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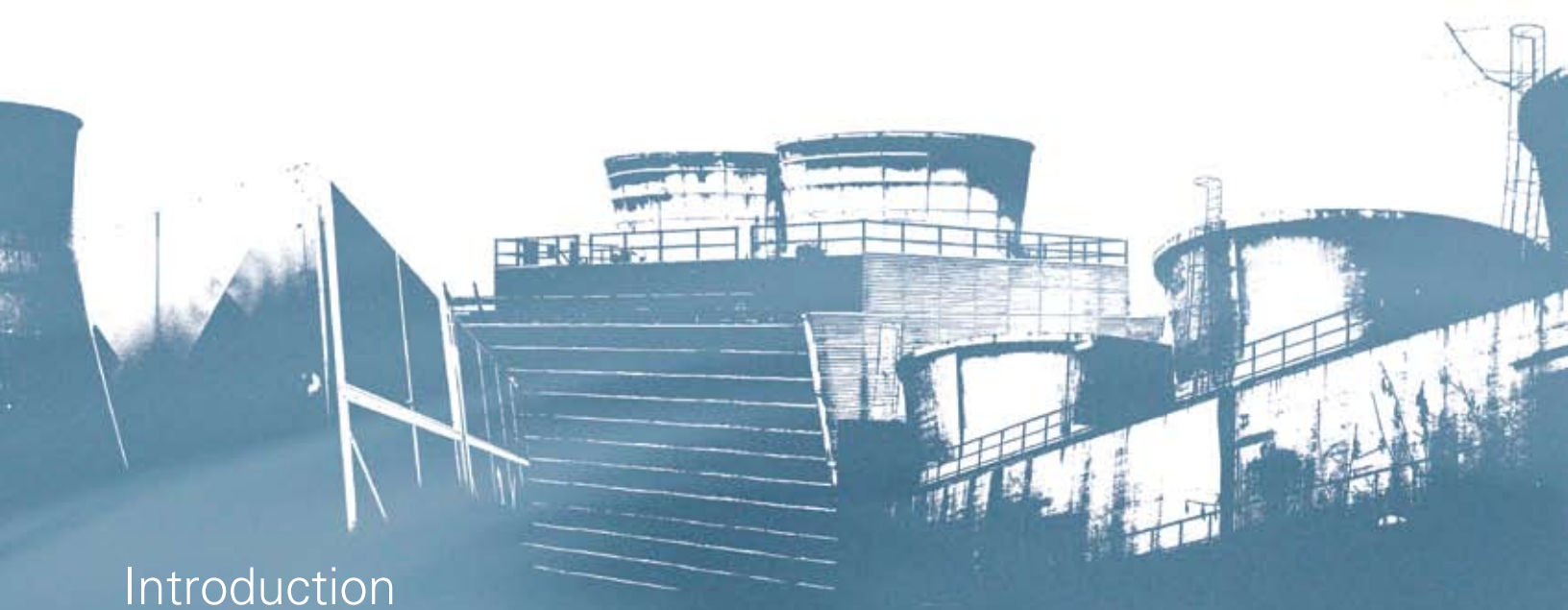
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Developing Cooling Water Treatments - Part I

Robert R. Cavano, Scranton Associates, Inc.



Introduction

Following is the first in a series of articles to help an industrious reader design, produce, and apply scale and corrosion control treatments over a wide range of cooling water conditions. This program is unique in that it ends up with whole number quantities of each ingredient, resulting in greater convenience, speed, and economy for the small batch manufacturer. And it is just fine for large batches too! The approach permits the final formulas to end up within acceptable limits determined by the theories we present.

Such precision in production weights provides for complete accuracy in the percentages calculated for prescribing and testing treatments!

In Part I, the first of four installments, expectations are offered in regard to scale and/or corrosion, the specific forms these afflictions can take, and the exploration of the preferred techniques and materials available for addressing them. Particular attention is given to the merits of the phosphonates, both the scale preventative type and the corrosion control versions.

Next (in what will no doubt be the eagerly awaited Part II), we consider additional corrosion inhibiting materials, as well as dispersants for contaminants and scaling agents from the raw water and in the complexes formed by the inhibitors we add. Synergism will be seen when these two types of raw materials are combined in the recommended proportions.

