

Water and Wastewater Disinfection Using On-Site Generated Hypochlorite

Leonard W. Casson, Ph.D., P.E., DEE
Professor
Department of Civil and Environmental Engineering
University of Pittsburgh

Introduction

Chlorine is the most common disinfectant used in water and wastewater treatment systems in the United States, although the use of ultraviolet light and ozone are becoming more common. Historically, gaseous chlorine was the most prevalent form of chlorination in the United States; however, the use of an aqueous solution of sodium hypochlorite is increasing in water and wastewater treatment applications due to safety concerns associated with the use, storage and transportation of chlorine gas. The implementation of the Risk Management Plan (RMP) by the USEPA for the storage of hazardous chemicals (June 1999) and the re-registration of chlorine gas by the USEPA Office of Pesticide Programs as a pesticide (Fall 2001) also has accelerated the use of sodium hypochlorite in the water and wastewater treatment industry. It should be noted that while the disinfection of drinking water using either ultraviolet light or ozone can be viable alternatives to gaseous chlorine, additional disinfection will be required to provide the USEPA mandated disinfectant residual in drinking water distribution systems.

Sodium hypochlorite solution is typically applied at concentrations up to 15% by weight chlorine. Problems associated with the use of sodium hypochlorite may include availability of sodium hypochlorite in some areas, high transportation costs, increasing production costs, a lack of long-term stability and the final pH of the chlorinated water. The rate at which sodium hypochlorite concentration decays during storage is a function of the hypochlorite concentration and storage temperature. On-site electrochemical generation of low strength sodium hypochlorite (0.8% chlorine concentration) may mitigate some of the problems associated with sodium hypochlorite storage and transport. However, storing large volumes of low-concentration sodium hypochlorite and adding these low-concentrations of sodium hypochlorite has many disadvantages that may include high salt usage, large storage requirements and increased salt concentrations in the finished water. In light of these disadvantages, on-site electrochemical generation of atmospheric pressure chlorine gas and sodium hydroxide and /or high strength sodium hypochlorite (12 % chlorine) is a viable solution to the problems discussed above.

It is the goal of this document to provide information concerning the on-site generation of high strength sodium hypochlorite via the absorption of on-site electrochemically generated chlorine gas and caustic. The on-site generated high strength sodium hypochlorite discussed in this paper is an ETC trademarked product produced by the Klorigen™ process and will be referred to using the name Ultra Pure Hypochlorite™. This paper will discuss the following:

- Basic principles of disinfection;
- Reaction chemistry of elemental chlorine and sodium hypochlorite in water;
- The basics of electrochemical generation of atmospheric pressure chlorine gas and sodium hydroxide and /or Ultra Pure Hypochlorite™;
- Recent and pending regulations affecting disinfectant selection;
- Typical hazards associated with common disinfectants used in water and wastewater treatment processes; and
- Differences between electrochemical generation of Ultra Pure Hypochlorite™, on-site generation of 0.8 percent sodium hypochlorite, and commercial bulk sodium hypochlorite.

This paper also will discuss the role of disinfectant choice in the water or wastewater vulnerability assessment process.

Basic Principles of Disinfection

Disinfection in water and wastewater treatment systems may be defined as the destruction of pathogens (e.g., bacteria, viruses, protozoan or amoebic cysts) to provide public health protection.

Design considerations and operational factors for disinfectant systems are as follows: the type of microorganisms to be inactivated; the concentration of the microorganisms in the water; the water quality (i.e., suspended solids concentration, particle size distribution, chemical composition, pH, and temperature) in which disinfection will occur; the variability of the water quality; the type of disinfectant chosen for application; the dose or concentration of the disinfectant applied; and the contact time of the disinfectant with the water.

Generally, the adequacy of disinfection in water and wastewater treatment systems is determined by the product “CT” where, “C” is the final residual concentration of the disinfectant in the water and “T” is the contact time which is exceeded by 90 percent of the fluid (Haas, 1999). “CT” values necessary to achieve varying levels of disinfection in water treatment systems have been published in USEPA guidance documents for chlorine and chlorine compounds, ozone, chlorine dioxide and chloramines (Malcolm Pirnie and HDR Engineering, 1991). It should be noted that CT values published in the above referenced document also include an acceptable margin of safety for design purposes.

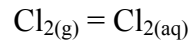
Typical Disinfection Alternatives

Typical disinfectant alternatives for use in water and wastewater applications include chlorine and chlorine compounds (chlorine gas, chloramines, sodium hypochlorite, calcium hypochlorite and chlorine dioxide), ozone and Ultra Violet radiation. Sodium hypochlorite application methods can be divided into the following categories: 1) bulk supplied commercial grade sodium hypochlorite, 2) on-site generated low strength sodium hypochlorite, 3) on-site generation of ultra pure (high strength) hypochlorite. In addition to these application methods, atmospheric pressure chlorine gas can also be generated on-site and used as an on-demand system (no storage of gas required) for water or wastewater treatment applications.

Basic Chemistry of Elemental Chlorine and Sodium Hypochlorite in Water

Chlorine is used in water and wastewater treatment processes as both a disinfectant and an oxidizing agent. Chlorine may be applied as gaseous chlorine that is dissolved in water, aqueous sodium hypochlorite or solid calcium hypochlorite. All three forms of chlorine application are chemically equivalent due to the rapid equilibrium between HOCl (hypochlorous acid) and OCl⁻, (hypochlorite ion) when they are injected into water.

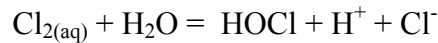
Elemental chlorine (Cl₂) is a dense gas that condenses to a liquid when subjected to pressures in excess of its vapor pressure. As a result, commercial shipments of chlorine are made in pressurized tanks to reduce shipment volume. When the pressurized chlorine liquid is dispensed, the pressure is reduced to vaporize the compressed liquid chlorine into a gas for application. The dissolution of gaseous chlorine in water forms aqueous chlorine. This reaction may be expressed by Henry's law and the corresponding Henry's Law Constant (H).



