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The Use of Zinc for Corrosion Control in Open Cooling Systems

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**Carbosperse™ K-700
Water Treatment Polymers****

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* Formerly BFGoodrich Performance Materials

** Formerly Good-Rite K-700 water treatment polymers

Introduction

Increasingly strict environmental regulations, enacted initially to protect the aquatic environment and most recently to protect people from airborne aerosols, have severely restricted the use of chromate in open recirculating cooling systems. These restrictions have been development slowly and predictable over the last one or two decades and in response, the water treatment service industry generated two main replacement technologies – the high pH/all-organic and the stabilized phosphate approaches. Each of these is a viable option under certain operating conditions but both have a common problem – limited positive corrosion protection.

Chromate/zinc programs were well known for their positive, forgiving corrosion protection. All-organic approaches generally contain little or no corrosion inhibitor package and rely heavily on creating a non-corrosive aqueous environment in the cooling tower by operating at elevated pH and hardness levels. Stabilized phosphate programs do have a positive corrosion inhibitor in their mixed phosphate packages but it is, relative to chromate/zinc, a very weak approach. Both replacement technologies fail to give adequate corrosion protection under similar water and operating conditions.

Some of the conditions that are most troublesome to these technologies are:

1. Corrosion protection for mild steel tubed heat exchangers.
2. Corrosion protection of higher temperature areas of a system.
3. Protection of systems operating at high chloride levels.
4. Protection of systems operating at high sulfate levels.
5. Protection of systems operating with low levels of calcium hardness.

The problem is magnified in systems that must operate with two or more of the troubling conditions. At some point, neither of the technologies will meet the performance expectations of the client company and alternatives must be sought.

An often overlooked alternative is the use of relatively low levels of zinc in these systems. This alternative is generally overlooked because of the perception that zinc has been regulated into oblivion with chromate because of its toxicity. Toxicity? Zinc is hardly toxic at all. It is allowed to be used at up to 5 ppm in drinking water for corrosion control. It is a commonly recommended ingredient in stress relief medication. It's good for mammals to ingest relatively large amounts of zinc on a regular basis – look at your vitamin pills. There is, however, a problem with the use of zinc.

Zinc containing water, when discharged into waterways, has a tendency to precipitate the zinc and that fluffy, gelatinous, adhesive precipitate can occlude the gills of marine organisms. This phenomenon is a purely physical blinding of the membranes with the resultant interference in respiration capability. This fact has led the federal EPA to recommend the limit for the direct discharge of zinc to 1.0 ppm. Most states are following this recommendation but there are some exceptions. If the discharge goes to a POTW, that POTW must be consulted but it is likely that the allowable levels will be higher because of its removal in the treatment process. The conclusion should be that

you shouldn't rule out the use of zinc without doing some preliminary investigation of the local discharge situation and regulations; it is highly likely that a zinc program of some sort can be utilized at almost every location.

In the Tower

In a cooling tower, a zinc based water treatment program may contain materials from the following general list:

1. Zinc
2. Phosphate(s)
3. Phosphonate(s)
4. Polymeric Dispersants
5. Yellow Metal Corrosion Inhibitors
6. Specialty Chelants
7. Molybdates

The levels and/or specific types of these materials may vary with various water quality criteria. I would like to first address each of these material classes separately before trying to coordinate their application with water "shape."

Zinc

Zinc, as noted earlier, is a relatively insoluble mineral as noted by Stumm and Morgan in 1970 (Figure 1). This insolubility is caused by the precipitation of zinc hydroxide whose K_{sp} is 1.2×10^{-17} . With the rapid increase in hydroxide ion level over a pH of 7.8, the solubility of zinc decreases remarkably rapidly as the pH rises. However, this is not the curse that most people consider. It is the mechanism through which an effective cathodic corrosion inhibitor functions.

