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Developing Cooling Water Treatments – Part III

Robert R. Cavano, Scranton Associates Inc.

Controlling Deposits and Corrosion

In previous installments of this series, the author has strongly advocated for combinations of chemicals to treat cooling tower waters. Now we move on to the difficult task of developing strategies for choosing the best levels of each ingredient for a particular system. Important issues of concentration, cycling, and feeding are also introduced, so that the active content will be present at the proper levels.

Specific Challenges

It is appropriate that we examine the metal particulates and hardness complexes which may cause trouble in a recirculating cooling water system and suggest ways to best neutralize, counteract, complex or disperse them.

Calcium Carbonate

Although polymers perform well as threshold agents for calcium carbonate, other materials, particularly the phosphonates, are more efficient. It is important to stabilize calcium carbonate before it precipitates rather than try to disperse the resulting complexes after it forms. Initial control of calcium carbonate can be provided by the phosphonates, assisted by polymers,

with terpolymers stabilizing the system and supplying versatile, yet expensive, reserves.

Boffardi and Schweitzer¹ confirm this, suggesting that:

“One would not use the copolymer (AA/ SA) exclusively for calcium carbonate control since the other building blocks (phosphonates and homopolymers) are more efficacious.”

In what follows, the use of the “greater than” symbol “>” is meant as “better than,” “>>” is meant as “much better than,” and “=” is meant as “approximately equal to.” At this stage, the ranked products are based on 100% active with no considerations of cost.

Much of the information in this article was taken from the bar graphs in various technical articles, where visual impact sometimes masked the relatively minor significance of performance differences. In most cases, however, the general trends are instructive.

Results with some of the products suggested for calcium carbonate inhibition were compared. They indicated that commercially available copolymers and terpolymers did not perform as well as phosphonates and homopolymers. One evaluation of commonly used building blocks indicated (at pH 8 and 10) that:

HEDP (100) > AMP (67) > PMA (49) > PAA (18) > SA/AA (13)

In cases where regulations prohibit the discharge of phosphorus, the polymers become the best alternative. Zuhl and Amjad² indicated that under conditions of high hardness and alkalinity, the solvent-reacted polyacrylates were more effective as a calcium carbonate inhibitor than the aqueous-reacted versions. Under more moderate conditions, the difference between the two types was narrowed. Enlarging the range of materials tested, it was found that HEDP and the homopolymers were better than the co- and ter-polymers for this function.

HEDP (94) > Solvent reacted PAA (81) > PMA (79)
> AA/SA (70) > AA/SA/SSS (59)

It appears that carboxyl content in polymers is necessary for calcium carbonate inhibition, and that the higher the carboxyl contents of a polymer, the better the performance.

PMA, at times, exhibited the best crystal distorting properties of all of the commonly available scale inhibitors. Claims that it exhibits dispersion activity superior to polyacrylate and phosphonates may indeed be true for calcium carbonate, but for other dispersant challenges it may be limited. When PMA is used, it is often formulated with a phosphonate and possibly another polymer (polyacrylate).

Calcium Sulfate

It was recognized at an early date¹ that polyacrylates were the best choice for treating calcium sulfate. The relative effectiveness was found to be:

PAA (100) > SA/AA (76) > AMP (71) = PMA (71) >> HEDP (11)

Sulfuric acid is no longer extensively used for alkalinity reduction and, as a result, problems with calcium sulfate are not as common as they once were. It became possible to eliminate the acid when new polymer technology allowed better management of the more alkaline waters.

Later publications³ confirmed these results to some extent:

PMA (98) = SS/AA-B (98) > PAA-2M (92) > AA/SA/SSS (70)
> SA/AA-A (66) > HEDP (6)

Because of its relatively high solubility, calcium sulfate by itself is not usually a primary scaling concern. Calcium carbonate, however, may “be an effective site for nucleation for (calcium sulfate) crystallization.”⁴

Calcium Polyacrylate

Since polyacrylates are known to have moderate sequestering abilities, the formation and precipitation of their complexes can become a problem. In addition, such loss of free polyacrylate diminishes dispersing power. The ability to resist these tendencies is somewhat reflected in a material’s calcium tolerance.

Zuhl and Amjad² report that a lower molecular weight polyacrylate (2000 amu) has over 50% greater calcium tolerance than does a higher molecular weight (5000 amu) version, and that the solvent-reacted polyacrylates have about 25% greater tolerance than the aqueous. These concerns are most pertinent when the polyacrylates are used alone and less so when they are used with phosphonates and copolymers.

