

This document is based on observations made on April 4, 2005 at CORROSION 2005. For a more detailed version, contact www.nace.org for a reprint of Paper No. 05063.

INHIBITOR CHOICE & DOSAGE **(For Scale Control in Cooling Towers)**

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I. Introduction

Our challenge today is to develop chemical formulas that will control scale in cooling tower waters at the lowest total cost. Sadly and reluctantly, we learned of, and are obliged to expose, those purveyors of phosphonates and polymers who eagerly carry us over the threshold into orgies of short-lived, excessive-treatment bliss. Such high levels have negative consequences that extend far beyond the obvious economic ones and add to our mounting aversion to reckless additions

A. Scale control chemicals introduced (often at high levels) to solve one problem are often seen to create new problems due to:

1. The limitations of threshold mechanisms;
2. The low solubility of certain complexes.

B. High concentrations of scale inhibitors (and of corrosion inhibitors!) may cause corrosion to mild steel and copper alloys.

II. How Can We Develop Treatments?

First, we attempt to establish a treatment range where we can satisfactorily control calcium carbonate precipitation. It will be bounded by a point where the water is under-saturated and treatment is, in general, not required, and another point beyond which traditional treatments may not be effective (and indeed may be harmful). In this paper, we focus on phosphonates and polymers (often in combination) to help us achieve our objectives within that range.

Phosphonates inhibit scale formation by being adsorbed onto active crystal sites, where they arrest growth. To some extent, phosphonates have the ability to disperse iron and silt, but there are also definite and unforgiving upper limits to these mechanisms.

Polymers distort whatever crystals are formed and prevent their aggregation by including relatively large, irregular forms into the scale lattice. The homopolymers act effectively as dispersants for suspended solids, but have little ability to control complexes formed with phosphorus from the water supply or introduced by chemical additions.

III. Methods To Determine Dosage

Establishing optimal dosage levels is of great importance to us for reasons of both performance and economy. LSI, RSI, and PSI values have regularly been used to estimate the dosages for scale inhibitors, but the vagaries of these measures (as described in our *Saturation, Stability, and Scaling Indices [SSSI]*) must be fully understood and compensated for.

If a proper treatment is applied at a proper rate, scaling constituents will be dispersed at concentrations considerably higher than those attainable without treatment -- at “threshold” dosages, far below the stoichiometric requirements for chelation.

Without treatment, scale will occur to varying degrees below a RSI/PSI of 6.0 or above an LSI of 0.0. Our task is to relate treatment dosage to the severity of the scale formation we have predicted for a desired or mandated level of cycling

A number of different approaches to this challenge have been offered. We borrow heavily from the work of Paul Puckorius, Dan Vanderpool, and Rob Ferguson, and will attempt to bring part of their valuable contributions together in this one place.

IV. Do Treatment Chemicals Have and Impact On The Indices?

It is essential that we know how the various chemicals already present in a cooling water system will influence the validity of indices determined for that water.

“All (of those) indices are effective for untreated waters or waters treated with ‘solubilizing’ scale inhibitors ... (They) can only be used accurately with treatments (phosphonates and acrylates) that solubilize calcium carbonate.”

If the treatment programs use zinc or molybdate, and no phosphate is present, the predominant scaling species remains calcium carbonate. The “solubilizing” additives (AMP, HEDP, and PAA), in contrast, are especially effective on these salts and also in reducing the indices.

With a phosphate based program, none of the indices can be used because calcium phosphate is the controlling scaling species, rather than calcium carbonate. Even if the phosphate derives only from the degradation of phosphonates, the index is inaccurate to the extent of that phosphate present.

When scale inhibitors of the “crystal modification” type are in use, the indices no longer give accurate information about scaling tendencies. These products usually impact the scaling indices by shifting them back to a “stable” water value for the indices (~0.0 or ~6.0).

