# Cost-effective new liquid halogen biocide with better performance and reduced corrosivity

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**Abstract**

Halogen biocides, though widely used and largely effective, are corrosive and are unsatisfactory in controlling surface attached microbes, such as slime. A newly patented product, composed of stabilized chlorine and unreacted bromide, controls surface attached microbes, is much less corrosive and is much more cost-effective than other halogen biocides.

**Introduction**

The formation of slime often occurs in water systems such as in cooling water towers, industrial water supply systems, and paper-making processes. This formation results from the growth and proliferation of bacteria, fungi, algae, etc. The proliferation of such microorganisms and the formation of slime bring about serious problems. In paper manufactories, it may give rise to slowdowns in operations and deterioration of products such as by changes in color of manufactured paper. A reduction in the efficiency of heat exchange, which is critical for cooling capacity in cooling systems, may occur. Ornamental fountains may become far less attractive. And in cooling towers of buildings, the genus legionella may be rapidly spread, creating an unsanitary environment. All these problems found in industrial water systems are mainly related to surface attached microbes such as slime, algae, etc., rather than free floating ones.

Oxidizing biocides and non-oxidizing biocides have been typically used to prevent the contamination of water system by microorganisms. Oxidizing biocides, which have oxidizing capabilities, act as a biocidal agent against microorganisms by oxidizing their proteins, while non-oxidizing biocides work by inhibiting the metabolism of microorganisms.

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 damage when it is applied to 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 systems with long holding time indices or high cycle of concentrations.

Other significant 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 water treatment engineers.

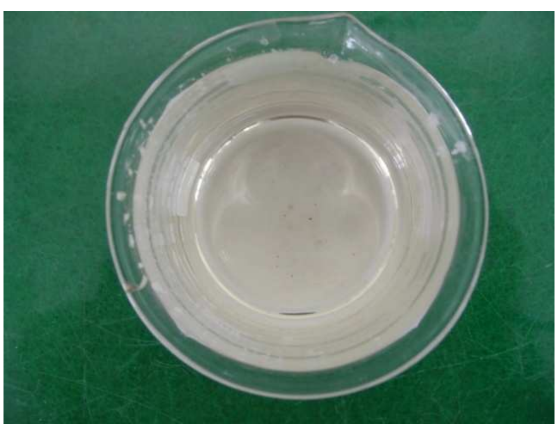
A newly patented halogen biocide composed with stabilized chlorine and unreacted bromide was introduced in the US market in the early 2008 (Shim and Kim, 2002) (Shim and Kim, 2008). This product is a single-feed, ready-to-use, liquid halogen biocide for industrial and institutional water treatment applications. 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. This product is much less corrosive to metal parts than other halogen biocides.

**Bromine biocide is produced in-situ within the slime, bio-film**

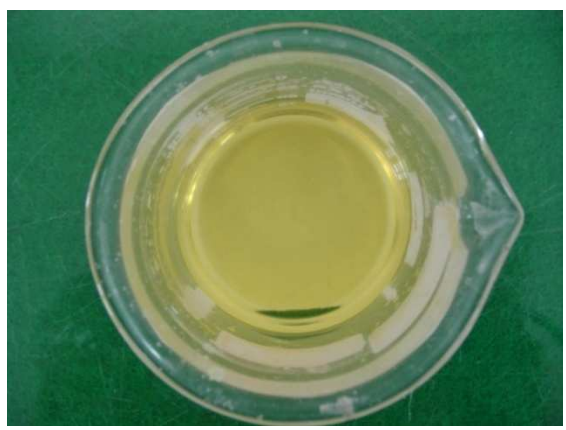
The product is a stable liquid composed of sulfamate stabilized chlorine and sodium bromide. The product is a highly alkaline liquid as other liquid halogen products such as sodium hypochlorite solution and liquid stabilized bromine products. The pH of the product is above 12.5. Stabilized chlorine, in the form of chlorosulfamate, does not react with bromide in this high alkaline pH. However, stabilized chlorine and bromide in the product react to produce bromine at a lower pH, 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 automatically when the product is diluted in industrial water systems. Since the pH range of typical industrial water systems are between 6.5 to 9.2, this bromine generation occurs automatically in the water systems when the product is introduced.