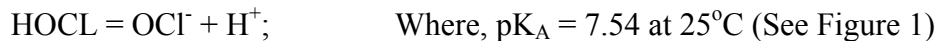
$$H \text{ (mol/L-atm)} = [\text{Cl}_{2(\text{aq})}]/P_{\text{Cl}_2}$$

where, H is Henry's Law Constant, [Cl₂(aq)] is the molar concentration of aqueous chlorine, and P_{Cl₂} is the partial pressure of chlorine in the gas phase in equilibrium with the liquid (measured in atmospheres).

When aqueous chlorine is combined with water it rapidly forms hypochlorous acid, protons, and chloride ions according to the following equation.



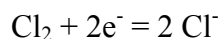
Hypochlorous (HOCl) acid is a relatively weak monoprotic acid that may dissociate according to the following equation.



Free available chlorine is a term used to refer to the concentrations of molecular chlorine (Cl₂), hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻) in water expressed as available chlorine. The term available chlorine is used to express the relative amount of chlorine present in chlorine gas, or hypochlorite salts. Available chlorine is expressed by determining the electrochemical equivalent amount of Cl₂ to the compound present in water (Haas, 1999).

The distribution of free chlorine in water between hypochlorous acid and hypochlorite ion as a function of pH is shown in Figure 1 below. Note that at very high pH values, almost all the free chlorine exists as hypochlorite ion. At very low pH values, almost all the free chlorine exists as hypochlorous acid. Equal quantities of hypochlorous acid and hypochlorite ion exist at the pK_A value of 7.54.

Based upon the equation shown below, one mole of elemental chlorine is capable of reacting with two electrons to form chloride:



Since one mole of hypochlorite (OCl⁻) also reacts with two electrons to form chloride (as shown below), one mole of hypochlorite is electrochemically equivalent to one mole of

elemental chlorine. Thus, one mole of elemental chlorine and one mole of hypochlorite both contain approximately 71 g of available chlorine (Haas, 1999).

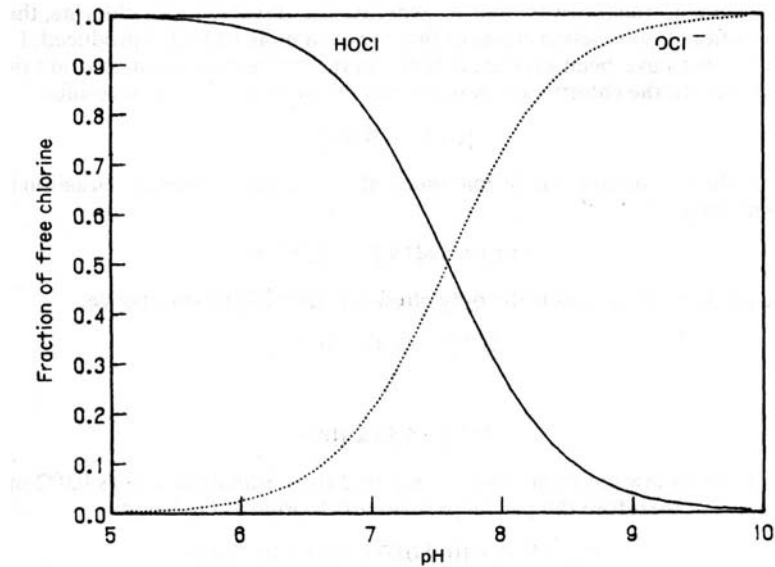


Figure 1 Effect of pH on the fraction of hypochlorous acid and hypochlorite ion at 20°C (Haas, 1999).

Chlorine Demand Reactions

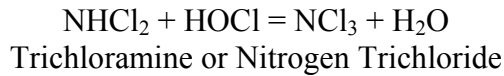
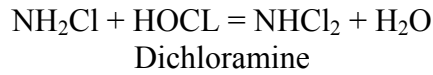
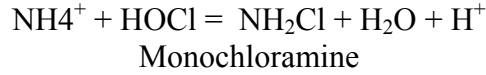
The amount of chlorine added to water for disinfection purposes is termed the dose. The dose is usually reported in pounds of chemical applied per day for water and wastewater applications. The dose may also be reported in terms of mass per unit volume for a given application. Some fraction of the applied disinfectant will react with substances (both organic and inorganic) in the water causing a reduction in the amount of disinfectant remaining in the water (this disinfectant reduction is termed the “demand”). The amount of disinfectant remaining in the system after a set time period is called the residual and usually reported in mg/L or ppm. The following equation expresses the relationship discussed above:

$$\text{Dose} = \text{Demand} + \text{Residual}$$

Chlorine demand reactions will be divided into two sections for purposes of discussion. First, chlorine reactions with ammonia and their significance to disinfection practice will be presented and discussed. Next, chlorine reactions with organic and inorganic matter will be presented and discussed.

Demand Reactions with Ammonia - When free chlorine is added to water in the

presence of ammonia, it reacts in a stepwise manner to form monochloramine (NH₂Cl); dichloramine (NHCl₂); and trichloramine (NCl₃), also known as nitrogen trichloride (Davis and Cornwell, 1998).



The sum of these three compounds in water is defined as the “combined chlorine residual” in water. The distribution of the species among the three chloramine species is a function of time, temperature, pH and the initial Cl₂:NH₄-N ratio.

Figure 2 is a schematic of a breakpoint chlorination curve. This schematic may be divided into three zones. Zone 1 is where all chlorine added to the water results in the formation of chloramines. This zone occurs at chlorine doses below a Cl₂:NH₄-N ratio of 5. Within this zone there is no change in the nitrogen concentration in the water. Chloramines are oxidized in Zone 2. A loss of nitrogen in the water also occurs in Zone 2. The breakpoint occurs at a Cl₂:NH₄-N ratio of 7.6 where all of the chloramines have been oxidized and Zone 3 begins. In Zone 3, all chlorine added to the water exists as free chlorine. The breakpoint indicates the amount of chlorine that must be added to a water containing ammonia before a stable free chlorine residual can be obtained.

