

4. CHLORINE DIOXIDE

Since the beginning of the twentieth century, when it was first used at a spa in Ostend, Belgium, chlorine dioxide has been known as a powerful disinfectant of water. During the 1950s, it was introduced more generally as a drinking water disinfectant since it provided less organoleptic hindering than chlorine. Approximately 700 to 900 public water systems use chlorine dioxide to treat potable water (Hoehn, 1992). Today, the major uses of chlorine dioxide are:

- CT disinfection credit;
- Preoxidant to control tastes and odor;
- Control of iron and manganese; and
- Control of hydrogen sulfide and phenolic compounds.

4.1 Chlorine Dioxide Chemistry

4.1.1 Oxidation Potential

The metabolism of microorganisms and consequently their ability to survive and propagate are influenced by the oxidation reduction potential (ORP) of the medium in which it lives (USEPA, 1996).

Chlorine dioxide (ClO_2) is a neutral compound of chlorine in the +IV oxidation state. It disinfects by oxidation; however, it does not chlorinate. It is a relatively small, volatile, and highly energetic molecule, and a free radical even while in dilute aqueous solutions. At high concentrations, it reacts violently with reducing agents. However, it is stable in dilute solution in a closed container in the absence of light (AWWA, 1990). Chlorine dioxide functions as a highly selective oxidant due to its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO_2^-) (Hoehn et al., 1996). The pKa for the chlorite ion, chlorous acid equilibrium, is extremely low at pH 1.8. This is remarkably different from the hypochlorous acid/hypochlorite base ion pair equilibrium found near neutrality, and indicates the chlorite ion will exist as the dominant species in drinking water. The oxidation reduction of some key reactions are (CRC, 1990):



Other important half reactions are:



In drinking water, chlorite (ClO_2^-) is the predominant reaction endproduct, with approximately 50 to 70 percent of the chlorine dioxide converted to chlorite and 30 percent to chlorate (ClO_3^-) and chloride (Cl^-) (Werdehoff and Singer, 1987).

4.2 Generation

4.2.1 Introduction

One of the most important physical properties of chlorine dioxide is its high solubility in water, particularly in chilled water. In contrast to the hydrolysis of chlorine gas in water, chlorine dioxide in water does not hydrolyze to any appreciable extent but remains in solution as a dissolved gas (Aieta and Berg, 1986). It is approximately 10 times more soluble than chlorine (above 11°C), while it is extremely volatile and can be easily removed from dilute aqueous solutions with minimal aeration or recarbonation with carbon dioxide (e.g. softening plants). Above 11 to 12°C , the free radical is found in gaseous form. This characteristic may affect chlorine dioxide's effectiveness when batching solutions and plumbing appropriate injection points. Other concerns are the increased difficulty in analyzing for specific compounds in the presence of many interfering compounds/residual longevity and volatility of gaseous compounds. In the gaseous form, the free radicals also react slowly with water. The reaction rate is 7 to 10 million times slower than that of the hydrolysis rate for chlorine gas (Gates, 1989).

Chlorine dioxide cannot be compressed or stored commercially as a gas because it is explosive under pressure. Therefore, it is never shipped. Chlorine dioxide is considered explosive at higher concentrations which exceed 10 percent by volume in air, and its ignition temperature is about 130°C (266°F) at partial pressures (National Safety Council Data Sheet 525 – ClO_2 , 1967). Strong aqueous solutions of chlorine dioxide will release gaseous chlorine dioxide into a closed atmosphere above the solution at levels that may exceed critical concentrations. Some newer generators produce a continuous supply of dilute gaseous chlorine dioxide in the range of 100 to 300 mm-Hg (abs) rather than in an aqueous solution (National Safety Council, 1997). For potable water treatment processes, aqueous solutions between 0.1 and 0.5 percent are common from a number of current generation technologies.

Most commercial generators use sodium chlorite (NaClO_2) as the common precursor feedstock chemical to generate chlorine dioxide for drinking water application. Recently, production of chlorine dioxide from sodium chlorate (NaClO_3) has been introduced as a generation method where in NaClO_3 is reduced by a mixture of concentrated hydrogen peroxide (H_2O_2) and concentrated sulfuric acid (H_2SO_4). Chlorate-based systems have traditionally been used in pulp and paper applications, but have recently been tested full-scale at two U.S. municipal water treatment plants. This is an emerging technology in the drinking water field and is not discussed in this guidance manual.

4.2.2 Chlorine Dioxide Purity

Chlorine dioxide generators are operated to obtain the maximum production (yield) of chlorine dioxide, while minimizing free chlorine or other residual oxidant formation. The specified yield for chlorine dioxide generators is typically greater than 95 percent. In addition, the measurable excess chlorine should be less than 2 percent by weight in the generator effluent. Generator yield is defined as (Gordon et al., 1990):

$$\text{Yield} = \frac{[\text{ClO}_2]}{[\text{ClO}_2] + [\text{ClO}_2^-] + \left(\frac{67.45}{83.45}\right)[\text{ClO}_3^-]} \times 100$$

Where: $[\text{ClO}_2]$ = Chlorine dioxide concentration, mg/L.

$[\text{ClO}_2^-]$ = Chlorite concentration, mg/L.

$[\text{ClO}_3^-]$ = Chlorate concentration, mg/L.

$\left(\frac{67.45}{83.45}\right)$ = Molecular weight ratio of ClO_2^- to ClO_3^- .

Since any chlorite ion fed to the generator may result in the formation of ClO_2 , ClO_2^- , or ClO_3^- , the purity of the resultant mixture can be calculated using the concentrations of each of the species from appropriate analytical measurements. The determination of purity requires neither flow measurement, mass recoveries, nor manufacturer-based methods to determine production “yield,” “theoretical yield,” “efficiency,” or conversion for any precursor feedstock. This approach does not require flow measurements that can introduce up to 5 percent error in the calculations.

Utilities that use chlorine dioxide should measure excess chlorine (as FAC) in the generator effluent in addition to the ClO_2^- related species. FAC may appear as false ClO_2 residuals for CT purposes, or result in the formation of chlorinated DBPs if high, relative to the ClO_2 level in the generated mixture. Excess chlorine is defined as:

$$\text{Excess Cl}_2 = \frac{[\text{Cl}_2]}{[\text{ClO}_2] + [\text{ClO}_2^-] + \left(\frac{67.45}{83.45}\right)[\text{ClO}_3^-] \times \frac{70.91}{2 \times 67.45}} \times 100$$

Where: $\frac{70.91}{(2 \times 67.45)}$ = stoichiometric and molecular weight ratio of Cl_2 to ClO_2^- .

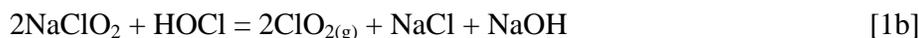
The following represents a summarily simpler equation that substantially resolves the problems of different equipment-specific calibration methods, chlorine-contaminated ClO_2 , or low efficiency conversion of either chlorite- or chlorate-based precursor material.

$$\text{Purity} = \frac{[\text{ClO}_2]}{[\text{ClO}_2] + [\text{FAC}] + [\text{ClO}_2^-] + [\text{ClO}_3^-]} \times 100$$

This practical (weight-based) calculation permits a variety of approved analytical methods (discussed in section 4.6) to be used to assess generator performance on unbiased scientific principles, rather than non-standardized manufacturer specifications.

4.2.3 Methods of Generating Chlorine Dioxide

For potable water application, chlorine dioxide is generated from sodium chlorite solutions. The principal generation reactions that occur in the majority of generators have been known for a long time. Chlorine dioxide can be formed by sodium chlorite reacting with gaseous chlorine ($\text{Cl}_{2(\text{g})}$), hypochlorous acid (HOCl), or hydrochloric acid (HCl). The reactions are:



Reactions [1a], [1b], and [1c] explain how generators can differ even though the same feedstock chemicals are used, and why some should be pH controlled and others are not so dependent on low pH. In most commercial generators, there may be more than one reaction taking place. For example, the formation and action of hypochlorous acid as an intermediate (formed in aqueous solutions of chlorine) often obscures the “overall” reaction for chlorine dioxide production.

Table 4-1 provides information on some types of available commercial generators. Conventional systems react sodium chlorite with either acid, aqueous chlorine, or gaseous chlorine. Emergent technologies identified in Table 4-1 include electrochemical systems, a solid chlorite inert matrix (flow-through gaseous chlorine) and a chlorate-based emerging technology that uses concentrated hydrogen peroxide and sulfuric acid.

Table 4-1. Commercial Chlorine Dioxide Generators

| GENERATOR TYPE | MAIN REACTIONS Reactants, byproducts, key reactions, and chemistry notes | SPECIAL ATTRIBUTES |
|---|--|---|
| ACID-CHLORITE: (Direct Acid System) | $4\text{HCl} + 5\text{NaClO}_2 \rightarrow 4\text{ClO}_{2(\text{aq})} + \text{ClO}_3^-$ <ul style="list-style-type: none"> • Low pH • ClO_3^- possible • Slow reaction rates | Chemical feed pump interlocks required. Production limit ~ 25-30 lb/day. Maximum yield at ~80% efficiency. |
| AQUEOUS CHLORINE- CHLORITE: (Cl_2 gas ejectors with chemical pumps for liquids or booster pump for ejector water). | $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow [\text{HOCl} / \text{HCl}]$ $[\text{HOCl}/\text{HCl}] + \text{NaClO}_2 \rightarrow \text{ClO}_{2(\text{g})} + \text{H}/\text{OCl} + \text{NaOH} + \text{ClO}_3^-$ <ul style="list-style-type: none"> • Low pH • ClO_3^- possible • Relatively slow reaction rates | Excess Cl_2 or acid to neutralize NaOH. Production rates limited to ~ 1000 lb/day. High conversion but yield only 80-92% More corrosive effluent due to low pH (~2.8-3.5). Three chemical systems pump HCl, hypochlorite, chlorite, and dilution water to reaction chamber. |
| RECYCLED AQUEOUS CHLORINE OR "FRENCH LOOP" TM (Saturated Cl_2 solution via a recycling loop prior to mixing with chlorite solution.) | $2\text{HOCl} + 2\text{NaClO}_2 \rightarrow 2\text{ClO}_2 + \text{Cl}_2 + 2\text{NaOH}$ <ul style="list-style-type: none"> • Excess Cl_2 or HCl needed due to NaOH formed. | Concentration of ~3 g/L required for maximum efficiency. Production rate limited to ~ 1000 lb/day. Yield of 92-98% with ~10% excess Cl_2 reported. Highly corrosive to pumps; draw-down calibration needed. Maturation tank required after mixing. |
| GASEOUS CHLORINE- CHLORITE (Gaseous Cl_2 and 25% solution of sodium chlorite; pulled by ejector into the reaction column.) | $\text{Cl}_{2(\text{g})} + \text{NaClO}_{2(\text{aq})} \rightarrow \text{ClO}_{2(\text{aq})}$ <ul style="list-style-type: none"> • Neutral pH • Rapid reaction • Potential scaling in reactor under vacuum due to hardness of feedstock. | Production rates 5-120,000 lb/day. Ejector-based, with no pumps. Motive water is dilution water. Near neutral pH effluent. No excess Cl_2 . Turndown rated at 5-10X with yield of 95-99%. Less than 2% excess Cl_2 . Highly calibrated flow meters with min. line pressure ~ 40 psig needed. |
| GASEOUS CHLORINE- SOLIDS CHLORITE MATRIX (Humidified Cl_2 gas is pulled or pumped through a stable matrix containing solid sodium chlorite.) | $\text{Cl}_{2(\text{g})} + \text{NaClO}_{2(\text{s})} \rightarrow \text{ClO}_{2(\text{g})} + \text{NaCl}$ <ul style="list-style-type: none"> • Rapid reaction rate • New technology | Cl_2 gas diluted with N_2 or filtered air to produce ~8% gaseous ClO_2 stream. Infinite turndown is possible with >99% yield. Maximum rate to ~1200 lb/day per column; ganged to >10,000 lb/day. |
| ELECTROCHEMICAL (Continuous generation of ClO_2 from 25% chlorite solution recycled through electrolyte cell) | $\text{NaClO}_{2(\text{aq})} \rightarrow \text{ClO}_{2(\text{aq})} + \text{e}^-$ <ul style="list-style-type: none"> • New technology | Counter-current chilled water stream accepts gaseous ClO_2 from production cell after it diffuses across the gas permeable membrane. Small one-pass system requires precise flow for power requirements (Coulombs law). |
| ACID/PEROXIDE/CHLORIDE | $2\text{NaClO}_3 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + \text{O}_2 + \text{NaSO}_4 + \text{H}_2\text{O}$ | Uses concentrated H_2O_2 and H_2SO_4 . Downscaled version; Foam binding; Low pH. |

Source: Adapted from Gates, 1998.

