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DOCUMENT

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 odour at the Niagara Falls water treatment plant. Today, there is increased interest in chlorine dioxide as an oxidant and disinfectant for drinking water. Recently, this interest has been stimulated by the publication of the final disinfectants and Disinfection Byproducts Rule (DBPR) as part of the EPA's National Primary Drinking Water Regulations.

This rule sets a maximum contaminant level (MCL) of 0.08 mg/L for total trihalomethanes (TTHM). The EPA has identified chlorine dioxide as an alternative or supplemental oxidant-disinfectant that is one of the most suitable for TTHM treatment and control.

It is also worth noting that the EU set a residual consent limit of 0.5 ppm for drinking water applications.

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 odours.

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 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).

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 10 mg/L dose of chlorine.

Figure 1
Comparison of the bactericidal effects of chlorine and chlorine dioxide on *A. aerogenes* at different temperatures and pH, with five minute contact

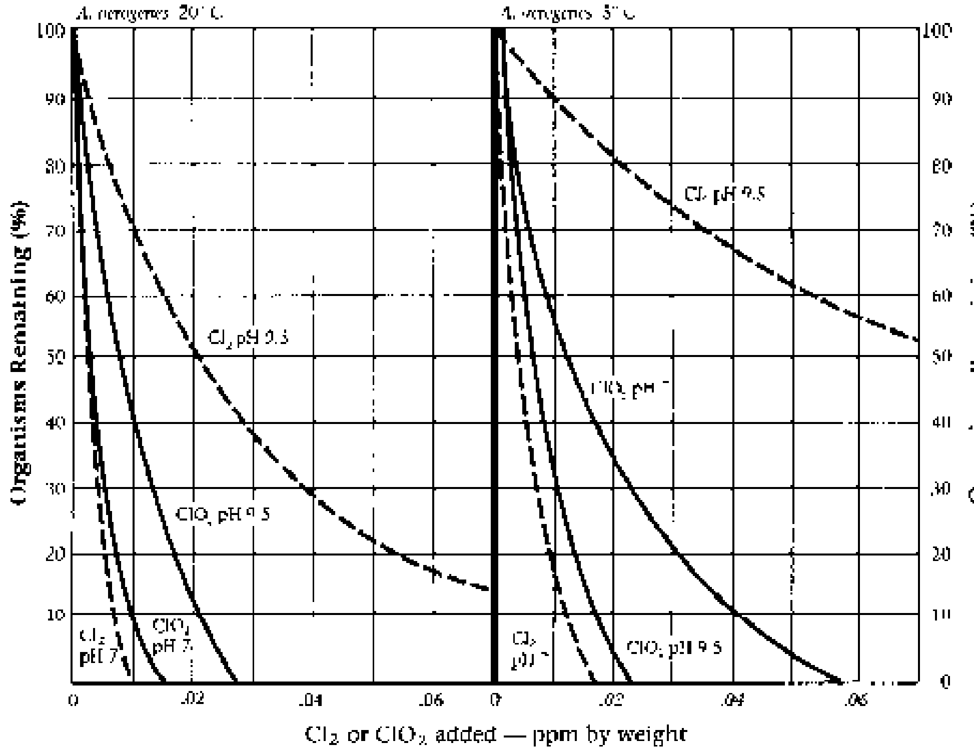


Figure 2
Comparison of the bactericidal effects of chlorine and chlorine dioxide on *E. coli* at different temperatures and pH, with five minute contact