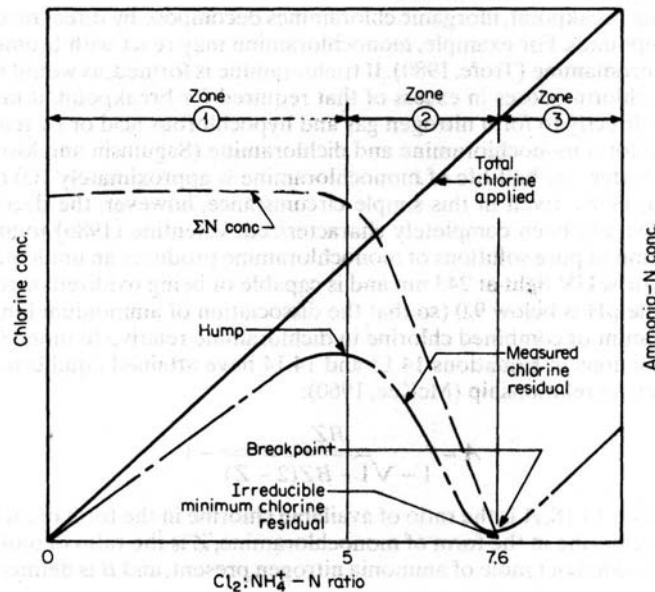


Figure 2 Idealized schematic of a breakpoint chlorination curve (White, G.C., 1978).

Demand Reactions with Organic and Inorganic Matter - Chlorine can react with both inorganic and organic material to form a variety of substances. Morris (1967) determined that organic amines react with free chlorine to form organic monochloramines. Murphy (1975) indicated that phenols, amines, aldehydes, ketones, and pyrrole groups are susceptible to chlorination. Granstrom and Lee (1957) observed that phenol could be chlorinated by free chlorine to form chlorophenols. More recently, Krasner (1986) determined that free chlorine was capable of removing tastes and odors associated with organic sulfur compounds. Wojtowicz (1979) summarized the reaction rates for free chlorine residuals and inorganic compounds

Disinfection Kinetics

Microorganism inactivation during disinfection is based upon the initial work of Chick (1908) who developed the relationship between microbial inactivation by chemical disinfectants and chemical reactions. Watson (1908) proposed an equation that related the rate constant of inactivation (k) to the disinfectant concentration (C). Gyurek and Finch (1998) presented a detailed overview of the principles of disinfection modeling in 1998.

On-Site Electrochemical Generation of Atmospheric Pressure Chlorine Gas and Sodium Hydroxide and /or Ultra Pure HypochloriteTM

Electrochemical generation of ultra pure hypochlorite is a multistep process using a chlor-alkali separated cell process. This process is widely used by major chemical companies (e.g. Dow Corporation, Occidental Chemical Corporation and PPG) for the production of commercial quantities of chlorine and sodium hydroxide. These commercial quantities of chlorine and sodium hydroxide are precursors of commercial grade sodium hypochlorite (bleach). More recently, Electrolytic Technologies Corporation has applied this technology to the water and wastewater treatment industry using the KlorigenTM process to generate atmospheric pressure chlorine gas, sodium hydroxide (caustic) and/or Ultra Pure HypochloriteTM on a much smaller scale than by the chemical companies listed above.

Figure 3 is a schematic of a typical separated electrolytic cell used for the generation of chlorine gas at atmospheric pressure and 15% sodium hydroxide (caustic). The chlorine gas can be used directly for disinfection. The caustic can be used in a treatment facility for pH adjustment or softening applications. Alternatively, the chlorine gas and caustic can be combined, using the Powell Process, into ultra-pure sodium hypochlorite (up to 12% concentration). The process description for the generation of chlorine gas at atmospheric pressure and caustic is as follows:

- Salt is combined with pre-conditioned (i.e. low hardness) water to form saturated brine;
- The brine is then purified prior to entering the electrolytic cell;
- AC power is rectified to DC and supplied to the electrolytic cell;
- Chlorine gas and sodium hydroxide are primary products of the electrolytic process;
- Brine, saturated with chlorine gas is discharged from the cell to a separation vessel from which chlorine gas is extracted under vacuum;

- Sodium hydroxide (“caustic soda”) is discharged from the cell using a controlled flow of de-mineralized dilution water to produce a final concentration of 15 percent;
- The chlorine gas and sodium hydroxide can be used independently or combined in-situ to form high strength (12%) sodium hypochlorite (Ultra-Pure Hypochlorite™); and
- Chlorine production is proportional to the power supplied.

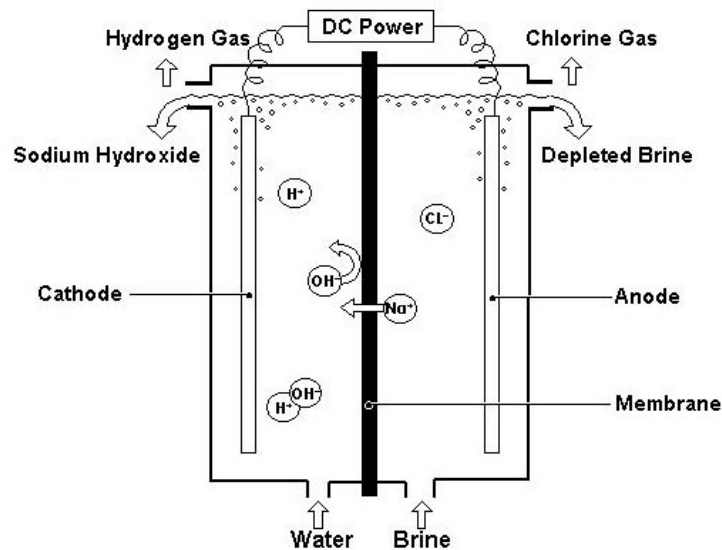


Figure 3: Typical Separated Electrolytic Cell Schematic.

Although the separated electrolytic cell shown in Figure 3 is the key component for the generation of chlorine gas at atmospheric pressure and caustic, other ancillary components are required to operate the cell. Figure 4 is a simple schematic of the key components of the on-site chlorine and caustic generation system.

