_S^2 + U_{DR}^2)^{1/2} \quad (17.9)$$

$$U_{Val} = (U_{IN}^2 + U_S^2 + U_{DR}^2)^{1/2}, \quad (17.10)$$

where

U_{Val} = uncertainty of validation,

U_{SP} = uncertainty of set point,

U_{IN} = uncertainty of interpolation of the dose-monitoring equation,

U_S = uncertainty of sensor value, and

U_{DR} = uncertainty of the fit of the dose–response curve.

If the U_S is less than 10% (using Eq. 17.11) and the U_{DR} is less than 30% (using Eq. 17.5 or less than 15% using standard statistical methods), these terms can be removed from the above equations. The sensor uncertainty is determined by comparing duty sensor measurements to calibrated reference sensors during the validation process by using the equation below:

$$U_S = \left[\frac{S_{duty}}{S_{Ref,avg}} \right], \quad (17.11)$$

where

S_{duty} = intensity measured by a duty sensor, and

$S_{Ref,avg}$ = average UV intensity measured by reference sensors (minimum of two).

U_{SP} and U_{IN} are calculated via Equations (17.12) and (17.13), respectively:

$$U_{SP} = \frac{t \times SD_{RED}}{RED} \times 100\%, \quad (17.12)$$

where

RED = average RED value measured for each test condition,
 SD_{RE} = standard deviation of the RED values for each test condition, and
 t = t-statistic at a 95% confidence interval,

$$U_{IN} = \frac{t \times SD}{RED} \times 100\%, \quad (17.13)$$

where

RED = RED calculated from dose-monitoring equation,
 SD = standard deviation of the difference between the observed RED
 and the calculated RED from the dose-monitoring equation, and
 t = t-statistic at a 95% confidence interval.

The validated dose is then determined by dividing the RED by the validation factor, as presented in Equation (17.14):

$$Validated\ Dose = RED/VF \quad (17.14)$$

where

RED = RED calculated with the dose-monitoring equation for the calculated dose-monitoring approach or the minimum RED for the UV intensity set point monitoring approach, and
 VF = validation factor.

NWRI/AwwaRF Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse.³⁸ Chapter 3 of the *NWRI/AwwaRF Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse* (hereon referred to as the *NWRI Guidelines*) reviews the validation procedures for UV systems for the disinfection of water and water reuse. The following sections review the challenge microorganisms utilized in the biosimetry testing and UV dose requirements for disinfection at PWSs; validation location and test stand considerations; dose-monitoring approaches and associated validation test conditions; sampling and data-recording requirements; collimated beam analysis; and biosimetry data analysis.

Challenge Microorganisms and UV Dose Requirements. Unlike the *UVDGM*, the testing procedures established in the *NWRI guidelines* are based on the use of a single challenge organism, MS2 bacteriophage, for the validation of UV systems for drinking water applications. Since these guidelines are not a descendant of a federal regulation (like the *UVDGM* and the

LT2ESWTR), it does not build upon or establish UV dose values that are required for the log inactivation of target pathogens. Instead, the NWRI testing protocol solely provides a validation approach that can be used to deduce delivery of a MS2-based RED as a function of the operational conditions of a UV system.

Validation Location and Test Stand Considerations. The NWRI guidelines state that validation testing must be conducted by an independent third party and witnessed by an independent, experienced, registered engineer. The validation facilities must be acceptable to the appropriate regulatory agency. Off-site validation testing with a finished drinking water source is allowed if the UV system is disinfecting filtered surface water or groundwater. However, if the UV system is treating unfiltered surface water, an on-site validation must be conducted to address the site-specific impact of particulates on the dose requirements. As is the case with the *UVDGM*, validation testing must be conducted with a full-scale reactor, having the same wetted dimensions as the reactor(s) to be installed at the disinfection facility of a PWS.

The validation test stand piping configuration is not prescribed in these guidelines. However, the protocol requires that the installation configuration be recorded, noting that the tested arrangement will constitute the conditions under which the biosimetry results are valid.

Dose-Monitoring Approaches and Validation Test Conditions. The NWRI guidelines do not provide guidelines on specific dose-monitoring strategies other than outlining specific water quality and reactor operational parameters that must be continuously monitored. These parameters include flow rate, UVT, turbidity, UV intensity and operational UV dose.

The performance of the UV reactor is validated at a minimum sensor reading over a specified flow rate range. The minimum sensor reading is achieved by using two methodologies. The first approach operates the lamps at full output and reduces the UVT of the water to achieve the minimum sensor reading. The second approach achieves the minimum sensor reading by lowering the output of the lamps while the UVT is maintained at a high UVT. The methodology that results in a test having the lowest MS2 log inactivation is deemed the limiting factor for sensor sensitivity, and will be utilized to achieve the minimum sensor reading for the following biosimetry testing.

A minimum of four flow rate test conditions are included in the reactor validation, including the operational minimum and maximum as well as a minimum of two intermediate flow rates. The maximum interval between two flow rates cannot exceed 150% of the lower flow rate. Each test condition is conducted three times, resulting in a minimum of 12 test conditions for a single minimum sensor value. More test conditions can be required, depending on the size of the flow rate range and/or evaluation of multiple minimum sensor

values. Additional testing may also be conducted to determine the impact of changes to the UVT and sensor readings on the operational UV dose.

Sampling and Data Recording. During each replicate test condition, three samples must be collected from the influent and effluent of the UV reactor. An additional influent sample must also be collected for collimated beam testing. During validation, the flow rate, UVT, electrical supply voltage, lamp power consumption, and UV intensity must be continuously monitored and recorded. In addition, the water temperature, pressure, and head loss across the UV reactor must be measured for each replicate test condition.

The cross-sectional velocity profile of the UV reactor must also be established 0.3 m upstream and downstream of the UV lamps of a single reactor or reactor series (if multiple reactors are validated). The water velocity is measured in a grid with the points spaced 6–12 cm apart. For reactors smaller than 25 cm wide, a minimum grid size of four points is required, with larger reactors requiring a minimum grid size of nine points. At each validated flow rate, three velocity measurements are conducted at each point in the grid.

Collimated Beam Analysis. The NWRI guidelines recommend that the collimated beam test should incorporate a zero dose control and a minimum of five dose points ranging from 20 to 150 mJ/cm², with a minimum interval of 25 mJ/cm². The collimated beam procedure should be conducted within 24 h of sample collection, and the microbial concentration should be analyzed directly following UV exposure.

The UV dose delivered to a sample during collimated beam analysis is calculated in the NWRI guidelines via Equation (17.15):

$$D = I_0 R t \left| \frac{1 - e^{-kd}}{kd} \right|, \quad (17.15)$$

where

D = UV dose (mJ/cm²),

R = reflectance at the air–water interface (unitless),

I_0 = average UV intensity (mW/cm²) from measurements conducted before and after sample exposure at the center of the sample surface,

t = exposure time (s),

k = absorbance coefficient (cm⁻¹), and

d = depth of sample (cm).

The absorbance coefficient can be determined from the absorbance of the water sample as measured with a spectrophotometer via Equation (17.16):

$$k = (2.3)(A_{254}), \quad (17.16)$$

where

k = absorbance coefficient, and
 A_{254} = absorbance at 254 nm.

For the MS2 dose–response curve to be constructed, the log inactivation for each collimated beam dose exposure must first be calculated by using Equation (17.17):

$$LI = -\log \left| \frac{N}{N_0} \right|, \quad (17.17)$$

where

LI = log inactivation,
 N = concentration of MS2 in a sample after UV exposure, and
 N_0 = concentration of MS2 in a zero dose control (no UV exposure).

The resulting log inactivation is used to develop the MS2 dose–response curve by plotting MS2 log inactivation as a function of UV dose. The dose response of the challenge MS2 must fall within the area bound by two dose response equations stated in the NWRI guidelines, as presented in Figure 17.25. This QA/QC check is to verify if the propagation, preparation, and enumeration of the MS2 stock result in the production of a homogenous, monodispersed culture having acceptable disinfection kinetics and dose–response curve.

Biodosimetry Data Analysis. Velocity profile testing is conducted with three measurements at each grid location in the cross section of the UV reactor. The mean measured velocity of each location should not vary by more than 20% from the theoretical average velocity determined by dividing the flow rate by the cross-sectional area. If the measured velocity is outside these

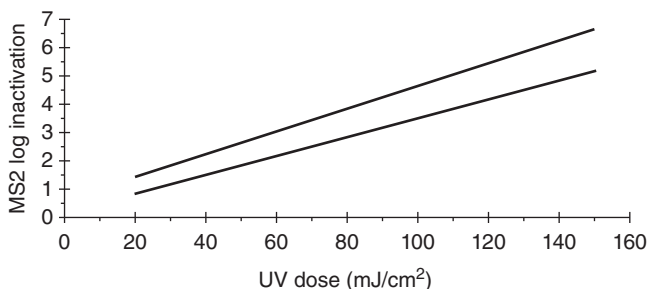


Figure 17.25. NWRI guidelines MS2 upper- and lower-bound dose–response curves.

bounds, an alternate profile is acceptable should it be demonstrated to provide satisfactory performance and the same profile is measured on-site in the reactor(s) at the UV facility during performance testing.

The log inactivation occurring in the reactor for each biosimetry test condition is determined in the same manner as the *UVDGM*, via Equation 17.17 using the average influent and effluent MS2 concentrations. For the uncertainty associated with the biosimetry testing process and application of these validation results to operational systems to be accounted for, the MS2 inactivation value associated with each flow rate is determined as the lower 90% confidence value by using the Student *t* distribution.

The delivered UV dose associated with each validated flow condition is calculated with the associated dose–response curve that was generated from the collimated beam analysis and the lower 90% MS2 log inactivation value. Validation results are plotted as the delivered UV dose as a function of flow per lamp, as presented in Figure 17.26.

Interpolation of UV reactor performance between evaluated flow rates and sensor readings is permitted. Extrapolation of UV system performance outside of the validated flow rates and sensor readings is not permitted, and any such operational conditions would require additional validation testing.

Central European Validation Protocols.^{73–75} The Central European validation procedures include those developed by the Austrian Standards Institute (ÖNORM: Österreichisches Normungsinstitut) and the German Technical and Scientific Association for Gas and Water (DVGW: Deutscher Verein des Gas- und Wasserfaches e.V.). Although the ÖNORM and DVGW validation protocols utilized the same basic biosimetric techniques as the *UVDGM* and NWRI guidelines, the protocols differ in several aspects.

The ÖNORM and DVGW protocols allow the use of a single organism, *Bacillus subtilis* spores, as the challenge microorganism, with standardized safety factors applied to the biosimetry results to account for validation uncertainty. Full-scale UV systems for drinking water installations in Austria and Germany must be validated and deliver a standardized UV dose of

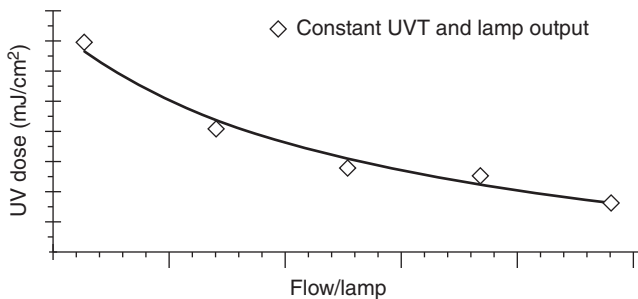


Figure 17.26. Delivered UV dose as a function of flow per lamp.

40 mJ/cm² for a minimum 4-log inactivation of human pathogens typically transmitted in water (including bacteria, *Cryptosporidium*, and a majority of viruses).

Testing is conducted at official test centers in Austria and Germany, with the validation test stand consisting of a 90 degree bend located directly upstream of the UV reactor to replicate “worst case” hydraulic scenarios through the UV reactor. The dose-monitoring strategy employed by these UV systems is based on the UV intensity set point approach. Utilizing this approach, a UV system is delivering a dose of 40 mJ/cm² or greater when the intensity is maintained at or above the set point, with a flow rate not exceeding a maximum validated value. ÖNORM protocols allow for additional flexibility in UV system controls through the addition of an online UVT monitor to the dose-monitoring strategy.

These validation protocols are similar to the *UVDGM* procedures associated with the validation of reactors employing the UV intensity set point monitoring approach. Testing is conducted over a series of flow rates, with the intensity set point attained in two different manners: (a) reducing of the UVT while maintaining lamps at 100% power, and (a) reducing the lamp output while maintaining the UVT at a high value. The lowest flow rate resulting in the delivery of 40 mJ/cm² is validated as the maximum flow rate for the associated UV system operational conditions.

If an online UVT monitor is provided as part of the dose-monitoring strategy, an alternate ÖNORM protocol allows for validation of UV systems, with the RED determined at various combinations of flow rate, UVT, and UV intensity. This alternate procedure requires that the output of the lamps be reduced to a relative value that is representative of that associated with the end of a lamp’s operational lifetime.

Additional Drinking Water Validation Protocols. The Drinking Water Systems Center of the USEPA’s Environmental Technology Verification (ETV)⁷⁶ Program developed a testing protocol for the validation of UV reactors for the disinfection of high-quality water (less than 10 NTU turbidity and greater than 70% UVT), with the latest version released in January 2003. The UV validation protocol was developed by National Science Foundation (NSF) International under a cooperative agreement with the USEPA and can be found as part of the *Protocol for Equipment Verification Testing for Inactivation of Microbiological Contaminants*.⁷⁷ There are also verification protocols for ozone, advanced oxidation and halogen disinfectants.³⁰

This document does not review the ETV protocol in detail since a vast majority of UV disinfection systems in the United States are currently validated in accordance with the *UVDGM* protocols. In addition, only a handful of ETV compliant validations have been historically conducted due to the fact that the disinfection performance and reports generated as part of the ETV program are available to the public and can be accessed on the ETV web site.

Due to the sensitivity of the models generated during validation testing and UV manufacturers' desire to limit the distribution of this information, the UV verification program of the ETV experienced limited use. The program has only resulted in a total of three validated drinking water UV systems conducted between 1999 and 2002,⁷⁸ with no additional testing conducted following the release of the 2003 draft *UVDGM*.

Wastewater and Water Reuse Validation. Formal UV system validation protocols for water reuse and wastewater applications in the United States consist of the NWRI/AwwaRF UV Disinfection Guidelines for Drinking Water and Water Reuse and the USEPA Design Manual for Municipal Wastewater Disinfection, respectively. The following sections provide a detailed review of the NWRI and USEPA protocols as well as an overview of a recent movement in the UV industry in the United States for the development of a uniform validation protocol for the UV disinfection of wastewater and water reuse applications.

*NWRI/AwwaRF Ultraviolet Disinfection Guidelines for Drinking Water and Water Reuse.*³⁸ Chapter 3 of the NWRI Guidelines reviews the validation procedures for UV systems for the disinfection of water and water reuse applications. The validation procedures for water reuse are identical to those for drinking water, with the following exceptions.

CHALLENGE MICROORGANISMS AND UV DOSE REQUIREMENTS. For water reuse applications, the design of the UV disinfection system depends on the type of upstream filter technologies utilized at the treatment facility. There are three general categories of filtration in the NWRI guidelines, including (a) media filtration: nonmembrane filtration, including granular, cloth, or alternate synthetic media, (b) membrane filtration: microfiltration (MF) and ultrafiltration (UF), and (c) reverse osmosis (RO). The UV dose and water quality requirements associated with these three filtration categories are presented below in Table 17.9.

VALIDATION LOCATION AND TEST STAND CONSIDERATIONS. The type of source water utilized for validation testing is also a function of the filtration technology of the intended application of the UV system, as presented in Table 17.10.

Unlike the NWRI procedures for drinking water, scaling is allowed between the size of the validated UV reactor and that of the full-scale system installed at a treatment facility for reuse applications. However, the scale-up factor is limited to 10 times the number of lamps used in the validation reactor. In addition, a velocity profile measured from the validation and full-scale systems must either be within 20% of the theoretical velocity or be equivalent to one another to assure similar disinfection performance between the two systems.

