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CHLORINE DIOXIDE

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ABSTRACT

Acceptance of chlorine dioxide as an oxidant and disinfectant for drinking water in the United States has grown significantly over the past 20 years; several hundred plants now use chlorine dioxide. In Europe, use of chlorine dioxide is widespread; in Italy, over 30 percent of the water works utilize chlorine dioxide and in Germany, over 10%. The major advantage of chlorine dioxide is that it improves taste and odor and reduces organic by-product formation, such as trihalomethanes (THM's). In addition, chlorine dioxide exhibits efficacy over a wide pH range. The use of chlorine dioxide to disinfect drinking waters is expected to continue to grow in the United States.

This paper describes chlorine dioxide as an effective alternative disinfectant for drinking water systems. Chlorine dioxide's properties and characteristics as they relate to efficacy, kinetics, pH, reaction with metals, by-products and analytical techniques are described. Parameters involved in the generation of chlorine dioxide are described and the regulatory status of chlorine dioxide and disinfection by-products is reviewed.

1. Introduction

1.1 Primary and secondary disinfection overview

In the United States, chlorine dioxide (ClO_2) was first used as a drinking water disinfectant 50 years ago. The first reported use was in 1944 at a water treatment plant in Niagara Falls, New York (Aieta and Berg, 1986). Since that time, use of chlorine dioxide has expanded to other applications including industrial and food processing water treatment. The chlorine, along with chloramines, chlorine dioxide and ozone are the most widely used disinfectants in municipal drinking water systems today. Chlorine dioxide is a distant third in the United States according to a recent survey of the American Water Works Association (AWWA – Skadsen, 1998). The following tables review chlorine dioxide as a primary and secondary disinfectant. The data demonstrates that chlorine dioxide is primarily used as a primary disinfectant and oxidant.

Table 1. Primary Chlorine Dioxide Disinfectant Use in the U.S.

Disinfectant	Number of systems	(%) Population
Chlorine dioxide	760	10

Table 2. Secondary Disinfectant Use in the US

Disinfectant	Number of systems	Percent (%)
Chlorine	592	64
Monochloramine	174	19
Chlorine dioxide	9	1
No disinfectant	150	16

In Europe, ClO_2 is more widely used as a secondary disinfectant. A survey of German water treatment plants (Table 3) reflects that most plants disinfect with sodium hypochlorite, followed by chlorine and then chlorine dioxide (Haberer, 1994a).

Table 3. Disinfectant Use in Germany

Disinfectant	Number of plants	Percentage (rounded)
Sodium Hypochlorite	754	53
Chlorine	368	27
Chlorine dioxide	133	9
Others (ozone, silver, chloramines, combinations)	179	11
Total	**1434**	**100**

The typical THM concentrations were between 1 and 4 µg/l, and in less than 10% of the plants, the guideline value of 10 µg/l was exceeded.

Table 4. Median THM Concentrations in Germany and the US

Country	Disinfectant	Year	Number of Analysis	Median THM (mg/l)
Germany	All chlorine products	1991	700	1.5
	chlorine	1991	239	3.0
	sodium hypochlorite	1991	351	1.0
	chlorine dioxide	1991	75	0.5
US	NORS[1]	1975	80	41
	NOMS[2]	1977	113	45
	AWWARF[3]	1987	727	55
	USEPA[4]/CDHS[5]	1988	35	40

1 NORS = National Organics Reconnaissance Survey
2 NOMS = National Organic Monitoring Survey
3 AWWARF = AWWA Research Foundation
4 USEPA = US Environmental Protection Agency
5 CDHS = State of California Department of Health Services

It is interesting to note that along the river Rhine in Germany, 13 of 16 major water treatment plants use chlorine dioxide (Haberer-1994b). The stated reason for the use of chlorine dioxide is related to low formation of chloroform in the presence of organic precursors. This is very understandable if one views the current standards for trihalomethanes (THM's) in Europe (Table 5).

