Advanced Chlorine Technology for Cooling Towers

A stabilized chlorine-based biocide for cooling water is capable of removing problematic surface slime and biofilm that chlorine leaves behind. By Justin Shim, Justeq LLC

Chlorine frequently is used as a cooling tower biocide because it is cost effective and controls bacteria counts in bulk water. However, chlorine also is corrosive to metals because it is highly oxidizing, and it has additional problems such as causing vapor lock and quickly degrading.

Introduced in the United States in 2008, a stabilized, chlorine-based cooling water biocide product can eliminate many of the most common problems with chlorine for water treatment. The single-feed, ready-to-use liquid biocide for industrial water treatment applications penetrates into slime masses and produces bromine in situ to break up slime masses from within. Chlorine is significantly less effective in controlling surface-attached micro-organisms such as slime.

In addition, the stabilized, chlorine-based biocide has a minimal odor and can be stored for long periods of time with minimal degradation, simplifying feeding. Less corrosive than bleach, the biocide can be dosed at a rate that is one-third to one-fifth the amount of bleach that is needed. This — combined with the fact that the need for supplemental biocides is reduced — makes the stabilized, chlorine-based biocide more cost effective than bleach (figure 1).

Basic Product Mechanism

The stabilized chlorine-based product only creates bromine in situ when placed in cooling water. Stabilized chlorine — in the form of chlorosulfamate — does not react with bromide in the product while in storage because the pH of the product is alkaline, similar to other liquid halogen products such as chlorine bleach or stabilized bromine. The pH of all these liquid halogen products is above 12.5 to make them stable. The stabilized chlorine and bromide in the product only react to produce bromine at a lower pH, below a pH of 11, and the reaction rate increases as the pH lowers.

When this highly alkaline product is added to cooling water, the two ingredients in the product — stabilized chlorine and bromide — produce bromine because the pH range of typical cooling water is between 8.0 and 9.2. Bromide ions, used to form the bromine, are regenerated after the bromine is consumed within the water system. The regenerated bromide then reacts with stabilized chlorine to produce bromine once again. This recycling mechanism conserves bromide, making the stabilized chlorine product economical.

Biofilm Removal Efficacy

The stabilized chlorine-based biocide is capable of removing problematic surface slime and biofilm that chlorine leaves behind. Even though chlorine is an effective sanitizer to control planktonic microbes, it cannot remove pre-formed slime or biofilm on system surfaces. The reason is that chlorine is consumed at the outer surfaces of slime layer before the chlorine penetrates into the mass, and the mass is left intact.

However, problems in industrial water systems are not usually caused by free-floating microbes but by attached ones that form insulating layers on the heat transfer surfaces. Thus, chlorine is relatively ineffective against the most problematic slime masses for water systems. As a result, most cooling towers resort to using non-oxidizing biocides and bio-dispersants to improve the system cleanliness.

Unlike active chlorine, stabilized chlorine diffuses into the slime layer easily. The diffusion rate of chlorosulfamate through a slime mass is almost as fast as chloride ions. This means that the concentration of stabilized chlorine present inside a slime mass is the same as the concentration in the bulk water when a certain concentration of stabilized chlorine is maintained in the bulk water. Bromide ions, which are introduced in the water with the product, also are present within the slime mass in the same concentration as in the bulk water because bromide is not consumed by the slime during the diffusion process. Bromine (HOBr) then is generated within the slime mass when the chlorosulfamate and bromide react. This bromine generation within slime or biofilm makes this product effective in cleaning up system surfaces and maintaining clean conditions. This fact substantially reduces or even eliminates the need for supplemental non-oxidizing biocides or bio-dispersants (figure 2).