Figure 1. pH Effect on Bromine Generation



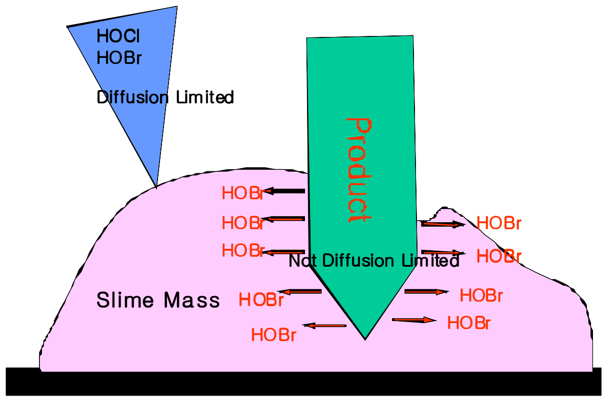
**Neat Product**



**pH Adjusted to 9**

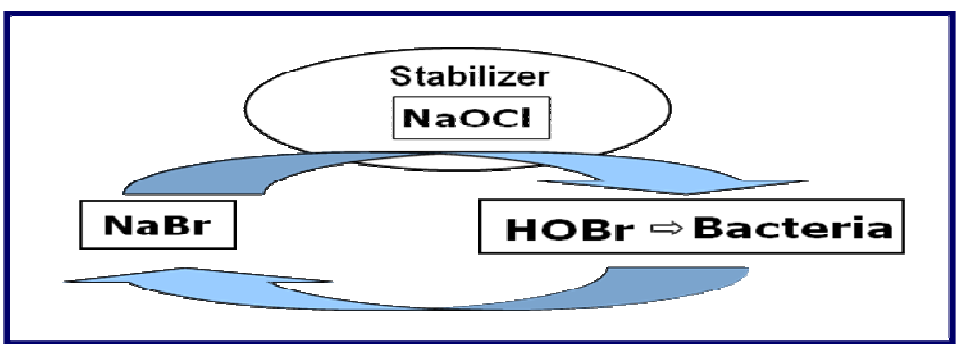
The in-situ bromine production mechanism within slime and bio-film was described in the paper presented at the 2009 AWT Annual Convention and Exposition in Hollywood, Florida, by the author. (Shim, 2009) Unlike regular chlorine, stabilized chlorine diffuses into the slime layer very easily. The diffusion 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




Bromide ions are reproduced and released when the bromine is consumed within the slime mass. This reproduced bromide then reacts with the stabilized chlorine, as before, to produce the biocide, bromine. Thus, the bromide is continuously recycled to combine with the stabilized chlorine to produce bromine. This cyclical process creates an exceptionally economical product because sodium bromide is the most expensive ingredient to produce this product. This recycling mechanism is depicted in Figure 3.

Figure 3. Bromide recycling mechanism




**Field Test**

This product was tested at a large refinery cooling tower. The operating conditions are shown in Table 1. Since make-up for this system was low hardness water with calcium concentration of 44ppm (as $CaCO_3$), the cycle of concentration was maintained at ~15.

Table 1. Operating Conditions of the cooling tower

| | |
|---|---|
| Recirculation Rate | ~40,000gpm |
| Holding Volume | ~1,000,000gallon |
| Delta Temperature | 18$^o$F |
| Cycle of Concentration | ~15 |
| Corrosion Inhibitor Program | Low Zinc Phosphate with Tolyl Triazole |
| Scale Inhibitor Program | Anionic Polymer and Phosphonate |
| pH | 7.7 – 8.2 |

Bio-control for this system was performed by a typical method for large industrial cooling towers before this trial started. Industrial grade (12% chlorine) bleach was continuously fed to maintain 0.1 to 0.25ppm residual free chlorine and 60ppm of 1.5% isothiazolone was slug-fed every two weeks. Aerobic bacteria count performed by dip-slide method usually showed between $10^4$ – $10^5$CFU/ml.

A field trial was conducted by using the new biocide for a month. The new biocide contains 6.7% chlorine concentration. This new product was slug-fed once a day at 23ppm of holding volume. The old and new methods are shown in Table 2.

Table 2. Biocide Treatment

| Old Method | New Method |
|---|---|
| • Continuous Feed of ~12% Chlorine Industrial Grade Sodium Hypochlorite: ~22,000 pound/month**<br>• 1.5% Isothiazolone: 60ppm/2week | • New Product was slug-fed: Once/day, 23ppm in Holding Volume: ~5,800 pound/month |

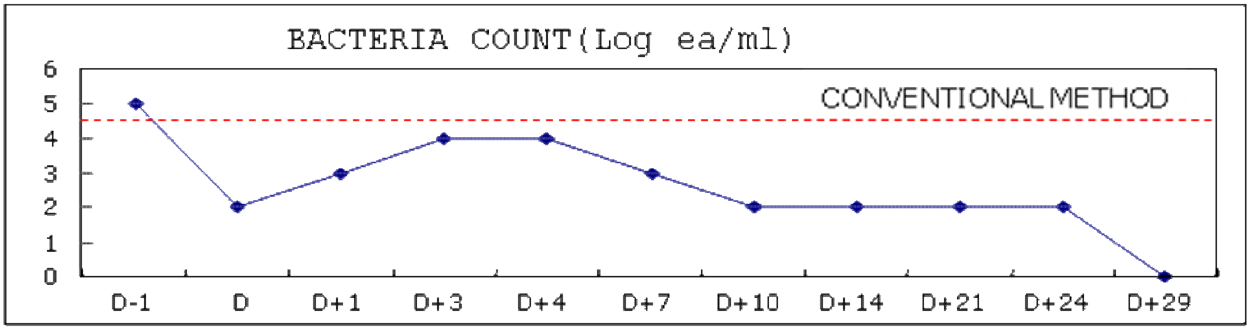
** Free residual chlorine was maintained at 0.1 – 0.25 ppm