At the cathodes, oxygen is reduced with the generation of hydroxyl ions. This locally high concentration of hydroxyl ions causes the zinc from the water to precipitate at that cathodic thereby passivating that site with a zinc hydroxide corrosion inhibitive film (deposit?). This cathodic passivation effectively interrupts the redox electrocouple and minimizes the reaction at the anode where the metal loss actually occurs.

This is generally a simple and self-limiting deposition reaction that with proper level control, can give very good corrosion protection with a minimum of fouling. Inspection of the commercially available zinc containing programs reveals that they all utilize similar levels of insoluble zinc. They all target approximately 0.5 ppm insoluble zinc. This level, when added to the soluble level in Figure 1, creates a desired "added" level of zinc as indicated by Figure 2.

This zinc can be added as any zinc containing salt, but most people use either zinc sulfate or zinc chloride as the source. Zinc chloride is readily available as a 50% aqueous solution for ease of handling and safety as well as economy.

Phosphate

Phosphate is used primarily in zinc based cooling water programs that will be operated at a pH of 8.4 or less. The reason for its inclusion is very simple. As the pH of the circulating water drops, the solubility of zinc rises very rapidly minimizing its corrosion inhibitive properties. The inclusion of phosphate at these lower pH levels results in the formation of mixed zinc hydroxide/phosphate inhibitive films at the cathode. The reason for this is the fact that zinc phosphate is even less soluble ($K_{sp} = 9.1 \times 10^{-33}$) than the zinc hydroxide.

This phosphate is generally added as orthophosphate but occasionally you will encounter some programs utilizing a polyphosphate. The advantage of using a polyphosphate is unclear.

The levels of orthophosphate encountered in most commercially available zinc programs are represented in Figure 3. A close examination of Figures 1 and 2 would show sharp changes in the slopes at a pH of 7.6 to 7.8. It is because of this that zinc containing programs are seldom run below pH 7.6 and that appears to be the consensus of the various water treatment companies.

Phosphonates

Most traditional zinc programs utilize the “normal” phosphonates at the “normal” levels – AMP or HEDP at 3 to 5 ppm. There have been articles promoting the use of PBTC to stabilize the zinc solution and citing specific ratios of PBTC to zinc (4:1). It’s hard to imagine, given the corrosion inhibition mechanism and the zinc levels recommended in Figure 2, why you would want to stabilize excessive amounts of soluble zinc or to pay the premium to do so. For the most part, the authors of those papers have reverted to the normal levels and types of phosphonates under the cloud of “over stabilization of zinc.”

Polymeric Dispersants

Polymers are an integral part of any zinc containing program. If you accept that these programs will generate a certain amount of insoluble zinc, then polymers are the appropriate technology to “crystal modify” and disperse the small amount of zinc that does precipitate. This is necessary to prevent excessive deposition of that precipitated material in heat exchangers or low flow areas of the system.

As indicated in Figure 4, various polymers have differing efficacies when it comes to “stabilizing” zinc in water solutions. The word “stabilizing” is somewhat of a misnomer. None of these polymers significantly increases the solubility of zinc hydroxide or zinc phosphate in cooling water. They merely minimize precipitated particle sizes and

effectively disperse them throughout the system. If you eliminated all of the precipitated zinc sales between 0.22u and 0.45u in the subject solutions of Figure 4, you would find levels that closely approach those of solubility.

The normally encountered levels of the chosen polymer will be in the 4 to 6 ppm range for the most efficacious products or correspondingly higher levels of less effective materials.

Yellow Metal Corrosion Inhibitors

Yellow metal corrosion inhibitors (YMCI) are sometimes used in conjunction with zinc or zinc phosphate based cooling water treatment programs. These programs generally exhibit effective copper or admiralty corrosion inhibition without the inclusion of YMCI but some local conditions may warrant their use.