4.1.1.1 Commercial Generators

The conventional chlorine-chlorite solution method generates chlorine dioxide in a two-step process. First, chlorine gas is reacted with water to form hypochlorous acid and hydrochloric acid. These

acids then react with sodium chlorite to form chlorine dioxide. The ratio of sodium chlorite to hypochlorous acid should be carefully controlled. Insufficient chlorine feed will result in a large amount of unreacted chlorite. Excess chlorine feed may result in the formation of chlorate ion, which is an oxidation product of chlorine dioxide and not currently regulated.

Acid-Chlorite Solution - Chlorine dioxide can be generated in direct-acidification generators by acidification of sodium chlorite solution. Several stoichiometric reactions have been reported for such processes (Gordon et al., 1972). When chlorine dioxide is generated in this way, hydrochloric acid is generally preferred (Reaction [1c]).

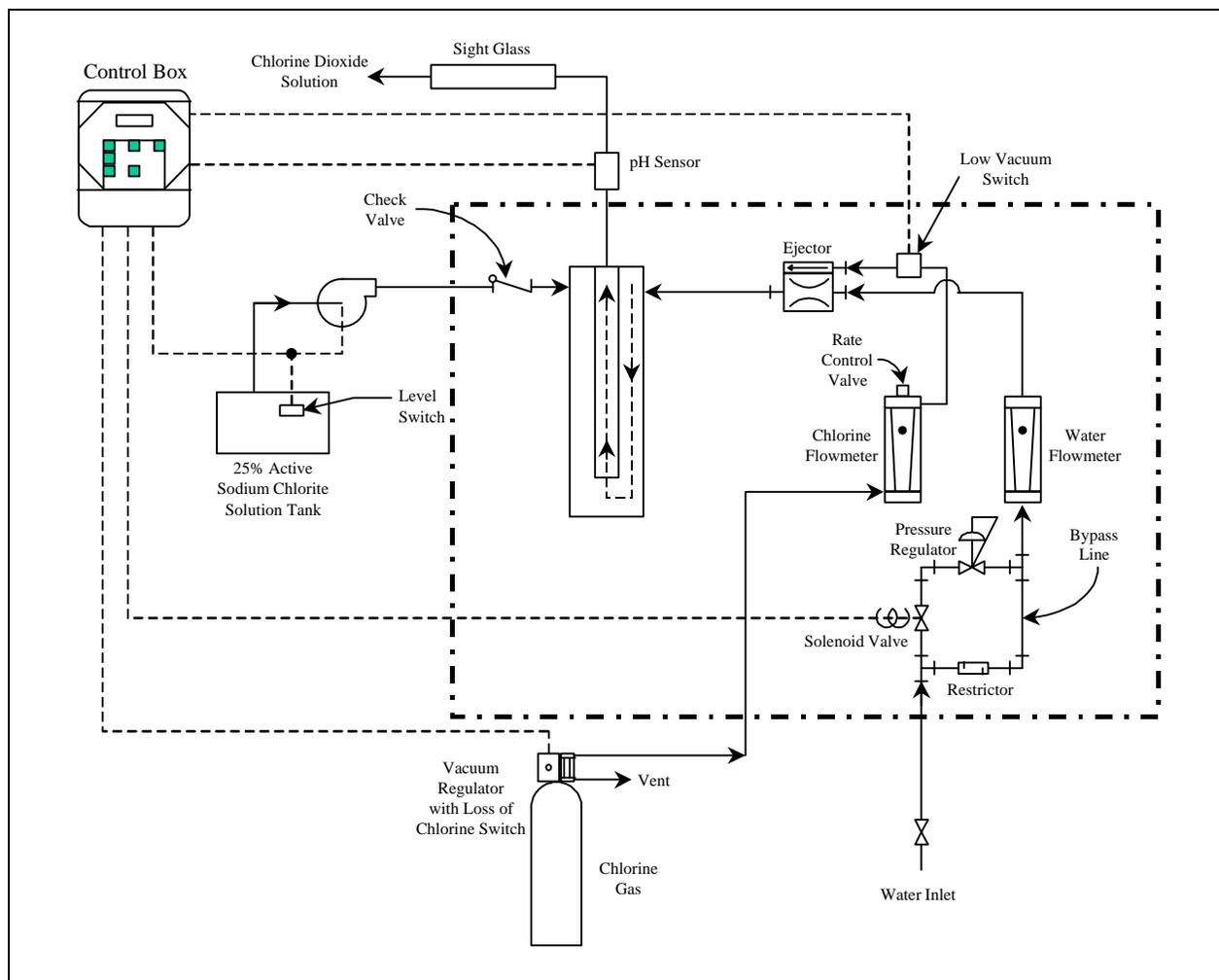
Aqueous Chlorine-Chlorite Solution - Chlorite ion (from dissolved sodium chlorite) will react with hydrochloric acid and hypochlorous acid to form chlorine dioxide in these systems, commonly referred to as conventional systems (Reaction [1b]):

Figure 4-1 shows a typical chlorine dioxide generator using aqueous chlorine-chlorite solution (Demers and Renner, 1992).

If chlorine gas and chlorite ion are allowed to react under ideal conditions (not usually formed in aqueous chlorine type systems), the resulting pH of the effluent may be close to 7. To fully utilize sodium chlorite solution, the more expensive of the two ingredients, excess chlorine is often used. This approach lowers the pH and drives the reaction further toward completion. The reaction is faster than the acid-chlorite solution method, but much slower than the other commercial methods described in the following discussion.

Recycled Aqueous Chlorine or “French Loop”™ - In this aqueous chlorine design, shown in Figure 4-2, chlorine gas is injected into a continuously circulating water loop. This eliminates the need for a great excess of Cl₂ gas to be fed to the generator since the molecular chlorine will dissolve in the feed water, and thus maintain a low pH level of the feed water. Loop-based generators keep chlorine at or above saturation levels. The low pH condition results in high yields of chlorine dioxide (greater than 95 percent at design production rate) (Thompson, 1989). Chlorine in the generator effluent may react with chlorine dioxide to form chlorate if allowed to stand in batch storage too long. The “French Loop” type of generator is more difficult to operate due to system start-up and control of sodium chlorite feed rate (meter pump), chlorine feed rate (rotameter), and the recirculating loop (pump). Newer designs incorporate a second batching tank for continuous aqueous chlorine storage, thus removing many of these startup or recycling difficulties.

Gaseous Chlorine-Chlorite Solution - Sodium chlorite solution can be “vaporized” and reacted under vacuum with molecular gaseous chlorine. This process uses undiluted reactants and is much more rapid than chlorine solution:chlorite solution methods (Pitochelli, 1995). Production rates are more easily scaled up, and some installed systems have reported producing more than 60,000 pounds per day.



Source: Demers and Renner, 1992.

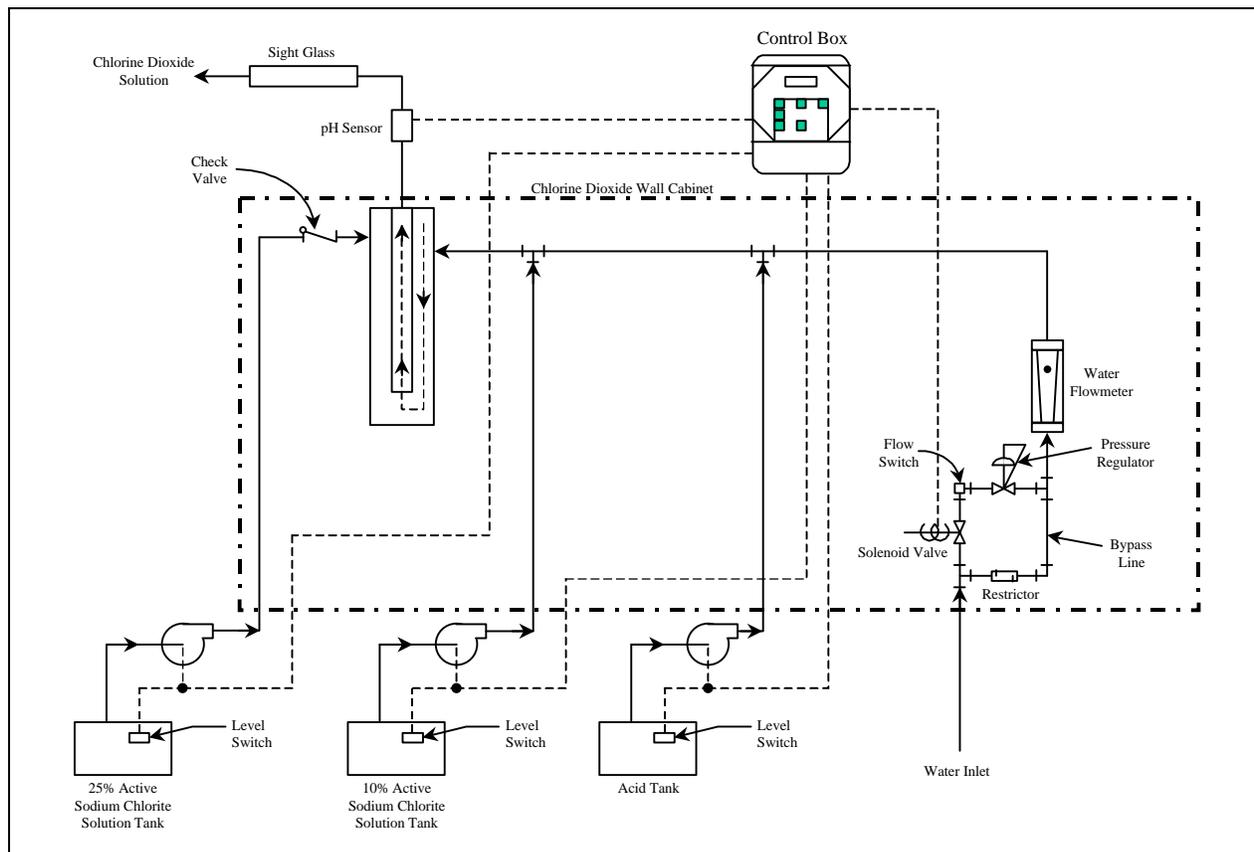
Figure 4-1. Conventional Chlorine Dioxide Generator When Using Chlorine-Chlorite Method

The acid-sodium hypochlorite-sodium chlorite method of generating chlorine dioxide is used when chlorine gas is not available. First, sodium hypochlorite is combined with hydrochloric or another acid to form hypochlorous acid. Sodium chlorite is then added to this reaction mixture to produce chlorine dioxide.

4.1.1.2 pH Effects on Chlorine Dioxide Generation

If hypochlorous acid is formed, one of the byproducts of its reaction with sodium chlorite in solution is sodium hydroxide. Since sodium hydroxide is also a common stabilizer of sodium chlorite feedstock, the resulting pH of the mixture can be too high. A high pH slows the formation of chlorine dioxide and impels less efficient chlorate-forming reactions. This is the same process in which chlorite and hypochlorite ions react in drinking water to form chlorate ion. This neutralizing effect of caustic may be influenced by different stabilizers used in each of the types and sources of

sodium chlorite which are approved for use in drinking water under AWWA Standard B303-95 (AWWA, 1995).



Source: Demers and Renner, 1992.

Figure 4-2. Chlorine Dioxide Generation Using Recycled Aqueous Chlorine Method

In very low pH aqueous chlorine solutions, chlorous acid (and not the chlorite ion) may be directly oxidized to chlorine dioxide as shown in reaction [1d]. At this low pH, gaseous chlorine remains "dissolved" in the water at concentrations higher than the normal occurrence, and allows reaction [1a] to proceed.

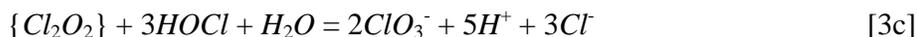


4.1.1.3 Chlorate Byproduct Formation

One of the most undesirable byproducts in generators is the chlorate ion (ClO_3^-). Chlorate production is possible through reactions with the intermediate dimer, $\{\text{Cl}_2\text{O}_2\}$. Rather than the chlorite ion being simply "converted" to chlorine dioxide, reactions [1a] through [1d] can result in the supposed formation of the unstable, unsymmetrical intermediate dimer, $\{\text{Cl}_2\text{O}_2\}$ or $\{\text{Cl}^-\text{ClO}_2\}$ as shown in reaction [2] (Emmenegger and Gordon, 1967).



