OxyChem®

Basic Chemicals

Sodium Chlorite
Treatment of Cooling Water with Chlorine Dioxide

Introduction

Chlorine dioxide, which has a long history of use in drinking water disinfection, is increasing its share of the cooling tower microbiological control market. In large measure, this is the result of chlorine dioxide's benefits when compared to other cooling tower biocides: it acts rapidly; is less sensitive to cooling water contamination and pH changes; has few side reactions and is environmentally friendly. This brochure covers the theory and practical application of chlorine dioxide to cooling towers.

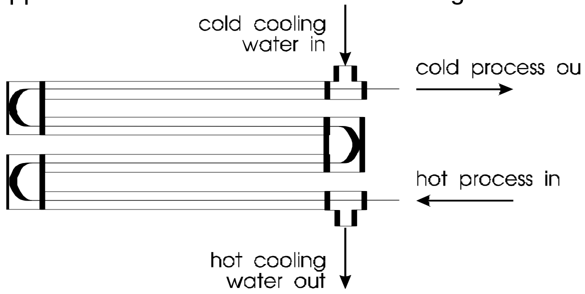


Figure 1. Heat Exchanger

Cooling Systems

A cooling system exists to remove heat from a process. This process may be a physical, chemical, or mechanical process. Heat is picked up by a recirculated fluid from a heat exchanger. A heat exchanger, shown in Figure 1, is a device in which the recirculated water is separated from the hot process fluid by a thin heat-conducting surface. Heat moves from the hot process fluid through the exchanger surface raising the temperature of the cooling water. From the heat exchanger the hot cooling water goes to the top of the cooling tower, shown in Figure 2, it is sprayed over the fill and slowly falls to the sump. The fan at the top of the tower induces a draft, which causes water evaporation and cooling. From the sump cool water is pumped back to the heat exchanger.

Cooling System Treatment

Treatment of cooling systems has two basic objectives: to protect and extend the life of the cooling system and to insure good heat transfer and removal. Any fouling of the heat exchanger surface by scale, debris, or microbiological growth decreases the heat transfer efficiency. Corrosion destroys heat exchanger surfaces and causes leaks that result in mixing of the cooling water and the process fluid. Consequently, there are three components to a cooling water treatment program: 1) microbiological control, 2) scale and deposit control and 3) corrosion control. The treatment used for each component must be selected based upon its

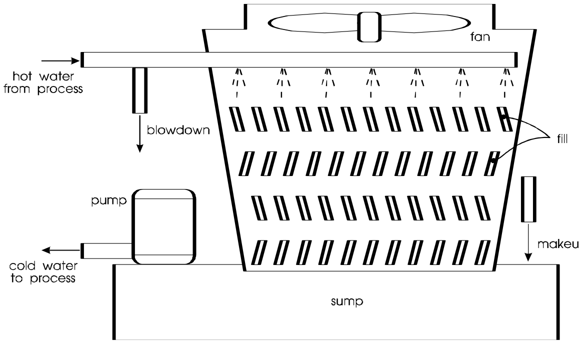


Figure 2 - Cooling Tower

performance and its compatibility with the other treatment components. Since biological control chemicals can be aggressive, react with and alter other treatment chemicals, a brief overview of corrosion and scale control and the chemicals used will be given before focusing on microbiological controls.

Corrosion Control

Corrosion is the process by which solid elemental metals or alloys are converted to oxides or other compounds, which are frequently soluble. The rusting of iron is a typical corrosion process. Corrosion occurs at sites that are connected by an electron (e-) flow through the metal. Different types of chemical reactions occur at these surfaces. An oxidation reaction or the loss of metal (Equation 1a) occurs at the anode; a reduction reaction (Equation 1b) occurs at the cathode. Electron flow and both surface reactions are required for corrosion to occur.

1a. Anode Reaction

$$Fe^0 \rightarrow Fe^{+2} + 2e^-$$

1b. Cathode Reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4HO^-$$

1c. Net Corrosion Reaction

$$2Fe^- + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

Chemical corrosion treatments function by forming a passivating (or insulating) barrier at either the anode or cathode surfaces. This stops the surface reactions and prevents corrosion. Common corrosion treatment chemicals are given in Table 1.

