

Water Chlorination/ Chloramination Practices and Principles

MANUAL OF WATER SUPPLY PRACTICES

M20

Second Edition



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AWWA MANUAL M20

Second Edition



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MANUAL OF WATER SUPPLY PRACTICES—M20, Second Edition

Water Chlorination/Chloramination Practices and Principles

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Contents

Figures, v

Tables, ix

Foreword, xi

Acknowledgments, xiii

Chapter 1 History of Chlorination and Chloramination 1

Origin of Water Disinfection, 1
Rationale of Water Disinfection, 2
Evolution of Chlorination Materials, 3
Evolution of Chlorination Control Practices, 3
Discovery of Trihalomethanes, 4
Historical Development of Chloramine, 4
Evolution of Chloramination Materials, 5
Evolution of Chloramination Control Practices, 5
Disinfection Regulations in the United States, 6
International Disinfection Regulations, 6
The Future, 6
References, 7
Additional Sources of Information, 7

Chapter 2 Properties of Chlorination Chemicals 9

Chlorine Gas, 9
Sodium Hypochlorite, 12
Ammonia Gas, 15
Ammonia Solutions, 16
References, 17
Additional Sources of Information, 17

**Chapter 3 Chlorination Water Chemistry and Disinfection
Mechanisms 19**

Chlorination Chemistry, 19
Disinfection Mechanism, 25
Disinfection Methods, 27
References, 30
Additional Sources of Information, 30

**Chapter 4 Chlorine and Ammonia: Handling, Storage,
Feed Equipment, and Systems 31**

Gas Chlorination Facilities, 31
Handling and Storing Chlorine Gas, 32
Feeding Chlorine Gas, 36
Liquid Hypochlorite Facilities, 50
Ammonia Gas (Anhydrous Ammonia) Facilities, 56
Aqua Ammonia Facilities, 58
Common Facilities for Liquid Chemicals, 60
Ancillary Equipment, 61
References, 69

Chapter 5 Chlorine and Ammonia Safety	71
Safety-Related Chemical and Physical Properties—Chlorine, 71	
Medical Aspects and First Aid—Chlorine, 84	
Sodium Hypochlorite Safety Considerations, 86	
Ammonia Gas Safety Considerations, 90	
Aqua Ammonia (Ammonium Hydroxide) Safety Considerations, 93	
Chlorine and Ammonia Facility Requirements, 94	
References, 96	
Additional Sources of Information, 96	
Chapter 6 Chlorine/Chloramine Disinfection Strategies	97
Microbial/Disinfection By-products Dilemma, 97	
Optimizing the Chlorination/Chloramination Disinfection Process, 104	
Distribution System Chlorination (Booster or Secondary Chlorination), 112	
Treatment Plant Chlorination/Chloramination Strategies, 116	
References, 120	
Additional Sources of Information, 121	
Appendix A Dechlorination	123
Dechlorination Practices, 124	
Chemical Feed Techniques, 131	
References, 136	
Appendix B CT Values for Inactivation of <i>Giardia</i> and Viruses by Free Chlorine and Other Disinfectants.	137
Appendix C Chlorine Residual Test Methods	143
Purpose of Test, 143	
List of Simplified Methods, 144	
Simplified Procedures, 144	
References, 154	
Appendix D Disinfection (Chlorination) of Facilities	155
List of AWWA Manuals, 157	
Index, 159	

Figures

- 1-1 US typhoid mortality and disease rates, 2
- 2-1 Vapor pressure of liquid chlorine, 10
- 2-2 Volume–temperature relation of liquid chlorine in a container loaded to its authorized limit, 11
- 3-1 Hypochlorous acid/hypochlorite distribution versus pH, 20
- 3-2 Breakpoint curve, 23
- 3-3 Disinfection versus free available chlorine residuals. Time scale is for 99.6 to 100 percent kill. Temperature was in the range of 20 to 29°C, with pH as indicated, 29
- 3-4 Disinfection versus free available chlorine residuals. Time scale is for 99.6 to 100 percent kill. Temperature was in the range of 0 to 5°C, with pH as indicated, 29
- 4-1 Chlorine cylinder, 32
- 4-2 Chlorine ton container, 32
- 4-3 Chlorine ton container truck, 32
- 4-4 Chlorine tank car, 33
- 4-5 Lifting beam with motorized hoist for ton containers, 34
- 4-6 Ton containers stored on trunnions, 35
- 4-7 Chlorination feed equipment located in a separate room, 35
- 4-8 Two-cylinder scale, 36
- 4-9 Portable beam scale, 37
- 4-10 Combination trunnion and scale for a ton container, 37
- 4-11 Standard cylinder valves: poured-type fusible plug and screw-type fusible plug, 38
- 4-12 Standard ton container valve, 38
- 4-13 Auxiliary tank valve connected directly to container valve, 39
- 4-14 Chemical induction mixers use a high-speed impeller to create a vacuum to draw the chemical, gas, or liquid into intimate contact with water to be treated. Some mixers have an open impeller design and some are closed, 40

- 4-15 Compound-loop control, 46
- 4-16 Perforated diffuser for pipelines larger than 3 ft (0.9 m) in diameter, 47
- 4-17 Chlorine scrubber test process flow and instrumentation diagram, 48
- 4-18 Chlorine scrubber system, 49
- 4-19 Example of total cylinder containment, 50
- 4-20 Chemical feed pump hydraulic drive, 51
- 4-21 On-site hypochlorite flow diagram, 52
- 4-22 On-site hypochlorite generation systems use only salt, water, and electric power to generate sodium hypochlorite, 54
- 4-23 Ammonia vacuum-feed systems with antipluggage options, 57
- 4-24 Truck delivery methods, 59
- 4-25 Typical horizontal aqua ammonia storage tank, 60
- 4-26 Automatic chlorine residual analyzer, 62
- 4-27 Automatic switchover unit, 64
- 4-28 Typical installation of switchover system, 64
- 4-29 Liquid chlorine changeover system, 65
- 4-30 Chlorine/ammonia vaporizer, 66
- 4-31 Chlorine vaporizer, 67
- 4-32 Propeller mixer in open channel flow showing location of baffles, 68
- 5-1 Air pack with positive-pressure mask, 75
- 5-2 Chlorine Institute emergency kit B, 83
- 6-1 Number of regulated contaminants, 103
- 6-2 Impact of L/W on T_{10}/T ratio, 105
- 6-3 Effect of perforated baffles on the T_{10}/T ratio of circular clearwells, 106
- 6-4 Examples of poor baffling conditions in basins, 106
- 6-5 Examples of average baffling conditions in basins, 107
- 6-6 Examples of superior baffling conditions in basins, 107

- 6-7 Common chlorination points in a conventional filtration plant, 111
- 6-8 Network map with potential booster chlorination locations, 113
- 6-9 Breakpoint chlorination curve, 114
- 6-10 Booster chlorination breakpoint curve, 1 hr incubation, 114
- 6-11 Blend-residual curve for San Joaquin Reservoir chlorinated effluent and diemer chlorinated effluent (5 min contact time), 115
- 6-12 Conventional treatment, surface water, 117
- 6-13 Direct and in-line filtration treatment, surface water, 118
- 6-14 Dissolved air flotation/filtration treatment, surface water, 118
- 6-15 Typical chlorinator deep-well installation showing booster pump, 119
- 6-16 Zebra mussel sightings distribution as of 2004, 120
- A-1 “Bazooka” venturi dechlorination feeder, 133
- A-2 Mat for dechlorination of trenches during main breaks, 134
- A-3 Diffuser for dechlorination of hydrant or blowoff waters, 134

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Tables

1-1	Utilities with long experience of chloramines use, 5
2-1	Physical properties of chlorine, 11
2-2	Primary factors affecting sodium hypochlorite stability, 13
2-3	Half-life values of liquid bleach: varying temperature, pH, and concentration, 14
2-4	Physical properties of ammonia, 16
2-5	Properties of aqueous (aqua) ammonia, 30 percent by weight, 16
3-1	Chlorination disinfection by-products, 24
3-2	Common disinfection methods, 27
5-1	Chlorine exposure levels and effects on humans, 73
5-2	Summary of PPE recommendations for tasks involving potential exposure to gaseous or liquid chlorine, 78
5-3	Recommended criteria to evaluate selected PPE components for tasks involving liquid or gaseous chlorine, 78
5-4	Hazard summary for a hypothetical water system, 80
5-5	Typical emergency action checklist, 82
5-6	Summary of Hazmat responders training requirements, 83
5-7	Summary of PPE recommendations for tasks involving potential exposure to 3–20 percent sodium hypochlorite below 100°F, 89
5-8	Recommended criteria to evaluate PPE components for tasks involving 3–20 percent sodium hypochlorite, 90
5-9	Physiological effects of ammonia, 91
6-1	Surface Water Treatment Rule disinfection requirements, 104
6-2	Baffling classifications, 108
A-1	Nonchemical dechlorination methods, 125
A-2	Comparison of dechlorination agents, 126
A-3	Dechlorination chemical reactions with free chlorine, 127

- A-4 Dechlorination chemical reactions with chloramines, 128
- C-1 Calibrating comparator standard using potassium permanganate, 146
- C-2 Dilution table for various strengths of residual chlorine, 150
- C-3 Calculating free available chlorine from amperometric titration results, 150
- C-4 Calculating free available chlorine from titration results, 153

Foreword

This publication is the second edition of the American Water Works Association (AWWA) Manual M20; the original manual was titled *Water Chlorination*. This manual provides information on chlorination and chloramination practices for the disinfection of drinking water. It does not cover the use of chlorine as an oxidant or as a disinfectant for pipeline and appurtenances.

The first edition was published in 1973 and was prepared to accompany an AWWA workshop on chlorination, which was part of a comprehensive operator's training program developed by an AWWA *ad hoc* committee and the AWWA Office of Education.

Major portions of the second edition have been adapted from two AWWA publications: *Water Treatment*, second edition, Principles and Practices of Water Supply Operations; and the *Chlorination/Chloramination Handbook* by G.F. Connell. In addition, significant contributions were obtained (with permission) from publications of the Chlorine Institute, the US Environmental Protection Agency, the Awwa Research Foundation, and the *Handbook of Chlorination and Alternative Disinfectants*, fourth edition, by Geo. Clifford White. AWWA thanks the authors and publishers of these resources for the use of their materials.

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Chapter 1

History of Chlorination and Chloramination

Chlorine was “discovered” in 1744 in an obscure laboratory in Sweden (AWWA 1973). Sixty-six years later in 1810, chlorine was identified as a chemical element and was named from the Greek word *chloros* (pale green), because of its characteristic color. However, it was not until several decades later that its use as a disinfectant was recognized.

Until the germ theory of disease was established around the mid-1880s, odors were thought to be responsible for transmitting diseases. As such, it was widely believed that the control of odors would limit the spread of infections. There is no question that the earliest applications of chlorine were aimed at controlling foul odors (Baylis 1935), even though, because of the unsophisticated techniques used, the chlorinous odor imparted to the treated water was sometimes just as, or more, objectionable than the odor it was meant to remove. It was not until well into the 1890s that chlorine and chlorine-containing products were evaluated and demonstrated to be effective disinfectants.

ORIGIN OF WATER DISINFECTION

Undoubtedly the disinfection of water has been practiced for millennia, although probably with little or no understanding of the principles involved. Historical records indicate that the boiling of water had been recommended at least as early as 500 B.C. The earliest recorded use of chlorine directly for water disinfection was on an experimental basis, in connection with filtration studies in Louisville, Ky., in 1896. It was employed for a short period in 1897 in England, again on an experimental basis, to sterilize water distribution mains following a typhoid epidemic.