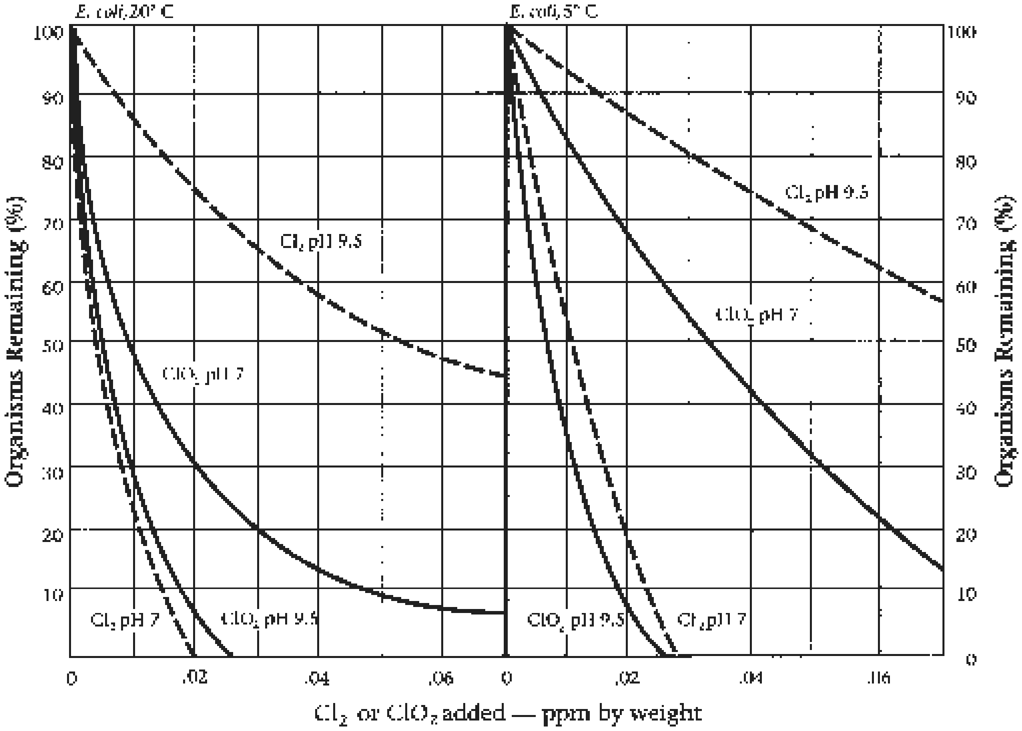


Figure 3
Comparison of the bactericidal effects of chlorine and chlorine dioxide on *Ps. aeruginosa and Staph. aureus* at different pH. with five minute contact

