TECHNICAL DATA SHEET

TECHNICAL & ENVIRONMENTAL SERVICES

Treatment Of Drinking Water With Chlorine Dioxide (ClO_2)

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. This interest is being stimulated by the Environmental Protection Agency (EPA) amendments[1,2] to the National Interim Drinking Water Regulations.

These amendments set a maximum contaminant level (MCL) of 0.10 mg/l for total trihalomethanes (TTHM). In 1983, they listed chlorine dioxide as an alternative or supplemental oxidant-disinfectant that was one of the most suitable for TTHM treatment and control.

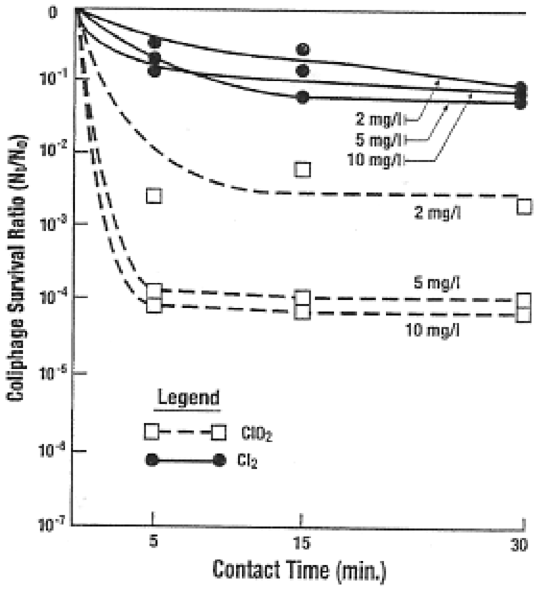
In contrast with chlorine, the reactions of chlorine dioxide with humic substances (the precursors of trihalomethanes) do not result in the formation of THMs. For this reason, chlorine dioxide treatment has become a preferred method where it is necessary to control TTHMs, along with taste and odors.

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 documented[3] in the laboratory, in pilot studies and in full-scale studies using potable and waste water. 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 waste water effluents, and is superior to chlorine in the treatment of viruses commonly found in secondary waste water 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.

Figure 4
***In Situ* coliphage survival in secondary effluent at three doses and three contact times**

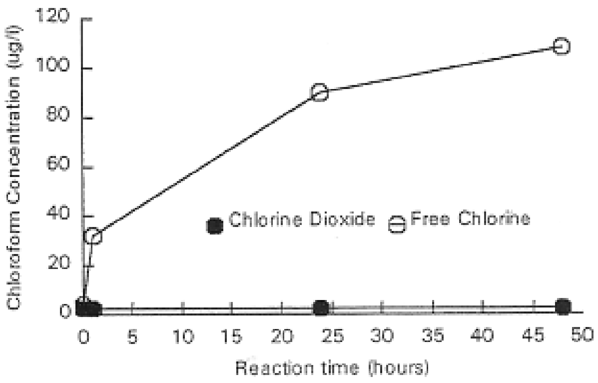


When applied for disinfection (as opposed to oxidation), a disinfectant must provide specified levels of microorganism kills or inactivations as measured by reductions of coliforms, heterotrophic plate count organisms and *Legionella* bacteria. Disinfection is currently defined by the EPA[4] to mean 99.9 percent reduction in *Giardia làmblia* cyst levels and 99.99 percent reduction in enteric virus concentrations. 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.

An amendment to the Safe Drinking Water Act[4] (SDWA) required compliance with MCL goals for *Giardia lamblia,* viruses and *Legionella*. The published CT values required by 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.

Figure 5

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



Chlorine Dioxide For Control Of THMs

Recent studies have determined that when chlorine is used to treat surface waters which contain decayed natural (i.e. humic) substances, it produces chloroform and other chloro- and bromo-organic derivatives which are known collectively as trihalomethanes (THMs).

Both the International Agency for Research in Cancer (IARC) and the National Toxicology Program (NTP) have classified chloroform as an animal carcinogen. Therefore, water treatment methods are being modified to prevent the formation of THMs or to reduce them to be in compliance with the EPA Maximum Concentration Level (MCL) of 0.10 mg/l for total trihalomethanes (TTHMs). For this purpose, chlorine dioxide is an excellent alternative or supplemental oxidant-disinfectant. Its use is supported by the amendments to the National Primary Drinking Water Regulations,[2] cited in the introduction section above.

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.

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 raw water supply would be for primary disinfection and/or oxidation. Then free or combined chlorine or chlorine dioxide is added after filtration as a disinfectant residual.

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 are: Evansville, Indiana;[5] Hamilton, Ohio;[6] and Galveston, Texas[7]. These case histories demonstrate the versatility and effectiveness of chlorine dioxide for THM control in municipal water treatment systems.

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 - 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). No chlorophenols are observed; simple organic acids (such as maleic and oxalic acids) are the remaining by-products. 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.[8] 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:

$$ClO_2 + 5Fe(HCO_2)_2 + 2H_2O \rightarrow$$
$$5Fe(OH)_3 + 10CO_2 + Cl^- + H^+$$

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

Chlorine dioxide has also been reported to oxidize organically-bound iron.[9] 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.