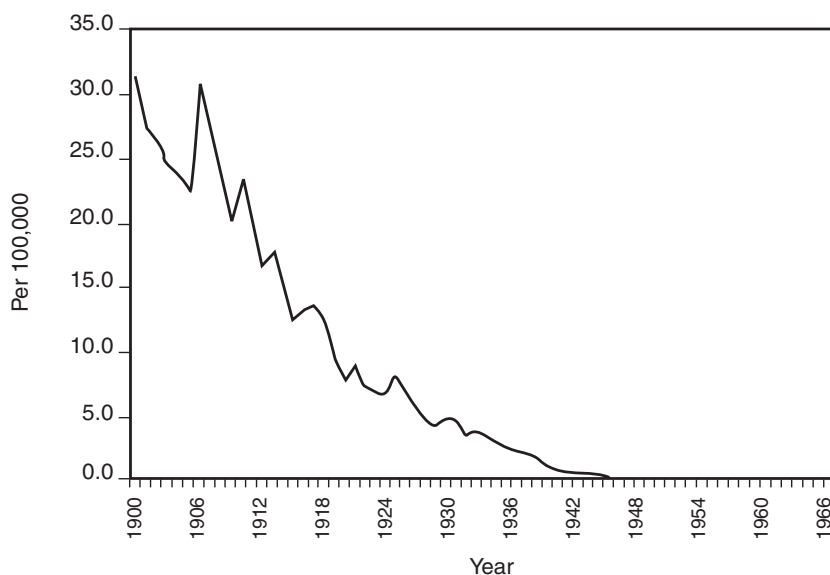
The first *continuous* use of chlorine for water disinfection was in 1902 in Belgium for the dual objective of aiding coagulation and making water biologically “safe.” In North America, the first continuous, municipal application of chlorine to water was in 1908 to disinfect the 40-mgd (151-ML/d) Boonton Reservoir supply of the Jersey City, N.J., water utility. Contested in the courts, the practice was declared to represent a public health safeguard, and this action paved the way for its rapid extension to other public water supplies throughout North America and elsewhere.

RATIONALE OF WATER DISINFECTION

Waterborne diseases, such as typhoid, dysentery, and cholera, occurred with regularity in US water systems in the 1800s. The incidence rates were high in the early 1900s (e.g., more than 25,000 typhoid deaths in 1900) but decreased rapidly with the onset of chlorination (e.g., less than 20 deaths in 1960) (Laubusch 1964), as shown in Figure 1-1. The data provide similar results for other organisms.

With such a dramatic drop in illnesses and fatalities following the onset of chlorination, the need for feeding these chemicals was well justified. To date, chlorine has emerged as the disinfectant of choice primarily because of its effectiveness (Race 1918), efficiency, economy of operation, convenience, and the persistence of a chlorine residual. The unique properties of chlorine also make its use an acceptable technique for taste-and-odor control, algae and slime control, water-main disinfection, and many other purposes. However, chlorine has come under intense scrutiny because some of the by-products of the disinfection process may be carcinogenic. In spite of this, chlorine is expected to remain in wide use.

Water disinfection, as now ordinarily considered, involves specialized treatment for the destruction of harmful, and otherwise objectionable, “nuisance” organisms. Classically, disinfection processes have been employed to destroy or inactivate disease-producing (pathogenic) organisms—more particularly bacteria of intestinal origin. Such organisms can survive for weeks in the environment at temperatures near 70°F (21°C), or possibly even for months at lower temperatures. In addition to temperature influences, their survival in water depends on environmental, physiological, and morphological factors, such as pH, oxygen and nutrient supply, dilution, competition with other organisms, resistance to toxic influences, and ability to form spores. Whether these organisms actually will cause disease in humans upon ingestion depends on their virulence and concentration and also on the individual’s vulnerability or susceptibility to them.



*Based on Vital Statistics of the United States 1937, 1938, 1943, 1944, 1949, 1960, 1967, 1976, 1987, 1992, Historical Statistics of the United States—Colonial Times to 1970 Part 1.

Source: *HealthSentinel.com*.

Figure 1-1 US typhoid mortality and disease rates

Water disinfection also encompasses the destruction of disease-producing organisms other than intestinal bacteria, but it does not necessarily imply the complete destruction of *all* living organisms (i.e., *sterilization*). Water disinfection processes seldom have been carried to the point of sterilization, which has been largely confined to the medical field. Among the other disease-producing organisms important in regard to water disinfection are a variety of viruses, intestinal protozoa, and some macro-organisms. In addition, many nuisance organisms of aesthetic or economic significance, both plant and animal, are sometimes vulnerable to disinfection and can be partially or completely controlled by suitable treatment.

EVOLUTION OF CHLORINATION MATERIALS

During the infancy of water chlorination, the only commercial sources of chlorine were dry chlorine-containing *compounds*, such as chlorinated lime (also called chloride of lime and bleaching powder) and sodium hypochlorite bleach solutions. The poor stability and variable effective chlorine content of the compounds then available caused many operating difficulties, and often inadequate disinfection dosages were used. Moreover, the comparatively crude equipment feeders yielded erratic results.

In 1909, liquid chlorine (the element in compressed form) became available commercially, and in the following year it was employed experimentally for water disinfection in Fort Myer, Va. The chlorine was added to the water by using a simple dry-gas feeder. In 1912, the first full-scale successful use of liquid chlorine was undertaken to control a recurring outbreak of typhoid in Niagara Falls, N.Y. In this case, a solution feeder was used. Two years later, improved equipment developed by C.F. Wallace and M.F. Tiernan to measure chlorine gas, dissolve it in water, and apply the solution was installed in Boonton, N.J., replacing the use of sodium hypochlorite bleach. These developments paved the way for the future extension of water disinfection techniques utilizing liquid chlorine.

Hypochlorite water chlorination gradually decreased in popularity, but it received renewed interest in 1928 with the commercial availability of high-test calcium hypochlorite, which was a more stable and active material than the various bleaching powders and solutions previously available. Today, there are three principal sources of chlorine for water disinfection and other chlorination treatment: (1) in elemental form, as a liquefied compressed gas (in commerce); (2) as “high-test calcium hypochlorite”; and (3) as chlorine bleach solutions (not to be confused with elemental liquid chlorine or with water solutions of chlorine gas).

EVOLUTION OF CHLORINATION CONTROL PRACTICES

Improvements in chlorine disinfection materials and in chemical feeders substantially contributed to the popularity and widespread adoption of water chlorination. Originally disinfection dosages were based largely on the application of fixed amounts of chlorine. Soon it became apparent that provisions were not being made for the effects of variations in water quality and the fluctuation in chlorine demand.

Gradually, the concept of varying chlorine dosage on the basis of residual chlorine was established, and iodometric methods for qualitative and quantitative assay of residual chlorine were developed. The use of orthotolidine as a qualitative indicator of residual chlorine was proposed in 1909, and later its use was extended quantitatively by the development of colorimetric standards. Between 1917 and 1919, chlorine disinfection was established on a scientific basis when the suitability and reliability of the orthotolidine test for even the smallest water supplies were demonstrated. Since then, a better understanding of water chlorination processes has brought many refinements in that test and in the development of other tests, such as the orthotolidine-arsenite colorimetric test to distinguish forms of residual chlorine, amperometric differential

titration, and various other differential chemical tests for available chlorine. In recent years, the use of orthotolidine reagent has been discontinued in favor of the safer and more stable *N,N*-diethyl-*p*-phenylenediamine (DPD) method. DPD is commonly used both for color comparison and titrimetric chlorine testing.

DISCOVERY OF TRIHALOMETHANES

As chlorination processes gained further acceptance, new discoveries were limited to refinements in the existing methods and chemistry (Connell 1996). It wasn't until the 1970s that trace organic chlorination by-products were discovered. In Holland, Rook identified that the reaction of chlorine with organic materials dissolved in water produced a class of compounds called trihalomethanes (THMs) (Connell 1996). The organics, usually humic and fulvic acids that originate in decaying vegetative growths, can be found in agricultural runoffs, aquifers, and natural vegetation.

The THMs were identified as possible cancer-causing agents, and their discovery in drinking water raised concerns about chlorination. Research began on the nature of the reactions that produce THMs, the concentrations of THMs considered unacceptable in drinking water, and methods to reduce or prevent their formation. The great rush of scientific work produced sufficient data to lead regulatory bodies in Europe and North America to set acceptable THM concentration levels in finished water and to determine ways to minimize THM formation in existing plants.

HISTORICAL DEVELOPMENT OF CHLORAMINE

It is likely that chloramines formed accidentally in wastewater and in waters containing natural ammonia for some time before this reaction was characterized. In the early 1900s, the chlorine-ammonia combination received attention when it was found that the cost of chlorination might be reduced if ammonia was added (Race 1918). The practice of chloramine treatment was adopted in 1916 at the treatment plant in Ottawa, Ont. The first installation in the United States was in 1917 in Denver, Colo. Both locations used ammonia and hypochlorite and noted improvements in taste and reductions in after-growth in the distribution system.

Additional utilities adopted the use of chlorine-ammonia in the years that followed, as listed in Table 1-1, and more than 400 utilities were using the process by 1938. Breakpoint chlorination was discovered in 1939, and thereafter, the use of chloramines declined. Chloramine usage was further reduced during World War II when ammonia was in short supply.

Chloramines were then used sparingly until the 1970s when trace organic chlorination by-products were discovered (THMs). As discussed earlier in this chapter, THMs are produced from the reaction of chlorine with natural organic materials (humic and fulvic acids) and were also identified as possible carcinogens.

Subsequent to the discovery of THMs in drinking water, chloramination received renewed attention because it produces less THMs than *free* chlorine under most conditions. Haloacetic acids (HAAs) were identified as chlorination disinfection by-products and a group of five of these compounds were regulated in 1998. This further supported the use of alternate disinfectant such as chloramines.

A common disinfection strategy is to provide primary disinfection with chlorine or another strong disinfectant and then use chloramine as the residual disinfectant. This combination reduces chlorine by-product formation that would occur in the distribution system but still satisfies the need to ensure microbiologically safe drinking water. The widespread use of chloramines may be affected in the future, however, as new information is available on the by-products of chloramination.

Table 1-1 Utilities with long experience of chloramines use

City	Approximate Start of Chloramination
Denver, Colo.	1917
Portland, Ore.	1924
St. Louis, Mo.	1934
Boston, Mass.	1944
Indianapolis, Ind.	1954
Minneapolis, Minn.	1954
Dallas, Texas	1959
Kansas City, Mo.	1964
Milwaukee, Wis.	1964
Jefferson Parish, La.	1964
Philadelphia, Pa.	1969
Houston, Texas	1982
Miami, Fla.	1982
Orleans Parish, La.	1982
San Diego, Calif.	1982

Source: Trussell and Kreft 1984.

EVOLUTION OF CHLORAMINATION MATERIALS

The first observations of chloramine formation were in waters that contained ammonia. In addition, wastewater disinfection with chlorine often resulted in the formation of chloramines. Ammonia was initially added to water as aqua ammonia (liquid ammonium hydroxide) or ammonium salt solutions. Precipitation of calcium from water near the point of application prevented the widespread use of compressed ammonia gas. This issue was resolved and the use of anhydrous ammonia (gas) is now commonplace. The four forms of ammonia currently in common use are anhydrous ammonia (NH_3), aqua ammonia (NH_4OH), ammonium chloride (NH_4Cl), and ammonium sulfate ($[\text{NH}_4]_2\text{SO}_4$).

EVOLUTION OF CHLORAMINATION CONTROL PRACTICES

Chloramine residual testing was conducted originally using the same methods used for free chlorine. The total residual was determined by iodometric titration. It wasn't until the use of orthotolidine that speciation of the various forms of residual chlorine could be determined. This led to improvements in the dosage control of both chlorine and ammonia. Subsequently, the development of amperometric differential titration led to an even better understanding of the chemistry of the chlorine residual compounds. Today DPD is the most common test indicator for chlorine residual analysis, and it is possible to use DPD to differentiate some chloramine compounds.