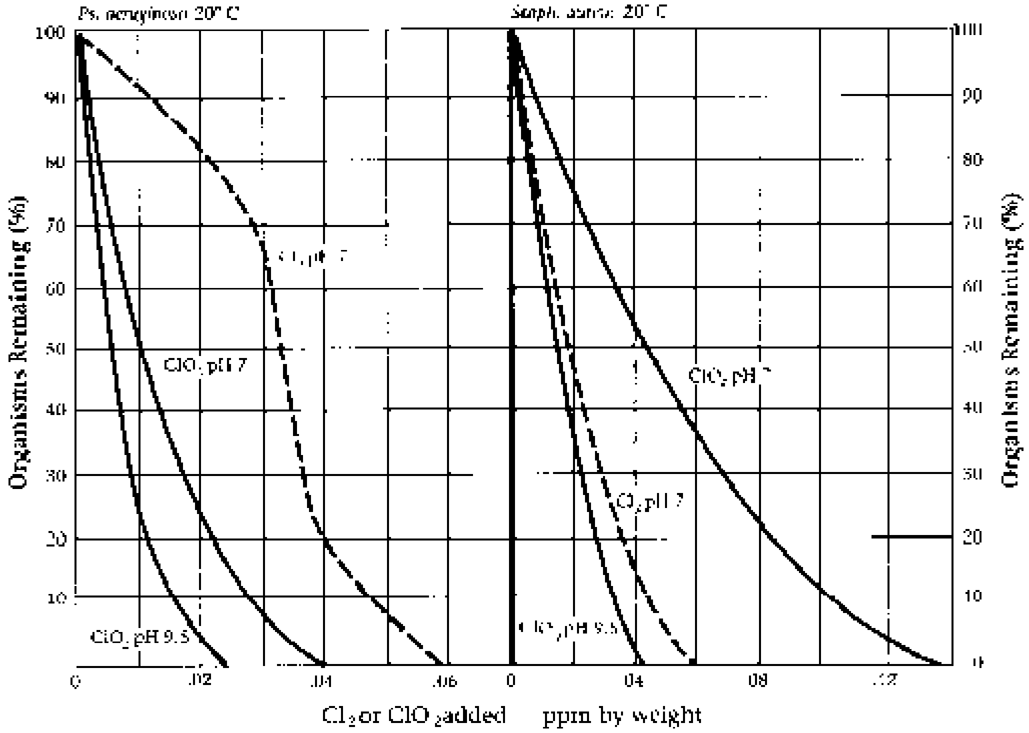
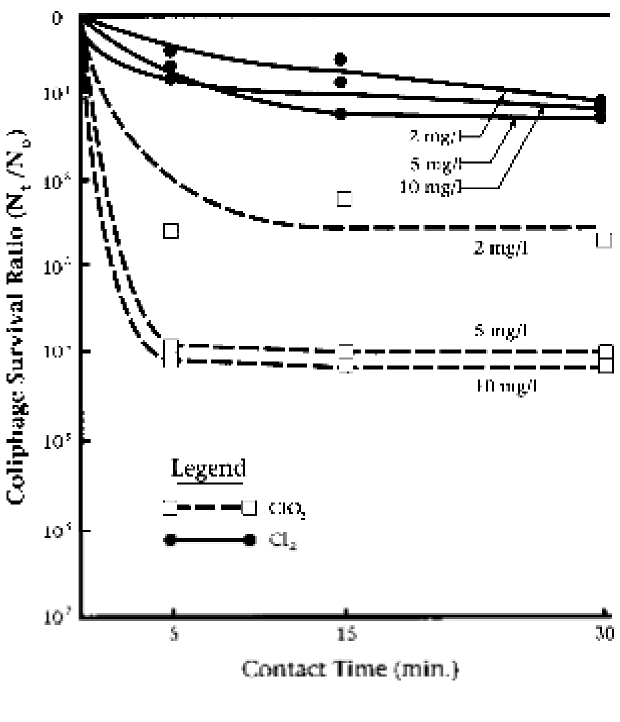


Figure 4
In situ coliphage survival in secondary effluent at three doses and three contact times



TASTE AND ODOUR CONTROL

Many potable water plants have experienced unpleasant tastes and odours in finished waters with descriptions such as medicinal, musty, earthy, fishy, metallic or rotten egg. These odour causing compounds have been identified as Geosmin, 2-methylisoborneol (MIB), pyrazine chlorophenols, actinomycetes, sulfur species or other odorous by- products of microscopic organisms. These substances generally are produced in raw waters by various algae or bacterial micro-organisms.

Chlorine dioxide is effective at oxidizing low-threshold-odour compounds like Geosmin and MIB at typical treatment dosages. Chlorine dioxide has an advantage in that its use for controlling tastes and odours will not chlorinate organics.

New regulations like the Stage One and Stage Two Disinfectant and Disinfection Byproduct (DBP) Rules, limiting trihalomethanes (THMs) and haloacetic acids (HAAs) levels, have severely curtailed the use of traditional chlorine treatment resulting in the need to re-evaluate taste and odour treatment strategies to include chlorine dioxide.

EASY SOLUTION

Chlorine dioxide's selective chemistry allows it to instantaneously react with oxidizable material to kill algae and bacteria that produce bad taste and odours in water. Chlorine dioxide is also excellent at destroying odour-causing biofilms that are not removed by chlorine treatment, and attach to piping and basins. In some cases, properly designed chlorine dioxide programs may not always show measured reductions of specific odorous substances but many systems report improved taste and odour characteristics resulting from the removal of micro-organisms that produce the particular odour versus the traditional chlorination treatment of these odorous substances.

