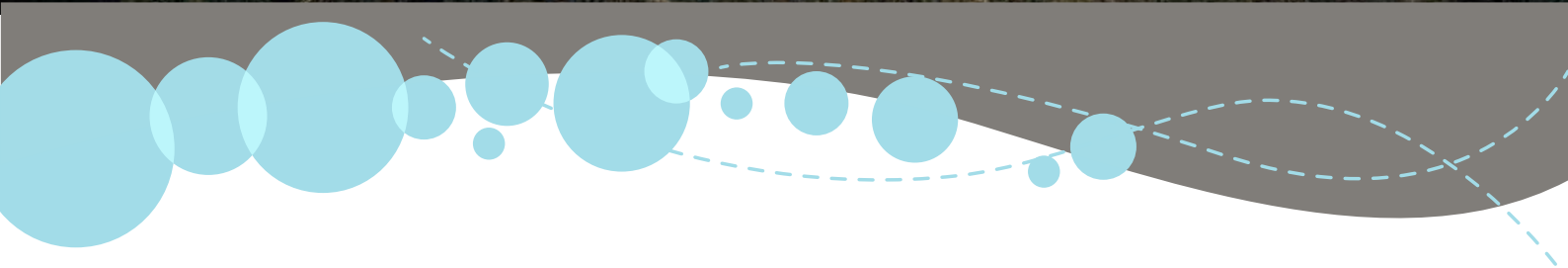


Application Of CHLORITAB IN COOLING TOWER



Introduction

Due to high temperatures and permanent scrubbing of nutrients, cooling towers shape a perfect environment in which microorganisms can thrive. The circumstances in cooling towers are ideal for the growth of Legionella bacteria. Controlling and preventing the growth of microorganisms in a cooling tower system is extremely important for health reasons and required to keep the system running under optimal operating conditions. The presence of the microorganisms may cause the system to breakdown, need to be replaced more rapidly and decrease the efficiency of the heat transfer.

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.

Cooling Systems

A cooling system exists to remove the 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, 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, 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 3) Corrosion Control.

The treatment used for each component must be selected based upon its 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 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.



Corrosion Control:

Corrosion is the process by which solid elemental metals or alloys are converted to



Chemical corrosion treatments function by forming a positive (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	$NaO-[PO_3Na]_xNa$	Cathodic Protection
Silicates	$(Na_2O)_3 \cdot (SiO_2)_{10}$	Anodic Protection
Triazoles	$R-C_6H_4N_3$	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. Three types of chemicals are used to control scale and deposits: chelants, sequesterants, and dispersants. Scale may be controlled by any type of treatment; deposits must be controlled by dispersants. 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.

Dispersants 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	Dispersant
Poly Maleic Anhydride	Dispersant
Poly Maleic Anhydride Copolymers	Dispersant
Poly Methacrylate	Dispersant
Poly Phosphate	Sequesterant

Microbiological Control:

Microbiological control is perhaps the most important portion of cooling tower water treatment program. Failure of microbiological control program causes microbial fouling, corrosion of metal and rot of tower wood. Three main types of organisms are found in cooling systems: bacteria, algae and fungi. 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 and 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. Micro biocides 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 micro biocides. 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 micro biocide 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. Quaternary ammonium salts
4. Various organo sulfur compounds

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

Table No 4
Non-Oxidizing Biocides

Material	Formula	Form	% Active	Min. Dose	Max. Dose	Feed Time	Min. pH	Max. pH
Methylene-bis-Thiocyanate	SCN-CH ₂ -SCN	suspension	10	25 ppm ¹	50 ppm ¹	1/wk	6	8
Tetrahydro 3,5-Dimethyl-2H-1,3,5-Thiadiazine-2-Thione	C ₅ H ₁₀ N ₂ S ₂	solution	24	30 ppm ¹	60 ppm ¹	1/wk	6.5	14
Na Dimethyl-Dithio-Carbamate	C ₃ H ₅ NS ₂ Na	solution	30	20 ppm ¹	40 ppm ¹	1/wk	7	14
Dibromo-Nitrilo-Propionamide	C ₃ H ₂ N ₂ OBr	solution	20	6 ppm ¹	15 ppm ¹	1/wk	6	8
(Chloro) Methyl-Isothiazolinones	C ₄ H ₁₁ NOSCl, & C ₄ H ₉ NOS	solution	1.15	25 ppm ¹	50 ppm ¹	1/wk	6	9.5
Glutaraldehyde	O=CH(CH ₂) ₃ CH=O	solution	45	25 ppm ¹	100 ppm ¹	1/wk	6	14
Alkyl-Benzyl-Dimethyl Ammonium Chloride	RC ₆ H ₅ (CH ₂) ₃ NCl	solution	9.4	30 ppm ¹	120 ppm ¹	1/wk	6	14
Diethyl-Dimethyl Ammonium Chloride	(C ₂ H ₅) ₂ (CH ₂) ₂ NCl	solution	50	30 ppm ¹	120 ppm ¹	1/wk	6	14

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.

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 interferes with material transport; and by binding with proteins, which interferes with energy production.

Quaternary ammonium salts: are narrow spectrum biocides that may be used over a pH range of 6 to 14. These salts function primarily as algacides, since the higher dosages required for bacterial control usually cause foaming problems in the cooling tower. Anionic polymers and organic contaminants interfere with their 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 micro biocides.

Carbamates - are good bactericides and algacides 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 bactericides, but only fair algacides. 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 interfere with the bio-chemistry of the cell resulting in its death.