Improvements in ammonia testing have also been important to control excess ammonia and to verify optimum chlorine:ammonia feed ratios. The Nessler method was used as early as 1930 to analyze wastewater for ammonia. This method used the formation of iodine and its characteristic color to determine the concentration of ammonia. The phenate method provides an alternative when some interferences are present. The ammonia-selective electrode method, developed in the 1970s, has made the routine testing of ammonia in water possible.

DISINFECTION REGULATIONS IN THE UNITED STATES

In 1974, the United States passed the Safe Drinking Water Act (SDWA). Amendments were added in 1986 and again in subsequent years that set further criteria for acceptable levels of THMs (Connell 1996). The SDWA also encouraged alternate treatment methods to achieve the now twin goals of disinfection and minimized THMs.

The Disinfectants and Disinfection By-Products Rule (USEPA 2001) established a maximum contaminant level (MCL) for THMs of 80 µg/L. The same rule set the MCL for HAAs at 60 µg/L. Maximum residual disinfectant levels were also set at 4.0 mg/L (ppm) for both chlorine and chloramine.

These regulations have caused utilities to carefully manage the use of chlorine. For example, the use of chlorine at the raw water intake is being reconsidered in favor of moving the point of addition closer to the clearwell. Intermediate points in the treatment plant would be considered on an as-needed basis. The addition of chlorine in conjunction with ammonia for use as the residual disinfectant in the distribution system is gaining popularity.

INTERNATIONAL DISINFECTION REGULATIONS

The World Health Organization (WHO) is a specialized agency of the United Nations. It publishes guidelines for drinking water quality that are used as a basis for the development of national drinking water standards. The 1998 guidelines include limits for disinfectants and disinfection by-products.

The European Union (EU) issued a directive (98/83/EC) that established minimum standards for water intended for human consumption. (More strict standards within the member states are allowed.) The directive includes disinfectants and disinfection by-product limits similar to the WHO guideline values.

The Netherlands has water systems operating without a residual in the distribution systems, indicating its great concern about the formation of THMs and other chlorinated by-products. The Netherlands' practices are not generally shared by the other European members. However, most of the practices of the EU states in the treatment of surface waters involve pretreatment with either ozone or chlorine dioxide, followed by chlorination of the finished waters.

Many countries have established their own drinking water quality standards. Most of these have adopted USEPA, EU, WHO, or a combination for their standards, yet the enforcement of standards varies widely from entirely voluntary to strict governmental oversight.

THE FUTURE

Chlorination practices will continue to be under scrutiny as more is learned about the effects of the disinfection process and the resulting disinfection by-products. Operation of surface water treatment plants and the quality of the water they produce will continue to be followed closely. Treated, potable water will continue to be examined in ever-increasing detail. New processes that will remove organic precursors will be discovered and used successfully.

Disinfection of drinking water is a vital component of the treatment and delivery system, and the protection of public health is the primary function of drinking water purveyors. It is a great challenge to provide microbiologically safe water and at the same time control disinfectant by-product production. Currently, scientific information is available to achieve these competing objectives. Further advancements, from scientific research, will undoubtedly lead the use of chlorine and chloramines in new directions in the future.

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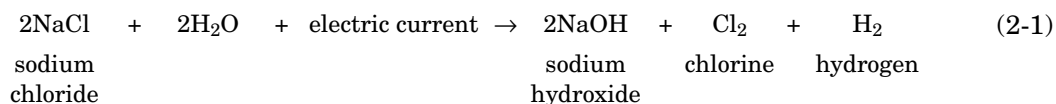
Chapter 2

Properties of Chlorination Chemicals

CHLORINE GAS

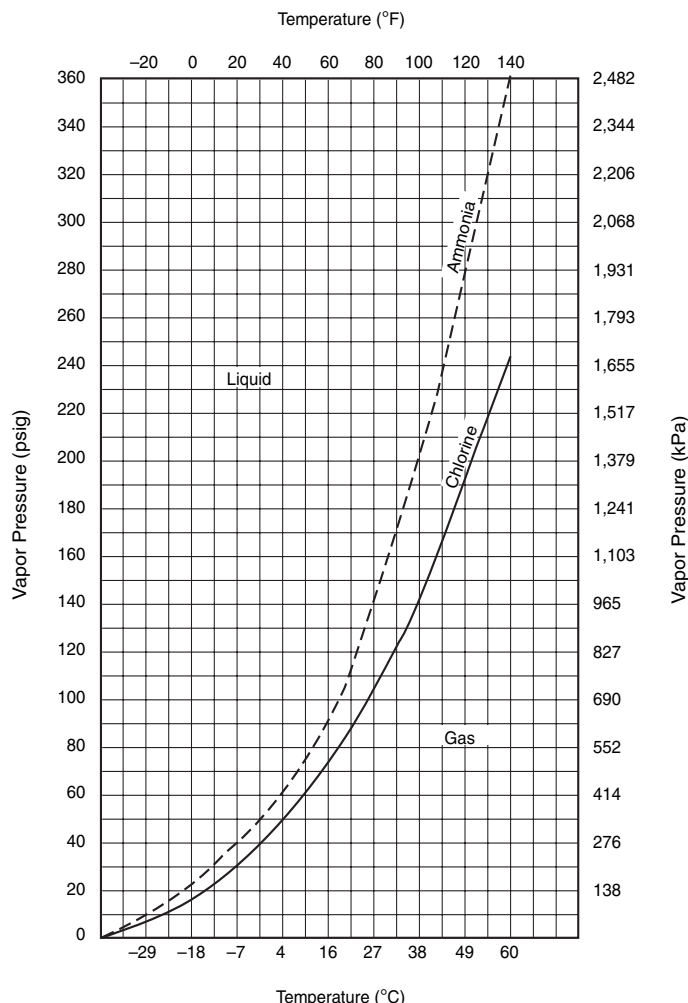
In the gaseous state, chlorine is greenish-yellow in color and has a pungent odor. The chemical symbol for chlorine is Cl and its atomic weight is 35.46. Chlorine, however, exists only as a two-atom molecule that is identified by the symbol Cl₂ and has a molecular weight of 70.92. It is neither explosive nor flammable, although as a strong oxidant, it supports combustion and reacts violently with many substances.

Pure chlorine does not exist naturally because of its reactivity. It is commercially produced by the electrolysis of sodium chloride brine. The chemical reaction is



Chlorine is stored and shipped as a liquefied gas under pressure, usually in 100- to 150-lb (45- to 68-kg) cylinders, ton containers, and tank cars. The compressed liquid is amber in color and approximately 1.5 times as heavy as water. If liquid chlorine is unconfined, it rapidly vaporizes to a gas. (One liquid volume yields approximately 450 volumes of gas.) The conversion of liquid to gas and subsequent expansion requires heat and can be self limiting by heat transfer to the liquid. As such, heat transfer through container walls limits gas withdrawal rates.

Because chlorine in a container may exist in gas, liquid, or both forms, any consideration of liquid chlorine includes that of chlorine gas. Chlorine gas is approximately 2.5 times as heavy as air. Therefore, released gas will initially settle to the lowest point in the container until mixed with the surrounding air. Figure 2-1 illustrates the temperature–pressure characteristics of chlorine. Note that when chlorine temperature increases, pressure also increases.



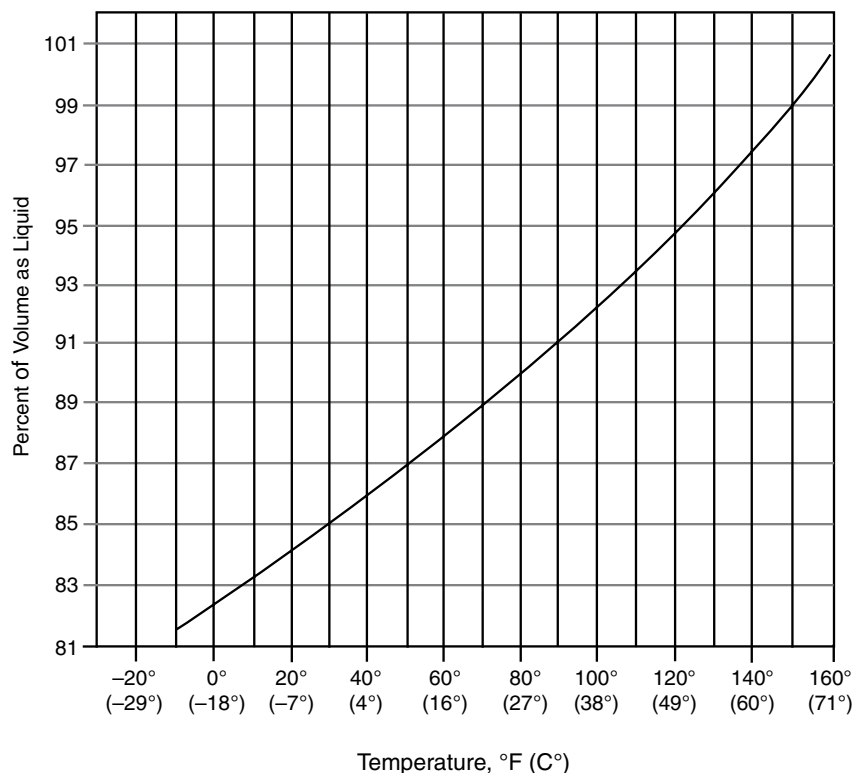
Source: Connell, 1996.

Figure 2-1 Vapor pressure of liquid chlorine

Figure 2-2 illustrates the volume–temperature characteristics of chlorine in a container loaded to the maximum authorized by the US Department of Transportation (USDOT). Note that a shipping container filled to its authorized maximum becomes completely full of liquid at approximately 154°F (68°C). Temperatures beyond that point may produce pressure that could result in hydrostatic rupture of the container. As such, safety devices are an integral part of chlorine containers. Fusible plugs are designed to melt at temperatures between 158 and 170°F (70 and 77°C), relieving excessive pressure accompanying temperature increases.

Chlorine is only slightly soluble in water; its maximum solubility is approximately 1 percent (10,000 ppm [mg/L]) at 49.3°F (9.6°C). Because the vapor pressure of chlorine increases with rising temperature, its solubility also decreases. The solubility drops to 4,000 ppm at 100°F (38°C) and to 0 ppm at 212°F (100°C). At temperatures below 49.3°F (9.6°C), chlorine can combine with water to form chlorine hydrate (sometimes called chlorine “ice”), which is a crystalline substance that may cause operational problems with direct feed chlorination. The maximum solubility for a given temperature should only be used for reference purposes. The actual useful solubility with minimal vapor pressure is considerably less: 3,500 mg/L is typically used as the maximum practical limit.

Table 2-1 summarizes some of the important physical properties of chlorine.



Adapted from the Chlorine Institute Chlorine Manual.

Figure 2-2 Volume-temperature relation of liquid chlorine in a container loaded to its authorized limit

Table 2-1 Physical properties of chlorine

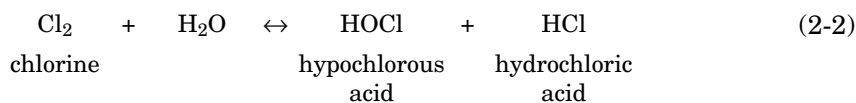
Boiling point (liquefying point) at 1 atm*	-29.15°F (-33.97°C)
Melting point (freezing point) at 1 atm	-149.76°F (-100.98°C)
Liquid density at 60°F (16°C)	88.8 lb/cu ft (1,422 kg/m ³)
Gas density at 34°F (1.1°C)	0.2006 lb/cu ft (3.213 kg/m ³)
Specific gravity (liquid) at 32°F (0°C)	1.468 (water = 1)
Specific gravity (gas) at 32°F (0°C)	2.485 (air = 1)
Water solubility at 70°F (21.1°C)	0.7 percent
Vapor pressures:	
at 32°F (0°C)	53.51 psi (368.9 kPa)
at 77°F (25°C)	112.95 psi (778.8 kPa)
at 129°F (43.9°C)	191.01 psi (1,316.8 kPa)

* 1 atmosphere = 14.696 psi (101.325 kPa).

