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Developing Cooling Water Treatments – Part IV

The Formulas

Robert R. Cavano, Scranton Associates Inc.

This article concludes our four-part series to develop high performance formulas for cooling water treatment. We have already learned about the scale and corrosion challenges we face and the tools we have to meet them. We reported earlier on underlying concepts, theories, and experiences with chemical treatments. This final installment will offer a set of specific formulas in a format that allows easy modification.

Introduction

A number of guidelines are provided here to assist in efforts to establish formulas for both scale and corrosion control. Slavish compliance to the formulas proposed is not necessary, but a careful evaluation is certainly expected.

Are there other ways to develop formulas? Of course far more than can be counted! One very productive approach has been developed by Rob Ferguson of French Creek Software, Inc.¹ In the programs, ion association models are developed to measure the driving force for calcium carbonate, calcium sulfate, calcium phosphate, and silica. They are used to predict the inhibitor dosage required “to delay precipitation or growth until after the water has passed through the system.”

Clearly, this introduces various influences on scaling such as the temperature, pH, flow rate, induction time, etc of the circulating water. Sequentially, and

even concurrently, models are developed for optimizing inhibitor levels. The limited solubilities of inhibitor complexes are shown and ranges of dosage are presented.

“The ... software ... checks to assure that sufficient polymer is present to control ... calcium phosphate scale potential created by the program. ... In all cases, the models ... balance corrosion inhibitor levels and performance with scale control agent dosage. ...Models... assure that sufficient scale control agents are present to control any fouling potential created by the treatment.”

II - Guidelines

We now turn to the approach we developed over many years and presented for your consideration in these four installments.

For the best results in choosing a treatment, it is necessary to know many things about a system and particularly the Calcite Saturation Index (CSI) and the iron and silt content. If such information is not available, we must estimate (in whatever terms or indices you choose) the extent of contamination and the vitality of the corrosive or scaling tendencies.

Where high calcium/alkalinity levels are present, and increased amounts of sulfate and chlorides are found, an “organic” program is often preferred.

This phosphonate/polymer type of product reduces the tendency for calcium carbonate to precipitate and allows a lower concentration of the dispersant polymer to be used. The following observations and warnings are, however, offered:

“The combination of orthophosphate and HPA can effectively control corrosion at relatively low concentrations. Using a blend of 10 mg/L of HPA, 5 mg/L of orthophosphate and sufficient polymer (5-10 mg/L), corrosion and fouling can be controlled in moderately hard water with a pH of 7.5.”²

“At a pH of 7.5 across the range of water hardness of 50 to 700 mg/L as calcium carbonate, a combination of 5 mg/L of HPA and 2 mg/L of zinc blended with an appropriate dispersant effectively inhibits corrosion. The same basic corrosion combination and 5-10 mg/L of a polymeric stabilizer inhibits corrosion when applied to severely scaling waters at a pH of 9.”²

“All organic programs (phosphonate/polymer) were ineffective in soft waters and in applications

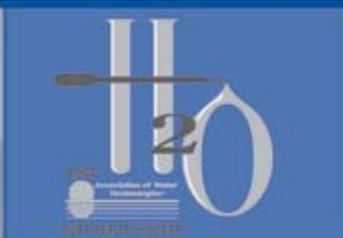
with high hardness/alkalinity (700 mg/L of calcium/500 mg/L of alkalinity as CaCO₃ or greater).”²

Scaling Categories to Be Considered

CSI readings are precise indicators for describing raw or treated waters. Calcium hardness, LSI, RSI, and PSI values may not always correspond to the CSI and are most suitable as very general indications of scaling tendencies.

Very Soft Water, No Scaling, High Corrosion, CSI < 2.0, 8 Cycles

In this category, special attention must be given to protection against corrosion, a difficult challenge if there are low levels of calcium. A scale preventive phosphonate is not usually needed here for calcium carbonate control, but PBTC is still appropriate because of its ability to control iron at low dosages, in addition to providing a reserve of scale inhibition properties. HPA is present, as in all formulas, as a

			
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very effective cathodic inhibitor, which also enhances other sources of scale and corrosion protection.

