



9707 Key West Avenue, Suite 100
Rockville, MD 20850
Phone: 301-740-1421
Fax: 301-990-9771
E-Mail: awt@awt.org

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Developing Cooling Water Treatments – Part II

Additional Contributions to Chemical Treatment

Robert R. Cavano, Scranton Associates Inc.

Additional Contributions to Chemical Treatment

Having established the theoretical bases in Part I, we will return to our task and review the importance of phosphonates to those efforts. We now turn to additional resources and to the proven benefits of combinations of raw materials.

Other Corrosion Reducing Materials

A number of other chemicals can help us to prevent corrosion.

A. Phosphates

For many years, we depended upon inexpensive (and often inadequate) inorganic phosphates for the protection of water circulating systems. Included in this category were the orthophosphates as anionic corrosion inhibitors and the complex phosphates as cathodic inhibitors. Phosphates of both types also appear, free of charge, in fertilizer run off or as present in municipal distribution systems. Orthophosphates, when provided as part of a treatment program, are usually supplied in the form of phosphoric acid or one of its sodium or potassium salts.

In general, complex phosphates are chosen for their initial and sustained solubility. The most widely used products are sodium hexametaphosphate (SHMP) and tetrapotassium pyrophosphate (TKPP). TKPP has especially good solubility, stability, and iron sequestering properties.

Smith and Sherwood¹ also observed that:

“For collective corrosion control, the ratio of calcium ion concentration needed to the polyphosphate concentration is at least 0.2 and preferably 0.5 ... Reversion of the polyphosphate to orthophosphate ... will only enhance overall protection due to the inhibitive properties of orthophosphate.”

At times, polyphosphates are used in a formula for convenience in manufacture or feeding, and their reversion is not necessarily objectionable since the change to the orthophosphate ions seems to improve overall performance. At high temperatures, polyphosphate reversion is rapid and almost complete, so feeding it alone can rapidly produce dianodic protection. Conversely, if the reversion rate is low, the addition of orthophosphate may become necessary.

Before the introduction of organic phosphorus programs, we reasoned that:

“Problems encountered with phosphate program operation occur at both ends of the water chemistry spectrum: lower system pH and softer water will result in accelerated corrosion rates on mild steel. Elevated pH or harder water will result in increased precipitation of calcium phosphate salts ...”²

Kessler³, extending this concept, also separated those programs into two categories, depending on phosphate content and pH range:

“Neutral pH programs operate in the pH range of 6.8 to 8.0 while alkaline programs operate at pH 8.0 and above. ... The neutral pH programs are also referred to as stabilized phosphate technology because they

rely on relatively high dosage of inorganic phosphate [10-20 ppm (mg/L)] for mild steel corrosion control.”

“Alkaline technology relies on lower concentrations of phosphate (2-8 mg/L) relative to stabilized phosphate programs, while sometimes also using zinc (1-3mg/L) for enhanced mild steel protection.”

Hartwick and Jovancicevic⁴ also described the operations of inorganic phosphate programs. Among the merits listed is that phosphates can be used for systems having as low as 50 mg/L CaH and up to some in excess of 1000 mg/L CaH (as CaCO₃). A dosage range of 10-16 mg/L as PO₄ is recommended for high level operations and 5-8 mg/L for the low.

Boffardi⁵ indicated that suitable treatment levels were approximately 15-18 mg/L expressed as total phosphate. He further stated that relative concentrations of orthophosphate and polyphosphate were not critical, with at least 20 % of either species being sufficient to create synergism in corrosion reduction.

The addition of HPA to a formula reduces the need for such high phosphate levels, yet, it allows the use of an alkaline phosphate technology if it is accompanied by an adequate polymer content for phosphate and phosphonate control.

B. Triazoles

Triazoles are needed for the primary protection of copper-based alloys and to help disperse and/or sequester stray copper ions. By deactivating free copper, these products also help to prevent galvanic corrosion and reduce particulate deposition.