Recent and Pending Regulations Affecting Disinfectant Selection

The implementation of the Clean Air Act (CAA) Risk Management Plan (RMP) for the storage of hazardous chemicals by the USEPA (June 1999) and the re-registration of chlorine gas by USEPA Office of Pesticide Programs as a pesticide (Spring 2001) has accelerated the use of liquid sodium hypochlorite in the water and wastewater treatment industry. Below is a brief discussion of each of these regulations. Note that sodium hypochlorite (on-site generation, storage, application, or training) is not affected by these recent or pending regulations.

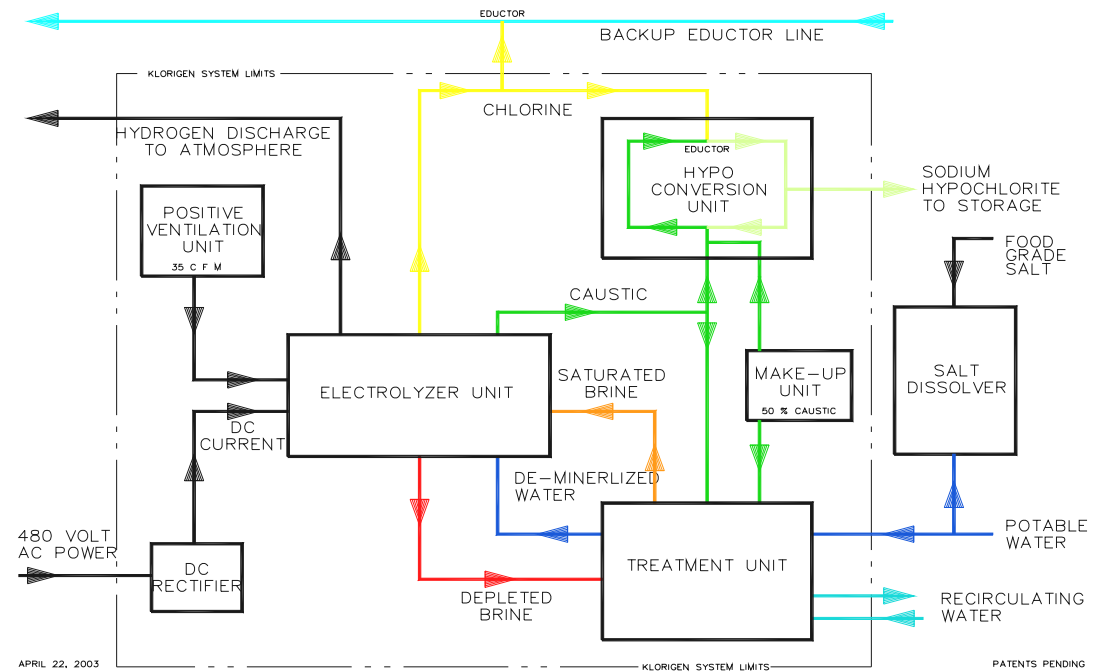


Figure 4: Simple Schematic of the Chlorine and Caustic Generation System

A portion of the schematic shown in Figure 4 is also shown as a photograph in Figure 5.

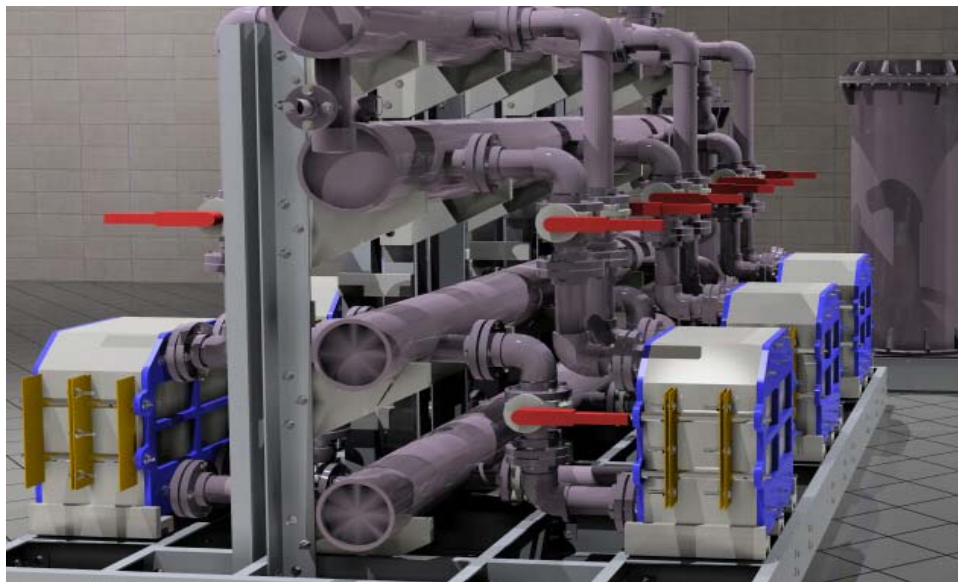


Figure 5: On-Site Chlorine and Caustic Generation System

CAA Risk Management Plan

Congress passed the Clean Air Act Amendments of 1990. One section of these regulations required the USEPA to publish regulations and guidance for chemical accident prevention at facilities using extremely hazardous substances. The Risk Management Program Rule (RMP Rule) was written to implement Section 112(r) of the CAA amendments. The RMP Rule was written based upon existing industry codes and standards. This rule requires companies of all sizes that use certain flammable and toxic substances to develop a Risk Management Program, which includes all of the following:

- A hazard assessment that details the potential effects of an accidental release, an accident history of the last five years, and an evaluation of worst-case and alternative accidental releases;
- A prevention program that includes safety precautions and maintenance, monitoring, and employee training measures;
- An emergency response program that spells out emergency health care, employee training measures and procedures for informing the public and response agencies (e.g., the fire department) should an accident occur; and
- By June 21, 1999, a summary of the facility's risk management program (known as a "Risk Management Plan" or "RMP") was required to be submitted to the USEPA, which makes the information available to the public. These plans must be revised and resubmitted every five years.