TABLE 17.9. NWRI Reuse Water Quality and UV Dose Requirements³⁸

Filtration Category	Design UV Dose (mJ/cm ²)	Minimum UVT (%/cm)	Maximum Turbidity (NTU)	Maximum TSS (mg/l)
Media filtration	100	55	≤2 (in 24-h period) ^a ; ≤5 (95% of time); not to exceed 10	5 ^b (max sample)
Membrane filtration	80	65	≤0.2 (95% of time); not to exceed 0.5	NA
Reverse osmosis	50	90	≤0.2 (95% of time); not to exceed 0.5	NA

^aBased on state of California water quality standards.

^bBased on state of Florida water quality standards.

NA, not applicable.

TABLE 17.10. NWRI Validation Source Water Requirements³⁸

Intended Application Water	Validation Source Water
RO-, UF-, or MF-treated water	Any finished drinking water
Media-filtered water	Granular media filtered reclaimed water (1 NTU minimum turbidity)

Biodosimetry Data Analysis. The procedure for the analysis of the log inactivation data for reuse applications also varies from that of drinking water. For reuse applications, the lower 75% confidence value of the measured log inactivation values for a single flow rate is utilized for the determination of the delivered UV dose.

*USEPA Design Manual for Municipal Wastewater Disinfection.*³⁹ The 1986 *USEPA Design Manual for Municipal Wastewater Disinfection* (here on referred to as the 1986 Design Manual) includes a section in Chapter 7 that presents a general protocol for the estimation of UV dose by the bioassay technique. This protocol represents one of the first biodosimetry-based validation procedures developed for wastewater applications in the United States. It should be noted that this protocol is extremely outdated and is not currently utilized for the evaluation of UV system disinfection performance. A review of this protocol has been included in this document to outline the first biodosimetry-based validation protocol developed in the United States for wastewater applications and to serve as an example of the progress made in the validation of UV systems, as exemplified by the current protocols, since this design manual was released in 1986.

The following sections review the challenge microorganisms utilized in the biodosimetry testing and UV dose requirements for disinfection at wastewater treatment facilities, validation location and test stand considerations,

dose-monitoring approaches and associated validation test conditions, sampling and data recording requirements, collimated beam analysis, and biodosimetry data analysis.

Challenge Microorganism and UV Dose Requirements. Research conducted by Johnson and Qualls⁷⁹ at the time that the 1986 Design Manual was released utilized *B. subtilis* spores as the challenge microorganism, and existing attempts at biodosimetric-based UV performance evaluations used these spores. Thus, the manual references this organism as a suitable candidate for biodosimetry and notes that alternative organisms, such as *Micrococcus lutea*, have successfully been utilized and demonstrated a dose response similar to that of coliforms. Biologically derived UV dose requirements for typical wastewater indicator bacteria are not provided in this protocol.

Validation Location and Test Stand Considerations. It is recommended that the validated UV system “closely simulate” the design of the full-scale installation. Scaling of the UV system size from the validated reactor to the full-scale installation is allowed, and, if the UV system design is modular, only a single module is required to be validated.

Although the manual notes the importance of the hydraulic impacts on UV system performance, no recommended piping arrangements are provided. It is recommended that the full-scale installation have a similar aspect ratio and inlet and outlet designs to those of the validated reactor. In addition, the manual notes the importance of the dispersion coefficient and RTD parameters in the evaluation of system hydraulics, which are reviewed in greater detail in the “Nonbiological, Mathematical-Based Modeling” section.

Dose-Monitoring Approaches and Validation Test Conditions. The 1986 Design Manual does not include a review of potential or suggested control strategies for UV systems in wastewater applications. The validation test conditions should include the expected hydraulic loads (flow/lamp) to be encountered at the full-scale installation, and the UV system should be sized to meet a desired dose at peak flow conditions. Biodosimetry testing should include the evaluation of three to four flow rates, tested in triplicate. As a minimum, the evaluated flow rates should bracket the peak design flow rate. Lamp output should be reduced to a value that is representative of that occurring at the end of lamp lifetime and the UVT should be adjusted to anticipated design conditions. The manual also recommends that RTD curves be developed for the validated UV reactor.

Sampling and Data Recording. For each replicate test condition, a minimum of three replicate influent and effluent samples should be collected for microbial analysis. Samples must be analyzed within 4 h of collection. A minimum of three dilutions of each sample must be plated in triplicate for the determination of the microbial concentration of influent and effluent samples. The

UVT at a wavelength of 253.7nm should be measured by using a spectrophotometer and standard methods.

Collimated Beam Analysis. The 1986 Design Manual recommends that the collimated beam test should be conducted on the microbial stock, which should be diluted to an approximate concentration of 10^5 org/100ml in buffered water. The dose-response curve should incorporate five to seven UV doses with each UV exposure (i.e., dose) conducted in triplicate. Each replicate set of UV doses should incorporate two zero dose controls, representing time zero and the longest sample exposure time. All exposed samples and controls are sampled in triplicate, with three dilutions of each sample plated in triplicate for determination of the microbial concentration.

The 1986 Design Manual does not present an equation to be used to determine the UV dose delivered by the collimated beam device, nor does it provide a detailed testing procedure. The dose-response curve is generated by calculating the log survival for each UV exposure (via Eq. 17.18 as a function of the collimated beam UV dose, as presented in Figure 17.27.

$$\text{Log Survival} = \log \left| \frac{N}{N_0} \right|, \quad (17.18)$$

where

N = concentration of MS2 in sample after UV exposure, and

N_0 = concentration of MS2 in zero dose control (no UV exposure).

Biodosimetry Data Analysis. The log survival of the challenge microorganism for each test condition is determined via Equation (17.16), with

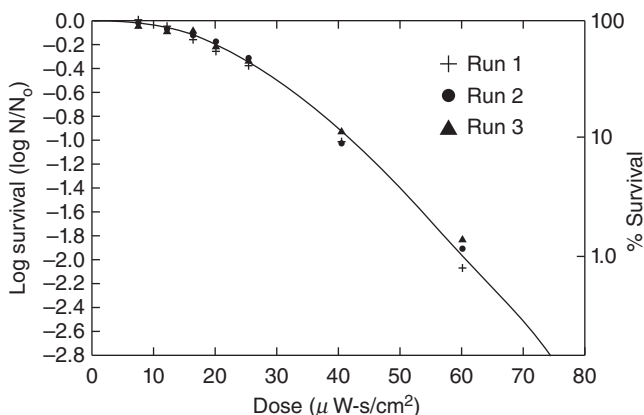


Figure 17.27. Log survival of *B. subtilis* as a function of UV dose.³⁹

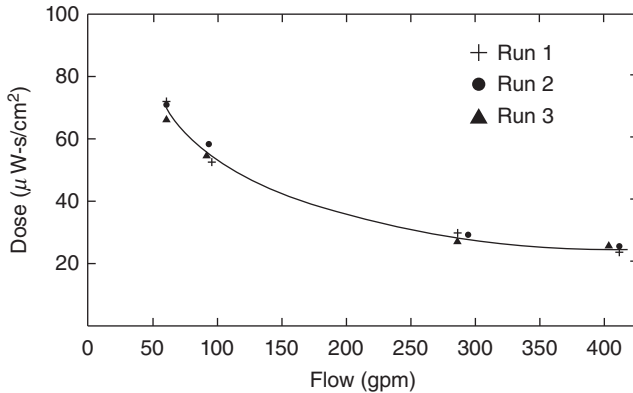


Figure 17.28. UV dose as a function of flow rate.³⁹

N_0 representing the influent concentration and N representing the effluent concentration. The UV dose associated with each test conditions is determined via the dose–response curve and the measured log survival. Validation results are presented as a plot of UV dose as a function of flow rate (at a constant lamp output and UVT), as presented in Figure 17.28.

Additional Wastewater/Water Reuse Validation Protocols. The Water Quality Protection Center of the USEPA’s Environmental Technology Verification (ETV) Program developed testing protocols for the validation of UV reactors for the disinfection of secondary wastewater effluent, reuse waters, and wet-weather flows. The UV validation protocols were developed by NSF International under a cooperative agreement with the USEPA.

The latest version of the *Verification Protocol of the Secondary Effluent and Water Reuse Disinfection Applications* was released on October 2002.⁷⁶ The verification protocols for secondary effluent and reuse waters are similar to the reuse protocols of the NWRI Guidelines, requiring the evaluation of secondary effluent disinfection performance to be conducted at 55%, 65%, and/or 75% UVT, and the evaluation of reuse disinfection performance at 55%, 65%, or 90% UVT, depending on the type of upstream tertiary treatment (media filtration, membrane filtration, or RO). It is important to note that these protocols require the use of MS2, or other organisms are being considered by UV industry, consultants, and regulators because of the shape of the dose–response curves of fecal and total coliforms.

The *Generic Verification Protocol for High Rate, Wet-Weather Flow Disinfection Applications, Draft 4.1* was released in July 2000.⁸⁰ Testing protocols are similar to the reuse and secondary effluent ETV protocols and consist of three required phases: (a) verification of disinfection performance at specific UVTs in a nonparticle bearing matrix, (b) verification

of disinfection performance at specific UVTs in a primary wastewater effluent matrix, and (c) verification of the efficacy of the cleaning system.

Due to the sensitivity of the models generated during validation testing and UV manufacturers' desire to limit the distribution of this information, the UV verification program of the ETV has been limited to a total of three validated UV systems for secondary effluent or water reuse, conducted in 2003, and a single validation test for wet-weather flows that began in 2000 and was cancelled prior to completion.

Development of a Uniform Wastewater Validation Protocol. Although many UV systems have been successfully implemented for the disinfection of wastewater applications, the variety of techniques utilized for the design and operation of these systems is a topic of concern. Manufacturers are using several different techniques for the sizing and operation of UV systems, ranging from theoretical-based mathematics (reviewed in the "Nonbiological, Mathematical-Based Modeling" section) to biodosimetry-based validation techniques in accordance with standardized and nonstandardized protocols. As a result, comparing UV system designs proposed by various manufacturers is not an easy task and can be host to a high level of uncertainty since engineers evaluating such designs are not typically able to compare such designs on an equal level.

In 2007, the UV industry in the United States became the host to a growing movement for the development of a current, uniform protocol for the validation of wastewater and water reuse UV systems. This movement has gained the support of various engineering consultants, UV manufactures, and UV testing facilities and has been driven by the UV Manufacturer's Council of the International Ultraviolet Association. As of early 2008, a draft protocol was under development, modeled after the *UVDGM*, and incorporating existing approaches published by the NWRI Guidelines and the *UVDGM*.⁸¹

The goal of this effort is the development of a modern, standardized approach that will be utilized by manufacturers for the validation of UV systems for all wastewater applications, including reuse, secondary effluents, and low-grade wet-weather flows.⁸¹ A validation approach based on the strengths of the *UVDGM* and NWRI protocols would allow for the development of performance models for the prediction of head loss, power consumption, and disinfection performance. Furthermore, such an approach would result in a design tool for UV manufacturers to safely and accurately design UV systems to attain required disinfection goals while accounting for the site-specific UV dose response of the target organism. In addition, the models developed for the design of the UV systems can also be implemented in the UV systems' control philosophy, allowing for reliable disinfection performance while minimizing the potential for excess dosing, resulting in more efficient operation and potential power savings.

Nonbiological, Mathematical-Based Modeling³¹

The design approach recommended by the 1986 USEPA *Design Manual for Municipal Wastewater Disinfection* utilizes a mathematically based UV process model for the design of UV systems. Due to the complexity of the model, the USEPA contracted HydroQual, Inc. of Mahwah, New Jersey, to develop a computer-based UV disinfection process design program, based on the approach outlined in the USEPA Design Manual.⁸² The program, UVDIS, remains in use by several UV manufacturers as a design tool for UV disinfection systems, in cases where bioassay or validation-derived sizing tools are not required.

As previously reviewed in Chapter 2 ("Background"), UV dose is ideally the product of the intensity of UV light that an organism is exposed to and the exposure time of that organism to the UV light, as presented in Equation (17.19):

$$D = It, \quad (17.19)$$

where

D = UV dose (mW-s/cm² = mJ/cm² or μ W-s/cm²),

I = UV intensity at a wavelength of 253.7 nm (mW/cm² or μ W/cm²), and

t = exposure time (s).

The level of inactivation of typical bacterial indicator organisms in wastewater in a UV reactor can ideally be demonstrated via the following first-order equation:

$$N = N_0 e^{-KIt}. \quad (17.20)$$

where

N = organism concentration following UV exposure (org/100ml),

N_0 = initial organism concentration (org/100ml),

K = inactivation rate (cm²/ μ W-s),

I = UV intensity at a wavelength of 253.7 nm (μ W/cm²), and

t = exposure time (s).

Equations (17.19) and (17.20) represent mathematical relationships associated with an ideal reactor, having an intensity field that is equally distributed and plug flow hydraulics, resulting in a homogenous velocity throughout the cross-section of the irradiation zone of the UV reactor. In real-world UV reactors, there exists a distribution in the intensity field and the velocity profile throughout a reactors' cross section and, thus, a distribution in the exposure time of a microorganism to the UV light. This results in a distribution in the

delivered UV dose and the associated microbial inactivation that occurs within UV systems.

The USEPA Design Manual UV process model is based on Equation (17.20) and it is modified to account for nonideal conditions and presented as Equation (17.21):

$$N = N_0 e^{\left[\frac{ux}{2E} \left[1 - \left[1 + \frac{4KE}{u^2} \right]^{1/2} \right] \right]} + N_p, \quad (17.21)$$

where

N_0 = initial organism concentration (org/100 mL),

X = UV reactor length, defined as the average distance traveled under direct UV exposure (cm),

u = water velocity (cm/s),

E = dispersion coefficient,

K = inactivation rate (s^{-1}), and

N_p = particle-associated microbial concentration not impacted by UV exposure (org/100 ml).

Furthermore, the water velocity (u) is calculated via Equation (17.22):

$$u = \left[\frac{x}{V_v/Q} \right], \quad (17.22)$$

where

V_v = reactor volume (l), and

Q = flow rate (l/s).

The dispersion coefficient (E) defines the hydraulic behavior of the UV reactor via the measurement of the distribution of time about the mean residence time. The dispersion coefficient is derived from RTD testing of a UV reactor and the following equation:

$$E = \left[\frac{ux\sigma^2}{2\theta^2} \right], \quad (17.23)$$

where

σ^2 = variance of the RED (s^2), and

θ = mean residence time (s).

The dispersion coefficient will approach unity with increasingly ideal plug flow conditions. The manual recommends a dispersion coefficient of less than 100 for effective UV system design.

The inactivation rate (K) can be determined as a function of the average UV intensity in the UV reactor via Equation (17.24):

$$K = a(I_{avg})^b, \quad (17.24)$$

where

I_{avg} = average UV intensity ($\mu\text{W}/\text{cm}^2$), and
 a, b = log–log regression coefficients of K and I_{avg} .

The average intensity is calculated via a mathematical approach, known as point source summation, which is based on the reactor dimensions, lamp configuration within the UV reactor, UV output of the lamps, and UV transmittance of the water. This calculation is complex, and various computer programs have been developed to determine the average UV intensity based on the point source summation method. One such program is the TULIP subroutine of UVDIS, which allows users to determine the average UV intensity for specific reactor configurations and wastewater conditions.⁸² This and other alternative intensity distribution modeling programs are currently utilized by UV manufacturers for the sizing of UV systems. The USEPA Design Manual also contains tables for the estimation of the average intensity for staggered, symmetrical, and concentric LP and LPHO UV reactor configurations. Once the average UV intensity is determined, it must be decreased to account for the loss of UV intensity associated with lamp aging and sleeve fouling, as presented in Equation (17.25):

$$I_{avg\ EOL} = I_{avg\ BOL} \times A_f \times F_f, \quad (17.25)$$

where

$I_{avg\ EOL}$ = end of lifetime average UV intensity ($\mu\text{W}/\text{cm}^2$),
 $I_{avg\ BOL}$ = beginning of lifetime average UV intensity ($\mu\text{W}/\text{cm}^2$),
 A_f = lamp aging factor, and
 F_f = sleeve fouling factor.

