Economical halogen biocide composed of stabilized chlorine and unreacted bromide

By Sang-Hea Shim, Ph. D., Justeq LLC

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Introduction

Problems found in industrial water systems that are caused by microbial activities are controlled by oxidizing and non-oxidizing biocides. Oxidizing biocides are extensively utilized because they are effective and relatively economical. Currently, there is a wide variety available in the market, including, for example, halogen biocides that release chlorine or bromine. Non-halogen oxidizing biocides include peracetic acid, peroxides, chlorine dioxide and ozone.

Chlorine is the most economical oxidizing biocide for industrial water systems. Sodium hypochlorite is the most widely utilized chlorine source because of treatment cost, safety and convenience. Chlorine is consumed on the surface layer of slime mass and is unable to penetrate deeply into the mass because of its high oxidizing property (Chen and Stewart, 1996). Though this may make chlorine effective in controlling floating (planktonic) micro-organisms, it is substantially less effective in controlling surface attached micro-organisms, such as slime. 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.

Chlorine is corrosive to metals because it is highly oxidizing. Therefore, the free chlorine concentration has to be strictly controlled to avoid the damage when it is applied for industrial water systems. The addition of chlorine in cooling water systems increases the chloride concentration and makes the water even more corrosive to metal parts. This problem is even more serious for the systems with long holding time indices or high cycle of concentrations.

The other problems with sodium hypochlorite are vapor lock and degradation with time. Maintaining industrial grade bleach with good active concentration and trouble-free pumping presents substantial problems for the water treatment engineers.

New economical halogen biocide

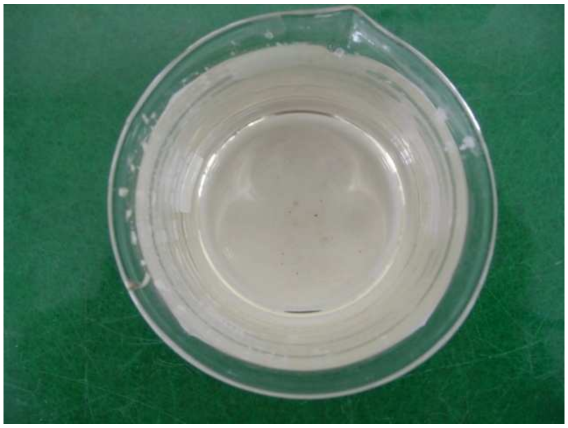
A new patented halogen biocide was introduced in the US water treatment market in the early 2008 (Shim and Kim, 2002) (Shim and Kim, 2008). This product is a single-feed, ready-to-use, liquid halogen biocide for industrial and institutional water treatment applications. The product is a mixture of stabilized chlorine and bromide, from which a bromine biocide is produced in-situ within the slime, bio-film and algae mass formed on system surfaces.

Stabilized chlorine, in the form of chlorosulfamate, does not react with bromide in the product because the pH of the product is very 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. Stabilized chlorine and bromide in the product react to produce bromine at a lower pH, such as below 11, and the reaction rate increases as the pH lowers.

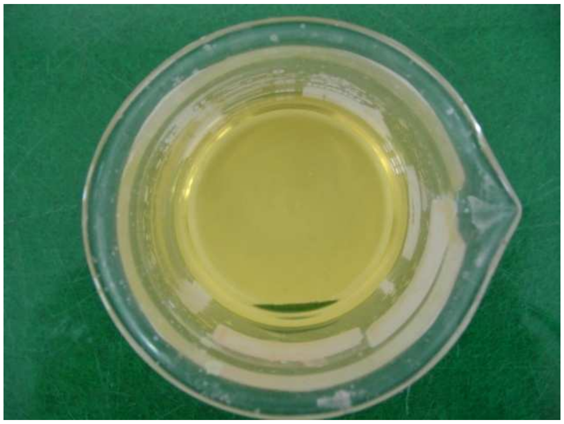
Figure 1 shows the effect of pH on the reaction of stabilized chlorine and bromide. The product in its container is clear in color like normal industrial chlorine bleach as shown in the figure. However, the color changes to yellow, evidence of the formation of bromine, when the pH of the product is lowered to 9 by adding sulfuric acid. This pH change occurs when the product is added into industrial water systems. Since the pH range of typical cooling water is between 8.0

to 9.2, this bromine generation occurs automatically in the cooling water when the product is introduced.