Table 1
Typical Corrosion Control Chemicals

Chemical	**Formula**	**Function**
Chromate	$NaCrO_4$	Anodic Protection
Molybdate	$NaMoO_4$	Anodic Protection
Poly Phosphate	$NaO\text{-}[PO_3Na]_x\text{-}Na$	Cathodic Protection
Silicates	$(Na2O)_3 \cdot (SiO_2)_{10}$	Anodic Protection
Triazoles	$R\text{-}C_6H_4N_3$	Copper Protection
Zinc	$ZnCl_2$	Cathodic Protection

Scale and Deposit Control

Scale and deposits have detrimental impact on the cooling systems, causing loss of heat transfer efficiency, flow restrictions, and system pluggages. The difference between scale and deposit is based upon their normal state in the cooling water. Dissolved solids cause scale; suspended solids cause deposits. Scale is formed from chemicals that exhibit inverse solubility, i.e. are less soluble as the water temperature increases and deposit on heat exchanger surfaces. The most common of these scale compounds is calcium carbonate. The chemistry of calcium carbonate scale formation is given in Equations 2a & 2b.

2a. $HCO_3^- + OH^- \rightarrow CO_3^= + H_2O$

2b. $Ca^{+2} + CO_3^= \rightarrow CaCO_3$

Three types of chemicals are used to control scale and deposits: chelants, sequesterants, and dispersents. Scale may be controlled by any type of treatment; deposits must be controlled by dispersents.

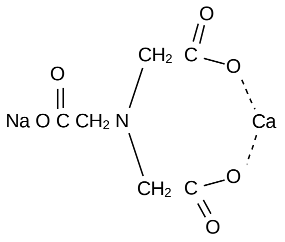


Figure 3
Chelated Calcium

Chelants function by forming a soluble compound (Figure 3), which prevents the formation of scale.

This type of treatment exhibits a fixed, integer (or stoichiometric) ratio between the calcium and the chelant.

In contrast, a *sequesterant* may be used at a sub-stoichiometric level. Under these conditions it does not prevent the formation of calcium carbonate, but it does modify the crystal structure of the scale making it non-adhering to heat exchanger surfaces.

Dispersents are low molecular weight polymers that prevent the agglomeration of scale and deposits. They function by changing the surface charge on deposits and scale particles. Common scale and deposit control chemicals are listed in Table 2.

Table 2
Typical Scale & Deposit Control Chemicals

Chemical	Type of Treatment
EDTA	Chelant
HEDP	Sequesterant
NTA	Chelant
PBTC	Sequesterant
AMP	Sequesterant
poly acrylate	Dispersent
poly maleic anhydride	Dispersant
poly maleic anhydride copolymers	Dispersant
poly methacrylate	Dispersant
poly phosphate	Sequesterant

Microbiological Control

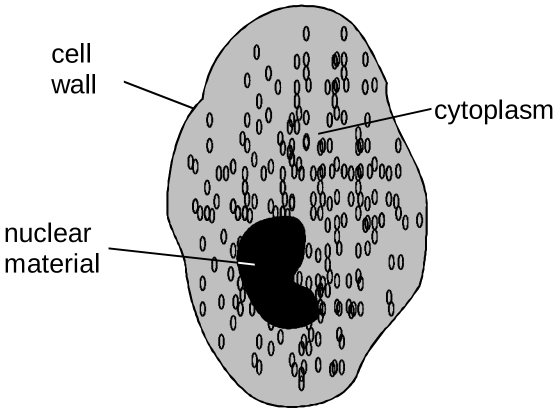


Figure 4
Organism Cell Structure

Microbiological control is perhaps the most important portion of a cooling tower treatment program. Failure of the microbiological control program causes microbiogical fouling, corrosion of metal, and rot of tower wood. Three main types of organisms are found in cooling systems: bacteria, algae, and fungi. While fungi are more complex, bacteria and algae share a common structure, which is shown in Figure 4.

The major components of all cells are the cell wall, the cytoplasm, and the nuclear material. While cells of higher organisms have more specialized components called organelles, understanding of microbiocides actions can be understood using the simplest cells. To survive and grow, microorganisms must keep their cellular material together; obtain food; excrete wastes; process the food into energy and cellular material; and reproduce. For the simplest cells the cell wall serves the dual purpose of keeping the cellular material together and energy synthesis. While both cytoplasm and nuclear materials have a role in the conversion of food to cellular matter, only the nuclear matter is involved in reproduction. Microbiocides kill microorganisms by attacking cellular sites and inhibiting necessary cellular functions. These products can be divided into two major groups based upon their mode of action: non-oxidizing biocides and oxidizing biocides.