Calcium Phosphonate

Recognizing the limited solubility of the phosphonates, it was discovered that a terpolymer inhibited the precipitation of calcium-HEDP much more effectively than did a copolymer, thus extending applications to higher cycles and more difficult waters. The superiority persisted as temperature, pH and hardness increased. Homopolymers had no appreciable influence on phosphonate stability.⁵

Amjad and others⁶ qualified these statements by warning that:

“... DCP (deposit control polymers) performance as a Ca-HEDP inhibitor strongly depends on polymer architecture.”

Among the polymers, the sulfonic acid-containing terpolymer was best, a similar copolymer next, then polymaleic anhydride, and a polyacrylate last.

Calcium Phosphate

AMPS[®] copolymers were found to be excellent dispersants for calcium phosphate when no iron was present. When is a higher price for the AMPS[®] terpolymers justified over the AMPS[®] copolymers? Where iron content is low, the copolymers perform as well as the terpolymers for calcium phosphate at a slightly lower dosage for the terpolymers.

One report⁶ found terpolymers to be almost twice as effective as the copolymers in the presence of 1.0 mg/L of iron. These tests showed an even more significant change when iron was increased to 2.5 mg/L, with the

terpolymer becoming about three times as effective. Both copolymers were far superior to the homopolymer polyacrylate under these circumstances.

Having accepted the superiority of copolymers and terpolymers over homopolymers for calcium phosphate control, is it possible to save money by extending copolymers with homopolymers.⁷ Tests indicate that such a blend would have to greatly favor the copolymer, making the economies of such blends questionable. Any savings would most likely be further reduced by the extra manufacturing expense of adding an additional ingredient.

It has been claimed⁷ that 10 mg/L of the copolymer AA/SA-25 was required to achieve 90 % inhibition of phosphate precipitation with no other contaminants present, and only 7.5 mg/L of the terpolymer AA/SA/SS was required to reach the same level of inhibition. Calculations indicate that at these dosage levels, the use of a terpolymer does not increase cost over the copolymer.

Another area of comparison might be between different versions of the AA/AMPS[®] copolymer. It is suggested that an improvement in the results can be achieved by using the AA/AMPS-40 product rather than the more common and inexpensive 25 % AMPS[®] version (~20-30). At current prices (2008) for AMPS[®] the two versions are, in fact, equivalent in cost. It should be noted, however, that only the 40% version is listed in CFR 173.310.

Amjad also tested various polymers for their effectiveness in preventing calcium phosphate precipitation when clay was present. A 7.5 mg/L of a terpolymer was better than 10 mg/L of a copolymer – with the terpolymer doing well (over 80 % inhibition) up to 100 mg/L of clay.⁶

As calcium phosphate saturations become higher, polymer requirements increase and control becomes more difficult. In order to remedy this situation, more sophisticated phosphonate programs were developed, including new products and combinations.

Soluble Iron

Iron, in all its forms and even at low concentrations, can seriously interfere with the dispersive capabilities of polymers and of other treatment chemicals. Sherwood and Smith¹³ showed that:

“Under the test conditions, calcium interferes with polyacrylic acid’s performance as an iron oxide

dispersant. ... AA/SA remains an effective dispersant even under high calcium ion concentration because it is relatively insensitive to the calcium ion.”

Particulate Iron

“Polymers are the most effective class of chemicals for dispersing particulate iron oxide. Polyphosphates and phosphonates exhibit poor dispersancy power.”⁸

In general, Amjad further concluded that for this function:

“terpolymer > copolymer > homopolymer”

Clay/Silt

Some homopolymers (especially materials such as 5000 molecular weight polyacrylates) are quite efficient for clay and silt dispersion, but the newer copolymers and terpolymers are even more effective and also resistant to interference from these same sources.⁹

Corrosion

Polymers will not provide much corrosion protection. Normally, at use concentrations, polymers by themselves are non-corrosive or less corrosive than available alternatives. Their ability to disperse and liquidize deposits, however, helps to keep the surfaces clean and resistant to the types of corrosion most closely associated with the presence of deposits.

While phosphonates are most typically used to prevent calcium carbonate precipitation, they have the additional benefit of providing limited cathodic corrosion inhibition, which is substantially improved when combined with powerful agents such as phosphates, molybdate, zinc or HPA. Corrosion control has been discussed more fully in Parts I and II of this series, and in the section below.

Guidelines for Chemical Choice

Bringing together the concepts considered so far, the following suggestions are offered for inclusion:

1. A phosphonate such as HEDP or PBTC is essential for the control of calcium carbonate, iron and silt.
2. Phosphates are well established components for corrosion inhibition.

