Educational Institute for

Equipment & Process Design

Oxidizing Biocide

Oxidizing and Nonoxidizing Biocides

Microbiocides fall into two broad groups:

Oxidizing biocides kill bacteria by destroying cells. Membranes are blocked so that the cells cannot metabolize. The more powerful oxidants actually break down (lyse) cell walls. Some less powerful oxidants can penetrate cell walls and oxidize internal cell structure. Chlorine and sodium hypochlorite (bleach solution) are by far the most widely used oxidizing biocides, followed by bromine compounds and other oxidants.

Oxidizing biocides can be applied as a continuous low-level dosage or as intermittent slug doses. Best results are usually obtained with low-level continuous dosages of 0.1 to 0.3 mg/L, plus, if needed, occasional higher slugs up to 1-2 mg/L for cleaning. Because of the reactivity of oxidizing biocides, residuals do not last long, so that to maintain a residual dosage, continuous feed is needed.

Nonoxidizing biocides do not destroy cells. Rather, they are absorbed through cell membranes into the cell, where they interfere with metabolic processes, mostly enzyme production. For this reason, nonoxidizing biocides are sometimes called metabolic biocides. A wide variety of organic compounds are used as microbiocides, including quaternary amines, sulfur compounds, aldehydes, nitrogen ring compounds (triazines) and others.

Nonoxidizing biocides are more expensive than oxidizing biocides, and larger dosages are required. However, because reactivity is lower, high dosages can be used to provide a residual that will often last for days.

Because of their toxicity, all biocides are registered with the U.S. Environmental Protection Agency and also with various state agencies. Dosages are specified on the label and special training and certification is required for operators who feed biocides to cooling systems.

Tables 4-9 and 4-10 contain lists of oxidizing and nonoxidizing biocides that are commonly used in cooling tower systems. All of these biocides and others are discussed in more detail later in this section.