Benzotriazole (BT, BZT) and tolyltriazole (TT, TTA) are the leading inhibitors for these functions. The most convenient forms are the sodium salt solutions at 50% (active tolyltriazole at 44 %), and 40 % active BZT (actually closer to 36 % active).

Other than for very special pretreatment requirements, TT and BZT are roughly equal in performance. TT is usually the first choice among the azoles because of price, but BZT has better solubility, especially at moderate pH values. Combinations of these triazoles may be advantageous, especially at the time of initial passivation.

Vanderpool⁶ and others indicate that the structure of the films is similar and that their formation is rapid for all of the major azoles. The quantity of azole con-

sumed in providing a protective film is small compared to that needed to protect copper containing metals, but generous reserves (2-5 mg/L) better guarantee against film breakdown and surges in demand:

“... common practice (is) ... to always maintain a constant residual of triazole ... of around 2.5 mg/L (as) active product.”⁷

C. Zinc and Molybdate

If calcium levels are below 20 mg/L, we probably have a corrosive system and should introduce zinc. Zinc also may be used in the calcite saturation index (CSI) 20-49 range but polyphosphates work equally well. Their combination into zinc phosphate had constituted the traditional “metal” program with the best pH range for multi-metal recirculating systems operating between 6.5 and 8.0. Zinc allows even better corrosion control in these soft waters when used in combination with other inhibitors such as the phosphonates (including HPA) and AMPS[®]-containing terpolymers.

Corrosion protection from zinc is of short duration because of zinc’s limited solubility⁸. Sherwood and Eastman⁹ show that it must be present at 1 mg/L or more to be effective and that zinc hydroxide precipitates at pH values above 7.5 unless sufficient AA/SA terpolymer is present. When introduced at levels of 1.0 to 3.0 mg/L into a system containing phosphate, it can yield excellent and prolonged anodic/cathodic protection. Such combinations generally utilize a rapid establishment of protection from zinc, with phosphates contributing later to more durable protection.

The proper terpolymer can stabilize zinc at pH levels as high as 9.0. For zinc to be fully available, a polymer/zinc ratio of as much as 3/1 is recommended¹⁰. Too little polymer allows zinc hydroxide to form and precipitate. At higher polymer levels, some feel that the metal may be over stabilized and consequently deprived of its inhibitive powers – a phenomenon not adequately documented.

Not only is zinc effectively dispersed by sulfonic acid-containing terpolymers, it also is synergistic with them when they are used for calcium phosphate control. This aspect of zinc usage was described by Amjad and others¹¹ as follows:

“...the presence of zinc greatly enhances the calcium phosphate inhibition of polymers AA/SA and AA/SA/SS.”

The synergistic effect of zinc is evident in these tests, allowing a reduction in AA/SA of 3 mg/L from the original 5 mg/L dosage, and a reduction of 2 mg/L for AA/SA/SS.

Molybdate can be helpful in corrosion control but often also requires the presence of zinc, phosphate, or phosphonates for greatest effectiveness. Molybdate has historically been used in combination with these other materials to prevent pitting and as an indicator, but its current high price disqualifies it from serious consideration as a general corrosion inhibitor.

Polymers for Dispersion

Polymers based on acrylates, acrylamides, AMPS®, etc., when used alone or in combination, have become essential dispersants in cooling water systems.

Where the water is soft, the chance of calcium phosphate formation is reduced, but the need for general dispersion and for control of stray metal continues and can be best provided by the terpolymers.

Several interesting observations have been made:

“The polymer requirement is determined by the calcium phosphate super-saturation. In general, more phosphate and less polymer are needed at lower pH and more polymer and less phosphate is needed at higher pH.”¹²

“It is possible to extend operations to more alkaline conditions by reducing the phosphate concentration and increasing or supplementing polymer usage with terpolymers.”¹³

While these comments may be applicable to some ternary systems (phosphate, polymer, alkalinity, for example), we have a limited ability to control pH in each system and must primarily match the quantities of terpolymer to those of phosphate or zinc.