In some generators that operate with relatively low initial reactant concentrations, a significant amount of chlorate is formed by reactions with $\{Cl_2O_2\}$, as shown in reactions [3a], [3b], and [3c].



Highly acidic (pH <3) reaction mixtures force the degradation of $\{Cl_2O_2\}$ to chlorate rather than chlorine dioxide, as well as the direct oxidation of chlorite to chlorate.

The overall reactions that describe chlorate ion formation are:



and



The following conditions may also produce the chlorate ion:

- Excessively high ratios of Cl_2 gas: ClO_2^- .
- Presence of high concentrations of free chlorine at low pH in aqueous solutions.
- Dilute chlorite solutions held at low pH.
- Base-catalyzed disproportionation of chlorine dioxide at high pH values (pH >11).
- Reaction mixtures that are highly acidic (pH <3).
- An excess of hypochlorous acid will directly oxidize chlorite ions to chlorate ions rather than to chlorine dioxide (independent of the rapid formation of the $\{Cl_2O_2\}$ intermediate).

4.1.4 Generator Design

As hypochlorous acid is formed under acidic conditions, the lowering of optimal concentrations of precursor reactants will also increase chlorate levels in the generator by promoting reaction [3b]. Therefore, if weak precursor feed stocks or high amounts of dilution water are added to the generator, chlorate will be more prevalent (according to reaction [3a]). These limitations explain why generators most often use ~25 percent chlorite solutions and gaseous (or near-saturated aqueous) chlorine. Higher strength solutions of sodium chlorite (e.g., 37 percent) also are more susceptible to crystallization or stratification at ambient temperatures as high as 25°C(78°F).

Due to these dilution effects, some systems function best as "intermittent batch" generators, (that produce high concentrations of chlorine dioxide) rather than as "continuous" generators (that produce lower concentrations (< 1g/L) of chlorine dioxide). The stored solutions are pumped or injected from

the storage tank. Cycling frequently avoids long-term (over 24 hour periods) storage of the generated solution.

Chlorine loop-type systems can obtain high conversion rates if excess chlorine is always present. Excess chlorine permits the molecular chlorine reaction mechanism (described above) to proceed. The low pH of the mixture also minimizes the contribution of OH^- formed via equation [1b] by neutralizing it. These solutions may still be contaminated with excess chlorine needed to drive the conversion of chlorite ion, but not to the same degree as found in simple aqueous chlorine systems when operated under dilute conditions. Chlorine-loop generators run best at high capacity since the chlorite ion is most available in this production mode.

Conventional or acid-enhanced generators produce chlorine dioxide through the intermediate $\{\text{Cl}_2\text{O}_2\}$ as long as relatively high concentrations of reactants (~above 20–30 g/L) are maintained in the reaction chamber prior to dilution. Vapor-phase, recycled loop, and solid chlorite-type generators that minimize dilute aqueous reaction conditions can obtain high efficiencies by preventing any chlorite ion from reacting in the "slower" steps described above. This is accomplished by establishing conditions that force the immediate reaction between chlorite ions and gas-phase or molecular chlorine at a rate hundreds of times faster than the Cl_2 hydrolysis in water. This essentially minimizes the impact of competitive chlorine hydrolysis or acidification on the dominant $[\text{ClO}_2^-:\text{Cl}_2 \text{ gas}]$ mechanism, and prevents the chlorite ion reacting with hypochlorous acid directly.

In all generators, large excess amounts of Cl_2 may result in the over-oxidization of chlorite and directly form chlorate in aqueous solution (reaction [4b]). Precursor chemical feed rates for the generators should always be adjusted to chart settings supplied with generators, notably with the continuous flow, direct gas injection systems. Re-calibration of these systems is sometimes needed on-site if feed stock sodium chlorite is not of the correct strength, or if pre-calibrated flow devices have been replaced.

If aqueous chlorine solutions are mixed with sodium chlorite feed stock solutions, the following mechanisms are dominant, which may affect the formation rates of chlorine dioxide:

- Chlorine gas reacts with water to form hypochlorous and hydrochloric acids, rather than directly with chlorite to form chlorine dioxide. (Water and chlorite both compete for the Cl_2 molecule simultaneously) (see equations [4.1a-c] and Section 6.1.1).
- Chlorate ion is formed (reactions [3a], [3b], and [3c]).
- Only 4 moles of chlorine dioxide are obtained from 5 moles of sodium chlorite via direct acidification (reaction [1c]). This may become important at low pH and high chloride ion levels.

The practical side of all of this is that different generators operate under different optimal conditions. For example, reactor columns should not be continuously flooded with excess water in vapor-phase systems. It is the main reason why dry chlorite-based generator reactor columns should not get wet. Over-dilution of the precursor reactants themselves will lower conversion efficiencies due to the

avored formation of chlorate over chlorine dioxide. Batch-type generation should always be carried out at maximal ClO_2 concentration with appropriate adjustments at the pump (located downstream of the reactor at the batch tank) for dosage or flow. Changes in chlorine dioxide concentrations in the batch tanks would then be minimized, and pump calibration does not need to include a broad range of chlorine dioxide levels. For the newer gas chlorine generators using dry sodium chlorite in an inert matrix, small amounts of humidifying water in the mixture do not interfere significantly with the simple gaseous $\text{Cl}_2:\text{ClO}_2^-$ reaction. These small traces of water allow for continuous exposure of ClO_2^- on the inert surfaces within the reactor column.

Chlorine dioxide generators are relatively simple mixing chambers. The reactors are frequently filled with media (Teflon™ chips, ceramic or raschig rings) to generate hydraulic turbulence for mixing. A sample petcock valve on the discharge side of the generator is desirable to allow for monitoring of the generation process.

The *Recommended Standards for Water Works* (GLUMRB, 1992) and drinking water design textbooks such as *Unit Processes in Drinking Water Treatment* by Masschelein (1992) are excellent sources for chlorine dioxide generation design criteria and application.

4.1.5 Chemical Feed Systems

Fiberglass Reinforced vinyl ester Plastic (FRP) or High Density Linear Polyethylene (HDLPE) tanks with no internal insulation or heat probes are recommended for bulk storage of 25 to 38 percent solution sodium chlorite. Nozzles should include truck unloading vents and local level and temperature indication. Transfer pumps should be centrifugal with 316 stainless steel, fiberglass, Hypalon™, wetted Teflon™ parts, or epoxy resins. The pump should be sealless or equipped with double mechanical seals. The recommended piping material is CPVC, although vinyl ester or Teflon™ piping systems are acceptable. Carbon steel and stainless steel piping systems are not recommended.

Depending upon system size, sodium chlorite can be purchased in 55-gallon drums, 275-gallon non-returnable totes, or in bulk quantities. A 30-day storage supply of sodium chlorite can easily be met for most small systems by using 55-gallon drums. A 55-gallon drum weighs approximately 600 lbs. Equipment should be provided such that one person can easily handle a drum. All gaseous chlorine or hypochlorite solution-related plumbing should follow Chlorine Institute directives.

Storage and chlorine dioxide systems typically include the following:

- Storage and feeding in a designated space.
- Use of non-combustible materials such as concrete for construction.
- Storage in clean, closed, non-translucent containers. Exposure to sunlight, UV light, or excessive heat will reduce product strength.

- Avoid storage and handling of combustible or reactive materials, such as acids or organic materials, in the sodium chlorite area.
- Secondary containment for storage and handling areas to handle the worse case spill with sumps provided to facilitate recovery.
- A water supply near storage and handling areas for cleanup.
- Inert material should be used in contact with the strong oxidizing and/or acid solutions involved in chlorine dioxide systems.
- Storage tanks with vents to outside.
- Adequate ventilation and air monitoring.
- Gas masks and first aid kits outside of the chemical areas.
- Reactor with glass view ports if it is not made of transparent material.
- Flow monitoring on all chemical feed lines, dilution water lines, and chlorine dioxide solution lines.
- Dilution water should not be excessively hard in order to avoid calcium deposits and should be near neutral pH.
- On-site and frequent testing of chemical solution strengths should be practiced to achieve efficient process control.
- Air contact with chlorine dioxide solutions should be controlled to limit the potential for explosive concentrations possibly building up within the generator. Chlorine dioxide concentrations in air higher than 8 to 10 percent volume should be avoided. Two methods can be applied: operation under vacuum or storage under higher positive pressure (45 to 75 psig) to prevent buildup of gas-phase ClO_2 in the head space. Bulk storage (batch) tanks containing ClO_2 should be suitably vented to atmosphere.

Sodium chlorite solution feed pumps are commonly diaphragm-metering pumps for liquid feed rate control. If centrifugal pumps are used, the only acceptable packing material is Teflon. If lubrication is needed, minimum quantities of fire-resistant lubricants should be used. Pump motors should be totally enclosed, fan-cooled (TEFC) with sealed-for-life bearings. Couplings should be of the greaseless type. Water lines for mechanical seals should have a pressure gauge and throttling valve on the outlet side. Visual means should be provided to verify adequate water flow. Each pump should include a calibration chamber.

Pipes carrying sodium chlorite should be provided sufficient support to minimize risk of overstressing joints. Flexible connections to pumps should also be provided to minimize risk of vibration damage. Pipe should be sloped to drainage points and valved hose connections provided at strategic points for efficient flushing and draining. Service water for flushing feed lines should be introduced only through temporarily connected hoses protected by a backflow preventer. Service water lines should include check valves. Hose connections from service water lines should have a vent valve to release pressure before the hose is disconnected after use.

Flows are frequently measured with magnetic flow meters, mass flow meters, or rotameters for precise control. Provisions should always be made for back-flow prevention. Sodium chlorite is extremely reactive, especially in the dry form, and care should be taken to protect against potentially explosive conditions.

Chlorine dioxide solution concentrations below about 10 g/L will not produce sufficiently high vapor pressures to present an explosion hazard under most ambient conditions of temperature and pressure. In water treatment, chlorine dioxide solution concentrations rarely exceed 4 g/L for temperatures less than 40°C, and treatment levels generally range from 0.1 to 5.0 mg/L. If temperatures exceed 50°C, storage tanks should be suitably vented due to the higher levels of ClO₂ possible. As cold service/potable water is typically used as generator dilution water, these conditions are rarely encountered.

4.1.6 Generator Power Requirements

Generator power requirements are similar to those for chlorination systems. For all generators (20 to 12,000 lb/day) power can be supplied from 120 VAC single phase, to 480 VAC three phase. Power demand will vary based upon make-up water pressure available to operate the venturi. Fractional horsepower metering pumps are required, based upon system configuration.

4.3 Primary Uses and Points of Application for Chlorine Dioxide

The calculation of CT for chlorine dioxide is similar to other disinfectants, with accurate determinations of residual concentrations being a prerequisite for effective disinfection. Primary disinfectant credit is achieved by the residual concentration and the effective contact time. It has been found in practice that because of the volatile nature of the gas, chlorine dioxide works extremely well in plug flow reactors such as pipe lines. It can be easily removed from dilute aqueous solution by turbulent aeration in rapid mix tanks or purging in recarbonation basins. CT credits should not be expected through a filter because the likelihood that no residual remains in the filtered water (DeMers and Renner, 1992). For post CT disinfection credit, chlorine dioxide can be added before clearwells or transfer pipelines. Ample sampling points should be included to allow close monitoring of residual concentrations. It is well known that chlorine dioxide is commonly destroyed by UV in basins exposed to sunlight or bright fluorescent lights. Therefore, protective design elements should be incorporated if such exposure is anticipated.

4.3.1 Disinfection

Before chlorine dioxide is selected for use as a primary disinfectant an oxidant demand study should be completed. Ideally, this study should consider the seasonal variations in water quality, temperature, and application points. Table 4-2 shows typical results for a single sample of a demand study completed on a surface water source.

The MRDL for chlorine dioxide is 0.8 mg/L and the MCL for chlorite is 1.0 mg/L per the D/DBP rule. This means that if the oxidant demand is greater than about 1.4 mg/L, chlorine dioxide may not be used as a disinfectant because the chlorite/chlorate ions byproduct, might exceed the maximum level allowed, unless inorganic byproducts (e.g., chlorite) are subsequently removed. There are numerous means to reduce excessive chlorite levels prior to chlorination in conventional water plants.