VERSATILE DISINFECTANT

Chlorine dioxide's use is not limited to just taste and odour problems in potable water systems. This versatile disinfectant also can be used as a primary disinfectant in potable water, as it reduces or controls bacteria, viruses, cysts and algae while being effective over wide temperature and pH ranges. Using chlorine dioxide will help optimize overall treatment efficiencies, including improved coagulation, reduced turgidities, improved particulate removals, increased CT values and lower THMs and HAAs.

Chlorine dioxide, when used as an oxidant for taste and odour problems in potable water treatment, is a powerful oxidant with CT values second only to ozone in biocide efficacy, but without the high capital expenditures and the ozonation byproducts. In addition, chlorine dioxide does not have the solids loading problem and the lengthy detention times associated with potassium permanganate. Using chlorine dioxide does not result in the formation of chlorinated or brominated disinfection byproducts like THMs or HAAs. A reduction byproduct of chlorine dioxide is chlorite ion, which is regulated under the Stage One and the Stage Two Disinfectant and Disinfection Byproduct (DBP) Rules at 1.0 mg/L maximum contaminant level (MCL). At typical dosage rates, chlorine dioxide can be used successfully to help control taste and odour problems without exceeding the MCL.

LOW CAPITAL/EASILY IMPLEMENTED

Chlorine dioxide cannot be shipped and must be generated on-site. XzioX unique two precursor system allows the user to safely generate a pure chlorine dioxide solution at the point of application. Chlorine dioxide is fed similarly to existing chlorine disinfection treatment systems often using the existing feed piping. The XzioX system is available for small scale uses all the way up to large municipal users by way of a specially developed automated solution to aid ease of use and safety.

ADDITIONAL USES

Chlorine dioxide's broad spectrum capabilities enable it to be used in a variety of potable water applications:

Iron and Manganese Oxidation
Chlorine dioxide instantaneously reacts with soluble iron Fe(III) and Mn(III,IV) precipitates that are easily removed by filtration. The use of chlorine dioxide will help optimize overall treatment efficiencies, including improved coagulation, reduced turbidities, and improved particulate removals, increased CT Values and lower THMs and HAAs.

Improved Disinfection Credits (C x T)

Trihalomethane (THMs) and Haloacetic Acids (HAAs) Control
Using chlorine dioxide does not result in the formation of chlorinated or brominated disinfection byproducts like THMs or HAAs. Chlorine dioxide is not a chlorinating agent and can be used as a primary disinfectant or as a raw water oxidant for THMs and HAAs precursor reduction in potable water treatment systems.

Colour Removal and Algae Control

Cryptosporidium Inactivation

Nitrification Control
Chlorine dioxide does not react with ammonia and is fully available to oxidize ammonia and nitrogen oxidizing bacteria (AOB & NOB). This selective chemistry will retain its full capacity without having to overcome any ammonia-related demand, allowing it to be fed at extremely low dosages. The use of chlorine dioxide allows the utility to continue to feed chloramines for residual microbial protection while still achieving the intended DBP compliance.

Additionally, the reduction byproduct of chlorine dioxide is chlorite ion, which has been proven to inhibit AOB and NOB in the distribution system. This would allow a facility to utilize chlorine dioxide for a number of disinfection or oxidative purposes on the raw water along with the benefits of nitrification control from the byproduct chlorite ion in the distribution system.

Zebra Mussel Control

APPROVALS

The use of chlorine dioxide is approved by U.S. EPA's Office of Ground Water and Drinking Water. The sodium chlorite precursor solutions carry U.S. EPA registrations and are ANSI/NSF Standard 60 Drinking Water Additive certified, as well as being EU and DWI approved.

The advantages of disinfection with chlorine dioxide are various: Especially for drinking water, which we all are depending on, it is essential to use a chemical which does not pose significant health risks.

