Non-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.

Biocide	Mechanism	Advantages	Disadvantages
Isothiazoline	Penetrates cell membrane to deactivate enzymes needed for cell to survive	Effective on both bacteria and fungi, persistent in system, synergism with oxidizers, activity over wide pH range	Inactivated by sulfide contamination, concentrated isothiazoline is a skin sensitizer
Glutaraldehyde	Crosslinking of two adjacent amino groups in cell wall proteins impairs cell function	Very effective in normal pH range of cooling water systems	Reacts with halogens, ammonia, and organic amines (but not quaternary amines), should not be applied in systems with these contaminants or with oxidizing biocides
2,2-dibromo-3-nitrilo propionamide (DBNPA)	Reacts with cellular membranes and enzymes, causing disruption of cell metabolism	Fast acting against bacteria	Lack of persistence, rapid hydrolysis at high pH (Fig. 19.19), high cost relative to other biocides, less effective for algae and fungi
Quaternary ammonium compounds (Quats)	Binds anionic components of cells and cell walls	Generally effective against bacteria, fungi, and algae, have surface-active dispersing properties	Can cause foaming and can inactivate anionic polymer dispersants

Section 2 : Common Non-Oxidizig Biocide

Isothiazolines

Alkyl isothiazolin-3-ones. Organo-sulfur group. Good, wide-spectrum bactericide and algaecide that is effective over a wide range of pH. Isothiazolines kill by inhibiting microbial respiration and food transport through the cell wall. It is recognized as an industry standard product for cooling systems but can be expensive. Isothiazolines are supplied to some markets as a 13.9% active concentrated blend (10.1% 5-chloro-2-methyl-4-isothiazolin-3-one and 3.8% 2-methyl-4-isothiazolin-3-one). It is always marketed to the end user, as a 1.5% active (1.11% + 0.39% to 1.15% + 0.35%)in-use blend. Isothiazolines are amber to yellow-green liquids that require every careful handling due to severe skin and eye irritant properties. They are effective against both general aerobic and spore-forming bacteria, over a pH range of 6.5 to 9.0. Isothiazolines are very effective algaecides and fungicides, but only at acid to slightly alkaline pH levels. Contact time is typically 5 to 6hours. Dose rate is typically 50 to 120 mg/L, for 1.5% active isothiazoline. Availability exists as several possible permutations of the product, under the KATHON™ brand from Rohm & Haas Company. Also, AMA®-215 (1.5%)from Vinings Industries, and as 33% aqueous dispersion of 1,2-benzisothiazolin-3-one (BIT), under the Proxel™ BD brand, from ICI PLC.BIT is also available as XBINX® from PMC Specialties Group, Inc. (U.S.).

Consumption:

System Volume: 7500 m^3

Required Dosage = 50 mg/l

Required Dosage per each injection $50 \frac{mg}{l} \times 7500\ m3 \times \frac{1000l}{m3} \times \frac{kg}{1000000mg} = 375 \frac{kg}{inj}$.

Glutaraldehyde

Pentane-1,5-dial. Aldehyde group. Glutaraldehyde is a good bactericide, especially with difficult and persistent organisms due to its good penetrating ability. It has limited effectiveness against algae and fungi. The kill mechanism is by cross-linking outer proteins of cell and preventing cell permeability. Glutaraldehyde is a fast-acting biocide (3 to 4 hours, perhaps 4 to 6 hours with difficult slimes), non-ionic, non-foaming, effective over a wide pH range (typically pH 6.5 to 9.0),. It is also effective against SRBs and biofilms. The half-life tends to be short, depending upon the particular cooling system parameters, but typically 4 to 12 hours. Careful evaluation is needed before application on some larger systems, especially as it may not be particularly cost effective. Glutaraldehyde is readily biodegradable. Typical use concentration is 100 to 125 mg/L at 45% active material, although heavily slimed cooling systems may need 200 to 300 mg/L as an initial, cleanup shock dose. It is an effective choice for biological control in air washers. Glutaraldehyde is probably a good biocide where the risk of *Legionella sp.* exists. Although concentrated glutaraldehyde reacts with ammonia, at typical in-use concentrations the rate of reaction is slowed and glutaraldehyde can be suitable for SRB and slime removal in large process systems, where 25 to 50 mg/L or more, of ammonia is present. This biocide is particularly associated with Aquacar® 515, 542, 545 (15, 42, 45% active product), from Union Carbide Corporation, a subsidiary of The Dow Chemical Company.

