

On-Site Generation of Hypochlorite

First Edition



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First Edition



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Manual of Water Supply Practices—M65, First Edition

On-Site Generation of Hypochlorite

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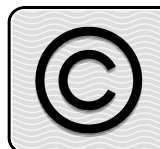
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Preface

A group of volunteers from the Disinfection Systems Committee of the American Water Works Association (AWWA) prepared this manual of practice. The need for a manual on on-site generation (OSG) of hypochlorite technology results from the increased use of bulk-delivered sodium hypochlorite and OSG as alternatives to chlorine gas for water disinfection. The goal of this first edition of M65 is to provide the reader with a general understanding of the principles of OSG, the differences between low-strength OSG systems and high-strength OSG systems, and the subsequent impact each of these systems has on design, construction, and maintenance for water and wastewater utilities. This manual covers the similarities and differences between OSG, bulk-delivered hypochlorite, and chlorine gas, but it does not endeavor to provide lengthy discussion surrounding well-documented chlorination practices, organic chlorine disinfection by-products, or chlorine dosing control. Appendix A provides the most currently available *CT* tables as an easy reference. We encourage interested readers to pursue additional information on chlorination and chloramination topics through other AWWA manuals or resources.

The contents of this manual include a history of OSG technology and definition of terms used in the manual (chapter 1); a comprehensive review of international and national guidance and regulation with respect to OSG (chapter 2); the chemical reactions associated with the electrolysis of sodium chloride to produce hypochlorite on-site (chapter 3); recent information regarding inorganic disinfection by-products produced by OSG and bulk-delivered hypochlorite (chapter 4); overview of the commercially available OSG electrolytic cells and systems (chapter 5); design, installation, and maintenance considerations for both low- and high-strength OSG systems (chapter 6); utility experiences with OSG (chapter 7); and economic comparisons of three different hypochlorite options (chapter 8). Each chapter can be read independently; therefore, there is some limited repetition among the chapters to provide necessary background of important concepts or reference to another chapter. Chapter 5 contains a summary table of chlorination technology attributes that pulls information from several of the proceeding chapters into one concise format. The index can be helpful in finding information on a subject of interest presented in different context throughout the manual.

This manual is designed to provide operators and engineering staff with an understanding of both low- and high-strength OSG systems and how they compare with other forms of chlorine currently available on the market. The manual should help operators, planners, management, and engineers gain enough background on the subject of OSG systems to improve their decision-making processes using a holistic risk management approach that considers not only triple-bottom-line approaches but also the specific regional situation when choosing a chlorination system.

The Disinfection Systems Committee is hopeful that M65 will meet the industry needs and will be a useful resource for a broad audience. As this is the first edition of AWWA Manual M65, *On-Site Generation of Hypochlorite*, the Disinfection Systems Committee and AWWA welcome comments and suggestions for improving future editions of this manual. Please send an email to AWWA at ETSupport@awwa.org or hard-copy correspondence to ETS, 6666 West Quincy Avenue, Denver, CO 80235-3098 to provide feedback on the contents of this manual.

—Susan Rivera, Ph.D.
Chair, M65 Subcommittee

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Chapter **1**

Overview

Susan Rivera and Rudolf Matousek

Various forms of chlorine are commonly used in drinking water and reuse applications for their ability to disinfect and maintain a residual level of disinfectant throughout the distribution system. The majority of utilities in the United States use chlorine gas during treatment, although approximately one-third of all drinking water treatment plants (DWTPs) in the United States use bulk hypochlorite for disinfection and around 8% of United States DWTPs use on-site hypochlorite generators or on-site generation (OSG) systems (AWWA 2008a, AWWA 2008b).

On-site generated hypochlorite, a water treatment disinfectant since the 1970s, initially was not widely embraced by the water industry because of intensive maintenance requirements and higher operating costs when compared with chlorine gas. Recent advances in OSG technology and increased concerns regarding the security and safety risks associated with chlorine gas have resulted in on-site generation of sodium hypochlorite becoming a more attractive and cost-effective option. Advantages of on-site generation over chlorine gas and bulk hypochlorite can include:

- Reduced volume of hazardous material that must be stored on-site
- Improved safety for the public and plant personnel
- Elimination of liabilities associated with transportation of hazardous materials
- Occupational Safety and Health Administration (OSHA) and US Environmental Protection Agency (USEPA) exemption from preparing emergency response plans

CHLORINE: FROM DISCOVERY TO COMMODITY CHEMICAL

The US Centers for Disease Control and Prevention list water chlorination and treatment as one of the ten greatest public health achievements of the twentieth century, and in 1997, *Life* magazine heralded water chlorination and filtration as “probably the most significant

public health advancement of the millennium.” Today, chlorine is by far the most common method used globally to disinfect water and wastewater. Looking back to its beginnings in the nineteenth century, however, the use of chlorine for water disinfection was considered revolutionary and, in some cases, heretical.

Chlorine was first discovered in 1774 by Carl Wilhelm Scheele, who thought the gas he produced was oxygen. In 1810, Sir Humphry Davy confirmed that Scheele’s gas was an element and proposed the name of *chlorine* based on the Greek word *chloros*, meaning green, greenish yellow, or yellowish green. The gas was liquefied by compression in 1805 by Thomas Northmore (*White’s* 2010). In subsequent generations a few visionaries, including John Snow (1813–1858), an English epidemiologist; John Leal (1858–1914), an American physician; and George Fuller (1868–1934), an American sanitary engineer, used chlorine as a chemical to reduce pathogens in water and improve public health. In 1908, Jersey City became the first US municipality to use chloride of lime (calcium hypochlorite) for continuous chlorination for the specific purpose of disinfection (McGuire 2013). Within six years of the successful use of chlorination in New Jersey, 73% of US municipal systems were using chloride-of-lime feed systems. This was an incredible paradigm shift that virtually eliminated typhoid, cholera, and other waterborne pathogens where chlorination and/or filtration were used. Since that time, pressurized tanks of liquid chlorine, now referred to as *chlorine gas*, delivered sodium hypochlorite, and on-site hypochlorite generators have replaced the chloride-of-lime systems. Chlorine and process monitoring systems also greatly improved in the twentieth century.

Origins of Chlorine Production

In 1831, English scientist Michael Faraday postulated the laws governing passing electric current through an aqueous salt solution and coined the word *electrolysis*. These fundamental laws are:

- The weight of a given element liberated at an electrode is directly proportional to the quantity of electricity passed through the solution.
- The unit quantity 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.

The first chlor-alkali processing plants: Bulk-delivered hypochlorite and liquid chlorine (chlorine gas). Chlorine was used as a bleaching agent from around 1785 by mixing Scheele’s gas in water and adding caustic potash. In 1789, Claude Louis Berthollet produced a type of chlorine lime. Charles Tennant (1768–1838) in Scotland performed experiments to produce another liquid bleaching agent then termed *chlorinated milk of lime*. This original product was greatly improved when it was dried to form bleaching powder. The first commercial production of chlorine using electrolysis, also known as the *chlor-alkali process*, began in 1890 by the Elektron Company (now Fabwerke-Hoechst A.G.) of Griesheim, Germany (*White’s* 2010). The first electrolytic plant in the United States was started at Rumford Falls, Maine, in 1892. In 1894, the Mathieson Chemical Company acquired the rights to the Castner mercury cell (Castner 1893) for the manufacture of bleaching powder at a demonstration plant in Saltville, Va. At first, the original electrolytic process was primarily used for caustic production, with chlorine as an unwanted by-product. By 1897, the Mathieson Chemical Company had started to make chlorine for domestic use, in large part to use the excess chlorine produced during caustic manufacture and to avoid dumping the waste into the Niagara River (*White’s* 2010). In 1909, the first commercial manufacturing of liquid chlorine began. This liquid was stored in 100-lb cylinders supplied from Germany. Tank cars with a capacity of 15 tons were manufactured

in the United States in 1909, as well. It was not until 1917 that 1-ton containers came into use for the US military (*White's* 2010). Today, there are over 500 chlor-alkali plants located in many parts of the world that produce both chlorine gas (also called *liquid chlorine*) and bulk-delivered hypochlorite.

Initial attempts to bringing the chlor-alkali plant to the site. While on-site generation was feasible at the turn of the twentieth century, the limitation was the electrode materials, carbon or platinum, the former which would dissolve in service, causing cell damage and poor product quality, and the latter too expensive for practical use. No cell developed during this period provided reliable on-site sodium hypochlorite generation. Not until the development of the dimensionally stable anode (DSA) for the chlorine industry in 1967, by independent Belgian scientist Henry Beer, was a reliable on-site generation cell practical (*White's* 2010). In 1971, J.E. Bennett, using a DSA anode, developed an unseparated electrolytic cell that was patented by Diamond Shamrock Corporation. Many variations in the electrodes and cell configurations have become available in the marketplace during the ensuing years for electrolysis of both dissolved salt solution and seawater as the system feedstock and will be expanded upon in the next section.

HISTORY, DEVELOPMENT, AND GROWTH OF OSG TECHNOLOGY

Electrolytic hypochlorite generation traces its roots back to the advent of chlor-alkali technology. The first recorded US electrolytic commercial plant went into production at Rumford Falls, Maine, in 1892 to produce caustic soda. It wasn't until the early part of the twentieth century that liquid chlorine (chlorine gas) was manufactured on a commercial basis, but only in very specialized applications due to the inefficiency of the systems available.

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 in the antiseptic treatment of open wounds led to the on-site generation of this solution in hospitals. One of the first electrolytic cells for this purpose was developed by Van Peurse and co-workers (1929). This cell was designed to produce the equivalent of the Carrell-Dakin solution (*White's* 2010).

In the 1930s Wallace and Tiernan, a company that would become a leader in OSG during that time, made electrolytic chlorinators as a safe means of chlorinating YMCA swimming pools when the pools were co-located in buildings where people slept. In the 1950s small electrolytic generators began appearing on the market for use in backyard swimming pools. The systems were attractive because they used readily available materials such as salt as a starting material and were safe. However, the cost of these units and the manufacturer's inability to provide satisfactory service discouraged wider use of this equipment. While safety and the ability to decentralize chlorine production were strong drivers in these examples, costs relative to compressed, bottled chlorine have traditionally been higher, ultimately limiting success in this field (*White's* 2010).

Up until the 1960s, the most troublesome and expensive components of the electrolytic systems were the electrodes. The first cells were made from carbon, which improved to graphite. Graphite was used as the universal anode material for the production of chlorine and hypochlorite in the early 1900s. Although graphite is gradually eroded and lost through reactions with oxygen and other elements, its low cost and availability made it preferable to anodes based on noble metals, which were known for their superior resistivity to corrosion and oxidation. Graphite anodes had a short life-span, lasting about 180 days. Developments in graphite and improved production methods provided anodes to meet industry's requirements at the time, although considerable research efforts continued to find a practical metal anode that would retain dimensional stability while generating chlorine.

Platinum metal as an anode was identified and employed in the early days of metal anodes after 1900. Cladding, or coating, platinum to copper and other substrate materials proved uneconomical because of the thickness of the platinum required to give a complete and reliable cover. In 1913, electrodes formed by applying noble-metal coatings to tungsten and tantalum were patented. The oxide-forming characteristics of these substrates eliminated the need for the coating to be pinhole free. Numerous methods were developed for applying the noble metals including vapor deposition and electroplating. Each of these manufactured electrodes had inherent problems with life, cost, or impurities leaching into the product. Extensive research culminated in the filing of European patents in 1958 where oxides of noble metals were used in coating of titanium, particularly ruthenium oxide in combination with other metals and oxides.