Biocidal Treatment Alternatives

Non-oxidizing Biocides
The first group is the organic microbiocides. This is a diverse collection of chemicals that are typically slow acting and are slug-fed, i.e., added weekly to achieve high concentration then allowed to decrease until the next addition. This type of treatment overdoses the microbiocide in the hope that an effective residual remains until most of the microorganisms in the water are dead. The chemical species used as non-oxidizing biocides are:

1. dibromo-nitrilo-propionamide
2. glutaraldehyde
3. quatenary ammonium salts
4. various organo-sulfur compounds

A summary of the properties and use of non-oxidizing biocides can be found in Table 4.

Dibromo-nitrilo-propionamide (DBNPA) is a broad-spectrum biocide that may be used over a pH range of 6 to 8. This product is not compatible with hydrogen sulfide, organic contaminants, or strong reducing agents. It achieves control by attacking the cell wall, which interfers with material transport and binding with proteins, which interfers with energy production.

Glutaraldehyde is a broad-spectrum biocide that may be used over a pH range of 6 to 14. This product is not compatible with ammonia or amines. Like DBNPA this product achieves control by attacking the cell wall, which interfers with material transport and binding with proteins, which interfers with energy production.

Quatenary ammonium salts are narrow-spectrum biocide that may be used over a pH range of 6 to 14. These salts function primarily as algicides, since the higher dosages required for bacterial control usually cause foaming problems in the cooling tower. Anionic polymers and organic contaminants interfer with the performance. They achieve control by attaching to and rupturing cell walls causing lysis or the release of all cell material.

Organo-sulfur compounds of various types are used as microbiocides.

> *Carbamates* are good bactericides and algicides that may be used over a pH range of 7 to 14 but are not compatible with chromates or dissolved iron. They achieve control by interfering with the electron transfer necessary for the cell's energy production.
>
> *Isothiazolinones* are good bacteriacides, but only fair algicides. They may be used over a pH range of 6 to 9 and are incompatible with chlorine and hydrogen sulfide. Like the carbamates they achieve control by interfering with the electron transfer necessary for the cell's energy production.
>
> *Thiocyanates* are broad-spectrum biocides that may be used over a pH range of 6 to 8 but can not tolerate dissolved iron. Like the carbamates they achieve control by interfering with the electron transfer necessary for the cell's energy production.
>
> *Thiones* are broad-spectrum biocides that may be used over a pH range of 7 to 14. Like carbamates, they are compatible with chromates. They achieve control by forming products that resemble microbial metabolites. These products interfer with the bio-chemistry of the cell resulting in its death.

Oxidizing Biocides
The second group, the oxidizing microbiocides, includes chlorine (gas, hypochlorites, & chloro-isocyanurates), bromine (NaBr-NaOCl, & bromo-chloro-methyl-hydantoin), and chlorine dioxide. These microbiocides rapidly react with both microbiological species and chemicals present in the water. This reactivity is both the strength and weakness of these products. Rapid reaction with microbiological species means a rapid and effective kill; rapid reaction with chemicals means consumption of the product for other than microbiological control. Since

chemical reactions are usually more rapid, only the portion of the product remaining after the chemical reaction (demand) is complete is available for microbiological control. This portion is usually called the residual and is related to the dose by the following Equation 3 below:

3. Residual = Dose - Demand

The demand of the cooling water depends upon 1) the level of microbiological growth in the cooling system, 2) chemical loading from process leaks, makeup water and the air, and 3) the chemistry of the product.

A summary of the properties and use of oxidizing biocides can be found in Table 5; discussion of the chemistry of disinfection with oxidizing biocides follows:

Oxidizing Biocide Disinfection Chemistry

Disinfection is the process of killing microorganisms to achieve microbiological control. Three oxidizing biocides dominate cooling tower treatment: chlorine, bromine and chlorine dioxide. The limitations, properties and chemistry of each oxidizing biocide will be discussed.

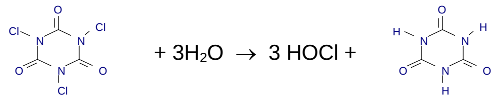
Chlorine Chemistry

As shown in Equation 4, chlorine reacts with water to form hydrochloric acid and hypochlorous acid (HOCl), which is the most active biocidal form of chlorine. Likewise metal hypochlorites (MOCl) and chloroisocyanurates are chlorine sources that react with water to form hypochlorous acid. Their reactions are summarized in Equations 5 and 6, respectively.

4. $Cl_2 + H_2 \rightarrow HCl + HOCl$

5. $MOCl + H_2O \rightarrow MOH + HOCl$

6.