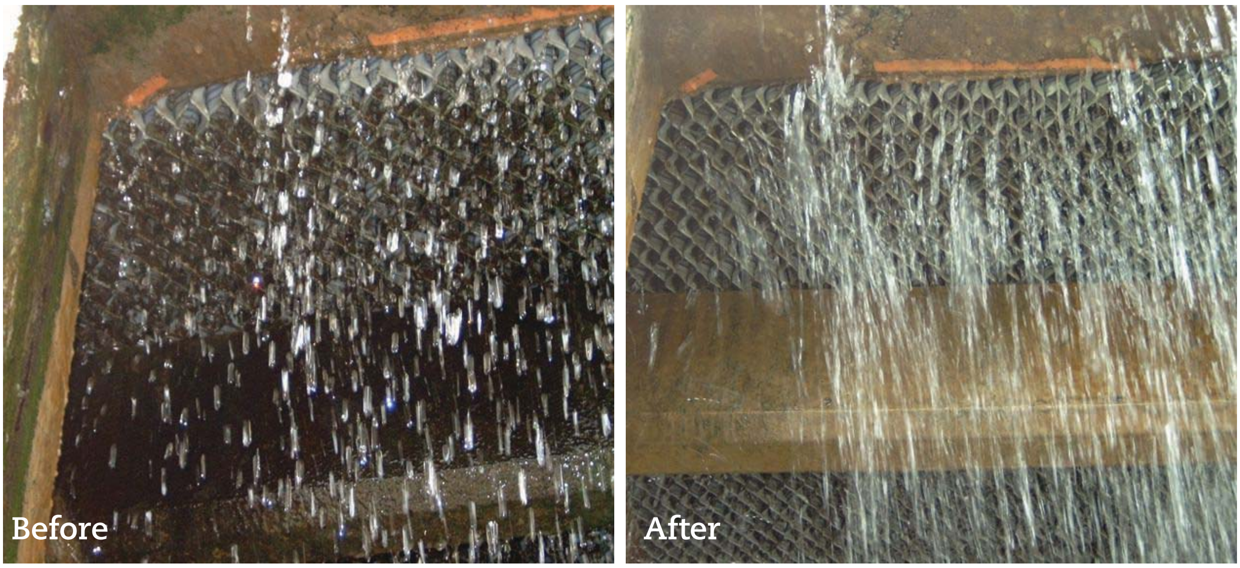

Figure 1. A large industrial cooling tower treated by the advanced chlorine technology showed much cleaner tower surfaces and better water flow.

Consumption Rate

Chlorine is consumed by halogen-demanding components in water, sunlight and evaporation. This waste requires the constant addition of chlorine into industrial cooling water systems. This increases treatment costs and makes water more corrosive because of the increased chloride concentration. Some systems with process contaminations cannot even use chlorine because it is consumed too quickly and chloride buildup is too high to maintain proper chlorine residual levels.

With the stabilized, chlorine-based cooling water biocide, about 5 percent of total halogen in the water is measured as free, indicating nearly all halogen exists as stabilized chlorine, chlorosulfamate. Chlorosulfamate reacts with the most halogen-demanding organics at a much slower rate than active chlorine, and it does not react with many halogen-demanding organics.

In addition, chlorosulfamate is consumed much less than active chlorine by sunlight and is hardly consumed by evaporation. This lower consumption makes the required dosage of the stabilized, chlorine-based cooling water biocide much lower than active chlorine, resulting in a lower usage cost. This advantage is even greater when a system has process contamination and shows a high halogen-demanding condition.

Metal Corrosion

Chlorine treatment in cooling water increases the corrosion rate of metal by both increasing the oxidation potential of water and increasing chloride ion concentration.

Chlorine concentration in water can be controlled by controlling ORP (oxidation reduction potential).

Figure 2. The stabilized, chlorine-based cooling water biocide penetrates into slime and produces bromine in situ to break up slime masses from within.

The highly oxidizing properties of chlorine increase the ORP of water. The increased electrochemical potential of the water thus increases the corrosion rate of metals. Therefore, in order to control corrosion, it is important to keep free chlorine concentration below 0.3 ppm to minimize this corrosive effect of chlorine.

Chlorine treatment also increases chloride ion concentration in water, causing it to be more corrosive to metals. For most cooling water systems, a 12.5 percent sodium hypochlorite solution is used for chlorination because it is safe to use and relatively more economical than chlorine gas or other solid chlorine sources. A sodium hypochlorite solution contains an equal mole ratio of sodium chloride and sodium hypochlorite. Chloride ions are additionally generated in the water when chlorine is consumed. The increase of metal corrosion due to higher chloride concentration is a significant problem for systems with high cycles of concentration and systems with process contaminations. Cooling water for these systems usually contains too much chloride from sodium hypochlorite and become too corrosive to metals, especially to copper alloys.