In the third installment (Part III), we begin intensive work on the challenges facing us, suggest strategies to meet them, and discuss the types of formulas we expect to develop. Concepts of concentration, cycling, and feeding will also be explored.

To conclude (Part IV), we ask for specific results and receive five different water conditions, plus suggested approaches to their treatment, including seven complete formulas. Detailed explanations are provided for the creation, use and modification of spreadsheets for these formulas.

These articles are based on an extensive mining of the available literature, as well as discussions with many practitioners in the field. A more detailed (and more heavily end-noted!) version (intended for internal use) was developed earlier but is mercifully condensed here for the reader's convenience.

Divergent opinions abound in this series and in most comparable efforts. In addition, some concepts, such as stabilization, are not yet as fully understood as we would like and are offered more tentatively. We solicit the readers' reactions to all of the ideas presented so that our knowledge and experience can be shared and thereby extended.

Introduction and History

Many years ago, we learned that the use of phosphates in water treatment would add gentle persuasion to our existing arsenal of the big guns of alkalinity. Solubility and reversion arose as major problems, to later be, in part, solved with stable organic phosphorus compounds. We had earlier seen that chromates could do it all, including combining synergistically with other inhibitors, as well as killing troublesome organisms.

In spite of earlier pledges of eternal fealty, our steamy dalliance with chelants cooled as we experienced negative corrosion inhibition. Phosphonates were considered for scale control but, at the beginning, only sparingly employed - to later become a staple for us. It was soon realized that newer types of phosphonate had significant and desirable corrosion reduction properties. Multi-functional copolymers became available and maintain prominence in the better products of today. [The term “copolymer” (as used here) refers to products with more than one type of functional group, be it two, three, or more.]

While there have been many advances in technology, respect must continue to be shown for the lore and legend of water treatment - for the tried and true techniques which served us so well for so long. The knowledge gained from the once dominant “phosphate programs” remains valuable and should still be recalled and revised, as needed.

Important recent accomplishments have not been in new product development alone, but more in improvements in combining, feeding and testing of established materials. As much as we now benefit from recent inventions and improved technologies, we continue to treasure and utilize the earlier discoveries.

The resulting selection and application of phosphates, phosphonates, and dispersant polymers (combined with azoles for non-ferrous metal protection) now allows us to provide an assortment of formulas for the protection of most cooling water systems; possibly supplemented with zinc at the corrosive end of the spectrum and high performance polymers at the scaling end.

Concepts of Interest

Threshold Treatment

One of our most useful resources is the concept of “threshold treatment.” It is a well established technique for inhibiting scale by introducing very small quantities

of appropriate chemicals, i.e. amounts not even remotely approaching the levels required for sequestration.

Threshold treatment allows us to provide excellent, but also affordable, results.

“Threshold” refers to the low level at which a treatment is successful, rather than to any particular mechanism for arriving at that condition. In fact, threshold mechanisms perform in vastly different ways for each of the various phosphonates and polymers.

When treatment levels extend beyond the threshold range, turbidity results, reflecting the insolubility of the complexes formed. Adhering to the generally accepted upper dosage standards for each phosphonate can usually help us to avoid this problem, and the presence of a suitable polymer can usually extend these limits.

Natural Inhibition

Fortunately, waters with a tendency to form scale also possess a degree of “natural” corrosion inhibition. Cognetti and others,¹ stressing the merits of PAPEMP for calcium carbonate dispersion under stress, indicated that:

“The strong (negative) correlation with calcium carbonate saturation indicates that the inhibition is due, at least in part, to a (thin) protective film of calcium carbonate. Good corrosion rates ... are obtained at saturations as low as 50 times calcium carbonate, while excellent corrosion rates ... are obtained above 100 times saturation.”

But “natural factors” may need to be supplemented and extended to prevent scale and corrosion, and this cannot always be done by alkalinity adjustment and calcium control.

Calcium Tolerance

“Calcium tolerance” describes the ability of a chemical to resist complexation with calcium. Such rejection is desirable since polymers and phosphonates used up in sequestration are then no longer available for dispersion. “Calcium tolerance” is also described as the opposite of “calcium binding power.”