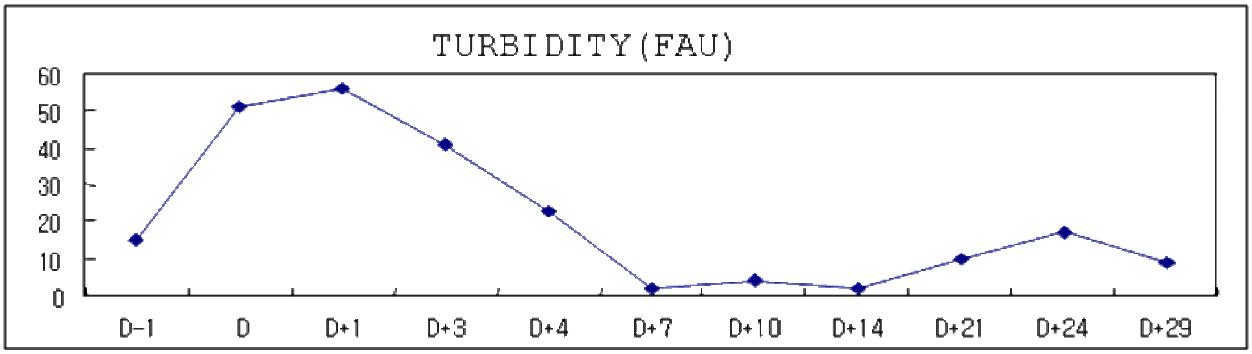
Aerobic bacteria count was measured by using dip-slide method. Bacteria count decreased at the first day of trial from $10^5$CFU/ml to $10^2$CFU/ml. However, it increased with time and reached a maximum of $10^4$CFU/ml on the third day. However, it then decreased to $10^2$CFU/ml after 10 days and stayed at that low bacteria count until the end of the trial.

Turbidity of the cooling water was measured once a day during the trial. Measured turbidity increased dramatically in the first two days of the trial from 15FAU to 57FAU. Turbidity of the system decreased with time after the peak value and reached below 10FAU at seventh day after the start of the trial. The bacteria count and turbidity measurement results are shown in Figure 4.

These bacteria and turbidity measurements showed the surface cleaning process by the new product. Bacteria count and turbidity increased when slime on the system surfaces were detached and dispersed into bulk water. Slime and bio-film that was not eliminated by the old treatment method and remained clinging to system surfaces were cleaned by the new biocide.

Figure 4.  Bacteria Count and Turbidity




This new product is much less corrosive than active chlorine because it is mainly chlorosulfamate and it has a much lower oxidizing property.  Chrorosulfamate is also less oxidizing than bromosulfamate which is the main ingredient of stabilized liquid bromine products in the current market.

Chloride build-up in cooling water makes cooling water more corrosive when chlorine is used for microbial control.  This problem becomes more serious when a system has a higher holding time index or cycle of concentration.  The system for this field trial was as high as 15.  Chloride concentration in the cooling water decreased when chlorine bleach was replaced by the new biocide.  The amount of the new biocide usage is about ¼ of the chlorine bleach previously used.  The new biocide also contains about 56% of the chloride and chlorine concentrations of chlorine bleach.  These two effects make the accumulation of chloride in cooling water decrease when chlorine bleach was replaced with the new biocide.  Chloride decrease with time during the trial was shown in Figure 5 and the total iron concentration change is shown in the same figure to show the effect on iron corrosion.  The figure clearly shows that iron corrosion decreased when chlorine bleach was changed to the newly developed biocide.

