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Chlorine alternatives: How do they compare?

A variety of biocides—both oxidizing and non-oxidizing—and techniques are available as environmentally benign substitutes for chlorination. Best choice depends on cooling-system design, raw-water quality, and economics

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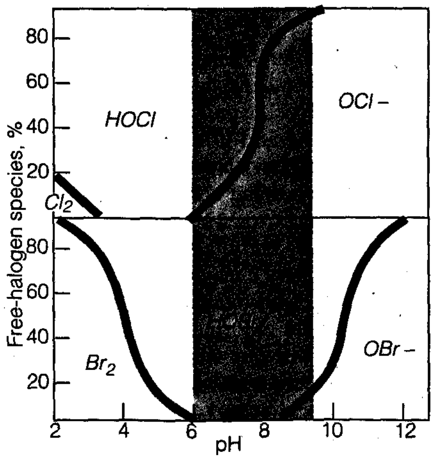
Cooling-water quality, system operating parameters, and environmental restrictions have greatly influenced the use of oxidizing biocides at utility powerplants. The most cost-effective of these is chlorine gas, yet environmental concern and international disasters have all but eliminated its use today. While substitutes have been applied to cooling-water systems, regulatory restrictions make their continued use questionable. Thus, it has become increasingly important to identify alternative biocides and application techniques that can effectively control cooling-water biofoulants and comply with permit requirements.

Water treatment for cooling systems now often incorporates sodium hypochlorite or bromine-producing biocides. Suspected toxicity, however, is bringing some bromine compounds into question. The US EPA is about to undertake a study of chlorine in all forms, intended to "prohibit, reduce, or substitute" its use. Concerned with this trend, the Cooling Tower Institute (CTI), National Assn of Corrosion Engineers (NACE), and some industries have initiated a program to communicate with EPA, Congress, and other branches of government the need to keep chlorine available for cooling-water bio-control. Tightening restrictions, however, have prompted the search for chlorine substitutes as well as for entirely different approaches to biofouling protection.

Although utility cooling-water systems are basically similar, they vary sufficiently from plant to plant to warrant special biocide program considerations. Similarities include the use of alloy tubing in condensers and heat exchangers, linings in the condenser circuitry, and mild steel in waterboxes and some tubesheets. Design differences, however, have a strong impact on treatment needs and costs. Regulations that preclude the use of more effective chemicals necessitate a resort to less effective products that can entail significantly higher costs. Operating procedures often can be modified to take advantage of certain system design features—and the possible use of generic rather than proprietary chemicals—to reduce treatment costs.

Cooling systems at fossil-fueled plants differ substantially from those at nuclear stations, where biocide restrictions are even more stringent. Design and operating conditions at nuclear plants must enter into the selection of biocide programs to ensure effective biofouling control throughout the cooling-water system. Heading the list of factors controlling biocide choice is the source of cooling water. Raw water is the usual source. Consisting of untreated river or lake water, it typically contains ammonia, suspended solids, and organics, so a relatively high oxidant demand—5 to 10 ppm—usually is required to ensure an oxidant residual.



HOBr, the active component in bromine-based oxidant (bottom), is far more predominant among free-halogen species over the pH range of interest (tinted) than HOCl in chlorine-based oxidant (top)

8.0	[illegible]	0.2-0.3
9.0	0.8-1.0	0.2-0.3

*With ammonia, bromine is five times more effective than chlorine

Systems are characterized by both a large capacity (typically 5-10-million gal) and long cycle time (capacity/circulation rate = 10 minutes or longer). These lead to considerable difficulty in maintaining the necessary oxidant treatment level. Use of film-pack fill instead of splash fill in cooling towers has led to excessive fouling with normal bio-treatment programs. This necessitates additional biocide attention to maintain cooling efficiency, possibly involving direct injection into the cooling tower. The use of cooling water for ash sluicing and dilution of radioactive waste can reduce the cycles of concentration (COC) in tower systems, which also affects on biocide use and effectiveness. Other factors include water aeration, periodic condenser cleaning, etc.

Significant changes over the past decade include an increase in cycles of concentration (from an average of 3 to 5 to as much as 8 or 10) and use of scale inhibitors as a total or partial replacement for acid. As a result, pH levels have risen to 7.5 and higher—possibly to 9.0, where chlorine is much less effective. Presence of higher levels of organics and dissolved and suspended solids also have reduced the potency of biocide chemicals. Regulatory restrictions on plant effluent have introduced major limitations on oxidative biocides. Thus, a free-oxidant discharge limit of 0.2 ppm for two hours per day, common not too long ago, has in many cases been replaced by tighter residuals limits. To continue using halogens at levels high enough to maintain condenser cleanliness, utilities in some regions are now required to subject effluent water to dehalogenation to meet discharge regulations.

Bromine-based oxidants

Bromine-based oxidants are effective substitutes for chlorine in cooling water that has a pH of 7.5 or higher or contains more than 2 ppm of ammonia. The bromine compound most commonly used is a bromide salt, usually sodium bromide, activated with either chlorine or sodium hypochlorite. The table compares its effectiveness to that of chlorine at various pH levels, as indicated by the amount required to obtain a residual.

This is also reflected in the chart, which graphs the proportions of free-halogen species vs pH for chlorine- and bromine-based oxidants. While the active component (HOCl) in chlorine-based oxidant is predominant below pH of 7.5, the active bromine ingredient (HOBr) predominates over the broader pH range of interest (tinted), making the latter the more effective biocide overall. Generation of bromine, accomplished by many utilities by bromide activation, requires equal molar amounts of bromide and chlorine. A higher ratio often is used to ensure complete conversion of the bromide to hypobromite or hypobromous ions to keep overall costs lower.