If one believes that a YMCI is needed, they are generally applied at levels lower than in other types of programs. Typically:

1. Tolyltriazole (1 to 2 ppm)
2. Benzotriazole (1 ppm)
3. Mercaptobenzothiazole (1.5 to 2.5 ppm)

Specialty Chelants

A variety of specialty chelants have been applied in these programs with varying levels of success. EDTA was used early to stabilize zinc but was soon dropped as the corrosive tendencies of the EDTA degradation products were realized. Later, other specialty chelants were tried but were successively dropped as the specter of “over stabilization” was realized and the wisdom of controlled addition and dispersion was discovered. Some of these materials are still formulated but are there largely as marketing hooks as opposed to being effective in the system.

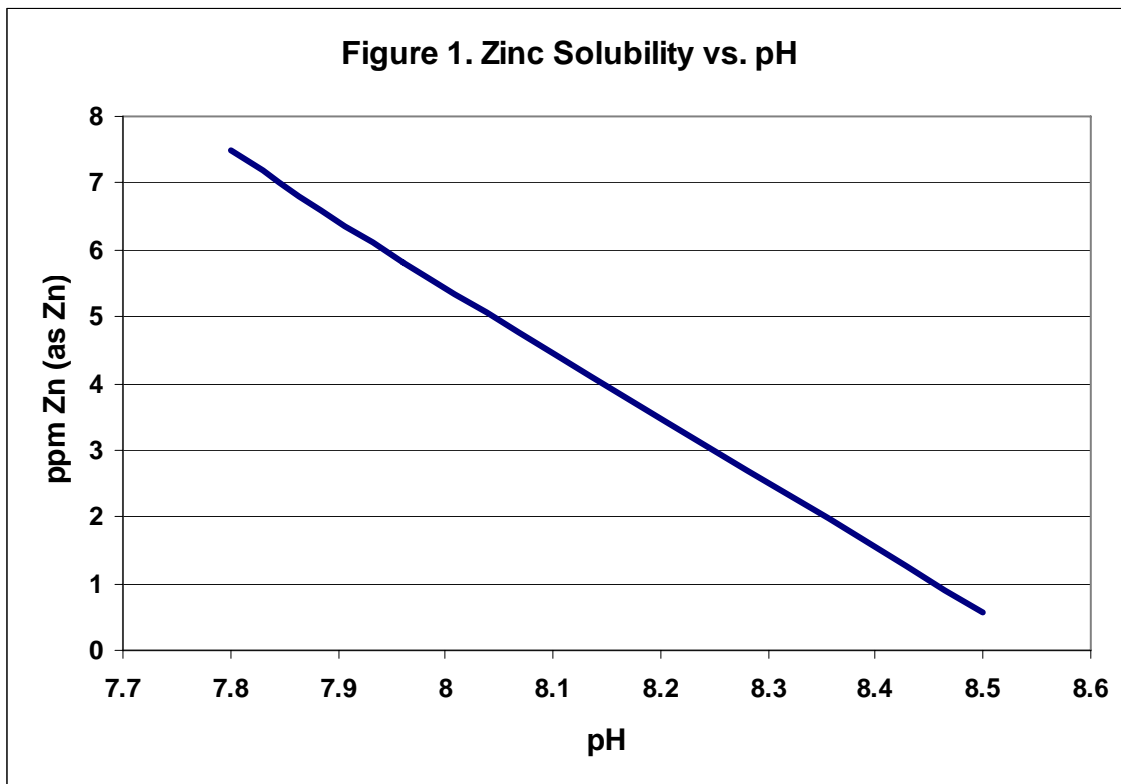
Molybdates

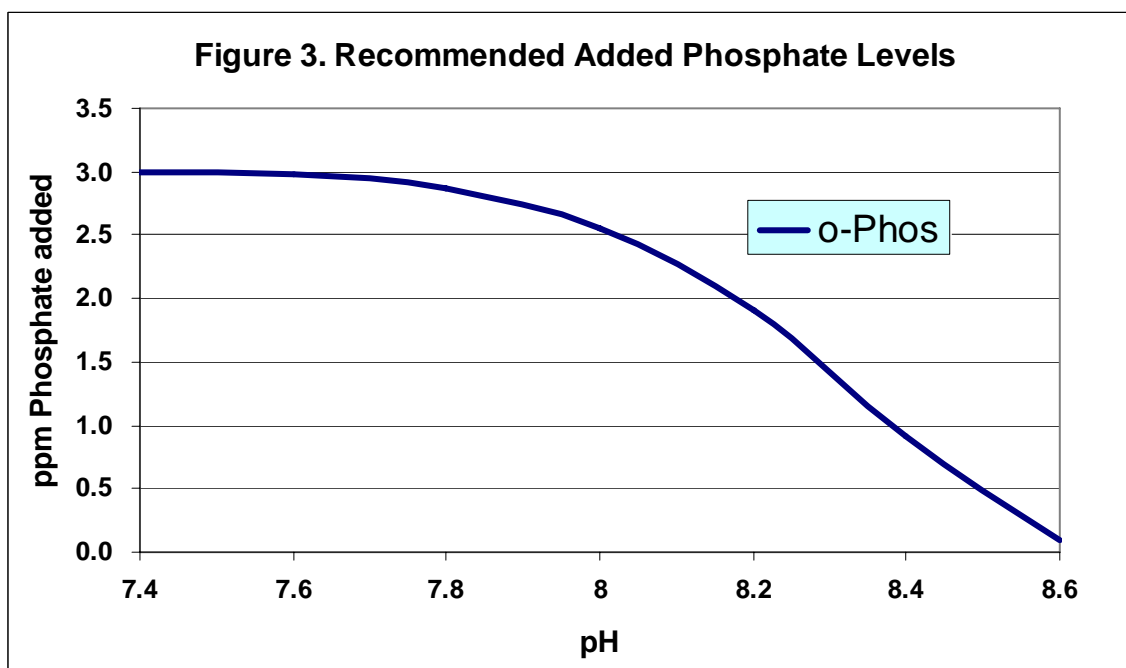
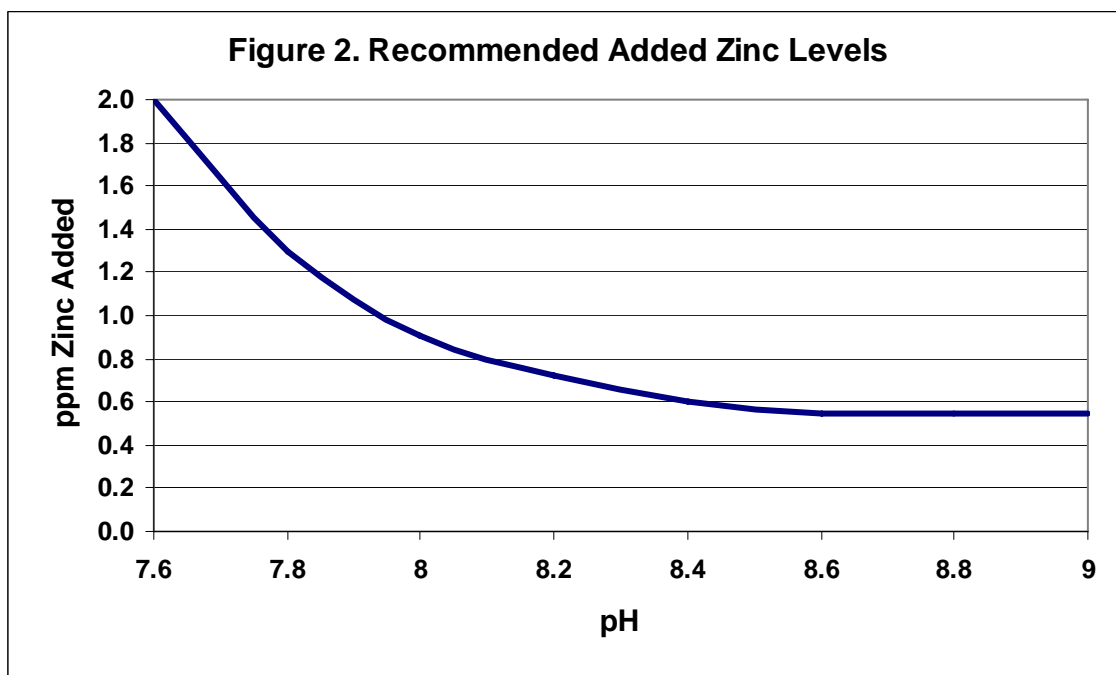
Numerous articles and references exist on the synergism of molybdates and zinc in cooling water treatments. When used in this context, molybdate is generally applied at the 3 to 5 ppm level.