The Risk Management Program was created to reduce chemical risk at the local level. The information included in the plan was intended to help local fire, police, and emergency response personnel (who must prepare for and respond to chemical accidents), and be useful to citizens in understanding the chemical hazards in communities. The USEPA anticipates that making the RMPs available to the public will stimulate communication between industry and the public to improve accident prevention and emergency response practices at the local level. A complete description of the Risk Management Plan can be found on the World Wide Web at:

<http://yosemite.epa.gov/oswer/ceppoweb.nsf/content/RMPoverview.htm>

The RMP rule defines threshold quantities (in pounds) of chemicals stored at a site as shown in Table 1. Exceeding these quantities at single location requires the development of a risk management plan. Industry guidance for wastewater treatment plants can be found at

<http://yosemite.epa.gov/oswer/ceppoweb.nsf/content/EPAguidance.htm#Wastewater>

Table 1: Threshold Quantities for the Clean Air Act Risk Management Plan

Chemical	Threshold Quantity (Pounds)
Chlorine	2,500
Chlorine dioxide	1,000
Chlorine monoxide	10,000
Chlorine oxide	10,000

A complete listing of regulated chemicals may be located at the following URL

[http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/title3.pdf/\\$file/title3.pdf](http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/title3.pdf/$file/title3.pdf)

USEPA Office of Pesticide Programs

<http://www.epa.gov/pesticides/>

On February 22, 1999, the USEPA Office of Pesticide Programs (OPP) issued a Re-registration Eligibility Decision (RED) on the pesticide pressurized chlorine gas. The RED required chlorine gas registrants to submit a revised labeling plan to the USEPA. This RED also allowed for re-examination of the required training and education procedures for people handling and dispensing pressurized chlorine gas. Although completion of this process was anticipated early in 2001, the process is still incomplete as of March 2003. No further progress has been made on this issue since 2001. It should be noted that, once progress begins again, the USEPA OPP would require an additional two-years to complete the Re-registration Eligibility Decision.

The USEPA OPP has received and examined comments by several trade groups, state governments, universities and individuals. The Antimicrobials Division of the OPP is in the process of obtaining information from State Agencies concerning possible methods of chlorine gas handling and dispensing training program implementation. Once the information gathering process is completed, a final decision on chlorine gas re-registration can be made. The current status of the re-registration decision may be found using the following URL:

<http://www.epa.gov/pesticides/reregistration/status.htm>

The outcome of this RED impacts the water and wastewater treatment industry as follows:

- To promote uniformity, the USEPA is re-examining the training required for all people handling and dispensing pressurized chlorine gas. Therefore, the training for water and wastewater treatment plant operators using chlorine gas may be affected or altered.
- Although the USEPA OPP would prefer not to require additional training (above that presently required) for water and wastewater operators, each State must determine how the RED will be implemented.

- No action regarding the changing of training requirements may be completed until the USEPA OPP finalizes the re-registration process.

In addition to the training issues, discussed above, possible public concern over the treating of drinking water with a chemical classified as a pesticide may be substantial. This increased concern may be the result of a perceived increased risk.

OSHA Process Safety Management Standard

The Occupational Safety and Health Administration (OSHA) Process Safety Management Standard of Highly Hazardous Chemicals; Explosives and Blasting Agents (29 CFR 1910.119) is a set of procedures in thirteen management areas designed to protect worker health and safety in case of accidental chemical releases. This rule is similar to the USEPA RMP.

Chlorine gas is regulated by both the USEPA RMP (discussed earlier) and OSHA PSM. On-site generated sodium hypochlorite is not included in either regulation. The threshold limit for chlorine gas to be regulated by OSHA PSM is 1,500 pounds. This threshold limit is 1,000 pounds less than the 2,500 pound threshold limit specified in the USEPA Risk Management Plan.

Local and State Regulations

In addition to the above federal regulations, State Regulators and local enforcement agencies (e.g., Local Fire Departments and Health Departments) may have more stringent regulations for the storage and transport of hazardous chemicals.

Public Law 107-188 – “Public Health Security and Bioterrorism Preparedness and Response Act of 2002”

In response to the attacks of September 11, 2001, Congress provided the USEPA with a supplemental appropriation of \$89 million to improve the safety and security of the Nation’s water supply and distribution systems. These funds were intended to reduce the vulnerability of large (serving over 100,000 people) drinking water systems to terrorist attacks and to enhance their security and ability to respond to emergency situations. Each of the large utilities that applied for a \$115,000 grant from the USEPA to complete a terrorism vulnerability assessment (VA), emergency response/operating plan (EOP), security enhancement plans and designs, or a combination of these efforts was fully funded.

In June 2002, Congress passed Public Law Number 107-188 the “Public Health Security and Bioterrorism Preparedness and Response Act of 2002”. This legislation stipulated that vulnerability assessments shall be conducted and emergency response plans shall be prepared or revised for all community water systems serving over 3,300 people. The timeline for completion of these vulnerability assessments is as follows:

- **March 31, 2003 for all (large) water systems serving a population of 100,000 or more,**
- **December 31, 2003 for all (medium sized) water systems serving a population of 50,000 or more but less than 100,000, and**
- **June 30, 2004 for all (small) water systems serving a population greater than 3,300 but less than 50,000.**

P.L. 107-188 directs that assistance or support shall be provided to all water systems to perform vulnerability assessments and develop or revise emergency response plans. P.L. 107-188 also directs the Water Protection Task Force of the U.S. EPA to provide guidance to community water systems serving a population of less than 3,300 people (very small systems) on how to conduct vulnerability assessments and prepare emergency response plans. Current information concerning the status of security related support for utilities and U.S. EPA's Strategic Plan for Homeland Security can be found at the following URL:

<http://www.epa.gov/safewater/security/index.html>

House Resolution 866 – “Wastewater Treatment Works Security Act of 2003”

More recently, H.R. 866, the “Wastewater Treatment Works Security Act of 2003”, was proposed to the 108th Congress on February 13, 2003 by Representative Young of Alaska. The House Transportation and Infrastructure Committee recently approved H.R. 866. If passed, this bill would provide funding for wastewater security work as outlined below:

- Authorizes 220 million dollars for direct grants to utilities for vulnerability assessments, emergency response plans and physical security enhancements;
 - The vulnerability assessments are not required, strictly voluntary;
 - \$150,000 maximum grant per utility with 25 percent matching funds required;
- Provides 15 million dollars for technical assistance for small systems; and
- Provides 5 million dollars or further vulnerability assessment tool creation and upgrades.