Boffardi and Schweitzer² supplied a list (later supplemented) of calcium tolerances. Calcium tolerance was shown at 9 for polyacrylate through 17 for HEDP, 42 for AMP, 75 for HPA, 100 for PBTC, 530 for PMA, and 1640 for the SA/AA copolymer. It is likely that the value for terpolymers

is even greater but such high levels may make insignificant additional contributions to stability.

They go on to say:

“The poor calcium tolerance of the phosphonates can be suppressed by the addition of the AA/SA (AA/AMPS) copolymer. This has the effect of keeping the phosphonate totally active in solution.”

AA/SA (AA/AMPS) copolymers, terpolymers, or quadpolymers have high calcium tolerances themselves and their addition to a formula makes major improvement in the calcium tolerance of phosphonates, and also of homopolymers such as polyacrylate and polymaleate.

Dispersion

While phosphonates primarily inhibit the formation of crystals, polymers distort crystal formation, prevent its further growth, and disperse the crystals. The homopolymers are excellent dispersants for calcium carbonate, silt, and iron, and under “normal” conditions, the dosage required for them is less than that for copolymers or terpolymers. When price is factored in, this difference becomes even greater. The

phosphonates are, however, in most cases, preferred to the polymers as the basic ingredient for scale control because of their superior inhibitive properties.

There is evidence that this advantage for homopolymers on calcium carbonate does not extend to calcium phosphate or to large quantities of iron and silt. While sodium polyacrylate is an excellent dispersant for the symmetric rhombic form of calcium carbonate, the more complex asymmetric triclinic calcium phosphate crystal seems to require the introduction of a copolymer.

Calcium phosphate, calcium phosphonate, iron, and silt are dispersed better and more economically by co/ter/quadpolymers than by homopolymers.

However, we have seen that phosphonates and polymers, while quite versatile, may not be able to do all of the required tasks at the same time if dosages are low.

“...when a polymer is tied up dispersing particles, it is not available to inhibit the formation of the scale forming salts. In addition, suspended solids can act as nuclei for the formation of calcium phosphate.”³

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As another facet of the dispersive properties of polymers, is that we expect polymers to carry inhibitors to the heated surfaces to facilitate film formation. As a part of this process, some zinc and phosphate stabilization is required and this may call for additional polymer.

Polymers, in their various configurations, perform many diverse functions including inhibition, stabilization and the general dispersion of organic and inorganic entities.

Deposit Formation and Control

Factors Influencing Scale

Calcium by itself does not determine scaling potential. The use of calcium hardness as a gauge is acceptable only when alkalinity is in a narrow, moderate range and when the selected formula possesses considerable adaptability.

pH/Alkalinity curves are helpful supplements to these hardness readings and can be developed for almost any system by formulas of the type:

$$\text{pH} = B \cdot \log(M \text{ Alk}) + A$$

The Kunz and Caplan curves reflect this type of formula. Plotting two or more pH/Alkalinity points determines a line useful for the prediction of pH in concentrated cooling tower waters. One approximation (Puckorius) is:

$$\text{pH} = 1.465 \log (M \text{ Alk}) + 4.54$$

Since it is possible to thereby establish these relationships between pH and M Alkalinity, either of them combined with any measure of total hardness will allow us to estimate the Langelier Saturation Index (LSI). It was the first significant index to be developed and later refinements were provided in the Ryznar Stability Index (RSI), and in the Puckorius Scaling Index (PSI).

Detection of deficiencies in most calculations of the LSI caused us to become skeptical about its interpretation and continued acceptance. The cause of the current resurgence in popularity for the LSI is that it is seen to approximate the common logarithm of the calcite saturation, CSI. ($\text{LSI} = \log \text{CSI}$)


The Calcite Saturation Index (CSI) is increasingly utilized to establish the upper and lower limits of scaling tendencies and to describe the expected intensity between these limits. Treatment ranges are confined

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in part by the (minimum) point where the water is undersaturated, and chemical treatment for scale is, in general, not required ($CSI < 2.0$). Another point exists above which traditional treatments will not be effective ($CSI > 200$), and which may, if overlooked, lead to harmful complacency. The resulting intermediate (treatable) range then becomes the primary target for our efforts.