The coefficients a and b are a function of the target microorganisms sensitivity to UV and are thus specific to individual wastewater sources. The USEPA Design Manual and UVDIS Users Manual recommend that this information be determined via site-specific pilot or bench-scale testing due to a high degree of variability observed in these coefficients from different installations. However, the UVDIS Users Manual does provide values for these coefficients that were derived from a study conducted at the Port Richmond water pollution control plant (WPCP) in New York City that may be adequate for “estimating purposes.”⁸²

The particle-associated microbial concentration not impacted by UV exposure (N_p) is a measurement of the microbial population that is associated with particles and will not be exposed to UV light in a UV reactor. These particle-associated microorganisms cannot be inactivated by UV disinfection and thus resulting in a UV-resistant residual population. The USEPA Design Manual quantitates the concentration of these microorganisms via a relationship with the suspended solids concentration of the wastewater, as presented in Equation (17.26):

$$N_p = cSS^m \quad (17.26)$$

where

SS = suspended solids concentration (mg/l), and
 c, m = log-log regression coefficients of effluent microbial concentration and suspended solids concentration.

Due to the variable nature of the concentration of these organisms and site-specific makeup of suspended solids of wastewater effluents, a high degree of variability in the N_p has been determined from various studies. As a result, the USEPA Design Manual recommends that this information be derived from site-specific pilot or bench-scale testing. The UVDIS Users Manual provides values for coefficients c and m based on the Port Richmond study, noting that these values provide a “reasonable estimate” of N_p for fecal coliforms.⁸²

Alternate, UVDIS-based, design approaches have also been used by UV manufacturers for sizing of UV systems. Due to the time and expenses associated with pilot testing, it is not always possible to determine coefficients a, b, c , and m based on site-specific studies. Since the release of the USEPA Design Manual, the increased experience gained by UV manufacturers has allowed for the sizing of UV systems in the absence of site-specific pilot testing.

Intensity distribution programs, such as the TULIP subroutine of UVDIS, are typically utilized for the determination of the average intensity, which is then decreased to account for the reduction in intensity associated with lamp aging and sleeve fouling. The EOL average intensity is then used in combination with Equation 17.9 to determine an average calculated dose. Bench-scale collimated beam studies may be conducted on a wastewater sample to determine the dose requirements to attain site-specific disinfection requirements with safety factors added to the dose requirement to account for nonideal intensity and velocity distributions. Alternatively, dose requirements can be derived from site-specific water quality measurements (UVT, suspended solids, particle size distribution) and experience from existing designs of similar wastewater quality and disinfection performance requirements.

Emerging Methods

In recent years, researchers have been developing alternative approaches to the biosimetry-based validation approach of UV reactors. These methods include UV dose models based on computational fluid dynamics (CFD) as well as the use of dyed microspheres as an alternative to microbiological indicators of UV dose for the validation of UV reactors. Due to the emerging nature of these alternative approaches, it is strongly advised that these methods be not used as a replacement of current biosimetry-based validation techniques. CFD and dyed microspheres represent promising technologies that are expected to continue to develop and improve in the future and can currently be implemented in combination with current approaches to aid in the validation of UV reactors.

CFD. CFD have been used to create models to predict microorganism trajectories through a UV reactor. When combined with UV intensity distribution prediction tools, the resulting CFD-I models can be utilized to predict the UV dose delivered to an organism as it travels through a UV reactor. Thus, these models allow not only for an estimation of the average UV dose delivered in a reactor (as is measured in biosimetry) but also for the determination of the dose distribution. The UV sensitivity of specific microorganisms can be evaluated, resulting in UV dose estimates that are unique to the UV dose response of target pathogens or indicator organisms of concern at individual treatment facilities.

Although CFD-I modeling has demonstrated a great deal of potential as a UV system sizing tool, several issues with this approach exist as reviewed in the *UVDGM*:³¹

- Little agreement exists on how to assess the credibility of CFD models.
- CFD-I models consist of a series of submodels including those for the prediction of turbulent flow, microbial transport, UV intensity, and microbial inactivation. Many options and approaches are available for each submodel, and no consensus has currently been reached on what methods are most suitable for UV dose delivery modeling.
- CFD-I modeling requires a multidisciplinary approach, requiring expertise in fluid mechanics, light physics, microbial inactivation, numerical modeling, and UV process engineering. A limited amount of individuals have such integrated expertise, resulting in challenges associated with the development of credible models and proper review of modeling reports by engineers and state regulators.

As a result, these models should not be used as a replacement for current biosimetry-based validation techniques but should rather be used to complement existing procedures. The *UVDGM* suggests that CFD-I models can

be used to predict the relative difference between validation-derived UV system performance and that occurring at an installation.

Such an approach can be utilized when comparing the impact of the piping arrangement utilized during UV system validation compared with an alternate configuration employed at a UV disinfection facility. CFD-I models should be used to assess if the UV dose delivery at the water treatment facility is equivalent to or in excess of that demonstrated during validation.³¹ If the analysis indicates that the dose delivery is reduced, an alternate configuration or additional validation testing is required to quantitate the UV dose associated with the piping arrangement. If the CFD-I analysis indicates that the dose delivery is greater at the water treatment facility, the validated dose should not be adjusted to take advantage of any excess potential treatment capacity.

In addition to assisting with the validation of UV reactors, CFD-I modeling has been utilized by UV manufacturers in the research and development of UV reactor configurations and optimization of existing designs prior to conducting validation testing.

Dyed Microspheres. Lagrangian actinometry is an emerging technique that uses dyed microspheres in place of challenge microorganisms in the validation of UV systems. The dye attached to the microspheres is sensitive to UV radiation. Upon UV exposure, the dye undergoes a photochemical reaction that yields a stable, fluorescent compound that can be measured by an instrument known as a flow cytometer.⁸³

During validation of a UV system, the microspheres are injected upstream of the UV system in a similar manner to microbial indicator organisms in biosimetry-based validation techniques. The dose response of the dyed microspheres is determined via collimated beam testing, which is conducted in a similar manner as the method prescribed in the *UVDGM*. Samples are collected from the effluent of the UV reactor at various test conditions and are subjected to a volume reduction process that includes membrane filtration, particle resuspension, and centrifugation.⁸⁴ Samples are then measured by a flow cytometer, which is capable of accurately measuring the fluorescence of tens of thousands of microspheres in a few minutes,⁸³ and these results are used to generate a fluorescence-intensity histogram for individual samples.⁸⁴

The measurement of a large population of the microspheres allows for the determination of the dose-distribution within a UV reactor. As was noted with CFD-I modeling, the measurement of the dose distribution of a UV reactor allows for organism-specific RED estimates to be developed for any microbe. Several successful studies have been conducted in which the average delivered dose as determined by microspheres was compared with that derived by biosimetry testing techniques in both LP and MP UV reactors.⁸³ In addition, studies have been conducted where microspheres have been used to calibrate CFD-I models.⁸⁴ Currently, a protocol is under development for the application of dyed-microspheres actinometry as part of a project

funded by the New York State Energy Research and Development Authority (NYSERDA), AwwaRF, New York City Department of Environmental Protection (NYCDEP), and others.⁸³

Although Lagrangian actinometry represents a potential alternative method for the validation of UV reactors, its use may be advantageous in alternative applications, including troubleshooting of reactor performance issues and assessment of potential corrective actions, and system optimization or revalidation of a UV system at a treatment facility.⁸³

OPERATION AND MAINTENANCE ACTIVITIES

Maintenance Activities

A number of maintenance activities need to be completed to ensure that the UV system will continue to function adequately. Operations staffs need to review these activities to ensure that the UV system will continue to function properly. The USEPA³⁰ recommends that the maintenance activities for UV systems in Table 17.11 be completed. The USEPA describes in detail the operational and maintenance activities that should be completed for UV system used in drinking water applications.³¹ The information presented in this chapter will assist mostly operations staff of UV at wastewater treatment facilities.

During start-up of the UV system, operational staff needs to review activities presented in Table 17.11 with specific vendor representatives. Vendors have specific requirements for their respective system. This may range from determining lamp replacement frequency to cleaning and maintenance of the reactor.

Treatment plant staffs need to understand that activities like cleaning and calibration of online instrumentation are critical to the successful operation of a UV system.

While not directly related to operation and maintenance, staffs need to understand the importance of following correct procedures for sampling and analytical procedures. Sampling of UV systems needs to be completed to ensure that no additional material is included in the samples. Clean sampling techniques may have to be implemented if the UV system has been designed to achieve high-level disinfection requirements. In addition, analytical procedures need to be followed (including quality control and assurance practices). Microbial testing is the key to monitoring the performance of any disinfectant. If appropriate sampling procedures are not followed either in the field or in the laboratory, results can be misleading. Samples should be collected in certified clean, sterile containers by using proper grab techniques and should be kept at a temperature of 4°C during transportation to the laboratory. Analysis should start within 6h of the time of collection. In some cases, rosolic acid may need to be added to the sample to ensure accurate counts based on methodologies described in *Standard Methods*. After collection, filled sample

TABLE 17.11. Recommended Typical Maintenance Activities for UV Systems^{30,31}

Frequency	Task/General Guideline	Action
Weekly	Check online UV transmittance analyzer calibration (if applicable)	Calibrate UV transmittance analyzer when manufacturer’s guaranteed measurement uncertainty is exceeded.
Monthly	Check sleeves, brushes, Teflon rings, and wipers for leaks or wear	Replace sleeves, seals, o-rings, or wiper seals if damaged or leaking.
Monthly	UV intensity calibration check	Check sensor calibration at the lamp power output utilized during routine operating conditions.
Monthly	Check cleaning efficiency	• Record UV intensity sensor reading. • Examine sleeves for streaks or remaining deposits. • Record UV intensity sensor reading after cleaning and compare with precleaned value. • Reclean or replace sleeves if intensity is not restored to precleaned value.
Semiannually	Check cleaning fluid reservoir (if applicable)	• Replenish solution if the reservoir is low. • Drain and replace solution if the solution is discolored.
Annually	Test trip GFI	Maintain GFI breakers in accordance with manufacturer’s recommendations.
Lamp/ Manufacturer specific	Replace lamps	Replace lamps when any of the following conditions occurs: • Initiation of low UV intensity after verifying that condition is caused by low lamp output • Initiation of lamp failure alarm • System not achieving permit requirements after exceeding guaranteed lamp run time
Manufacturer’s recommended frequency	Check flow meter calibration	If effluent weir or flume is available, manually check depth and compare with primary device measurement. Primary device should be calibrated at recommended frequency or when measurement uncertainty is exceeded.
When lamps are replaced	Properly dispose of lamps	Send spent lamps to a mercury recycling facility or back to the manufacturer.

Table 17.11. *Continued*

Frequency	Task/General Guideline	Action
When quartz sleeves are replaced	Properly dispose of quartz sleeves	Replace sleeves as recommended by the manufacturer or when damage, cracks, or excessive fouling occurs that would impede UV intensity.
Manufacturer's recommended frequency	Clean/Calibrate transmittance monitor (if installed)	Clean/Calibrate according to manufacturer's recommended frequency.

GFI, ground fault indicator.

TABLE 17.12. Training Highlights

1. Design flows and characteristics.
2. Alarm system.
3. Mechanical checks.
4. Electrical checks.
5. Control logic for PLC.
6. Replacement of basic components

bottles must be kept in the dark at all times. This can be accomplished by wrapping the bottles in aluminum foil.

Treatment plant operating staff should receive training in the proper operation of the UV equipment. The system manufacturer should provide the training, as each manufacturer has issues that are specific to its system. Key items to be addressed during training are listed in Table 17.12.

The plant staff should review the operation and maintenance manuals for the equipment before the training sessions begin. Manuals should also be reviewed following training to determine what materials may be missing or need to be clarified before the manuals are finalized.

Operation and Maintenance Manual. One of the key ways treatment plant staff can understand the procedures for operating an UV system is an operations and maintenance manual. This manual should be specific to the type of system that has been selected and installed. The manual should contain but not be limited to information on built drawings, manufacture-specific information, treatment objectives, regulatory and discharge requirements, description of equipment, start-up and shutdown recommendations from the manufacturer, and spare parts inventory. Draft copies of the manual should be available during start-up and training classes.

Functional Testing. Functional testing should take place to verify the proper installation of the sensors, lamps, ballasts, cooling system, analyzer, and cleaning system. The head loss should be verified. The manufacturer should conduct the functional testing and prepare a report documenting the results. Any modifications needed for compliance with the specifications should be made prior to conducting any performance testing. Additional information on functional testing of UV reactors is found in Chapter 6 of the USEPA *UVDGM*.³¹

Performance Testing. Performance testing is conducted to assess and verify the performance of the UV system. Testing should be carried out under actual operating conditions. Testing can be used to verify that the control system, power consumption, cleaning system, sensor operation, and online sensors all operate as specified. The USEPA *UVDGM*³² can be reviewed to learn about performance testing of UV systems.

Operational Issues

Operational Issues. Operationally, a number of activities need to be conducted by the staff. These include operation of power meters, temperature, elapse time, flow rate meters, and collection of water quality data.

Power Meter. One of the major ways to monitor the power demand of the UV lamps is to install a power meter. Power is critical to the operation of the UV system. Therefore, monitoring power will allow utilities to better understand and optimize both performance of upstream unit operations that influence water quality and selection of UV operation strategies to minimize power costs.

Temperature Measurements. On some UV systems, alarms are installed to monitor temperature. This is most frequently involved with monitoring water temperature in reactors using MP or LPHO lamps that could become unacceptably hot if flow through the reactor were to be stopped but the lamps were not shut off.

Elapse Time on Lamps. All UV systems have meters to measure the elapsed time on each lamp. The elapsed time can be used as an indicator of when lamps should be replaced. UV manufacturers usually state a useful life of the lamps based on operating hours. Replacing the lamps on schedule instead of waiting for compliance problems is recommended.

Flow Rate Meter. All UV systems need to be installed so that the equipment can operate within certain flow limits or be controlled by flow through them. A flowmeter needs to be available to produce an electronic signal that can be transmitted to the UV PLC. Operation and maintenance requirements from

the manufacturer of the flowmeter need to be followed to ensure that the UV system will operate correctly.

Collection of Water Quality Data. Operations staff needs to collect and review data on the UV system on a periodic basis. The most critical information that will be collected relates to compliance with permit or established guidance. This may range from collection of bacterial data from daily to once per month. Periodic checks need to be made of effluent transmittance, suspended solids, turbidity, flow, and particle size to verify that design values have not been exceeded.

TROUBLESHOOTING STRATEGIES

A number of activities can be implemented to allow a UV system to achieve the desired compliance requirements. These include process control modifications.

Process Control Modifications

The effectiveness of a UV disinfection system depends on the influent wastewater characteristics and on the upstream treatment processes. In wastewater, industrial users may discharge substances such as UV-absorbing organics or inorganics that inhibit the performance of the UV system, and upstream operations may contribute additional solids or organic material that interferes with disinfection. Table 17.13 presents a checklist of factors that could influence the performance of a UV system and should be understood before modifications to the process are undertaken.

Electrical System Modifications

Table 17.14 lists items to be checked by plant operations if the problems appear to be related to the electrical system.

TABLE 17.13. Process Checks

-
1. Effluent transmittance
 2. Effluent total suspended solids concentration/
turbidity
 3. UV spectra
 4. Effluent color
 5. Industrial dischargers
 6. Algae
 7. Iron/manganese/hardness
 8. Microbial testing procedures
-

TABLE 17.14. Electrical Checks

1. Lamps are energized.
2. Lamps are connected.
3. Useful lamp life
4. Ballast output

TABLE 17.15. Mechanical Checks

1. Cleaning system to ensure acceptable performance
2. Proper delivery of chemical
3. Online transmittance measurements
4. Online intensity measurements
5. Flowmeter calibration
6. Ballasts closed-loop cooling system

Mechanical System Modifications

Mechanical systems are critical to the operation of UV systems, and some of the checks are listed in Table 17.15. Quartz sleeves have to be cleaned on a regular basis. The primary maintenance task required in the operation of UV systems is cleaning the surfaces of the quartz sleeves due to the tendency of constituents in wastewater to foul the surfaces of the quartz sleeves. Consequently, mechanical and chemical cleaning systems are used to periodically clean the sleeves. Cleaning requirements are based on the reduction in measured intensity caused by the impedance of the transfer of UV light into the water flowing through the reactor.

HEALTH AND SAFETY FOR WATER AND WASTEWATER UV SYSTEMS

General

Although UV radiation was once an emerging technology area, this unit process is becoming a more commonly designed and operated disinfection process for water and wastewater treatment facilities in the United States. With the increasing implementation of UV systems comes more information concerning their design and operation.