By contrast, the stabilized, chlorine-based cooling water biocide shows low oxidizing potential and only about 5 percent of its total chlorine is measured as free. When total chlorine of water treated by the stabilized, chlorine-based biocide is 2 ppm, free chlorine is usually measured at only about 0.1 ppm. Metal corrosion by the oxidizing power of chlorine is greatly reduced by this method. Chloride ion buildup with the new product is about one-sixth to one-tenth of sodium hypochlorite because chlorine consumption using the product is less. These two effects — lower oxidizing potential and low chloride buildup — make the stabilized, chlorine-based cooling water biocide less corrosive than chlorine.

Bromine is generated within the slime mass.

Compatibility with Water Treatment Chemicals

The stabilized, chlorine-based cooling water biocide does not decompose corrosion and scale inhibitors like active chlorine. Most modern all-organic or phosphate-based cooling water treatment programs rely on phosphonate calcium carbonate scale inhibitors. These inhibitors will oxidize due to free halogen residuals created by chlorine, thus leading to scale and corrosion problems.

The low oxidizing nature of the stabilized, chlorine-based cooling water biocide eliminates the problem of corrosion and scale inhibitor decomposition. Furthermore, because of its low oxidation properties, relatively low cost phosphonates such as AMP can be used in place of phosphonates such as PBTC. In fact, the stabilized, chlorine-based cooling water biocide does not, at treatment concentrations, decompose even azole copper corrosion inhibitors. (Azole copper corrosion inhibitors usually are added in the product formulation in excessive amounts to compensate for the losses caused by halogen biocides such as active chlorine.) Because the product does not decompose azoles in cooling water, fewer amounts of azoles are needed and water treatment costs can be reduced.

pH Effect

It is well known that the effectiveness of chlorine decreases with an increase of pH in the cooling water to above 8 because a majority of available chlorine presents as OCl^- instead of HOCl, and OCl^- is a much weaker biocide than HOCl. Bromine technology has been applied to solve this problem. Sodium bromide is added together with chlorine to cooling water to produce bromine in situ, adding to treatment costs.

The stabilized, chlorine-based cooling water biocide produces bromine in slime and biofilm as well as in the cooling water. All the chlorine in the product is converted to bromine even though a small amount of bromide is used to produce the bromine because of the bromide regeneration mechanism explained earlier. This mechanism makes this product effective in pHs above 8.5.

Ammonia-Contaminated Conditions

Finally, the stabilized, chlorine-based cooling water biocide is more effective than chlorine in ammonia-contaminated conditions. Chlorine forms chloramine in cooling water contaminated by ammonia, and chloramine is a much weaker biocide than chlorine. Bromamine, which bromine forms in ammonia-contaminated water, is almost as strong a biocide as bromine. Because the product produces bromine as a biocide, ammonia contamination in cooling water does not influence the effect of the product.

In conclusion, most recirculating cooling water systems use a sodium hypochlorite solution instead of chlorine gas due to safety concerns. Industrial-grade sodium hypochlorite is generally a 12.5 percent solution and degrades to less than 10 percent in 6 to 8 weeks. This degradation is accelerated by temperature, sunlight and heavy metal impurities. It is common practice to purchase it frequently to minimize degradation losses.

Sodium hypochlorite solutions produce oxygen and this can cause major problems for engineers. If oxygen is formed in pump casings when the pump is not operating, the pump can gas lock. The gas formation will cause the pump to fail until the casing is vented. Because pumping systems are not typically designed to easily vent this gas, the process is typically time consuming. During the time the pumps are not operating, damage to pump seals and bearings in magnetic-drive pumps occurs because the pump is operating dry. Such problems can create significant maintenance expenses.

The storage stability of the stabilized, chlorine-based cooling water biocide means that less than 2 percent of available chlorine concentration is lost in an entire year. Not only does this allow engineers to purchase the product much less frequently, but the product produces less gas in pumping systems and gas lock is not a problem in almost all cases. **PC**

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