- Chlorine dioxide suppresses not only the forming of the volatile haloforms, but also reduces the generation of hardly or non-volatile organic halogen compounds considerably. Primarily the volatile haloforms such as chloroform, but also dichlorobromomethane, chlorodibromomethance and bromoforme, are suspected of being harmful to health, some even carcinogenic.

- Unlike chlorine, chlorine dioxide does not form any chlorophenols affecting taste and smell. It reacts neither with ammonium nor with amino compounds.

- Low concentrations of chlorine dioxide are applied as chlorine; it disinfects faster and its effect is due to its permanency in water also reliable in extensive networks of pipes.

The disinfection effect of inorganic agents such as chlorine dioxide depends on their redox potential. A high redox potential is decisive for effective decontamination. Chlorine dioxide is used for the oxidation treatment of water, for deodorising, fighting of algae and mucus, reduction of CSB/BSB and AOX for reasons of its high redox potential:

- The highly reactive chlorine dioxide has an oxidation capacity of more than 100 to 250% compared with chlorine.

- Destruction of chloramines by oxidation, no irritation of eyes, no special smell, pleasant ambient climate (chloramines lead to irritations of the mucous membranes, especially those of the eyes).

- No reaction with ammonia or ammonium ions.

- Strong algicide effect of chlorine dioxide: no necessity to use organic biocides.

- The disinfecting effect is not depending on the pH in the pH range from 6 to 10.

- Positive effect on the skin by oxygen transfer (no degreasing, no smell,…)

- Destruction of dirt and microbacteria deposits e.g. at the basin or in the pipes.

- Chlorine dioxide has outstanding bactericide and bacteriostatic characteristics.

- The germicide as well as the sporicide and the virucide effect of chlorine dioxide is outstanding.

ADVANTAGES OF CHLORINE DIOXIDE

Chlorine dioxide reacts more rapidly and completely than other available oxidizers.

Only chlorine dioxide does not form colloidal sulfur. Hydrogen peroxide, potassium permanganate and chlorine all require excess oxidizer and a basic pH to avoid colloidal sulfur formation.

Chlorine dioxide does not form chlorinated organic byproducts. While chorline is the least expensive oxidizer available, it cannot be used when organic compounds are present due to the formation of chlorinated organic byproducts. When chlorine can't be used, hydrogen peroxide has the lowest chemical cost.

Chlorine dioxide forms soluble byproducts. Potassium permanganate and catalyzed hydrogen peroxide (Fentons chemistry) result in high solids loading and significant disposal costs.

HOW DOES XZIOX PRODUCE CHLORINE DIOXIDE

The XzioX process uses 2 pre-cursor chemicals in much the same way a conventional Chlorine Dioxide generator does, but with some very important differences. The patented XzioX chemistry releases ClO_2 instantaneously, whereas a conventional Chlorine Dioxide generator or stabilised Chlorine Dioxide dosing system can take several hours to give its maximum yield of ClO_2.

The chlorine dioxide yield of the XzioX process is very high, converting around 95% of the pre-cursor chemical to ClO_2. This is higher than other processes and much higher than some so-called stabilised Chlorine Dioxide systems, which not only give a low yield but take a long time to do it. Another critical difference between XzioX and other chlorine dioxide systems is that it doesn't need a strong acid to work. The matching pre-cursor to XzioX is a special blend of food/drinking water approved weak acids, which is classified as non-hazardous. The patented XzioX chemistry is so different from the way conventional Chlorine Dioxide generators work.

COST COMPARISON AND SAVINGS

The cost of chlorine dioxide is dependent on the cost of the precursor chemicals-sodium chlorite or sodium chlorate-and the chemicals required to convert these chemicals into ClO_2. The cost of ClO_2 will also depend on the generation method employed. When compared to the cost of chlorine, the cost of ClO_2 is higher. However in those instances in which chlorine is not the preferred regulatory or environmental alternative, ClO_2 is a very attractive alternative. The capital equipment costs of generating ClO_2 are also far less than that of other alternatives like ozone which can also be used for water treatment.