Operators of UV technologies require special awareness and attentiveness to the UV nature of these technologies, as well as to routine safety practices around any technology that has electrical and mechanical components. In general, protective gloves, eyewear, and footwear are recommended when servicing UV equipment.

UV Light Exposure

UV light is damaging to body tissues. Thus, workers must not be exposed to UV through careless practices such as pulling illuminated UV modules or lamps from their position within reactors and turning on an open channel UV systems when the lamps are not immersed in the wastewater. Every attempt has been made in equipment design to ensure that UV does not reach operators who are standing beside the equipment while it is operating. However, a willful disregard for common sense can lead to unnecessary risk taking. Before any UV modules or lamps are removed or handled, the power must be off. If there is any reason to look directly at or be exposed to ignited UV lamps, proper UV absorbing eye or whole-face shields should be worn. All exposed skin should be covered with clothing that absorbs or reflects all of the UV light at the wavelengths given off by the lamps. Consult the UV system suppliers' operations manual for proper protective wear.

UV is electromagnetic radiation similar to radio waves, x-rays, and light. Immediate or prolonged exposure to UV light can result in eye injury, skin burn, premature skin aging, or skin cancer. Individuals who work with or in areas where UV sources are used are at risk for UV exposure if the appropriate shielding and protective equipment are not used. Although exposure to small amounts of UV radiation can have beneficial effects, such as vitamin D synthesis in the skin, overexposure can cause serious acute and chronic health effects.

The exposure limit of UV light for a worker is based on the wavelengths of the specific region of the UV spectrum to which the workers is exposed, the duration of the exposure, and the intensity of the light. However, germicidal lights (MP) may also emit more hazardous forms of UV light such as UV-B, and a potential for overexposure does exist for wastewater workers performing maintenance and operations of UV disinfection systems that use MP lamps. UV-B is typically the most destructive form of UV radiation because it has enough energy to cause photochemical damage to cellular DNA. UV-B and C effects can include sunburn, cataracts, and development of skin cancer. It should be noted, however, that the exposure to harmful UV radiation is reduced due to the absorbance of the UV light by a mere 2–5 in. of water, depending on the UVT. Further, all major UV manufacturers have programmed their lamps to automatically shut down as part of normal out-of-the-water maintenance (the methods for shutdown vary and should be confirmed for each type of UV system).

Workers may not be fully protected from UV light exposure by the manufacturers' shielding around the lamps, or the user may not be aware of the hazards of UV light. The purpose of a UV Light Safety Program is to ensure that the safeguards necessary to limit exposure have been implemented.

Perform a UV Safety Audit

One concept for improving the safety of a UV system is conducting a safety audit. This audit can have the following goals:

- Identify the sources and work procedures that may produce overexposure for workers
- Determine UV exposure levels for each work procedure and develop safe job procedures
- Carry out a UV radiation survey by a qualified person
- Determine exposure levels based on OSHA or other regulations
- Determine allowable exposure times based on OSHA or other regulations
- Determine safe viewing distances
- Identify appropriate personal protective equipment

The symptoms of UV overexposure to the skin are well known and are characteristically called sunburn. However, the signs and symptoms of overexposure to the eyes are not as widely known. They are as follows:

- A burning and painful sensation in the eye
- Sensitivity to light
- The sensation of a foreign object in the eye, sometimes described as sand in the eye
- Tearing

These symptoms usually develop several hours after the overexposure. If an eye or skin injury is suspected, a physician should examine the individual.

Acute Health Effects of UV Exposure

Sunburn is a reddening of the skin, with blistering and peeling in severe cases. Prolonged exposure causes a thickening of the skin's outer layer. People with lighter skin, hair and eyes have less pigment and are more sensitive to UV exposure.

Retinal injury possibly resulting in loss of sight may be caused by UV radiation in people who have cataract surgery. Preemployment placement and medical evaluations must be performed for workers in UV applications.

Immune systems may also be adversely affected by exposure to UV radiation. UV hypersensitivity may result from the use of certain prescription drugs such as common antibiotics. Workers who may be exposed to UV radiation should ask their physician about the possibility of sensitization when given any new prescriptions.

Chronic Health Effects of UV Exposure

A number of chronic health effects can occur to those who use and maintain UV systems. Chronic health effects include the following:

- Skin cancer—Excessive exposure to UV radiation over many years has been shown to increase a person's risk of developing skin cancer.
- Photoaging—Premature aging of the skin is caused by chronic exposures to UV radiation. The resulting changes in the skin include excessive wrinkling, dark spots, loss of elasticity, and a leathery appearance.
- Senile cataracts—Long-term UV exposure has been shown to be an important factor in the development of this disease.

Engineering Controls

Organizations using UV radiation for disinfection can help to prevent over-exposure of workers by following the basic control measures:

- Contain or confine UV radiation to a restricted area.
- Interlocked access so the UV is shut off when the protective enclosure is opened.

Administrative Controls

- Limited exposure times
- Increased distances between workers and the UV source
- Warning signs

Personal Protection

The keys to effectively reducing UV exposure are properly shielding the source and requiring that users wear the appropriate personal protection, as noted below.

- UV blocking eyewear such as goggles, face shields, and welding shields
- Long-sleeved, closely woven protective clothing
- Sunscreen with a high sun protection factor (SPF) and UV-A and UV-B blocking capability

Most UV light sources have the potential of causing photokeratitis (eye injury) with only short exposure periods and should therefore be used in a manner that limits exposure time. Many overexposures to UV light have occurred when the exposed individual was not aware of the hazards of the UV source. Accidental UV overexposures can injure unaware workers due to the

fact that UV is invisible and does not produce an immediate reaction. For eye and skin injuries to be prevented, sources of UV light must be conspicuously labeled with a warning sign attached to the housing of the source. Warning signs are available from commercial suppliers or may be available from the manufacturer of the UV light equipment. Reported UV accident scenarios often involve work near UV sources with protective coverings removed, cracked, or fallen off. Depending on the intensity of the UV source and length of exposure, an accident victim may end up with a lost-time injury even though they are totally unaware of the hazardous condition. Hazard communications training is important in helping to prevent accidental exposures in the workplace.

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18 Advanced Oxidation Processes

INTRODUCTION

Advanced oxidation processes (AOPs) have been defined as processes that involve generation of highly reactive radical intermediates, particularly the hydroxyl radical ($^{\circ}\text{OH}$).¹ Radicals are atomic or molecular species containing electrons that are unpaired with a complementary electron of opposite spin. The hydroxyl radical, the neutral form of hydroxyl (OH), is the most potent oxidant used in water treatment. It has an oxidation potential (E°) of 2.80V, compared with 2.07V for ozone, 1.50V for chlorine dioxide, and 1.36V for chlorine, and reacts very rapidly with most substances because of its unpaired electron. The high oxidation potential and reactivity of the hydroxyl radical make AOPs attractive for treatment of a variety of refractory contaminants.

Hydroxyl radicals are produced during normal ozonation through the decomposition of ozone (O_3). Consequently, oxidation during ozonation occurs by two reactions: direct oxidation by ozone and oxidation by the hydroxyl radical. Glaze et al.² noted that, for this reason, ozonation itself could be considered an AOP.

Oxidation reactions by ozone are slower (10^{-5} – $10^8 \text{M}^{-1} \text{s}^{-1}$) than oxidation reactions by the hydroxyl radical (10^8 – $10^{10} \text{M}^{-1} \text{s}^{-1}$). Under normal ozonation conditions, ozone is present at much higher concentrations than the hydroxyl radical. In contrast, AOPs are designed to favor hydroxyl radical formation and promote oxidation by $^{\circ}\text{OH}$.

Historical Perspective

One of the oldest AOPs is Fenton's reagent, discovered by H. J. H. Fenton in 1894.³ In Fenton's reagent, ferrous iron (Fe(II)) catalyzes decomposition of hydrogen peroxide to form the hydroxyl radical. This AOP has been limited primarily to the treatment of industrial wastewater because the ideal pH for the process ranges between 2 and 4.

AOPs more commonly used for municipal water and wastewater treatment were first developed in the 1970s by researchers who combined ozone with hydrogen peroxide (H_2O_2) or ultraviolet (UV) light to produce the hydroxyl

White's Handbook of Chlorination and Alternative Disinfectants, 5th edition,
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radical. Ozone is a powerful oxidant and disinfectant that has been used in water treatment for more than 100 years,⁴ but it is highly selective in its reactions with organic and inorganic compounds.⁵ It reacts slowly, for example, with the taste and odor compounds geosmin and 2-methylisoborneol (MIB),⁶ and ethers used as fuel additives.⁷

Interest in AOPs grew as researchers discovered that refractory contaminants could be oxidized more effectively by using H_2O_2 or UV in combination with ozone than by ozone alone. Prengle et al.,⁸ at Houston Research Inc., found that O_3 combined with UV (O_3/UV) improved the oxidation of pesticides, chlorinated solvents, complexed cyanides, and biological oxygen demand (BOD) and chemical oxygen demand (COD) compounds.^{9–10} Ozone combined with H_2O_2 ($\text{O}_3/\text{H}_2\text{O}_2$) was investigated for wastewater treatment by Nakayama et al.¹¹ and for drinking water treatment by Bollyky,¹² Brunet et al.,¹³ and Duguet et al.¹⁴ The initial body of research consistently showed that combining ozone with UV or H_2O_2 or UV with H_2O_2 to produce the hydroxyl radical enhanced oxidation of several organic and inorganic compounds compared with the use of ozone alone or any other oxidant.

Types of AOPs

AOP systems are typically classified as homogeneous or heterogeneous processes. Homogeneous AOPs use some combination of O_3 , H_2O_2 , and UV to produce the hydroxyl radical and have been the most widely used AOPs. Homogeneous systems include the following:

- O_3/UV systems
- $\text{O}_3/\text{H}_2\text{O}_2$ systems
- $\text{H}_2\text{O}_2/\text{UV}$ systems

Heterogeneous processes use hydrogen peroxide, UV, or both with a solid semiconductor or transition metal to produce hydroxyl radicals. Examples of heterogeneous processes include the following:

- $\text{Fe(II)}/\text{H}_2\text{O}_2$ systems (Fenton reaction)
- $\text{Fe(II)}/\text{H}_2\text{O}_2/\text{UV}$ systems (photo-Fenton reaction)
- TiO_2/UV systems

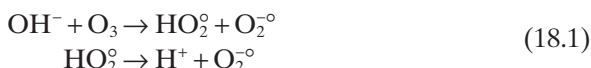
CHEMISTRY OF AOPS

There are many ways to produce the hydroxyl radical. Two commonly used AOPs, O_3/UV and $\text{O}_3/\text{H}_2\text{O}_2$, use the decomposition of ozone to generate hydroxyl radicals. Ozone is unstable and undergoes autodecomposition in a

spontaneous reaction involving several intermediate radical species, the most important of which is the hydroxyl radical. The decomposition of ozone can be initiated by natural organic matter (NOM), hydroxide ions (OH^-), H_2O_2 , or UV radiation. The hydroxyl radical can also be generated by photocatalytic (PC) reactions, such as those between hydrogen peroxide and UV. Heterogeneous processes involve the use of transition metals or solid semiconductors with hydrogen peroxide or UV to generate hydroxyl radicals.

Ozone Decomposition Initiated by Hydroxide

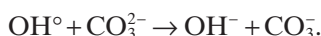
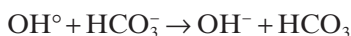
Decomposition of ozone is initiated by hydroxide in the following series of reactions:



This series of reactions has been referred to as autodecomposition or autocatalytic decomposition of ozone because decomposition through this pathway is self-propagating. The initial reaction in Equation 18.1 to produce the hydroperoxyl radical (HO_2°) and the superoxide radical ion ($\text{O}_2^{\circ-}$) starts a chain of reactions that leads to the production of the hydroxyl radical in Equation 18.3. Decomposition of ozone by the hydroxyl radical in Equation 18.4 produces more HO_2° , which further fuels the chain reaction. Consequently, many ozone molecules can be decomposed by a single decomposition step.

The rate of the chain reaction depends on several water characteristics, including alkalinity, temperature, and the composition and concentration of NOM. Because it is so reactive, the hydroxyl radical can be trapped in reactions with a number of common water constituents such as carbonate and bicarbonate. These radical scavengers slow down the rate of ozone decomposition and prolong ozone residual. Hoigné and Bader,¹⁵ for example, observed a 10-fold increase in ozone half-life from about 17 min in distilled water to 170 min in water with 2 mM of bicarbonate.

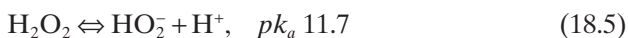
Carbonate and bicarbonate are among the most important hydroxyl radical scavengers because they are ubiquitous in natural waters. The reactions of the hydroxyl radical with bicarbonate and carbonate are as follows:



Adding a base to raise pH produces more hydroxide ions for initiation of ozone decomposition but it also increases the concentrations of bicarbonate and carbonate scavengers. Loss of hydroxyl radicals in reactions with carbonate and bicarbonate can offset any increases in oxidation efficiency that would otherwise be realized by raising pH.^{1,16} Consequently, hydrogen peroxide or UV is typically used with ozone rather than a base to promote the formation of hydroxyl radicals.

O₃/H₂O₂

Hydrogen peroxide can initiate the ozone decomposition cycle through the following reactions:



Hydrogen peroxide deprotonates to its conjugate base, HO_2^- , and H^+ in the pH regulated acid-base reaction of Equation 18.5. In Equation 18.6, HO_2^- reacts with ozone to form HO_2° and O_3^- , at which point the reactions of Equations 18.2 to 18.4 are initiated, resulting in hydroxyl radical formation and further decomposition of ozone. At neutral pH, most of the hydrogen peroxide is in the H_2O_2 form. Therefore, the rate of O_3 decomposition by H_2O_2 is limited by the deprotonation of H_2O_2 in Equation 18.5.

O₃/UV

The photolysis of ozone with UV in water results in the formation of hydrogen peroxide,¹⁷



and the *in situ* formed hydrogen peroxide initiates the ozone decomposition cycle described above. Although the $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/UV processes are mechanistically similar after formation of H_2O_2 in the latter, the O_3/UV process can be more effective for contaminants that absorb UV radiation. Glaze et al.¹ compared oxidation rates for O_3/UV treatment of tetrachloroethylene (PCE) and trichloroethylene (TCE), which have lower quantum yield than PCE. Oxidation rates for PCE increased with UV dose, while those for TCE were unaffected by UV dose. These researchers concluded that the O_3/UV process is, at the same time, an oxidation process and a photolysis process. Consequently, O_3/UV may be more cost-effective than $\text{O}_3/\text{H}_2\text{O}_2$ for compounds that are efficiently photolyzed.

H₂O₂/UV

The simplest method of generating hydroxyl radicals is photochemical cleavage of hydrogen peroxide with UV. Theoretically, two hydroxyl radicals are formed per quantum of radiation ($h\nu$) absorbed.



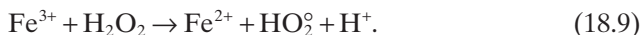
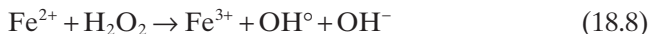
There are, however, several limitations to this process. The actual yield of radicals in Equation 18.7 is about 0.5 rather than 2 because hydroxyl radicals are consumed in radical–radical recombination reactions.



The $\text{H}_2\text{O}_2/\text{UV}$ process is further hampered by the low UV molar absorptivity of H_2O_2 , which is $20\text{ M}^{-1}\text{ cm}^{-1}$ at 254 nm compared with $3300\text{ M}^{-1}\text{ cm}^{-1}$ for ozone.¹ Consequently, a high concentration of H_2O_2 is required to generate enough radicals for effective treatment. Glaze et al.¹ concluded that $\text{H}_2\text{O}_2/\text{UV}$ was unlikely to be practical for treatment of drinking water or wastewater because of the accumulation of H_2O_2 that would occur.

Fe(II)/ H_2O_2 (Fenton Reaction)

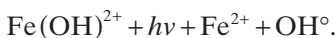
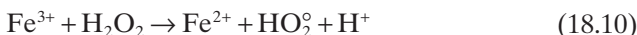
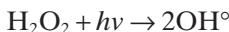
In the Fenton reaction, oxidation of ferrous iron (Fe(II)) to ferric iron (Fe(III)) catalyzes the decomposition of hydrogen peroxide to the hydroxyl radical (Eq. 18.8). The catalyst is regenerated by hydrogen peroxide (Eq. 18.9).



