

## How to Protect Open, Recirculating Cooling Systems

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### Corrosion Control

Corrosion of metal surfaces in cooling systems is minimized by adding inhibitors to the recirculating water as well as by managing the water chemistry itself. The selection of corrosion inhibitors is complex. The size and operation of a system, chemistry of the recirculating water, environmental discharge regulations, system metallurgy and program costs all must be considered when selecting a treatment program.

Open recirculating cooling systems can include mild steel, galvanized steel, stainless alloys, copper and copper alloys, and aluminum. These metals are subject to a range of corrosion problems such as generalized corrosion, galvanic attack, pitting, crevice attack and stress cracking.

The basic corrosion reaction is a well-defined electrochemical process. The corrosion cell is an electrochemical cell. At the anode of the corrosion cell, metal dissolves into the water as metal ions, as shown in the equation:

where:

$M$  represents the metal

$n$  is the valence of the corroding metal species

$e$  represents the liberated electron(s)

The anodic reaction is an oxidative reaction. The electrons lost at the anode flow through the metal to the cathode. At the cathode, electrons are removed by reducing reactions.

A wide range of corrosion inhibitors is available for use in cooling systems. Table 1 summarizes typical treatment dosages and uses. Inhibitors generally are classified as anodic or cathodic according to which electrochemical process they affect. Anodic inhibitors interfere with the dissolution of metal at the anode of the corrosion cell. Cathodic inhibitors interfere with the cathodic process. Numerous inorganic materials have been used as corrosion inhibitors. These include metals with relatively low toxicity such as molybdate and zinc as well as nonmetallic, inorganic materials such as phosphate, silicate and nitrite salts. Organic corrosion inhibitors primarily are azoles used to protect copper and copper alloys by forming thin films that stabilize the metal and limit or prevent oxidative reactions.

### Metallic Corrosion Inhibitors

**Chromate.** For many years, the most commonly used corrosion inhibitors were chromate salts because of their excellent anodic corrosion inhibition for mild steel and copper. However, regulatory action has severely restricted chromates, and they are no longer used for corrosion protection in U.S. cooling water systems.

**Molybdate.** Molybdate salts are chemically similar to chromate salts and act as anodic corrosion inhibitors in much the same way. Because of their low toxicity, they are easier to handle and more environmentally acceptable.

In open recirculating systems, water losses make treatment programs with high levels of molybdate uneconomical. However, some system operators claim that low levels of molybdate (~10 ppm [mg/L]) have a synergistic action when used in combination with other corrosion inhibitors. In such applications, molybdate also serves as a tracer to facilitate program monitoring.

**Zinc.** Zinc is widely used as a corrosion inhibitor, particularly in alkaline cooling water programs. In mildly to strongly alkaline aerated water, zinc hydroxide precipitates at the cathode of the corrosion cell, forming a physical barrier that blocks the reaction.

Zinc fed at rates of less than 5 ppm (mg/L) often is used in combination with anodic inhibitors to prevent both anodic and cathodic corrosion reactions. Although zinc has relatively low toxicity, its direct discharge to public bodies of water has been restricted in some regions.

### Nonmetallic Inorganic Corrosion Inhibitors

**Phosphate.** For many years, the use of phosphates was frustrated by an inability to maintain effective levels of soluble phosphate. Phosphate precipitated as calcium phosphate, resulting in corrosion as well as generalized fouling. The problem was solved by the development of a polymer technology that significantly increased calcium phosphate solubility. This polymer technology now is used widely and has become the standard for soluble, phosphate-based corrosion control programs.

Phosphates such as orthophosphate and polyphosphate salts -- frequently applied in combination -- are by far the most widely used nonmetallic inorganic corrosion inhibitors. Orthophosphates can provide either anodic or cathodic protection, depending on dosage and system pH levels. Polyphosphates at concentrations of less than 5 ppm (mg/L) can contribute to both cathodic and anodic corrosion inhibition.

Table 1. Many corrosion inhibitors are available for use in open, recirculating process cooling. The table summarizes selected typical treatment dosages and uses.

**Silica.** Silica is an effective inorganic corrosion inhibitor when applied at 25 to 50 ppm (mg/L) above naturally occurring background silica levels. Nontoxic and inexpensive, it functions by slowly forming a corrosion-resistant film at the metal surface.

**Nitrite.** Nitrite salts commonly are used as anodic corrosion inhibitors in closed recirculating systems but rarely, if ever, in open recirculating systems. Although they are easy to use and environmentally acceptable, nitrites are readily metabolized by various microbes that rapidly deplete residuals, resulting in a loss of corrosion protection. The tendency toward high microbial levels in open cooling systems, combined with frequent use of oxidizing biocides, means that nitrites are metabolized or chemically oxidized to nitrates and rendered ineffective for corrosion control.

## Organic Corrosion Inhibitors

The most common types of organic corrosion inhibitors are azole-based corrosion inhibitors. These are widely used in cooling systems to protect copper and copper alloys by forming a barrier film between the metal surface and water. In the case of mercaptobenzothiazole

Table 2. Cooling water pH control can be achieved by feed of acid or caustic or by controlling cycles of concentration. The table shows a comparison of neutral and alkaline systems.

objectionable odor.

Recent advances in azole technology have led to a halogen-resistant product for more-effective yellow metal protection. This modified azole is not degraded by halogen residuals. Because there is no breakdown reaction, effective azole and halogen residuals can be achieved at lower feed rates. The protective film formed by the modified azole is longer lasting than those produced by conventional azoles -- even in the absence of halogens. Environmental impact also is reduced because less halogen and copper are discharged.

Replacement of conventional chlorine-based programs by stabilized liquid bromine also has been proposed as a way to avoid the problem of azole degradation by chlorine, as well as the problem of halogen attack on organic-, phosphonate-based scale inhibitors. The choice is between using water treatment chemicals that are inherently halogen stable or replacing inexpensive commodity biocides with more costly stabilized liquid bromine.

### **Neutral and Alkaline Cooling Programs**

Most cooling systems operate best in a pH range of 6.8 to 9.0. For any given system, the operating pH range must be controlled (typically, +/-0.20 pH units of the target pH) to ensure optimal results from the treatment program. Cooling water pH control can be achieved by feed of acid or caustic or by controlling cycles of concentration. Table 2 shows a comparison of neutral and alkaline systems.

Neutral pH programs (pH less than 7.8) commonly rely on sulfuric acid for pH control. These programs permit the highest cycles of concentration to be achieved and are often the most economical. Neutral pH programs are especially well suited for makeup sources containing high levels of alkalinity combined with hardness and other dissolved solids.

Neutral pH programs provide a certain level of inherent protection against scaling. They also provide excellent corrosion protection as long as effective inhibitor levels and good pH control are maintained. However, corrosion can result from low pH excursions while the loss of acid feed, coupled with moderately high levels of anodic inhibitors, can lead to treatment-related fouling.

Alkaline treatment programs provide natural corrosion protection by slowing the production of hydroxyl ions and the overall cathodic reaction. With significant amounts of calcium hardness, calcium carbonate precipitates, forming a barrier film at the cathode.

Such programs carry a higher risk of calcium carbonate scale problems; however, advanced alkaline treatment programs can eliminate those concerns and allow some cooling systems to run entirely without acid for pH control, minimizing treatment costs and handling problems. The recent development of highly stable and soluble nonphosphonate-based scale inhibitors and halogen-stable corrosion inhibitors has dramatically improved the reliability and economics of such alkaline water treatment programs.

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### **Related Websites**

- BetzDearborn [www.betzdearborn.com](http://www.betzdearborn.com)

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