In what follows, we work with either the Calcite Saturation Index (CSI) or, where necessary, other, less precise indicators of prevailing scaling tendencies. If we are fortunate enough to have a complete raw water analysis, the cycled values and CSI can be determined from a WaterCycle® program. If not, whatever indications or estimates of scaling are available must be utilized.

Scale Control Phosphonates

First, we consider the water characteristics of a system to determine to what extent scaling conditions prevail and then to ascertain whether they will be receptive to treatment. Within the treatable range, we usually choose scale control phosphonates as the preferred initial additive. The most common versions, AMP, HEDP, and PBTC, in addition to inhibiting calcium carbonate scale, control iron and clay. However:

“...it has been well documented that under stressed conditions, phosphonates can react stoichiometrically with calcium ions leading to a precipitation of calcium phosphonate”⁴

The scale prevention properties of AMP and HEDP are well known, as are their shortcomings, including limited solubilities and poor resistance to oxidizers. This last problem is evidenced by reports of attack by chlorine on AMP and by bromine on HEDP, especially at high levels of oxidizer. PBTC is the most resistant of the phosphonates to this type of degradation.

Dosage of Scale Control Phosphonates

Much had been written about the phosphonates, but, until recently, almost no specific techniques had been offered for the determination of treatment levels. Dan Vanderpool⁵ now describes the concepts necessary to evaluate these materials for scale inhibition, and in so doing, quantifies effective dosages for them at varying levels of calcium, iron, and silt.

We turn to Vanderpool's approach for determining minimum phosphonate dosage. The results are summarized in following boxes. Required dosages

are listed in mg/L, with lower dosages indicating better (more economical) performance

Vanderpool^{6(b) 7(a, c-f)} suggests that:

- a) For low or no hardness, some phosphonate is still necessary for iron and silt control
- b) “... under typical cooling water conditions (say 5 cycles, 95 degrees F, pH 8, 20-50 times saturation, half life of 24 hours or less), there is little difference in the threshold performance by HEDP (0.08), AMP (0.19), and PBTC (0.23). The choice between the three depends on secondary properties of the phosphonate, in particular, halogenation, stability, and price.”
- c) If we encounter calcium carbonate alone (without iron or silt), HEDP (0.08-0.80) > AMP (0.19-1.30), > PBTC (0.23-2.32) for CSI values between 50 and 125

Too often, the impact of metals, either present in the make-up or appearing as corrosion by-products, is not adequately considered in the selection and dosage of standard phosphonates.

- d) Under most circumstances, some iron is present and the use of AMP then becomes uneconomical. For $Fe(OH)_3$ up to and including 0.3 mg/L, CSI 50, 104 °F, the order remains HEDP (0.21) > PBTC (0.31).
- e) For iron content above the 0.3 mg/L level, PBTC > HEDP. For iron $[Fe(OH)_3 > 1.0]$, CSI 50, 104 °F, PBTC (0.36) > HEDP (0.43), etc.
- f) As temperatures rise to 122 °F and above, HEDP recaptures the lead, HEDP (0.50) > PBTC (0.56). This difference is magnified as the temperature rises. We must, under these highly stressed conditions, be sure that the low solubility of HEDP and its salts is not exceeded.

The dosages listed are minimums and a cushion must be allowed, even at moderate CSI values, for degradation of the phosphonates by oxidizing biocides and other variations in water quality, temperature and alkalinity.

It has become clear that dosages of phosphonates as low as 3 mg/L active (and probably much lower), are highly effective for the described functions, and also

resist precipitation. If higher levels are introduced to prevent corrosion, more stable phosphonates (PBTC) and/or polymeric dispersants become necessary.

Sullivan and others⁸ point out, however, that:

“PBTC requires reaching a minimum ‘threshold’ concentration before activity is established. ...increasing the additive concentration to 3 ppm results in 100 % CaCO_3 threshold treatment being achieved...”

We calculated dosages for several sets of information, and in so doing, demonstrated that this process for phosphonate choice can be carried out for most types of water.