Chemical Properties

Although it is neither explosive nor flammable, chlorine is a strong oxidant and capable of supporting combustion of certain substances. It should be handled and stored away from other compressed gases (e.g., ammonia) and flammable materials.

When mixed with moisture or water, chlorine will hydrolyze to form a corrosive mixture of acids and strong oxidants shown as



The chemical reactivity of chlorine enables it to combine with many other chemicals. It reacts with most organic materials, sometimes with explosive results. Dry chlorine is not corrosive to metals such as carbon steel, nickel, lead, or copper, but it can react violently with other metals such as aluminum, tin, gold, and titanium. Stainless steels are subject to chloride stress corrosion and should not be used by water utilities for chlorine service. Moist chlorine is corrosive to most metals with the exception of gold, silver, platinum, titanium, and certain specialized alloys.

Some plastics, such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF), can be used with gaseous chlorine whether wet or dry. Dry liquid chlorine or gas under pressure will react with polyvinyl chloride (PVC), causing it to soften and reduce its structural integrity. PTFE and PVDF may be used in liquid chlorine service. Gaseous chlorine under vacuum, both wet or dry, is compatible with PVC, chlorinated polyvinyl chloride (CPVC), or acrylonitrile butadiene styrene (ABS).

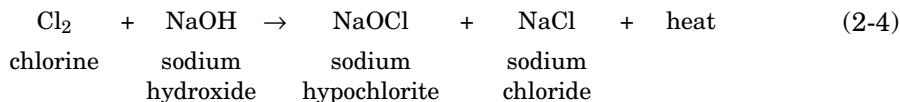
SODIUM HYPOCHLORITE

Sodium hypochlorite (NaOCl), often referred to as liquid bleach, is available only as a solution that contains 5–20 percent available chlorine. These solutions are clear to light yellow in color, are alkaline corrosive, and have a strong chlorinous odor. (The vapor above solutions contains a mixture of hypochlorous acid and chlorine monoxide.) The percent concentration typically used with hypochlorite is in terms of “trade percent.” This is different from a “weight percent,” which takes into consideration the solution’s specific gravity. Trade percent is expressed as

$$\text{trade percent} = \frac{\text{chlorine (g/L)}}{1,000} \times 100 \quad (2-3)$$

A 15 percent solution contains 1.5 lb/gal (180 g/L) of chlorine; a 10 percent solution contains 1 lb/gal (100 g/L), and so on.

Sodium hypochlorite is produced by reacting chlorine and sodium hydroxide as follows:



As noted earlier in this chapter, heat is generated during this reaction, which must be controlled to minimize the formation of chlorate at the onset and maximize stability during storage.

Unlike elemental chlorine, sodium hypochlorite is subject to decomposition. Table 2-2 lists the primary factors that affect stability.

Table 2-2 Primary factors affecting sodium hypochlorite stability

Factor	Relationship	Decomposition Products
Concentration	Stability increases inversely with concentration	Chlorate
Temperature	Stability increases inversely with temperature	Chlorate
Metallic impurities	Minimize Cu, Ni, Co concentrations	O ₂
pH	A pH between 11.5 and 13 is best	Chlorate
UV light	Minimize light exposure	Chlorate/O ₂

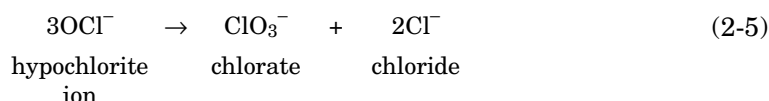
Based on the influencing factors listed in Table 2-2, the rate of decomposition of liquid hypochlorite has been studied (Gordon et al. 1995; Bommaraju 1994), and several equations have been developed to help predict the decomposition rate. (For additional details see the *Sodium Hypochlorite Manual* [Chlorine Institute 1995].) While helpful, these equations rely on a number of assumptions as well as accurate and consistent information, all of which may not be available. The best method to use in dealing with decomposition is to minimize the negative factors outlined in Table 2-2 and monitor the solution concentration. For a crude estimate, under moderate conditions, a 15 percent hypochlorite solution can conservatively be expected to degrade by approximately 0.5 percent per day. For example, 15 percent sodium hypochlorite at 77°F (25°C) has a 100-day half-life (i.e., it will degrade to half of its strength in 100 days). For comparison, at the same temperature, the half-life of 10 percent sodium hypochlorite is 220 days, and 5 percent is 790 days.

The three implications to sodium hypochlorite decomposition include

- the slow degradation of feed concentration,
- possible health consequences of high chlorate levels, and
- the evolution of oxygen that may complicate the feed.

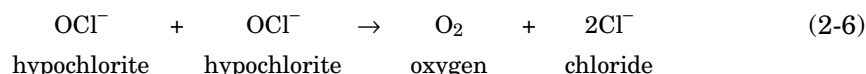
Because sodium hypochlorite solution concentration degrades with time, feed volumes must be increased to compensate. This is easily accomplished by adjusting the volumes manually (once a week is adequate under most conditions), or by providing residual feedback control as outlined in chapter 4. Concentration of new shipments of sodium hypochlorite should be checked daily for the first few days until stability can be characterized.

Chlorate is a by-product of decomposition, formed in the manufacturing process and during storage, as illustrated here:



The human health risk of chlorate has not been clearly defined in any definitive studies. For example, the 2002 edition of the *Drinking Water Standards and Health Advisories* (USEPA 2002) does not contain a listing for chlorate. However, high levels of chlorate have been associated with hemolytic anemia. Health Canada has proposed a guideline for chlorate in drinking water of 1.0 mg/L and the World Health Organization has a provisional guideline of 0.7 mg/L.

A second major degradation path, primarily catalyzed by transition metals such as Ni^{2+} , Cu^{2+} , and Co^{2+} , produces oxygen as follows:



While oxygen is not toxic, this degradation pathway can dramatically reduce the solution half-life and gas-bind chemical feed pumps resulting in cavitations and irregular feed rates. Metal concentrations in the sub-ppm levels can be a problem. Contamination can result from the manufacturing process, storage, transportation, feeding, or via dilution water. Particulates can be a major source of metal contamination, and filtration during the storage tank fill process can be an effective preventative measure. All metal (with the exception of titanium and tantalum) contact must be eliminated from storage vessels, piping, valves, and feed equipment.

Steps to Reduce Hypochlorite Degradation

Regardless of any other factors, sodium hypochlorite solutions will degrade with time. Any steps to minimize the time between manufacture, delivery, and use will maximize product strength and reduce chlorate formation. These steps will, however, involve trade-offs in product cost and operation time between deliveries.

The products of decomposition of most concern are chlorate and oxygen. There is no specific data showing that the expected levels of chlorate from hypochlorite would be hazardous to human health. However, it is prudent to minimize the formation of unintended by-products that may be of future concern. Oxygen, on the other hand, while not a toxicity issue, can complicate feeding.

A small reduction in hypochlorite solution concentration will greatly increase solution stability, as outlined in Table 2-3. However, care must be exercised to dilute hypochlorite solutions only with good quality waters. Using water that has been filtered and passed through a softener (cation exchange resin) to remove any solubilized metals is a good precaution. The pH must also be between 11.5 and 13.

Decreasing the temperature of hypochlorite solutions also has substantial benefit. As shown in Table 2-3, a 59°F (15°C) decrease in temperature increased stability over six times. While solution temperature is primarily a result of storage conditions, and options to reduce temperature may be limited, any reduction in temperature will have a measurable positive effect on solution stability. Such options may include

- specifying a maximum temperature of delivered hypochlorite,
- avoiding daylight heating by covering storage containers and feed piping, and
- considering practical heat exchangers and cooled storage areas.

Both oxygen and chlorate formation are catalyzed by ultraviolet (UV) light (sunlight). At the very least, the storage facility should be covered, preferably with reflective material, and storage containers made of or covered with opaque or UV blocking material.

Table 2-3 Half-life values of liquid bleach: varying temperature, pH, and concentration

Temperature		9.5 wt%	4.25 wt%	2.13 wt%
(°F)	(°C)	pH 13.0	pH 12.7	pH 12.4
95	35	66 days	300 days	2 years
68	20	1.5 years	6.5 years	17 years

Utilities should also establish minimum specifications for sodium hypochlorite deliveries to help in minimizing degradation products and rates. A hypochlorite specification may include the following requirements:

- a pH greater than 12,
- Ni^{2+} and Cu^{2+} concentrations less than 0.1 mg/L,
- a maximum chlorate concentration,
- a concentration greater than 12.5 percent (consider a lower concentration if cost per pound is comparable and feed and storage capacity can accommodate), and
- a solution temperature prior to delivery that is below 77°F (25°C).

The enforcement of a specification will greatly assist solution stability and predictability of degradation rate. For more detailed specification information, readers are directed to the AWWA Standard for Hypochlorites (B300, latest edition).

AMMONIA GAS

Ammonia is a gas at atmospheric pressure and ambient temperatures. It is not an element but rather a compound composed of the elements nitrogen and hydrogen. The chemical formula for ammonia is NH_3 and contains three atoms of hydrogen and one atom of nitrogen. Its molecular weight is 17. Small quantities of ammonia exist naturally. For commercial purposes, ammonia can be synthesized by a number of different processes that use hydrogen and nitrogen.

Ammonia has a pungent odor and, unlike chlorine, is colorless in both gaseous and liquid states. Ammonia liquefies at approximately the same temperature as chlorine but has a higher vapor pressure than chlorine at corresponding temperatures. The vapor pressure–temperature curve for ammonia is shown in Figure 2-1. To illustrate the difference in vapor pressure between chlorine and ammonia with changing temperatures, the dotted line in the figure represents the ammonia vapor pressure curve. The vapor pressure of ammonia is approximately 20 percent greater than chlorine at ambient temperatures and increases at a more rapid pace than chlorine at higher temperatures.

Unlike chlorine, reliquefaction of ammonia gas is not considered to be an operational problem. The boiling point, or vaporization point, of ammonia at atmospheric pressure is -28°F (-33.3°C).

Liquid ammonia is lighter than water with a density of 42.57 lb/ft³ (681.9 kg/m³) at -18°F (-28°C). Ammonia gas is lighter than air with a density of 0.555 lb/ft³ (0.8899 kg/m³) at -18°F (-28°C). Ammonia is approximately 36 times more soluble in water than chlorine: 250 lb/100 gal (299 g/L) or 34 percent by weight at 60°F (20°C).

Ammonia is classified by the USDOT as a corrosive gas. Chemically, ammonia is a relatively stable chemical compound and reactive only under specific conditions or with certain chemicals. Most common metals are unaffected by dry ammonia. In the presence of moisture, or when dissolved in water, ammonia will attack copper, zinc, and alloys containing these metals (e.g., brass and bronze). Ammonia will react with organics and inorganics to form ammonium salts. Reactions with chlorine can produce dangerous and/or explosive compounds, such as nitrogen trichloride. The physical properties of ammonia are listed in Table 2-4.

Ammonia is considered a respiratory irritant, although it does not have a cumulative effect. Ammonia's pungent odor provides an early warning to alert the individual to its presence. Although individual physiological responses may vary, the least perceptible odor is considered to be 5 ppm (by volume). The current (1993) OSHA-PEL level is 35 ppm, while the American Council of Government Industrial Hygienists (ACGIH) threshold limit value and short-term exposure limit (STEL) value are 25 ppm and 35 ppm, respectively.