There are limitations to the Fenton reaction, one being that the reaction is only effective in the pH range of 2–5.^{18,19} At higher pH, iron precipitates as ferric hydroxide ($\text{Fe(OH)}_{3(s)}$), and in this form, iron catalytically decomposes H_2O_2 into oxygen and water without forming hydroxyl radicals. Another limitation is that the catalyst regeneration reaction of Equation 18.9 is very slow, and, therefore, continuous addition of Fe(II) is needed to sustain the reaction.

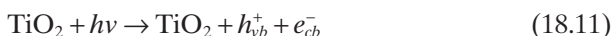
Fe(II)/ $\text{H}_2\text{O}_2/\text{UV}$ (Photo-Fenton Reaction)

Addition of UV to the Fenton reaction can improve oxidation efficiency by enhancing both catalyst regeneration and hydroxyl radical formation. The hydroxyl radical is produced in three ways during the photo-Fenton reaction: (a) photolysis of hydrogen peroxide, (b) the redox reaction between ferric iron and hydrogen peroxide, and (c) the photolytic reduction of ferric iron in Equation 18.10. In the last, the major ferric species in water, FeOH^{2+} , absorbs UV light, and is reduced to ferrous iron to complete the redox cycle. Thus, slow catalyst regeneration in Equation 18.9 of the Fenton reaction is overcome:



TiO₂/UV

Like other solids, semiconductor materials such as titanium dioxide (TiO₂) have an electronic band structure that includes a valence band almost completely occupied by electrons and an outer conduction band that is mostly empty. When TiO₂ molecules absorb UV in the TiO₂/UV PC oxidation system, light energy is converted to chemical energy. The increase in chemical energy causes an electron to jump from the valence band of the molecule to the conduction band, leaving an electron hole (h_{vb}^+) in the valence band (Eq. 18.11). The conduction band electron (e_{cb}^-) and the electron hole thus created are referred to as electron pair. Water is oxidized by the electron hole to form the hydroxyl radical in Equation 18.12, and oxygen is reduced by the electron to form the superoxide radical anion ($\text{O}_2^{\circ-}$) in Equation 18.13.

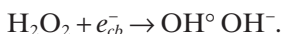
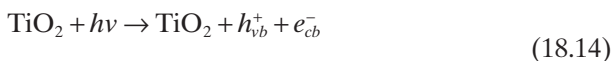


Reaction of the conduction band electron with oxygen prevents the recombination of the electron pair, which would preclude hydroxyl radical formation. It has been suggested that oxidation in the TiO₂/UV process is achieved by the hydroxyl radical and the superoxide anion radical.

In photoelectrocatalytic (PEC) oxidation, the efficiency of the TiO₂/UV system is enhanced by using an external circuit to drive photo-generated electrons to a counter electrode.²⁰ In typical PEC systems, the anode is a TiO₂ film electrode made by coating a conducting metal or glass with TiO₂, and the cathode is often a platinum (Pt) counter electrode.

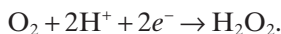
TiO₂/H₂O₂/UV

TiO₂/UV system efficiency can be enhanced by the addition of H₂O₂.²¹ In the TiO₂/H₂O₂/UV system, the conduction band electron is still photo-induced, but H₂O₂ improves oxidation efficiency by capturing the conduction band electrons to form the hydroxyl radical (Eq. 18.14):



The method of dosing is important because an excess concentration of H₂O₂ has been shown to reduce oxidation efficiency by acting as a scavenger

of hydroxyl radicals. Hydrogen peroxide can be generated electrochemically on a carbon electrode in PEC systems as an alternative to chemical dosing.²⁰



It has been suggested that electrochemical generation of H_2O_2 improves efficiency of the $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$ system by providing a continuous and appropriate supply of H_2O_2 .²⁰

USES IN DRINKING WATER AND WASTEWATER TREATMENT

AOPs typically are used in drinking water and wastewater treatment applications to oxidize organic contaminants that are difficult to treat with conventional processes. These refractory organic contaminants include a variety of volatile organic chemicals (VOCs), pesticides, and taste and odor compounds.

Such contaminants are not removed effectively by conventional drinking water coagulation/sedimentation/filtration treatment processes. Although they may be removed by advanced treatment technologies such as reverse osmosis and granular activated carbon (GAC) adsorption, an AOP may be more economical, particularly in cases where the treatment target is one or two contaminants.

Organic compounds that are resistant to biodegradation include polyaromatics, chlorinated hydrocarbon pesticides, and polychlorinated biphenyls. AOPs can be used to oxidize these contaminants, often with the goal of transforming them into more biodegradable products for subsequent biologic treatment.

In principle, organic contaminants can be completely oxidized by AOPs to carbon dioxide and water. A reduction in the measured concentration of the contaminant, however, does not mean that it has been completely oxidized. Rather, complete oxidation is indicated by commensurate reduction in total organic carbon (TOC) concentration. Typically, the oxidant dose or reaction time required for complete mineralization is not economical, and the treatment goal is to partially oxidize contaminants to compounds that are innocuous, more biodegradable, or both.

There has been no systematic research to establish the disinfection potency of the hydroxyl radical, and it is not a recognized disinfectant. This limitation can be overcome by achieving the necessary disinfection credits with ozone or UV before adding H_2O_2 .

Oxidation of VOCs

VOCs include compounds found in petroleum products such as benzene and xylene, degreasers and solvents such as PCE and TCE, and in fuel oxygenates

such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). In its review of contaminants in U.S. public water systems, the U.S. Environmental Protection Agency (USEPA)²² concluded that VOCs occur in about 30% of treated water supplies. AOPs have been found to be more effective for treatment of several VOCs than ozone alone or conventional biologic or physico-chemical processes.

Degreasers and Solvents. TCE and PCE are two of the most frequently encountered contaminants in groundwater and surface water systems.²⁷ Each is regulated under the USEPA National Primary Drinking Water Standards at a maximum contaminant level (MCL) of 5 $\mu\text{g/l}$.

Oxidation of TCE and PCE by the hydroxyl radical is more effective than oxidation with ozone. Glaze and Kang²³ reported that compared with ozone, $\text{H}_2\text{O}_2/\text{O}_3$ increased the oxidation rate of TCE by a factor of two to three and that of PCE by a factor of two to six. Likewise, Armstrong et al.²⁴ reported that $\text{H}_2\text{O}_2/\text{O}_3$ increased oxidation of TCE by a factor of two and oxidation of PCE by a factor of four compared with ozone.

AOPs can be used to achieve near complete or even complete removal of VOC contaminants. Topudurti et al.²⁵ conducted field evaluations with UV/ H_2O_2 for the treatment of a groundwater containing TCE, PCE, 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), and chloroform. They reported that the system achieved 99% removal of TCE and PCE, 96% removal of DCA, and 93% removal of TCA and chloroform. Li et al.²⁶ reported complete mineralization of TCE and its by-products, formic, oxalic, dichloroacetic, and monochloroacetic acids using UV/ H_2O_2 .

Suri et al.²⁷ compared several photocatalysts for the destruction of a variety of VOCs, including TCE. The most effective, platinized TiO_2 , reduced 10 mg/l of TCE to less than the detection concentration (1 $\mu\text{g/l}$) in 20 min using a 450-W lamp. The associated TOC concentration was reduced by 90%. By using sunlight as the light source, TCE was reduced to less than 1 $\mu\text{g/l}$ in 6 min.

The $\text{H}_2\text{O}_2/\text{O}_3$ process has been shown to be more efficient than ozone for oxidation of dioxane, another industrial solvent.^{28,29} Furthermore, compared with ozone, $\text{H}_2\text{O}_2/\text{O}_3$ increases the biodegradability of dioxane.^{28,30}

AOPs can also be used to remove VOCs from the off-gas of air strippers. The City of Pasadena³¹ investigated the use of UV and O_3/UV to remove TCE, PCE, and carbon tetrachloride from air stripper off-gas. Both were effective for TCE and PCE, but neither was effective for carbon tetrachloride. Following a cost analysis, the researchers concluded that air stripping with GAC treatment of the off-gas or AOP treatment of the liquid phase was less expensive than air stripping with AOP treatment of the off-gas. Van Craeynest et al.³² evaluated $\text{H}_2\text{O}_2/\text{O}_3$ for the destruction of TCE in the off-gas of an oxidative scrubber. The TCE-contaminated gas stream was mixed with an ozone-loaded gas stream and fed to a bubble column dosed with H_2O_2 . TCE removal efficiencies of up to 98% were reported.

Petroleum Products. AOPs provide effective treatment of phenols and chlorophenols. Gurol and Vatis³³ compared oxidation of mixtures of phenols by UV, O_3 , and O_3 /UV. TOC removal by UV alone was negligible, and O_3 reduced TOC by 30%. O_3 /UV, however, reduced TOC by more than 95%. Esplugas et al.³⁴ compared several AOPs for oxidation of phenol in laboratory tests. Fenton's reagent was found to be the most effective, followed by ozone and ozone in combination with UV or hydrogen peroxide. Photocatalysis with TiO_2 /UV or UV alone was least effective.

Several researchers (e.g., Zazo et al.³⁵) have noted that Fenton's reagent is an attractive means for treating phenols and chlorophenols in industrial wastewaters because Fe is a widely available, nontoxic, element, and hydrogen peroxide decomposes to environmentally safe by-products. De et al.³⁶ evaluated oxidation of initial concentrations of 100,000 mg/l of phenol, o-chlorophenol, and p-chlorophenol with Fenton's reagent. The process was reported to reduce the initial concentration of each contaminant by more than 90% in less than 10 min.

Duguet et al.³⁷ compared removal of chloronitrobenzene (CNB) from a contaminated groundwater source with O_3 and O_3 / H_2O_2 and reported that O_3 / H_2O_2 was significantly more effective. The initial CNB concentration averaged 1500 μ g/l. A 16 mg/l O_3 dose with a 40-min contact time resulted in 88% removal of CNB. A combination of 8 mg/l O_3 with 3 mg/l H_2O_2 reduced CNB by 99% after a 20-minute contact time.

Al-Momani³⁸ compared the degradation and biodegradability of 2,4-dichlorophenol (2,4-DCP) by Fenton's reagent (Fe(II)/ H_2O_2), UV, H_2O_2 , H_2O_2 /UV, and the photo-Fenton process (Fe(II)/ H_2O_2 /UV). The photo-Fenton process was most effective. Initial characteristics of the test sample were 100 mg/l 2,4-DCP and no BOD_5 . Fenton's reagent reduced the 2,4-DCP concentration by 58% and generated a BOD_5 of 6 mg O_2 /l. H_2O_2 , or UV alone had little effect on 2,4-DCP concentration (5% removal) and generated no BOD_5 . H_2O_2 /UV removed 15% of the initial 2,4-DCP and generated 3 mg O_2 /l BOD_5 . The photo-Fenton reaction resulted in 100% removal of 2,4-DCP and generated a BOD_5 of 11 mg O_2 /l.

Fuel Oxygenates. Groundwater contamination by MTBE and other oxygenated fuel additives has been a significant concern since their use became prevalent in the 1990s. MTBE is mobile and persistent in the subsurface because it is highly soluble (50 g/l) and resistant to biodegradation. Although the use of MTBE has been curtailed recently, large volumes of groundwater have been contaminated by it leaking from underground storage tanks.

MTBE is difficult to remove by air stripping or GAC adsorption³⁹ and is resistant to aerobic and anaerobic biological treatments.⁴⁰ The reactivity of MTBE with ozone is relatively low;⁴¹ however, it is effectively oxidized by AOPs.

Vel Leitner et al.⁴² compared oxidation of the fuel additives MTBE and ETBE with O_3 and O_3 / H_2O_2 . ETBE was oxidized more efficiently than MTBE,

and O_3 and O_3/H_2O_2 were equally effective for ETBE. Oxidation of MTBE, however, was more effective with O_3/H_2O_2 (99% removal) than with ozone (80% removal). The primary products of MTBE oxidation were *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), acetone (AC), and formaldehyde (FA).

Acero et al.⁴¹ compared oxidation of MTBE and its by-products TBF, TBA, AC, and FA with O_3 and O_3/H_2O_2 . The AOP O_3/H_2O_2 oxidized MTBE and its degradation products much more efficiently than ozone did. Rate constants for reactions with ozone ranged from 0.003 to $0.78 M^{-1}s^{-1}$, compared with rate constants of 1.3×10^8 to $1.9 \times 10^9 M^{-1}s^{-1}$ for O_3/H_2O_2 . Several other researchers have reported O_3/H_2O_2 to be more effective than ozone for the removal of MTBE.^{42–44}

Baus et al.⁷ compared the removal of four fuel oxygenates MTBE, ETBE, *tert*-amylmethylether (TAME), and *di*-isopropylether (DIPE) with O_3 , O_3/H_2O_2 , UV/ O_3 , and UV/ H_2O_2 . The comparative removal efficiency by all processes was as follows:

$$MTBE \ll TAME \approx ETBE < DIPE.$$

The removal of all compounds by ozone was negligible, and it was concluded that the formation of the hydroxyl radical was necessary for oxidation of these ethers. The best results were obtained with UV/ O_3 and UV/ H_2O_2 . MTBE was reduced by 90% in 5 min by UV/ O_3 and in 27 min by UV/ H_2O_2 .

Huling et al.⁴⁵ evaluated the Fenton reaction to oxidize MTBE on exhausted GAC, with the goal of regenerating the GAC for further MTBE adsorption. The GAC was first soaked in a ferric sulfate solution to allow Fe to diffuse into the GAC pores and then loaded with MTBE to exhaustion. The spent GAC was contacted with H_2O_2 to initiate the Fenton reaction between Fe(II) and H_2O_2 and to oxidize MTBE. Up to 29% of the MTBE sorbed to GAC was removed by the Fenton reaction. The researchers surmised that Fe did not fully penetrate into GAC pores, and, therefore, oxidation of MTBE occurred only near the pore openings. Consequently, the rate of oxidation was limited by the diffusion rate of desorbed MTBE from the interior of pores to the pore openings rather than by kinetics of the Fenton reaction.

Hung²¹ demonstrated oxidation of MTBE with TiO_2/UV and $TiO_2/H_2O_2/UV$. An initial MTBE concentration of 750 mg/l was reduced by as much as 80% in these experiments. In comparing the oxidants, MTBE degradation was enhanced by the addition of H_2O_2 . The degradation rate in the $TiO_2/H_2O_2/UV$ system was 2.8 times faster at pH lower than 5 but only 30% faster at pH higher than 5.

Oxidation of Pesticides

Pesticides encompass a broad range of contaminants that include algicides, antimicrobials, fumigants, fungicides, herbicides, insecticides, miticides, nema-

TABLE 18.1. Chemical Families and MCLs of Common Pesticides

Chemical Group	Example	EPA MCL (mg/l)
Aniline derivatives	Alachlor	0.002
Carbamate	Carbofuran	0.040
Chlorophenoxy compounds	2,4-D	0.070
Organochlorine	Chlordane	0.002
Organophosphate	Glyphosate	0.7
Pyridine, pyrimidine	Diquat	0.02
Triazine	Atrazine	0.003
Urea substituted	Diuron	no MCL

ticides, defoliants, and desiccants. These contaminants reach water sources through wastewater from manufacturing facilities and through agricultural and urban runoff. Many pesticides have an adverse effect on human health and aquatic life at low exposure levels, and contamination of groundwater and surface water sources by pesticides is a pervasive water quality concern.

Chemical families of common pesticides, examples in each group, and USEPA MCLs where applicable are listed in Table 18.1.