In corrosive water (low calcium, some chlorides and sulfates), a phosphate program is generally required, preferably one including cathodic inhibition. The addition of poly- or pyrophosphate will serve to enhance whatever protection is already being supplied by calcium.

Formula 801 – This formula is prescribed where there is not a lot of phosphate in the water supply. Zinc and HPA provide cathodic protection, phosphoric acid provides anodic protection.

Formula 802 – Similar to 801, except that phosphate as part of a municipal water supply provides more orthophosphate than is needed. Poly- or pyrophosphate is added to supply cathodic inhibition, which ultimately becomes additional anodic functionality.

Formula 803 – If zinc is not permitted, then an increase in poly- or pyrophosphate and HPA sup-

plies the needed cathodic protection, and polyphosphate degradation provides anodic protection.

Soft Water, Light Scaling, Some Corrosion, CSI 2-19, 6 Cycles

Progressing to less corrosive waters, we most likely will adopt a lower phosphate technology vigorously utilizing calcium and other sources of cathodic inhibition.

Considering waters with less than 20 times calcite saturation, Vanderpool³ indicated that calcium carbonate itself was not the major challenge, but rather the iron and silt that could precipitate onto calcium carbonate and other surfaces. Satisfactory treatment of these non-homogeneous particles requires smaller amounts of inhibitor once the tube and tower surfaces have been conditioned.

If an aqueous system has a CSI < 20, it is often desirable to include a metal such as zinc. The usual approach to application is 0.5 to 2.0 mg/L of cathodic zinc and an added inorganic phosphate at

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or near the ratio for PO_4/Zn of between 1/1 and 3/1 with HPA for further cathodic protection.

Formula 814 – Zinc may, at times, still be a valuable part of treatment in this range to supplement phosphates, phosphonates and polymers.

Moderate Scaling, Slightly Hard Water, CSI 20-84, 5 Cycles

Low phosphate programs also function well in moderately soft water applications if there is adequate alkalinity present. Some anodic protection results from the reversion of the poly- or pyrophosphates.

Corrosion inhibitor content can usually be reduced as hardness increases and increased cationic protection is received from its calcium. In the moderate intermediate hardness range of CSI = 50 and above, dosage levels for scale control should be kept at or above the amounts calculated in the Vanderpool approach. We counsel phosphonate dosages considerably above the levels calculated for low CSI values.

PBTC has been chosen because of its great stability in harder waters (e.g. $\text{RSI} < 4.5$). There are a number of dosage and cost considerations, but we know that PBTC can be used very well over a complete hardness range. Similarly, some maleate functionality may be needed at this time to reinforce the acrylic input.

Formula 825 – Zinc is omitted because of its limited solubility, since its cathodic protection is no longer needed, and because HPA and poly- pyrophosphates can perform more conveniently and economically in this range.

Heavy Scaling, Moderately Hard Water, CSI 85-149, 4 Cycles

Corrosion inhibitors can be further reduced and scale inhibitors increased as hardness increases. At hardness over 400 mg/L, inorganic phosphates should no longer be used. HPA provides cathodic protection, as does the large amount of calcium present.

For hard waters (CSI > 100), the solubility limitations on AMP and HEDP must be considered, particularly the latter. PBTC has both the best overall solubility and the greatest stability of the scale control phosphonates under these conditions

As cycles increase, the holding time increases (and possibly the dosage) leading to possible phosphonate break down, calcium phosphate/phosphonate scale, and reduced concentrations of scale inhibitor present in the system. In these cases, the feed of less phosphonate and more polymer is indicated, though the additional polymer would not be chosen solely for its phosphorus control properties.