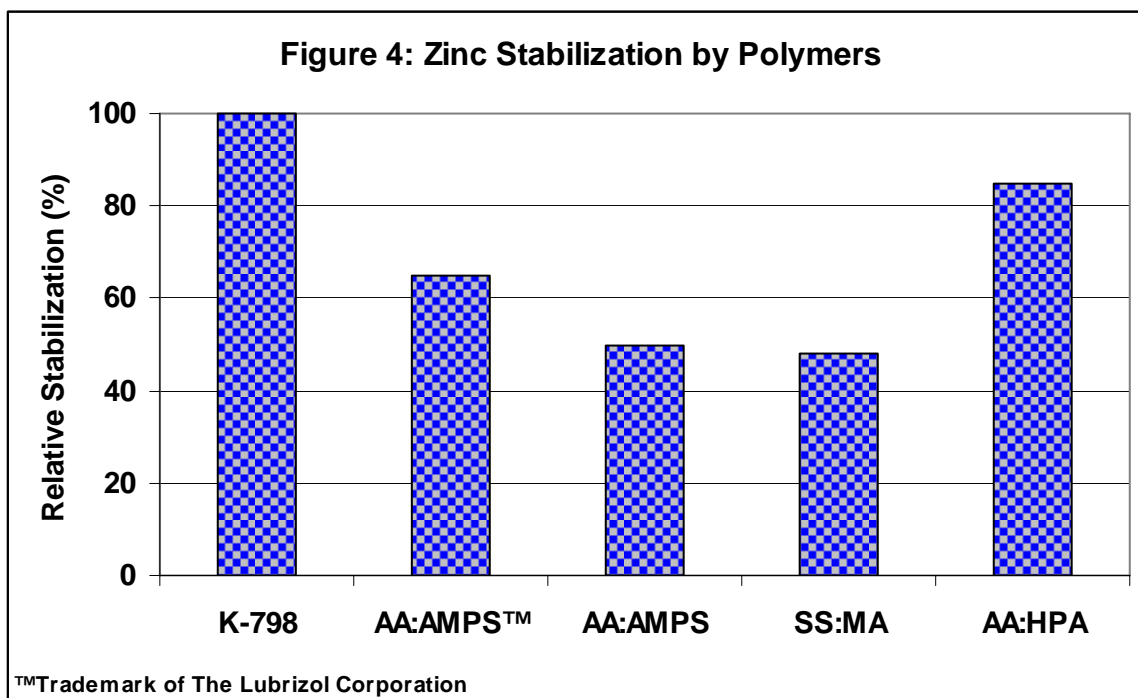
Theoretically, as an anodic inhibitor, molybdate should complement the use of zinc very well and our limited experience indicates that this is the case. However, much research needs to be done to optimize the levels of zinc, molybdate and probably phosphate.

Conclusion

The use of zinc containing cooling water treatments for the treatment of open recirculating cooling water systems is simple, safe and largely environmentally acceptable. The inclusion of a well designed and understood zinc based program in a product line utilizing modern dispersants to minimize deposition of the inevitably insoluble zinc is a necessity where local water quality or operating conditions dictate. The design and application of these programs are not mysterious – they merely conform to some basic principles of solubility and dispersion.







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