AOPs have been found to be more effective for oxidizing recalcitrant pesticides than ozone or UV alone. Early studies compared the effectiveness of O_3 with that of O_3/H_2O_2 . Ormad et al.⁴⁶ compared O_3 at high pH with O_3/H_2O_2 for the degradation of organochloride pesticides and examined the oxidation by-products. The contaminants tested were chlorobenzene, 1,2,4-trichlorobenzene (1,2,4-TCB), tetradifon, and dichlorobenzophenone. Ozone doses ranged from 0.2 to 1.3 mg O_3 per mg TOC, and the H_2O_2/O_3 dose ratio was 0.5. H_2O_2/O_3 was more effective for chlorobenzene and 1,2,4-TCB. The oxidants were similarly effective for tetradifon and dichlorobenzophenone. Relative removal efficiency of the pesticides by both oxidants was tetradifon > chlorobenzene > dichlorobenzophenone > 1,2,4-TCB. Neither oxidant reduced TOC by more than 10%, indicating that the compounds were not completely oxidized. The by-products formed included benzenemethanol, chlorobenzenemethanol, benzoic acid, chlorobenzoic acid, dichlorobenzoic acid, nitrobenzaldehyde, chloro-hydroxybenzaldehyde, chlorophenol, and trichlorophenol.

Lambert et al.⁴⁷ examined degradation of five herbicides with O_3 and O_3/H_2O_2 . In these experiments, a surface water sample was spiked with 2 $\mu\text{g/l}$ each of atrazine, benazolin, bentazone, imazapyr, and triclopyr. Consumed ozone doses were 1, 2, and 3 mg/l, and H_2O_2 was added at six mass ratios to consumed O_3 ranging between 0 and 1.0. Only bentazone was as effectively removed by O_3 without H_2O_2 . Removals of the other four pesticides increased as the mass ratio of H_2O_2 increased.

Muller and Jekel⁴⁸ evaluated AOPs for oxidation of atrazine based on energy consumption. The AOPs evaluated were O_3/UV , H_2O_2/UV , and O_3/H_2O_2 . These processes were also compared with UV and O_3 alone. Each

process was optimized for 90% atrazine removal. For H_2O_2 , equivalent energy consumption was calculated based on the cost of the chemical relative to the cost for electricity. Energy consumption ranged from 0.1 to 2.8 kWh/m^3 , and $\text{O}_3/\text{H}_2\text{O}_2$ required the least energy. Energy consumption values were 2.8 kWh/m^3 for UV, 1.7 kWh/m^3 for $\text{H}_2\text{O}_2/\text{UV}$, 0.9 kWh/m^3 for O_3/UV , 0.2 kWh/m^3 for O_3 , and 0.1 kWh/m^3 for $\text{O}_3/\text{H}_2\text{O}_2$.

In many subsequent studies, photo-assisted AOPs have been shown to be most effective for pesticides. Several researchers have reported superior performance of the photo-Fenton process compared with other AOPs for mineralization of a variety of pesticides. Benitez et al.⁴⁹ compared energy consumption by UV, $\text{H}_2\text{O}_2/\text{UV}$, and $\text{Fe(II)/H}_2\text{O}_2/\text{UV}$ for 70% removal of diuron. The energy consumed by $\text{Fe(II)/H}_2\text{O}_2/\text{UV}$ was 11% of the energy required for $\text{H}_2\text{O}_2/\text{UV}$ and 8% of the energy required for UV.

Badawy et al.⁵⁰ evaluated the removal of organo-phosphorus pesticides from wastewater using UV, $\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe(II)/H}_2\text{O}_2$, $\text{Fe(II)/H}_2\text{O}_2/\text{UV}$, and $\text{Fe(III)/H}_2\text{O}_2/\text{UV}$ and concluded that destruction of these contaminants was strongly accelerated by the photo-assisted oxidation processes. The sample water contained 50 mg/l each of fenitrothion, diazinon, and profenofos to simulate wastewater effluent from a pesticide-manufacturing facility. The relative treatment efficiency of the processes was $\text{Fe(II)/H}_2\text{O}_2/\text{UV} > \text{Fe(III)/H}_2\text{O}_2/\text{UV} > \text{H}_2\text{O}_2/\text{UV} \gg \text{Fe(II)/H}_2\text{O}_2 > \text{UV}$. Addition of UV in the photo-Fenton process significantly improved the efficiency of the Fenton reagent. TOC degradation after 90 min of treatment with the Fenton process at pH 3 after 90 min was 54% for fenitrothion, 13% for diazinon, and 46% for profenofos. The photo-Fenton process increased TOC removal to 87% for fenitrothion, 57% diazinon, and 90% profenofos at the same pH after 30 min.

Atrazine and alachlor are two of the more difficult pesticides to mineralize. Farre et al.⁵¹ compared $\text{Fe(II)/H}_2\text{O}_2/\text{UV}$, TiO_2/UV , and O_3/UV for removal of five common pesticides: alachlor, atrazine, chlorofenvinfos, diuron, and pentachlorophenol (PCP). The photo-Fenton process was the most effective for all of the pesticides except alachlor, which TiO_2/UV mineralized more effectively. In the first 15 min of contact time, the rate of mineralization, measured as TOC removal, ranged from 35 mg/l/s for PCP to 2.2 mg/l/s for atrazine. The rates of mineralization for the other two processes were 0.8–14 mg/l/s for TiO_2/UV and 0.4–23 mg/l/s for O_3/UV . Of the five pesticides, atrazine was mineralized least effectively by all processes, with 10%–30% TOC removal. For PCP, TOC removal ranged from 65% to 90%. In general, the pesticides were mineralized in descending order of $\text{PCP} > \text{chlorofenvinfos} > \text{diuron} > \text{isoproturon} > \text{alachlor} > \text{atrazine}$.

Kruithof et al.⁵² demonstrated successful treatment of atrazine with $\text{H}_2\text{O}_2/\text{UV}$. A $6 \mu\text{g/l}$ atrazine concentration was reduced to less than $1 \mu\text{g/l}$ by applying 25 mg/l of H_2O_2 , with UV at electric energies greater than 0.5 kWh/m^3 .

Removal of carbofuran with O_3 , UV, $\text{Fe(II)/H}_2\text{O}_2$, O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, and $\text{Fe(III)/H}_2\text{O}_2/\text{UV}$ was evaluated by Benitez et al.⁴⁹ The initial carbofuran concentration was 100 mg/l. Psuedo-first-order rate constants were estimated

from the results to compare processes. The photo-assisted AOPs had the highest reaction rates. The photo-Fenton reaction had the highest reaction rate ($>200 \times 10^{-4}/s$), followed by H_2O_2/UV ($43.5 \times 10^{-4}/s$), O_3/UV ($23 \times 10^{-4}/s$), O_3 ($7 \times 10^{-4}/s$), $Fe(III)/H_2O_2$ ($2.2\text{--}7.1 \times 10^{-4}/s$), and UV ($3.3 \times 10^{-4}/s$).

O_3 and O_3/UV were compared for their effect on the removal and biodegradability of the pesticide triadimenol by Lafi and Al-Qodah.⁵³ O_3/UV was more effective than O_3 alone both for oxidation of triadimenol and for increasing its biodegradability. The oxidation rate of triadimenol was 1.7 times faster with O_3/UV than with O_3 . COD remaining after biologic treatment was approximately twice as great in the O_3 -treated samples as in the O_3/UV -treated samples.

The oxidation of 4-chloro-2 nitrophenol by various AOPs was compared by Saritha et al.⁵⁴ The researchers reported the relative degradation efficiencies as follows: $Fe(II)/H_2O_2/UV > TiO_2/UV > H_2O_2/UV > Fe(II)/H_2O_2 > UV$. Trapido et al. compared oxidation of nitrophenols with ozone and combinations of ozone with hydrogen peroxide and UV. Relative reaction rates of the oxidants were as follows: $O_3/H_2O_2/UV > O_3/H_2O_2 > O_3/UV > O_3$. The reaction rates for $O_3/H_2O_2/UV$ were 2–14 times faster than oxidation with O_3 .

Oxidation of Taste and Odor Compounds

Geosmin and MIB are the two contaminants most commonly associated with taste and odor problems in drinking water supplies. Their appearance is typically seasonal and is triggered by hydrological changes in the watershed. While these contaminants are not regulated, they have a very low odor threshold (around 10 ng/l) and consequently are among the more frequently cited causes of consumer complaints.

Geosmin and MIB can be removed by adsorption to GAC or powdered activated carbon (PAC) and can be destroyed by oxidation. Selection of an adsorption process, an oxidation process, or both operated in series can depend on several factors, including other treatment goals and the frequency and severity of taste and odor events.

AOPs are more effective than ozone or other oxidants for oxidizing geosmin and MIB. The Metropolitan Water District of Southern California evaluated O_3 and O_3/H_2O_2 for the removal of geosmin and MIB at pilot scale.^{55,56} Water samples were spiked to achieve 100 ng/l concentrations each of geosmin and MIB. It was found that target removal rates could be achieved at significantly lower ozone doses when hydrogen peroxide was added at a ratio of 0.2 H_2O_2/O_3 . Removal of 90% of the contaminants was achieved with 36%–60% less O_3 by using H_2O_2/O_3 than by oxidation with O_3 alone. Similarly, the reduction in ozone use to achieve 80% removals with H_2O_2/O_3 ranged from 44% to 70%.

Glaze et al.⁵⁷ evaluated nine oxidizing agents for removal of six taste and odor compounds. The oxidizing agents included chlorine, chlorine dioxide, chloramines, potassium permanganate, hydrogen peroxide, ozone, and three

AOPs: $\text{O}_3/\text{H}_2\text{O}_2$, O_3/UV , and $\text{H}_2\text{O}_2/\text{UV}$. The taste and odor compounds were 1-hexanal, 1-heptanal, dimethyltrisulfide, 2,4-decadienal, geosmin, and MIB. The studies showed that chlorine, chlorine dioxide, chloramines, potassium permanganate, and hydrogen peroxide were not effective in controlling geosmin and MIB, but ozone and the AOPs were. Furthermore, it was concluded that the reaction responsible for the removal of geosmin and MIB by ozone was oxidation by the hydroxyl radical.

Oxidation of Disinfection By-Product (DBP) Precursors

AOPs have been evaluated for the removal of DBP precursors. Several researchers have shown that organic carbon is mineralized more effectively by AOPs than by ozone alone. Volk et al.⁵⁸ compared ozone, $\text{O}_3/\text{H}_2\text{O}_2$, and O_3/TiO_2 for reduction of dissolved organic carbon (DOC) in a fulvic acid solution. The initial DOC concentration was 2.8 mg/l. At an ozone dose of 6.5 mg/l, the O_3/TiO_2 system achieved the greatest DOC reduction (24%) followed by $\text{O}_3/\text{H}_2\text{O}_2$ (18%) and O_3 (15%).

Glaze et al.⁵⁹ evaluated the effects O_3 and O_3/UV on trihalomethane formation potential (THMFP) of two surface waters with high formation potentials. The raw water samples had TOC concentrations of approximately 9 mg/l and THMFP ranging from 540 to 700 $\mu\text{g}/\text{l}$. The researchers reported that O_3/UV was significantly more effective than O_3 alone for destruction of THM precursors. THMFP was completely dissipated after 100 min of photolytic ozonation at an ozone dose of 4.2 mg/l-min and a UV transfer of 0.2 W/l at 254 nm. The researchers noted that approximately 2–3 mg/l TOC remained in the samples even after THMFP was completely dissipated. This was attributed to the presence of organic compounds that were refractory to further oxidation but that did not react with chlorine to form THMs.

Sanly et al.⁶⁰ evaluated $\text{Fe(III)}/\text{UV}$, $\text{H}_2\text{O}_2/\text{UV}$, and $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{UV}$ for removal of DBP precursors from a humic acid (HA) solution. The HA solution had a DOC concentration of 10 mg/l, and a THM formation potential of 590 $\mu\text{g}/\text{l}$. The $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{UV}$ system achieved the greatest DOC removal (80%), followed by $\text{H}_2\text{O}_2/\text{UV}$ (40%) and $\text{Fe(III)}/\text{UV}$ (less than 10%). The researchers attributed this to more efficient hydroxyl radical formation for $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{UV}$. DOC removal increased with $\text{H}_2\text{O}_2:\text{Fe}$ molar ratio up to 10. Beyond a molar ratio of 10, there was no further increase in DOC removal, which was attributed to the scavenging effect on hydroxyl radicals by excess H_2O_2 .

Interestingly, the $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{UV}$ -treated sample did not have the lowest THM formation potential even though it had the lowest DOC concentration. THMFPs were 222 $\mu\text{g}/\text{l}$ for $\text{H}_2\text{O}_2/\text{UV}$, 397 $\mu\text{g}/\text{l}$ for $\text{Fe(III)}/\text{UV}$, and 438 $\mu\text{g}/\text{l}$ for $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{UV}$. It was theorized that iron broke organic compounds down into species that were more reactive with chlorine. To test this, Fe was added to $\text{H}_2\text{O}_2/\text{UV}$ -treated water, and THMFP was measured. THMFP for this sample was 348 $\mu\text{g}/\text{l}$, a significant increase from 222 $\mu\text{g}/\text{l}$. The researchers

pointed out that neither DOC nor UV absorbance predicted TTHM formation for the oxidized samples.

Kitis and Kaplan⁶¹ investigated the use of iron-coated pumice particles as a heterogeneous catalyst with H_2O_2 for removal of DOC. In these experiments, various concentrations of pumice (0–3000 mg/l) and H_2O_2 (0–1000 mg/l) were added to either natural surface water or a HA solution in completely mixed reactors. After 24 h of treatment, DOC reductions ranged from 35% to 73%. A pumice dose of 100 mg/l combined with 1000 mg/l of H_2O_2 decreased the DOC concentration from 6 to 3 mg/l. A combination of 3000 mg/l pumice and 1200 mg/l H_2O_2 reduced DOC in the same sample to 1.7 mg/l.

FACTORS AFFECTING SYSTEM PERFORMANCE

The performance of AOPs is affected by many factors, including the presence of hydroxyl radical scavengers, pH, water temperature, oxidant doses and ratios, and contact time. Because the hydroxyl radical is so reactive, all AOPs are affected by the presence of scavengers such as carbonate, bicarbonate, and NOM. Even hydrogen peroxide, a chemical used to promote hydroxyl radical formation, can act as an $^{\circ}\text{OH}$ trap. Consequently, a micropollutant targeted for removal must compete with all other scavengers present to react with $^{\circ}\text{OH}$. Scavengers also influence the effect of pH on AOP performance. The hydroxyl ion (OH^-) promotes hydroxyl radical formation. As Hoigné and Bader¹⁵ noted, however, this effect is often offset by the increased concentration of carbonate scavengers at higher pH. The influence of other factors varies among the AOPs.

$\text{O}_3/\text{H}_2\text{O}_2$

The respective concentrations of H_2O_2 and O_3 have a significant impact on oxidation efficiency in $\text{O}_3/\text{H}_2\text{O}_2$ systems. Hydrogen peroxide acts as a promoter as well as a scavenger of $^{\circ}\text{OH}$. Consequently, in many cases, oxidation efficiency of $\text{O}_3/\text{H}_2\text{O}_2$ has been shown to increase with $\text{H}_2\text{O}_2/\text{O}_3$ ratio until a maximum is reached where the scavenging effect of H_2O_2 exerts greater influence. Glaze et al.¹ reported that the oxidation rate of TCE with $\text{O}_3/\text{H}_2\text{O}_2$ increased up to an $\text{H}_2\text{O}_2/\text{O}_3$ molar ratio of 1.0 then began to decrease. Duguët et al.¹⁴ reported an optimum $\text{H}_2\text{O}_2/\text{O}_3$ ratio of 0.4 for the removal of CNB.

In the evaluation of $\text{O}_3/\text{H}_2\text{O}_2$ for oxidation of MIB and geosmin, Koch et al.⁵⁵ reported that the optimum $\text{H}_2\text{O}_2/\text{O}_3$ ratio varied by water source. Two sources were tested, State Project Water (SPW) and the Colorado River. The optimal ratio for SPW was 0.1–0.2, but the optimal ratio for Colorado River water continued to increase for $\text{H}_2\text{O}_2/\text{O}_3$ ratios between 0 and 0.5. This difference was attributed to the presence of more natural $^{\circ}\text{OH}$ promoters in SPW.

The effect of $\text{H}_2\text{O}_2/\text{O}_3$ ratio may be affected by the presence of hydroxyl radical scavengers, particularly background NOM. In surface water with

6.2 mg/l TOC, Lambert et al.⁴⁷ reported that no optimum was observed for $\text{H}_2\text{O}_2/\text{O}_3$ mass ratios up to 1.0 for degradation of five herbicides, including atrazine. Similarly, Muller and Jekel⁴⁸ reported that no optimum ratio was found when testing $\text{H}_2\text{O}_2/\text{O}_3$ mass ratios between 0.3 and 0.9 for degradation of atrazine in surface water with a DOC concentration of 6.2 mg/l.