Table 2-4 Physical properties of ammonia

Molecular Weight	17.03
Boiling point	-28.2°F (-33.4°C) at 1 atm
Freezing point	-107.9°F (-77.7°C)
Density (gas)	0.0555 lb/ft ³ (0.8899 kg/m ³) at -27.7°F (-33.2°C)
Density (liquid)	42.57 lb/ft ³ (681.9 kg/m ³) at -27.7°F (-33.2°C)
Flammability	Only within a range of 16–25 percent

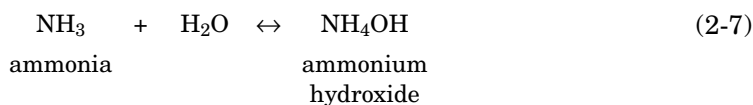
Source: Compressed Gas Association 1984.

Table 2-5 Properties of aqueous (aqua) ammonia, 30 percent by weight

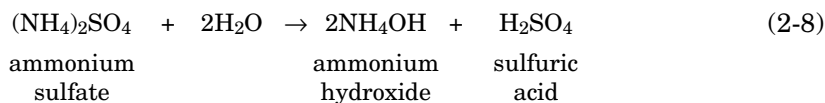
Specific gravity at 60°F (15°C)	0.8957
Density at 60°F (15°C)	26.31°Bé (Baumé) 55.7 lb/ft ³ (0.893 kg/L)
Boiling point at 1 atm (101.325 kPa)	82°F (27.8°C)

AMMONIA SOLUTIONS

Ammonia is available in forms other than as a compressed gas in cylinders. The most commonly used form is a solution of ammonia dissolved in water, usually referred to as aqueous or aqua ammonia. Other forms of ammonia are salts of ammonia solutions. Of these, the most frequently used is ammonium sulfate. The reaction of ammonia with water is shown here:



The product of this reaction is ammonium hydroxide, which is also produced from solutions of ammonia salts, as shown here:



Equation 2-7 is reversible and will release ammonia as a gas. In addition, solutions that produce ammonium hydroxide will also provide ammonia. Because ammonia is available from these solutions, ammonium salt solutions are used as a source of ammonia just as sodium hypochlorite is used as a source of chlorine. All ammonium salt or aqueous ammonia solutions have alkaline pH values. (The exact pH is a function of the solution concentration and temperature.) Because some ammonia gas evolves, a vapor pressure exists in aqueous ammonia and ammonium salt solutions, and all storage facilities must be suitably vented. Table 2-5 lists the properties of aqueous ammonia.

Both ammonium salt solutions and aqueous ammonia exhibit the same characteristics that would be expected from ammonia. The solutions should be treated as a respiratory irritant and handled with care. Irritation and redness may develop if the solutions come into contact with the skin.

For additional information on the properties and handling of chlorine, ammonia, and their solutions, see chapter 6. Also ask the chemical supplier to provide the latest available material safety data sheet (MSDS) for the appropriate chemical.

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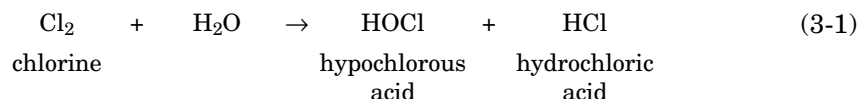


Chapter 3

Chlorination Water Chemistry and Disinfection Mechanisms

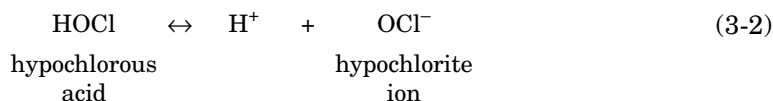
CHLORINATION CHEMISTRY

When chlorine gas (Cl_2) is added to water, a mixture of hypochlorous acid (HOCl) and hydrochloric acid (HCl) is formed, as shown here:

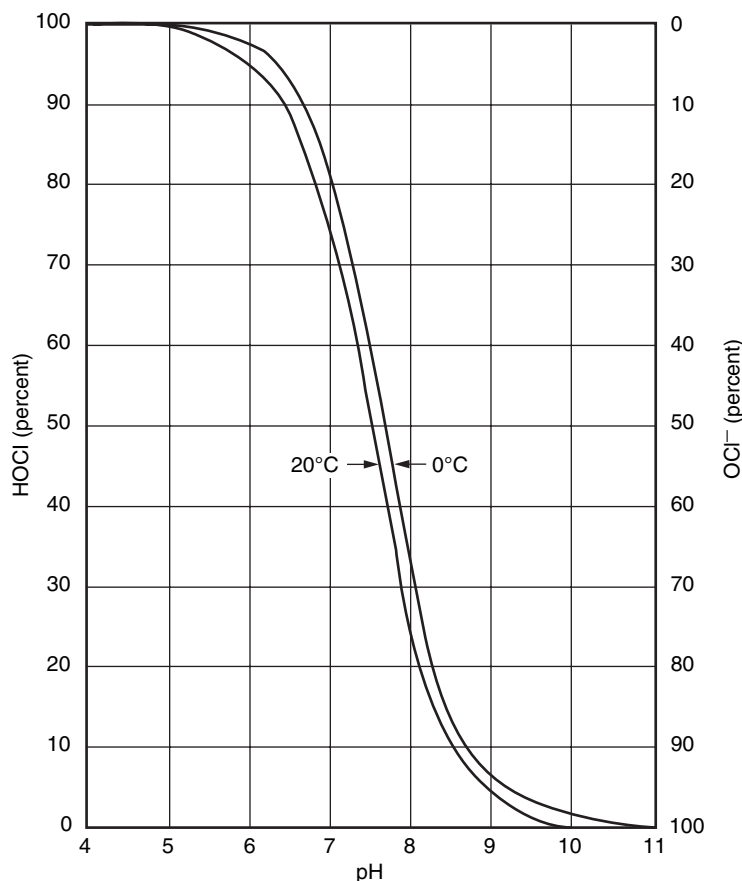


In dilute solutions and at pH levels above 4, the reaction illustrated in Eq 3-1 is displaced to the right. As the pH drops below 4, the percentage of available chlorine in the form of chlorine gas increases along with the vapor pressure. For every milligram per liter (part per million) of chlorine added, 0.7–1.4 mg/L of alkalinity is consumed. At typical chlorine dose rates (1–5 mg/L), the pH of the receiving water will be reduced but buffered by the water's natural alkalinity.

Once formed the HOCl instantaneously establishes equilibrium as follows:



As the pH rises above 7.5 (60°F [20°C]), an increasing percentage of free chlorine is in the form of hypochlorite ion. At a pH below 7.5, free chlorine is in the form of HOCl , as illustrated in Figure 3-1. As shown, temperature will also influence the equilibrium; the effect is particularly significant at a pH between 7 and 8. This reaction is independent of concentration, is completely reversible, and responds instantaneously to pH changes.



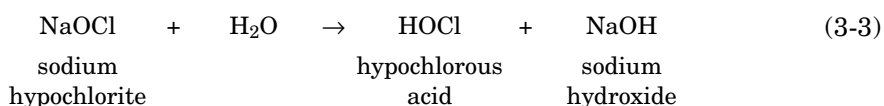
Source: Connell, 1996.

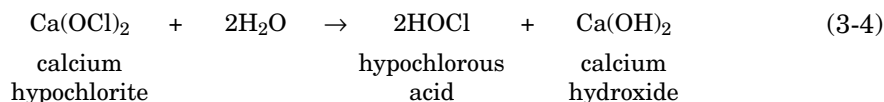
Figure 3-1 Hypochlorous acid/hypochlorite distribution versus pH

The combined concentration of HOCl and OCl⁻ is known as *free chlorine residual* (FCR). These two species, however, react quite differently. HOCl is a much stronger disinfectant, stronger oxidant, and more reactive than OCl⁻. HOCl will disinfect 100 times faster and oxidize compounds that OCl⁻ will not, but be consumed at a much higher rate. This creates a dynamic relationship in which HOCl is consumed and the remaining FCR re-equilibrates according to the relationship illustrated in Figure 3-1. In effect, OCl⁻ acts as a disinfectant buffer, adding HOCl as it is being consumed.

The speed of chlorine disinfection and durability of the residual is therefore strongly affected by the pH of the water being treated. In addition to being more reactive, HOCl is neutral and can more easily penetrate negatively charged bacterial surfaces and suspended particles protecting pathogens.

Chlorine may also be added as sodium hypochlorite or calcium hypochlorite. While there are obvious differences in feeding characteristics, and hypochlorite will add alkalinity as opposed to chlorine gas consuming alkalinity, once added to the receiving water the resulting residuals are indistinguishable from those added by chlorine gas as shown here:



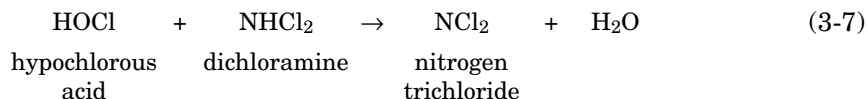
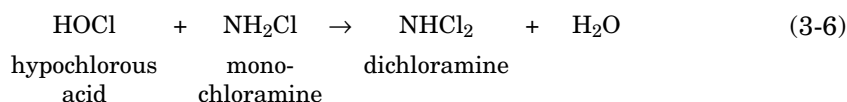
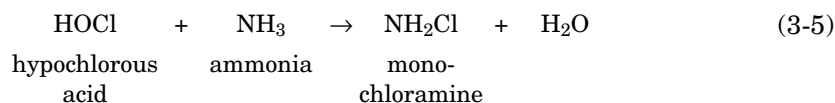


The reaction products of both chemicals produce HOCl, which will be distributed according to the HOCl and OCl⁻ pH relationship.

Chlorine Reactions With Other Compounds

The reactions of chlorine with other compounds are important to understand because these reactions generally exhibit a chlorine demand. This may directly affect the disinfection capability of the chlorine added to the water.

Reactions with ammonia. The reaction between chlorine and ammonia is of great significance in water chlorination processes, especially disinfection. When chlorine is added to water containing natural or added ammonia, the ammonia reacts with HOCl to form various chloramines that, like HOCl, retain the oxidizing capacity of chlorine (+1 oxidation state) but in a weaker configuration. The reactions between chlorine and ammonia may be represented as follows:



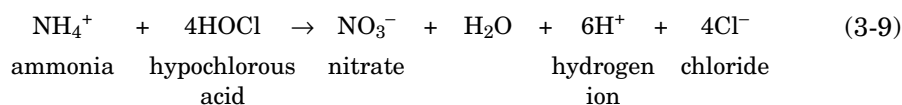
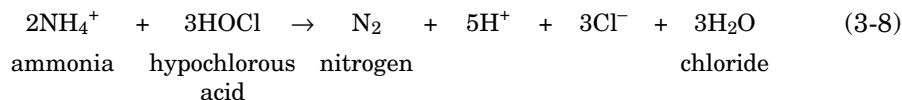
The distribution of the reaction products is governed by the rates of formation of monochloramine (NH₂Cl) and dichloramine (NHCl₂), which are dependent upon pH, temperature, time, and initial chlorine to ammonia (Cl:NH₃) ratio. In general, low Cl:NH₃ ratios and high pH levels favor monochloramine. Monochloramine is characterized as a weak disinfectant and oxidant, frequently used as a durable residual that will form lower levels of disinfection by-products (DBPs) and will produce the least detectable chlorinous taste and odor (T&O) of any of the chlorine residuals. Dichloramine has similar disinfection and oxidation characteristics to monochloramine but is characterized by a more intense T&O. Nitrogen trichloride (NCl₃) is practically insoluble in water, has a very intense T&O, and is known for its eye irritation/tearing effects at very low concentrations.

Chlorine also reacts with organic nitrogenous material, such as proteins and amino acids, to form organic chloramines. These compounds have little disinfection and oxidation value and are resistant to further oxidation. These residuals are sometimes referred to as “nuisance residuals” because they are virtually indistinguishable from inorganic chloramines with standardized analytical procedures.