With respect to chloride electrolysis, considerable strides were made to produce an anode that exhibited high chlorine current efficiently. One anode, made of a 70/30 wt% platinum-iridium coating displayed a key characteristic that allowed it to produce more chlorine than other types of anodes. The key characteristic is the low overpotential for chlorine evolution combined with a relatively high overpotential for oxygen. Overpotential is the extra voltage that must be applied to an electrode to initiate the desired electrode reaction in the electrolytic cell. Normally oxygen is produced, but if the overpotential is low, chlorine production can be maximized. Thus the platinum-iridium coating described above exhibited a high chlorine current efficiency. Unfortunately with time, changes occurred in the coating that negatively affect the electrochemical properties. In the production of sodium hypochlorite by the electrolysis of a weak brine solution (30 g/L NaCl), these platinum-iridium anodes exhibited wear rates of 0.3 μg per $\text{A}\cdot\text{h}$ (Hayfield and Jacob 1979). This high attrition rate is a key reason why platinum-iridium coatings are rarely used in commercial on-site applications.

The Breakthrough

Two major technological breakthroughs in the 1950s fostered a quantum change in the types of electrodes for the chlorine industry and subsequently on-site hypochlorite generation systems. First, in the 1950s, titanium became commercially available in large quantities. The excellent corrosion resistance of titanium in a variety of solutions and its self-oxidizing metal characteristics became key in electrochemical systems. The second major breakthrough was the development of the dimensionally stable anode (DSA) by Henri Beer. In 1965, Henri Beer coated titanium with catalytic materials, such as ruthenium and iridium, and then heated the components. The process created a dimensionally stable, long-lasting anode that ultimately spurred the chlor-alkali and on-site hypochlorite generation industry. The relatively low cost of these DSAs fueled innovation to develop comparably low-cost, efficient electrolytic cells and systems in the early 1970s. Early on-site hypochlorite production was with seawater and produced hypochlorite at 0.1 wt%.

The improvements in cost and efficiency of the OSG systems based on DSA technology coupled with the potential hazards of chlorine gas systems contributed to the popularity of OSG in the late 1970s. Other drivers were more stringent laws regulating the use of chlorine gas, such as the Uniform Fire Code and risk management plan (RMP) requirements in addition to restrictions on the transportation of chlorine gas. The OSG systems eliminated the need for transporting hazardous chemicals because the hypochlorite is generated at the point of use using salt and electricity. Also there is very little danger that a flow-through on-site hypochlorite generation system that manufactures 0.1 to 0.8 wt% hypochlorite could produce any situation that would be classified as a major leak. In many remote places of the world, on-site hypochlorite generation is the only practical way of obtaining disinfection since low-voltage electricity and salt or seawater are more accessible than bulk-delivered hypochlorite or chlorine gas. Finally, as distributed architecture and

water reuse continue to gain consideration in water planning and development, OSG often solves the problems associated with the need for frequent transport of bulk hypochlorite to multiple sites because of degradation concerns (see chapter 4).

More recently, high-strength hypochlorite systems that produce up to 15% hypochlorite have come into the market. These generators provide some flexibility for some utilities but can also require additional operator training due to their complexity. These systems will be covered in more detail throughout the manual.

ON-SITE GENERATION TECHNOLOGY NOW

This manual of practice focuses on the on-site generation (OSG) systems commonly used in the drinking water and reuse industry. Until recently, the OSG systems typically produced low-strength hypochlorite between 0.4–0.8%, or 4,000–8,000 ppm. This manual will also cover the recent introduction of OSG hypochlorite systems that produce product in the 12–15% range. The hypochlorite solutions produced from these systems are termed *high-strength OSG* and are similar in properties compared with bulk-delivered hypochlorite. Some confusion in the industry has ensued between the on-site generated high-strength hypochlorite and bulk-delivered hypochlorite. The major differences are that the on-site system can be tuned to produce a specific concentration of hypochlorite and caustic, if desired, whereas bulk-delivered hypochlorite is made at a chlor-alkali plant and then shipped to the desired location. The high-strength systems can also be configured to produce chlorine gas on-site, and this manual will describe these systems and how they compare with low-strength OSG and bulk-delivered hypochlorite in several chapters. However, because of the small installation base, these systems were not compared in the case-study (chapter 7) or economics (chapter 8) chapters.

Terms Used in This Manual

Hypochlorite is a commodity chemical, but it comes in many forms and each has advantages and disadvantages. While this manual focuses on the design, installation, and operations associated with on-site generated hypochlorite, it also compares OSG with bulk-delivered hypochlorite and chlorine gas. Calcium hypochlorite tablet feeders are not compared with OSG in this manual, but such systems are available as a method to deliver hypochlorite.

Trade versus weight percent. This manual will use trade percent throughout, unless otherwise noted. Hypochlorite stocks are frequently stored at concentrations ranging from 0.4–15 trade percent NaOCl measured as free available chlorine (FAC). Fifteen (15) trade percent is equivalent to 1.5×10^5 mg/L free available chlorine (FAC). Trade percent may be calculated using one of the following equations:

$$\text{trade percent} = \text{g/L Cl}_2 \div 10$$

$$\text{trade percent} = \text{percent of available Cl}_2 \text{ by weight} \times \text{specific gravity}$$

Weight percent of sodium hypochlorite is defined as the weight of sodium hypochlorite per 100 parts weight of solution. It can be calculated by converting weight percent of available chlorine into its equivalent as sodium hypochlorite. One way to calculate this is by multiplying by the ratio of their respective molecular weights as shown below:

$$\frac{\text{molecular wt NaOCl } A}{\text{molecular wt Cl}_2} = \frac{74.44}{70.91} = 1.05$$

$$\text{wt\% NaOCl} = \left(\text{wt\% available Cl}_2 \right) \times \frac{\text{molecular wt NaOCl}}{\text{molecular wt Cl}_2}$$

Percent available chlorine by weight may also be calculated by taking the trade percent and dividing by the specific gravity of the solution:

$$\% \text{ available chlorine by weight} = \text{trade \%} \div \text{specific gravity}$$

Table 1-1 shows some comparisons among some common trade percent values and their weight percent values.

Explanation of terms and definitions. One major source of confusion is that on-site hypochlorite generators and systems produce hypochlorite at different concentrations. These are 0.4%, 0.8%, and 12–15%. In this manual we classify the first two as low-strength OSG because the hypochlorite concentrations are <1% and the electrolytic cells are not separated by a membrane. High-strength on-site hypochlorite generation systems use more than one unit operation to produce hypochlorite in the 12–15% range and always use a separated electrolytic cell. These systems can also produce 15% sodium hydroxide, often called *caustic soda*. These systems are also referred to as *on-site generators*, which causes confusion. Adding further to the confusion is that bulk-delivered hypochlorite is typically provided as 12.5%, but the concentrations can range from 11–14%, depending upon the manufacturer. Because high-strength OSG systems are also available in this range, the reader is cautioned to avoid confusing these two forms of hypochlorite. In this manual of practice, we use the following terminology:

- **Bulk-delivered hypochlorite.** Hypochlorite that is made at a manufacturing facility and transported to the site. Typical concentration is 12.5% but can range from 11–20% when it leaves the manufacturing plant.
- **Delivered chlorine gas.** Chlorine gas that is delivered in a cylinder or by railcar and requires special handling. Chlorine gas is also commonly referred to as *liquid chlorine*.
- **High-strength OSG.** Describes an on-site generator that produces 12–15% hypochlorite (120,000–150,000 mg/L of NaOCl measured as free available chlorine). Some high-strength systems can be configured to produce chlorine gas.
- **Low-strength OSG.** Describes any on-site generator system that produces hypochlorite at <1% (10,000 mg/L of NaOCl measured as free available chlorine).
- **On-site generation (OSG).** General term to describe hypochlorite that is made on-site from salt.

In general, we will try to use these definitions throughout. However, in some cases, such as chapter 8 (economics), the concentration is explicitly defined in order to provide better cost comparisons. Table 1-2 describes the forms of chlorine and hypochlorite available in the marketplace.

Regulations, Guidelines, and Standards

Current regulations for most drinking water systems worldwide suggest or require some form of chlorination. Regulations surrounding chlorine disinfection in drinking water systems have been evolving for over 50 years, with strong guidance coming from international organizations such as the World Health Organization (WHO). Chlorine has inevitably prevented the spread of waterborne disease, nearly eradicating diseases such as typhoid and cholera. More recently, however, research regarding disinfection by-products has dominated the conversations, especially as analytical detection methods increase in sensitivity (ability to detect contaminants at extremely low concentrations) and regulations drive acceptable levels. Chapter 2 gives a broad review of international regulations as well as the

current and future US regulatory trends as they relate to chlorination in general and OSG in particular. More information regarding inorganic disinfection by-products produced by OSG and bulk-delivered hypochlorite can be found in chapter 4.

OSG Electrolytic Principles, Function, and Application

Chapter 3 delves into the chemical reactions associated with the electrolysis of sodium chloride (NaCl) using DSA technology to produce hypochlorite on-site. The water quality and features that limit the lifetime of an electrolytic cell, such as anode passivation, electrode wear, and the effect of inorganic and organic species on cell performance, are also covered. Chapter 5 then provides overview of the commercially available OSG electrolytic cells and systems, highlighting the differences, advantages, and potential disadvantages of each. Cell designs can be tubular or flat plate designs, but must all use a dimensionally

Table 1-1 Comparisons among some common trade percent values and their weight percent values

Trade % (g available Cl ₂ / 100-mL solution)	Mass to Volume Available Cl ₂ Equivalent (g/L)	lb/gal	wt%/wt Cl ₂ (g available Cl ₂ / 100-g solution)	wt%/vol NaOCl (g NaOCl/ 100-mL solution)	wt%/wt NaOCl (g NaOCl/ 100-g solution)	Specific Gravity
0.4	4	0.0334	0.39	0.42	0.41	1.018
0.8	8	0.0668	0.78	0.84	0.82	1.020
1	10	0.0836	0.97	1.05	1.02	1.026
5	50	0.42	4.64	5.25	4.87	1.078
6	60	0.50	5.50	6.30	5.77	1.091
11	110	0.92	9.47	11.55	9.95	1.161
12	120	1.00	10.22	12.60	10.73	1.174
12.5	125	1.04	10.59	13.12	11.12	1.180
15	150	1.25	12.40	15.75	13.01	1.210
16	160	1.34	13.09	16.80	13.75	1.222
20	200	1.67	15.74	21.00	16.52	1.271

Table 1-2 Forms of chlorine and hypochlorite available in the market*

Mode of Delivery	Low-Strength OSG	High-Strength OSG	Bulk-Delivered Hypochlorite	Delivered Chlorine Gas
Produced on-site from salt	Yes, typical concentrations are 0.4% and 0.8%.	Yes, typical concentra- tion is 12.5%. Chlorine gas can also be produced on-site from some of these systems.	No	No
Delivered as a liquid	No	No	Yes, concentration ranges from 11–20%, with a typical concentration of 12.5%.	No
Delivered as a gas (cylinder or railcar)	No	No	No	Yes

*Calcium hypochlorite tablet feeder systems are not included in this manual.

stable anode (DSA) technology to produce hypochlorite at the most efficient energy conversions and salt conversions. A summary table comparing the attributes of the various forms of aqueous chlorine and chlorine gas is also provided at the end of the chapter.