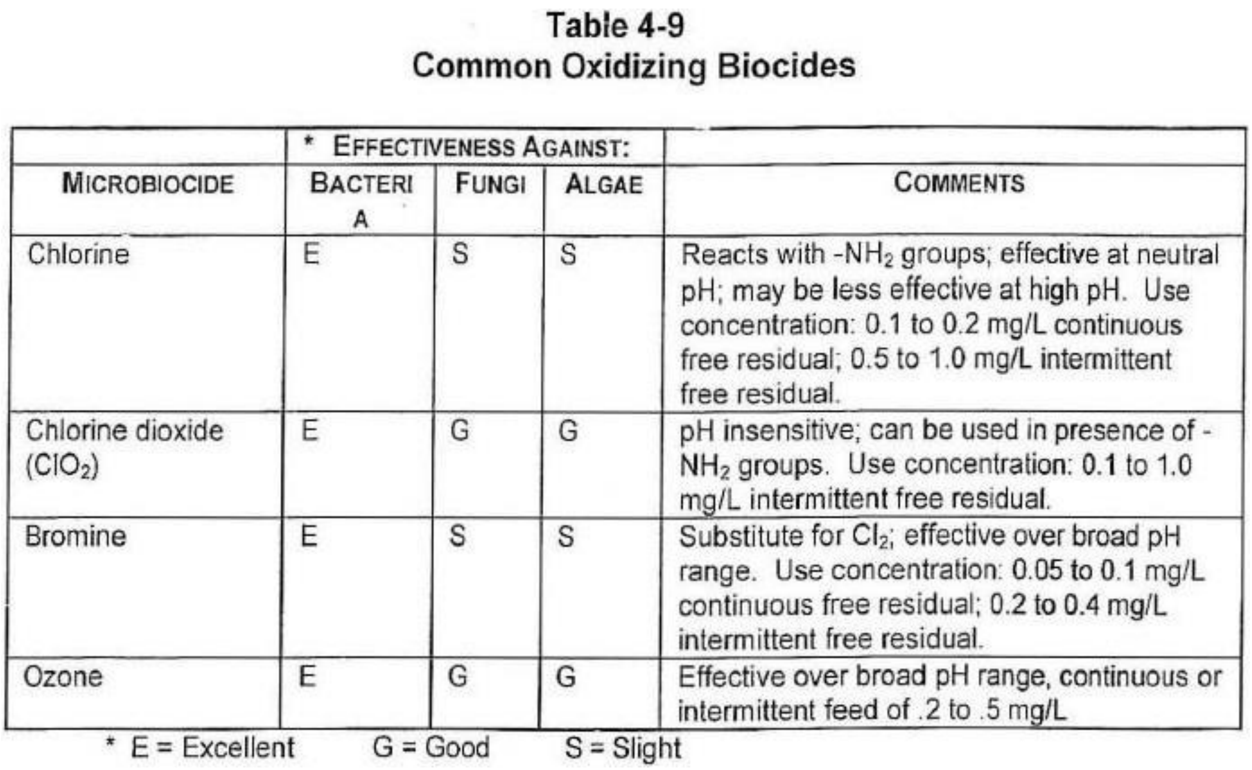

Table 4-9
Common Oxidizing Biocides

	* EFFECTIVENESS AGAINST:			
MICROBIOCIDE	BACTERIA	FUNGI	ALGAE	COMMENTS
Chlorine	E	S	S	Reacts with -NH$_2$ groups; effective at neutral pH; may be less effective at high pH. Use concentration: 0.1 to 0.2 mg/L continuous free residual; 0.5 to 1.0 mg/L intermittent free residual.
Chlorine dioxide (ClO_2)	E	G	G	pH insensitive; can be used in presence of -NH$_2$ groups. Use concentration: 0.1 to 1.0 mg/L intermittent free residual.
Bromine	E	S	S	Substitute for Cl_2; effective over broad pH range. Use concentration: 0.05 to 0.1 mg/L continuous free residual; 0.2 to 0.4 mg/L intermittent free residual.
Ozone	E	G	G	Effective over broad pH range, continuous or intermittent feed of .2 to .5 mg/L

* E = Excellent G = Good S = Slight

Table 4-10

COMMON NON-OXIDIZING BIOCIDES

	* EFFECTIVENESS AGAINST:			
MICROBIOCIDE	BACTERIA	FUNGI	ALGAE	COMMENTS
Organic bromine compounds (DBNPA)	E	S	S	pH range 6 to 8.5. Use concentration: 0.5 to 24 mg/L, intermittent feed
Methylenebis-thiocyanate (MBT)	E	S	S	Hydrolyzes above pH 8. Use concentration: 1.5 to 8 mg/ L, intermittent feed
Isothiazoline	E	G	G	pH insensitive; deactivated by -HS and -NH_2 groups. Use concentration: 0.9 to 13 mg/L, intermittent feed
Quaternary ammonium salts	E	G	G	Tendency to foam; surface active; ineffective in highly oil or organic-fouled systems. Use concentration: 8 to 35 mg/L, intermittent feed
Organic-tin/ quaternary ammonium salts	E	G	E	Tendency to foam; functions best in alkaline pH. Use concentration: 7 to 50 mg/L, intermittent feed.
Glutaraldehyde	E	E	G	Deactivated by -NH_2 groups; effective over broad pH range. Use concentration: 10 to 75 mg/L, intermittent feed
Carbamates	E	E	G	Broad spectrum activity; pH range 5 to 9. Good in high suspended solids systems; not compatible with chromate treatment programs. Use concentration: 15 to 100 mg/L
Dodecylguanidine (DGH)	E	E	G	Broad spectrum activity; pH range 6 to 9. Use concentration 25 to 100 mg/L
Triazines	NA	NA	E	Specific for algal control; must be used with other biocides. pH range 6 to 9. Use concentration: 2 to 7 mg/L

* E = Excellent G = Good S = Slight NA = Not Applicable

Biocide Demand

One important reason for regular tower cleanings is to maximize the effectiveness of biocides. Oxidizing biocides will react with many other materials in the cooling tower besides bacteria. Other organic chemicals, oxidizable inorganic chemicals such as ferrous iron, other reactive chemicals such as amines, suspended dirt and clay, etc. all will react with oxidizing biocides.

Nonoxidizing biocides also react with substances other than bacteria. These are mostly polar organic molecules that have an affinity for surfaces. They adsorb readily on suspended solids, so that the amount available for free circulation in the water is reduced.

These concepts can be quantified in terms of "demand". The demand for any biocide in a specific system is the amount, in mg/L, that must be added to the system water before a measurable free residual can be maintained in the system. With oxidizing biocides, the demand is easily measured by laboratory amperometric titration to the first appearance of a stable free residual. In field situations, where a quick demand number is needed to estimate required dosages, for example, DPD tests can be used for a rough demand estimate.