Table 4-2. Surface Water Chlorine Dioxide Demand Study Results

| Dose (mg/L) | Time (min) | ClO ₂ (mg/L) | ClO ₂ ⁻ (mg/L) | ClO ₃ ⁻ (mg/L) |
|-------------|------------|-------------------------|--------------------------------------|--------------------------------------|
| 1.4 | 3 | 0.47 | 0.76 | 0.05 |
| | 10 | 0.30 | 0.98 | 0.06 |
| | 20 | 0.23 | 1.08 | 0.07 |
| | 40 | 0.16 | 1.11 | 0.07 |
| | 60 | 0.11 | 1.11 | 0.07 |

Source: DeMers and Renner, 1992.

Note: *Raw water sample, 23°C, 8.5 pH.

Typical dosages of chlorine dioxide used as a disinfectant in drinking water treatment range from 0.07 to 2.0 mg/L. For plants using chlorine dioxide, median concentrations of chlorite and chlorate were found to be 0.24 and 0.20 mg/L, respectively in an EPA survey (USEPA, 1998), the standard is 1.0 mg/L.

4.3.2 Taste and Odor Control

A common application of chlorine dioxide in drinking water in the United States has been for control of tastes and odors associated with algae and decaying vegetation. Chlorine dioxide is also effective in destroying taste and odor producing phenolic compounds. The recommended location for application of chlorine dioxide for this purpose will depend on raw water quality, the type of treatment plant and any other purposes for chlorine dioxide addition. In conventional treatment plants, it is recommended that chlorine dioxide be added near the end of or following, the sedimentation basin. If the raw water turbidity is low (for example, less than 10 NTU), chlorine dioxide can be added at the beginning of the plant. Some utilities follow this practice because chlorine dioxide is effective in controlling algae growth in flocculation and sedimentation basins that are exposed to sunlight (DeMers and Renner, 1992). Such application during periods of darkness may be more successful for nuisance algae control.

4.3.3 Oxidation of Iron and Manganese

Chlorine dioxide can be used to oxidize both iron and manganese. Chlorine dioxide reacts with the soluble forms of iron and manganese to form precipitates that can be removed through sedimentation and filtration. Chlorine dioxide reduces to chlorite ion in this reaction (Knocke et al., 1993). About 1.2 mg/L of chlorine dioxide is required to remove 1.0 mg/L of iron, and 2.5 mg/L of chlorine dioxide are required to remove 1.0 mg/L of manganese. For high concentrations of iron and manganese, the use of chlorine dioxide is limited to the 1.0 mg/L chlorite/chlorate ion byproduct, as

described before. Ferrous iron may be added prior to conventional coagulation to chemically reduce chlorite ion (to chloride ion) and improve the overall flocculation process.

4.4 Pathogen Inactivation and Disinfection Efficacy

For water treatment, chlorine dioxide has several advantages over chlorine and other disinfectants. In contrast to chlorine, chlorine dioxide remains in its molecular form in the pH range typically found in natural waters (Roberts et al., 1980). Chlorine dioxide is a strong oxidant and disinfectant. Its disinfection mechanisms are not well understood, but appear to vary by type of microorganism

4.4.1 Inactivation Mechanisms

Gross physical damage to bacterial cells or viral capsids has not been observed at the low concentrations of chlorine dioxide typically used to disinfect drinking water. Therefore, studies have focused primarily on two more subtle mechanisms that lead to the inactivation of microorganisms: determining specific chemical reactions between chlorine dioxide and biomolecules; and observing the effect chlorine dioxide has on physiological functions.

In the first disinfection mechanism, chlorine dioxide reacts readily with amino acids cysteine, tryptophan, and tyrosine, but not with viral ribonucleic acid (RNA) (Noss et al., 1983; Olivier et al., 1985). From this research, it was concluded that chlorine dioxide inactivated viruses by altering the viral capsid proteins. However, chlorine dioxide reacts with poliovirus RNA and impairs RNA synthesis (Alvarez and O'Brien, 1982). It has also been shown that chlorine dioxide reacts with free fatty acids (Ghandbari et al., 1983). At this time, it is unclear whether the primary mode of inactivation for chlorine dioxide lies in the peripheral structures or nucleic acids. Perhaps reactions in both regions contribute to pathogen inactivation.

The second type of disinfection mechanism focuses on the effect of chlorine dioxide on physiological functions. It has been suggested that the primary mechanism for inactivation was the disruption of protein synthesis (Bernarde et al., 1967a). However, later studies reported the inhibition of protein synthesis may not be the primary inactivation mechanism (Roller et al., 1980). A more recent study reported that chlorine dioxide disrupted the permeability of the outer membrane (Aieta and Berg, 1986). The results of this study were supported by the findings of Olivieri et al. (1985) and Ghandbari et al. (1983), which found that the outer membrane proteins and lipids were sufficiently altered by chlorine dioxide to increase permeability.

4.4.2 Environmental Effects

Studies have been performed to determine the effect of pH, temperature, and suspended matter on the disinfection efficiency of chlorine dioxide. Following is a summary of the effects these parameters have on pathogen inactivation.

4.4.2.1 pH

In comparison to chlorine, studies have shown that pH has much less effect on pathogen inactivation for viruses and cysts with chlorine dioxide than with chlorine in the pH range of 6 to 8.5. Unlike chlorine, studies on chlorine dioxide have shown the degree of inactivation of poliovirus 1 (Scarpino et al., 1979) and *Naegleria gruberi* cysts (Chen et al., 1984) increase as the pH increases.

The results of studies on *E. coli* inactivation are inconclusive. It has been found that the degree of inactivation by chlorine dioxide increases as pH increases (Bernarde et al., 1967a). However, an earlier study found that the bactericidal activity of chlorine dioxide was not affected by pH values in the range of 6.0 to 10.0 (Ridenour and Ingols, 1947). A recent study on *Cryptosporidium* found that inactivation of oocysts using chlorine dioxide occurred more rapidly at a pH of 8.0 than 6.0. At a similar CT value, the level of inactivation at pH of 8.0 was approximately twice that at a pH of 6.0 (Le Chevallier et al., 1997). Another study found that chlorine dioxide efficacy increases for *Giardia* inactivation at higher pH levels and that this may be the result of chemical or physical changes in *Giardia* cyst structure rather than pH effects on chlorine dioxide disproportionation (Liyanage et al., 1997). More research is needed to further clarify how pH impacts the effectiveness of chlorine dioxide.

4.4.2.2 Temperature

Similar to chlorine, the disinfection efficiency of chlorine dioxide decreases as temperature decreases (Ridenour and Ingols, 1947). This finding is supported by the data from Chen et al. (1984) shown in Figure 4-3 for the inactivation of *Naegleria gruberi* cysts. The curve shows the CT required to achieve 99 percent inactivation for temperatures between 5 and 30°C.

In a more recent study, LeChevallier et al. (1997) found that reducing the temperature from 20°C to 10°C reduced the disinfection effectiveness of chlorine dioxide on *Cryptosporidium* by 40 percent, which is similar to previous results for *Giardia* and viruses. Gregory et al. (1998) found that even under the most favorable conditions (i.e., at a pH of 8.5), required doses to achieve 2-log *Cryptosporidium* inactivation do not appear to be a feasible alternative, requiring doses of more than 3.0 mg/L with a 60 minute detention time. At neutral pH levels, the required doses may be more than 20 mg/L.

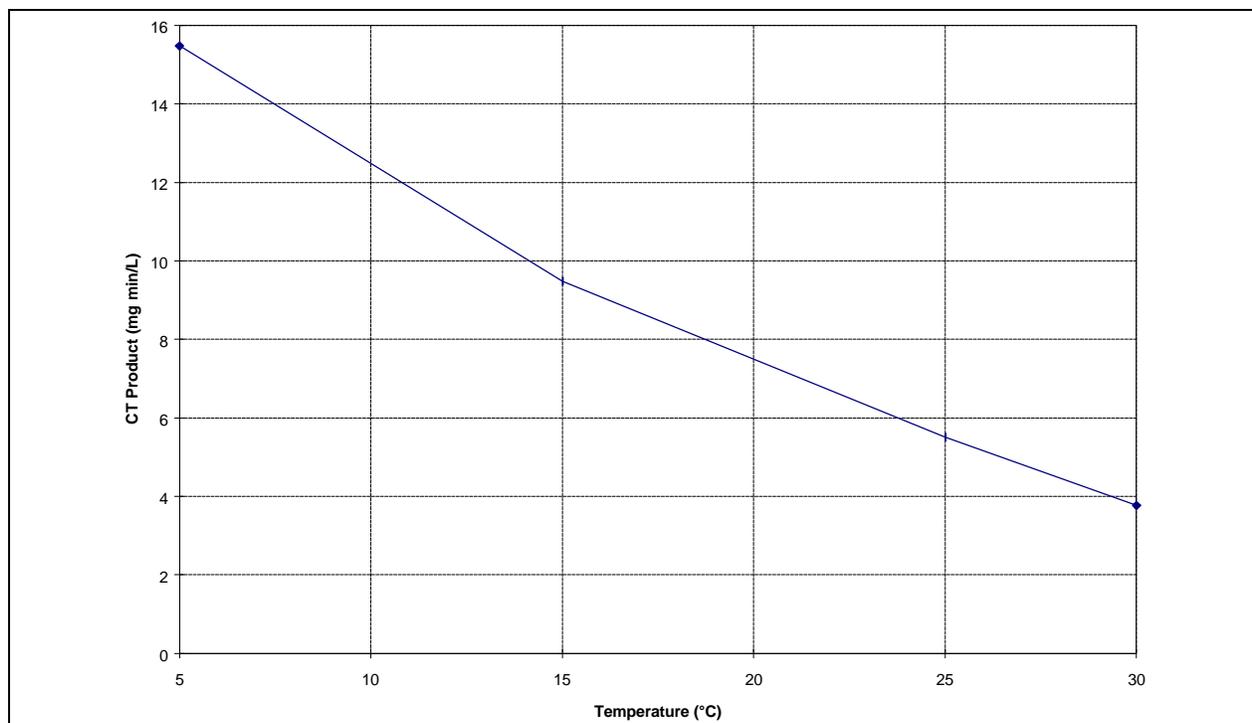


Figure 4-3. Effect of Temperature on *N. Gruberi* Cyst Inactivation at pH 7

4.4.2.3 Suspended Matter

Suspended matter and pathogen aggregation affect the disinfection efficiency of chlorine dioxide. Protection from chlorine dioxide inactivation due to bentonite was determined to be approximately 11 percent for turbidities equal to or less than 5 NTUs and 25 percent for turbidities between 5 and 17 NTUs (Chen et al., 1984).

Laboratory studies of poliovirus 1 preparations containing mostly viral aggregates took 2.7 times longer to inactivate with chlorine dioxide than single state viruses (Brigano et al., 1978). Chen et al. (1984) also found that clumps of *Naegleria gruberi* cysts were more resistant to chlorine dioxide than unclumped cysts or clumps of smaller size.

4.4.3 Disinfection Efficacy

Several investigations have been made to determine the germicidal efficiency of chlorine dioxide since its introduction in 1944, as a drinking water disinfectant. Most of the investigations were carried out as a comparison to chlorine; some studies have compared chlorine dioxide and ozone. Chloride dioxide is a more effective disinfectant than chlorine but is less effective than ozone.