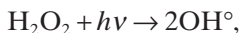
O_3/UV

Oxidation of a contaminant with O_3/UV can occur by direct oxidation with ozone, photolysis, or oxidation by the hydroxyl radical. The relative contribution of each mechanism depends on oxidation conditions, water quality characteristics, the extent to which UV is absorbed by the contaminant, and the contaminant's reactivity to light induced transformation. The desired AOP reaction is oxidation by the hydroxyl radical.

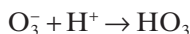
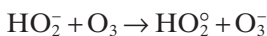
The first step in hydroxyl radical formation is photolysis of O_3 to form H_2O_2 :



The hydrogen peroxide thus formed *in situ* can lead to hydroxyl radical production in two ways, by photolysis of hydrogen peroxide,



or through a chain reaction initiated by the hydrogen peroxide conjugate base, HO_2^- ,



The HO_2^- pathway is the more important one because the molar absorption coefficient of O_3 is much higher (3300 Mol/L·s) than that of H_2O_2 (17.9 Mol/L·s). Consequently, in carbonate-free water, hydroxyl radical formation increases with pH. As the carbonate concentration of water increases, this effect is increasingly negated through hydroxyl radical scavenging by carbonate and bicarbonate.

Beltran et al.⁶² compared atrazine removal at pH 2 with that at pH 7. Hydroxyl radical formation and atrazine removal were greater at pH 7 because hydrogen peroxide remains in its nondissociated form at pH 2 and does not react with ozone to form hydroxyl radicals. Similarly, Oh et al.⁶³ reported that hydroxyl radical formation was much faster at pH 7 than at pH 3. H_2O_2 concentration increased as O_3 concentration decreased until reaching a maximum concentration when O_3 was completely dissipated. At this point, H_2O_2 concentration decreased as hydroxyl radical formation occurred. Oh et al.⁶³

suggested monitoring H_2O_2 concentration as a means of optimizing O_3/UV . Lafi et al.⁵³ reported increased removal of triadimenol with pH. Removal was much greater at pH 7 than at pH 4 but increased only slightly from pH 7 to pH 11.3.

O_3/UV performance is also affected by the $\text{O}_3:\text{UV}$ dose ratio. Hydroxyl radical formation increases with O_3 dose until an optimal dose is reached. Beyond the optimal O_3 dose, excess H_2O_2 acts as a hydroxyl radical scavenger, and oxidation efficiency decreases. Oh et al.⁶³ reported an optimum ratio of 2 einstein/l/s per mol/l/s O_3 but noted that this optimum could vary by water source, depending on the UV-adsorbing constituents present.

The rate of ozone decomposition, and hence hydroxyl radical formation, increases with light intensity. Wittman et al.⁶⁴ reported that ozone decomposition occurred approximately four times faster at a light intensity of 9.7×10^{-5} einstein/s than at 4.12×10^{-7} einstein/s. Garoma and Gurol⁶⁵ reported that oxidation of MTBE increased as light intensity increased at a fixed ozone dose. Three light intensities (1.35, 2.73, and 4.28 W/l) were tested with three ozone doses (24, 39, and 51 mg/l). At each ozone dose, MTBE removal increased as light intensity increased.

$\text{H}_2\text{O}_2/\text{UV}$

Efficiency of $\text{H}_2\text{O}_2/\text{UV}$ depends on the rate of hydroxyl radical formation during photolysis of H_2O_2 . As the background UV absorbance of water increases, hydrogen peroxide must compete with more constituents for photon energy. Hence, hydroxyl radical formation decreases as UV absorbance of the water increases.

Hydroxyl radical formation increases as light intensity increases. Ozone, however, absorbs UV light at a much higher rate than H_2O_2 does. Consequently, PC hydroxyl radical formation is more efficient with O_3/UV than with $\text{H}_2\text{O}_2/\text{UV}$.^{1,66}

Fenton and Photo-Fenton Reactions

Oxidation efficiency in the Fenton and photo-Fenton reactions is affected by pH, the ratio of H_2O_2 to Fe(II) dose, and for the photo-Fenton reaction, light intensity. Efficiency is affected by pH in several ways. The distribution of Fe species is pH dependent, and the efficiency of the Fenton reaction is affected by Fe speciation. More $\text{Fe}(\text{OH})^+$ is formed at low pH, and the activity of $\text{Fe}(\text{OH})^+$ is higher than that of Fe^{2+} in the Fenton and photo-Fenton reactions. Consequently, the ideal pH for both reactions is around 3.^{38,50} The Fenton reaction is hindered at high pH by the disassociation and autodecomposition of H_2O_2 . In the photo-Fenton reaction, efficiency is also decreased at pH greater than 4 by the precipitation of ferric hydroxide, which decreases process efficiency by hindering the transmittance of UV light. At pH lower than 3,

oxidation efficiency is decreased by hydroxyl radical scavenging by hydrogen ions.

Oxidation efficiency is affected by the ratio of $\text{H}_2\text{O}_2/\text{Fe(II)}$ dose. Badawy et al.⁵⁰ evaluated the effect of $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratio of oxidation of three pesticides with the Fenton and photo-Fenton reactions. TOC removal was optimized at a $\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratio of 100 in the Fenton reaction and at a ratio of 50 in the photo-Fenton reaction. Al Momani³⁸ reported that the oxidation rate of 2,4-DCP increased as H_2O_2 doses increased from 15 to 50 mg/l at a fixed Fe(II) dose of 10 mg/l ($\text{H}_2\text{O}_2/\text{Fe(II)}$ molar ratios of 2.5–8.2). In the photo-Fenton process, too much iron can add color to the water and hinder absorption of UV light. De et al.³⁶ reported that changing Fe dose had a greater impact than changing H_2O_2 dose on mineralization of phenol and chlorophenol compounds.

Khan et al.⁶⁷ evaluated the effect of pH, reaction time, and $\text{Fe}^{2+}:\text{H}_2\text{O}_2:\text{DOC}$ mass ratio on mineralization and biodegradability of p-nitrophenol. Experiments were conducted with $\text{Fe}^{2+}:\text{H}_2\text{O}_2:\text{DOC}$ mass ratios of 1:10:1, 10:10:1, and 10:100:1 and pH values of 2, 3, and 4. At each $\text{Fe}^{2+}:\text{H}_2\text{O}_2:\text{DOC}$ ratio, pH 3 was the optimum pH for biodegradability enhancement. The increase in biodegradability occurred very rapidly, and there was little change after the first 30 s. The $\text{Fe}^{2+}:\text{H}_2\text{O}_2:\text{DOC}$ ratio of 10:10:1 resulted in the greatest increase in biodegradability (70%). The other two ratios resulted in a 50% increase in biodegradability. DOC was reduced most effectively at pH 4, and at a $\text{Fe}^{2+}:\text{H}_2\text{O}_2:\text{DOC}$ ratio of 10:10:1. DOC reduction ranged from 3% to 10% at pH 2, from 10% to 20% at pH 3, and from 20% to 40% at pH 4. Most of the DOC removal occurred in the first 10 min of reaction time, and, at reaction times of 10–50 min, there was little difference among DOC removals.

Benitez et al.⁶⁸ evaluated the oxidation of phenylurea herbicides by the Fenton and photo-Fenton processes. In each, oxidation was more effective at pH 3.3 than at pH 2 or 4, and degradation increased as $\text{H}_2\text{O}_2:\text{Fe}$ molar ratios increased in the range of 1:1–1:10.

TiO_2/UV

Oxidation efficiency of TiO_2/UV is affected by the catalyst (TiO_2) dose, pH, light intensity, initial contaminant concentration, and the type of electron acceptor. Saritha et al.⁵⁴ reported that maximum oxidation efficiency occurred at pH 7 for oxidation of 4-chloro-2 nitrophenol (4C–2–NP). The process was least effective at low pH. Efficiency steadily increased between pH 2 (20% removal) and pH 7 (80% removal) and decreased slightly between pH 7 and 10 (75% removal). In the same study, it was reported that degradation increased to an optimal TiO_2 dose then decreased with higher doses. Degradation increased from 47% at a TiO_2 dose of 0.1 g to 86% at the optimal dose of 3 g. Degradation decreased from 86% at 3 g to 45% at a dose of 0.5 g. The effect of decreasing degradation at doses beyond the optimum was

attributed to the aggregation of TiO_2 particles, causing a loss of interfacial area between the solution and catalyst, and to the reduction in UV transmittance caused by the light-scattering effect of particles.

An optimum TiO_2 dose was also reported by Suri et al.,²⁷ but the optimum dose depended on the initial concentration of the contaminant. The optimum TiO_2 dose for an initial toluene concentration of 0.1 mg/l was 0.01% by weight. For initial toluene concentrations of 1 and 10 mg/l, however, the optimum TiO_2 dose was 0.1%. Doses greater than the optimum resulted in a significant decrease in oxidation efficiency in each case. The researchers reported similar behavior for the destruction of TCE and methyl ethyl ketone. An optimum dose was found for each and the optimum dose depended on the initial concentration of the contaminant.

The TiO_2 /UV rate of oxidation increases with light intensity. Suri et al.²⁷ compared oxidation of TCE at incident light intensities of 193 $\mu\text{einsteins/l}\cdot\text{min}$ with that of 280 $\mu\text{einsteins/l}\cdot\text{min}$. The initial TCE concentration was reduced by 90% after 10 min at the lower intensity and after 2 min at the higher intensity light.

Oxidation efficiency of the TiO_2 /UV process can be improved by adding H_2O_2 as an electron acceptor. In this role, H_2O_2 reacts with the conduction band electron to prevent its recombination. Hydroxyl radical formation during this reaction further enhances TiO_2 /UV oxidation efficiency.

REGULATIONS

The USEPA has promulgated a series of interrelated drinking water regulations to address the trade-offs between limiting chronic health risks from exposure to DBPs and avoiding acute health risks from exposure to pathogens. Although these regulations have greater application to traditional disinfection practices, AOPs also provide disinfection and generate DBPs.

Pathogen inactivation is addressed in the EPA National Primary Drinking Water Regulations under the Surface Water Treatment Rule, the Interim Enhanced Surface Water Treatment Rule, and the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR). In the USEPA approach, microbial inactivation is related to treatment conditions through CT tables, where C is the residual disinfectant concentration and T is contact time.

Although the hydroxyl radical is a potent disinfectant, its lack of a residual makes it impossible to obtain CT credit. Disinfection credit, however, can be obtained for O_3 or UV in $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/UV processes. CT credit can be obtained for ozone by measuring its residual and contact time before H_2O_2 or UV is added to accelerate ozone decomposition. In terms of the CT calculation, this is analogous to obtaining free chlorine disinfection credit before adding ammonia to form chloramines. The ozone contact time and residual need not be great because the CT requirements for inactivation of viruses and *Giardia* with ozone are low relative to other disinfectants. For example, at

10°C, the CT for 0.5-log inactivation of *Giardia* is 0.22 for ozone compared with 22 for free chlorine. Under the same conditions, the CT for 2-log inactivation of viruses is 0.5 for ozone and 3.0 for free chlorine.

The purpose of LT2ESWTR is to reduce the risk of exposure to *Cryptosporidium*. The rule requires monitoring water supplies for *Cryptosporidium* and additional treatment of supplies with the highest risk levels. The USEPA has determined that UV is a feasible treatment for up to 4-log inactivation of *Cryptosporidium*. Consequently, O₃/UV systems that meet EPA requirements can receive *Cryptosporidium* disinfection credits for ozone and UV. Credits for UV inactivation of *Giardia* are comparable to those for *Cryptosporidium*, but it is likely that the requirement for *Giardia* inactivation would be met by ozone.

The Stage 1 and Stage 2 Disinfectants and Disinfection By-products Rules were promulgated to provide protection against potential risks for cancer and reproductive and developmental health effects associated with DBPs. These rules establish MCLs for total trihalomethanes (TTHMs), five haloacetic acids (HAA5), and bromate (BrO₃⁻). These DBPs were selected for regulation because they are the most frequently encountered, and it was assumed that steps to limit their formation would also control the formation of other DBPs.

AOPs that involve ozone decomposition can generate the same DBPs as ozone, namely, aldehydes, ketones, and carboxylic acids. In waters containing bromide, brominated DBPs can also be formed. These include bromate, bromoform, brominated acetic acids and acetoneitriles, bromopicroin, and cyanogen bromide (if ammonia is present).

Reports on the effects of the hydroxyl radical on bromate formation have been mixed. Song et al.⁶⁹ reported that the addition of H₂O₂ during ozonation could increase or decrease bromate formation, depending on other water quality characteristics. Similar results were reported by Von Gunten and Hoigné.⁷⁰ Symons and Zheng,⁷¹ however, reported that no bromate formation occurred with H₂O/UV even though the test waters were spiked with unnaturally high bromide concentrations (1–5 mg/l). They attributed this to the absence of ozone due to direct formation of hydroxyl radicals through photolysis of H₂O₂.

EQUIPMENT AND GENERATION

Several of the AOPs comprise combinations of ozone and UV. Ozonation is covered in Chapter 15 of this text, and UV is covered in Chapter 17. The reader is referred to these chapters for discussion of the equipment required for generation of ozone and UV.

Several AOPs (O₃/H₂O₂, UV/H₂O₂, Fe(II)/H₂O₂, Fe(II)/UV/H₂O₂, and TiO₂/UV/H₂O₂) require a hydrogen peroxide feed system. In the O₃/H₂O₂ process, hydrogen peroxide can be added before ozone, after ozone, or

concurrently with ozone. Addition of H_2O_2 after ozone has the benefit of maximizing the CT credit for ozone if the system is engineered to have a treatment volume dedicated to O_3 contact.

A chemical storage and metering system is required to feed hydrogen peroxide. Hydrogen peroxide is easier to handle than other disinfectants because it is not flammable or explosive and is chemically stable under normal storage conditions. It decomposes to oxygen and water with no toxic residue.

Hydrogen peroxide is available in concentrations of 35%, 50%, and 70%. The most common strength in the water and wastewater treatment industry is 50% hydrogen peroxide, which has a density of 10lb/gal and a freezing point of -62°F . Hydrogen peroxide continuously degrades, but the process is slow (1%–5% per year, depending on the concentration, grade, and amount of impurities). The by-products are off-gas consisting mainly of oxygen and some hydrogen. The degradation rate is accelerated by impurities and high temperatures. Proper materials of construction and cleaning prior to use are critical to prevent contamination of the chemical and corrosion of equipment.

Bulk truckload deliveries of hydrogen peroxide range from 4000 to 4500 gal. Storage tanks are typically Type 304L or 316L stainless steel. Special grades of aluminum and high-density polyethylene are also suitable under certain conditions. The storage tanks should be provided with filters on the vent and a trapped overflow to prevent impurities from entering the tank.

Piping systems for hydrogen peroxide are typically of Type 304L or 316L stainless steel piping and valves. Pipelines must be equipped with relief valves at points where the peroxide could become trapped between closed valves and equipment. The pressure of liquid peroxide trapped between two closed valves will steadily increase because of the generation of oxygen gas during degradation until it exceeds the pressure rating of system piping and valves. Vented ball valves should be used to prevent pressure buildup inside the valve (between the ball and the valve body) in the open or closed position.

Metering pumps used for feeding hydrogen peroxide are typically either diaphragm or peristaltic type. The off-gas produced during degradation can cause vapor lock in diaphragm metering pumps. Normally, the peroxide feed rates are very small, which makes development of vapor lock more likely. Use of diaphragm metering pumps requires special suction venting, degassing heads, and appropriately sized piping. For pump discharge pressures of 25 psi and less, peristaltic-type pumps should be considered because they are not affected by the off-gas.

Some utilities dilute peroxide upon receipt to reduce its degradation rate and to make it safer to handle. The dilution should be carried out with high-purity deionized water to prevent contamination of the peroxide and spontaneous off-gassing.

All metallic equipment and piping for storage, handling, and feeding hydrogen peroxide must be thoroughly cleaned and passivated, typically

with nitric acid, before being placed into service. The passivation process protects the hydrogen peroxide from being contaminated by the metal surface and protects the metal surface from being corroded by the hydrogen peroxide.