OSG Design, Installation, Operations, and Maintenance

The first part of chapter 6 covers the design and installation of both low-strength OSG systems (0.4–0.8%) and high-strength OSG systems (12–15%). Specific considerations for providing redundant OSG system and power are discussed. One of the key advantages of OSG is that the solutions are generated on-site so that dangerous chemicals do not need to be stored or handled. Methods to provide redundancy and contingency plans in the event that the generator or one of its key components (electricity or salt) is missing are also covered along with additional information on hydrogen gas and electrical mitigation strategies. The chapter also discusses the operation and maintenance (O&M) associated with OSG systems. The frequency of needed maintenance will be discussed so that the reader can understand the annual time commitments associated with OSG.

OSG Case Studies and Economics

Chapters 7 and 8 cover case studies and evaluate the economics of choosing a low-strength OSG compared to a high-strength OSG. These chapters have collected real-world data from operators and consulting engineers in the form of survey questionnaires and interviews. Chapter 7 incorporates the experiences of utilities that have already implemented OSG hypochlorite technology at their facilities. A range of system sizes and a number of US geographical locations were included in the survey, which asked questions regarding the system in place, cost data, and subjective questions on the system benefits and concerns. Financial and subjective comments were compiled so that anonymity would be preserved yet the information could serve to inform a utility considering a change from bulk-delivered hypochlorite or chlorine gas.

Chapter 8 uses actual cost data from two different consulting engineering firms. Both capital and operations and maintenance costs are considered and compared for bulk-delivered hypochlorite 12% solution, on-site generated hypochlorite from a low-strength system (0.8% solution), and on-site generated hypochlorite from a high-strength system (12%).

Holistic Risk Management

While separately evaluating the chemical, regulatory, safety chemical storage, and economics of hypochlorite systems and chlorine is helpful, more utilities are finding that a holistic risk management approach that considers not only triple-bottom-line approaches, but also the specific regional situation, is necessary. These concepts are addressed throughout the manual, with specific attention to these ideas in chapters 2 and 5.

New technology breakthroughs and improvements. To address the potential need to minimize inorganic by-product formation during OSG, manufacturers are investigating process changes and new materials that might lower the cost of electrodes or produce more efficient generators. For example, one manufacturer is conducting a National Science Foundation (NSF) research study in collaboration with industry leaders to further investigate the factors that affect oxyhalide production in OSGs. This manufacturer is also actively integrating patented automatic self-cleaning technology to remove common electrode surface deposits, such as calcium carbonate. Operators are not required to acid wash the cells manually. Other companies are investigating new types of DSA electrodes to increase hypochlorite production and methods to save energy during the electrolysis process.

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Chapter **2**

Standards and Regulations

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Drinking water disinfection is a ubiquitous process used by water systems internationally. The World Health Organization (WHO) publishes guidelines for drinking water quality that serve as a basis for the development of drinking water standards in many nations. The *2011 WHO Guidelines for Drinking-Water Quality* contains information regarding the use of chlorine to disinfect water and recommended limits for disinfectants and disinfection by-products (DBPs) associated with chlorination. Other national and international organizations including American Water Works Association (AWWA), NSF International (NSF), and the Chlorine Institute Inc. (CI) provide industry guidance related to chlorination, which can influence the selection of a particular type of chlorine and practices associated with its use.

In the United States, the Safe Drinking Water Act (SDWA) is the principal regulatory framework for achieving appropriate levels of disinfection and maintenance of a secondary residual to protect public health without creating unwanted levels of DBPs. The SDWA is not the only relevant regulation for chlorine disinfection practices because water quality is not the only consideration when operating chemical treatment systems, including on-site generation (OSG) units. Other considerations include protection of employees, the public, and the environment, as well as economics. Therefore, regulatory requirements under the Clean Air Act (CAA), Occupational Safety and Health Act (OSHA), and Clean Water Act (CWA) must also be considered when choosing, designing, and operating a chlorination option.

The intent of this chapter is to summarize key requirements of national and international standards and regulations that are relevant to the planning, selection, design, and operation of OSG systems for the treatment of public drinking water supplies and reclaimed water for potable use.

USEPA SAFE DRINKING WATER ACT AND RELEVANT RULES

Overview

The SDWA was first signed into law December 16, 1974, and it has subsequently been amended in 1986, 1988, 1996, and 2002. The act authorizes the US Environmental Protection Agency (USEPA) to establish minimum standards related to the drinking water supply, treatment, and distribution for the protection of public health. These standards may be either health-based numeric criteria known as a maximum contaminant level (MCL), or when it is not possible to set an MCL, a treatment technique (TT), which sets operational controls that can be reliably monitored and thus manage the water quality issue of concern.

The SDWA, like most environmental regulations, is implemented through a system of primacy agencies, where individual states establish and enforce requirements that are at least as stringent as the federal requirements. States also have general duties beyond implementing the federal regulations, which include ensuring that water systems are appropriately designed and constructed. Consequently, many states have unique water treatment plant design and construction approval processes that are relevant to installing or modifying an OSG system to support disinfection objectives. One group of 10 states has developed a set of common standards known as the *10 States Standards*. Illinois, Indiana, Iowa, Ohio, Minnesota, Missouri, Michigan, New York, Pennsylvania, and Wisconsin (as well as Ontario, Canada) created and adopted the “Great Lakes, Upper Mississippi River Board of State and Provincial Public Health and Environmental Managers, Recommended Standards for Water Works” in 1950. The *10 States Standards* is updated every few years and is comprehensive in its detail for design.

Table 2-1 summarizes the existing SDWA regulatory framework by water system type, identifying the applicability of key regulations to the various types of systems. Of those rules listed in the table, three primary sets of regulations are most pertinent to OSG system selection and design as they relate to chlorine or chloramine disinfection:

- Surface Water Treatment Rule (SWTR) and subsequent revisions
- Ground Water Rule (GWR)
- Disinfectants and Disinfection By-products Rules (DBPRs)

Each rule is currently *effective*, meaning that systems that are constructing new facilities must comply with the provisions set forth in each rule during the initial design, as they modify existing facilities, or as they bring new water supplies online. Further discussion on each statute is provided below in addition to a brief introduction to potential future SDWA regulations that may impact OSG systems.

Surface Water Treatment Rule and Subsequent Revisions

The primary purpose of the SWTR is to minimize the risk of human exposure to microbial contaminants in drinking water by requiring all water treatment plants that use either surface water or groundwater under the direct influence (GWUDI) of surface water as a source of supply to provide adequate disinfection and, under most conditions, also filtration. The initial SWTR and its subsequent revisions contain a number of design and operating requirements for filtration and disinfection processes. For OSG system design and operation, the two most directly relevant requirements are: (1) to achieve, at a minimum, the required inactivation of microbial contaminants (or primary disinfection credits) at the treatment plant through the application of the *CT* concept (disinfectant concentration multiplied by contact time) and (2) to provide a secondary disinfectant residual to minimize the potential for bacterial regrowth in the distribution system.

Table 2-1 SDWA regulatory framework

Rule	Community Water Systems*		Noncommunity Water Systems†	
	Surface Water/ Groundwater Under Direct Influence	Groundwater	Surface Water/ Groundwater Under Direct Influence	Groundwater
Surface Water Treatment Rule (1989, as amended 1998, 2002, 2006)‡	All systems that practice conventional or direct filtration as well as unfiltered surface water supplies	Does not apply	All systems that practice conventional or direct filtration as well as unfiltered surface water supplies	Does not apply
Total Coliform Rule (1989, as amended 2013)	All	All	All	All
Ground Water Rule (2006)	Only to groundwater sources operated by such systems	All groundwater supplies	Only to groundwater sources operated by such systems	All groundwater supplies
Stage 1 Disinfectants and Disinfection By-products Rule (1998)	All systems applying chemical disinfectant(s)	All systems applying chemical disinfectant(s)	Nontransient systems applying chemical disinfectant(s)	Nontransient systems applying chemical disinfectant(s)
Stage 2 Disinfectants and Disinfection By-products Rule (2006)	All systems that apply or receive water with a chemical disinfectant(s)	All systems that apply or receive water with a chemical disinfectant(s)	Nontransient systems that apply or receive water with a chemical disinfectant(s); transient, non-community water systems (TNCWSs) that treat with chlorine dioxide	Nontransient systems that apply or receive water with a chemical disinfectant(s); TNCWSs that treat with chlorine dioxide
Lead and Copper Rule (1991, as amended 2000, 2007)	All systems	All systems	Nontransient systems	Nontransient systems

* A community water system (CWS) is defined as a public water system that serves at least 15 service connections used by the same population year-round or regularly serves at least 25 year-round residents.

† A noncommunity water system is either:

- A nontransient noncommunity water system (NTNCWS), which is defined as a public water system that regularly supplies water to at least 25 of the same people at least six months per year, or
- A transient noncommunity water system (TNCWS), which is defined as a public water system that does not regularly supply water to at least 25 of the same people at least six months per year.

‡ Revisions of the SWTR include, in chronological order, the Interim Enhanced Surface Water Treatment Rule (IESWTR), Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR), and Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR).

Disinfectant CT. The SWTR requires at least 99.9% (3-log) removal and/or inactivation of *Giardia lamblia* and at least 99.99% (4-log) removal and/or inactivation of viruses. Physical removal is achieved via filtration, and inactivation is achieved via disinfection. In the SWTR, the USEPA defined the technologies eligible for disinfection credit for these indicators as chlorine, chloramines, chlorine dioxide, ozone, and ultraviolet light (UV). As such, through proper design and operation, OSG systems can serve as an effective means for achieving compliance with the SWTR.

In lieu of direct monitoring for *Giardia lamblia* and viruses, the SWTR adopted the concept of CT, expressed in units of milligram-minute/liter, to evaluate inactivation via

chemical disinfection. The SWTR provides the following explicit instructions for the calculation of *CT*:

1. The temperature of the disinfected water measured at least once per day at each residual disinfectant concentration sampling point.
2. If the system uses chlorine, the pH of the disinfected water must be measured at least once per day at each chlorine residual disinfectant concentration sampling point.
3. The disinfectant contact time(s) (*T*) must be determined for each day during peak hourly flow.
4. The residual disinfectant concentration(s) (*C*) of the water before or at the first customer must be measured each day during peak hourly flow.

Higher disinfectant residual concentrations and/or additional contact time are needed to achieve a higher log inactivation. The minimum *CT* requirements for primary disinfection processes vary depending upon the type of treatment employed, as illustrated in Table 2-2. These requirements are consistent through the SWTR, Interim Enhanced Surface Water Treatment Rule (IESWTR), and Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR), but become more complicated in the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR). Required *CT* for systems practicing chlorination or chloramination can be determined using the *CT* tables provided in appendix A. Based on the chemical application point and the desired level of inactivation, the *CT* value can then be used to calculate the required chlorine dosage to adequately size an OSG system. The USEPA SWTR Guidance Manual (1991) offers additional guidance for determining *CT*.

