Sodium Chlorite

Treatment of Drinking Water with Chlorine Dioxide

Introduction

Chlorine dioxide is a powerful oxidizing agent, generated from sodium chlorite. Its selective reactivity makes chlorine dioxide useful in many water treating applications for which chlorine and other oxidizing agents are unsuitable.

Chlorine dioxide was first used in municipal drinking water treatment in 1944 to control taste and odor at the Niagara Falls water treatment plant. Today, there is increased interest in chlorine dioxide as an oxidant and disinfectant for drinking water.

Code of Federal Regulations 40 CFR §141.64, which cites the maximum contaminant levels for disinfection byproducts sets a maximum contaminant level (MCL) of 0.08 mg/L for total trihalomethanes (TTHM).[1] The EPA has identified chlorine dioxide as an alternative or supplemental oxidant-disinfectant that is one of the most suitable for TTHM treatment and control[2].

In contrast with chlorine, the reactions of chlorine dioxide with humic substances (the precursors of trihalomethanes) do not result in the formation of THMs. For this reason, chlorine dioxide treatment has become a preferred method where it is necessary to control TTHMs, along with taste and odors.

Chlorine Dioxide as a Water Disinfectant

Chlorine dioxide is an extremely effective disinfectant and bactericide, equal or superior to chlorine on a mass dosage basis. Its efficacy has been well documentedin the laboratory, in pilot studies and in full-scale studies using potable and wastewater[3]. Unlike chlorine, chlorine dioxide does not hydrolyze in water. Therefore, its germicidal activity is relatively constant over a broad pH range (See Figures 1, 2, and 3 on Page 6 and 7).

At pH 6.5, doses of 0.25 mg/L of chlorine dioxide and chlorine produce comparable one-minute kill rates for the bacterium *Escherichia coli.* At pH 8.5, chlorine dioxide maintains that same kill rate, but chlorine requires five times as long. Thus, chlorine dioxide should be considered as a primary disinfectant for high pH, lime-softened waters.

Chlorine dioxide has also been shown to be effective in killing other infectious bacteria such as *Staphylococcus aureus* and *Salmonella.* Chlorine dioxide is as effective as chlorine in destroying coliform populations in wastewater effluents and is superior to chlorine in the treatment of viruses commonly found in secondary wastewater effluents (Figure 4). When *Poliovirus I* and a native coliphage were subjected to these two disinfectants, a 2 mg/L dose of chlorine dioxide produced a much lower survival rate than did a 10 mg/L dose of chlorine[4].

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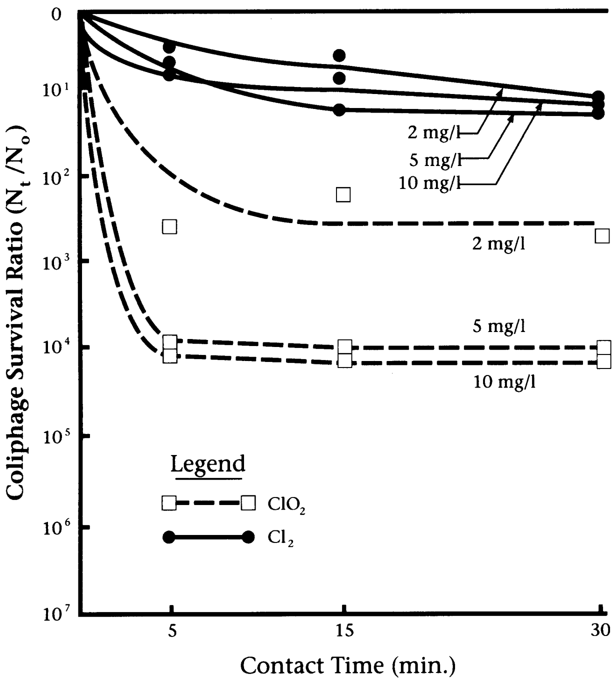
Figure 4

In situ coliphage survival in secondary effluent at three doses and three contact times