Consequently, the disinfection chemistry of all chlorine releasing species will be defined by the chemistry of hypochlorous acid. There are two important aspects to this chemistry: 1) pH response, and 2) reactions with ammoniacal compounds (ammonia and amines).

pH Response

Hypochlorous acid reacts with bases to form hypochlorite ion (OCl^-), which has only 5% of the biocidal activity of hypochlorous acid. As can be seen in Figure 5 the percentage of hypochlorous acid and the consequent biocidal efficacy decrease with increasing water pH. The hypochlorous acid fraction drops from 79% at pH 7 to 28% at pH 8. Since many cooling towers operate near pH 8.0 for corrosion control, this response is significant.

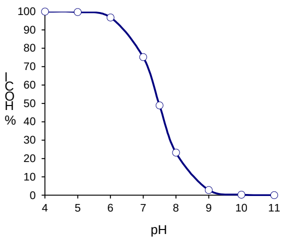


Figure 5. pH Response

Ammoniacal Reactions

Chlorine (in all its forms) reacts rapidly with ammonia and amines to form chloramines, which have 1% the biocidal efficacy of hypochlorous acid. This is a stepwise reaction which forms a mixture of mono-, di- and tri-chloramine. These reactions, which are summarized in Equations 7a-c, require 7.6 parts of chlorine for every part of ammonia-N to form trichloramine or nitrogen trichloride (NCl_3).

7a. $HOCl + NH_3 \rightarrow NH_2Cl + H_2O$

7b. $HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$

7c. $HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$

Chlorine's Limitations

As a result of its response to pH and its reaction with ammoniacal compounds, chlorine's use in cooling towers has limitations. Simply increasing the chlorine dosage in the presence of high pH or ammonia levels is not advisable since this causes increased metal corrosion, wood delignification and higher levels of total dissolved solids (TDS). In addition, many water treatment chemiclas are attacked by chlorine. Among these are triazole corrosion inhibitors and the scale inhibitors EDTA, NTA and AMP. Finally, in the presence of organic material chlorine can form THM's (trihalomethanes). These compounds have been shown to be carcinogenic and are currently limited to 100 ppb in drinking water.

Table 4
Non-Oxidizing Biocides

	Material	Formula	Form	% Active	Min. Dose	Max. Dose	Feed Time	Min. pH	Max. pH
1	Methylene-bis-Thiocyanate	SCN-CH_2-SCN	suspension	10	25 ppm[1]	50 ppm[1]	1/wk	6	8
2	Tetrahydro 3,5-Dimethyl-2H-1,3,5-Thiadia-zone-2-Thione	$C_5H_{10}N_2S_2$	solution	24	30 ppm[1]	60 ppm[1]	1/wk	6.5	14
3	Na Dimethyl-Dithio-Carbamate	$C_3H_6NS_2Na$	solution	30	20 ppm[1]	40 ppm[1]	1/wk	7	14
4	Dibromo-Nitrilo-Propionamide	$C_3H_2N_2OBr$	solution	20	6 ppm[1]	15 ppm[1]	1/wk	6	8
5	(Chloro) Methyl-Isothiazolinones	C_4H_4NOSCl, & C_4H_5NOS	solution	1.15	25 ppm[1]	50 ppm[1]	1/wk	6	9.5
6	Glutaraldehyde	$O=CH(CH_2)_3CH=O$	solution	45	25 ppm[1]	100 ppm[1]	1/wk	6	14
7	Alkyl-Benzyl-Dimethyl Ammonimum Chloride	$RC_6H_5\ (CH_3)_3NCl$	solution	9.4	30 ppm[1]	120 ppm[1]	1/wk	6	14
8	Dioctyl-Dimethyl Ammonimum Chlorite	$(C_8H_{17})_2(CH_3)_2\ NCl$	solution	50	30 ppm[1]	120 ppm[1]	1/wk	6	14