Inorganic phosphates can no longer be used at or above these CSI values.

Formula 836 – Scaling becomes a greater challenge with corrosion a lesser concern.

Very Heavy Scaling, Hard Water, CSI 150-199, 3 Cycles

One definition of “stress” in water is the existence of high levels of hardness, alkalinity, or solids (those of greatest concern being calcium, iron, phosphate or silica). These adverse conditions result when there is poor quality

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make-up water, corrosion products are measurably high, or greater cycles of concentration are being pursued.

Attempts to deal with scale formation under stressed circumstances have moved in the direction of using more sophisticated phosphonates or even to abandoning phosphonate technology completely in favor of polymers. The high dosages specified for some phosphonates under these circumstances may cause us to ask whether we are still adhering to the threshold philosophy.

“AMP and HEDP do not perform effectively in preventing CaCO₃ scaling under the water chemistries evaluated (LSI 2.76 to 2.89 and 180x to 223x calcite saturation, respectively). PBTC exhibits better inhibitor activity than AMP and HEDP, especially in moderately stressed conditions (i.e.180x calcite saturation).”⁴

“It has been found that under high stressed water chemistries ... neither phosphonates nor any type of traditional polymeric inhibitors

completely prevents the precipitation of CaCO₃. It has also been observed that blends of terpolymer (K-798) with PBTC exhibit synergistic influence on the precipitation of CaCO₃.”⁵

“Under the harsh and stressful conditions, dispersants and crystal modifiers such as polymers/ copolymers become more critical for a successful treatment program than threshold inhibitors such as the phosphonate. Stability and compatibility of these antiscalants become important considerations for the product formulation. Concerns about ... calcium tolerance ... rule out the use of the traditional workhorses such as polyacrylates and polymethacrylates. Concerns about hydrolysis, calcium tolerance and stability against oxidizing biocides rule out the use of some phosphonates.”⁶

Versaflex ONE (VF-1) is described as a good dispersant for stressed waters, especially when combined with PBTC and possibly a terpolymer.

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Formula 847 – Consider maleates and sophisticated polymers as supplements or to partially replace the more standard ingredients.

Explanation of Process

Production formulas for treatments generally show weight percentages for commercial version of each ingredient. If this product is added to the system at the rate of 100 milligrams per liter (mg/L), it is thereby introduced into the system as parts per million (mg/L) corresponding to the percentage it constitutes in the formula.

If we are to properly determine system concentrations, adjustments must be made to convert to a fully active specification from the weaker strength commercial materials being used. Establishing these values is difficult since the differing modes of product specification - either 100% active or as “product” - are not always clearly stated.

Cycles of concentration (COC) must also be factored into these determinations. COC are usually determined from the ratio of make up water to blow down or from comparison of chlorides or molybdate in the system water to that in the feed water. While this reflects well the loss through evaporation, drift, leakage and blow down, it does not adequately represent the reactions such as complex formation, precipitation, and plating out.

Mass balance is the most accurate way of fully controlling the level of dosage to be applied. As part of the process, the concentration in the recirculating water can be calculated from the actual product usage and blow down or water loss. Chemical dosage should be validated by chemical testing and confirmed by these balances.

There is expected to be some reduction in active components as they react with the materials in the system and impurities in the water. If chemical testing shows that there is excessive residual after this loss, product dosage should be lowered and results observed to confirm that desired levels are being maintained.

Where molybdate is used as a monitoring method, its loss to the system is generally minimal. When used as a tracer, it would commonly call for a lower

product usage rate than needed because the other active components deteriorate more readily.

Many operators elect to feed one pint of treatment for each 1000 or 2000 gallons of make-up water. Again, the conversion is straightforward, but time consuming. The calculation of PO₄ content is also routine but troublesome. Knowledge of the quantities of organic phosphorus and complex phosphates and of their degree of activity, and phosphate content are often necessary for determining test levels.