When applied for disinfection (as opposed to oxidation), a disinfectant must provide specified levels of microorganism kills or inactivations as measured by reductions of coliforms, heterotrophic plate count organisms and *Legionella* bacteria. Under current regulations, the disinfection treatment must be sufficient to ensure at least a 99.9 percent (3-log) removal and/or inactivation of *Giardia lamblia* cysts and 99.99 percent (4-log) removal and/or inactivation of enteric viruses[5]. Disinfection is expressed as a CT value (i.e., a function of Concentration x Contact Time). At the CT values necessary for chlorine dioxide to inactivate 99.9 percent of *Giardia lamblia* cysts, the simultaneous inactivation of 99.99 percent of enteric viruses is also assured.

These regulations also establish treatment technique requirements in lieu of MCLs for *Giardia lamblia,* viruses, and *Legionella*. The published CT values (40 CFR 141.74) required for various disinfectants to achieve these goals show that chlorine dioxide is more effective than chlorine or monochloramine. Over the pH 6-9 range, chlorine dioxide is at least twice as effective as free chlorine is at pH 6. At pH 7-9, free chlorine becomes progressively less effective than chlorine dioxide. Chlorine dioxide is also substantially more effective than monochloramine.

Chlorine Dioxide for Control of THMs

In 1974, researchers first observed the formation of trihalomethanes (THMs) during chlorination of natural waters. These THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) are produced when free chlorine or bromine reacts with natural organic matter in the water.

The subsequent identification of THMs in chlorinated water supplies led to concerns over their potential health effects. These concerns include potential reproductive effects and the classification of chloroform, bromodichloromethane and certain other disinfection byproducts (DBPs) as carcinogens.

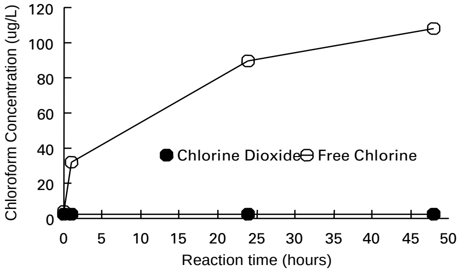
In 1979, the EPA established a THM Maximum Contaminant Level (MCL) of 0.10 mg/L, causing water utilities to begin searching for alternatives to chlorine for oxidation and disinfection of water. By 2004, the EPA not only lowered the MCL for total trihalomethanes (TTHMs) to 0.08 mg/l, but also extended the MCL to all size systems[1]. In addition, a MCL of 0.06 mg/L was established for haloacetic acids (HAA5). As a result, there is an increased emphasis on the modification of water treatment methods to prevent or reduce the formation of THMs and other DBPs to ensure compliance with the EPA rule. For this purpose, chlorine dioxide is an excellent choice as either an alternative or supplemental oxidant-disinfectant.

The key to understanding why chlorine dioxide is so effective can be found in the differences in the reactions of chlorine dioxide and chlorine with THM precursors, such as humic and fulvic acids. Chlorine dioxide reacts primarily by oxidation; however, chlorine reacts by both oxidation and electrophilic substitution to yield volatile and nonvolatile chlorinated organic substances (THMs).

Many treatment methods have been developed to remove THMs once they have been formed by chlorine treatment. However, chlorine dioxide treatment method is superior in preventing or substantially reducing their initial formation. Figure 5 compares the effect on chloroform formation when water containing humic acid is treated with chlorine dioxide and chlorine.

Figure 5

Chloroform production in water containing 5 mg humic acid
dosed with chlorine dioxide or free chlorine



Chlorine dioxide reacts with THM precursors to make them unreactive or unavailable for THM formation. This means that pretreatment with chlorine dioxide has an inhibiting effect on THM formation when chlorine is subsequently used for treatment.

