AQUARIUS

An Introduction to the Biocides Applied in Cooling Systems

1. Oxidizing Biocides. "Oxidizing biocides" is a term describing microbiocides that oxidize or irreversibly "burn up" the bio-organisms. Oxidizing biocides also destroy nutrients that the microorganisms require for growth. Avoid addition of excess amounts (over-feeding) of oxidizing biocides because they are corrosive to metal and wood in the cooling system and have the potential to destroy some scale and corrosion inhibitors. The various oxidizing biocides are described below.

1.a. Chlorine: Chlorine (Cl_2) compounds are the most effective industrial oxidizing biocides and the most widely used. Chlorine is available as a chlorine gas, dry calcium hypochlorite, liquid sodium hypochlorite, plus several other dry products that release chlorine. When chlorine is introduced into water, it hydrolyzes to form hypochlorite ion (OCl^-) and hypochlorous acid (HOCl); it is the latter chemical that is the stronger oxidizing biocide. The most commonly used chlorine-based biocide is liquid sodium hypochlorite.

1.b. Bromine: Bromine (Br_2) compounds are very similar to chlorine compounds. Although more expensive than chlorine compounds, their main advantage is that bromine is more effective at higher pH ranges (7.5 or greater) than chlorine. Bromine has a lower vapor pressure than chlorine and is 6 times as soluble in water, making it less subject to vaporization loss from a cooling tower. When bromine is introduced to water, it hydrolyzes to form hypobromite ion (OBr^-) and hypobromous acid (HOBr); A pH range of 7.5 to 10.0 is considered optimal for the use of bromine. In water, bromine degrades more rapidly than chlorine. Recent developments in bromine chemistry have resulted in the production of a bromine solution (liquid).

1.c. Ozone. Ozone is a very strong oxidizing biocide that, if properly applied, can provide effective control of microorganisms in cooling tower systems; however, because of safety and operational problems, it is neither the most economical method nor the preferred method for microbiological control in cooling towers under normal operations. Ozone can increase metal corrosion and does not prevent scale.

1.d. Chlorine Dioxide. Chlorine dioxide (ClO_2) is gas generated by mixing several chemicals. It is considered as one of the most effective biocides but is not commonly used on commercial cooling systems due to the complexity of its production and safety concerns associated with its production and handling.

1.e. Hydrogen Peroxide. Hydrogen peroxide (H_2O_2) is a liquid that is usually used at a concentration of 30% in water. Hydrogen peroxide is considered one of the most environmentally friendly oxidizing biocides because it degrades to water; however, concentrated hydrogen peroxide will react in a violent manner when it comes into contact with organic chemicals and materials. Table 1 provides guidelines for selecting oxidizing microbiocides.

2.Non-Oxidizing Biocides. Non-oxidizing biocides are microbiocides that act as "poisons"; they disrupt the metabolic or reproductive processes of micro- and macro-organisms and are therefore toxic. Non-oxidizing biocides are organic compounds that are very toxic to organisms, including human beings and animals. They are usually liquids, but some are available as dry products (e.g., pellets, solids). A major consideration for their use is their persistence with respect to the discharge limitations for water (effluent) containing these toxic substances. Also, when choosing and applying a non-oxidizing biocide, you must consider the cooling tower system's operating parameters, such as pH and retention time. The applied dosages of microbiocides should never exceed EPA maximum limits, which are always printed on the container labels. Control programs often combine both oxidizing and non-oxidizing biocides. The most important aspect of bio-fouling control is to match the non-oxidizing biocide to the problematic organism. Table 2 provides guidelines for non-oxidizing biocide effectiveness.

Table 1. Guidelines for Oxidizing Microbiocide Effectiveness

Microbiocide	Bacteria Types				Fungi	Algae	Comments
	Slime Forming		Iron Depositing	Corrosive			
	Spore Formers	Non-Spore Formers					
Chlorine	P	E	E	N	P	F	Dangerous to handle; corrosive to metal; available as dry, gas or liquid; less effective at higher pH (>7.5)
Bromine	F	E	E	N	P	F	Can be produced from bromides; very effective at pH 6.0-10.0; very effective with ammonia; less volatile than chlorine
Ozone	E	E	E	F	G	P	Very volatile; can attack wood, PVC, copper, and gaskets
Chlorine Dioxide	G	E	E	N	P	F	Must be produced onsite; very volatile; not sensitive to pH; does not react with ammonia and many organics
Peroxide	G	G	G	F	P	F	Does not add TDS; degrades to water

E=Excellent G=Good F=Fair P=Poor N=Not Effective

Table 2. Guidelines for Non-Oxidizing Microbiocide Selection

Microbiocide	Bacteria Types				Fungi	Algae	Comments
	Slime Forming		Iron Depositing	Corrosive			
	Spore Formers	Non-Spore Formers					
Quaternary ammonium salts	E	E	E	G	P	G	Effective pH 6.5-9.2; foaming potential; reacts with anionics
Organotin plus quaternaries	E	E	E	G	P	G	Effective pH 6.5-9.2; foaming potential; reacts with anionics; tin compounds often restricted
Dibromo-nitrilo-propionamide	E	E	E	G	N	P	Effective pH 6.5-7.5; degrades quickly; uses glycol solvent
Methylene bis thiocyanate	E	E	G	E	P	P	Effective pH < 7.5; deactivated with high pH
Isothiazoline	E	E	G	G	G	G	Effective pH 4.5-9.3; dangerous to humans
Dodecylguanidine	E	E	G	G	G	G	Effective pH 6.5-9.5
Glutaraldehyde	E	E	G	E	G	G	Effective pH 6-10
Terbutylazine	N	N	N	N	N	E	Very effective algaecide; blocks photosynthesis
Carbamates	E	E	G	G	G	F	Eff. pH 7-9; corrodes copper

E=Excellent G=Good F=Fair P=Poor N=Not Effective