In the O_3/UV and H_2O_2/UV systems, water dosed with O_3 or H_2O_2 is fed to a UV reactor, as described in Chapter 17. In contrast to UV for disinfection, however, UV doses are designed to optimize hydroxyl radical formation.

Historically, Fenton's reagent was applied in batch mode. Today, however, it is applied in sequential batches and by continuous flow. A typical system consists of a reactor, chemical storage tanks, and chemical feed systems for ferric sulfate, hydrogen peroxide, acid, and lime or sodium hydroxide. The reactor is typically constructed of Type 304 or 316 stainless steel. Packaged Fenton's systems are available from equipment manufacturers.

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APPENDIX

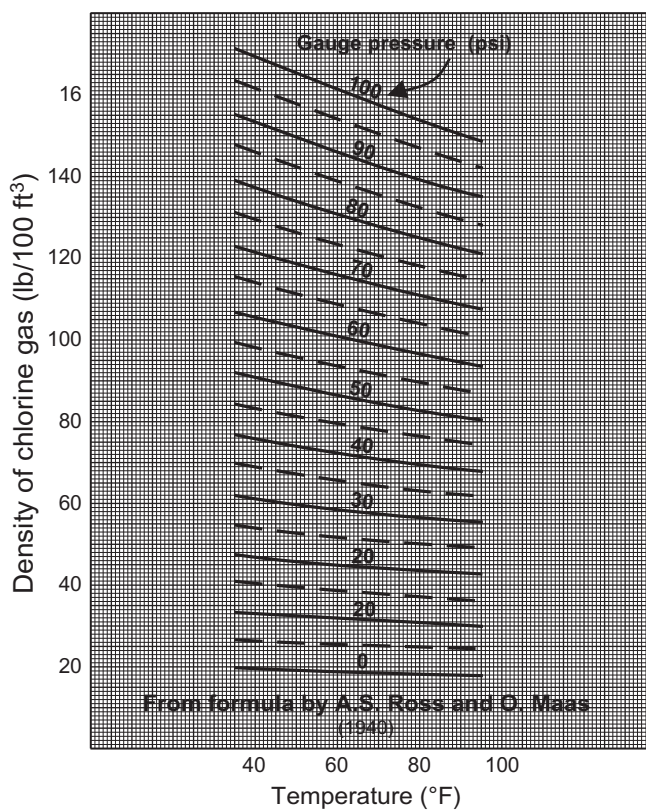


Figure A1. Density of chlorine gas under pressure (calculated from a formula by Ross, A.S. and Mass, O. The density of gaseous chlorine. *Canadian Journal of Research* 1940;18B:55–65).

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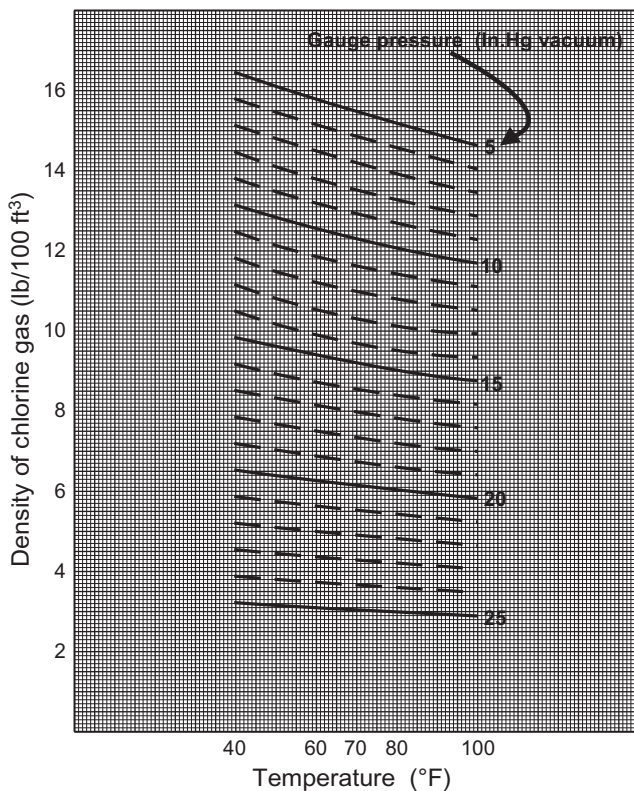


Figure A2. Density of chlorine gas under vacuum (from Ross, A.S. and Mass, O. The density of chlorine gas. *Canadian Journal of Research* 1940;18B:55–65).

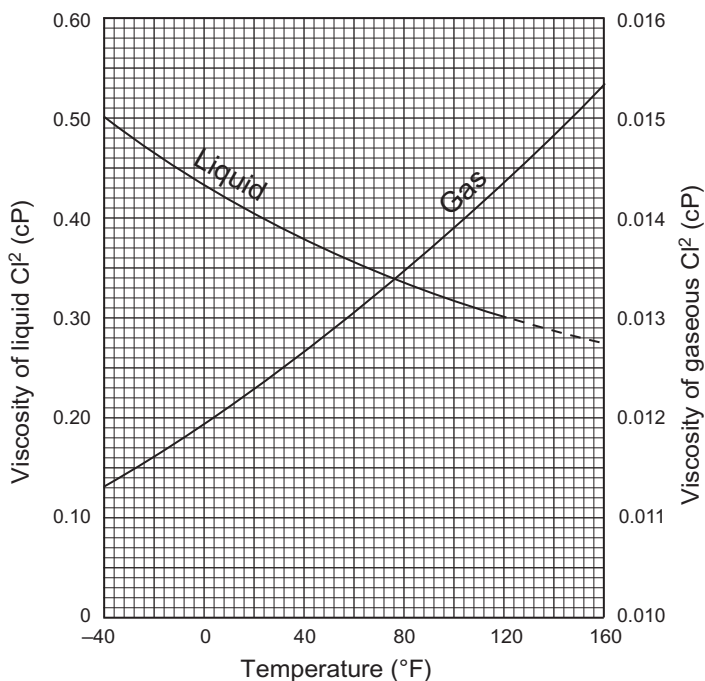


Figure A3. Viscosity of chlorine liquid and gas (from Steacie, E.W.R. and Johnson, F.M.G. The viscosities of the liquid halogens. *Journal of the American Chemical Society* 1926;47:756).

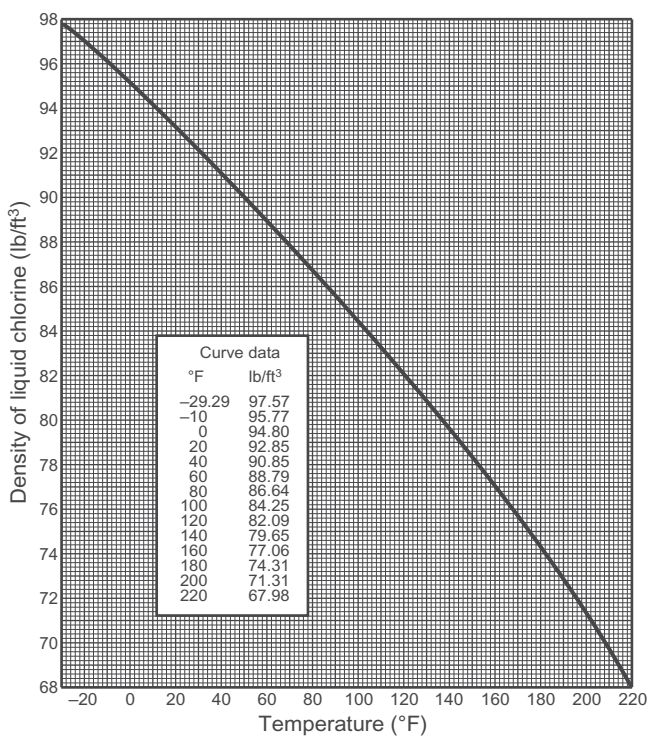


Figure A4. Temperature–density relation of liquid chlorine (from Kapoor, R. and Martin, J. Thermodynamic properties of chlorine. Engineering Research Institute, University of Michigan, 1957).

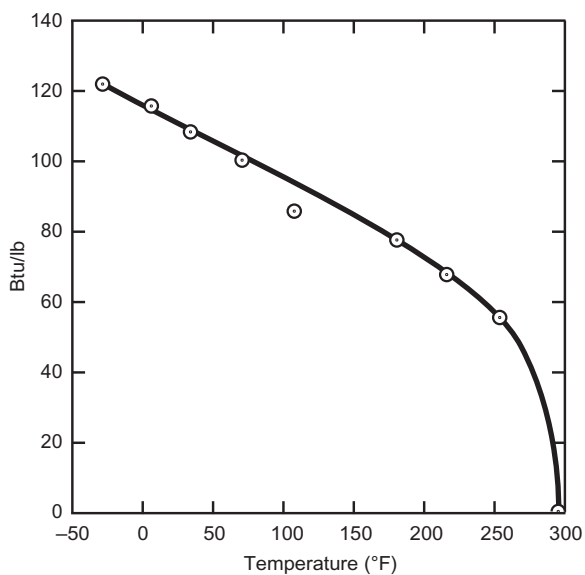


Figure A5. Latent heat of vaporization of liquid chlorine (from Pellaton, M. Constantes physiques du chlore. *Journal de Chemic Physique* 1915;13:426).

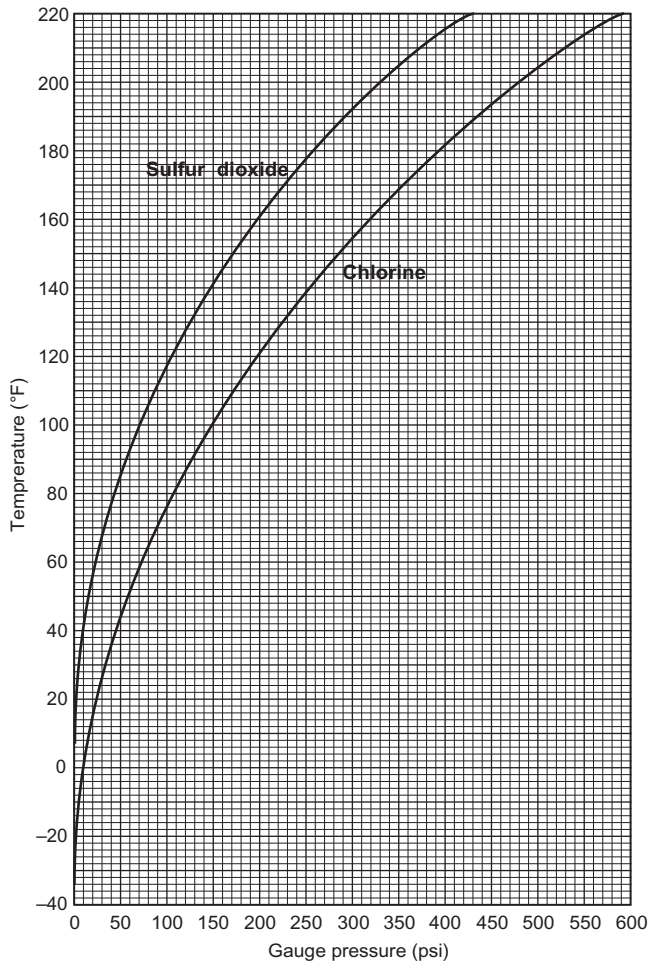


Figure A6. Vapor pressure versus temperature of liquid chlorine and sulfur dioxide.

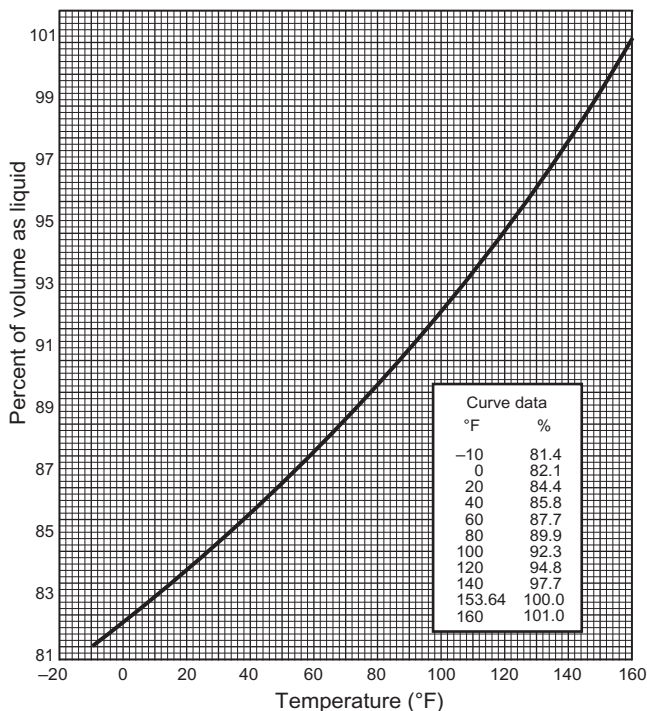


Figure A7. Volume–temperature relation of liquid chlorine in container loaded to its authorized limit (from Kapoor, R. and Martin, J. Thermodynamic properties of chlorine. Engineering Research Institute, University of Michigan, 1957).

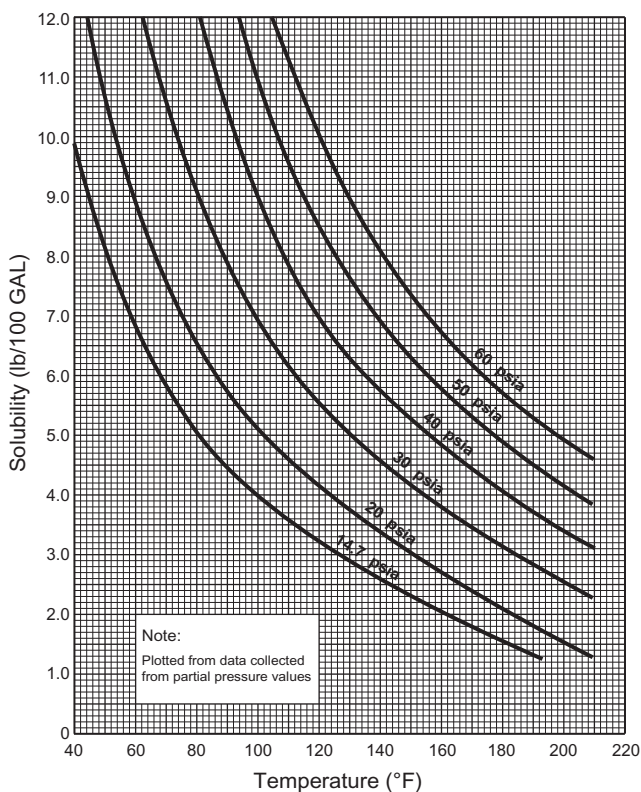


Figure A8. Equilibrium solubility of chlorine in water (from Adams, F.W. and Edmonds, R.G. Absorption of chlorine by water in a packed tower. *Industrial and Engineering Chemistry* 1937;29: 477).

CONVERSION FACTORS

	U.S. (English System)
1 ppm	=8.34 lb/mg
1 gpm	=1440 gpd
1 gpm	=0.0022 cfs
1 gal	=0.832 Imperial gal
1 gal	=0.1337 ft ³
1 gal	=8.34 lb
1 ft ³	=7.48 gal
1 mgd	=1.547 cfs
1 mgd	=694.44 gpm
1 cfs	=0.646 mgd
1 cfs	=448.8 gpm
1 day	=1440 min
1 day	=86,400 s
1 hp	=550 ft·lb/s
1 psi	=2.04 in.Hg at 60°F
1 psi	=2.31 ft H ₂ O
1 acre	=43,560 ft ²

	U.S. to Metric
1 in	=2.54 cm
1 ft	=0.3048 m
1 in ³	=16.387 cm ³
1 ft ³	=0.0283 m ³
1 oz	=0.0295 l
1 gal	=3.7854 l
1 gal	=0.003785 m ³
1 lb (mass)	=0.45359 kg
1 oz	=28.349 g
1 W·h	=3600 J
1 hp	=746 W
1 lb (force)	=4.448 N
1 gpm	=0.063 l/s
1 cfs	=2446.6 m ³ /d
1 cfs	=0.02832 m ³ /s
1 mgd	=3785.4 m ³ /d
1 psi	=6.893 kPa
1 ppm (by wt) × specific gravity	=mg/l

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