In tests, samples of raw Ohio River water were treated with 2-3 mg/L of chlorine dioxide and stored for 48 hours. The samples were then treated with 8 mg/L of chlorine. The samples pretreated with chlorine dioxide showed a 50 percent (50%) reduction in THM formation when compared with an untreated sample.[3]

These findings can be the basis of water treatment practices designed to minimize THM formation. Most often, chlorine dioxide for THM control is a replacement for prechlorination. The addition of chlorine dioxide to the raw water supply would be for primary disinfection and/or oxidation. Then, free or combined chlorine or chlorine dioxide is added after filtration to provide a disinfectant residual in the distribution system.

With such treatment, THM precursors are oxidized by the chlorine dioxide. The next treatment steps (coagulation, settling and filtration) remove the oxidized precursors before final chlorination. Preoxidation dosages with chlorine dioxide are typically 30 to 50 percent of the required prechlorination dosages. Postchlorination dosage, however, might be slightly higher than the dosage without using chlorine dioxide. This modification of standard chlorination practices can result in a 50 to 70 percent (50% - 70%) decrease in TTHMs.

Chlorine dioxide is not only economical but is also effective in preoxidation and disinfection. Typically, there is a lower oxidant demand for chlorine dioxide than for chlorine. This is an indication that chlorine dioxide is more selective and less reactive than chlorine.

Specifically (unlike chlorine), chlorine dioxide does not react with ammonia to produce chloramines. Since chloramines are poor disinfectants, their formation increases consumption of chlorine needed for water treatment.

Three well-documented case histories: Evansville, Indiana; Hamilton, Ohio; and Galveston, Texas demonstrate the versatility and effectiveness of chlorine dioxide for THM control in municipal water treatment systems.[6,7,8]

Chlorine Dioxide for Taste and Odor Control

Chlorine dioxide is far superior to chlorine for destroying phenols, algae, sulfides, iron, and manganese contaminants. For this reason, it continues to be used to control taste and odor in municipal water supplies.

Phenols - Surface water often contains phenols from industrial effluents. When chlorine is used for disinfection, chlorophenols are formed. These lead to taste and odor problems.

Ortho-Chlorophenol - Recognized as the most offensive of the phenolic compounds, it is objectionable at concentrations as low as 1-2 ppb. Treatment with chlorine dioxide can destroy chlorophenols. Proper application requires several parts of chlorine dioxide per part of chlorophenol.

In solutions with chlorine dioxide in excess, the principal by-product is *p*-benzoquinone (45 to 65 percent). While no chlorophenols are observed, simple organic acids (such as maleic and oxalic acids) are the remaining byproducts. At pH 7, the phenol reaction is rapid and complete, with all phenols consumed.

Algae - Chlorine dioxide has been shown to be effective in controlling algae growth. In one study, chlorine dioxide was found to be more effective than copper sulfate, at comparable treatment costs.[9] Chlorine dioxide is believed to attack the pyrrole ring of the chlorophyll. This cleaves the ring and leaves the chlorophyll inactive. Since algae cannot function without chlorophyll metabolism, they are destroyed. The reaction of chlorine dioxide with algae and their essential oils forms tasteless, odorless substances.

Algae control is carried out by adding chlorine dioxide to the reservoir at night (to prevent decomposition of chlorine dioxide by sunlight). The algae killing action is fast enough to be effective before the sun rises. A dosage of 1 mg/L has been reported to control algae populations.

Manganese - Manganese ions in water supplies can cause stained clothes, "black" water, water main incrustation and debris at users' taps. Though chlorine can be used to control these problems, it reacts so slowly that manganese ions may still be in the water distribution system after 24 hours. Chlorine dioxide reacts much more rapidly with manganese, oxidizing it to manganese dioxide:

$$2ClO_2 + 5Mn^{+2} + 6H_2O \rightarrow 5MnO_2 + 12H^+ + 2Cl^-$$

Manganese dioxide is insoluble in water and can be filtered out before it leaves the treatment plant. To remove one part manganese requires 2.45 parts of chlorine dioxide. Best results are obtained when the pH is greater than 7.