Figure 5.  Chloride and Total Iron Change During the Trial

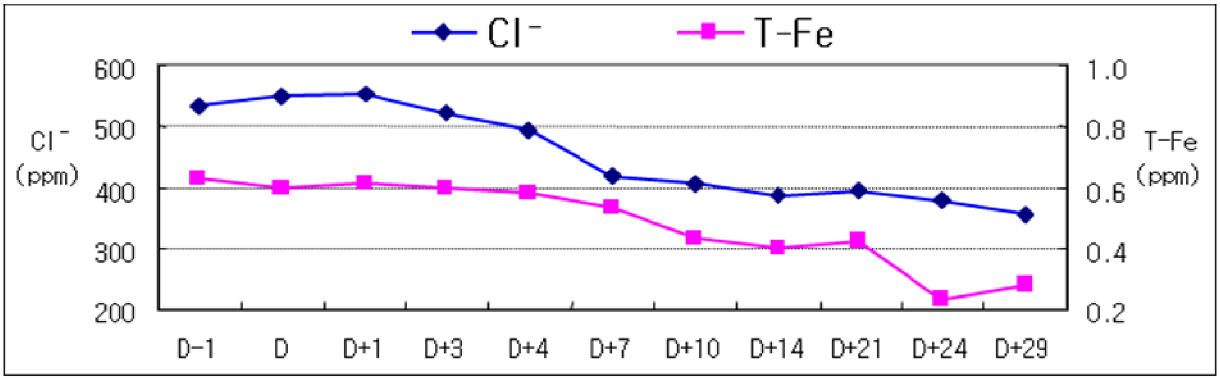



Table 3 summarizes chloride and total iron concentration changes with the application of the new biocide.  Even though the decrease in iron concentration with the new biocide suggests reduced system corrosion, electrochemical corrosion measurements were performed to find more quantitative information by using the Tafel method.

Table 3 Water Analysis

| | Make-Up | Theoretical value at COC = 15 | Cooling Water (Initial) | Cooling Water (Final) |
|---|---|---|---|---|
| $Ca^{++}$ (mg/L as $CaCO_3$) | 44 | 660 | 645 | 633 |
| $Cl^-$ (mg/L as Cl) | 18 | 270 | 510 | 302 |
| Total $Fe^{++}$ (mg/L as Fe) | 0.01 | 0.15 | 0.62 | 0.28 |

Table 4 summarizes test conditions and results of the Tafel measurements.  The results showed a substantial effect of chloride concentration on mild steel corrosion.  Therefore, the new biocide product is less corrosive than chlorine bleach, which is being used for most large industrial cooling towers by two mechanisms.  The new biocide product is less corrosive because it is much less oxidizing than conventional chlorine bleach and it creates a far less corrosive environment because it builds-up less chloride in cooling water.

Table 4.  Tafel Measurement Conditions and Results

| | Conventional Treatment Condition | New Biocide Condition |
|---|---|---|
| Temperature ($^oF$) | 105 | 105 |
| pH | 8.2 | 8.2 |
| Ortho-$PO_4$ (mg/L as $PO_4$) | 8 | 8 |
| $Zn^{++}$ (mg/L as Zn) | 1.5 | 1.5 |
| PBTC (mg/L as PBTC) | 4 | 4 |

| | | |
|---|---|---|
| Tolyl-triazole (mg/L as TT) | 2 | 2 |
| Polymer (mg/L as polymer) | 6 | 6 |
| $Ca^{++}$ (mg/L as $CaCO_3$) | 660 | 660 |
| **$Cl^-$ (mg/L as Cl)** | **510** | **302** |
| **Mild Steel Corrosion (mpy)** | **2.7** | **1.2** |

**Discussion**

Even though a chlorine biocide is a very effective and economical option for industrial cooling water treatment, a problem has been realized that it has limited performance in controlling surface-attached microbes. This problem is related to the highly oxidizing property of active chlorine. The field trial performed at a large industrial cooling tower using the newly developed biocide composed of stabilized chlorine and unreacted bromide showed that this new product can effectively control slime on the surfaces of the system. The trial also showed that the amount of the new biocide needed to effectively control bio-related problems of a cooling tower is about one quarter of the industrial grade chlorine bleach that was used previously. It is also noted that non-oxidizing biocide application that is necessary to make chlorine bleach satisfactory for bio-control may not be needed or can be reduced.

Another important effect of the new biocide is that it is much less corrosive than chlorine. Low corrosivity of the product compared with chlorine is caused by a far lower oxidizing property and lower chloride contribution in the treated cooling water.

Industrial chlorine bleach is not stable to store in ambient temperatures and is especially difficult to use during summer seasons. Active chlorine concentration drops quickly when temperature increases. Another problem with chlorine bleach is that it produces gas so that a special pump with a degassing head has to be utilized. By contrast, the storage stability of the new product is very long and one year storage stability test results show that it loses only 3% of the active chlorine concentration. In addition, a special degassing head pump is not needed for this product for most usages.

**Conclusion**

The field trial by the new biocide product showed that the new product outperformed the conventional biocide application practice which is composed of continuous chlorine bleach and intermittent non-oxidizing biocide slug-feed. The new method was not only more effective for bio-control but also reduced corrosivity of the cooling water substantially.

This new product composed of stabilized chlorine and bromide is very economical and convenient to use. The low cost of the product is possible because low bromide quantities are needed for the production because bromide is recycled in the biocidal process, and the lower dosages are required when compared to chlorine bleach. These two cost-saving mechanisms allow for a substantial reduction in the amount of non-oxidizing biocide expenses.

**Abstracts**

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