Table 5. Current Regulations for THMs

Country	TTHM (µg/L)	Chloroform (µg/L)	Dichlorobromomethane (µg/L)
	MAC	**MAC**	**MAC**
Austria	30		
Belgium	100		
Canada	350		
Finland		200	60
France		30	
Germany	10		
Great Britain	100		
Ireland	100		
Luxembourg	50		
Norway	100		
Sweden	50		
Switzerland	25		
U.S.A.	100		
EEC Directive (1995)		40	15

* MAC: Maximum Admissible Concentration

Water utilities in the US continue to improve their disinfection practices by providing adequate microbial protection while minimizing disinfectant by-products. The amendments of the Safe Drinking Water Act include the promulgation of the Disinfectant/Disinfectant Byproduct Rule (D/DPB). The D/DBP rules are being implemented in two phases, Stage I and Stage II. Stage I is proposed to take effect in November 1998 and requires compliance for surface water systems that serve more than 10,000 people. Stage II will be promulgated in May of 2002 and will consider additional scientific, applications and research data. Table 6 reflects proposed levels of disinfectants and their byproducts.

Table 6. Proposed US Maximum Contaminant Levels in the Future

		Stage I	Stage II
Disinfectant	Chlorine Chloramine Chlorine Dioxide	4 ppm 4 ppm 0.8 ppm	
Byproducts	Total Trihalomethanes Haloacetic Acids (HAAs) Bromate Chlorite	80 ppb 60 ppb 10 ppb 1 ppm	40 ppb

2. Properties of chlorine dioxide

Chlorine dioxide is a yellowish-green gas with a molecular weight of 67.46. It is stable and highly soluble in aqueous solutions up to 20 g/l. In addition to its biocidal properties, chlorine dioxide improves the quality of drinking water i.e. odor neutralization, color removal, iron and manganese oxidation. One of the more interesting properties of chlorine dioxide is its biocidal efficacy, which is exhibited over a wide pH range (3 to 9). Chlorine dioxide is ultra violet light sensitive (Junli et al., 1997) and exhibits increasing oxidative capacity with increasing acidity.

$$ClO_2 + 4H^+ + 5e = Cl^- + 2H_2O \qquad (2)$$

Since chlorine dioxide exists as an unstable gas, the product cannot be compressed and shipped in cylinders like chlorine gas. Chlorine dioxide must be produced on-site by use of a mechanical generator. Chlorine dioxide is most commonly generated by reacting sodium chlorite with chlorine gas (2-chemical system) or by reacting sodium chlorite with sodium hypochlorite and hydrochloric acid (3-chemical system).

Two Chemical Chlorine Dioxide Generation Process

$$2NaClO_2 + Cl_2 = 2ClO_2 + 2NaCl \quad (1)$$

$$5NaClO_2 + 4HCl = 4ClO_2 + 2H_2O + 5NaCl \quad (2)$$

Three Chemical Chlorine Dioxide Generation Process

$$NaOCl + 2HCl = Cl_2 + NaCl + H_2O \quad (1a)$$
$$2NaClO_2 + Cl_2 = 2Cl0_2 + 2NaCl \quad (1b)$$
$$\text{Net - } 2NaClO_2 + NaOCl + 2HCl = 2ClO_2 + 3NaCl + H_2O \quad (1c)$$

Chlorine dioxide has several physio-chemical effects on the constituents often found in water. These effects are summarized in Table 7.

Table 7. Effects of ClO_2 in Treatment of Drinking Water

Substance	Reaction
Selected natural and synthetic organics	Can react to form chlorite
Iron and manganese	Oxidized
Color	Removed
THMFP	Lowered
Organics	Oxidized
Phenols	Oxidized to quinones -

3. Use in water treatment

Chlorine dioxide is very useful in treating drinking water. Where chlorine disinfectants react with various substances via oxidation and electrophillic substitution, chlorine dioxide reacts only by oxidation (Aieta and Berg, 1986). As a result, use of chlorine dioxide can result in reduced THM formation in finished water. Higher levels of THM's experienced in chlorine dioxide treated waters are often attributed to poor chlorine dioxide generator performance, i.e. excess chlorine feed to the generator (Anderson et al., 1982).

Production of chloroform occurs over time in a distribution system, where the age of the water can exceed several days (Figure 1).