Iron - Iron can be a problem, either from the effects of its presence in the water alone, or because iron-bearing water has promoted the growth of iron bacteria. Chlorine dioxide rapidly oxidizes Fe^{+2} to Fe^{+3}, which is precipitated as iron hydroxide:

$$ClO_2 + 5Fe(HCO_3)_2 + 2H_2O \rightarrow$$
$$5Fe(OH)_3 + 10CO_2 + Cl^- + H^+$$

As with manganese, best results are obtained under neutral to alkaline conditions.

Chlorine dioxide has also been reported to oxidize organically bound iron.[10] Excess free chlorine residuals (>5 mg/L) could not control the iron bacteria, presumably because the organically bound iron was chlorine-unreactive, and yet remained bio-available to the bacteria in the attached biofilms. Chlorine dioxide has been used to control these biofilms. It removes the attached bacteria and exposes them to the disinfectant while the iron is being oxidized.

Sulfides - Chlorine dioxide is not typically used to remove sulfides from potable water. However, it does rapidly oxidize hydrogen sulfide to sulfates in the pH range 5-9.

EPA Registration

When used as the parent chemical for on-site production of chlorine dioxide in pesticidal applications, sodium chlorite is governed by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). This means that the *sodium chlorite* sold for this purpose must be registered with the EPA under a label or labels which list this usage.

Pesticidal uses of chlorine dioxide generated by sodium chlorite are biocidal, disinfective or sanitizing in nature. Examples of such uses include bactericide or slimicide in treatment of drinking water; processing plant flume water; rinse water in produce packing facilities; as a slimicide in recirculating cooling waters; and as a microbicide in oil recovery operations.

OxyChem technical sodium chlorite products are registered for these applications under the following EPA Registration Numbers:
5382-42 Technical Sodium Chlorite Dry
5382-45-31% Active Sodium Chlorite Solution
5382-43 Technical Sodium Chlorite Solution 31.25
5382-44 Technical Sodium Chlorite Solution 18.75
21164-6 Akta Klor 25
21164-9 Akta Klor 7.5

Generation of Chlorine Dioxide

Chlorine dioxide can be generated by activating sodium chlorite ($NaClO_2$) with an oxidizing agent or an acid source.[10] The most commonly available oxidant is chlorine, which reacts with sodium chlorite as follows:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

From the above equation, 1.34 lb of pure sodium chlorite will react with 0.5 lb of chlorine to produce 1.0 lb of chlorine dioxide. However, since dry technical sodium chlorite is 80% active, the reaction takes 1.68 lb of Technical Sodium Chlorite Dry. Usually, a slight excess of chlorine should be used to ensure that the reaction solution has a pH value between 2-4. This will produce chlorine dioxide more efficiently.

In some applications, a two-fold excess of chlorine can be used for maximum yield of chlorine dioxide. However, for treatment of potable water where the formation of trihalomethanes is a concern, only an amount of chlorine slightly in excess of the theoretical should be used. Alternatively, the addition of a small amount of muriatic acid (HCl) or other mineral acid may be used for pH adjustment.

If chlorine is not readily available, chlorine dioxide can also be prepared by mixing sodium hypochlorite bleaching solution with sodium chlorite and an acid:

$$\begin{aligned}&2NaClO_2 + NaOCl + H_2SO_4 \rightarrow\\&2ClO_2 + NaCl + Na_2SO_4 + H_2O\end{aligned}$$

The reaction with sulfuric acid as shown in the above reaction, produces the highest purity chlorine dioxide. Other inorganic and organic acids may be used, and hydrochloric acid reportedly produces the most efficient generation of chlorine dioxide with the three-product reaction.[11] Regardless of the acid used, a slight excess is needed to maintain a pH of 2-4.

Chlorine dioxide may also be generated by acidifying a solution of sodium chlorite with hydrochloric acid as shown below:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 2H_2O + 5NaCl$$

This reaction represents the easiest method of generating chlorine dioxide. It can often be used by simply mixing sodium chlorite into water systems which are slightly acidic (pH 4-5).