[1] ppm based upon product
[2] C = continuous, I - intermittent

Table 5
Oxidizing Biocides

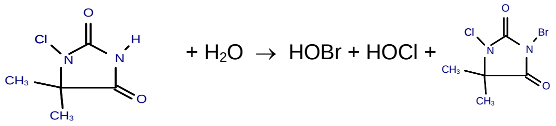
	Material	Formula	Form	% FAC	Required Residuals		Feed Type	Min. pH	Max. pH
					Min. Dose	Max. Dose			
1	Chlorine Dioxide	ClO_2	solution	---	0.2 ppm	0.5 ppm	C	5	9
2	Chlorine	Cl_2	gas	100	0.5 ppm[2]	1.0 ppm[2]	C	6	7.5
3	Calcium Hypochlorite	$Ca(OCl)_2$	solid	65	0.5 ppm[2]	1.0 ppm[2]	C	6	7.5
4	Sodium Hypochlorite (Industrial)	NaOCl	solution	12	0.5 ppm[2]	1.0 ppm[2]	C	6	7.5
5	Sodium Hypochlorite, (Domestic)	NaOCl	solution	5	0.5 ppm[2]	1.0 ppm[2]	C	6	7.5
6	Lithium Hypochlorite	LiOCl	solid	35	0.5 ppm[2]	1.0 ppm[2]	C	6	7.5
7	Trichloro Isocyanuric Acid	$(CONCl)_3$	solid	89	0.5 ppm[2]	1.0 ppm[2]	C	6	7.5
8	Sodium Dichloro Isocyanuric Acid	$(CON)_3Cl_2Na$	solid	56	0.5 ppm[2]	1.0 ppm[2]	C	6	7.5
9	Bromo, Chloro, Dimethyl Hydantoin	$C_5H_6N_2O_2ClBr$	solid	---	0.2 ppm[3]	0.5 ppm[3]	C	7	10
10	Sodium Bromide- "Chlorine"	NaBr only (see above for Cl_2 & NaOCl pricing)	varies	38% NaBr	2.0 ppm[4]	4.0 ppm[4]	C	7	10

(1) C = Continuous, I = Intermittent
(2) as free available chlorine (FAC)
(3) as free available halogen (FAX)
(4) product dose = 3.81 times chlorine demand, then cut chlorine feed to 50-80%

Bromine Chemistry

One of the oxidizing biocides that has been used to overcome the deficiencies of chlorine is bromine. Bromine is applied in two common forms: 1) bromo-chloro-methyl-hydantoin and 2) the reaction of sodium bromide with sodium hypochlorite. Both methods form hypobromous acid (HOBr) in water.

8a.



8b. $NaBr + NaOCl + HCl \rightarrow HOBr + 2\ NaCl$

Like chlorine, the biocidal species is the oxyacid, hypobromous acid. The pH curve for hypobromous acid is shifted up approximately one pH unit, i.e., the fraction of hypobromous acid present at pH 8.5 is equal to the fraction of hypochlorous acid present at pH 7.5. While bromine also reacts with ammoniacal compounds to form bromamines, there is a significant difference between the biocidal activity of bromamines and chloramines. Bromamines are potent biocides, while chloramines are not. But like chlorine, bromine reacts with organic materials, whether treatment chemical or contaminants. Consequently, bromine overcomes only some of chlorine's deficiencies as cooling water treatment.

Chlorine Dioxide Chemistry

Chlorine dioxide's chemistry is best summarized not by what it reacts with so much as by what it does not react with. Chlorine dioxide does not react with water nor does its chemical form or biocidal activity change with changes in pH. Chlorine dioxide also does not react with ammoniacal, or most organic contaminants and treatment chemicals present in the cooling water. Consequently, the dosage required for biocidal control remains fairly constant over a wide range of cooling water conditions. This makes chlorine dioxide an excellent choice for cooling water that has a high pH or that has high levels of organic or ammoniacal contamination.

Chlorine dioxide's poor stability means that it can not be shipped; it must be generated at the point of application from sodium chlorite ($NaClO_2$) and other chemicals. Two methods of generation are used in the US: 1) Chlorine-Chlorite Generation and 2) Acid-Chlorite Generation. Each of these generation methods will be examined.

Chlorine-Chlorite Generation

Chlorine dioxide is generated from chlorine and chlorite by the reaction of sodium chlorite and hypochlorous acid:

9a. $2\ NaClO_2 + HOCl + HCl \rightarrow 2\ ClO_2 + 2\ NaCl + H_2O$

Hypochlorous acid may be obtained in two ways: by the hydrolysis of chlorine (Equation 4) or by the acidification of sodium hypochlorite (Equation 9b). Irrespective of the source of hypochlorous acid used, generator operated for cooling tower applications use at least 5% excess chlorine to drive the reaction with typical conversions of sodium chlorite to chlorine dioxide exceeding 90%.