Measuring the demand for nonoxidizing biocides is harder, because analytical methods are not available for all biocides. Nonoxidizing biocides are usually dosed based on system volume, and if possible, the measured residual is compared with calculated values. If tests are available, analytical measurements of biocide residuals vs. time are a good way to detect the presence of biofilm or other microbiological deposits in a system.

Chlorine and Hypochlorous Acid

Chlorine gas reacts with water (hydrolyses) to form hypochlorous acid (HOCl) and hydrochloric acid (HCl).

$$Cl_2 + H_2O = HOCl + HCl \qquad (4\text{-}45)$$

Hypochlorous acid is the active biocide. Hypochlorous acid is a very weak acid (chapter 1). It dissociates in water to produce hydrogen and hypochlorite ions:

$$HOCl \leftrightarrow H^+ + OCl^- \qquad (4\text{-}46)$$

This is an equilibrium reaction that goes in both directions. Since the hydrogen ion concentration of a water solution is defined by the pH (chapter 1), the pH also determines the amount of dissociation – that is, the relative amounts of hypochlorite ion and undissociated hypochlorous acid – in the solution. In low pH (acid) solutions, the equilibrium in equation (4-46) will be forced to the left, and the hypochlorous acid will be mostly undissociated. In alkaline solutions (high pH), hydrogen ions will be neutralized and the reaction will be pulled to the left, towards hypochlorite ion.

This is very important, because as explained above, unionized hypochlorous acid is the active biocide. The hypochlorite ion has some biocidal activity, but it is roughly one-tenth as effective as the unionized acid. Thus, the efficacy of chlorine (hypochlorous acid) as a biocide is pH sensitive.

Table 4-11 below shows the availability of hypochlorous acid as a function of pH, based on the equilibrium in equation (4-46):

Table 4-11
Ionization of Hypochlorous Acid

pH	%HOCl	%OCl$^-$
6.5	95	5
7.0	90	10
7.5	50	50
8.0	24	76
8.5	9	91
9.0	3	97
9.5	0	100

Table 4-11 shows that at pH 8, only 24 percent of the hypochlorous acid is available in unionized form as an active biocide. As the pH increases above 8, this percentage drops off rapidly. This explains why cooling towers operating above pH 8 require significantly more chlorine feed to maintain biological control.

However, it is not true that chlorine is not effective in alkaline solutions; it just takes a lot more to do the job. The additional chlorine impacts handling, discharge, total dissolved solids, and corrosion rates.

Chlorine and sodium hypochlorite, discussed below, react with ammonia to form a series of chloramines. The chloramines are very stable compounds that do not release chlorine easily. This can create a large demand for chlorine in systems containing ammonia contamination. Monochloramine has some biocidal activity. Municipalities sometimes add small amounts of ammonia to water to help carry chlorine residuals to the far ends of long distribution systems.

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Chlorine also reacts readily with many organic molecules to form chlorinated organic compounds that create environmental problems when discharged. For this reason, large industrial plants and utility stations that discharge directly to waterways are restricted in the amount of chlorine they can use and discharge, or they may be required to dechlorinate their discharge water. This is done by adding sodium sulfite to reduce the chlorine to chloride ions.

Sodium Hypochlorite (Bleach Solution)

Commercial sodium hypochlorite solution is simply a nominal 12 percent solution of sodium hypochlorite, the sodium salt of hypochlorous acid, in excess caustic. Retail laundry bleach is the same thing, as a 3 percent solution, but the term "bleach" is also loosely used to refer to the commercial 12 percent solution.

Sodium hypochlorite solutions are unstable and gradually decompose, especially when exposed to light and high temperatures. Solutions stored in warm places may lose as much as half their activity in approximately six months. Old solutions should therefore be tested before use to determine their activity.

When added to water, sodium hypochlorite ionizes to produce hypochlorite ions, and some of the hypochlorite will react with water to produce hypochlorous acid. All of these equilibria are controlled by the pH of the solution, as explained above:

$$NaOCl = Na^+ + OCl^- \qquad (4\text{-}47)$$

$$OCl^- + H_2O \leftrightarrow HOCl + OH^- \qquad (4\text{-}48)$$

Calcium Hypochlorite [$Ca(OCl)_2$]

Calcium hypochlorite is a solid compound. It dissolves in water to produce hypochlorous acid and calcium hydroxide:

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2 \qquad (4\text{-}49)$$

The hypochlorous acid ionizes as explained above.