The IESWTR and later LT1ESWTR and LT2ESWTR expanded upon the original requirements of the SWTR to include *Cryptosporidium*. Currently, water treatment plants must provide total *Cryptosporidium* removal and/or inactivation based on influent *Cryptosporidium* concentrations as summarized in Table 2-3. Under the LT2ESWTR, inactivation of *Cryptosporidium* can be achieved via ozone, chlorine dioxide, or UV. Chlorine, however, and subsequently OSG cannot be used to meet the additional *Cryptosporidium* requirements of LT2ESWTR. Rather as the LT2ESWTR requirements are applied in a site-specific fashion, the effect on OSG design and operation is one of balancing multiple disinfectants instead of explicitly changing inactivation requirements for *Giardia lamblia* or viruses. Additionally, significant changes in disinfection practices (e.g., moving the point of disinfection or changing the type of disinfectant) may require systems to conduct disinfection profiling and benchmarking. This includes developing a disinfection profile for *Giardia* or virus inactivation achieved on a daily basis over one year or more. These data are then used to set a benchmark for design of treatment modifications.

Secondary disinfectant residual. All surface water systems including GWUDI systems are required to maintain a minimum disinfectant residual throughout the distribution system. A common method to maintain a secondary residual is with the use of chlorine or chloramines. Community and nontransient noncommunity water systems that use chlorine or monochloramine must measure the residual disinfectant level in the distribution system at the same point in the distribution system and at the same time as total coliforms are sampled. No more than 5% of those samples may be below detection in any monitoring period. “Below detection” is addressed differently in various states with some states providing an explicit numeric value. For example, in Texas, residual disinfectant levels must be equal to or greater than 0.2 mg/L when free chlorine is used or 0.5 mg/L when monochloramine is used.

Monitoring and reporting. Ongoing demonstration of compliance with *CT* and secondary disinfectant residual requirements is required as a component of routine reporting.

Individual states will have additional operational monitoring requirements that impact chemical feed rates, water flows, and water quality conditions that bear on disinfection processes. Utility-specific requirements should be considered when automating OSG systems for compliance monitoring and reporting.

Ground Water Rule

The federal GWR as finalized in 2006 does not require disinfection in all cases. Instead, it establishes a set of triggers that the states can use to require a system to replace its current source, apply additional treatment, or take other risk management steps if certain triggers are reached. The triggers are (1) identification of a sanitary defect by the state, (2) positive fecal indicator results from well samples, or (3) an evaluation of the hydrogeologic setting by the state. This is a challenging regulatory framework to implement; consequently, some states extended existing provisions or added new provisions for mandatory disinfection of groundwater systems (e.g., Colorado, Florida, Kentucky, and Pennsylvania).

Table 2-2 Minimum disinfection requirements SWTR, IESWTR, and LT1ESWTR

Filtration Treatment Process Employed	Minimum Required Log Inactivation Credit by Disinfection Treatment	
	<i>Giardia</i>	Viruses
Conventional	0.5	2.0
Direct	1.0	3.0
Slow sand	1.0	2.0
Diatomaceous earth	1.0	3.0
Reverse osmosis	0.0	1.0
Nanofiltration	0.0	1.0
Ultrafiltration	0.0	4.0
Microfiltration	0.0	4.0
Pretreatment plus bag or cartridge	1.0	4.0
Conventional filtration followed by bag or cartridge	0.5	2.0
No filtration	3.0	4.0

Table 2-3 LT2ESWTR *Cryptosporidium* treatment requirements

System's Bin Classification	Conventional Filtration (Including Softening)	Direct Filtration	Slow Sand or Diatomaceous Earth Filtration	Alternative Filtration Technologies
Bin 1 (<0.075 oocysts/L)	No additional treatment	No additional treatment	No additional treatment	No additional treatment
Bin 2 (≥ 0.075 to <1.0 oocysts/L)	1-log treatment	1.5-log treatment	1-log treatment	*
Bin 3 (≥ 1.0 to <3 oocysts/L)	2-log treatment	2.5-log treatment	2-log treatment	†
Bin 4 (≥ 3.0 oocysts/L)	2.5-log treatment	3-log treatment	2.5-log treatment	‡

* As determined by the state such that total *Cryptosporidium* removal and inactivation is at least 4.0 log.

† As determined by the state such that total *Cryptosporidium* removal and inactivation is at least 5.0 log.

‡ As determined by the state such that total *Cryptosporidium* removal and inactivation is at least 5.5 log.

Disinfectant CT. Those systems that are using treatment to comply with the GWR must provide 4-log removal/inactivation of viruses. The regulatory language encourages disinfection using free chlorine and recognizes the use of membranes and UV disinfection. With respect to CT, the chemical disinfectant inactivation requirements for viruses use the original SWTR CT tables.

Monitoring and Reporting. Monitoring and reporting expectations parallel those established under the SWTR. Specific requirements are determined by the state.

Disinfectants and Disinfection By-products Rules

The Stage 1 and Stage 2 DBPRs were established to minimize exposure to harmful by-products resulting from disinfection practices including chlorine, chloramines, chlorine dioxide, and ozone.¹

Stage 1 DBPR. The Stage 1 DBPR establishes MCLs, maximum contaminant level goals (MCLGs), maximum residual disinfectant levels (MRDLs), and maximum residual disinfectant level goals (MRDLGs) for chemical disinfectants and the concentrations of DBPs in finished water and in drinking water distribution systems as shown in Table 2-4.

Systems using free chlorine or chloramines must comply with the requirements for THMs and HAAs. Compliance with the TTHM and HAA5 MCLs is based on a running annual average (RAA) of quarterly averages of samples taken in the distribution system associated with a particular water treatment plant as identified in coordination with the primacy agency. Although the Stage 1 DBPR includes MCLs for chlorite and bromate, these contaminants are only regulated contaminants for systems that use chlorine dioxide or ozone, respectively, in any part of their treatment process. Some utilities are also adding chlorite for nitrification control (Blute et al. 2013, McGuire et al. 2009). These entities should consider the chlorite MCL as well. Water utilities providing primary and secondary disinfection via a chlorine-based disinfectant (e.g., sodium hypochlorite) are not required to monitor for these contaminants. However, both chlorite and bromate can be concerns when sodium hypochlorite is used. Bromate, for example, is present in sodium hypochlorite supplies due to the presence of naturally occurring bromide ions in the salt used to manufacture the sodium hypochlorite. Chlorite is also a known by-product from the production and storage of sodium hypochlorite. As such, careful consideration must be given when selecting and designing chlorine disinfection systems using bulk bleach or on-site generated hypochlorite. Refer to chapter 4 for additional information on the mechanisms for formation of these inorganic impurities in OSG systems compared with bulk bleach systems.

Stage 2 DBPR. The Stage 2 DBPR requires some systems to complete an initial distribution system evaluation (IDSE) to characterize DBP levels in their distribution systems and identify locations to monitor DBPs for Stage 2 compliance. The Stage 2 DBPR did not change any of the Stage 1 DBPR MCLs; however, it did change the calculation method for determining compliance with the TTHM and HAA5 standards. Under the Stage 1 DBPR, compliance with the TTHM and HAA5 MCLs was determined based on a RAA, which averaged TTHM and HAA5 monitoring results across multiple sampling locations. Under the Stage 2 DBPR, compliance is based on a locational running annual average (LRAA), where the running annual average concentration at each compliance monitoring location must be less than the MCL. This approach is intended to provide more equitable water quality relative to DBPs to a utility's customers regardless of where they live in the distribution system. The Stage 2 DBPR also shifted monitoring sites from locations generally representative of the distribution system to locations where high TTHM and HAA5 observations are expected to occur based on monitoring results and/or modeling.

Table 2-4 Stage 1 DBPR MRDLGs, MRDLs, MCLGs, and MCLs

Disinfectant Residual	MRDLG (mg/L)	MRDL (mg/L)	Compliance Based On
Chlorine	4 (as Cl ₂)	4.0 (as Cl ₂)	Annual average
Chloramine	4 (as Cl ₂)	4.0 (as Cl ₂)	Annual average
Chlorine dioxide	0.8 (as ClO ₂)	0.8 (as ClO ₂)	Daily samples
Disinfection By-products	MCLG (mg/L)	MCL (mg/L)	Compliance Based On
Total trihalomethanes (TTHMs)	N/A	0.080	Annual average
Chloroform	0.07		
Bromodichloromethane	0		
Dibromochloromethane	0.06		
Bromoform	0		
Haloacetic acids (HAA5s)	N/A	0.060	Annual average
Monochloroacetic acid	0.07		
Dichloroacetic acid	0		
Trichloroacetic acid	0.2		
Bromoacetic acid	N/A		
Dibromoacetic acid	N/A		
Chlorite	0.8	1.0	Monthly average
Bromate	0	0.010	Annual average

N/A—not applicable

Additionally, the Stage 2 DBPR requires that operational evaluation levels (OELs) be calculated each monitoring period for each Stage 2 DBPR monitoring site according to the following equation:

$$\text{OEL} = (\text{Q1} + \text{Q2} + 2 \cdot \text{Q3}) / 4$$

Where:

Q1 = Stage 2 TTHM or HAA5 compliance measurement for the quarter before the previous quarter

Q2 = Stage 2 TTHM or HAA5 compliance measurement from the Stage 2 compliance location for the previous quarter

Q3 = Current quarter Stage 2 TTHM or HAA5 compliance measurement

If the TTHM or HAA5 OEL exceeds the Stage 2 DBPR MCL of 80 µg/L or 60 µg/L, respectively, an operational evaluation must be conducted to identify how the excursion(s) can be reduced. This evaluation must include the raw water supply, water treatment facilities, and distribution system.

Potential Future Regulations

Chlorate. Chlorate is an impurity in hypochlorite solutions that results from the decay of hypochlorite with time and elevated temperature. The USEPA may make a determination to regulate chlorate in the third cycle of SDWA Regulatory Determinations with a proposed rule two years after a decision to regulate is made. Chlorate is regulated as a

pesticide under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and that regulatory process identified drinking water as the primary route for human exposure. In addition, California established a notification level (NL) for chlorate at 0.8 mg/L. At this time, it is not clear if the USEPA will set an MCL for chlorate; however, the USEPA is using 0.21 mg/L as a health reference level (HRL) in its regulatory deliberations. Refer to chapter 4 for additional discussion on chlorate.

Perchlorate. Perchlorate is another impurity present in sodium hypochlorite solutions. In February 2011, the USEPA issued a final determination to regulate perchlorate. Based on the SDWA, the USEPA had been expected to release a proposed rule by February 2013, with a final rule following in late 2014 or early 2015; however, in early 2013, the USEPA expressed a need for additional data before an MCL for perchlorate could be proposed. As such, a proposed rule is not anticipated until late 2015 or 2016 at the earliest. In the interim, the USEPA has established a health advisory level of 0.015 mg/L for perchlorate. Additionally, several states have already adopted a provisional limit, including Massachusetts (MCL of 0.002 mg/L) and California (0.006 mg/L). Additional states have set various guidelines or health goals that range from 0.004 to 0.051 mg/L. New York, for instance, requires that utilities notify the state if perchlorate is detected at or above 0.005 mg/L and take appropriate action if detected at or above 0.018 mg/L. Refer to chapter 4 for additional discussion on perchlorate.

The AWWA Government Affairs web page (<http://www.awwa.org/legislation-regulation.aspx>) and references therein may be a useful resource for more current information on regulatory actions.