It has been said that:

“...with higher polymer concentrations, the polymer must be properly balanced with the phosphate concentration. Too high a polymer level can result in over-stabilization of the phosphates and in increased corrosion rates: too low a concentration can result in bulk precipitation of the calcium salts, fouling the system.”¹⁴

Chang¹⁵ discussed many properties of the polyacrylate homopolymer in evaluating it for possible

use in detergents. His comments on calcium stabilization probably also apply to zinc. His results predict some degree of sequestration and describe the difficulties in determining those levels.

“The binding powers [Calcium Ion Binding Power (CBP)] for polyelectrolytes did not correspond to the formation of complexes with a simple stoichiometry. In most cases, more than one equilibrium is involved.”

Alternatively, stabilization ratios for a single metal/polymer system can be estimated empirically, but determining the amount of polymer required for other functions may be a more difficult problem. The mechanisms involved are complex and each terpolymer varies from the others in many important aspects.

It seems unlikely that the high tolerance terpolymers would form a very strong bond with calcium, zinc, or phosphate. Might it be that polymer redundancy from over-dosage is costly but perhaps less risky than having an excess of phosphates or phosphonates?

In any event, we have tentatively chosen to specify polymer content to match the total amounts of phosphate and metal present and the total orthophosphate which might evolve from degradation.

At this point, we may ask what that matching ratio should be, or more simply, what levels of terpolymer should be used.

Ion association model saturation levels can be used for predicting calcium phosphate scale formation and for determining dosage. Investigations of this type are recommended but, in the interests of brevity, we turn to some more rough and ready recommendations for phosphate control. Ratios of active terpolymer to PO₄ of between 1:1 and 3:1 are usually recommended, depending on the levels of particulate contaminants, the amount of phosphorus complexes, and the dispersion and stabilization requirements for inhibitors such as zinc.

A general guide is shown in Table 2:

Table 2: Terpolymer Dosage

Function	Active Terpolymer/(PO ₄ +Zinc)
Low Hardness & Particulate	1.0 mg/L
Higher Hardness, Phosphate, Iron, Zinc	1.5 mg/L
More Stress and Contaminants	2.0+ mg/L

Combinations

The introduction of phosphonates made a highly significant contribution to the field of water treatment. It soon became evident that their combination with phosphates produced better scale and corrosion protection than the individual contributions might have led us to expect. Combinations of this type also allowed reduction in total phosphorus requirements and became a harbinger of other valuable discoveries.

Dividends from this discovery were, at times, diminished by poor calcium phosphate and calcium phosphonate solubility, a shortcoming to later be compensated for by the introduction of highly effective copolymers and terpolymers.

We had learned from many sources that the presence of the proper AA/SA copolymers and terpolymers can cause substantial improvement in the performance and calcium tolerance of phosphonates (HEDP in one example¹⁶). These sulfonic acid-containing and AMPS[®]-based copolymers are effective for dispersing zinc, calcium phosphate and calcium phosphonate, thereby allowing the other components of a formula to fully execute their originally designated functions.

Therefore, these polymer/phosphonate blends synergistically impeded the tendency for calcium carbonate to precipitate and permitted lower dosages of dispersant polymers.

“...because there are two possible and distinct mechanisms (stabilization and dispersion), it is reasonable to suggest that the reason combination products are so successful is that they can take advantage of both of these mechanisms.”¹⁷

Subsequent investigations and patents¹⁸ continued to demonstrate that blending phosphonates with polymers greatly improved treatment results and this approach is now accepted practice¹⁹.

HPA performance as a corrosion inhibitor was greatly improved by being part of an anodic/cathodic combination with the phosphates and with the strongly cathodic zinc. Adding HPA to a scale preventative phosphonate (HEDP) can also prove rewarding.

Success in combining these many pairs of materials was a precursor to even better performance and protec-


tion. Since good things often come in threes, it was not at all difficult to anticipate the next development!