Dry bromine-release compounds, such as the bromo-chlorodimethyl and methylethyl hydantoins and the chloro-isocyanurate/bromide mixtures, are cost-effective when the handling of liquid or gaseous chemicals is undesirable. These have been used successfully in both large utility and smaller industrial cooling-tower systems.

Chlorine dioxide, ozone

Chlorine dioxide (ClO_2) is another chlorine alternative, particularly when cooling water contains amines (ammonia) and some organics. Effective over a wide pH range, especially between 8 and 11, ClO_2 must be generated on-site. Dissolved in water and added to the cooling system, it has 2.6 times the oxidizing power of chlorine. ClO_2 is quickly consumed when organics are present, but very effective for bio-control at residuals of one-half to one-fifth those of chlorine or bromine. It is particularly cost-effective in the presence of ammonia, with which it does not react.

Ozone, the remaining potential alternative to chlorine, has received considerable attention as a biocide both for air-conditioning cooling-tower systems and as a stand-alone corrosion/scale/biofouling preventive. Ozone—O_3 chemically—is a gas generated by subjecting dry air or O_2 to an electric discharge (corona); it is first dissolved in water, then added to cooling water. A good biocide and occasionally successful in controlling scale and corrosion, it does not require chemical handling, degrades to form O_2, does not add to cooling-water TDS, and is very effective for control of *Legionnaires' disease*. Among the characteristics that limit its application to large utility cooling systems: high volatility; rapid degradation at pH above 7.5 and temperatures above 104F; reaction with many organics, and corrosivity to copper alloys.

Despite these problems, increasing experience and application of economic guidelines could establish ozone as a viable, environmentally attractive alternative to chlorine. Ongoing studies under sponsorship of EPRI, American Society of Heating, Refrigerating, and Air Conditioning Engineers, NACE, and CTI are directed at various aspects of ozone use in cooling-tower systems.

Non-oxidants as substitutes

Use of non-oxidizing biocides in utility cooling water has been effective for biocontrol, without the help of chlorine or other oxidants. Most often, they are used as a supplementary biocide to produce a broader organism-control spectrum than provided by chlorine or bromine alone. Occasionally, a non-oxidizing biocide has found use as the sole control agent, particularly when oxidant demand is high. Quaternary ammonium salts and certain aldehydes are among the forms most commonly used.

These toxic non-oxidizing biocides are very effective, but not as economical as chlorine and most other oxidants except to deal with certain specific problems. Examples are Asiatic clams and other marine macrofoulants. They can be cost-effective when a high oxidant demand occurs (over 20 ppm) in cooling water, or when sulfate-reducing bacteria (SRB) and other corrosive microorganisms present a major problem.

Generally, non-oxidizing biocides constitute suitable chlorine alternatives only for specific sites or situations. Some are quite persistent, and will be found in the effluent unless removed or deactivated. Research into new approaches to control technology is under way on several fronts. Specific non-oxidizing inhibitors, for example, are being developed that are adsorbed on component surfaces to render them bio-resistant. A major advantage is that these inhibitors are not discharged with the system effluent.

Mechanical alternative

In some treatment techniques, a high biocide dosage (such as 10 ppm chlorine) is directed at a limited section of the condenser-box tubesheet for several minutes, then moved to another section to repeat the application, and so on. Delivery systems for "targeted treatment," as the method is known, typically cover about 10% of the total area. One design works much like an automobile windshield wiper, while others use a network of stationary pipes. The entire condenser is gradually treated several times a day.

Because only a small area and water volume are treated at one time, dilution of the biocide with the remaining water reduces its concentration in the discharge. This does not truly constitute a chlorine alternative, but it is a method that usually enables the use of any oxidant in compliance with discharge limitations.

Evaluation leads to choice

Realistic comparison of candidate chlorine alternatives requires consideration of very specific conditions of the cooling-system design and operation, water quality, and any applicable restrictions. Costs, technology, safety, and social and political influences all enter into the evaluations and the decision-making process in choosing the most logical and practical alternative to chlorine.

There are many possibilities that should be considered, including both mechanical methods and chemical treatment. With improvement, ozone may prove to be a viable chlorine alternative for the entire cooling-water system. Even newer biocide technologies are beginning to emerge. The use of coatings on condenser tubing may prove feasible, providing not only resistance to biomass accumulation but corrosion protection as well.

How best to proceed? In the short term, it makes sense to continue "as is" until driven to an alternative approach. At that point in time, the best control method and/or chemical should be determined for the specific system conditions present. As for general rules regarding cost-effectiveness, several apply: The most effective alternative to chlorine *gas* is sodium hypochlorite, hands down. But, with ammonia at 2 ppm (or higher) or pH above 7.5, bromine chemistry is the choice and ClO_2 a close second. Bromine from bromide activation is the most flexible of all and usually the most cost-effective, but dry bromine-release agents can move to the fore if chemical-feed and -handling costs are high.

ClO_2 can edge out bromine, particularly if both ammonia and high pH occur or in cooling water with high organic loading. Ozone is currently not in the running for utility plants larger than 100 MW or so, unless regulations prohibit use of chlorine and bromine compounds and capital cost is not a major factor. Non-oxidizing biocides only offer an alternative to chlorine in special cases.

Although the future may provide new options, with proper evaluation and study you can identify the best of several alternatives already available for your particular cooling-water system.

Edited by Sheldon Strauss