S. 779 – “Wastewater Treatment Works Security and Safety Act”

On April 3, 2003, Senator Jeffords introduced S. 779, the “Wastewater Treatment Works Security and Safety Act” into the Senate. This bill is similar to H.R. 866, discussed above, with one notable exception. If passed, this bill would require all wastewater collection and treatment systems in the United States serving 25,000 people or more to conduct a Vulnerability Assessment no later than April 1, 2004. In addition, this pending legislation would require these utilities to update their emergency response plans 180 days after completing their vulnerability assessments.

Differences Between On-Site Generated Ultra Pure Hypochlorite™ and Other Disinfection Alternatives

This section discusses the considerations for high-pressure gaseous chlorine, commercial grade sodium hypochlorite, low-strength on-site generated sodium hypochlorite, mixed oxidant systems and on-site generated Ultra-Pure Hypochlorite™ for water and wastewater disinfection applications.

High Pressure Gaseous Chlorine

Chlorine is the most common disinfectant used in water and wastewater treatment systems in the United States. Historically, gaseous chlorine was the most prevalent form of chlorination. The use of aqueous sodium hypochlorite is increasing in water and wastewater treatment applications due to safety concerns associated with the use, storage and transportation of chlorine gas. When using pressurized chlorine gas for water and wastewater disinfection, the following should be considered:

- Pressurized chlorine gas is regulated by the USEPA Clean Air Act Risk Management Plan;
- A hazard may exist for the community due to the possibility of an accidental large-scale release of chlorine gas during transport and handling of cylinders;
- Pressurized chlorine gas is regulated by the Occupational Safety and Health Administration Process Safety Management Standard of Highly Hazardous Chemicals; Explosives and Blasting Agents;
- Pressurized chlorine gas may be affected by the USEPA Office of Pesticide Programs (OPP) when a Re-registration Eligibility Decision (RED) on the pesticide chlorine gas is finalized. This pending decision may require specific training and licensing for handling of pressurized chlorine gas;
- Possible public concern over the treating of drinking water with a chemical classified as a pesticide may be substantial. This increased concern may be the result of a perceived increased risk; and
- Chlorine gas cylinders may provide a potential target for terrorists wishing to cause damage to a water or wastewater treatment system or to the local community.

Commercial Grade Sodium Hypochlorite

Chemical manufacturers can produce sodium hypochlorite at concentrations as high as 16 weight % chlorine. However, typical commercial grade sodium hypochlorite concentrations are between 12 and 15 weight % chlorine. Concerns associated with the use of commercially produced sodium hypochlorite include high transportation costs, and a lack of long-term stability.

The stability of a sodium hypochlorite solution is dependent upon the following:

- The concentration of the hypochlorite solution;
- The alkalinity and pH of the hypochlorite solution;
- Storage temperature of the hypochlorite solution;
- Concentration of impurities (e.g., Ni^{2+} and Cu^{2+}) that may catalyze hypochlorite decomposition; and
- Exposure to sunlight.

The rate of reduction in the strength of a sodium hypochlorite solution increases with increasing hypochlorite strength, increasing solution temperature and increasing holding time. The half-life of sodium hypochlorite (time to reach half of the original concentration) at ambient temperatures varies between 60 and 1,700 days for solutions of 18 and 3 percent, respectively (Baker, 1969 and Laubusch, 1963). Based upon these data, a factor of six reduction in sodium hypochlorite concentration (18% to 3%) resulted in an almost 30 fold increase in sodium hypochlorite stability.

Data from Gordon et al., (1997) indicates that, as expected, the free available chlorine concentration reduction increases with increasing sodium hypochlorite strength and increasing temperature. Reductions in free available chlorine concentration of 12 percent and 10 percent were observed at 13°C in the 28-day holding period. No significant change in concentration was observed in the 5 percent solution at 13°C after the 28-day period. As expected, data at 27°C show a higher reduction in free available chlorine concentration for the 15 and 10 percent free available chlorine solutions. Although reductions in free available chlorine concentrations as high as 28 percent were observed for the 15 percent solution at 27°C after 28 days, no significant change was observed for the 5 percent sodium hypochlorite solution.

Typically, commercial grade sodium hypochlorite is held for 14 days at a concentration of approximately 15 percent. On-site generated Ultra Pure Hypochlorite™ is typically stored for only one day at a concentration of 12 percent providing for a very stable free available chlorine concentration. Based upon the above data, it can be reasoned that if sodium hypochlorite is to be held for extended periods of time, it should be held at lower strength concentrations.

Reductions in concentration of sodium hypochlorite in the storage tank may make it difficult for some operators to apply the correct chlorine dose. An incorrect chlorine dose may result in an insufficient residual being maintained in a drinking water distribution system (a health risk) or an excess of chlorine being discharged from a wastewater treatment plant into a receiving water (an environmental quality issue).

Gordon et al., (1995a) reported that the role of transition metals in the decomposition of sodium hypochlorite is complex. However, the maximum concentration of transition metals should be limited to less than 0.1 mg/L of Ni^{2+} and 1 mg/L Cu^{2+} in stored sodium hypochlorite. Ferric iron and manganese, when present alone, are effective catalysts for sodium hypochlorite decomposition. It should be noted that on-site generated sodium hypochlorite is less susceptible to transition metal effects due to its lower initial concentration and the short time from production to application.