3. Zinc, having strong cathodic functionality and synergism with other inhibitors, makes a major contribution under highly corrosive conditions.
 4. HPA, because of its excellent solubility, stability, and corrosion inhibition, should be used all across the treating spectrum.
 5. Terpolymers are highly effective for dispersing phosphate and phosphonate complexes, as well as iron, zinc and silt.
 6. All formulas should contain PBTC, HPA, and a terpolymer as a result of the above described individual effectiveness, and because of their extensive synergism.
 7. Azoles protect non-ferrous metals and also prevent metallic contamination, and should be present in most formulations.
2. Complexes of calcium with AMP and HEDP have limited solubility, as do zinc and phosphates. These tendencies are greater as pH and temperature rises. PBTC is the most resistant to these insolubility problems. Advanced copolymers are a helpful addition.
 3. HEDP and AMP have poor resistance to oxidizers, the latter because it contains nitrogen. In particular, chlorine attacks AMP and bromine attacks HEDP, with PBTC being the most resistant. A similar problem arises with HPA, but the addition of monoethanolamine is helpful, as is the introduction of a closer control on feeding rates and techniques.

Caveats

To use the available materials most wisely and economically:

1. Avoid overdosing—the affliction of our industry (and many others)!

Concentration and Feeding

Concentration

Initially, a critical decision is made on how much of each chemical is needed in a system. The rest of the work becomes mere mechanical calculations to arrive at proper feed rates for a selected product and degree of cycling. Chemical concentrations may be indicated in a number of ways and must, at times, reconcile one with the other:

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NO-Reagents / **NO**-House Formulas
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1. Production formulas are stated as percent by weight of commercial chemical, e.g., percentage of 60% HEDP solution to be incorporated into the formula.
2. Specifications for chemical content in a system are usually stated as mg/L, based on 100% active materials. These values are obtained by adjusting commercial products for their degree of activity. For example, 1.0% of 60% HEDP solution results in 0.6% of active HEDP. If specified as PO₄, 1.0% of 60% HEDP is 0.553% as PO₄. The concentration in the system is related to the number of cycles. For example, 0.6% of active HEDP at 5 cycles of concentration results in 3.0% active HEDP.

Cycling

Clearly, estimates of cycling are necessary to establish a correspondence between the targeted system concentration of a chemical and the amount to be fed with the make-up. If the make-up water calcium and alkalinity levels are highly susceptible to change, cycles of concentration must be carefully monitored and adjusted to maintain maximum adherence to a treatment program and assure trouble-free operation.

In general, cycles of concentration will be between 2 and 8, determined by water analysis and interpreted by a program such as WaterCycle[®]. Cycling based on such calculations can usually tolerate moderate variation. For example, if a formula is based on 5 cycles of concentration, good results can still be obtained from 4 cycles, particularly if the dosage rate is increased by 25% ($5/4 = 1.25$).

The cost savings which can be obtained by increased cycling are well recognized, especially at the lower levels (e.g. from 2-5). There are, however, several limitations that must be acknowledged:

1. Certain salts (silicate, calcium) may be particularly abundant in a water supply and allow only a small number of cycles before precipitation begins.
2. Systems with large water loss from drift or leakage develop high cycles of concentration even when there is little blow down.
3. In general, increases in cycling are accompanied by higher pH and its attendant reduced corrosion. The solids left behind, however, may increase corrosion and scaling tendencies, negating, to some extent, any anticipated savings.

High cycling is not always desirable! Experience has shown that for systems operating above about 8 cycles, treatment dosages must often be greatly increased (at additional cost) and that there is risk of increasing concentrations beyond threshold levels.

Feeding

Instructions for feeding cooling water treatment chemicals are usually given as 100 mg/L of a formula described in percentage of commercial strength raw materials. Since balances for weighing milligrams and a stock of one liter flasks are not readily available in most production locations, many operators find that the addition of one pint of treatment for each 1000 gallon multiple of water added is a convenient way to introduce treatment.

Clearly, one pint for 500 gallons would double the concentration and one pint for 2000 gallons would cut it in half. Similar results could be obtained by maintaining the dosage rate but cutting the production formula, as well as (where possible) concentrating it. For larger systems, one gallon could be used to treat 10, 8, 6, or 4,000 gallons.