4. $Cl_2 + H_2O \rightarrow HOCl + HCl$

9b. $NaOCl + HCl \rightarrow HOCl + NaCl$

Acid-Chlorite Generation

When solutions of sodium chlorite are acidified with hydrochloric acid (HCl) they react to form chlorine dioxide:

10. $5\ NaClO_2 + 4HCl \rightarrow 4\ ClO_2 + 5NaCl + 2\ H2O$

This type of generation sacrifices some chlorine dioxide yield to obtain greater purity and ease of operation. The chlorine dioxide produced by this type of generator contains virtually no chlorine. Typical conversions of sodium chlorite to chlorine dioxide are 80%.

Chlorine Dioxide Treatment

Since the primary function of a biocide is to protect the heat exchangers and other metal parts of the cooling system, chlorine dioxide should be applied directly into the suction of the cooling system's recirculating pump. Alternatively, it may be applied beneath the water in the sump as close to the pump intake as possible. Depending upon how critical the cooling system is, two different treatment schemes may be used: an intermittent treatment scheme and a continuous treatment scheme. Since both treatment schemes are based upon establishing a chlorine dioxide residual, to be effective the chlorine dioxide demand of the cooling water must be known. Typically, the chlorine dioxide demand is determined over a 5-minute time interval. Equation 3 shows the relationship between chlorine dioxide demand, dose and residual.

3. Residual = Dose - Demand

Intermittent Treatment

An intermittent treatment program may be used for less critical cooling systems. This program applies chlorine dioxide three times a day (dawn, dusk, and midnight) at a dose sufficient to achieve a 0.5-1.0 ppm chlorine dioxide residual. This dose is based upon the cooling system recirculation rate. The duration of each dosing period is half an hour or four turnovers of the total cooling system volume, whichever is greater.

Continuous Treatment

A continuous treatment program, which is much more expensive, can be used for critical cooling systems. This program applies chlorine dioxide continuously at a dose sufficient to achieve a 0.1 - 0.2 ppm chlorine dioxide residual. This dose is again based upon recirculation rate.

Chlorine Dioxide Treatment Example

DPD Method

Both chlorine and chlorine dioxide react with DPD to give a red-colored solution. The intensity of the red color is proportional to their concentrations. Glycine, NH_2CH_2COOH, is added prior to the DPD to react with and mask chlorine in the sample. If a test kit calibrated for chlorine is used, the result must be multiplied by

The water of an industrial cooling tower with a total system volume of 65,000 gallons and a recirculation rate of 22,000 gpm had a chlorine dioxide demand of 0.36 ppm ClO_2. The following table and calculation give the estimated daily chlorine dioxide requirement for both intermittent and continuous treatment.

Table 6
Chlorine Dioxide Treatment Example

	Intermittent Treatment	Continuous Treatment
Treatment Time, hrs/day	1.5	24
Dosage, ppm ClO_2	1.36	0.56
Total Volume Treated, mgpd	1.98	31.7
ClO_2 required, lbs/day	22.50	148

$$\text{lbs/day } ClO_2 = \frac{\text{Dose (ppm)} \times \text{Minutes Treated/Day} \times \text{Recirc. Rate} \times 8.34 \text{ lbs/gal}}{1{,}000{,}000 \text{ lbs/million lbs}}$$

Chlorine Dioxide Analysis

While chlorine dioxide concentrations may be determined by many different methods, two methods have been commercialized and are in widespread use: the DPD (N,N-diethyl-*p*-phenylenediamine) method and the CPR (chlorophenol red method). Since the DPD method is normally used to also determine chlorine concentrations, it is widely available. However, it must be modified so that it reads only chlorine dioxide. In contrast, the CPR method is not as widely used but is specific for chlorine dioxide.

1.9 to correct for the higher equivalent weight of chlorine dioxide.

CPR Method

The CPR method specifically determines chlorine dioxide concentration based upon its ability to convert red CPR to a colorless product. The amount of the red CPR that is bleached is proportional the chlorine dioxide concentration.

Chlorine Dioxide Service

The implementation and administration of a chlorine dioxide treatment program for cooling tower microbiological control requires several different steps. Consequently, many plants have found it cost effective to employ a water service company to implement and administer their chlorine dioxide programs. These companies typically provide the following services: 1) determine the chlorine dioxide demand of the water; 2) size, design, and provide the chlorine dioxide generator; 3) determine the optimum application point and treatment strategy; 4) install and start-up the generator; and 5) provide monthly service visits to maintain and adjust the generator.

Further Information

More detailed information for sodium chlorite, make a request through the OxyChem Technical Service Department.
Call or write:

OxyChem
Technical Service Department
6200 S. Ridge Rd.
Wichita, Kansas 67215
800-733-1165 option #1
OxyChem_Tech_Service@oxy.com