Figure 1. pH Effect on Bromine Generation



Neat Product

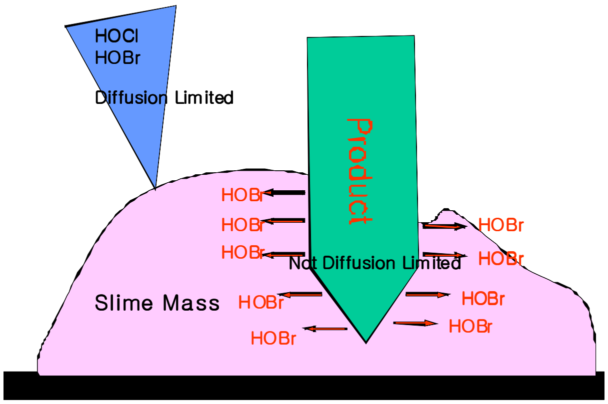


pH Adjusted to 9

Available chlorine is consumed within slime as bromine

Unlike regular chlorine, stabilized chlorine diffuses into the slime layer very easily. The diffusion rate of chlorosulfamate through a slime mass is almost as fast as chloride ions (Stewart et al, 2001). It took 6 minutes for chlosulfamate to pass 1mm of slime layer. This is very close to the diffusion rate of chloride ions, which took 5 minutes to pass the same thickness of slime layer. 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, 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. Therefore, bromine (HOBr) is generated within the slime mass as in the bulk water. This is shown in Figure 2.

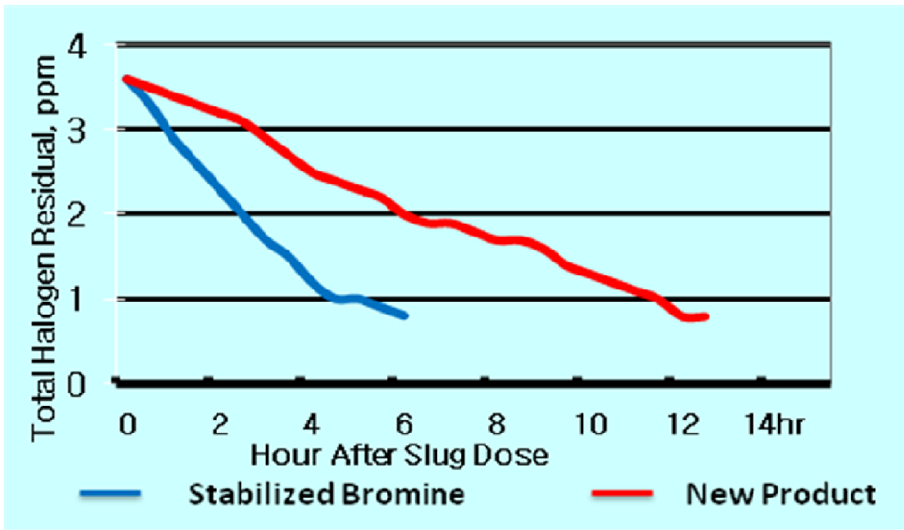
Figure 2. Bromine generation within slime



The consumption rate of the product is lower than other halogen biocides

Only about 5% of the total halogen concentration in the cooling water with the use of this new product is measured as a free halogen residual. This is true because there is an equilibrium among stabilized chlorine, bromide and the reaction product, bromine. This produced bromine is measured as the free halogen. In the clean bulk water phase of cooling systems, this low concentration of bromine is consumed relatively slowly. However when bromine is produced inside slime or an algal mass, bromine consumption is fast due to the high halogen demand of the organics. This causes a reaction equilibrium shift when bromine is consumed within the slime or algal mass, which accelerates bromine production. The lower pH inside the slime mass compared to the bulk water promotes even greater preferential bromine generation within the slime mass. Subsequently the majority of the available halogen in the cooling water treated with this new product is consumed within the slime or algae mass itself, disintegrating them to clean the surfaces. This exceedingly efficient use of the available halogen in the product results in the product lasting two to three times longer than other stabilized bromine products. Figure 3 shows the total chlorine consumption rates of stabilized bromine and this new product at a cooling tower.

