OxyChem®

Basic Chemicals

Sodium Chlorite
Cooling Water Treatment with Chlorine Dioxide

Introduction

Chlorine dioxide (ClO_2) is effective as both a disinfectant and an oxidant in water treatment. Chlorine dioxide is a broad-spectrum microbiocide effective over a wide pH range. Unlike chlorine, chlorine dioxide does not react with organic materials to form trihalomethanes (THMs). Chlorine dioxide is also non-reactive with ammonia-nitrogen and with most treatment chemicals (corrosion and scale inhibitors) present in cooling water systems.

Chlorine dioxide is effective in the control of microbiological growths in industrial cooling waters under conditions unfavorable to chlorine. It is particularly effective in systems having a high pH, ammonia-nitrogen contamination, persistent slime problems, or where the microbial contamination is aggravated by contamination with vegetable or mineral oils, phenols or other high chlorine-demand producing compounds.

Application Description

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. From the heat exchanger the hot cooling water goes to the top of the cooling tower, shown in Figure 1, 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.

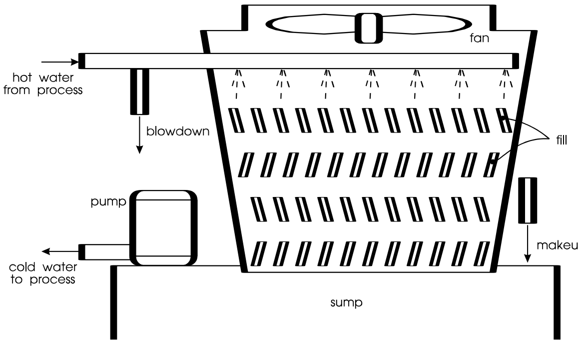

Figure 1 - Cooling Tower

Cooling System Treatment

Treatment of a cooling system 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.

Microbiological control is arguably the most important portion of a cooling tower treatment program. Failure of the microbiological control

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program causes microbiological fouling, corrosion of metal, and rot of tower wood.

Microbial Treatment Alternatives

Biocide products can be divided into two major groups based upon their mode of action: non-oxidizing biocides and oxidizing biocides.

Non-oxidizing Biocides

Non-oxidizing or organic biocides include dibromo-nitrilopropionamide, glutaraldehyde, quaternary ammonium salts and various organo-sulfur compounds. Organic biocides are a diverse collection of chemicals that are typically slow acting and are slug fed, i.e., added periodically to achieve high concentration, then allowed to decrease until the next addition. With this type of treatment, the biocide is dosed to maintain a residual for an appropriate contact time to achieve an effective kill. Repetitive treatments allow those strains of bacteria, which are fairly resistant to the biocides, to predominate in a system.

Oxidizing Biocides

The second group, the oxidizing biocides, includes chlorine (gas, hypochlorites, & chloro-isocyanurates), bromine (NaBr-NaOCl, & bromo-chloro-methyl-hydantoin), and chlorine dioxide. These 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 is complete is available for microbiological control (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.

Three oxidizing biocides dominate cooling tower treatment: chlorine, bromine, and chlorine dioxide.

Chlorine

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.

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

Consequently, the disinfection chemistry of all chlorine releasing species will be defined by the chemistry of hypochlorous acid. Hypochlorous acid reacts with bases to form hypochlorite ion (OCl^-), which has only 1/20 to 1/300 of the biocidal activity of hypochlorous acid depending upon the organism tested. 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 decrease in efficacy is significant.

Chlorine also (in all its forms) reacts rapidly with ammonia and amines to form chloramines, which have 1% the biocidal efficacy of hypochlorous acid. In addition, many water treatment chemicals are attacked by chlorine. Among these are triazole corrosion inhibitors and the phosphonate AMP scale inhibitors along with other polymeric disinfectants. Finally, in the presence of organic material chlorine can form harmful trihalomethanes (THM's).

Bromine

Bromine is applied both solid and liquid forms. Both types of products form hypobromous acid (HOBr) in water.