Recall that all volumetric calculations depend on the density of the treatment chemical. To derive the feed rates for these alternatives, there are several relationships:

1. One pound (#) = 453.6 grams (g)
100 mg = 1/4536 pounds = 0.22×10^{-3} pounds
2. One gallon (gal) = 3.785 liters (L) = 8 pints (p)
1 Liter = 1/3.785 gallons = 0.2642 gallons
3. "P" = pounds per gallon (#/gal) for each particular treatment

Volumetric Feeding Rates ("F") Are Not Hard to Calculate!

$$\text{"F"} (1 \text{ pint per } 1000 \text{ gal}) = (P) \times (10^2) \times (0.2642) \times (10^3) / (8) \times (0.22) \times (10^3)$$

$$= (15.0) \times (P) \text{ mg/L of treatment}$$

$$= (7.5) \times (P) \text{ mg/L when one pint is added for each } 2000 \text{ gallons.}$$

It is important that the formula used in production is stated in mg/L, ppm, or percent by weight. This format allows the percentage of each ingredient in the production formula (adjusted for the feed rates and cycling) to

determine the mg/L (ppm) at which it will appear in a system.

As an example, the feed rate of one pint of a product (weighing 9.1 #/gal and designed to be fed initially at 100 mg/L for every 2000 gallons of make up water), results in 68.25 mg/L of the treatment ($9.1 \times 7.5 = 68.25$). Close correspondence to the original guidelines (mg/L) could, in this case, be obtained by feeding one pint for each 1365 gallons.

If operating conditions will not tolerate the number of cycles expected, this may indicate that hardness is higher than anticipated or that there are other limiting factors. This requires increasing dosage or switching to a formula better suited to the water being used. Be aware that in a new system, residuals are slow to develop and must be patiently monitored and acted upon. ☹️

Robert R. Cavano is President of Scranton Associates Inc. Mr. Cavano has been the recipient of many awards for his contribution to the water treatment industry, and especially his technical contributions to AWT. He can be contacted by phone at (216) 252-2120 or by email at bcavano@scrantonassociates.com.

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The purpose of this quiz is to ensure the CWT (Certified Water Technologist) has read and understands the technical paper or article. The quiz answers are based strictly on the content and perspective of this article. The AWT and Certification Committee make no representation to the factual content of the article. Each article has been reviewed and the Certification Committee has made every attempt to avoid articles with misleading statements. Any questions concerning the scoring of any quiz will be referred back to the article for clarification.

The Analyst - Summer 2008 - "Developing Cooling Water Treatments - Part III" by Robert R. Cavano, Scranton Associates, Inc..

1. It was recognized at an early date¹ that _____ were the best choice for treating calcium sulfate.
 - a. zinc chlorides.
 - b. polyacrylates
 - c. orthophosphates
 - d. erythorbates.

2. Among the polymers, the sulfonic acid-containing terpolymer was best, a similar _____ was next best.
 - a. homopolymer
 - b. copolymer
 - c. polymaleic anhydride
 - d. polyacrylate

3. One report found terpolymers to be _____ as effective as the copolymers in the presence of 1.0 mg/L of iron
 - a. half
 - b. equally
 - c. almost twice
 - d. more than three times

4. _____, in all its forms and even at low concentrations, can seriously interfere with the dispersive capabilities of polymers and of other treatment chemicals
 - a. Molybdate
 - b. Azole

- c. Carbohydrazide
 - d. Iron
5. A phosphonate such as HEDP or PBTC is essential for the control of _____, iron and silt.
- a. copper
 - b. aluminum
 - c. zinc chloride
 - d. calcium carbonate
6. Zinc, having strong cathodic functionality and synergism with other inhibitors, makes a major contribution under _____ conditions.
- a. high hardness
 - b. highly scaling
 - c. highly corrosive
 - d. high alkalinity
7. HPA, because of its excellent solubility, stability, and corrosion inhibition, should be used _____.
- a. on low hardness waters only
 - b. on high hardness waters only
 - c. where bleed off rates are low
 - d. all across the treating spectrum
8. Terpolymers are highly effective for dispersing phosphate and phosphonate complexes, as well as _____.
- a. silicates
 - b. aluminum
 - c. iron, zinc and silt
 - d. azoles
9. _____ protect non-ferrous metals and also prevent metallic contamination, and should be present in most formulations.
- a. Terpolymers
 - b. Phosphonates
 - c. Azoles
 - d. Polyacrylates
10. All formulas should contain PBTC, HPA, and a _____ as a result of the above described effectiveness, and because of their extensive individual synergism
- a. copolymer
 - b. terpolymer
 - c. polymaleic anhydride
 - d. polyacrylate