CHEMICAL SAFETY AND SECURITY IN THE UNITED STATES

The USEPA's CAA Risk Management Plan (RMP) Rule and OSHA's Process Safety Management (PSM) program were designed to minimize potential risks associated with hazardous chemicals. Facilities that use, manufacture, store, or handle regulated substances above certain threshold quantities (TQs) are required to develop a written plan to identify and prevent potential hazards associated with accidental releases of such substances. Both programs require multiple preventive measures, including training, compliance audits, and hot work permits, in addition to the development of an emergency response plan and program in order to minimize impacts to the public and the environment should a release occur. The RMP Rule also requires eligible facilities to develop an RMP for worst-case and alternative release scenarios, and complete a hazard assessment that documents any releases that occurred within the five years prior to submission of the RMP.

Threshold quantities for chemicals that may be used or produced during an OSG process are summarized in Table 2-5. OSG systems including those that produce dilute or concentrated sodium hypochlorite or chlorine gas do not typically use chemicals that are subject to the requirements of the USEPA RMP Rule or OSHA PSM program since the process chemicals are either not chemicals of concern or because the chemicals do not exceed the threshold quantities as listed under section 112(r) of the CAA RMP Rule or OSHA's PSM program. An exception could be the storage of hydrochloric acid for high-strength OSG systems for larger installations. However, state or local agencies may have adopted more stringent requirements, and as such, readers are strongly advised to carefully review all state and local standards and regulations.

Table 2-5 USEPA RMP and OSHA PSM threshold quantities for chemicals used or produced by OSG systems

Chemical	CAS No.	Threshold Quantity (lb)	
		RMP	PSM
Chlorine	7782-50-5	2,500	1,500
Hydrochloric acid (37% or greater)	7647-01-0	15,000	Not listed
Hydrochloric acid (less than 37%)	7647-01-0	Not listed	Not listed
Hydrogen	1333-74-0	10,000	Not listed
Sodium bisulfite	7631-90-5	Not listed	Not listed
Sodium chloride	7647-14-5	Not listed	Not listed
Sodium hydroxide	1310-73-2	Not listed	Not listed
Sodium hypochlorite	7681-52-9	Not listed	Not listed

CAS No.—Chemical Abstract Service Registry number

OSHA also implemented the Hazard Communication Standard (HCS), which includes requirements for labeling hazardous materials, safety data sheets (SDSs), and employee training on worker safety. Utilities must also comply with state or local requirements related to the design and construction of liquid chemical storage and handling facilities. Industry standards generally recommend providing covered or enclosed areas out of the sunlight, proper ventilation of storage tanks, spill containment areas around storage tanks and metering equipment, and secondary contained piping, particularly for large quantities of stored chemicals. For OSG systems that require multiple liquids for generation (see chapter 3 for more information), mitigation measures to minimize the risk of cross-contamination should be incorporated into the design and include defining clear unloading protocols, color-coded delivery piping, clear labeling of chemical tanks and piping, and separate keys for unlocking each chemical delivery connection. In addition, adequate containment areas around transfer stations are advised. Primacy agencies with responsibility for implementation of the Resource Conservation and Recovery Act (RCRA) also require registration of all underground storage tanks, and in most instances, state or local fire ordinances contain registration and permit requirements for select aboveground storage tanks storing hazardous liquids above a certain volume threshold. Bulk liquid storage regulations may vary by region, and as such, it is necessary to understand all state and local policies regarding bulk liquid storage and handling. Refer to chapters 4, 6, and 8 for additional discussion on chemical safety.

INTERNATIONAL STANDARDS AND REGULATIONS

Water Quality

Several prominent countries and international organizations have developed guidelines or enforceable regulations comparable to those of the United States related to drinking water quality and disinfection that are as illustrated in Table 2-6. These parameters are particularly pertinent to the design and operation of OSG systems. Although this list may not be comprehensive, it is intended to capture well-established standards in addition to regulations or guidelines from countries with existing OSG installations for the treatment of drinking water.

Table 2-6 Summary of key international water quality standards and regulations for various organizations and countries

Applicable Standards	World Health Organization	Australia	Canada	Emirate of Abu Dhabi	European Union	New Zealand	Republic of South Africa	Singapore	United States
	World Health Organization, <i>Guidelines for Drinking Water Quality</i> (2011)	<i>Australian Drinking Water Guidelines, Paper 6</i> (2011)	Health Canada, <i>Guidelines for Canadian Drinking Water Quality</i> (2010)	Emirate of Abu Dhabi, <i>Water Quality Regulations</i> (2009)	Council Directive 98/83/EC (1998)	New Zealand, <i>Drinking-Water Standards for New Zealand</i> (2005) (Revised 2008)	<i>South African Water Quality Guidelines</i> (1996); South African National Standard 241—Drinking Water (2011)	Singapore, <i>Environmental Public Health Regulations</i> (Quality of Piped Drinking Water) (2008)	US Safe Drinking Water Act (as of March 2013)
Microbiological									
<i>Cryptosporidium</i>	No guideline established; recommend implementing control measures to reduce risk	No guideline established; recommend implementing a multiple barrier approach	No guideline established; recommend at least 3-log removal/inactivation if providing treatment	Not listed	Not listed	Less than one infectious (oo)cyst per 100 L of sample	0 per 10 L	Not listed	Minimum of 2-log removal/inactivation required under IESWTR; additional treatment may be required under LT2ESWTR
<i>Giardia</i>	No guideline established; recommend implementing control measures to reduce risk	No guideline established; recommend implementing a multiple barrier approach	No guideline established; recommend at least 3-log removal/inactivation if providing treatment	Not listed	Not listed	Less than one infectious (oo)cyst per 100 L of sample	0 per 10 L	Not listed	Minimum of 3-log removal/inactivation
<i>Escherichia coli</i>	0 per 100 mL	0 per 100 mL	0 per 100 mL	0 per 100 mL	0 per 100 mL	<1 per 100 mL	0 per 100 mL	0 per 100 mL	See Total Coliforms
Total Coliforms	No guideline established	No guideline established	0 per 100 mL	0 per 100 mL	Not listed	No guideline established	≤10 per 100 mL	Not listed	No more than 5.0% positive in monthly samples (includes fecal coliform and <i>E. coli</i>)

(Table continued on next page.)

Table 2-6 Summary of key international water quality standards and regulations for various organizations and countries (continued)

	World Health Organization	Australia	Canada	Emirate of Abu Dhabi	European Union	New Zealand	Republic of South Africa	Singapore	United States
Microbiological									
Heterotrophic Plate Count	No guideline established	No guideline established	No guideline established	10 per 1 mL at 37°C	Not listed	Not listed	≤1,000 per mL	Not listed	No more than 500 bacterial colonies per mL
Viruses	No guideline established; recommend implementing a control measures to reduce risk	No guideline established; recommend implementing a multiple barrier approach	No guideline established; recommend at least 4-log removal/inactivation if providing treatment	Not listed	Not listed	No guideline established	0 per 10 L	Not listed	Minimum of 4-log removal/inactivation
Disinfectant (mg/L)									
Chlorine (as Cl ₂)	5	5	No guideline established	Not listed	Not listed	5	≤5	5	4
Residual Chlorine (as Cl ₂)	>0.2	>0.5	No guideline established	0.20–0.50	Not listed	Not listed	Not listed	>0.5	>0.2
Disinfection By-products (mg/L)									
Bromate	0.01	0.02	0.01	0.01	0.01	0.01	Not listed	0.01	0.010
Chlorate	0.7	No guideline established	1	0.7	Not listed	0.8	Not listed	0.7	Not regulated
Chlorite	0.7	0.8	1	0.7	Not listed	0.8	Not listed	0.7	1.0
Haloacetic Acids (HAAs)	Not listed	Not listed	0.08	Not listed	Not listed	Not listed	Not listed	Not listed	0.060
Monochloroacetic Acid	0.02	0.15	0.08	Not listed	Not listed	0.02	Not listed	0.02	Included under HAAs
Dichloroacetic Acid	0.05	0.1	0.08	Not listed	Not listed	0.05	Not listed	0.05	Included under HAAs

(Table continued on next page.)

Table 2-6 Summary of key international water quality standards and regulations for various organizations and countries (continued)

	World Health Organization	Australia	Canada	Emirate of Abu Dhabi	European Union	New Zealand	Republic of South Africa	Singapore	United States
Disinfection By-products (mg/L)									
Trichloroacetic Acid	0.2	0.1	0.08	Not listed	Not listed	0.2	Not listed	0.2	Included under HAAs
Monobromoacetic Acid	No guideline established	Not listed	0.08	Not listed	Not listed	Not listed	Not listed	Not listed	Included under HAAs
Dibromoacetic Acid	No guideline established	Not listed	0.08	Not listed	Not listed	Not listed	Not listed	Not listed	Included under HAAs
Total Trihalomethanes (TTHMs)	The sum of the ratio of the concentration of each THM to its respective maximum value must be ≤ 1	0.25	0.1	The sum of the ratio of the concentration of each THM to its respective maximum value must be ≤ 1	0.1	The sum of the ratio of the concentration of each THM to its respective maximum value must be ≤ 1	Not listed	The sum of the ratio of the concentration of each THM to its respective maximum value must be ≤ 1	0.080
Bromodichloromethane	0.06	0.25	0.1	0.06	0.1	0.06	0.1	0.06	Included under TTHMs
Bromoform (Tribromomethane)	0.1	0.25	0.1	0.1	0.1	0.1	0.1	0.1	Included under TTHMs
Chloroform (Trichloromethane)	0.3	0.25	0.1	0.3	0.1	0.4	0.3	0.3	Included under TTHMs
Dibromochloromethane	0.1	0.25	0.1	0.1	0.1	0.15	0.06	0.1	Included under TTHMs

World Health Organization. The WHO, an agency of the United Nations responsible for public health, has developed a comprehensive set of guidelines related to drinking water quality that are intended to assist policymakers around the world to ensure sound drinking water practice. These guidelines have been established for various microbial, chemical, radiological, and aesthetics-based contaminants. The guidelines also contain recommended design and operating criteria for various disinfection processes. For example, a minimum disinfectant residual concentration of 0.5 mg/L and contact time of at least 30 min (at a pH of 8.0) is recommended for effective disinfection via free chlorine. Recommended limits for DBPs formed as a result of chlorination are also included.

Australia. *Australian Drinking Water Guidelines* were developed by the National Health and Medical Research Council in collaboration with the National Resource Management Ministerial Council to provide individual communities and regulatory agencies with a structure for proper treatment and management of drinking water supplies. The guidelines propose limits for microbial, physical, and chemical parameters in drinking water to ensure supplies are safe for human consumption. In addition, the guidelines include recommendations for selecting and monitoring the effectiveness of various treatment processes including disinfection via chlorination and chloramination. These are nonenforceable standards. Each state or territory may choose to implement any or all of the guidelines. Readers are advised to consult the individual state or territory for additional information on drinking water requirements related to disinfection and OSG practices.