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. However, like chlorine, bromine reacts with organic materials, whether treatment chemical or contaminants. Brominated organics may be more harmful than chlorinated organics. Consequently, bromine overcomes only some of chlorine's deficiencies as a cooling water treatment biocide.

Chlorine Dioxide

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 ammonia-nitrogen 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 is generally 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: 1) an intermittent treatment scheme and 2) 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 demand is determined over a five-minute period. The relationship between chlorine dioxide demand, dose and residual is as follows.

Residual = Dose – Demand

Economic Comparison with other Biocides

A comparison of chlorine dioxide and other oxidizing biocides should be conducted from the perspective of performance rather than on a cost per pound of chemical basis. When chlorine dioxide is evaluated in this way, it becomes more cost competitive with alternative biocide programs, especially in systems, which operate at high pH or are contaminated with organics. The higher the contamination level the more economically viable chlorine dioxide becomes.

For a clean system, the amount of chlorine dioxide required to treat a system would commonly be 1/4 to 1/5 of that of chlorine. For a contaminated system, the amount required may be as low as 1/20. Figure 2 gives an indication of chlorine dioxide economics versus the economics of other common oxidants based on system contamination.

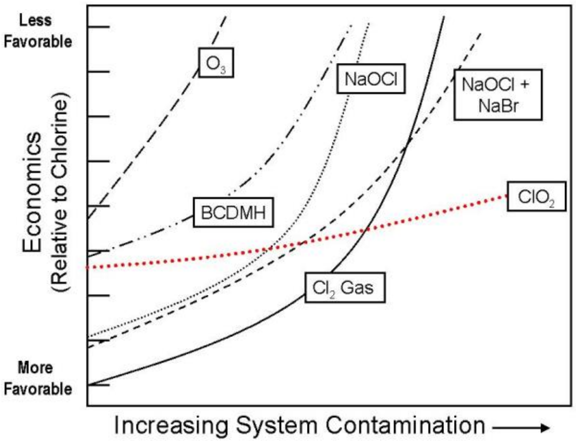

Figure2: Economic Comparison

Advantages of Chlorine Dioxide

- Chlorine dioxide is effective over a broad pH range.
- Chlorine dioxide does not react with organics to form THMs.
- Chlorine dioxide does not react with ammonia-nitrogen.
- Chlorine dioxide is effective at lower dose rates in contaminated systems compared to alternative biocides.
- Chlorine dioxide does not react with triazole corrosion inhibitors.
- Chlorine dioxide is very effective for biofilm and algae control.
- Chlorine dioxide may reduce the requirement for microbial control chemicals in the cooling water.

Feed Requirements
For control of bacterial slime and algae in industrial recirculating and one-pass cooling systems, the required dosages will vary depending on the exact application and the degree of contamination present. The required chlorine dioxide residual concentrations range is between 0.1 and 5.0 ppm. Chlorine dioxide may be applied either continuously or intermittently. The typical chlorine dioxide residual concentration range is 0.1 - 1.0 ppm for continuous doses, and 0.1 - 5.0 ppm for intermittent doses. The minimum acceptable residual concentration of chlorine dioxide is 0.1 ppm for a minimum one-minute contact time.

Method of Feed
Sodium chlorite is converted to chlorine dioxide through a chlorine dioxide generator. Chlorine dioxide solutions should be fed to the cooling tower drip pan (cold water well) or other feed point that permits adequate mixing and uniform distribution. The feed point should be well below the water level to prevent volatilization of the chlorine dioxide.

Chlorine Dioxide Analysis
Residual chlorine dioxide concentrations must be determined by substantiated methods, which are specific for chlorine dioxide. Two suitable methods are published in *Standard Methods for the Examination of Water and Wastewater*[1]*:*

4500-ClO_2 D	DPD-Glycine Method
4500-ClO_2 E	Amperometric Method II

Further Information
More detailed information on sodium chlorite is available on request through OxyChem Technical Service Department. Call or write to:

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References

1. *Standard Methods for the Examination of Water and Wastewater,* APHA, AWWA and WEF, Washington, D.C. (20th Ed., l998).

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