4.4.3.1 Bacteria Inactivation

Quantitative data were published as early as the 1940s demonstrating the efficacy of chlorine dioxide as a bactericide. In general, chlorine dioxide has been determined to be equal to or superior to chlorine on a mass-dose basis. It was demonstrated that even in the presence of suspended matter,

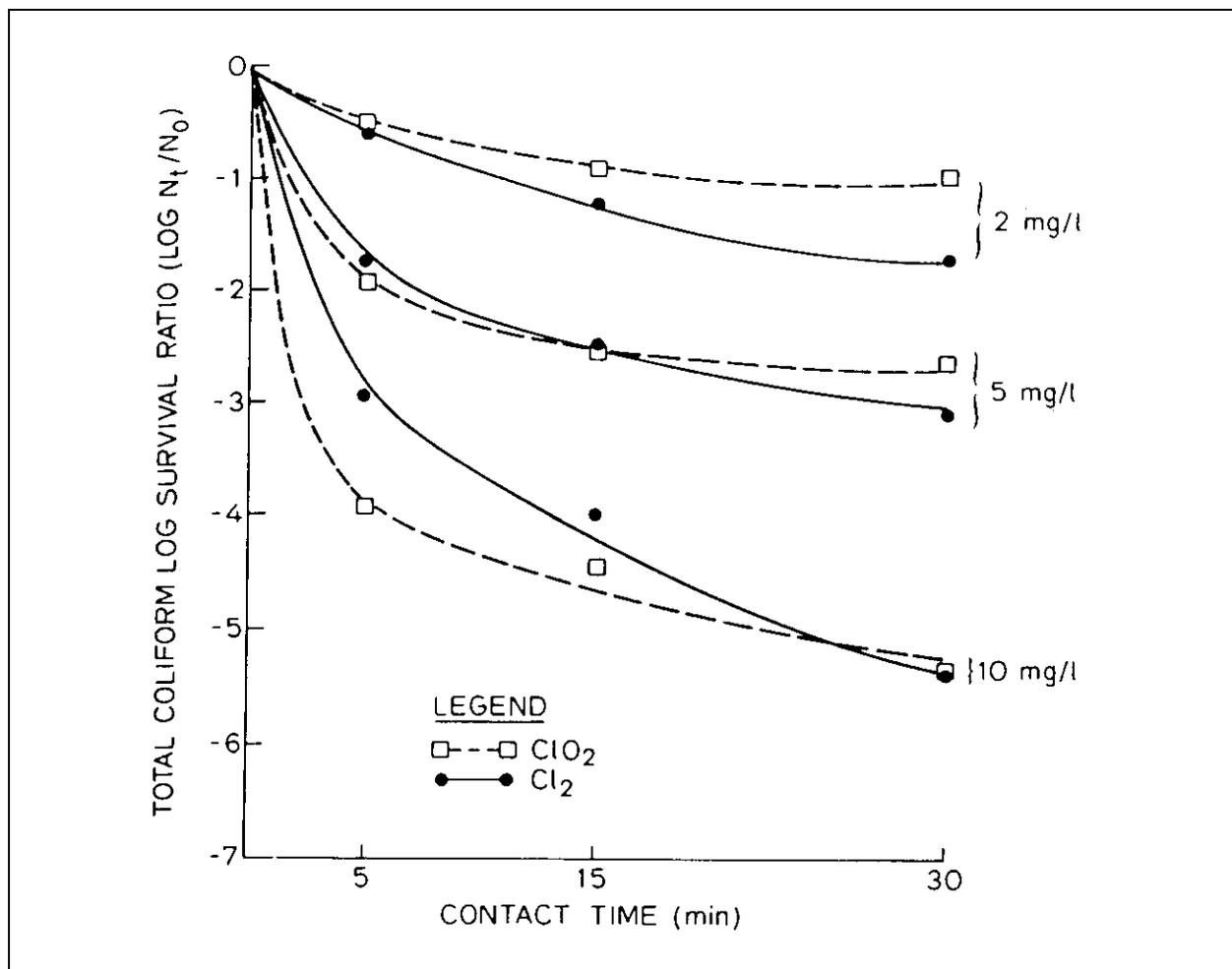
chlorine dioxide was effective against *E. coli* and *Bacillus anthracoides* at dosages in the range of 1 to 5 mg/L (Trakhtman, 1949). Ridenour and Armbruster (1949) reported that an orthotolidine arsenite (OTA) chlorine dioxide residual of less than 1 mg/L was effective against *Eberthella typhosa*, *Shigella dysenteriae*, and *Salmonella paratyphi* B. Under similar pH and temperature slightly greater OTA residuals were required for the inactivation of *Pseudomonas aeruginosa* and *Staphylococcus aureus*.

Chlorine dioxide was shown to be more effective than chlorine at inactivating *B. subtilis*, *B. mesentericus*, and *B. megatherium* spores (Ridenour et al., 1949). Moreover, chlorine dioxide was shown to be just as effective or more effective than chlorine at inactivating *Salmonella typhosa* and *S. paratyphi* (Bedulivich et al., 1954).

In the early 1960s several important contributions were made by Bernarde et al. (1967a and 1967b). Chlorine dioxide was found to be more effective than chlorine at disinfecting sewage effluent and the rate of inactivation was found to be rapid.

A comprehensive investigation of chlorine dioxide as disinfectant was performed by Roberts et al. (1980). The investigation was performed using secondary effluents from three different wastewater treatment plants. One of the objectives was to determine the relationships between dosages and contact times and bactericidal efficiency. Dosages were compared for 2, 5, and 10 mg/L of chlorine dioxide and chlorine. The contact times selected were 5, 15 and 30 minutes. Results of the investigation are shown in Figure 4-4. As shown, chlorine dioxide demonstrated a more rapid coliform inactivation than chlorine at the shortest contact time of 5 minutes and higher concentrations. However, after 30 minutes of contact time, chlorine dioxide was equal or slightly less efficient than chlorine as a bactericide.

Oliveri et al. (1984) studied the effectiveness of chlorine dioxide (and chlorine) residuals in inactivating total coliform and f2 coliphage virus in sewage introduced to a water distribution system. Initial chlorine dioxide residuals between 0.85 and 0.95 mg/L resulted in an average 2.8-log inactivation of the total coliform and an average 4.4-log inactivation of the f2 coliphage virus, over a contact time of 240 minutes.



Source: Roberts et al., 1980.

Figure 4-4. Comparison of Germicidal Efficiency of Chlorine Dioxide and Chlorine

4.4.3.2 Protozoa Inactivation

The disinfection efficiency of chlorine dioxide has been shown to be equal to or greater than chlorine for *Giardia* inactivation. Based on a 60 minute contact time, chlorine dioxide doses in the range of 1.5 to 2 mg/L are capable of providing a 3-log *Giardia* inactivation at 1°C to 25°C and pHs of 6 and 9 (Hofmann et al., 1997). Depending on the temperature and pH, *Cryptosporidium* has been found to be 8 to 16 times more resistant to chlorine dioxide than *Giardia* (Hofmann et al., 1997). Although some *Cryptosporidium* oocysts remained viable, one group of researchers found that a 30-minute contact time with 0.22 mg/L chlorine dioxide could significantly reduce oocyst infectivity (Peeters et al., 1989). In contrast, other researchers have found that CT values in the range of 60 to 80 mg·min/L were necessary to provide 1- to 1.5-log inactivation (Korich et al., 1990; Ransome et al., 1993). Finch et al. (1995) reported that the CT values for 1-log inactivation was in the range of 27 to 30 mg·min/L. For 2-log inactivation, the CT value was approximately 40 mg·min/L, and 70 mg·min/L for 3-log inactivation. Finch et al. (1997) found 3-log inactivation of *Cryptosporidium* oocysts with initial chlorine dioxide residual concentrations of 2.7 and 3.3 mg/L for contact times of 120 minutes, at pH of 8.0 and a temperature of 22°C.

Both Chen et al. (1985) and Sproul et al. (1983) have investigated the inactivation of *Naegleria gruberi* cysts by chlorine dioxide. Both studies concluded that chlorine dioxide is an excellent disinfectant against cysts and that chlorine dioxide is better than or equal to chlorine in terms of inactivation. Chlorine dioxide was found to be superior to chlorine at higher pHs. However, the authors cautioned that the CT required for 2-log inactivation was much higher than normally employed for water treatment at that time.

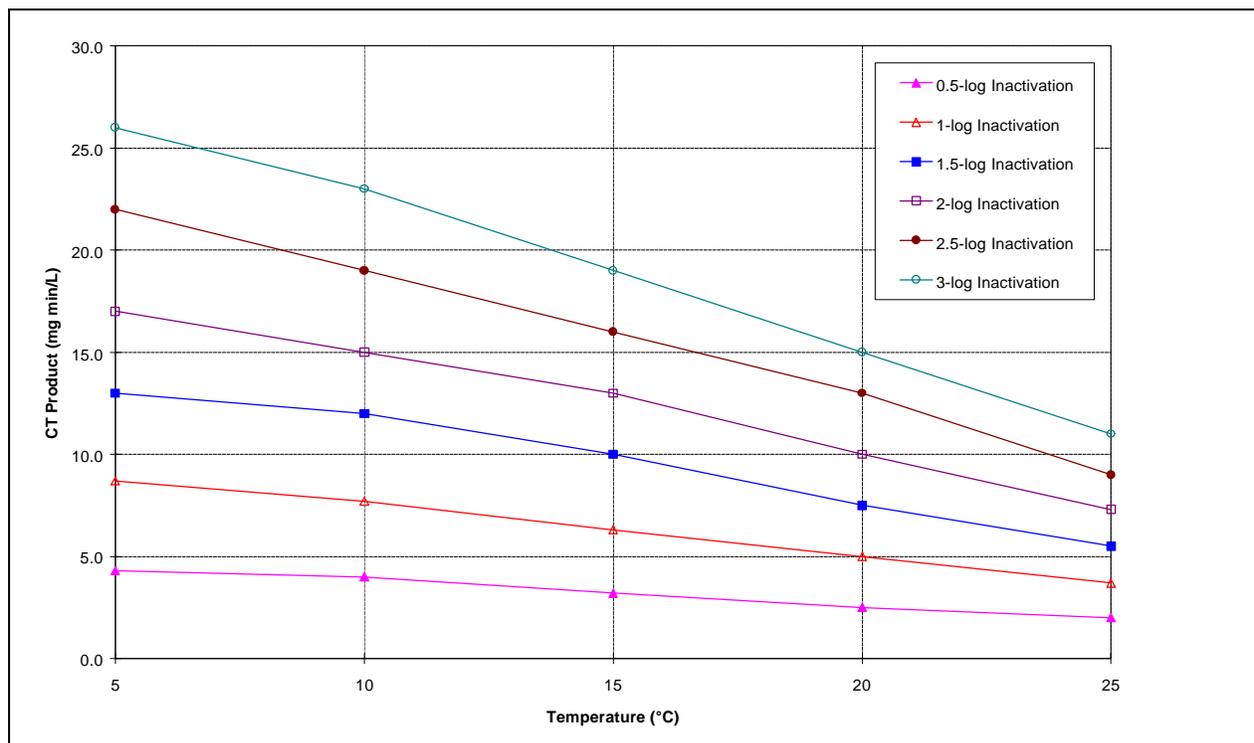
4.4.3.3 Virus Inactivation

Chlorine dioxide has been shown to be an effective viricide. Laboratory studies have shown that inactivation efficiency improves when viruses are in a single state rather than clumped. It was reported in 1946 that chlorine dioxide inactivated *Poliomyelitis* (Ridenour and Ingols, 1946). This investigation also showed that chlorine dioxide and free chlorine yielded similar results. Other studies have verified these findings for poliovirus 1 (Cronier et al., 1978) and *Coxsackie* virus A9 (Scarpino, 1979). At greater than neutral pHs (where hypochlorite ion is the predominant species) chlorine dioxide has been found to be superior to chlorine in the inactivation of numerous viruses such as echovirus 7, coxsackie virus B3, and sendai virus (Smith and McVey, 1973). Sobsey (1998) determined CT values based on a study of Hepatitis A virus, strain HM 175. The study found 4-log inactivation levels are obtainable at CT values of less than 35 at 5°C and less than 10 at a temperature of 25°C.

4.4.3.4 CT Values

Chlorine dioxide is regarded as a strong disinfectant that is effective at inactivating bacterial, viral, and protozoan pathogens. CT values for *Giardia* and virus inactivation are shown in Figure 4-5 and Figure 4-6, respectively (AWWA, 1991).

CT values shown in Figure 4-5 are based on disinfection studies using in vitro excystation of *Giardia muris*. Average CT values for 2 log removal were extrapolated using first order kinetics and multiplied by a safety factor of 1.5 to obtain the CT values for other log removal CT values. Due to the limited amount of data available at pH values other than 7, the same CT values are used for all pHs. Because chlorine dioxide is more effective at a pH 9 than at a pH of 7, the CT values shown in Figure 4-5 are more conservative for higher pHs than for lower pHs. A lower safety factor was used to derive the CT values for chlorine dioxide than for ozone due to the fact that the chlorine dioxide values were derived from *Giardia muris* studies, which are more resistant than *Giardia lamblia*.