Calcium hypochlorite is not commonly used as a biocide except in small cooling towers. Care should be taken that calcium hypochlorite is completely dissolved and not collecting on the bottom of the tower basin. The high chlorine levels in such deposits can cause severe corrosion damage.

Chlorine Dioxide

Chlorine dioxide is widely used as a bleaching agent in the papermaking industry, and as a microbiocide in large industrial cooling towers and municipal systems. Chlorine dioxide is an unstable gas that must be generated on site and used immediately. For water treatment purposes, chlorine dioxide is normally generated from the reaction of sodium chlorite with sodium hypochlorite and hydrochloric acid:

$$NaOCl + HCl + 2NaClO_2 \quad = \quad 2ClO_2 + 2NaCl + NaOH \qquad (4\text{-}50)$$

This reaction involves handling hazardous chemicals, and the generated chlorine dioxide must be carefully controlled. For these reasons, chlorine dioxide has not been considered safe for use in small industrial and commercial systems. However, other methods have been developed that do make chlorine dioxide available safely for small systems:

- Stabilized chlorine dioxide: These are simply solutions of sodium chlorite, sometimes with added caustic. When these solutions are mixed with hydrochloric acid in a tank, the chlorite ion slowly reacts with the acid to produce chlorine dioxide in solution. About 50 to 75 percent conversion can be obtained over about one hour reaction time, and the chlorine dioxide solution can then be diluted into a cooling water sidestream for use. Batch generation in this way is convenient for preparing chlorine dioxide for one-time use as a sterilizing or cleaning agent, but it is not cost-effective for continuing on-line use of chlorine dioxide as a microbiocide.

- Electrochemical generation: Sodium chlorite can be electrochemically oxidized to chlorine dioxide in a flow-through cell. This is a convenient way to prepare chlorine dioxide as needed for on-line use. Conversion is about 75 percent complete, so that the product solution contains about 25 percent unreacted sodium chlorite. The method is simple and safe, but the cells require frequent replacement.

- Dilute solutions: The standard chemical reaction (equation 4-50) can be modified for safe handling by using dilute solutions and premixing reactants. Proprietary solutions and equipment for doing this permit generating low levels of chlorine dioxide instantly as needed, with 100 percent conversion. This method should become readily available for use as interest in chlorine dioxide increases.

Chlorine dioxide is a powerful oxidizing agent, but it is more selective than chlorine. Chlorine dioxide does not react with many organic species, so that the system demand is usually lower than for chlorine. It does not form chlorinated organic compounds. Chlorine dioxide does not react with water, as does chlorine. Therefore, the biocidal effectiveness of chlorine dioxide is independent of pH – an important advantage in treating alkaline cooling systems. Finally, unlike chlorine, chlorine dioxide does not react with ammonia to form chloramines.

BROMINE AND BROMINE DERIVATIVES

Bromine Reactions in Water

Bromine reacts with water just like chlorine, and hypobromous acid is the active biocide. There are, however, important differences:

- Hypobromous acid (HOBr) is much less stable than hypochlorous acid. Sodium hypobromite cannot be stored and shipped commercially.
- Bromine is a weaker oxidizing agent than chlorine, but it is equally or more effective as a biocide. Because HOBr reacts less readily than HOCl, it appears to have better ability to penetrate biofilms and slimes.
- Bromine reacts with ammonia, as does chlorine, but the resulting bromamines are unstable and readily release bromine to solution. Therefore the bromamines are biocidally as effective as hypobromous acid, and ammonia in solution dos not create a "demand" for bromine.
- HOBr is a weaker acid than HOCl. Therefore it does not ionize as readily. Whereas only 24 percent of HOCl remains unionized at pH 8 (Table 4-11), 83 percent of bromine remains unionized (Table 4-12). This means that bromine, as HOBr, is a more effective biocide in alkaline cooling water systems.