Consumption:

System Volume: 7500 m^3

Required Dosage = 50 mg/l

Required Dosage per each injection $100\frac{mg}{l} \times 7500\ m3\ \times \frac{1000l}{m3} \times \frac{kg}{1000000mg} = 750\frac{kg}{inj}$.

Quats (ADBACs)

Alkyldimethylbenzylammonium chloride (also known as alkylbenzyldimethyl ammonium chloride or benzalkonium chloride). Quaternary ammonium compound group. There are many popular products in this group that are widely available. The primary amine salts are of limited benefit in cooling systems, but diamine quats are effective. Quats are cationic, surface active products with a tendency to foam, especially above pH 8.0. The kill mechanism is due to the cationic nature, whereby an electrostatic bond is formed with the cell wall, which affects permeability and protein denaturing. Quats are effective algaecide and reasonably good bactericide, and can be applied over a wide range of pH (optimum pH 6.5-8.5). At typical in-use concentrations, diamines will help maintain clean cooling systems, and reduce populations of general algal and bacterial organisms. However, they tend to have only a bacteriostatic effect over *Pseudomonas sp*. and SRBs. An advantage of quats is their relatively low-cost. The disadvantage is that quats are deactivated by high hardness (typically over 500 mg/L), chlorides, oil, dirt, silt and debris. Quats have poor compatibility with polyanionics polymers. Typical end-user product is 10% active strength quat in an alkaline solution, with a dose rate of 50 to 100 mg/L. Contact time is typically 4 to 6 hours. Examples of quat concentrates are Barquat® OJ50 and OJ80 (50 and 80% active ADBAC), from Lonza Inc., Synprolam™ 35DMBQC 50 and 80 (50 and 80% active) from ICI PLC, Arquad™ B-100, from Akzo Nobel B.V. Examples of diamines are Redicote® E9, Duomeen® C and Arquad® DMMCB-50, from Akzo Chemicals BV.

Consumption:

System Volume: 7500 m^3

Required Dosage = 50 mg/l

Required Dosage per each injection $50\,\frac{mg}{l} \times 7500\ m3 \times \frac{1000l}{m3} \times \frac{kg}{1000000mg} = 375\,\frac{kg}{inj}$.

DTEA, DTEA II

2-(Decylthio)ethanamide. Alkylthio amine group. This is one of the few, genuinely new biocides to enter the market in recent years. DTEA or DTEA IIwas designed to operate effectively under a wide range of pH levels (pH 6 to10 or greater), but especially for the higher pH's now common with "AllOrganic" and similar, high alkalinity tolerant inhibitor programs. It was also designed as a specific sessile bactericide, biofilm remover and biofilm growth control agent. DTEA or DTEA II functions by forming reversible Chelant complexes with the salts and inorganic ions found in biofilm structures, which severely weakens the biofilm and reduces its adhesiveness. DTEA or DTEA IIare highly surface active and can be thought of as a "biocidal soap" to be used for clean-up programs (biofilm debris will quickly be in evidence and foaming may occur), as a biocide component with chlorine (although it is not recommended to be used at the same time as chlorine) and as a maintenance biostat. Application rates are typically 50 to 100 mg/L. It is consumed and decays rapidly in heavily fouled systems (typically in 3 to 4 hours), consequently, it is recommended to slowly add the complete dose over a four-hour period. DTEA or DTEA II is manufactured as a 15% active material. It is distributed primarily through AMSA Corp. in the U.S.

Consumption:

System Volume: 7500 m^3

Required Dosage = 50 mg/l

Required Dosage per each injection $50\frac{mg}{l} \times 7500\ m3 \times \frac{1000l}{m3} \times \frac{kg}{1000000mg} = 375\frac{kg}{inj}$.