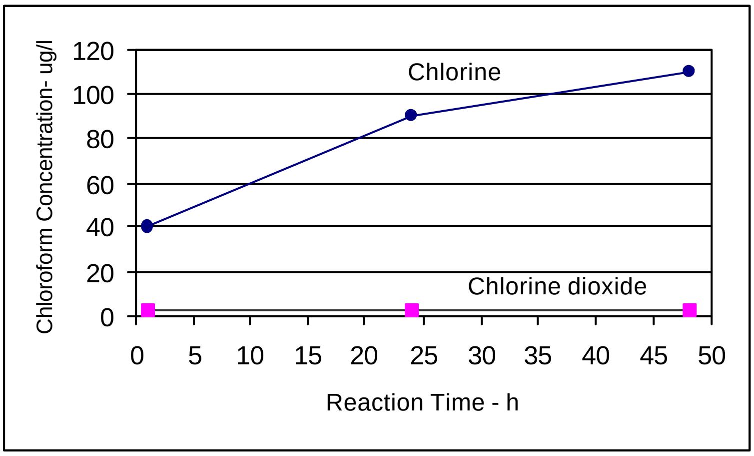

Figure 1. Chloroform Production by Chlorine and Chlorine Dioxide in Water with 5 mg/L Humic Acid (Symons, 1981)

Chlorine dioxide produces by-products in the form of chlorites and chlorates. Chlorites and chlorates both oxidize hemoglobin and chlorite is a hemolytic (red blood cell) agent (Anderson et. al, 1982). The proposed Maximum Contaminant Level (MCL) in the United States for chlorite is 1.0 mg/l, while the chlorate ion is currently unregulated. Data from German water treatment plants indicates that the average chlorite concentration is well under 200 **g/l in Germany (**Haberer, 1994).

Table 8 notes examples of European contaminant limits of chlorine dioxide and sodium hypochlorite.

Table 8. Examples of European Regulations on $NaClO_2$ and ClO_2

Country	**$NaClO_2$**	**ClO_2**	Max. Allowable Quantity (mg/L)	Residual Conc. at end of treatment plant
Belgium	**X**		5	
Germany		**X**	0.4	Min = 0.05 mg/L, max = 0.2 mg/L
Great Britain				Max = 0.5 mg/L as sum of ClO_2 + $NaClO_2$ + $NaClO_3$
Spain	**X**		30	
Sweden		**X**	0.7	

4. Modes of action

4.1 Microbiocidal action

Chlorine dioxide is a stronger disinfectant than chlorine and chloramine. Ozone has greater microbiocidal effects, but limited residual disinfection capability. Recent research in the United States and Canada demonstrates that chlorine dioxide destroys enterorviruses, *E. coli*, amoebae and is effective against cryptosporidium cysts (Finch et al., 1997).

Chlorine dioxide exists in the water as ClO_2 (little or no dissociation) and thus is able to permeate through bacterial cell membranes and destroy bacterial cells (Junli et. al, 1997b). Its action on viruses involves adsorbing onto and penetrating the protein coat of the viral capsid and reacting with the viral RNA. As a result, the genetic capability of the virus is damaged (Junli et. al, 1997a). In comparison to chlorine, chlorine dioxide can be more effective as a disinfectant due to the fact that chlorine exists in the water as HOCl or OCl^-. As a result, bacterial cell walls are negatively charged and repel these compounds, leading to less penetration and absorption of the disinfectant into the membranes.

Table 9 shows the biocidal efficacy, stability and effect of pH for the four most common disinfectants.

Table 9. Biocidal Efficacy, Stability, and pH effect

Disinfectant	Biocidal Efficacy	Stability	Effect of pH Efficacy (pH=6-9)
Ozone	1	4	Little influence
Chlorine Dioxide	2	2	Slightly increases with Increase in pH
Chlorine	3	3	Decreases considerably With pH increase
Chloramines	4	1	Little influence

Table 9 demonstrates that ozone, while having the strongest oxidation potential, is the least stable of the four noted compounds. Also noted is the fact that chloramines may be the least effective biocide, but exhibit the longest residual time.

Selection of a disinfectant or selection of combinations of disinfectants must include a balanced view of the overall requirements of a specific water plant and distribution system.

4.2 Oxidant action

The oxidant action of chlorine dioxide often improves the taste, odor, and color of water. Chlorine dioxide reacts with phenolic compounds, humic substance, organics, and metal ions in the water.