Chlorine dioxide has proved economical and effective when treating waters high in ammonia or organic nitrogen and in the destruction of phenol-based taste and odour causing compounds. Essentially, this is because chlorine dioxide is not affected by pH, thus it is a cost effective means of water treatment when the pH is high.

Chlorine dioxide is about 5 to 10 times more expensive than chlorine. Chlorine dioxide is usually made on site. The cost of chlorine dioxide depends upon the price of the chemicals that are used to produce chlorine dioxide. Chlorine dioxide is less expensive than other disinfection methods, such as ozone.

Chlorine dioxide is the alternative for cost-saving disinfection. It can be integrated very well into process systems technologically, as it can be automatically measured and controlled. In the sectors of disinfection and in the water and waste water fields very big savings are possible, simultaneously increasing the operating safety and protection of the environment.

While Chlorine Dioxide has been around and used in water disinfection for some 50 years, mostly in Europe, it has only recently seen renewed interest in municipal water treatment applications in the USA. The main reason it hasn’t been used more is price: it costs 5-10 times more than chlorine. The reason for the renewed interest is its efficacy, safety and environmental credentials.

Chlorine dioxide is a disinfectant that directly reacts with the cell wall of microorganisms. The reaction is not as dependent on time or concentration. Compared to chlorine, the chlorine dioxide concentration needed to effectively kill microorganisms is much lower and microorganisms cannot build up any resistance against chlorine dioxide. Also, chlorine dioxide remains in its molecular form in the pH range typically found in natural waters and it is far more effective in treating the water for cysts and controlling biofilms.

Since Chlorine dioxide does not react with ammonia, nitrogen, amines or other oxidizable organic matter, it generates fewer harmful byproducts. Chlorine dioxide does not produce THMs and produces only a small amount of total organic halide. The inorganic disinfection-by-products chlorite and chlorate are produced, but these can be quite easily removed with the addition of a little ferrous sulfate.

For the purpose of our application, Chlorine dioxide is about the only thing you can add to water that will kill cryptosporidium. Some data as follows: 0.3 – 0.4 ppm of Chlorine dioxide completely deactivates tough Cryptosporidium oocysts in less than 20 minutes. Also, according to the Dept. of Microbiology and Immunology at the U. Arizona, in a report entitled Effects of ozone, chlorine dioxide, chlorine, and monochloramine on Crypto viability, ozone and chlorine dioxide more effectively inactivated oocysts than chlorine and monochloramine did. Exposure to 1.3 ppm of chlorine dioxide yielded 90% inactivation after 1 h, while 80 ppm of chlorine required approximately 90 min for 90% inactivation.

A common and effective approach to lowering DBP's is to optimise the physical removal of organic precursors before adding any disinfectant. This approach can also minimize the potential for the occurrence of taste-and-odour events. It appears to be more effective in establishing a true disinfectant residual for C x T credits in the case of CIO2. This initial removal of most particulate-phase constituents before primary disinfection results in more cost-effective application of CIO2, but it does not override CIO2's use as a preoxidant in the treatment train.

COMPARISON BETWEEN DISINFECTANTS

COST COMPARISON

The table (Myers, 1990) below compares the cost of treating water with chlorine dioxide and ozone. Chlorine dioxide treatment is more costly than chlorine in most cases, but is often less costly than ozone.

Little information relative to the comparative costs for various disinfecting options for water treatment plants is available in the literature. Table 10 summarizes information (1980) relative to capital, operating and maintenance costs for several alternative disinfectants. Recent data submitted to the USEPA by the Chemical Manufacturers Chlorine Dioxide panel indicate that this tabulated data is still of qualitative value. Not unexpectedly, the cost per gallon of water treated increases significantly for smaller systems.