Canada. Health Canada's Water Quality and Health Bureau, on behalf of the Federal-Provincial-Territorial Committee on Drinking Water, is the federal organization responsible for developing the *Guidelines for Canadian Drinking Water Quality*. Similar to MCLs established in the United States, these guidelines are designed to protect public health by establishing maximum acceptable concentrations (MACs) for microbiological, physical, chemical, and radiological parameters in drinking water. These are nonenforceable federal standards. In Canada, the establishment of drinking water legislation is the responsibility of the individual provinces and territories. Each province or territory may choose to adopt a portion or all of the MACs established under the *Guidelines to Canadian Drinking Water Quality* or develop entirely new levels. To date, only two of the twelve provinces and territories (Alberta and Nova Scotia) have adopted the *Guidelines to Canadian Drinking Water Quality* in their entirety as enforceable drinking water regulations. In addition, each province/territory is responsible for developing a set of drinking water requirements related to treatment, monitoring, and reporting. While the individual requirements vary across Canada, the overarching nationwide goal is to employ a multibarrier approach to protect public drinking water by reducing or preventing contamination at the source, during treatment, and throughout distribution. At a minimum, this typically includes requirements for disinfection to reduce exposure to microbiological contamination in water sources. Readers are advised to consult the individual province or territory for additional information on drinking water requirements related to disinfection and OSG practices.

Emirate of Abu Dhabi Water Quality Regulations. In 2009, the Regulation and Supervision Bureau for the Water, Wastewater, and Electricity Sector in the Emirate of Abu Dhabi developed the *Water Quality Regulations 2009* to ensure safe drinking water was provided to all customers throughout the Emirate. The regulations established maximum limits for select microbial, inorganic, and organic contaminants in drinking water based on WHO guidelines. The regulations include requirements for monitoring and record-keeping for water suppliers. While the regulations do not directly discuss treatment or disinfection, they do state that "the water does not contain any element, organism, or substance at a concentration or value which would be detrimental to public health" and they do contain limits for various DBPs.

European Union. In 1998, the EU issued Council Directive 98/83/EC, which established minimum standards for water intended for human consumption. Although disinfection is not explicitly required, the directive includes limits for microbiological parameters and DBPs similar to the WHO guidelines. Member states are also encouraged to minimize DBP formation but not at the expense of disinfection. Member states may adopt stricter standards as well as limits for additional parameters. In general, most member states require disinfection of surface water supplies via chlorine, chlorine dioxide, ozone, or UV, but do not require disinfection of groundwater supplies. Only some member states require that a minimum disinfectant residual be maintained at all times in the distribution system. Other states, such as the Netherlands, employ strategies that include the use of only high-quality water supplies and biologically stable distribution system materials, in addition to distribution system operational strategies, such as flushing, to minimize the potential for bacterial regrowth.

New Zealand. *Drinking-Water Standards for New Zealand (2005)* were developed based on WHO guidelines and include recommended maximum values for microbial, radiological, and chemical parameters including DBPs. The guidelines are enforceable and apply to all drinking water providers regardless of source, treatment type, or distribution system size. The guidelines require that some form of disinfection be provided for all sources, with the exception of groundwater. The guidelines also include requirements for monitoring disinfection efficiency at the plant and in the distribution system in addition to reporting and corrective action requirements.

Republic of South Africa. The *South African Water Quality Guidelines* were established in 1996 and provide target water quality ranges (TWQR) for various microbial, physical, chemical, and aesthetic parameters. The guidelines recommend disinfection via chlorination or chloramination and that an adequate residual be maintained to minimize any bacterial regrowth or biological corrosion.

Drinking water must also comply with the requirements set forth in the South African National Standard (SANS) 241 Drinking Water Specification. The specification establishes maximum allowable concentrations for select parameters monitored at the point of delivery. Values were established based on WHO guidelines.

Singapore. Recently, the government of Singapore promulgated the Environmental Public Health Act, which established standards for the quality of drinking water in piped systems. The act also includes information on development of sampling and safety plans. Although the act does not plainly require disinfection, the national water agency in Singapore (PUB) provides disinfection of its water supplies prior to distribution.

Drinking Water Treatment Systems and Chemicals

Many nations have also adopted regulations related to the purity of chemicals and components used in the treatment of drinking water. Most are based on the widely accepted standards developed by NSF International and the American National Standards Institute (ANSI). The primary standards relevant to OSG systems include NSF/ANSI Standard 60: Drinking Water Treatment Chemicals—Health Effects, and NSF/ANSI Standard 61: Drinking Water System Components—Health Effects. Other standards may be applicable to plumbing and electrical components of an OSG system; however, these are not discussed in this chapter. Some jurisdictions, including many states within the United States, require the use of NSF-compliant products in drinking water systems, and as a result, readers are advised to consult the individual state or territory for additional information.

NSF/ANSI Standard 60. NSF/ANSI Standard 60 establishes minimum requirements for chemicals added to water during treatment (e.g., bulk sodium hypochlorite or chlorine gas) to minimize adverse health effects from the chemicals or contaminants found in the chemicals that are likely to be present in the finished water. To receive NSF certification, a

sample of the product must be analyzed for specific contaminants, such as select metals. The analysis of each contaminant must be performed in accordance with the methods and sample preparation procedures specified in NSF/ANSI Standard 60. The concentration of each contaminant (once normalized to reflect the most probable concentration that will be present in the finished drinking water) must not exceed the specific product allowable concentration (SPAC). Hypochlorite chemicals produced by a utility via an OSG system cannot be certified to NSF/ANSI Standard 60 because of uncertainties associated with the preservation and source of the salt used in the generation process. However, NSF International can certify the salt used in the OSG process.

A revised edition of NSF/ANSI Standard 60 was published in 2012. Two key revisions incorporated into this version are as follows:

- The SPAC for bromate, a regulated DBP, was lowered from 0.005 mg/L to 0.003 mg/L. This reduction was included to reduce the likelihood that finished water from utilities using hypochlorite and ozonation, both of which are sources of bromate in drinking water, contains bromate at a concentration near the MCL of 0.010 mg/L. As a result, all hypochlorite chemicals (e.g., bulk-delivered sodium hypochlorite and calcium hypochlorite) shall meet the bromate SPAC of 0.003 mg/L to receive NSF/ANSI Standard 60 certification. Utilities should be aware that certifications provided by a manufacturer at the time of production may not reflect the amount of bromate present after storage and transport to the facility because the hypochlorite degrades over time, forming additional bromate (see chapter 4 for more information on hypochlorite degradation).
- A bromide impurity requirement for sodium chloride used in electrolytic chlorinator applications was added. NSF International recognized that bromide in the salt used to produce the brine solution that feeds the generator could potentially contribute to the formation of bromate in OSG solutions and revised the standard to address this concern. Note that OSG solutions can also contain bromate if bromide is present in the water used to form the brine solution. To achieve and maintain NSF/ANSI Standard 60 certification, manufacturers must test for bromide in the salt and provide a specification that states the maximum bromide concentration in the salt. Sodium chloride products for use in electrolytic generation systems must not contain any more than 54 mg/kg of bromide when the generated sodium hypochlorite product is applied at the maximum use level (MUL) of 10 mg Cl_2 /L. This is based on the assumption that 3.5 lb of salt per 15 gal of water is needed to produce 1 lb of free available chlorine. It should be noted that (1) most OSGs use 2.5–3.0 lb of salt to generate 1 lb of FAC, and (2) higher concentrations of bromide in the salt are allowed when lower feed rates or lower concentrations of product are applied (i.e., between 2 and 10 mg Cl_2 /L) as long as the total concentration of bromate in the finished water does not exceed the SPAC of 0.003 mg/L. This standard revision has not resulted in a special bromide salt specification by manufacturers, in large part because of the variability associated with identifying what the feed rate at a specific site will be and uncertainties in predicting the final bromate concentration in the finished water. Utilities or engineers are encouraged to contact salt and OSG manufacturers with specific dose and flow information during the procurement processes to assess bromate formation from various salt types. See chapter 4 for additional information regarding bromide concentrations in commercially available salt and bromate formation potentials during OSG.

Table 2-7 lists the contaminants of concern and SPACs associated with electrochlorination salt under NSF Standard 60. All certified products are tested annually for the specified contaminants of concern.

Table 2-7 NSF/ANSI Standard 60 specific product allowable concentrations for contaminants contained in salt used during OSG of sodium hypochlorite*

Regulated Contaminant	Specific Product Allowable Concentration
Metals	
Antimony (mg/L)	0.0006
Arsenic (mg/L)	0.001
Barium (mg/L)	0.2
Beryllium (mg/L)	0.0004
Cadmium (mg/L)	0.0005
Chromium (total) (mg/L)	0.01
Copper (mg/L)	0.13
Lead (at tap) (mg/L)	0.0015
Mercury (inorganic) (mg/L)	0.0002
Selenium (mg/L)	0.005
Thallium (mg/L)	0.0002
Radionuclides	
Beta particle and photon activity (mrem/yr)	0.4
Gross alpha particle activity (pCi/L)	1.5
Inorganics	
Bromate (mg/L) [†]	0.003

Source: NSF/ANSI Standard 60 (2012), Table D1 (NSF International 2012).

* Only facilities using ozone are required to monitor for bromate.

† Bromide present in electrochlorination salt forms bromate, a possible contaminant of concern, during aqueous chlorine manufacturing processes. As a result, salts are analyzed for bromide, not bromate.

NSF/ANSI Standard 61. NSF/ANSI Standard 61 establishes minimum requirements to minimize adverse health effects from contaminants that are passed into drinking water from contact with products during treatment, storage, transmission, or distribution. On-site sodium hypochlorite generators can be certified to NSF Standard 61. The OSG unit can be tested for NSF Standard 61 certification with a specific ingredient (i.e., salt type) if specified in the manufacturer's user manual or with a generic product.

POTABLE REUSE

Supply challenges, whether they result from diminishing access to freshwater supplies or extreme weather events, have encouraged many utilities and communities to pursue potable reuse opportunities. Several organizations provide industry guidance, regulatory information, and technical resources related to potable reuse including WaterReuse, the WHO, and the USEPA, which recently published the 2012 *Guidelines for Water Reuse*. These guidelines contain internationally recognized standards for best practices in water reuse and include a discussion of the types of reuse applications, requirements for treatment and monitoring, and criteria for the design and construction of reuse systems.

Indirect potable reuse, where reclaimed water is used to augment a public water system's source of supply (i.e., groundwater recharge), has become increasingly popular in

areas where water scarcity is a concern (e.g., Southern California and West Texas). As of this manual's publication, direct potable reuse, where reclaimed water is introduced directly into a public water system's treatment facility or distribution system, has only been used at a few installations in the United States (e.g., Big Spring, Texas), but interest in this approach is growing quickly, particularly where indirect reuse through groundwater recharge is unfeasible. In the United States, the degree of treatment required for water reuse is dependent on its intended use and state-specific regulations.

Disinfection is a key component of any reuse strategy to ensure the protection of public health and can be achieved via several methods including, but not limited to, chlorination, UV, and ozone. The efficacy of chlorination is based on a *CT* approach similar to drinking water regulations. As such, the design and operation of OSG systems for potable reuse applications are therefore driven by the required chlorine dosages needed to meet the required *CT*, but should also consider all applicable, and often conflicting, drinking water treatment regulations. The specific method used to calculate *CT* and required *CT* value are determined by the state or local governing body and vary based on application.