The loss of strength in sodium hypochlorite solutions may also result in the formation of undesirable by-products (e.g., chlorate) (Bolyard et al, 1992). Bolyard et al., (1992 and 1993) reported that the mass concentration of chlorate ranges from 1.7 to 220 percent of the mass concentration of free available chlorine. However, the concentration of chlorate in stock solutions is a function of solution strength, aging time, temperature, pH and the presence of metal catalysts (Gordon et al, 1993 and 1995).

Gordon et al, (1997) also presented data concerning chlorate ion formation in commercial sodium hypochlorite held in the dark in glass containers for 28 days. As expected, these data indicate that increasing chlorate ion formation was observed with increasing sodium hypochlorite strength. Again, as with the stability information (discussed above) less chlorate ion is formed in lower strength sodium hypochlorite (e.g., 5 percent free available chlorine) than in commercial strength sodium hypochlorite regardless of temperature.

Presently, chlorate ion is not regulated in the current USEPA Primary Drinking Water Regulations. However, as of January 1, 2002, chlorite ion is regulated for systems using chlorine dioxide as a disinfectant. The maximum contaminant level for chlorite is 1.0 mg/l and the maximum contaminant level goal is 0.8 mg/L. It should be noted that the chlorate ion is not listed in the USEPA Candidate Contaminant List (CCL) for drinking water. However, perchlorate is listed in the CCL.

Gordon et al., (1997) developed a computer-based sodium hypochlorite decomposition model (the Gordon-Adam Model) that was also shown to be a good predictor of chlorate ion formation in stored sodium hypochlorite. Following extensive testing of the model, Gordon recommended three basic strategies for minimizing chlorate ion concentration and increasing the stability of commercial grade sodium hypochlorite as follows:

- Dilute concentrated sodium hypochlorite immediately after delivery;
- Use lower storage temperatures; and
- Avoid sunlight during storage.

When using commercial grade bulk sodium hypochlorite for water and wastewater disinfection applications, the following should be considered:

- Hypochlorite concentration degradation with increasing time and temperature;
- Possible chlorate ion formation with sodium hypochlorite degradation;
- Specialized storage requirements (no sunlight, etc.);
- Increased storage requirements (2.5 to 3 times due to dilution from 12 or 15% to 5% to reduce degradation);
- Transportation considerations associated with routine deliveries of commercial grade bulk sodium hypochlorite;
- Increased safety and security procedures following September 11, 2001 make chemical deliveries and driver identification verification more time consuming; and
- These routine deliveries also provide a method for unauthorized persons to gain

access to the treatment plant.

Low-Strength On-Site Generated Sodium Hypochlorite

Generation of low-strength on-site generated sodium hypochlorite occurs using an unseparated brine electrolyzer. In this electrolytic cell the anode and cathode have no separator device, such as a membrane, to prevent the chlorine and sodium hydroxide (caustic) from reacting together to make a weak solution (0.8%) of sodium hypochlorite. Typically, this type of unseparated electrolyzer system contains a salt dissolver that makes a concentrated brine solution of approximately 300g/L using softened water and salt. The concentrated brine solution is then diluted to a concentration of 30 g/L using the softened water. The diluted brine solution is passed through an electrolytic cell, which produces sodium hypochlorite at a concentration of between 7 to 9 g/L (0.7 to 0.9% chlorine). Power for use in the cell is converted from AC into DC by a power supply and rectifier. An acid cleaning system is also connected to the cell. Acid cleaning is usually performed on the cell on a monthly basis as a result of the salt quality.

After passing through the electrolytic cell, the sodium hypochlorite solution enters a hypochlorite degassing and storage system. This system allows the wet secondary hydrogen gas generated in the electrolytic cell to be diluted and vented. The system also allows for storage of at least one days supply of sodium hypochlorite necessary for disinfection. The hypochlorite is then pumped from the storage system to the dosing point where additional chemicals (e.g. acid for pH reduction) may be added.

When using low strength on-site sodium hypochlorite for water and wastewater disinfection applications, the following should be considered:

- The system requires frequent (monthly) maintenance;
- The concentration of sodium hypochlorite generated by the unseparated cell system is only 0.8 percent. This concentration is less than ultra-pure on-site generated sodium hypochlorite by a factor of approximately 15;
- Due to the lower concentration of sodium hypochlorite, 15 times more storage capacity is required to meet requirements for disinfection redundancy; and
- Excess sodium (i.e., a ratio of 2:1 of Cl_2) – excess brine/chloride passes into the treatment stream.

Mixed Oxidant Systems

In addition to on-site sodium hypochlorite generation from a brine solution in both separated and unseparated electrolytic cells, an unseparated electrolytic cell was developed and is marketed by MIOX Corporation that claims to generate a number of mixed oxidants in addition to low-strength sodium hypochlorite. This system is basically a parallel plate, electrolytic hypochlorite generator. The cell for generation of the hypochlorite uses a titanium-based anode that depends on a ruthenium oxide/iridium oxide electrocatalytic coating for the generation of chlorine by brine electrolysis (Trumm, 1994).

In his work, Trumm (1994) used wet chemistry tests to analyze for chlorine, chlorine dioxide, and ozone in sodium hypochlorite generated by the MIOX system. Trumm observed ample chlorine production for almost any operating condition in the MIOX system. However, “no appreciable concentrations of chlorine dioxide or ozone were found” in the effluent from the MIOX generation system (Trumm, 1994).

In another study, Gordon (1998) evaluated oxidants and by-products resulting from the electrolysis of a brine solution. Initially, Gordon determined that free available chlorine might have been interfering with accepted measurement methods for chlorine dioxide and ozone. Thus, improved selected methods for measuring chlorine dioxide and ozone were developed and tested using zero-headspace devices in this study.

In his final analysis of effluent from the MIOX sodium hypochlorite generator, Gordon (1998) determined the following:

“No chlorine dioxide was detected. No ozone was detected. No hydrogen peroxide was detected”

Even, if these additional oxidants, discussed above and unmeasured by Gordon, were being produced by the MIOX system, Gordon (1998) determined that ozone and chlorine dioxide would react in solution with the sodium hypochlorite generated by the system on a millisecond timescale, thus rendering them ineffective for use as oxidants.