Commercial generators are available based on all three activation reactions discussed above. Complete discussions of the reactions and generators can be found in a number of references.[12]

Methods of Analysis

In addition to other monitoring requirements, 40 CFR §141.64[1] also requires that water systems using chlorine dioxide for disinfection or oxidation must monitor their system for chlorine dioxide and chlorite. Chlorine dioxide solutions and the oxidized chlorine species may be analyzed by a number of different methods, depending on the selectivity, sensitivity and accuracy required in the analysis. Each of these procedures has some limitations either in detection limits, interferences, or reliability or in the difficulty or cost to perform. The selection of an analytical method will be based on the requirements for the analysis, and the species being analyzed.

Chlorine Dioxide For compliance monitoring for residuals of chlorine dioxide, one of the two approved methods specified in 40 CFR §141.131(c) must be used:
DPD Method, 4500-ClO_2 D, or
Amperometric Method II, 4500-ClO_2 E.[13]

Where approved by the state, systems may also measure residual disinfectant concentrations of chlorine dioxide by using DPD colorimetric test kits.

Sodium Chlorite For compliance monitoring for chlorite, water systems must use one of three approved methods specified in 40 CFR §141.131(b):
Amperometric Method II, 4500-ClO_2 E;
Ion Chromatography, EPA Method 300.0[14], or
Ion Chromatography, EPA Method 300.1[15].

The regulations further specify that Amperometric Titration may be used for routine daily monitoring of chlorite at the entrance to the distribution system, but that Ion Chromatography must be used for routine monthly monitoring of chlorite and for additional monitoring of chlorite in the distribution system.

SAFETY AND HANDLING

The following summary of health and safety information is not intended to be complete. For complete information, read the current Safety Data Sheet (SDS). To obtain an SDS, contact the OxyChem Technical Service Department.

Toxicological Properties

Sodium chlorite is toxic by ingestion. Sodium chlorite may cause anemia by oral exposure and has low toxicity by dermal exposure. OxyChem sodium chlorite has an oral LD_{50} (rat) of 165 mg/kg. Sodium chlorite products have a dermal LD_{50} (rabbit) of greater than 2 g/kg. Sodium chlorite can produce severe irritation or burns to the skin and eyes. Corneal damage can occur if not washed immediately from the eyes.

Personal Protection

When handling sodium chlorite, chemical goggles, face shield, neoprene gloves, chemical resistant apron or suit, and chemical resistant boots should be worn. Wear a NIOSH/MSHA approved acid gas respirator with a dust/mist filter if any exposure is possible. Local exhaust is required where exposure to dust or mist might occur. If sodium chlorite is spilled on clothing, remove and wash contaminated clothing at once to avoid the potential of fire.

First Aid

Eyes: Immediately flush eyes with large amounts of water for at least 15 minutes while frequently lifting the upper and lower eyelids. Consult a physician immediately.

Skin: Remove contaminated clothing. Immediately flush exposed skin areas with large amounts of water for at least 15 minutes. Consult a physician if burning or irritation of the skin persists. Contaminated clothing must be laundered before re-use.

Ingestion: DO NOT induce vomiting. Drink large quantities of water. Consult a physician immediately. DO NOT give anything by mouth if the person is unconscious or having seizures.

Inhalation: Move patient to fresh air and monitor for respiratory distress. If cough or difficulty in breathing develops, administer oxygen, and consult a physician immediately. In the event that breathing stops, administer artificial respiration and obtain emergency medical assistance immediately.

Notes to Physician: Chlorine dioxide vapors are emitted when sodium chlorite contacts acids or chlorine. If these vapors are inhaled, monitor patient closely for delayed development of pulmonary edema which may occur up to 48-72 hours post-inhalation.

Following ingestion, neutralization and use of activated charcoal is not indicated.

Storage and Handling

Do not contaminate sodium chlorite with incompatible materials such as dirt, organic matter, oxidizers, reducing agents, chemicals, soap products, solvents, acids, paint products, or combustible materials. Do not store or transport sodium chlorite with incompatible materials. Contamination may start a chemical reaction with generation of heat and emission of chlorine dioxide (a poisonous, explosive gas). A fire or explosion may result. Rinse empty containers thoroughly with water and dispose of in accordance with label instructions.