Figure 3. Total chlorine decay with time in a cooling tower



Bromide ions are reused within treated water

Bromide is the most expensive ingredient to produce this product and other stabilized liquid bromine products. However, the amount of bromide used to produce this product is greatly reduced because the bromide is regenerated when the produced bromine is consumed in the treated water. The bromide ions produced by the consumption of bromine reacts with stabilized chlorine to produce bromine once again. This bromine is then consumed within the slime or algal mass, which produces bromide ions, which then reacts with the stabilized chlorine again to produce bromine. Therefore, the most expensive ingredient is greatly conserved. In addition, this cyclical phenomenon happens within the slime mass more than in the bulk water as explained above. This makes the product even more economical and efficient.

Low corrosivity

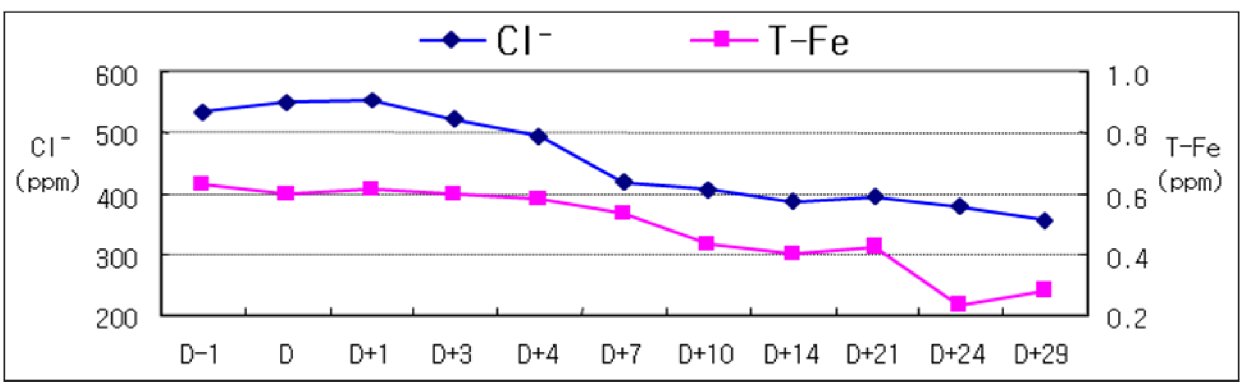
Oxidizing biocides are corrosive to metal parts of the industrial water systems mainly due to their oxidizing properties. Halogen biocides such as chlorine or bromine are known to be corrosive to metals because of their high oxidizing potentials. Stabilized bromine products are less corrosive because of their lower oxidizing potential. However, they are still corrosive to metal parts because around 50% of the total halogen in treated water exists as free residual halogens.

Only about 5% of the total chlorine in the water treated by the new product is measured as free chlorine (actually bromine). This low free halogen makes the product much less corrosive than other oxidizing biocides. Free bromine concentration, measured as chlorine, in the cooling water treated by this product is usually less than 0.1ppm.

Chlorine builds up chloride concentration when it is used for industrial water systems. It is especially troublesome when the holding time index is longer. Higher chloride concentration makes water more corrosive. The application of the new product reduces the chloride build-up to about 1/5 of regular chlorine bleach.

This low free halogen concentration and low chloride build-up makes this new product much less corrosive than other oxidizing halogen biocides. Figure 4 shows the decrease of chloride and total iron concentrations (which indicates corrosion) in the cooling water of a large refinery cooling tower when chlorine bleach was switched to the new product. The circulation rate of the tower was 40,000gpm and the average cycle of concentration was about 6. The calculated chloride concentration by cycle of concentration from pure make-up was about 270ppm. These results demonstrate the lower corrosion effect of the new product compared with conventional chlorine bleach.