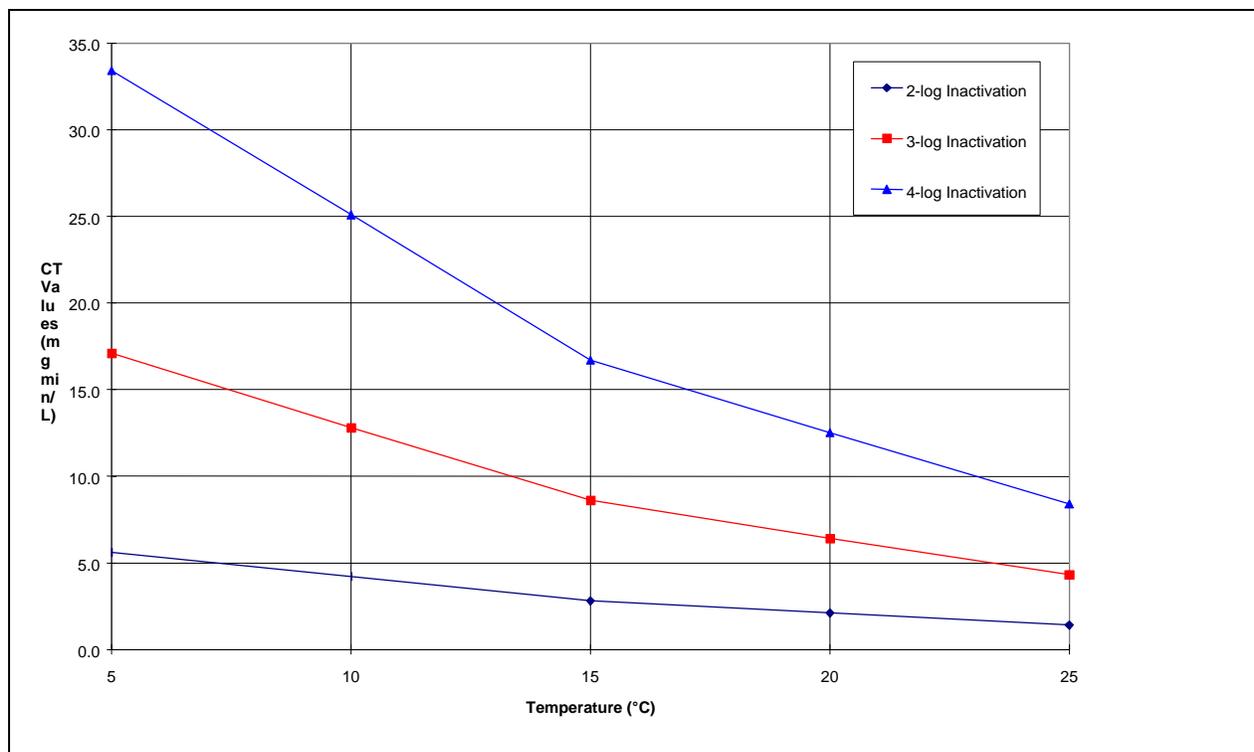


Source: AWWA, 1991.

Figure 4-5. CT Values for Inactivation of *Giardia* Cysts by Chlorine Dioxide

CT values shown in Figure 4-6 were obtained by applying a safety factor 2 to the average CT values derived from the studies on hepatitis A virus, strain HM 175 (Sobsey, 1988). CT values at temperatures other than 5°C were derived by applying a twofold decrease for every 10°C increase in temperature.

Figure 4-7 and Figure 4-8 show the relationship between CT products and log inactivation of *Cryptosporidium* at 20 and 10°C, respectively, and pHs of 6 and 8. CT values shown in Figure 4-7 and Figure 4-8 indicate that oocysts were more rapidly inactivated at pH 8 than 6 and that temperature does impact the disinfection efficiency of chlorine dioxide. Reducing the temperature from 20 to 10°C reduced the disinfection effectiveness by 40 percent. Finch (1997) is studying *Cryptosporidium* inactivation under laboratory conditions using a variety of different disinfectants, one of which is chloride dioxide.



Source: AWWA, 1991.

Figure 4-6. CT Values for Inactivation of Viruses by Chlorine Dioxide

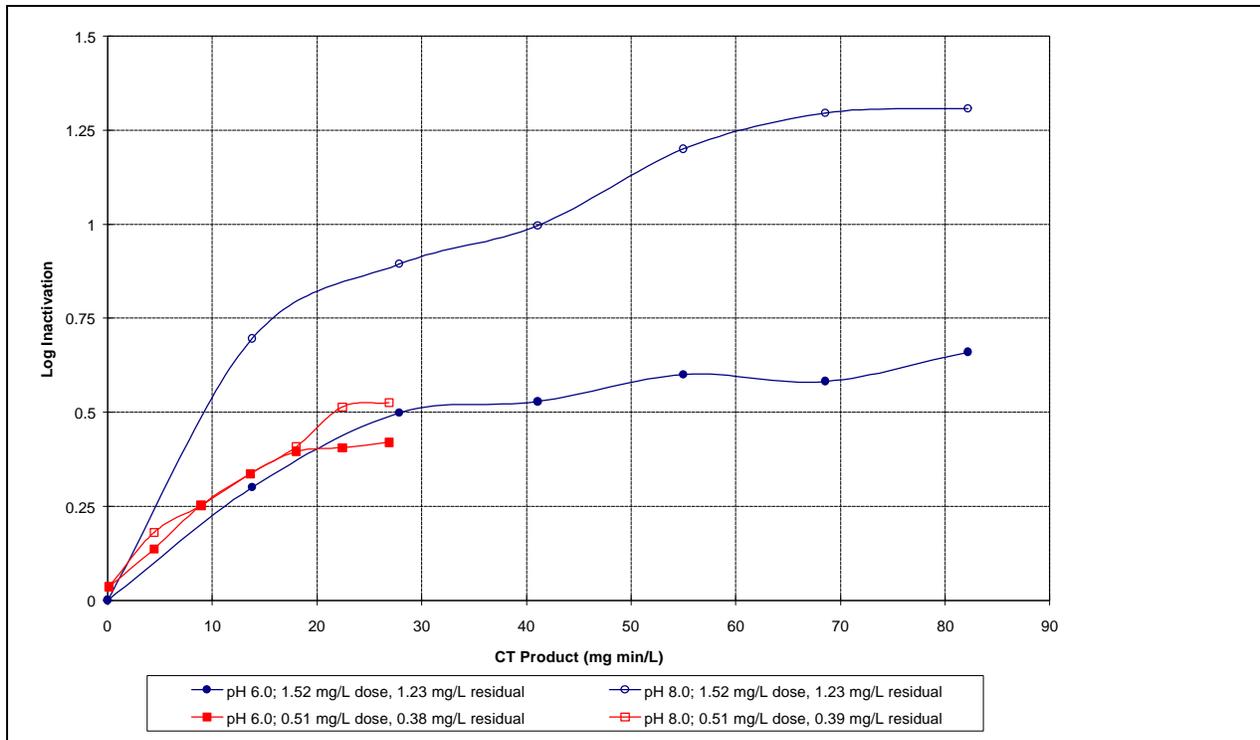
4.5 Chlorine Dioxide Disinfection Byproducts

Byproducts from the use of chlorine dioxide include chlorite, chlorate, and organic DBPs. This section discusses the formation of these byproducts and methods to reduce or remove these DBPs. The use of chlorine dioxide aids in reducing the formation of TTHMs and HAAs by oxidizing precursors, and by allowing the point of chlorination to be moved farther downstream in the plant after coagulation, sedimentation, and filtration have reduced the quantity of NOM.

4.5.1 Production of Chlorite and Chlorate

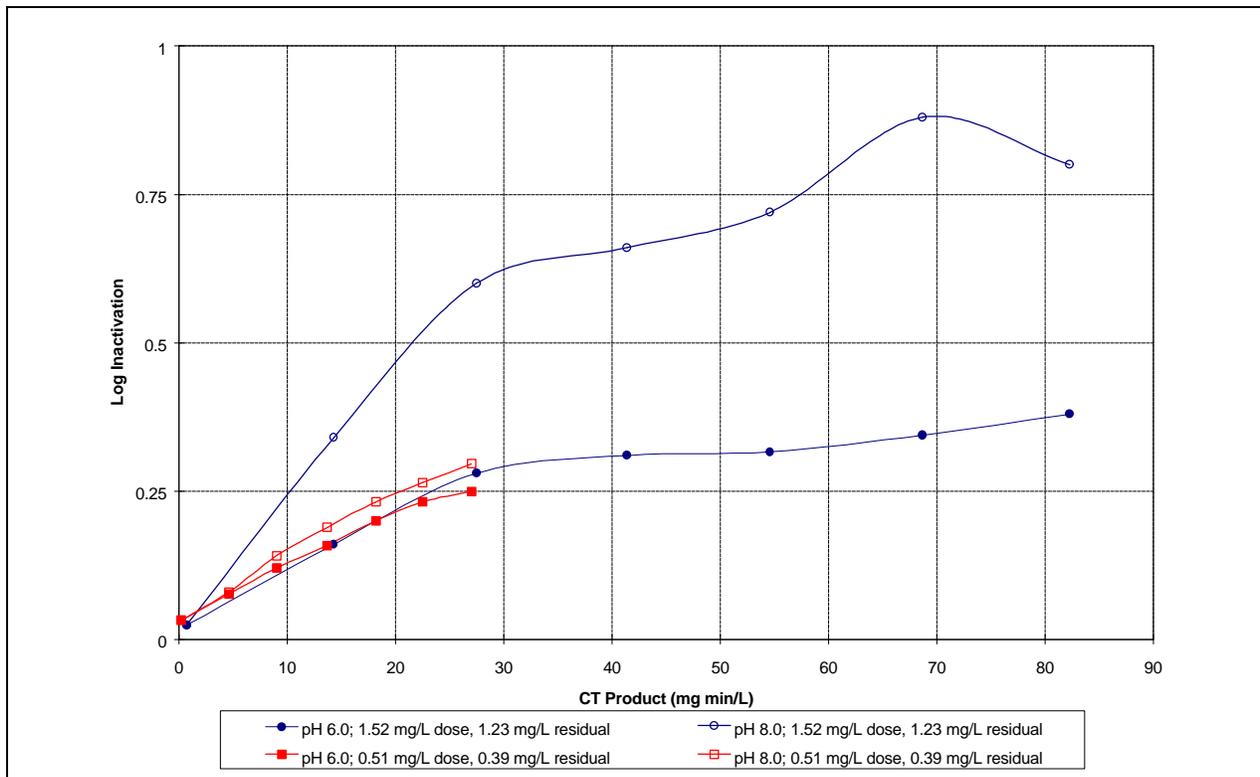
Chlorite and chlorate are produced in varying ratios as endproducts during chlorine dioxide treatment and subsequent degradation. The primary factors affecting the concentrations of chlorine dioxide, chlorite, and chlorate in finished drinking water involve:

- Dosage applied/oxidant demand ratio.
- Blending ratios of sodium chlorite and chlorine during the chlorine dioxide generation process.
- Exposure of water containing chlorine dioxide to sunlight.



Source: LeChevallier et al., 1996.

Figure 4-7. *C. parvum* Inactivation by Chlorine Dioxide at 20°C



Source: LeChevallier et al., 1996.

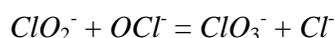
Figure 4-8. *C. parvum* Inactivation by Chlorine Dioxide at 10°C

- Reactions between chlorine and chlorite if free chlorine is used for distribution system residual maintenance.
- Levels of chlorate in sodium chlorite feedstock.

Incomplete reaction or non-stoichiometric addition of the sodium chlorite and chlorine reactants can result in unreacted chlorite in the chlorine dioxide feed stream. Dilute chlorine dioxide solutions are stable under low or zero oxidant-demand conditions. The quantity of chlorate produced during the chlorine dioxide generation process is greater with excess chlorine addition. Likewise, a low or high pH can increase the quantity of chlorate during the chlorine dioxide generation process. See Section 4.2, "Generation," for a detailed discussion of the chemistry of chlorine dioxide generation.