SELECTING DISINFECTANTS

Disinfection has been an integral component of water treatment for over a century. During that same time the process and related operation requirements have required an increasingly complex need to balance competing priorities relative to selecting the most appropriate disinfection technology. The decision to implement and design an OSG system should be evaluated through the use of a holistic evaluation, which considers all environmental, social, and economic factors to aid in the decision-making process. These factors may include:

- Regulatory requirements (e.g., water quality, permitting)
- Public health impacts (e.g., emissions from power demands/carbon footprint)
- Worker and community impacts (e.g., potential releases of hazardous chemicals)
- Vulnerability/security (e.g., potential thefts of chemicals or attacks on drinking water treatment systems)
- Supply availability/reliability (e.g., ability to obtain the necessary components and consumables)
- Operations and maintenance costs (e.g., energy costs, chemical costs)
- Operational complexity

Multiple resources have been developed to support utilities and communities in making such decisions, such as AWWA's *Selecting Disinfectants in a Security-Conscious Environment* (2009). This reference provides a framework for assessing safety and security risks associated with various disinfectants. This guide, published in 2009, describes a step-by-step process to evaluate disinfection options that meets the unique needs of each system. This resource builds on existing water sector engineering practices, manuals of practice, costing tools, and public communication techniques to

- Address federal and local statutory and regulatory disinfection objectives
- Reflect local circumstances
- Compare disinfection options consistently
- Consider operational, process, and supply-chain reliability as well as environmental, operator, and community safety considerations

- Provide transparency in the decision-making process
- Incorporate appropriate risk communication within the decision-making process and the community

The guide details a five-step process for selecting disinfectants:

1. **Assess Current Situation.** Identify existing and future disinfection requirements and regulations and the ability of the existing disinfection process to meet them. Review past water quality and security assessments and recommendations and determine which recommendations have been or are planned to be implemented. Use the information gathered to establish system disinfection goals and objectives.
2. **Identify Options.** Use a screening process to determine which disinfection options are feasible to carry forward for detailed evaluation.
3. **Evaluate Options.** Evaluate each disinfection option identified as feasible in Step 2 by defining and then comparing and contrasting the attributes, costs, advantages, and disadvantages of each option. This evaluation can reflect on design considerations such as reducing the quantity of hazardous substances stored on-site, the reliability and efficiency of potential disinfectant system options, and simplifying treatment processes where possible.
4. **Select Option.** Use the results of the evaluation along with decision-making tools to select the preferred disinfection method.
5. **Implement Selected Option.** Design, install, construct, and start up the facilities and equipment required

Several additional references or tools are currently available to help utilities assess the OSG systems and compare OSG with other disinfectants, and include:

- *Hypochlorite Assessment Tool.* In light of potential future water quality regulations, it is essential that utility operators and managers understand that contaminants such as chlorite, chlorate, perchlorate, and bromate can be formed in hypochlorite solutions, and thus to support utility risk management a predictive model has been developed by the AWWA. This tool is specifically designed for modeling the degradation of bulk hypochlorite and not OSG hypochlorite, but is still a key resource in supporting utility risk management when considering various disinfection methods. The hypochlorite assessment tool is now available to AWWA members at <http://www.awwa.org/hypochlorite>.
- *Life-Cycle Assessment Tools.* Commercially available software, such as GaBi, can help assess environmental impacts of alternative disinfectants. Impacts may include global warming potential or human toxicity potential.
- *USEPA's Emergency/Incident Planning, Response, and Recovery.* Various resources related to water utility preparedness, response, and recovery are available at <http://water.epa.gov/infrastructure/watersecurity/emplan/index.cfm>.

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ENDNOTE

1. It should be noted that there is a difference between THM (trihalomethanes), TTHM (total trihalomethanes), HAA (haloacetic acids), and HAA5 (a term referring to the five haloacetic acids regulated in the United States). THM and HAA are general terms to describe two different classes of organic disinfection by-products. HAA5 and TTHM are used in US regulation, specifically. Haloacetic acids (five; HAA5) mean the sum of the concentrations in milligrams per liter of the haloacetic acid compounds (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid), rounded to two significant figures after addition. Total trihalomethanes (TTHM) means the sum of the concentration in milligrams per liter of the trihalomethane compounds (trichloromethane [chloroform], dibromochloromethane, bromodichloromethane, and tribromomethane [bromoform]), rounded to two significant figures.

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Chapter **3**

Electrolytic Cell Reactions and Principles of Operation

Andrew K. Boal, Rudolf Matousek, and Wesley L. Bradford

At the heart of every on-site generation (OSG) system is an electrolytic cell that accomplishes the electrochemical production of chlorine. Inside the electrolytic cell, chloride ions from the sodium chloride brine are oxidized using a current passed through the cell. Through this electro-oxidation process, the sodium chloride (NaCl) brine that is used as a feedstock to the on-site generator is converted into a disinfectant solution containing aqueous chlorine. In the equation below, aqueous chlorine is shown as sodium hypochlorite.



While the basis of OSG production of aqueous chlorine is relatively simple, the electrolytic process can be influenced by system design in addition to the brine chemistry parameters that affect both the chemical form of the oxidant-containing solution as well as the operational functionality of the OSG system itself. Sections of this chapter will provide additional insight into the chemistry and engineering aspects of cell operations and will cover the following topics:

- **Brine Electrolysis Chemistry** provides a description of the chemical transformations that occur within the electrolytic cell of an OSG system.
- **Types of Electrolysis Systems** includes discussion of the various types of electrolysis systems and the different chemical products that can be produced through sodium chloride brine electrolysis.

- **Electrolytic Cell Materials of Construction** provides information on the materials typically used to build electrolytic cells.
- **Feedstock Quality Impacts on Cell Performance** details the impact common impurities in water and salt have on the OSG system and how to prevent problems from arising.
- **Cell Maintenance** describes typical cell maintenance procedures.
- **Hydrogen Handling Practices** discusses the by-product of hydrogen gas that is produced in all OSG systems and how the hydrogen production is safely handled.

The complete OSG system configurations are not shown in this chapter. Please see chapters 5 and 6 for more specific information on the design, installation, and operation of the commercially available OSG system configurations.

BRINE ELECTROLYSIS CHEMISTRY

Electrolytic cells are classified into two groups: *separated* and *unseparated*. Unseparated cells consist of two or more electrodes that are immersed in a brine stream based on sodium chloride (NaCl) that is usually pumped through the cell (Figure 3-1). Typically, the electrodes in the electrolytic cell have a titanium core with a precious metal (Group VIII) oxide coating on the anode and are known as *dimensionally stable anodes* (DSAs). DSAs are discussed in greater detail later in this chapter. In the electrolytic cell, there is both a primary anode and a primary cathode: these are the electrodes that are electrically connected to the power supply that drives electrolysis in the cell.

Basic Reactions

Unseparated cells. Unseparated cells are also sometimes referred to as *undivided* cells. The overall chemical reaction that occurs within an unseparated electrolytic cell is the production of sodium hypochlorite (NaOCl) and hydrogen (H₂) gas from a sodium chloride (NaCl) solution in water:



At the anode surface, where oxidation occurs, chloride ions from the salt are oxidized to initially produce dissolved chlorine gas (Cl₂):



Once produced, the chlorine gas rapidly dissolves in and reacts with water (hydrolyzes) to produce both hydrochloric acid (HCl) and hypochlorous acid (HOCl):



As a result of these reactions, both chemical and electrolytic, the pH of the solution near the anode surface tends to be acidic due to the production of protons.

Electrochemical reactions taking place at the cathode surface use water as an electron acceptor, which is reduced to produce both hydrogen gas (H₂) and hydroxide ions (OH⁻):



Because of the formation of hydroxide ions during this process, the solution near the cathode typically is caustic (pH greater than 12). The hydrogen gas that is evolved at the

cathode surface must be safely removed from both the OSG system and the produced oxidant solution, a topic that is covered in a later portion of this chapter. In the *undivided* cell of most OSG systems, in which the solutions at the anode and cathode are free to mix, the hydroxide ions that are produced at the cathode will combine with the acids produced at the anode, resulting in the formation of hypochlorite.



By rewriting these equations for both charge and molar balance, the overall chemical transformation described in Eq 3-1 is realized.

An electrolytic cell containing only a primary anode and cathode is known as a *monopolar cell*. Most cells contain *intermediate plates* placed between the primary electrodes that also engage in electrolysis; this geometry is known as a *bipolar cell*. The intermediate plates have an anode side and a cathode side. Conceptually, in a bipolar cell, the voltage field between the primary electrodes is divided by equally spaced intermediate plates that are electrically connected only through the electrolyte. Each pair of intermediate plates forms a *compartment*, and the voltage drop between each intermediate plate drives electrolysis inside each compartment. The logic behind the design of a bipolar cell is compelling: the same electrons (or current) passing through the complete cell (the assembly of all compartments) are used by each compartment to generate the desired product—in this case, aqueous chlorine. The primary advantages of the bipolar cell are high production of chlorine within a small total cell volume and reduced current compared with a monopolar cell with comparable chlorine production. Bipolar cells also use less expensive power supplies compared with monopolar cells with similar production capacities. Additionally, the energy losses at hard electrical connections of the cell with the power supply are minimized because of the decreased number of these connections in a bipolar cell, providing further advantage.

Separated cells. A separated cell is an electrolytic cell in which the anode and cathode sides of the cell are separated by a membrane that allows for current to flow from anode to cathode but does not allow the solutions contained within the anode and cathode compartments to mix (Figure 3-2). The electrochemical reactions that occur in a separated cell are the same as those that occur in an unseparated cell. At the anode surface, chloride ions are oxidized to produce Cl_2 according to Eq 3-2, while water is reduced at the cathode surface to produce hydrogen and hydroxide ions according to Eq 3-4. Because the solutions formed in either compartment of a separated cell cannot mix due to the membrane, separated cells will have two product outputs instead of the one output typical of an unseparated cell. Depending on the specifics of an OSG using a divided cell, the anode product can be either a low-pH HOCl solution or gaseous Cl_2 , with Cl_2 gas being the most common product of this type of cell. Gaseous Cl_2 will evolve from the anode product as the pH of the anolyte output decreases. All separated electrolytic cells produce high-pH NaOH solutions, along with hydrogen gas, from the cathode compartment.

Chlorine speciation and the formation of chlorine gas. Speciation of aqueous chlorine produced by OSGs into the HOCl and ClO^- states depends on the pH of the chlorine solution (Figure 3-3). Since both protons (in the form of HCl and HOCl) and hydroxide ions are produced during the electrolysis of NaCl brines, it might be expected that the pH of the chlorine solution produced by an unseparated electrolytic cell would be unchanged from the pH of the brine used as a feed source. However, the pH of the chlorine solutions produced through electrolysis of sodium chloride brines is typically slightly basic with a pH between 9 and 10, which results in hypochlorite being the primary chlorine species present in the produced solution. The origin of the elevated pH found in most electrochemically produced aqueous chlorine solutions can result from different mechanisms.

Small amounts of chlorine loss as chlorine gas during generation can lead to an imbalance of the amount of protons and hydroxide ions produced. Alternatively, differences in the efficiencies in the anode and cathode reactions can lead to elevated hydroxide ion production since there are more competing reactions on the anode compared with the cathode. The actual pH of an electrolytically generated aqueous chlorine solution from an unseparated electrolytic cell will depend on the pH and alkalinity of the water used to feed the OSG system. In a separated system, as the pH approaches 4, chlorine gas begins to evolve from solution as shown by the solid gray line in Figure 3-3. This property can be advantageous if the system is designed to produce and safely capture chlorine gas.