In October of 1995, Gill applied for a U.S. Patent (granted on January 20, 1998)²⁰ describing a way to completely control calcium carbonate and calcium phosphate in a high pH, high scaling water. It recommended a mixture of PAPEMP (a scale preventing phosphonate)/Aquatreat AR-540 (a dispersant ter/quad polymer)/Belcor 575 (a corrosion inhibiting phosphonate), in ratios such as 1/2/1. Gill also reported remarkable reduction in phosphonate demand for systems treated with these combinations. Gill and others²¹ later supported these findings with laboratory and field results, particularly describing their success under stressed conditions.

Most cooling tower applications benefited greatly from the presence of multiple functionalities such as those described above, including two, three, and four part combinations.

Debate continues as to whether any mixture can be as effective as a single multi-functional molecule (such as PBTC or some of the new copolymers and terpolymers). In addition, structural limitations may keep us from combining multiple groups into one molecule with as much flexibility as we can obtain from blending individual polymers and/or phosphonates. Even if it were possible to incorporate a number of desired functionalities at the ratios we designate, it would be difficult to decide upon that unique molecule which would be most suitable for all of the problems.

The movement to ever more complex terpolymers has, in general, been rewarding, but is not without problems. There is evidence that most multi-component (if also multi-functional) formulas are versatile and forgiving, with the various ingredients able to cover for one another to some extent. But water pipes must be protected and the piper must always be paid. As we continue to design more complex remedies, we also increase the number of formulas in our line and the cost of maintaining and stocking them.

We strongly commend the advantages of adding multiple function components, whether introduced in a single product or as several distinct products! 

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Robert R. Cavano is the President of Scranton Associates Inc. Bob can be reached at (216) 252-2120 or via email at bcavano@scrantonassociates.com.

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1. For collective corrosion control, the ratio of calcium ion concentration needed to the polyphosphate concentration is at least 0.2 and preferably 0.5. Reversion of the polyphosphate to orthophosphate will only enhance overall protection due to the inhibitive properties of _____.
 - a. zinc
 - b. orthophosphate
 - c. sulphite
 - d. erythorbate

2. Problems encountered with phosphate program operation can occur at both ends of the water chemistry spectrum: Elevated pH or harder water will result in _____.
 - a. accelerated corrosion rates on mild steel
 - b. increased precipitation of calcium phosphate salts
 - c. higher than normal bacteria growth
 - d. increased turbidity

3. Common practice is to always maintain a constant residual of triazole of around ___ mg/L as active product."
 - a. 0.5
 - b. 1.0
 - c. 2.5
 - d. 5.0

4. If calcium levels are below 20 mg/L, we probably have a corrosive system and should introduce _____.

- a. zinc.
 - b. copolymers
 - c. terpolymers
 - d. tolytriazole
5. The polymer requirement is determined by the calcium phosphate super-saturation. In general, more phosphate and less polymer are needed _____.
- a. with soft water
 - b. with hard water
 - c. at higher pH
 - d. at lower pH
6. HPA performance as a corrosion inhibitor was greatly improved by being part of an anodic/cathodic combination with phosphates and with _____.
- a. acryamides
 - b. tolytriazole
 - c. strongly cathodic zinc
 - d. polyacrylate homopolymer
7. Triazoles are needed for the primary protection of copper-based alloys and to help disperse and/or sequester _____.
- a. orthophosphate
 - b. phosphate
 - c. calcium ions
 - d. stray copper ions
8. Among the merits listed is that phosphates can be used for systems having as low as ___mg/L CaH and up to some in excess of 1000 mg/L CaH (as CaCO₃).
- a. 5
 - b. 10
 - c. 50
 - d. 100
9. A dosage range of ___ mg/L as PO₄ is recommended for high level hardness operations.
- a. 1-2
 - b. 2-4
 - c. 10-16
 - d. 20-32
10. For zinc to be fully available, a polymer/zinc ratio of as much as ___is recommended.
- a. 2/1
 - b. 3/1
 - c. 8/1
 - d. 10/1