Figure 4. Chloride and Total Iron Reduction



Easy to Use

Liquid biocides are conveniently used for the industrial water treatment by using metering pumps. However, most the oxidizing halogen biocides develop vapor lock in the pumps because of excessive gas formation. This makes it necessary to use special degassing head pumps. The new product generates much less gas and regular metering pumps are sufficient to pump the product.

The one year storage stability test performed in room temperature showed that only 4% of the active ingredient of the product was lost. Excellent storage stability and low gas generation make this product uniquely easy to use in the field.

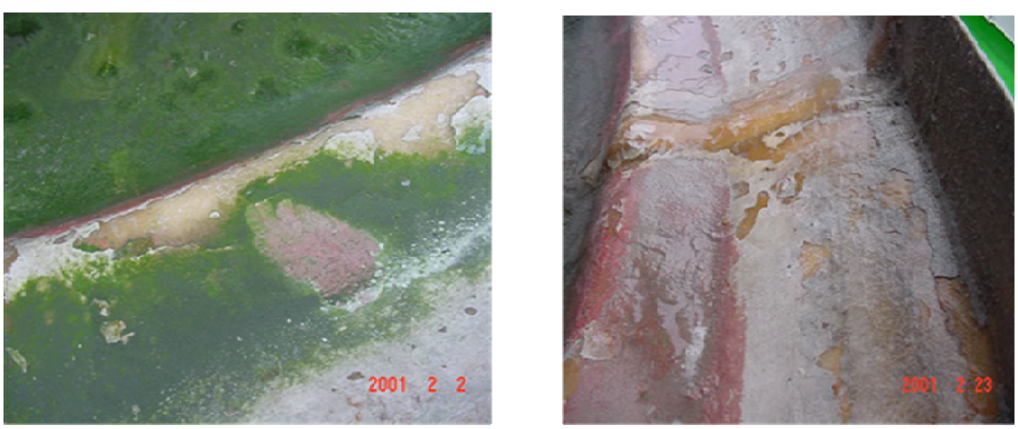
Compatible with Water Treatment Chemicals

Most modern all-organic or phosphate based cooling water treatment programs normally rely heavily on phosphonate calcium carbonate scale inhibitors; many of which are not stable in the presence of free halogen residuals, which can lead to their oxidization and subsequent scale and corrosion related problems. The very low oxidizing nature of the new product eliminates the problem of corrosion and scale inhibitor decomposition. The new product does not decompose even azole copper corrosion inhibitors at the treatment concentrations. Copper corrosion inhibitors, azoles, are usually added in the product formulation in excessive amounts to compensate the loss in the cooling water by halogen biocides. Since the new product does not decompose azoles in cooling water, fewer amounts of azoles are needed to formulate cooling water treatment products. Therefore, water treatment costs can be substantially reduced.

Algae Control

Even for surfaces not continuously in contact with the circulating water, the stabilized chlorine present on a wet surface is sufficient for this new product to generate bromine, thereby eliminating slime and algae and preventing re-growth (Figure 5). This is not the case with other halogen based biocides, where, unless surfaces are continuously wetted, they lose their biocidal efficacy too quickly to prevent slime and algae proliferation.

Figure 5. Algae control on wet area without continuous contact with circulating water



Conventional

New Product

Conclusions

This new product composed of stabilized chlorine and bromide is very economical and convenient to use. The low cost was achieved by reduced raw material costs by using much lower bromide quantities for the production, which is recycled in the biocidal process, and the lower required dosage compared to other halogen biocides. In addition, low cost scale inhibitors can be used with this product because this product does not decompose any phosphonates for water treatment applications. Stable liquid product let the service engineers use conventional metering pumps without degassing heads.

Many industrial cooling water systems have converted to this product from the conventional commodity chlorine bleach because of these advantages. Most large cooling tower customers buy bleach for themselves directly from commodity chemical suppliers while water treatment companies provide service, and sodium bromide, nonoxidizing biocides or bio-dispersants. Sales revenues can potentially increase dramatically for a water treatment company if it supplies this new product and the customer does not have to handle the bleach themselves.

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