The breakpoint reaction. The breakpoint is described as the point at which chlorine demand has been satisfied, combined chlorine compounds have been destroyed, and as additional chlorine is added, a free chlorine residual is produced. The breakpoint reaction is important in understanding the formation of chloramines (when ammonia is present or is added) because the formation of chloramines is a primary

element of this reaction. In some cases, organic compounds present in the water may also combine with chlorine to form chloro-organic compounds that may exhibit the characteristics of a combined chlorine residual.

If water contains ammonia (either naturally or added), and a free chlorine residual is desired, the ammonia can be removed by oxidation with chlorine to produce primarily nitrogen gas and some nitrate by the breakpoint reaction. While there are a number of reaction steps that take place in this process, two of the predominant reaction sequences are summarized as follows:



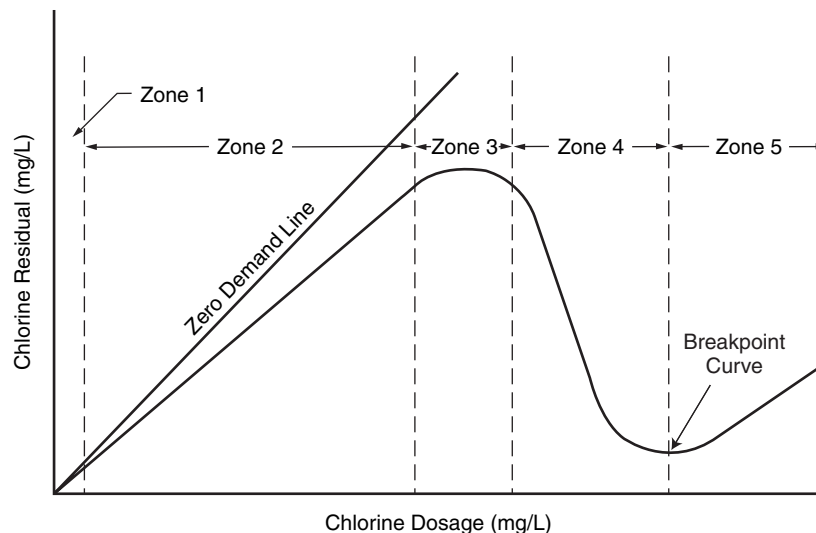
Ideally, the breakpoint reaction should take place at a pH between 7.0 and 7.5, but it will also continue at a slower rate down to a pH of 6.5 and as high as 8.5. Adequate chlorine must also be added to complete the reaction (empirically found to be approximately 8.5 mg/L [ppm] chlorine per mg/L [ppm] $\text{NH}_3\text{-N}$). Additional chlorine may also be required to satisfy a number of side reactions, including the creation of minor products such as nitrogen trichloride, and other chlorine demands (caused by organic and other compounds). The only other reaction requirement is time. The breakpoint reaction is not instantaneous and may take 30 min or longer to run to completion. If free chlorine disinfection or oxidation is needed, adequate reaction time must be provided.

The ammonia breakpoint reaction is a series of steps in which monochloramine is formed first and then converted by HOCl to dichloramine, which is followed by a dichloramine decomposition reaction resulting in primarily nitrogen gas and nitrate. Organic compounds may combine with chlorine to form chloro-organic compounds that may also be destroyed as more chlorine is added.

The breakpoint curve illustrates the breakpoint reaction and is shown in Figure 3-2. This curve plots the chlorine dosage in milligrams per liter along the horizontal axis and the total (free and combined) chlorine residual in milligrams per liter along the vertical axis. The line plotted at a 45° angle is called the zero demand line and represents the ideal situation in which all chlorine added to the water is measured as a free chlorine residual in the water. In zero demand water, there is no loss of chlorine addition due to chlorine demand.

The presence of reducing agents and other inorganic chlorine demand-causing compounds will consume any initial chlorine dosage, which results in zero chlorine residual until this demand is satisfied. This section of the zero demand curve is identified as zone 1 in Figure 3-2. Once this initial demand is met in the presence of ammonia (and organic compounds), any additional dosage will be measured as combined chlorine residual. This residual will increase in proportion to the increase in dosage and is identified as zone 2. In this zone, monochloramine is the primary chlorine form.

As the chlorine-to-ammonia molar ratio surpasses 1:1, more and more dichloramine is formed, the dosage/residual relationship will cease to be linear, and the amount of combined and total residual increase will flatten out, as shown by zone 3. In this zone, the proportion of dichloramine increases to a point where it begins to decompose (along with any chloro-organic compounds that may have formed).



Source: Connell, 1996.

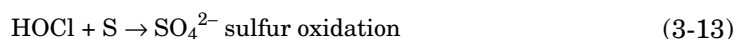
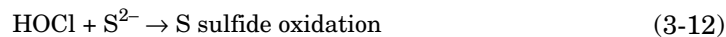
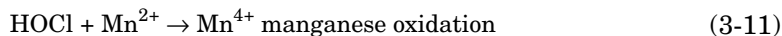
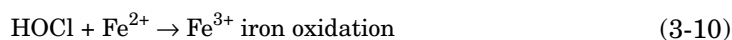
Figure 3-2 Breakpoint curve

Subsequent increases in chlorine dosage will convert an increasing proportion of monochloramine to dichloramine, which subsequently decomposes resulting in a roughly 2-mg/L drop in residual for each milligrams per liter added, as shown by zone 4. This continuing decrease of total residual will taper off and the chlorine residual will reach a minimum point after which it will once again increase with continued chlorine addition. This minimum point is called the *breakpoint* and represents that point in the treatment process at which all ammonia compounds (and most chloro-organic compounds) have been oxidized. Any further chlorine addition will increase the residual chlorine as free chlorine, as identified in zone 5. Combined chlorine residual predominates in zones 2, 3, and 4, while free chlorine residual predominates in zone 5. It is again important to point out that these reactions are not instantaneous. Time must be allowed for the reaction to go to completion before the results follow the breakpoint curve.

Some waters treated by the breakpoint process may never reach a zero residual because organic nitrogen compounds (or other chloro-organic compounds) present resist the oxidation by chlorine. This organic nitrogen is sometimes referred to as an *irreducible minimum*.

Each water plant must determine its own breakpoint curve. Analysis of the water for the various forms of chlorine at different chlorine dosages allows for the determination of the particular breakpoint curve for the water. Procedures from *Standard Methods for the Examination of Water and Wastewater* (APHA, et al., latest edition) should be followed for these determinations.

Inorganic oxidation reactions. The oxidation of soluble iron, manganese, and sulfides is a common use of chlorine in water treatment. Once oxidized iron, manganese, and sulfides form insoluble compounds, they then can be removed by filtration prior to distribution. The following are unbalanced equations that illustrate the oxidation products from chlorination:



When iron and manganese are oxidized, they are transformed from a colorless soluble ion to a red and a dark brown precipitate, respectively. If allowed to be oxidized by oxygen or chlorine addition at a customer's tap, the result is the staining of surfaces and cloths and, in some cases, the formation of scales that can eventually restrict flow. Iron is readily oxidized by both free and combined chlorine. Manganese is far more difficult to oxidize (requiring free chlorine, an optimal pH of 10, and 2–3 hr contact time). Approximately 0.6 mg/L chlorine is required to oxidize 1 mg/L of iron. (This reaction consumes 0.9 mg/L of alkalinity.) To oxidize 1 mg/L of manganese requires approximately 1.3 mg/L chlorine (3.4 mg/L alkalinity is consumed). Some organically combined manganese is even more resistant to oxidation.

Sulfide, primarily from wells, is highly toxic and produces a characteristic rotten-egg odor that makes the water unpalatable. With sulfides, there are two reaction steps possible. The first reaction, shown in Eq 3-12, produces colloidal sulfur. The second reaction, shown in Eq 3-13, produces a soluble sulfate ion that has no taste or odor and is not considered objectionable at low concentrations. Which reaction dominates will depend on the pH level and chlorine-to-sulfide ratio. The sulfate-forming reaction will be favored at a low pH (optimum 6.0) and high chlorine-to-sulfide ratio. Sulfur formation is favored at a high pH and low chlorine-to-sulfide ratio. Although oxidation of sulfide is relatively easy, the overall chemistry is complex and its removal without causing objectionable T&O can be difficult (requiring more elaborate treatment processes that are beyond the scope of this discussion).

Organic oxidation reactions. Reactions of chlorine with some organics produce DBPs. The most common are trihalomethanes (THMs). THMs include chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Some of these compounds are classified as probable human carcinogens (Fielding et al. 1993). The current maximum contaminant level (MCL) for THMs in drinking water is 0.080 mg/L (80 µg/L) (USEPA 1996). Another group of DBPs are haloacetic acids (HAAs), which include a number of compounds (11 or more). The five most common HAAs are grouped for regulatory purposes (dichloroacetic acid, monochloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid) and the MCL is 0.060 mg/L. Other products of chlorine-organic reactions have also been identified (Kleinjans 1991). Table 3-1 is a list of some of the generally recognized DBPs.

Table 3-1 Chlorination disinfection by-products

Trihalomethanes	Haloacetic Acids
Chloroform	Dichloroacetic acid
Bromodichloromethane	Monochloroacetic acid
Dibromochloromethane	Trichloroacetic acid
Bromoform	Monobromoacetic acid
Haloacetonitrile	Dibromoacetic acid
Dichloroacetonitrile	Tribromoacetic acid
Trichloroacetonitrile	Bromochloroacetic acid
Bromochloroacetonitrile	Bromodichloroacetic acid
Dibromoacetonitrile	Dibromochloroacetic acid
Tribromoacetonitrile	Others
Cyanogen halides	Chloral hydrate
Halopicroins	Haloketones

Source: Fielding et al. 1993.

Many factors influence the formation of DBPs, including contact time (CT), temperature, pH, precursor type and concentration, disinfectant type and concentration, ratio of oxidant to precursor, and concentrations of bromide and ammonia. In addition, naturally occurring humic and fulvic acids are known precursors for DBP formation.

Chlorine can be used as a preoxidant for the removal of T&O and color. Current regulations, however, limit the use of chlorine for this purpose because of the possible high production of undesirable DBPs. Generally, the use of pretreatment methods that remove DBP precursors or inhibit the formation of DBPs is the preferred water treatment strategy. These methods may include one or more of the following: filtration, lime softening, preoxidation with ozone, chlorine dioxide, permanganate, relocation of the point of chlorination, enhanced coagulation, membrane filtration, activated carbon treatment, or ultraviolet (UV) irradiation.

The reaction rates with organic compounds are generally slower than those with inorganic compounds and are often more difficult to quantify because the rate, demand, and end products may vary considerably with reaction conditions and type of precursor. The chlorine requirements are best established by laboratory jar testing to determine the desired treatment level.

Typically, chlorine requirements change periodically in surface water treatment plants. The complexity of new regulations may require pilot plant evaluation to effectively determine the best overall treatment and the most effective role for chlorine. When chlorine is used in the presence of organic compounds, the reaction products are of concern and the results should be reviewed with this in mind.

DISINFECTION MECHANISM

Disinfection is the treatment process used to destroy or inactivate disease-causing (pathogenic) organisms (Von Huben 1995). The consequences of waterborne disease range from mild illness to death. Disinfection should not be confused with sterilization. Sterilization is the complete destruction of all living microorganisms. It has been found that treatment for turbidity removal and subsequent disinfection to control disease-causing organisms is sufficient to protect public health.

Inactivating Pathogens in Water

Most pathogens are accustomed to living in the temperatures and conditions found in the bodies of humans and warm-blooded animals. In general, their ability to survive outside of this environment is limited, but some do survive long enough to cause infections if ingested in drinking water. Certain viruses and protozoans that form cysts can survive for surprisingly long periods, even under adverse conditions. Some pathogenic organisms also tend to be somewhat resistant to certain disinfection processes, so disinfection alone cannot always be assumed to ensure safe drinking water.