Dry sodium chlorite. Do not expose to moisture during storage. Dry product may clump due to the hygroscopic nature of the material. Store in the original container, in a cool, dry, well-ventilated area away from direct sunlight. Always replace cover tightly. Mix only into water using a clean, dry scoop reserved for this product alone.

Keep away from flame or any burning material (such as a lighted cigarette). If fire occurs, extinguish with plenty of water. Cool any unopened drums near the fire by spraying water on them.

Sodium chlorite solutions. Store in clean, closed, non-translucent containers. Exposure to sunlight or ultra-violet light will reduce product strength.
Do not allow solution to evaporate to dryness; this product becomes a fire or explosion hazard if allowed

to dry and can ignite on contact with combustible materials.

Spill and Leak Procedures

In the event of a spill or leak, remove all sources of ignition. Wear NIOSH/MSHA approved positive pressure, self-contained breathing apparatus with a chemically impermeable, fully encapsulated suit. Follow OSHA regulations for respirator use (see 29 CFR 1910.134).

Sodium chlorite in the dry form is a fire or explosion hazard if contaminated with combustible material. Clean up in a manner to avoid contamination. Spilled material should be picked up, by using a clean, dry, scoop or shovel and placed into a clean, dry, container. Do not return spilled material to the original container. Isolate the recovery container outside or in a well-ventilated area and hold for proper waste disposal. Do not seal the container. Flush any residual material with large quantities of water.

Sodium chlorite solutions also becomes a fire or explosion hazard if allowed to dry and can ignite on contact with combustible material. Continue to keep damp until spilled material is contained by diking or absorbing with clay, soil, or non-flammable commercial absorbents. Do not return spilled material to original container. Place in a clean container and isolate outside or in a well-ventilated area. Do not seal the container. Flush any residual material with large quantities of water.

Disposal

Dispose in accordance with all applicable regulations. Do not put product, spilled product, or filled or partially filled containers into the trash or waste compactor. Contact with incompatible materials could cause a reaction and fire. Contact OxyChem Technical Service to obtain neutralization instructions. Sodium chlorite is toxic to fish and aquatic organisms. Keep out of water supplies and sewers. If sodium chlorite is spilled or becomes a waste, it must be disposed of in accordance with local, state, and Federal regulations by a NPDES permitted out-fall or in a permitted hazardous waste treatment, storage, and disposal facility.

Shipping Information

Special blends are available upon request. OxyChem Technical Sodium Chlorite is registered with the EPA for a number of pesticidal applications as governed by FIFRA, as amended.

- Technical Sodium Chlorite Dry is available in 100-lb drums.
- 31% Active Sodium Chlorite Solution is available in railcars, tank trucks, 330-gallon non-returnable totes, and 55-gallon drums.
- Technical Sodium Chlorite Solution 31.25 is available in railcars, tank trucks, 330-gallon non-returnable totes, and 55-gallon drums.
- Special blends are available upon request.

Figure 1

Comparison of the bactericidal effects of chlorine and chlorine dioxide on *A. aerogenes* at different temperatures and pH, with five minute contact