If a suggested formula is not acceptable for any reason, further steps must be taken. When it is necessary to increase the amount of active treatment in a system, and the basic formula is felt to be well balanced, a larger dosage is suggested. Otherwise, a new formula should be chosen or developed.

Formulas are not so precisely and conclusively established as to prevent specifying a range of chemical levels in the system rather than providing an exact figure. We therefore feel comfortable in choosing whole number values for both production batches and for laboratory evaluations.

With this in mind, we choose even number quantities of pounds for each material in a 55 gallon batch. It is clear that production scales are most accurate at full pound values. These figures are then divided by two to obtain whole numbers (in grams) for the assembly of laboratory batches.

The Spreadsheets

We propose the use of spreadsheet technology to facilitate future changes in these formulas without sacrificing any of the original basic relationships. After any such change, the product must be laboratory tested for stability and the specific gravity determined. The spreadsheet then automatically shows values for:

1. Percentage of each commercial product in a formula
2. Parts per million of 100% active (for each chemical) material in the system
3. Parts per million of phosphate (as PO₄) in the system.

Shown in Table 1 is a model spreadsheet for Formula 814 and attached instructions for creating similar ones for the seven formulas listed. Detailed spreadsheets for all of the formulas can be obtained from the author at Scranton Associates Inc.

The formulas listed in Table 1 constitute our initial recommendations. Please note that while we designate particular commercial versions of raw materials, substitution of equivalent products should also yield good results. There are an infinite number of combinations of these ten ingredients possible and the reader may make selections which differ from those made by the author. In any event, the process itself and references cited are of primary importance and should help you to make your final decision.

Spreadsheet Construction

Instructions

1. Open Excel or another spreadsheet program
 2. Under “File,” select “page set up” and
 - a. From “sheet,” choose “gridlines” and “columns and headings”
 - b. From “page,” choose “portrait”
1. Enter information as shown on the model
 2. Under “Format,” choose “cell” and then “border” to create boxes, etc.

Procedures

1. Enter data into boxes with solid outlines
2. $D12 = (100 * C12) / (\$C\$25)$ and then drag
3. $D11 = 100 - \text{SUM}(D12:D20)$
4. $D21 = \text{SUM}(D11:D20)$
5. $C24 = C23 * 8.33$ (8.33#/gal for water)
6. $C25 = C24 * 55$ (55 Gallon Drum); or $(C24 * 55) - 1$ if C25 shows odd
7. $F11 = 0$
8. $F12 = C12 * E12 * 272.8 * \$H\$5 / \$G\$42$ reflects one pint per 2000 gal
9. $H14 = F14 * 0.561$; $H15 = F15 * 0.728$; $H16 = F16 * 0.351$; $H17 = F17 * 0.610$
10. $H27 = \text{SUM}(H11:H20)$
11. $F28 = 1.5 * (H27 + F13)$
12. $G42 = 2000$ unless changed

Table 1: Seven Formulas (Pounds of each ingredient in a 55 Gallon Drum)

Ingredients	801	802	803	814	825	836	847
Soft Water	338	348	374	337	382	376	356
50% Caustic Soda Solution	120	120	60	120	60	60	60
50% Zinc Chloride Solution	8	6	0	8	0	0	0
Tetrapotassium Pyrophosphate	0	2	4	0	2	0	0
75% Phosphoric Acid	4	0	0	4	0	0	0
50% PBTC Solution	4	4	4	6	6	12	10
Belcor® 575 (HPA)	12	12	16	10	10	10	12
Versaflex ONE	0	0	0	0	0	0	20
44% TTA Solution	6	6	6	8	8	12	16
Carbospense™ K-798	26	22	24	26	26	16	18

Cycles of Concentration	8	8	8	6	5	4	3
Net Wt. in 55 Gal Drum	518	520	488	519	494	486	492

Derivation of 0.1364 and 272.8 Factors for Conversion to mg/L active in system (“P” = treatment pounds per gallon)