Numerous inorganic and biological materials found in raw water will react with chlorine dioxide (Noack and Doerr, 1977). Chloride (Cl^-) and chlorite (ClO_2^-) ions are the dominant degradation species arising from these reactions, although chlorate (ClO_3^-) can appear for a variety of reasons when chlorine dioxide is used (Gordon et al., 1990; Werdehoff and Singer, 1987). The immediate redox reactions with natural organic matter play the dominant role in decay of chlorine dioxide into chlorite in drinking water (Werdehoff and Singer, 1987). Chlorite ion is generally the primary product of chlorine dioxide reduction. The distribution of chlorite and chlorate is influenced by pH and sunlight. Approximately 50 to 70 percent of the chlorine dioxide consumed by oxidation reactions is converted to chlorite under conditions typical in water treatment (Rav-Acha et al., 1984; Werdehoff and Singer, 1987). The application of 2 mg/L chlorine dioxide is expected to produce 1 to 1.4 mg/L of chlorite (Singer, 1992).

Chlorite is relatively stable in the presence of organic material but can be oxidized to chlorate by free chlorine if added as a secondary disinfectant (Singer and O'Neil, 1987).



Chlorate is therefore produced through the reaction of residual chlorite and free chlorine during secondary disinfection.

In addition, chlorine dioxide also disproportionates under highly alkaline conditions ($\text{pH} > 9$) to chlorite and chlorate according to the following reaction:



In water treatment processes that require high pH, such as softening, chlorine dioxide should be added after the pH has been lowered (Aieta et al., 1984).

The occurrence of photochemical decomposition of chlorine dioxide can affect the ultimate concentrations of chlorine dioxide, chlorite, and chlorate in water treated with chlorine dioxide. Moreover, generally, sunlight may increase chlorate concentrations in uncovered storage basins containing water with chlorine dioxide residuals. Exposure to ultraviolet light will also change the potential reactions between chlorine dioxide and the bromide ion.

4.5.2 Organic DBPs Produced by Chlorine Dioxide

Chlorine dioxide generally produces few organic DBPs. However, Singer (1992) noted that the formation of non-halogenated organic byproducts of chlorine dioxide has not been adequately researched, and expected that chlorine dioxide will produce the same types of oxidation byproducts that are produced through ozonation. The application of chlorine dioxide does not produce THMs and produces only a small amount of total organic halide (TOX) (Werdehoff and Singer, 1987).

A study was conducted in 1994 by Richardson et al., to identify semivolatile, organic DBPs produced by chlorine dioxide treatment in drinking water. Samples were taken from a pilot plant in Evansville, Indiana that included the following treatment variations:

- Aqueous chlorine dioxide;
- Aqueous chlorine dioxide, ferrous chloride, (FeCl_2), chlorine (Cl_2), and dual media filtration (sand and anthracite);
- Gaseous chlorine dioxide; and
- Gaseous chlorine dioxide, ferrous chloride (FeCl_2), chlorine (Cl_2), and dual media filtration (sand and anthracite).

Using multispectral identification techniques, more than 40 different DBPs (many at sub-nanogram/L [ng/L] levels) were identified including carboxylic acids and maleic anhydrides isolated from XADTM concentrates, some of which may be regulated in the Stage 2 DBPR. THMs were not found after chlorine dioxide was added to the water; however, THMs did show up during subsequent chlorination.

4.5.3 Chlorine Dioxide DBP Control Strategies

EPA recommends that the total concentration of chlorine dioxide, chlorite, and chlorate be less than 1.0 mg/L as Cl_2 (USEPA, 1983). In addition, chlorine dioxide concentrations exceeding 0.4 to 0.5 mg/L contribute to taste and odor problems (AWWA, 1990). Due to these issues, the use of chlorine dioxide to provide a disinfectant residual is somewhat limited in moderate to high TOC water. In low oxidant-demand water, however, ClO_2 residuals may last several days.

Once formed, chlorate is stable in finished drinking water. No known treatment exists for removing chlorate once it is formed. However, three strategies (Gallagher et al., 1994) that have been proven effective for chlorite removal are:

- Adding reduced-sulfur compounds such as sulfur dioxide and sodium sulfite (not recommended).
- Applying either granular activated carbon (GAC) or powdered activated carbon (PAC).
- Adding reduced iron salts, such as ferrous chloride and ferrous sulfate.

Chlorite removal from drinking water through sulfur dioxide and other sulfur-based reducing agents has been reported effective, but not desirable. A study of chlorite removal by sulfur dioxide indicates that a lower pH level yields higher chlorite removal, and chlorite removal efficiencies increase as the sulfur dioxide dose increases. Unfortunately, this removal process forms significant levels of chlorate when sulfur dioxide and metarsulfite are utilized. Therefore, it is concluded that treatment with sulfur dioxide and metarsulfite is not desirable for chlorite removal (Dixon and Lee, 1991). In addition, sodium thiosulfate results in effective chlorite reduction, but the degree of removal is highly dependent upon pH and contact time and relatively high dosages are required. Again, this application of sodium thiosulfate is not desirable because the required dosages are too high (Griese et al., 1991).

The addition of ferrous iron in drinking water is effective for chlorite removal, with chloride the expected byproduct. Chlorite reduction occurs quickly in the pH range of 5 to 7, and complete reduction occurs within 3 to 5 seconds. Excess reduced iron remaining in solution reacts with dissolved oxygen at neutral pH, but under acidic conditions (pH < 6.5) the stability of the soluble iron can create aesthetic (staining) problems if excess iron is used. Special consideration should be given to ferrous iron dosage requirements so that the secondary MCL for iron is not exceeded (Knocke and Iatrou, 1993).

Chlorite can be controlled by PAC at relatively high dosages (10 to 20 mg/L) and low pHs (5.5 to 6.5). Unless PAC is used for other purposes, such as odor control, it requires large doses and is not cost effective. PAC brands can differ in their capacity to reduce chlorite.

GAC can remove chlorite but breakthrough may occur relatively early. The removal of chlorite by GAC appears to be a result of adsorption and chemical reduction (Dixon and Lee, 1991). There is an initial high removal efficiency due to chlorite adsorption. As the adsorptive sites are occupied, chemical reduction on the GAC surface becomes the primary removal mechanism. This results in an initial high removal efficiency. Although chlorite levels exiting the GAC filters are low, the chlorate levels are high, most likely a result of reactions in the GAC filters between chlorite and free chlorine. According to studies, the capacity of GAC beds is low, and if free chlorine and chlorite ion are present in the GAC influent, chlorate ion will form. The most effective way to operate GAC for chlorite reduction and avoid chlorate is to minimize production run times and have no chlorine present in the filter.

4.6 Status of Analytical Methods

In addition to the monitoring requirements that apply regardless of the disinfectant used, the DBPR requires that water systems that use chlorine dioxide for disinfection or oxidation must also monitor their system for chlorine dioxide and chlorite.

4.6.1 Chlorine Dioxide and Chlorite Analytical Methods

For compliance monitoring for chlorine dioxide, systems must use one of the two methods specified in 40 CFR §141.131(c), including (1) DPD, Standard Method 4500-CLO₂ D, or (2) Amperometric Method II, Standard Method 4500-CLO₂ E. Where approved by the state, systems may also measure residual disinfectant concentrations for chlorine dioxide by using DPD colorimetric test kits.

For compliance monitoring for chlorite, systems must use one of the three methods specified in 40 CFR §141.131(b), including (1) Amperometric Titration, Standard Method 4500-CLO₂ E, (2) Ion Chromatography, EPA Method 300.0, or (3) Ion Chromatography, EPA Method 300.1. The regulations 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, monitoring of chlorate and monthly additional monitoring of chlorate in the distribution system.

Details of these analytical procedures can be found in:

- *Standard Methods for the Examination of Water and Wastewater*, 19th Edition, American Public Health Association, 1995.
- *Methods for the Determination of Inorganic Substances in Environmental Samples*. USEPA. 1993. EPA/600/R-93/100.
- *USEPA Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0*. USEPA. 1997. EPA/600/R-98/118.

Table 4-3 summarizes the analytical methods approved for use for chlorine dioxide and chlorite and provides some background information for each method.

4.6.2 Chlorine Dioxide Monitoring for Systems Using Chlorine Dioxide

For chlorine dioxide monitoring, community, non-transient non-community, and transient non-community water systems that use chlorine dioxide for disinfection or oxidation, are required to take daily samples at the entrance to the distribution system. For any daily sample that exceeds the chlorine dioxide MRDL of 0.8 mg/L, the system must take additional samples in the distribution system the following day at the locations specified in the DBPR, in addition to the daily sample required at the entrance to the distribution system.

Additional sampling is to be performed in one of two ways, depending on the disinfectant that is used to maintain a disinfectant residual in the distribution system. If chlorine dioxide or chloramines are used to maintain a disinfectant residual, or if chlorine is used to maintain the residual and there are no disinfection addition points after the entrance to the distribution system (i.e., no booster chlorination), the system must take three samples as close to the first customer as possible, at intervals of at least six hours. If chlorine is used to maintain a disinfectant residual and there are one or more disinfection addition points after the entrance to the distribution system, the system must take one sample at each of the following locations: (1) as close to the first customer as possible, (2) in a location representative of average residence time,

and (3) as close to the end of the distribution system as possible (reflecting maximum residence time in the distribution system). Chlorine dioxide monitoring may not be reduced.

If any daily sample taken at the entrance to the distribution system exceeds the MRDL, and on the following day one (or more) of the three samples taken in the distribution system exceed the MRDL, the system is in violation of the MRDL. The system must take immediate corrective action to lower the level of chlorine dioxide below the MRDL, and must notify the public of the acute violation pursuant to 40 CFR §141.32. The system must also report to the State pursuant to 40 CFR §141.134.

If any two consecutive daily samples taken at the entrance to the distribution system exceed the MRDL, the system is also in violation of the MRDL and must notify the public of the non-acute violation pursuant to 40 CFR §141.32. The system must also report to the State pursuant to 40 CFR §141.134.

4.6.3 Chlorite Monitoring for Systems Using Chlorine Dioxide

For chlorite monitoring, community and non-transient non-community water systems that use chlorine dioxide for disinfection or oxidation are required to take daily samples at the entrance to the distribution system. For any daily sample that exceeds the chlorite MCL of 1.0 mg/L, the system must take additional samples in the distribution system the following day at the locations specified in the DBPR. These additional samples are to be collected at: (1) a location as close to the first customer as possible, (2) a location representative of average residence time, and (3) a location as close to the end of the distribution system as possible (reflecting maximum residence time in the distribution system).

In addition, systems using chlorine dioxide must take a three-sample set each month in the distribution system similar to the three locations required if the chlorite MCL is exceeded in the sample collected at the entrance to the distribution system. Specifically, these three-sample sets are to be collected: (1) in a location near the first customer, (2) in a location representative of average residence time, and (3) at a location reflecting maximum residence time in the distribution system. Any additional routine sampling must be conducted in the same three-sample sets at the specified locations. This monthly sampling requirement may be reduced to quarterly after one year of monitoring where: (1) no individual chlorite sample taken in the distribution system has exceeded the MCL and (2) the system has not been required to conduct follow-up monitoring as a result of a daily sample collected at the entrance to the distribution system. These systems can remain on an annual schedule until either the daily sample or any of the three individual quarterly samples exceed the MCL, at which time, the system must revert to monthly monitoring.

If the arithmetic average of any three-sample set exceeds the chlorite MCL of 1.0 mg/L, the system is in violation of the MCL and must notify the public pursuant to 40 CFR §141.32, in addition to reporting to the State pursuant to 40 CFR §141.134.

4.7 Operational Considerations

As with all disinfectant selections, the primacy agency should be consulted when selecting disinfectants. Certain states have their own operational, maintenance, and monitoring requirements

for the application of chlorine dioxide. California prohibits the use of chlorine dioxide in ground water systems, according to Merkle et al., 1997. Also, in Texas, the Texas Natural Resources Conservation Commission (TNRCC) requires the public water supply to sign a bilateral agreement which outlines a detailed operator qualifications requirement, testing methods, and procedures, monitoring locations, testing frequency and reporting procedures. The chlorine dioxide concentration leaving the water treatment plant must be less than 0.8 mg/L and the chlorite concentration in the distribution system must be less than 1.0 mg/L.

State requirements must be reviewed to determine the cost-effectiveness of utilizing chlorine dioxide as part of the overall water treatment scheme. Analytical testing and reporting requirements may have significant labor and cost impacts.