Some pathogens can be inactivated by simply storing water in open tanks for extended periods of time. Some pathogens are removed by sedimentation in those tanks, and others experience natural die-off. This is not usually a practical treatment method because of the large investment required for the storage facilities and reliability of the process. In addition, the water is subject to contamination and other nuisance organisms—such as algae—while in storage.

Water disinfection strategies are usually divided into two categories: surface water and groundwater. Surface water is characterized as containing a higher degree of suspended material, higher organic levels, diverse natural and man-made contaminants, variable quality, and subject to a wider variety of pathogens, including most notably *Giardia* and *Cryptosporidium*. Groundwater is generally characterized by low levels of organics and consistent quality. Groundwater is also subject to higher levels

and broader types of inorganic compounds, with viruses and bacteria being the pathogens of concern, albeit at low levels.

Surface water treatment is the more involved of the two because the water has not benefited from the natural filtering process of groundwater. Particulate matter (mineral and organic) as well as larger disinfectant-resistant organisms such as *Giardia* and *Cryptosporidium* must be removed by physical separation, primarily sedimentation and filtration. Higher organic levels and oxidation pretreatment requirements also require higher levels and longer contact times for oxidative disinfectants, which may aggravate DBP formation and complicate disinfection. Surface water may also be subject to rapid quality changes. It is not uncommon for surface water plants to use chlorine dioxide, ozone, or permanganate for oxidative pretreatment, followed by free chlorine disinfection and chloramine residual disinfection.

The longer contact time required for inactivation of *Giardia* and the outright resistance of *Cryptosporidium* to inactivation by chlorine present some of the most difficult disinfection challenges to water treatment operators. Treatment is further complicated by the difficulty in testing for these pathogens, making it almost impossible to monitor disinfection performance on a real-time basis. Treatment strategies generally involve a combination of filtration and disinfection designed to achieve a minimum total log reduction.

Disinfection of groundwater is far easier to achieve because water quality changes little over long periods of time. Disinfection programs are generally consistent and, therefore, easier to monitor and control. The pathogens of concern are viruses and bacteria that are relatively easy to inactivate. (Exceptions are in parts of the Southeast and in isolated aquifers elsewhere.) In most groundwater sources, the DBP precursor concentrations are generally low so that in many waters free chlorine can be used without risk of violating DBP regulations. However, it is important to point out that every water system has unique characteristics that must be taken into account to achieve the best water quality.

Detecting Pathogens in Water

Detecting various types of pathogens such as viruses and protozoan cysts is time-consuming and often requires involved analytical techniques. Alternatively, indicator organisms such as fecal coliform and total coliform are used for routine monitoring, and relatively simple, inexpensive tests are available for detecting their presence. These tests, however, only indicate the likelihood that water is contaminated by feces from a warm-blooded animal and, therefore, possibly contains pathogens. All public water systems are required by federal and state regulations to collect representative samples from the distribution system periodically for coliform analysis.

This inability to conduct routine tests for the presence of specific disease-causing microorganisms has been recognized in the US Environmental Protection Agency's (USEPA) Surface Water Treatment Rule, which is discussed later in this chapter. In essence, the rule requires a "treatment technique" for all systems using surface water sources. The technique must consist of one or more methods of treatment that will ensure almost complete removal and/or inactivation of the most resistant pathogenic organisms. In other words, establishing an MCL for pathogenic organisms is not practical because the tests for their presence cannot be completed in a timely manner. Compliance with regulations is based on properly operating the treatment process known to remove or inactivate the organisms.

DISINFECTION METHODS

A 1999 survey revealed the following US disinfection practices in larger water treatment plants (a large majority of smaller water treatment facilities generally use a form of chlorine):

Chlorine gas	83.3 percent*
Sodium hypochlorite	18.3
Sodium hypochlorite (onsite)	2
Chlorine dioxide	8.1
Ozone	5.6
Chloramines	29.4
UV	< 1

*The total percentage is greater than 100 percent because some utilities use several disinfection practices.

Although chlorination is the most common disinfection method, other methods are available and can be used in various situations as described in Table 3-2.

Refer to the *Interim Voluntary Security Guidance for Water Utilities* (AWWA 2004) when evaluating options for disinfection method.

Chemical Treatment

Although the primary use of chemical oxidants is for disinfection, these chemicals also serve other purposes during the disinfection process. In some cases, the choice of chemicals used in a treatment system is dictated by the ability of the chemicals to perform these secondary functions, which include

- control of biological growth in pipelines and basins;
- control of tastes and odors;
- removal of color;
- aids to flocculation; and
- oxidation of iron, manganese, and sulfides.

Aside from oxidizing disinfectants, oxidants such as potassium permanganate and oxygen can be used solely for their oxidation properties.

Table 3-2 Common disinfection methods

Disinfectant Type	Primary Application
Chloramines	Potable water
Iodine	Potable water in emergencies
Bromine	Nondrinking water uses
Chlorine dioxide	Potable water
Ozone	Potable water
Filtration/membranes	Potable water
Ultrasonic/ultrasound	Nondrinking water uses
Ultrahigh frequency	Nondrinking water uses
UV/advanced oxidation processes	Potable water
Ionized radiation (gamma, electron beam)	Nondrinking water uses
Cations of heavy metals (silver)	Nondrinking water uses
Biocides	Nondrinking water uses

Chlorine and Chlorine Compounds

Chlorination is by far the most common form of disinfection currently practiced in the United States. It is the only disinfectant recognized as an acceptable residual disinfectant. When properly understood and correctly operated, the chlorination process is a safe, practical, and effective way to destroy many disease-causing organisms (Figures 3-3 and 3-4).

Principle of Disinfection by Chlorination

The effectiveness of chlorination depends primarily on four factors: concentration (C), contact time (T), pH, and temperature. These factors are combined in a relationship called a CT or concentration (in milligrams per liter) multiplied by the time (in minutes) at a given pH and temperature. CTs have been established for a number of pathogens, disinfectants, and levels of inactivation achieved. (See appendix C.)

The effectiveness of chlorination is also related to the temperature of the water. At lower temperatures, bacterial kill and all chemical reactions in general tend to be slower. However, chlorine is more stable in cold water, and the residual will remain for a longer period of time, compensating to some extent for the lower rate of disinfection. Other factors being equal, all disinfection processes are more effective at higher water temperatures. As temperatures change seasonally, this relationship must be included when adjusting the chlorine dosage.

It is essential that the operator understand and use these relationships in order to obtain the most effective disinfectant. The pH of the water should be checked routinely. This is particularly important if the pH of the water is being raised during disinfection to control corrosion.

It is important to recognize that the use of chlorine as the disinfectant is only one part of the multiple barrier treatment process. In fact, the USEPA acknowledges this in the drinking water regulations under the Safe Drinking Water Act (SDWA). Of equal importance is the need for improved physical removal by sedimentation and filtration. A combination of proper disinfection and improved removal by filtration often provides the most optimum treatment sequence. Chlorination alone, for example, is not recognized as an effective means for *Cryptosporidium* inactivation (Finch 1997).

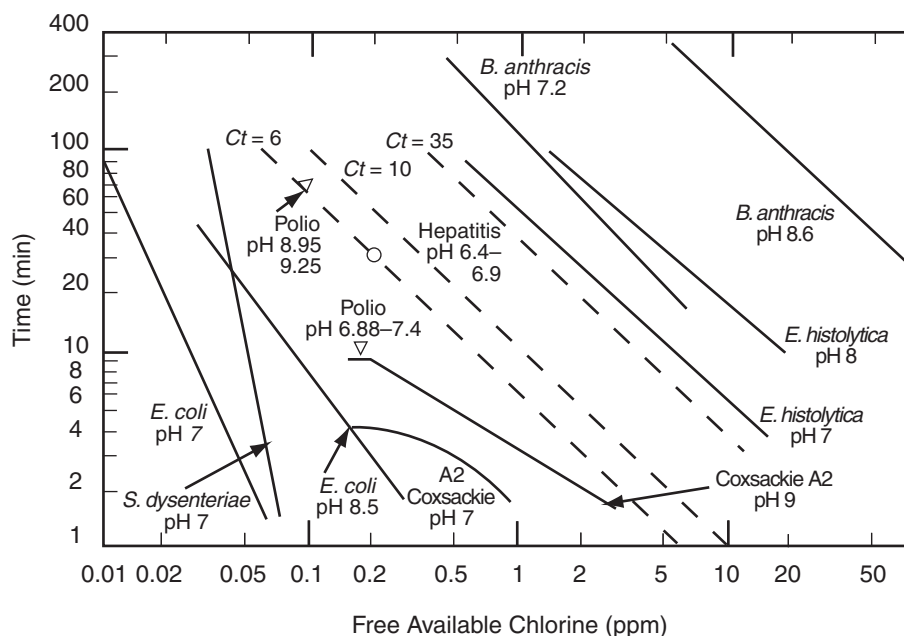
Residual disinfection. All surface waters and most groundwater systems are required to maintain a measurable residual disinfectant to guard against recontamination, control biofilms and biological growth, meet the USEPA Coliform Rule, and provide an indicator of system integrity and quality. Only chlorine and chloramines are accepted universally as residual disinfectants.

The USEPA's maximum residual disinfection levels (MRDLs) are 4 mg/L for chlorine and chloramines, and 0.8 mg/L for chlorine dioxide.

Interference Substances

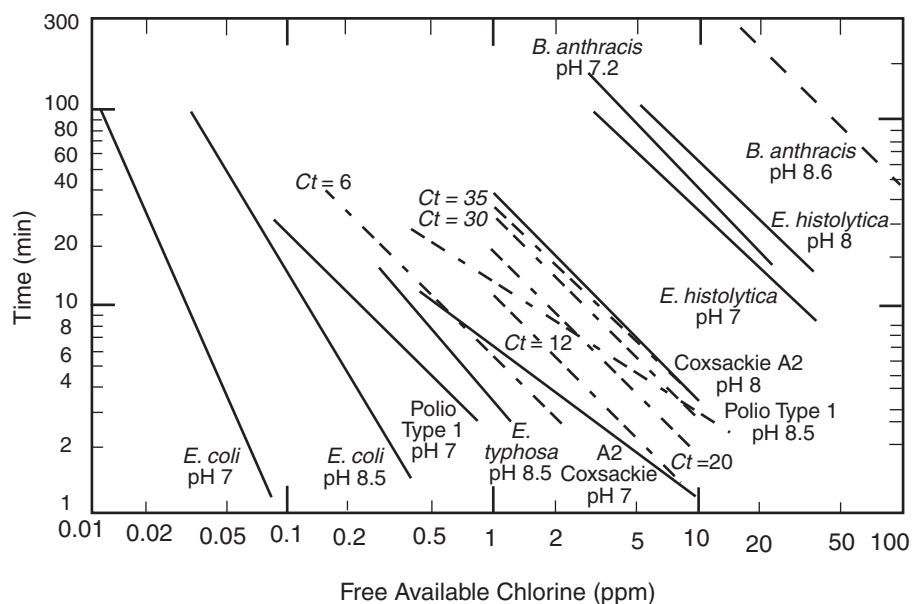
Chlorine acts as an effective disinfectant only if it comes in contact with the organisms to be killed. Turbidity, caused by tiny particles of minerals or organic matter suspended in the water, can prevent good contact and protect the pathogens from the effects of chlorine. Therefore, for chlorination to be effective, turbidity must be reduced to very low levels.

As discussed earlier, chlorine reacts with other substances in water, such as organic matter and ammonia. Because these compounds result in the formation of combined residuals, their concentrations are an important factor in determining chlorine dosages.