Table 4-12

Ionization of Hypobromous Acid

PH	%HOBr	%OBr^-
6.5	100	0
7.0	100	0
7.5	94	6
8.0	83	17
8.5	60	40
9.0	33	67
9.5	11	89

Figure 4-30 compares the ionization of HOBr and HOCl vs. pH, using the data from tables 4-11 and 4-12. From this graph, it is easy to see that HOBr ionizes at much higher pH levels than does HOCl. Since the unionized acids provide most of the microbiological activity, this explains why HOBr is a more active biocide in cooling water systems operating above pH 8. There are also microbiological kill data indicating that even at equal molar concentrations of HOBr and HOCl, and at the same pH, HOBr is a more efficient microbiocide.

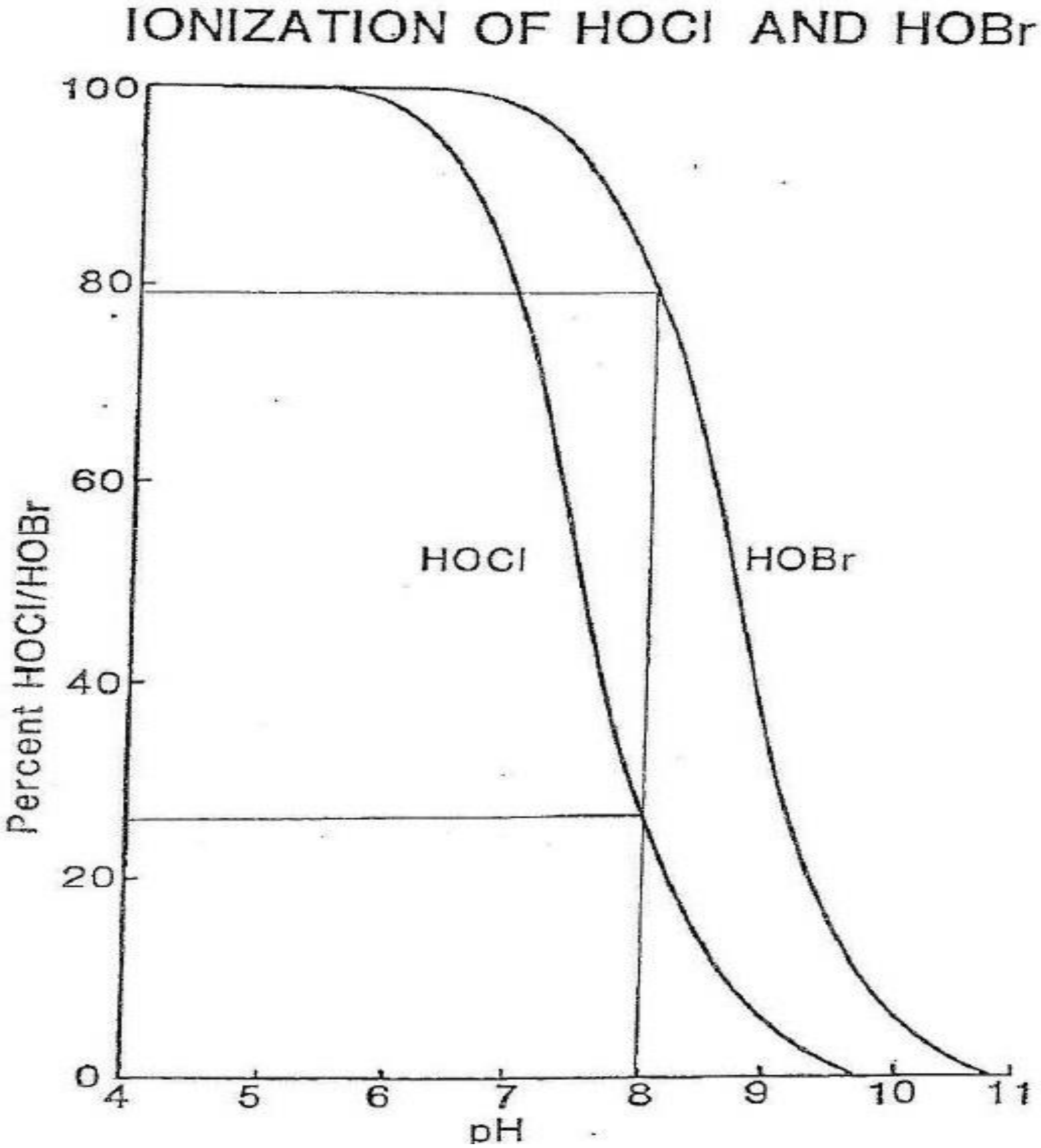

Figure 4-30. Effect of pH on ionization of hypochlorous and hypobromous acids.