Table 4-3. Analytical Methods for Chlorine Dioxide and Related Compounds

| Method | Basis | Interferences | Limits |
|--|---|--|---|
| DPD as Test Kits Colorimetric (SM-4500-ClO ₂ G) | Colored oxidation product. Use of color comparator is not recommended. Use instrument detection. | Mn ₂ ⁺ , other Cl ₂ , related oxidants. | > 0.1 mg/L |
| DPD-glycine Method Colorimetric (SM 4500- ClO ₂ .D) | Colored product, free Cl ₂ is masked with glycine as chloraminacetic acid. | ClO ₂ ⁻ slowly; other oxidants. | > 0.1 mg/L |
| DPD-FAS Titrimetric method (SM 4500- ClO ₂ .D) | DPD color titration with standard FAS until red color is discharged. | Iron, other oxidants. | > 0.1 mg/L |
| 5-Step Amperometric Method 4500-ClO ₂ .E | I ⁻ oxidation; pH control and gas purging steps. Skilled analyst needed. | Suitable for ClO ₂ generated solution. Low levels not okay. | ~ PQL ClO ₂ : 0.1-0.05 mg/L; ClO ₃ ⁻ at 0.5 mg/L |
| Ion Chromatography (EPA Method 300.0 or 300.1) Conductivity | Must use AS9 column, ext. standards & suppression. | No other oxidants. Chloramines, ClO ₂ ⁻ , OCl ⁻ & HOCl undetectable. | ~ 0.05 mg/L |
| Two-step Amperometric Method 4500-ClO ₂ .E | I ⁻ Oxidation; pH control. Amendable to operator-based dosage control. Practical method. | Cu ₂ ⁺ , Mn ₂ ⁺ , NO ₂ ⁻ Accounts for free Cl ₂ , NH ₂ Cl, ClO ₂ ⁻ species. | > 0.1 mg/L, not ClO ₃ ⁻ |

Source: Gates, 1998.

Notes: SM = Standard Methods

4.7.1 Process Considerations

The basic components of chlorine dioxide generation systems include:

- Aqueous hypochlorite solution storage and feed system;
- Sodium chlorite storage and feed system;
- Acid storage and feed system (for Direct-Acidification generators);
- Chlorine storage and feed system;
- Chlorine dioxide generator; and
- Chlorine dioxide feed piping and dispersion equipment.

Sodium chlorite storage and feed systems are basically liquid systems that consist of a storage tank(s) and solution feed pumps. Outside storage of 25 percent solutions (or greater) of sodium chlorite is not recommended in cold climates since stratification may occur below 4°C (40°F). Any ice formation may also damage the storage tanks. In some cases, storage might be separated into bulk tanks and smaller operational or day tanks that are filled periodically. Storage of dark drums for long periods in hot climates should be avoided since sodium chlorite decomposition will occur. In the storage area, light fixtures, switches, wiring, and conduit runs should be located to avoid the risk of sodium chlorite spilling on them.

4.7.2 Generator Operation

A manual chlorine dioxide feed system may be used where the chlorine dioxide dose remains fairly constant. The reagent chemicals are manually set for the desired chlorine dioxide capacity at a ratio of chemicals optimized for maximum chlorine dioxide yield. Some generating systems can produce 95 percent pure chlorine dioxide solutions at full design capacity, but purity can vary when the feed rate is changed. Turndown capacity may be limited by precision of the flow metering devices, typically 20 percent of rate capacity. Purity can vary when the feed rate is changed significantly. Feed water alkalinity, operating conditions, and pH also can affect yield. The ratio of reagent chemicals should be routinely adjusted for optimum operation. Chlorine dioxide generators can be provided with automated control to provide modulation of chlorine dioxide feed rates based upon changes in flow (flow paced) and chlorine dioxide demand (residual control). The automatic modulation of the generators to meet a demand setpoint varies with manufacturer. Generally, vacuum and combination systems are limited by the hydraulic requirements of the venturi and the optimum reaction conditions for chlorine dioxide generation. A chemical metering pump or injector system is then used with a batch production system to control the applied dose of chlorine dioxide.

4.7.3 Feed Chemicals

Chlorine dioxide is generated when sodium chlorite is either oxidized or acidified, or both, under controlled pH and temperature conditions. Commonly, solutions of 25 percent active sodium chlorite or less are used in chlorine dioxide generators. The major safety concern for solutions of sodium chlorite is the unintentional and uncontrollable release of high levels of chlorine dioxide. Such levels may approach detonation or conflagration concentrations by accidental acidification.

The feedstock acid used by some of the generators is only one source of accidental chemical acidification. Accidental mixing with large amounts of any reducing agent or oxidizable material (such as powdered activated carbon or flammable solvents) also represents a significant hazard. The AWWA Standard B303-95 (a) includes an outline of some of these materials (AWWA, 1995).

Another concern when handling and storing sodium chlorite solutions is crystallization, which occurs as a result of lower temperatures and/or higher concentrations. Crystallization will plug pipelines, valves, and other equipment. Sodium chlorite solution should not be allowed to evaporate to a powder. If dried, this product becomes a fire hazard and can ignite in contact with combustible materials. A sodium chlorite fire may result in a steam explosion if too much water and inappropriate fire-fighting techniques are used to quench such a fire. As the temperature of burning sodium chlorite is around 2200°C, water quickly turns to steam. Because thermal breakdown products of sodium chlorite at high temperatures include molecular oxygen, appropriate techniques are required to correctly extinguish closed containers or large amounts of dry material that has been ignited.

Stratification of sodium chlorite in holding tanks may also occur and would influence the chlorine dioxide yield. If stratification occurs in the bulk tank, sodium chlorite changes from high density to

low density as it is fed. The density will continue to change until the material is re-mixed. In stratified tanks, excess chlorite would be fed to the generator since the bottom of the tank will have denser material, and this material would have more chlorite than required. Similarly, the bulk tank would later discharge too little chlorite.

Although infrequent, such stratification is not readily apparent and may likely remain unnoticed by operations unless the generator performance is evaluated frequently. If stratification or crystallization occurs in bulk delivery trucks, the entire content should be warmed prior to delivery so that the sodium chlorite is re-mixed. Operators should be aware of the possibility of stratification and crystallization during delivery conditions.

Sodium chlorite is commercially available as a 38 percent or 25 percent solution. Chemical and physical properties are given in Table 4-4.

Table 4-4. Properties of Sodium Chlorite as Commercially Available

| | 38% Solution* | 25% Solution* |
|--|------------------------------|--------------------|
| Sodium Chlorite, (%) NaClO ₂ | 38 | 25 |
| Sodium Chloride, (%) NaCl | 1.5-7.5 | 1-4.5 |
| Inert Ingredients, mixture of other sodium salts (%) | 3-4 | 3-4 |
| Water (%) | 55-61 | 68-74 |
| Appearance | Slightly cloudy, pale yellow | Clear, pale yellow |
| Density @ 35°C (lb/gal), typical | 11.4 | 10.1 |
| Crystallization Point (°C) | 25 | -7 |

* Source: Vulcan Chemicals

For systems handling the 38 percent solution, storage tanks, piping and pumps will require a heated enclosure, or heat tracing and insulation. The 25 percent solution may not require any special protection except in cold climates.

The ideal production of 1.0 pound of chlorine dioxide requires 0.5 pounds of chlorine and 1.34 pounds of pure sodium chlorite. Chlorine gas is available as a nearly 100 percent pure chemical on a weight basis. Gas flow metering devices are typically limited to +/- 5 percent accuracy at full rated capacity. For example, a 100 pound per day flow tube would allow between 20 and 30 pounds of chlorine to flow if set at 25 pounds per day (i.e., 25 +/- 5 percent of maximum flow capacity). Sodium chlorite is supplied commercially as a pre-mixed aqueous solution of various strengths. The 25 percent solution is the most commonly used grade for potable water treatment.

Pure chlorine dioxide solutions (very dark amber and oily in appearance) are very dangerous and are likely to detonate if exposed to oxidizable materials or vapors, or even to bright lights. They are extremely uncommon except perhaps in very specific laboratory setup systems using concentrated sodium chlorite and concentrated acid mixtures. Such laboratory generation methods are not

recommended for the uninitiated laboratory analyst or operator. Inexperienced personnel should not mix strong acid and strong sodium chlorite solutions together unless they are familiar with the purgeable extraction methods for sodium chlorite and have a safely designed setup under a fume hood.

4.8 Summary

4.8.1 Advantages and Disadvantages of Chlorine Dioxide Use

The following list highlights selected advantages and disadvantages of using chlorine dioxide as a disinfection method for drinking water (Masschelein, 1992; DeMers and Renner, 1992, Gallagher et al., 1994). Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

Advantages

- Chlorine dioxide is more effective than chlorine and chloramines for inactivation of viruses, *Cryptosporidium*, and *Giardia*.
- Chlorine dioxide oxidizes iron, manganese, and sulfides.
- Chlorine dioxide may enhance the clarification process.
- Taste and odors resulting from algae and decaying vegetation, as well as phenolic compounds, are controlled by chlorine dioxide.
- Under proper generation conditions (i.e., no excess chlorine), halogen-substituted DBPs are not formed.
- Chlorine dioxide is easy to generate.
- Biocidal properties are not influenced by pH.
- Chlorine dioxide provides residuals.

Disadvantages

- The chlorine dioxide process forms the specific byproducts chlorite and chlorate.
- Generator efficiency and optimization difficulty can cause excess chlorine to be fed at the application point, which can potentially form halogen-substitute DBPs.
- Costs associated with training, sampling, and laboratory testing for chlorite and chlorate are high.
- Equipment is typically rented, and the cost of the sodium chlorite is high.
- Measuring chlorine dioxide gas is explosive, so it must be generated on-site.
- Chlorine dioxide decomposes in sunlight.
- Chlorine dioxide must be made on-site.
- Can lead to production noxious odors in some systems.

4.8.2 Summary Table

Table 4-5 summarizes considerations and descriptions for chlorine dioxide use.

Table 4-5. Summary for Chlorine Dioxide

| Consideration | Description |
|-------------------------|--|
| Generation | Chlorine dioxide must be generated on-site. In most potable water applications, chlorine dioxide is generated as needed and directly added or injected into a diluting stream. Generators are available that utilize sodium chlorite and a variety of feedstocks such as Cl ₂ gas, sodium hypochlorite, and sulfuric or hydrochloric acid. Small samples of generated solutions, up to 1 percent (10 g/L) chlorine dioxide can be safely stored if the solution is protected from light, chilled (<5°C), and has no unventilated headspace. |
| Primary Uses | Chlorine dioxide is utilized as a primary or secondary disinfectant, for taste and odor control, TTHM/HAA reduction, Fe and Mn control, color removal, sulfide and phenol destruction, and Zebra mussel control. |
| Inactivation Efficiency | Chlorine dioxide rapidly inactivates most microorganisms over a wide pH range. It is more effective than chlorine (for pathogens other than viruses) and is not pH dependent between pH 5-10, but is less effective than ozone. |
| Byproducts Formation | When added to water, chlorine dioxide reacts with many organic and inorganic compounds. The reactions produce chlorite and chlorate as endproducts (compounds that are suspected of causing hemolytic anemia and other health effects). Chlorate ion is formed predominantly in downstream reactions between residual chlorite and free chlorine when used as the distribution system disinfectant. Chlorine dioxide does not produce THMs. The use of chlorine dioxide aids in reducing the formation of TTHMs and HAAs by oxidizing precursors, and by allowing the point of chlorination to be moved farther downstream in the plant after coagulation, sedimentation, and filtration have reduced the quantity of NOM. |
| Point of Application | In conventional treatment plants, chlorine dioxide used for oxidation is fed either in the raw water, in the sedimentation basins, or following sedimentation. To limit the oxidant demand, and therefore chlorine dioxide dose and the formation of chlorite, it is common to add chlorine dioxide following sedimentation. Concerns about possible taste and odor complaints have limited the use of chlorine dioxide to provide a disinfectant residual in the distribution system. Consequently, public water suppliers that are considering the use of chlorine dioxide for oxidation and primary disinfectant applications may want to consider chloramines for secondary disinfection. |
| Special Considerations | An oxidant demand study should be completed to determine an approximate chlorine dioxide dosage to obtain the required CT value as a disinfectant. In addition to the toxic effects of chlorine, chlorine dioxide gas is explosive at levels > 10% in air. The chlorine dioxide dosage cannot exceed 1.4 mg/L to limit the total combined concentration of ClO ₂ , ClO ₂ ⁻ , ClO ₃ ⁻ , to a maximum of 1.0 mg/L. Under the proposed DBP regulations, the MRDL for chlorine dioxide is 0.8 mg/L and the MCL for chlorite is 1.0 mg/L. Regulations concerning the use of chlorine dioxide vary from state-to-state. |

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