1. $C_{12}/P^{*}55$ = Fraction of formula attributed to C_{12}
2. $C_{12}^{*}P/P^{*}55^{*}8$ = Converted from gallons to pints
3. $C_{12}/55^{*}8$ = Since “P” values cancel out
4. $C_{12}/55^{*}8^{*}2000^{*}8.33$ = Converted from pounds to 2000 gallons
5. $C_{12}^{*}10^6/55^{*}8^{*}2000^{*}8.33 = 0.1364^{*}C_{12}$ = Converted to mg/L.
6. $C_{12}^{*}10^6/55^{*}8^{*}8.33/\$G\$42 = \text{mg/L conversion for varying gallons treated.}$
7. Then $F_{12} = C_{12}^{*}E_{12}^{*}272.8^{*}\$H\$5/\$G\$42$.

Applications

1. Once the program is set up, we need only vary the pounds in Column C, the COC, and possibly the polymer multiplier used in F20. If the changes are substantial, a new specific gravity must be determined.
2. Column H of the spreadsheet calculates PO_4 content for use in determining terpolymer requirements and for possible use in testing. 

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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. Scranton Associates Inc. has moved to a new facility at 17647 Foltz Industrial Parkway, Strongsville, OH 44149. Mr. Cavano can be reached at his new phone number at (440) 572-2277.

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

1. "The combination of _____ and HPA can effectively control corrosion at relatively low concentrations.
 - a. zinc.
 - b. orthophosphate
 - c. bromine
 - d. molybdate.

2. "All organic programs (phosphonate/polymer) are ineffective in applications with hardness/alkalinity in excess of _____ as CaCO₃.
 - a. 400 mg/L of calcium/200 mg/L of alkalinity
 - b. 500 mg/L of calcium/300 mg/L of alkalinity
 - c. 600 mg/L of calcium/400 mg/L of alkalinity
 - d. 700 mg/L of calcium/500 mg/L of alkalinity

3. In very soft water conditions, (CSI < 2.0), special attention must be given to protection against _____.
 - a. bacteria
 - b. biofilms
 - c. corrosion
 - d. scaling

4. In corrosive water (low calcium, some chlorides and sulfates), a phosphate program is generally required, preferably one including _____ inhibition
 - a. bacterial
 - b. calcium
 - c. anodic
 - d. cathodic

5. In soft water, light scaling some corrosion conditions, (CSI 2-19), , we most likely will adopt a lower phosphate technology vigorously utilizing _____ and other sources of cathodic inhibition.
 - a. oxidizing biocides
 - b. non-oxidizing biocides
 - c. iron
 - d. calcium

6. In Moderate Scaling, Slightly Hard Water, CSI 20-84, 5 Cycles, low phosphate programs also function well if there is adequate _____ present.
 - a. molybdate
 - b. magnesium
 - c. alkalinity
 - d. chlorides

7. In Heavy Scaling, Moderately Hard Water, CSI 85-149, 4 Cycles, scale inhibitors should increase as hardness increases, and the corrosion inhibitor content can _____.
 - a. stay the same
 - b. be increased as well.
 - c. be eliminated
 - d. be reduced

8. In Very Heavy Scaling, Hard Water, CSI 150-199, 3 Cycles, consider incorporating _____ and sophisticated polymers as supplements, or to partially replace the more standard ingredients.
 - a. AMP
 - b. HEDP
 - c. maleates
 - d. phosphoric acid

9. Where molybdate is used as a monitoring method, its loss to the system _____.
 - a. is dependent on hardness levels
 - b. increases as pH increases
 - c. is generally minimal
 - d. is considerable

10. When high hardness and alkalinity levels are present and increased amounts of sulphate and chlorides are found, _____ program is often preferred

- a. a zinc phosphate
- b. an all organic
- c. a molybdate.
- d. a phosphate only