Phosphonates for Corrosion Prevention

As a result of mounting dissatisfaction with the performance of phosphates as corrosion inhibitors, the industry began to investigate products based on organic phosphorus compounds. This led to the introduction of a different type of phosphonate, hydroxyl phosphonocarboxylic acid (HPA), whose 50 % active commercial version is Belcor 575.

“The unique feature of HPA in comparison to other phosphonates is that the corrosion inhibition is not activated by the formation of a calcium complex but rather by the corrosion process itself. Further, the fact that corrosion inhibition by HPA is not solely dependent on calcium complex formation also explains why its corrosion control properties are not compromised in soft water.”⁹

“The phosphonates ‘extend’ the solubility of CaCO_3 as well as forming (stable) calcium phosphonate salts. These two processes help to inhibit corrosion by permitting operation under highly buffered conditions.”¹⁰

Resistance to reversion over time or when subjected to high temperatures are other special assets of HPA. It is degraded by oxidizing biocides, especially if fed continuously at high rates, but its stability may be improved by utilizing other feeding techniques or by the introduction of monoethanolamine or sulfamic acid.

Commercial HPA products contain some orthophosphate (<3 %), which reduces the total organic phosphorus content but, in return, contributes some anodic protection.

For these many reasons, HPA has become the most widely accepted standard for comparison of corrosion inhibitors.

We now offer some recommendations for HPA dosage when it is applied along with phosphate and/or zinc:

- 1) In high hardness water, where corrosion is low and phosphate complexes quickly become insoluble, HPA is desirable, both for its corrosion prevention properties and for its ability to enhance the solubility and performance of phosphates and other phosphonates (Less than 3 mg/L of HPA).
- 2) For moderate hardness waters, the need for corrosion protection increases and some HPA is required to supplement the phosphates and to guarantee adequate cathodic protection (3-5 mg/L of HPA).
- 3) Very soft water needs all the corrosion protection help it obtains from HPA, phosphates, and zinc (More than 5 mg/L of HPA).

HPA is able to reduce corrosion over a wide range of water conditions! We strongly believe that HPA, because of its great versatility and stability, warrants consideration for just about every cooling water application. ☺

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

1. A well established technique for inhibiting scale by introducing very small quantities of appropriate chemicals, is referred to as, _____ treatment
 - a. sequestration
 - b. threshold
 - c. dispersion
 - d. natural

2. The strong (negative) correlation with calcium carbonate saturation indicates that the inhibition is due, at least in part, to a (thin) protective film of calcium carbonate. Good corrosion rates are obtained at saturations as low as ____ times calcium carbonate.
 - a. 1
 - b. 5
 - c. 50
 - d. 100

3. AA/SA (AA/AMPS) copolymers, terpolymers, or quadpolymers have high calcium tolerances themselves and their addition to a formula makes major improvement in the calcium tolerance of _____.
 - a. molybdate
 - b. zinc
 - c. phosphonates
 - d. chelents

4. When a polymer is tied up dispersing particles, it is not available to inhibit the formation of the scale forming salts. In addition, suspended solids can act as nuclei for the formation of _____.
- corrosion
 - fungi
 - algae
 - calcium phosphate
5. For moderate hardness waters, the recommended HPA dosage (when applied with zinc and/or phosphate) is _____mg/L of HPA.
- <3
 - 3-5
 - >5
 - 6-7
6. For high hardness waters, the recommended HPA dosage (when applied with zinc and/or phosphate) is _____mg/L of HPA.
- <3
 - 3-5
 - >5
 - 6-7
7. While phosphonates primarily inhibit the formation of crystals, _____ distort crystal formation, prevent its further growth, and disperse the crystals.
- zincs
 - molybdates
 - Polymers
 - HPAs
8. For very soft waters, the recommended HPA dosage (when applied with zinc and/or phosphate) is _____mg/L of HPA.
- <3
 - 3-5
 - >5
 - 6-7
9. The homopolymers are excellent dispersants for calcium carbonate, silt, and iron, and under "normal" conditions, the dosage required for them is _____ that for copolymers or terpolymers.
- equal to
 - less than
 - more than
 - not related to

10. The fact that corrosion inhibition by HPA is not solely dependent on calcium complex formation also explains why its corrosion control properties are not compromised in ____ water.”

- a. Low pH
- b. High pH
- c. hard
- d. Soft