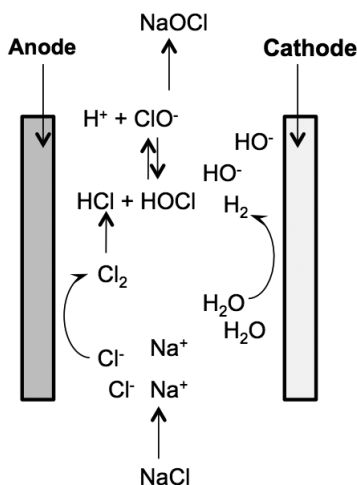


Figure 3-1 Drawing of primary anode and cathode of a monopolar unseparated cell and the basic reactions that occur on these electrode surfaces

Source: Courtesy of MIOX Corporation

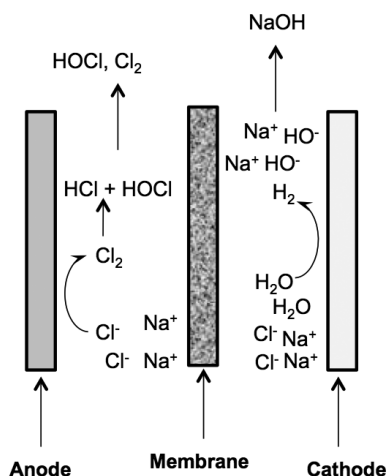


Figure 3-2 Drawing showing a separated cell and the electrochemical transformations that occur in the anode and cathode compartments of the cell

Source: Courtesy of MIOX Corporation

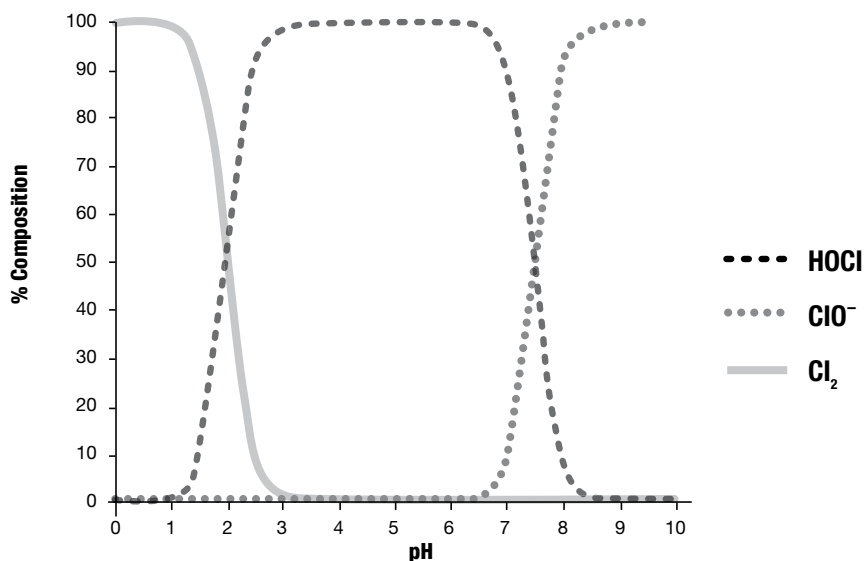


Figure 3-3 Relationship between solution pH and chlorine speciation

Source: Courtesy of MIOX Corporation

Parasitic Reactions

Any reaction within the electrolytic cell that results in an undesired product, i.e., some compound other than chlorine or another oxidant that is usable for water treatment, or that destroys a desired product, and that uses electrons in the process is called a *parasitic reaction*. In electrolysis where the products remain in solution, parasitic reactions potentially limit the efficiency of the OSG system. Three major parasitic reactions occur during the electrolysis of sodium chloride brines: anodic production of oxygen gas, anodic oxidation of hypochlorite ions, and cathodic reduction of hypochlorite ions.

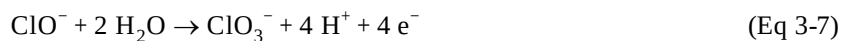
Anodic production of oxygen gas is an undesirable but unavoidable process that occurs through the oxidation of water (H_2O). Typically, this reaction consumes about 5% of the electrons passed in the cell:



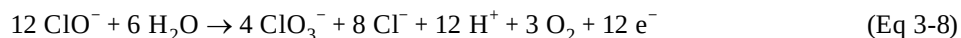
At the cathode the primary known parasitic reaction is:



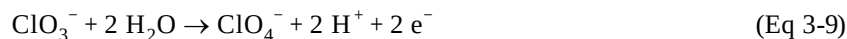
The cathodic reduction of ClO^- is the primary limitation on the ability of the cell to produce the desired product. Additional parasitic anodic reactions can occur that consume the hypochlorite produced through the oxidation of chloride. These reactions are relatively rare and are covered in more detail in chapter 4. Anodic oxidation of hypochlorite results in the production of chlorate ions (ClO_3^-):



This reaction rarely goes to completion and is also reported (Robertson et al. 1983) to have stoichiometry as follows:



The chlorate ions produced in these reactions can be further oxidized to produce perchlorate ions (ClO_4^-):



As the concentration of the hypochlorite anion (OCl^-) rises in the electrolyzed brine, formation of chlorate (ClO_3^-) increases and formation of perchlorate (ClO_4^-) can also occur. The exact production mechanism of both chlorate and perchlorate during brine electrolysis is not clear at this time (Snyder et al. 2009). Chlorate concentrations are presently unregulated in potable water, although interest in regulation is growing (see chapters 2 and 4). Some states have adopted provisional limits, guidelines, or health goals for perchlorate in drinking water, but a final rule from the USEPA is not expected until 2016 (see chapter 2). A national survey of perchlorate occurrence from several different types of OSG systems showed that the perchlorate concentrations were below a level of concern (see chapter 4 for more detail).

Other Potential Oxidants

Aside from the production of chlorine and hydrogen described above, a number of electrochemical transformations can occur on the electrode surfaces leading to the limited production of oxidants and chemical products beyond hydrogen and chlorine. Other potential oxidant products of NaCl brine electrolysis include chlorine dioxide (ClO_2), ozone (O_3), and hydrogen peroxide (H_2O_2). Measured potentials (relative to the normal hydrogen electrode; NHE) at the anode of some electrolytic cells are sufficient to provide the energy requirements for the formation of these products. However, oxidants other than free available chlorine (FAC) are difficult to detect because of the large Cl_2 matrix that can interfere with most analytical techniques. Neither ClO_2 nor O_3 has been detected in electrolyzed NaCl brines (Gordon et al. 2002). Both O_3 and H_2O_2 have been detected in nonchloride brines electrolyzed using similar electrodes and under similar operating conditions to those in OSGs (Jeong et al. 2006), suggesting that both may be produced during electrolysis of NaCl brines but either are short-lived, degrade to other oxidant forms, or are undetectable against the high-chlorine concentrations of on-site generated solutions.

In addition to those already discussed, the regulated disinfection by-product bromate (BrO_3^-) can potentially be produced during NaCl electrolysis. Bromate has a USEPA MCL of 10 $\mu\text{g/L}$ in potable water but is currently only a regulatory concern for utilities using ozone (see chapter 2). The main determining factor in the concentration of bromate produced is the concentration of bromide (Br^-) in the brine that is feeding the cell, as these bromide ions can be converted into bromate during electrolysis. Bromide in the brine is present from sodium bromide (NaBr) impurities in the salt used to prepare the brine solutions but can also be present in some sources of water used to prepare the brine. A more in-depth discussion of chlorate, perchlorate, and bromate is presented in chapter 4.

Measures of Cell and System Performance

The electrolysis process and energy requirements for production of FAC from NaCl quantitatively follow well-established principles of electrochemistry and physics. Some terms used in this discussion are defined as follows:

- Coulomb (C): a quantity of electric charge or electrons.
- Ampere (A): rate of charge flow (coulombs/second); 1 ampere = 6.238×10^{18} electrons/second. The ampere is a unit of current, which is sometimes expressed as “I.”
- Faraday constant (F): 96,493 coulombs/equivalent of electrolysis product.

- Faradaic efficiency (FE): measure of the fraction of total coulombs of electrons passed through the brine and used to make desired product.
- Power (watts, W): rate of energy flow in joules/second (watt).
- Energy (joules, J): electrical work; 1 joule = 1 watt•second.

The objective of electrolysis in an OSG cell is to convert as much of the Cl^- in the brine as possible to FAC while minimizing both the use of energy and salt to yield an efficient process. Several efficiency parameters can be calculated by making relatively simple measurements of the operational parameters of the OSG system.

Faradaic efficiency. *Faradaic efficiency* (FE) is a way to measure how efficiently the electrons passed through the brine were used in the electrolytic process. Coulombs passed is determined by measuring the current (amperes, I) passed through the cell in a measured time (seconds). The mass of FAC is then determined by measuring the volume of solution produced during that time, measuring the FAC concentration in the solution, and calculating the mass of FAC produced. The FE is the ratio of the mass of FAC actually produced to the coulomb-equivalent mass, and is calculated as:

$$\text{FE} = \text{FAC mass (g)} / [(\text{coulombs passed} / 96,493 \text{ coulombs/eq}) \times 35.453 \text{ g/eq of FAC}] \quad (\text{Eq 3-10})$$

The FE approaches unity only in the first few seconds of electrolysis. As the desired products accumulate in the solution, the FE declines due to parasitic reactions as described above, the most important of which is the reduction of ClO^- at the cathode. Actual FE of an OSG system using an unseparated electrolytic cell is highly dependent on operating conditions and system design and is typically in the range of 0.6 to 0.9.

Salt conversion efficiency. The *salt conversion efficiency* (SCE) is the mass of salt (NaCl) required to produce a unit mass of measured FAC. The SCE together with the FAC dosing requirements are used to estimate the rate of salt usage and the amount of salt that must be purchased by the OSG system user. SCE is determined by measuring the mass of NaCl consumed by an OSG system over a period of time as well as the mass of FAC produced by that cell over the same timeframe and is calculated as:

$$\text{SCE} = \text{NaCl mass} / \text{FAC mass} \quad (\text{Eq 3-11})$$

SCE values are also used to calculate the NaCl, and therefore total dissolved solids (TDS) increase in the treated water by injection of the FAC solution, and can be calculated by:

$$\text{NaCl added (mg/L)} = \text{FAC dose (mg/L)} \times \text{SCE} \quad (\text{Eq 3-12})$$

OSG system manufacturers typically measure the SCE of each of their systems before the system is shipped to the client, to ensure operation within specifications, and publish the SCE for each model of system. SCE values in the range of 3 are typical for most OSG systems using an unseparated electrolytic cell.

Energy conversion efficiency. *Energy conversion efficiency* (ECE) is the amount of energy ($\text{kW}\cdot\text{h}$) required to produce a unit mass of FAC. The measurement is normally made on the electrolytic cell only; the energy requirements of a full system are larger, but the electrolytic cell typically uses >90% of the total energy consumption of an OSG system. The energy used by a cell is calculated by measuring the voltage (V) and current (I) across the cell over a fixed time (t) and calculating the energy used (after suitable conversions of units to yield $\text{kW}\cdot\text{h}$) as:

$$\text{energy} = V \times I \times t \quad (\text{Eq 3-13})$$