Source: Baumann and Ludwig, 1962.

Figure 3-3 Disinfection versus free available chlorine residuals. Time scale is for 99.6 to 100 percent kill. Temperature was in the range of 20 to 29°C, with pH as indicated.



Source: Baumann and Ludwig, 1962.

Figure 3-4 Disinfection versus free available chlorine residuals. Time scale is for 99.6 to 100 percent kill. Temperature was in the range of 0 to 5°C, with pH as indicated.

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Chapter 4

Chlorine and Ammonia: Handling, Storage, Feed Equipment, and Systems

GAS CHLORINATION FACILITIES

Chlorine gas (Cl_2) is approximately 2.5 times as dense as air (Von Huben 1995). It has a pungent, noxious odor and a greenish-yellow color, although it is visible only at a very high concentration. Chlorine gas is irritating to the eyes, nasal passages, and the respiratory tract and it can kill a person in a few breaths at concentrations as low as 0.1 percent (1,000 ppm [mg/L]) by volume. Its odor can be detected at concentrations above 0.3 ppm.

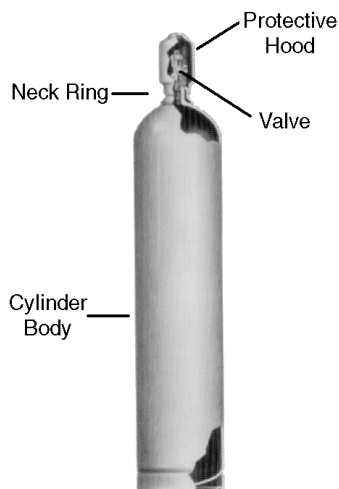
Chlorine liquid, which is approximately 99.5 percent pure chlorine, is created by compressing chlorine gas. The liquid is amber in color and approximately 1.5 times as dense as water. It can be purchased in cylinders, containers, tank trucks, and railroad cars, as shown in Figures 4-1 through 4-4.

Liquid chlorine changes easily to a gas at room temperatures and pressures. One volume of liquid chlorine will expand to approximately 460 volumes of gas. Dry chlorine gas will not corrode steel or other metals, but it is extremely corrosive to most metals in the presence of moisture.

Chlorine will not burn. But, like oxygen, *it will support combustion*—that is, it takes the place of oxygen in the burning of combustible materials. Chlorine is not explosive, but it will react violently with greases, turpentine, ammonia, hydrocarbons, metal filings, and other flammable materials. Chlorine will not conduct electricity, but the gas can be very corrosive to exposed electrical equipment. Because of the inherent hazards involved, chlorine requires special care in storage and handling.

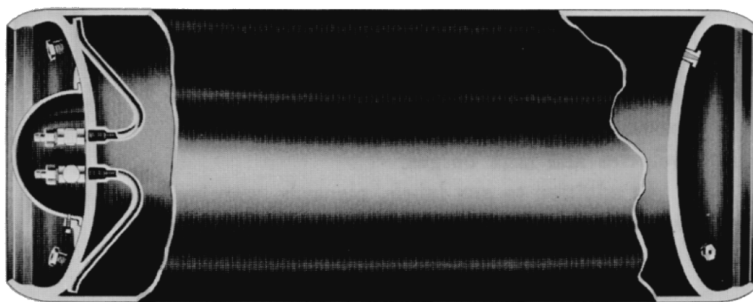
HANDLING AND STORING CHLORINE GAS

Safe handling and storage of chlorine are vitally important to the operator and to the communities immediately surrounding a treatment plant, because an error or accident in chlorine handling can cause serious injuries or even fatalities. The containers commonly used to supply chlorine in smaller water treatment plants are 150-lb (68-kg) cylinders. Larger plants find it more economical to use ton containers. Some large plants are equipped to draw chlorine directly from tank cars.



Courtesy of the Chlorine Institute, Inc.

Figure 4-1 Chlorine cylinder



Courtesy of the Chlorine Institute, Inc.

Figure 4-2 Chlorine ton container



Courtesy of PPG Industries, Inc.

Figure 4-3 Chlorine ton container truck



Courtesy of the Chlorine Institute, Inc.

Figure 4-4 Chlorine tank car

The decision of whether to use cylinders or ton containers should be based on cost and capacity. The cost per pound (kilogram) of chlorine in cylinders is usually substantially more than that of chlorine in ton containers. If a plant's needs for chlorine are lower than 50 lb/d (23 kg/d), cylinders should usually be selected. For systems that use large amounts, ton containers will probably be more economical.

Cylinders

Chlorine cylinders hold 150 lb (68 kg) of chlorine and have a total filled weight of 250–285 lb (110–130 kg). They are approximately 10.5 in. (270 mm) in diameter and 56 in. (1.42 m) high. As illustrated in Figure 4-1, each cylinder is equipped with a hood that protects the cylinder valve from damage during shipping and handling. The hood should be properly screwed in place whenever a cylinder is handled, and should be removed only during use.

Cylinders are usually delivered by truck. Each cylinder should be unloaded to a dock at truck-bed height if possible. If a hydraulic tailgate is used, the cylinders should be secure to keep them from falling.

Cylinders must never be dropped, including “empty” cylinders, which actually still contain some chlorine. The easiest and safest way to move cylinders in the plant is with a hand truck. The hand truck should be equipped with a restraining chain that fastens snugly around the cylinder about two thirds of the way up. Slings should never be used to lift cylinders, and a cylinder should never be lifted by the protective hood because the hood is not designed to support the weight of the cylinder.

Cylinders should not be rolled to move them about a plant. Tipping the cylinders over and standing them up can lead to employee injury. In addition, the rolled cylinders might strike something that could break off the valve.

Cylinders can be stored indoors or outdoors. If cylinders are stored indoors, the building should be fire resistant, have multiple exits with outward-opening doors, and be adequately ventilated. Outdoor storage areas must be fenced and protected from direct sunlight, and they should be protected from vehicles or falling objects that might strike the cylinders. If standing water accumulates in an outdoor storage area, the cylinders should be stored on elevated racks. Avoiding contact with water will help minimize cylinder corrosion.

Some operators find it convenient to hang “full” or “empty” identification tags on cylinders in storage, so that the status of the chlorine inventory can be quickly determined. Other plants maintain separate storage areas for full and empty cylinders, but all cylinders, full or empty, should receive the same high level of care. In addition, protective hoods should be placed on empty and full cylinders in storage. Even when a cylinder no longer has sufficient chlorine for plant use, a small amount of gas remains and could escape if the cylinder or valve was damaged. Both full and empty cylinders should always be stored upright and secured with a chain to prevent them from tipping over.

Ton Containers

The ton container is a reusable, welded tank that holds 2,000 lb (910 kg) of chlorine. Containers weigh about 3,700 lb (1,700 kg) when full and are generally 30 in. (0.76 m) in diameter and 80 in. (2.03 m) long. As shown in Figure 4-2, the ends are concave. The container is crimped around the perimeter of the ends, forming good gripping edges for the hoists used to lift and move them. The ton container is designed to rest horizontally both in shipping and in use. It is equipped with two valves that provide the option of withdrawing either liquid or gaseous chlorine. The upper valve draws gas, and the lower valve draws liquid.

Handling the heavy containers is, by necessity, far more mechanized than handling cylinders. Containers are loaded or unloaded by a lifting beam in combination with a manual or motor-operated hoist mounted on a monorail that has a capacity of at least 2 tons (1,815 kg), as shown in Figure 4-5. To prevent accidental rolling, containers are stored on trunnions, as illustrated in Figure 4-6. The trunnions enable the container to be rotated so that it can be positioned correctly for connection to the chlorine supply line.

Ton containers can be stored indoors or outdoors and require the same precautions as chlorine cylinders. The bowl-shaped hood that covers the two valve assemblies when the tank is delivered should be replaced each time the container is handled, as well as right after it has been emptied.

The chlorine storage area should provide space for a 30- to 60-day supply of chlorine. Some systems feed chlorine directly from this storage area. When ton containers are used, the chlorination feed equipment is usually housed in a separate room, as shown in Figure 4-7.

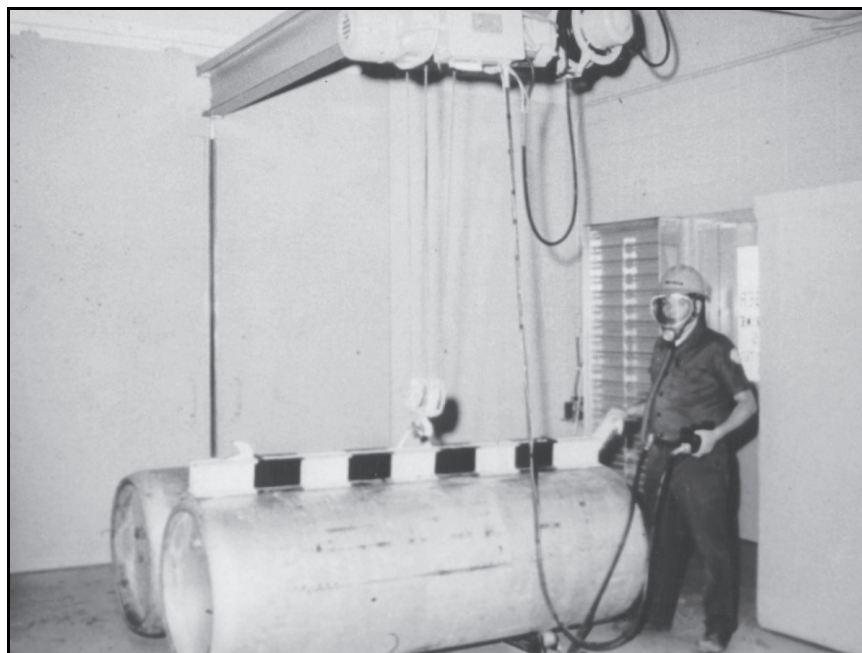
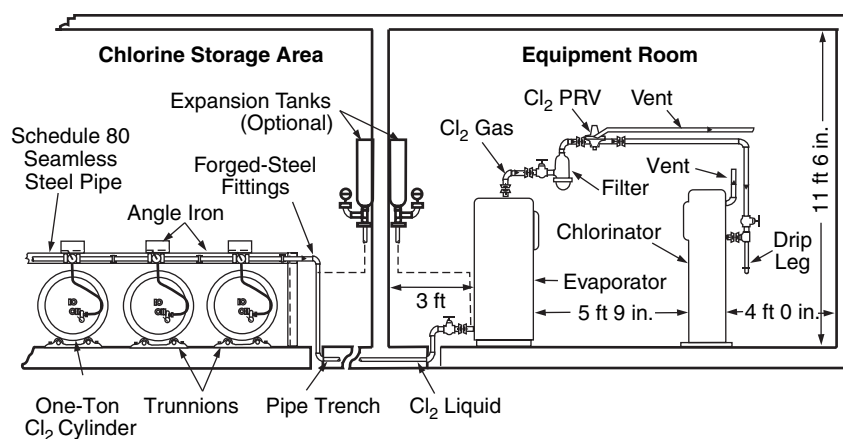


Figure 4-5 Lifting beam with motorized hoist for ton containers



Figure 4-6 Ton containers stored on trunnions



Source: *Handbook of Chlorination* by Geo. Clifford White, copyright © 1972 by Van Nostrand Company. Reprinted by permission of the publisher.

Figure 4-7 Chlorination feed equipment located in a separate room

Tank Cars/Rail Cars

Chlorine is available in tank cars and rail cars for very high capacity needs. Semi-trailer tank cars come in various sizes but many have a capacity of 25 tons. Rail cars also vary in size but a common capacity is 90 tons. These large storage containers require special unloading systems that consist of the following:

- unloading platform,
- storage tank and sun shield,
- weighing device,
- air padding system,
- eductor,