Figure 4-30. Effect of pH on Ionization of hypochlorous and hypobromous acids.

Sodium bromide (NaBr) is an inorganic salt that is readily soluble in water. Sodium bromide is not a biocide, but it reacts with sodium hypochlorite to produce hypobromous acid.

$$NaOCl + NaBr = NaOBr + NaCl \tag{51}$$

This is a dual-feed approach. Solutions of sodium hypochlorite and sodium bromide are mixed in a reaction chamber where the reaction goes to completion very quickly, and the mixture is then pumped into the cooling system.

The concentrations of the two reacting solutions, and the pumping ratios, can be set to produce either a mixture of HOCl and HOBr or complete conversion to HOBr. The molecular weight of NaOCl is 74.5, and the molecular weight of NaBr is 103 (chapter 1). The ratio is 1:1.3. If the two solutions are pumped together in this ratio of active components, conversion will be complete. About 10 percent excess sodium hypochlorite should be used to ensure complete reaction.

Bromochlorodimethyl Hydantoin (BCDMH)

BCDMH is a white to off-white solid. It is sparingly soluble in water. BCDMH reacts with water to eventually release equal moles of HOBr and HOCl:

$$BCDMH + H_2O = HOBr + HOCl + DMH \tag{52}$$

In practice, BCDMH pellets are placed in a bromine feeder, where they slowly dissolve or erode as water flows through the feeder. Water flow can be controlled by a timer or by an ORP (oxidation-reduction potential) controller for maintaining a continuous residual.

Liquid Bromine Products

Hypobromous acid can be stabilized by reacting it with sulfamic acid to produce a stable complex compound. The same end product can be made starting with bromine chloride (BrCl), a reaction product of bromine and chlorine. "Stabilized bromine" solutions prepared by these methods are widely used in cooling water applications.

These products are simple to pump and control, an advantage over BCDMH and NaBr + NaOCl. The disadvantage is that because the liquid is stabilized, it does not release active HOBr quickly. HOBr is released gradually, so that it is difficult to maintain a free oxidizing residual with these products. As with any oxidizing biocide, microbiological control is not reliable unless a free oxidizing residual can be maintained in the water.

OTHER OXIDIZING MICROBIOCIDES

Ozone

Ozone (O_3) is an unstable gas that readily converts to oxygen. Therefore it must be generated on-site for immediate use. The most common generation method is electrical corona discharge. Dry air or oxygen is passed through a high voltage electrical field to produce ozone. The conversion is low, about 4.5% using air or 12% using oxygen.

$$3O_2 = 2O_3 + \text{heat} \qquad (4\text{-}53)$$

Ozone is partially soluble in water. It is the most powerful of the oxidizing biocides used in cooling water. Ozone degrades as a function of pH, being unstable at pH 6 and instantly degrading at pH 10. Degradation produces hydroxyl radicals ($OH^{\cdot}$), which are even more powerful oxidizers than ozone. Note: Hydroxyl radicals ($OH^{\cdot}$) are not the same as the familiar hydroxide ion (OH^-). Effective dosages can be as low as 0.02 to 0.05 mg/L, but the feed rate should be at least 0.1 mg/L to help account for losses and demand.

The half-life of ozone is cooling towers is very short, typically 5 to 20 minutes, because of its reactive nature and volatility. It is therefore almost impossible to maintain a free ozone residual in the water.

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is not a common biocide in cooling water. In-situ generation of peroxide can be achieved with peracetic acid (CH_3COOOH). This acid reacts in water to produce acetic acid (CH_3COOH) and hydrogen peroxide. Hydrogen peroxide can be used very effectively on a batch basis to remove biofilm and slime in seriously fouled systems.

Iodine

Iodine is a halogen, like bromine and chlorine, with similar chemistry. Iodine is a solid at room temperature, but with a considerable vapor pressure. It is normally handled in solutions. Iodine is useful as a medical antiseptic, and it has seen limited use as a packaged biocide for small cooling systems.