Table10. Cost Comparison of Disinfectants

COSTS	SYSTEM CAPACITY				
	1 mgd	5 mgd	10 mgd	100 mgd	150 mgd
CAPITAL COST (c/1000 gal)*					
Chlorination (2mg/L)	2.19	0.88	0.62	0.26	0.24
Ozone-air (1mg/L)	2.90	1.36	1.11	0.76	0.73
Ozone Oxygen (1 mg/L)	4.46	1.50	1.08	0.61	0.58
Chlorine Dioxide (1 mg/L)	1.9	0.76	0.51	0.22	0.20
Chloramine (1mg/L)	1.70	0.62	0.42	0.17	0.15
OPERATING COST (c/1000 gal)*					
Chlorination (2mg/L)	1.06	0.56	0.46	0.32	0.31
Ozone-air (1mg/L)	2.785	1.08	0.77	0.40	0.38
Ozone Oxygen (1 mg/L)	2.87	1.17	0.88	0.52	0.49
Chlorine Dioxide (1 mg/L)	1.55	1.18	1.12	1.03	1.02
Chloramine (1mg/L)	0.63	0.25	0.19	0.10	0.10
TOTAL COST (c/1000 gal)					
Chlorination (2mg/L)	3.25	1.44	1.08	0.58	0.55
Ozone-air (1mg/L)	5.68	2.44	1.88	1.16	1.11
Ozone Oxygen (1 mg/L)	7.33	2.67	1.96	1.13	1.07
Chlorine Dioxide (1 mg/L)	3.45	1.94	1.63	1.25	1.22
Chloramine (1mg/L)	2.33	0.87	0.61	0.27	0.25

COMPARISON OF CxT VALUES OF THE DISINFECTANTS

Table 11 shows the amount of time (T) needed for a concentration (C) of residual disinfectant to inactivate a microorganism. The concentration is typically measured in mg/L, and the time is measured in minutes.

Table 11. CxT Values

Microorganism	Chlorine (pH 6-7)	Chloramine (pH 8-9)	Chlorine Dioxide (pH 6-7)	Ozone (pH 6-7)
E. Coli	0.034-0.05	95-180	0.4-0.75	0.02
Polio 1	1.1-2.5	768-3740	0.2-6.7	0.1-0.2
Rotavirus	0.01-0.05	3806-6476	0.2-2.1	0.006-0.06
Phage f2	0.08-0.18	Nd	Nd	Nd
Cysts of G. *lamblia*	47-150	2200*	26*	0.5-0.6
Cysts of G. *muris*	30-630	1400	7.2-18.5	1.8-2.0

*99.99% inactivation at pH = 6-9, 90% inactivation at pH = 7 and at 25oC, nd: no data

The most effective disinfectants are those which have the lowest CxT values. This table indicates that the most effective disinfectant is ozone. Chlorine dioxide is noted as the second most effective disinfectant.

COMPARISON OF DISINFECTANTS FOR GIARDIA AND CRYPTOSPORIDIUM

The table below shows the effectiveness of the disinfectants on problematic microorganisms such as Cryptosporidium.

Table 12. CxT Values for Problematic Microorganisms (mg/L*min)

Microorganism	Chlorine (pH 6-7)	Chloramine (pH 8-9)	Chlorine Dioxide (pH 6-7)	Ozone (pH 6-7)
Giardia 0.5 log inactivation pH 6-9, 5o C	16-47	365	4.3	0.3
Cryptosporidium pH 7, 25o C	7200 1 log inactivation	7200 2 log inactivation	78 1 log inactivation	5-10 2 log inactivation

This table shows ozone the most potent disinfectant, with chlorine dioxide second.

Chlorine dioxide is more expensive than chlorine but it is an excellent disinfectant and exhibits greater stability over wide pH ranges. Chlorine dioxide provides residual disinfection in the distribution system but is often used as a primary disinfectant. In the cases where chlorine dioxide is used as a primary disinfectant, chlorine is often used as a secondary disinfectant to provide additional microbial protection in the distribution system. The combination of chlorine dioxide and other disinfection technologies often provides an economical means to reduce disinfection by-products, while providing adequate microbial protection in the distribution system.