For example, iron is oxidized by chlorine dioxide so that it precipitates out of the water in the form of iron hydroxide. The precipitate is then easily removed by filtration.

$$ClO_2 + 5Fe(HCO_3)_2 + 3H_2O = 5Fe(OH)_3 + 10Cl_2 + Cl^- + H^+ \qquad (3)$$

Chlorine dioxide reacts with organics, typically by oxidation reactions, and forms few chlorinated organic compounds. Free chlorine, in the presence of organic precursors can form trihalomethanes (THM's) and other halogenated compounds (Aieta and Berg, 1986).

Phenolic compounds present in drinking water are due mainly to contamination from industrial sources. Such molecules, even when present in concentrations of micrograms per liter, give an unpleasant odor and taste. Chlorine dioxide reacts rapidly with phenols. This reaction may vary in different systems.

1) The formation of quinones or chloroquinones.
2) The breaking of the aromatic ring and the formation of aliphatic derivatives.

Humic acid, a THM precursor, is oxidized by chlorine dioxide thus minimizing halogenated compound formation in secondary treatment (Aieta and Berg, 1986).

5. Chlorine dioxide problems

The majority of problems associated with chlorine dioxide center around two areas:

1) Chlorine dioxide generation equipment.

There is no industry standard for the performance of chlorine dioxide generators. Generator efficiency is defined not only in terms of the conversion of sodium chlorite to chlorine dioxide, but also by the generation of byproducts such as chlorate ion, free chlorine and excess chlorite. Without proper generator performance, these byproducts can exit the chlorine dioxide generator in excess and diminish intended results. Additionally, poor generator performance will result in higher than desired operating costs. Modern chlorine dioxide generators are capable of consistently performing at desired levels when properly applied and operated.

2) Proper analysis of chlorine dioxide and its byproducts.

Because chlorine dioxide reactions involve the formation chlorite ion byproduct, a simple test kit cannot provide required analytical data. The analysis of the chlorine dioxide generator stream and finished water are required to quantify the dosage and byproducts accurately. It is necessary to speciate chlorine dioxide, chlorite ion and free chlorine, specifically in the generator stream to determine both yield and efficiency. The recommended method to determine generator yield and efficiency is the four-step amperometric titration procedure. Test kits are available for concentrations less than 5 mg/l in finished water, but have limitations and interferences.

6. Comparison between disinfectants

6.1 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.

Table 10. 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

6.2 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 25^{o}C, 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.

6.3 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, 5^{o} C	16-47	365	4.3	0.3
Cryptosporidium pH 7, 25^{o} 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.

7. Summary of the advantages and disadvantages of chlorine dioxide

7.1 Advantages

- Effective against many microorganisms and is more potent than chlorine over a short contact time.
- Stronger oxidant and contributes to the removal of odor, color, and bad taste.
- Limits/reduces trihalomethane formation.

7.2 Disadvantages

- Costs more than chlorine.
- Chlorite and chlorate byproducts are formed.
- Must be generated on-site.

8. Conclusion

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 in the U.S., 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.

In the United States, the primary goal is to provide adequate microbial protection in drinking water systems while minimizing undesirable disinfectant by-products. To meet this goal, a balanced view of alternative disinfection technologies must be realized and applied.

9. References

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10. Additional references

Three good reference books on chlorine dioxide are:

Gates, D. The Chlorine Dioxide Handbook, 1998, American Water Works Association, ISBN 0-89867-942-7.

Masschelein, W.J. Chlorine Dioxide,1979, Ann Arbor Science Publishers, ISBN 0-250-40224-6.

George, D.B. Case Studies of Modified Disinfection Practices for Trihalomethane Control, 1990, AWWA Research Foundation, ISBN 0-89867-515-4.

The first book, second in AWWA's Water Disinfection Series, provides an in-depth look, from theory to practical application, at a technology that offers both distinct advantages and issues of concern. Written by a leading expert in the field, well illustrated.

The second book is an academic reference book describing the formation and use of oxychlorine compounds in water treatment, and other uses such as the treatment of textiles, flour, food products, and the purification of air.

The third book describes 5 water treatment plants that had difficulties meeting the trihalomethane standards and retrofitted their chlorination systems to produce chlorine dioxide.