Oxidizing Biocides:

The second group, the oxidizing micro biocides, includes Chlorine (gas, hypo chlorites, & chloro - isocyanurates), Bromine (NaBr-NaOCl, & bromo-chloro-methyl-hydantoin), and Chlorine Dioxide. These micro biocides 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

Table No- 5
Oxidizing Biocides

Material	Formula	Form	% FAC	Required Residuals		Feed Type	Min. pH	Max. pH
				Min. Dose	Max.Dose			
Chlorine Dioxide	ClO ₂	solution	---	0.2 ppm	0.5 ppm	C	5	9
Chlorine	2 Cl ₂	gas	100	0.5 ppm ²	1.0 ppm ²	C	6	7.5
Calcium Hypochlorite	Ca(OCl) ₂	solid	65	0.5 ppm ²	1.0 ppm ²	C	6	7.5
Sodium Hypochlorite (Industrial)	2 NaOCl	solution	12	0.5 ppm ²	1.0 ppm ²	C	6	7.5
Sodium Hypochlorite, (Domestic)	NaOCl	solution	5	0.5 ppm ²	1.0 ppm ²	C	6	7.5
Lithium Hypochlorite	LiOCl	solid	35	0.5 ppm ²	1.0 ppm ²	C	6	7.5
Trichloro Isocyanuric Acid	(CONCl) ₃	solid	89	0.5 ppm ²	1.0 ppm ²	C	6	7.5
Sodium Dichloro Isocyanuric Acid	(CON) ₃ Cl ₂ Na	solid	56	0.5 ppm ²	1.0 ppm ²	C	6	7.5
Bromo, Chloro, Dimethyl	C ₅ H ₆ N ₂ O ₂ ClBr	solid	---	0.2 ppm ³	0.5 ppm ³	C	7	10
Sodium Bromide- "Chlorine"	NaBr only (see above for Cl ₂)	varies	38	2.0 ppm	4.0 ppm	C	7	10

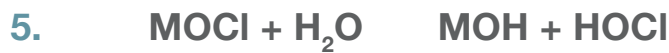
1- c = continuous, I = Intermittent, 2 = As Free available Chlorine (FAC) 3 = As free available Halogen, 4 - Product dose = 3.81 times chlorine demand then cut chlorine feed to 50-80 %

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



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

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).



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 chemicals are attacked by chlorine. Among 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

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 by **2) the reaction of sodium bromide with sodium hypochlorite**. Both methods form hypobromous acid (HOBr) in water.

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.

Cooling tower Treatment with CHLORITAB :

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 CHLORITAB three times a day (dawn, dusk and midnight) at a dose sufficient to achieve a 0.2-0.4 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 CHLORITAB continuously at a dose sufficient to achieve 0.1 - 0.2 ppm chlorine dioxide residual. This dose is again based upon recirculation rate.

CHLORITAB Treatment Example

The water of an industrial cooling tower with a total system volume of 100 m³. The following table and calculation gives the estimated daily **CHLORITAB** requirement

Sr.No.	Hold Up volume	Required dose of CHLORITAB	CHLORITAB Required – Kg / Cycle / Hr
1	100000	0.3 ppm	0.3 Kg
2	100000	0.4 ppm	0.4 Kg
3	100000	0.5 ppm	0.5 kg

Calculation of CHLORITAB dose:

$$\text{CHLORITAB required} = \frac{\text{Required dose rate (ppm)}}{100000} \times \text{Quantity of Water}$$

CHLORITAB 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 **CHLORITAB** demand of the water
- 2) Size, design and provide the **CHLORITAB** system
- 3) Determine the optimum application point and treatment strategy

Advantages of CHLORITAB (Chlorine Dioxide Tablets) :

The goal of using **CHLORITAB** is to increase microbiological control, eliminate the frequent ‘shock’ treatments with hazardous biocides, save money on chemicals and clean up the heat ex- change surfaces so they would operate at maximum efficiency. The advantages of **CHLORITAB** in cooling water treatment are :

- The cooling tower system will operate at maximum efficiency, as chlorine dioxide effectively removes the insulating biofilms layer from the heat exchange surfaces in the chillers.
- Corrosion rates throughout the system decrease dramatically resulting in an i mprovement in the operating condition of the plant and life of the cooling tower.

- **CHLORITAB** strips insulating biofilms and prevents biofilm after growth in cooling towers. The removal of biofilm prevents damage to and corrosion of equipment and piping and causes the pumping efficiency to be improved.
- **CHLORITAB** replaces toxic, slow acting and less effective non-oxidizing biocides (e.g. ammonium bromide is under increasing regulatory scrutiny).
- **CHLORITAB** is capable of removing blue-green algae whereas chlorine is not.
- **CHLORITAB** is the best available technology for Legionella prevention and control.
- **CHLORITAB** does not chlorinate organic molecules meaning no toxic pollutants (like THMs), nor does it form chloramines with ammonia-nitrogen, providing a lower demand for chlorine dioxide. This means that the dosage required for biocidal control remains fairly constant over a wide range of cooling water conditions.
- **CHLORITAB** is effective at lower dose rates in contaminated systems compared to alternative biocides.
- **CHLORITAB** does not react with triazole corrosion inhibitors.
- The biocidal activity is constant over a wide pH-range (2-10), whereas chlorine becomes corrosive in alkaline pH range. No acids are required to adjust the pH.

Contact Us:

SVS AQUA TECHNOLOGIES

Plot No. 43/44/45, Gut No. 411,
Village Urawade, Taluka - Mulshi,
District Pune - 412111, Maharashtra.
Ph.:+91-8007716655 / 020-22923390
Email: info@svsaqua.com ; www.svsaqua.com