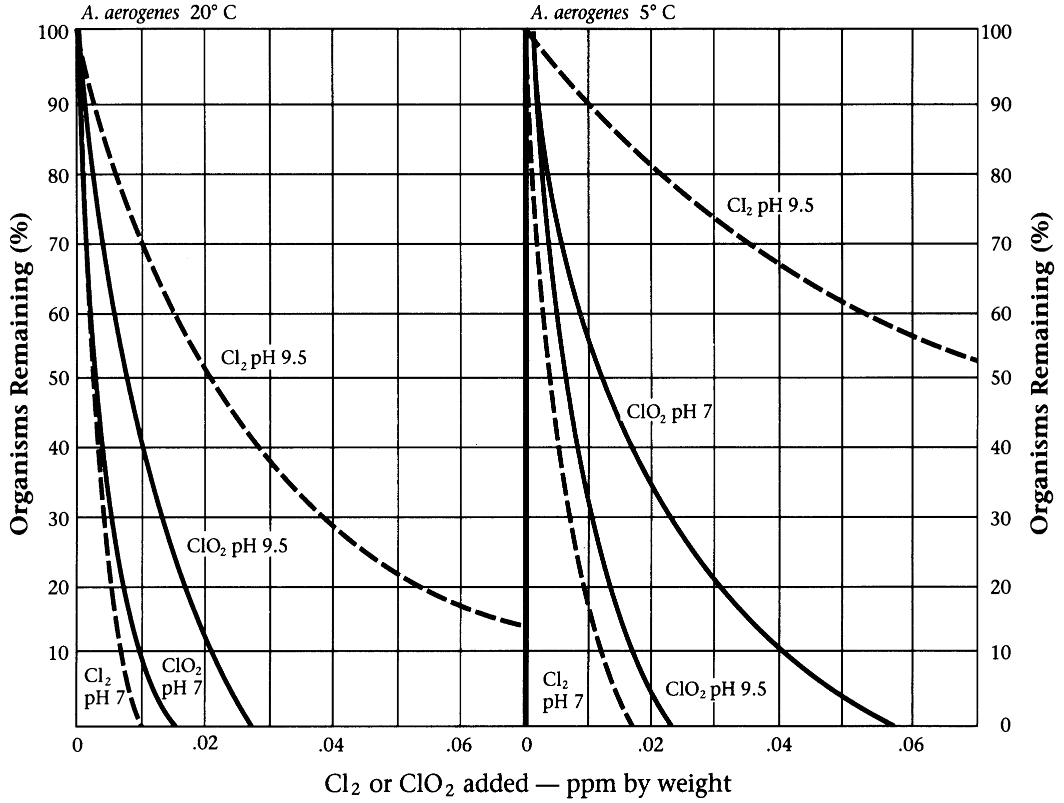


Figure 2

Comparison of the bactericidal effects of chlorine and chlorine dioxide on *E. coli* at different temperatures and pH, with five minute contact