In addition to the studies discussed above, work published by Casteel et. al, (1999) and Venczel et al., (1997) determined that sodium hypochlorite generated from a brine source provided effective disinfection of *Clostridium perfringes*, *Cryptosporidium parvum* oocysts, and other microbes in water. Since these studies used a MIOX system to generate sodium hypochlorite from a brine solution, many have attributed the effective reduction in *Cryptosporidium* and other microorganism concentrations to the possibility of mixed oxidants being generated by the MIOX system. However, Casteel et. al., states the following in their conclusions:

An important data gap for the disinfection technology of mixed oxidants electrically generated from brine is that the chemical composition of the oxidant mixture is inadequately characterized. ...Additional studies are needed to account for departures from first-order inactivation kinetics and to determine the effectiveness of mixed oxidants under a wider range of water quality conditions.

On-Site Generated Ultra-Pure Hypochlorite™ (Chlor-Alkali Process)

On-site generation of either atmospheric pressure chlorine gas and caustic or Ultra-Pure Hypochlorite™ has many advantages in light of the current and pending regulations discussed above and the information presented in this paper:

- Not regulated by the USEPA Clean Air Act Risk Management Plan;
- Not regulated by the Occupational Safety and Health Administration Process Safety Management Standard of Highly Hazardous Chemicals; Explosives and Blasting Agents;
- No public risk due to the transport of hazardous chemicals;
- No storage of hazardous chemicals;
- Quarterly maintenance is performed on this system rather than monthly maintenance, with no shutdown required.
- Chlorine gas produced in this process is delivered at atmospheric pressure rather than high pressure;
- The system can be designed to produce either atmospheric pressure chlorine gas and caustic or Ultra-Pure Hypochlorite™;
- The concentration generated by the on-site ultra-pure system is approximately 15 times greater than the concentration generated by the on-site low-strength sodium hypochlorite; and
- Unspent chloride and sodium do not enter a stream being treated with Ultra Pure Hypochlorite™.

The Role of Disinfectant Choice in the Water or Wastewater Vulnerability Assessment Process

Today everyone in the United States must deal with the effects of potential terrorism in their everyday environment. There are many businesses, institutions, facilities and groups of people that feel the need to be protected against terrorist attacks similar to those our nation experienced on September 11, 2001 in New York and Washington, DC and on the US Postal Service later that same year. Among the most critical areas needing protection are our nations potable (drinking) water supply and distribution systems and wastewater collection and treatment systems. There is no need to try to explain the magnitude of the terror that would be experienced in our community if we were to wake up one morning and find out that we could not use our drinking water system or could not dispose of our waste. During natural disasters such as hurricane Andrew, local areas have had to resort to the use of bottled water for relatively brief periods of time, but, during a wide spread terrorist attack, large population areas as well as hospitals, nursing homes, etc. might be affected.

The latest USEPA guidance concerning vulnerability assessments required for all community water supplies in the United States includes six basic elements. Although these elements are conceptual in nature and not intended to be used as a detailed outline for a vulnerability assessment, they do provide some insight into the role of disinfectant choice in the vulnerability assessment process. The six elements required for the performance-based

vulnerability assessment process are as follows:

1. Characterization of the water system, including its mission and objectives;
2. Identification and prioritization of adverse consequences to avoid;
3. Determination of critical assets that might be subject to malevolent acts that could result in undesired consequences;
4. Assessment of the likelihood (qualitative probability) of such malevolent acts from adversaries;
5. Evaluation of existing countermeasures; and
6. Analysis of current risk and development of a prioritized plan for risk reduction.

Since disinfection choice and operation are an integral component of all water and wastewater treatment systems, they must be included in each of the six elements listed above. The nature and extent of the involvement of disinfection choice and operation in the vulnerability assessment process will vary among systems based upon a number of factors, including system size, potential population affected, source water, treatment complexity, system infrastructure and other factors. Safety evaluations of the system may highlight a need for a change in disinfectant or a modification of current disinfection operational procedures.

Summary and Conclusions

A summary of the advantages of on-site generated Ultra-Pure Hypochlorite™ over other alternates is shown below in Table 2. As shown above, on-site generation of either chlorine gas at atmospheric pressure and caustic or Ultra-Pure Hypochlorite™ has numerous advantages over other alternates for use in water and wastewater systems as described previously in this paper. Please note that mixed oxidant systems were not included in Table 2 due to a lack of supporting data regarding the existence of mixed oxidants generated by these types of systems.

Table 2 Comparison of Disinfectants for Water and Wastewater Disinfection

Item of Concern	Disinfectant Choice			
	High Pressure Gaseous Chlorine	Commercial Grade Sodium Hypochlorite	Low-Strength On-Site Hypochlorite	Ultra-Pure Hypochlorite™
Regulated by USEPA Clean Air Act RMP	Yes	No	No	No
Regulated by the OSHA Administrative Process	Yes	No	No	No
Transport of Hazardous Chemicals	Yes	No	No	No
Storage of Hazardous Materials	Yes	No	No	No
Requires Frequent Maintenance (Monthly or More)	Yes	Yes	Yes	No
Chlorine Gas Above Atmospheric Pressure	Yes	N/A	N/A	No
Possible Public Concern of Pesticides	Yes	No	No	No
Chlorine Gas Cylinders May Provide Targets For Terrorists	Yes	No	No	No
Concentration of Sodium Hypochlorite Less Than 10 %	No	No	Yes	No
Loss of Strength With Time and Temperature	No	Yes	No	No
Possible Formation of Chlorate Ion Upon Degradation	No	Yes	N/A	N/A
Specialized Storage Requirements - Sunlight Protection	No	Yes	No	No
Security Concerns Related to Numerous Deliveries	No	Yes	No	No
Large Storage Capacity Required Due to Low Strength	No	No	Yes	No
Unspent Chloride/Sodium Passed into Treatment Stream	No	No	Yes	No

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