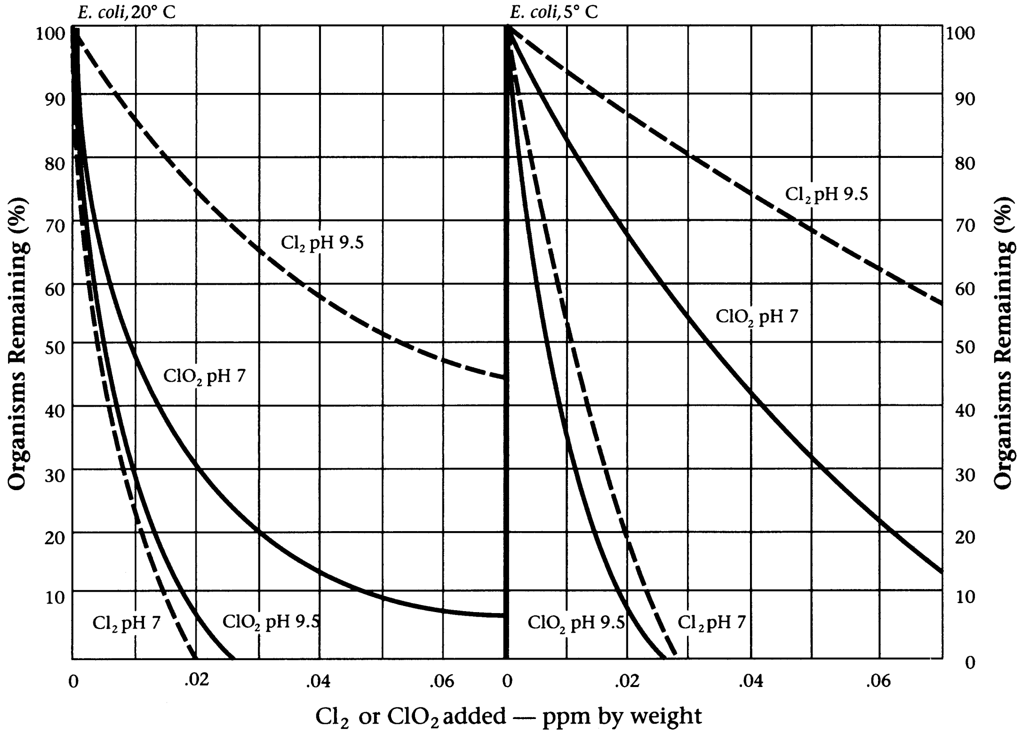
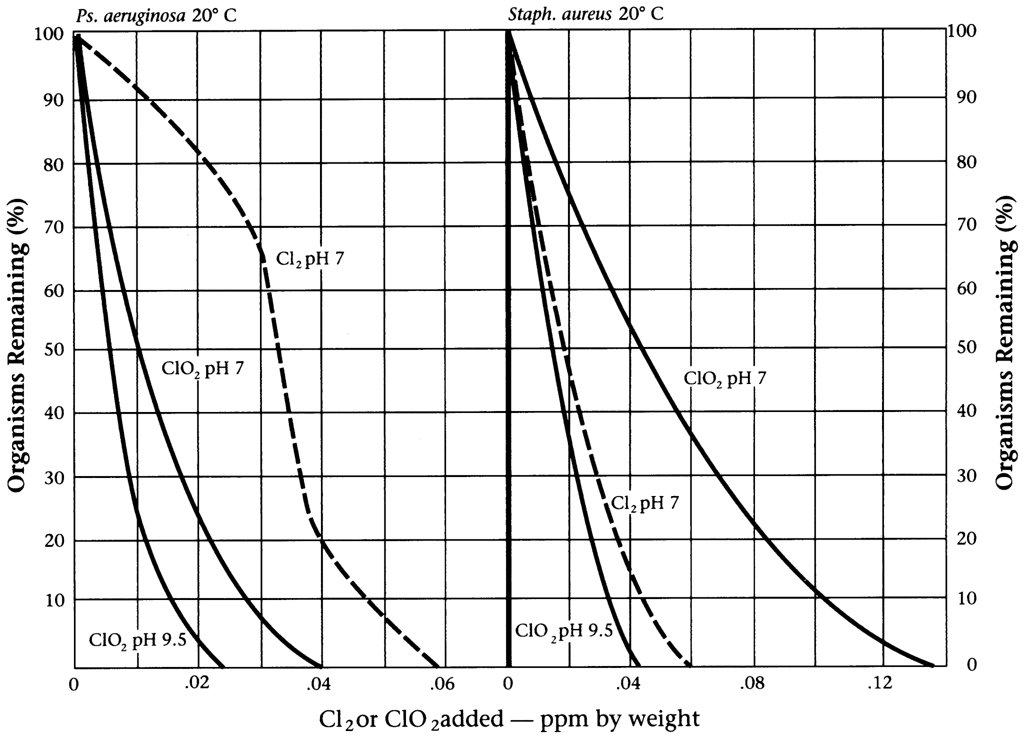


Figure 3

Comparison of the bactericidal effects of chlorine and chlorine dioxide on *Ps. aeruginosa and Staph. aureus* at different pH, with five minute contact



Further Information

More detailed information on sodium chlorite is available upon request through the OxyChem Technical Service Department. Call or write to:

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Wichita, Kansas 67215
800-733-1165 opt. 1
OxyChem_Tech_Service@oxy.com

References

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13 *Standard Methods for the Examination of Water and Wastewater,* APHA, AWWA and WEF, Washington, D.C. (20th Ed. 1998).

14 *Methods for the Determination of Inorganic Substances in Environmental Samples*. USEPA. 1993. EPA/600/R-93/100

15 USEPA Method 300.1, *Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0*. USEPA. 1997. EPA/600/R-98/118.