V. More About “Solubilizing” Inhibitors

When a phosphonate and/or polyacrylate are used, an indicator value which is scale forming without treatment can be tolerated without scaling. A shift in the permissible PSI occurs from 6.0 to a value of 4.6 with 2 ppm HEDP or 4.0 with 1.8 ppm of PBTC, and, at those dosages, does not allow scale to form. When 3 ppm of HEDP is carried in the circulating water, a PSI of about 4.1 -- normally a severe scaling level -- results in no scaling.

The phosphonates are limited in how much scale inhibition they can provide before the precipitation of their complexes when the RSI/PSI value goes below 3.9. There often is a clear requirement for dispersants such as sulfonated styrenes (SSMA), AMPS copolymers (such as AA/SA), or other polymeric crystal modifiers.

VI. What Are “Crystal Modifying” Inhibitors?

Inhibitors known as “crystal modifiers” engender sludge or soft scale. They preclude the productive use of indices because they modify the calcium carbonate scale crystals to a non-adherent form, one that will not stick to heat transfer surfaces -- but rather fall out and be removed from the water. When an index value is calculated for these programs, it is close to neutral (RSI/PSI = 5.8-6.0), and consequently of no use in measuring scaling intensity.

These inhibitors are described in the literature as sulfonated polystyrenes and polymaleics. The use of 3-5 ppm active of either can prevent scale very effectively even at pH levels of 8.5-9.5 and stability index levels of 3.5-4.0. It is believed that the newer copolymers are also a part of this class, though dosage levels for them have not yet been published.

Some treatment programs utilize mixed systems, “solubilizing inhibitors” along with “crystal modifiers”. This means that the system is in a solubilizing mode before it exceeds the capabilities of solubilizing inhibitors and passes into a precipitating mode.

VII. Suggestions From Puckorius

Most of the work on the two types of scale inhibitor described above was done by Puckorius and his associates. At an early date, they supplied specific dosages of HEDP, PBTC, and PAA to optimize scale prevention over a range of indices. Since these relationships do not adhere to any known mathematical relationships, they must be used with caution and continue to be modified on the basis of experience. Note that the levels indicated are for 100% active chemical in the system, not in the make-up for all three of these approaches. Calculation of the feed rate should then be done with adequate consideration of the cycles of concentration. No scaling is expected at the following levels:

Table VII
Dosage for Calcium Carbonate Scale Prevention

Scaling	LSI	RSI/PSI	HEDP	PBTC	PAA
			(100% Active Basis)		
None	0.0	> 5.8	0.0	0.0	0.0
Slight	0.2	5.6 - 5.7	0.2	0.1	0.5
Moderate	0.5	5.3 - 5.5	0.5	0.3	1.0
Strong	1.0	4.7 - 5.2	1.0	0.5	2.2
Very Strong	1.5	4.3 - 4.6	2.0	1.2	4.0
Severe	2.0	4.1 - 4.2	3.0	1.8	x
Very Severe	2.5	3.9 - 4.0	x	2.4	x
Highly Stressed	> 2.7	< 3.9	x	x	x
Activity of Commercial Product			60	50	50
% PO ₄ in Commercial Product			55.3	17.6	x

Polyacrylates show a lower level of effectiveness than the phosphonates for calcium carbonate control. Furthermore, higher levels of polyacrylate can create an increase in scale, this time, some of it as calcium polyacrylate. Polyacrylic Acid (PAA) will hold calcium carbonate in solution or dispersion to a PSI of 4.6 at dosages of 4 ppm, but will not be effective at lower PSI values.

We should note that a dosage of active HEDP very much above 3 ppm allows formation of calcium phosphonate. This establishes 4.1 as the lowest PSI we can effectively treat with HEDP. When the scaling indicator is so low that HEDP can not do the job satisfactorily, or temperatures are above 140° F and alkalinities also high, replacement of HEDP with PBTC is recommended.

We see that PBTC is effective at about one half the dosage of HEDP. HEDP is 18.1% P, and PBTC is 5.7% P so the replacement of AMP by PBTC on an equal weight basis reduces P content to one-third of what it was ($5.7/18.1 = 0.32$). This responds well to most regulations on phosphate disposal. The replacement increases the actives price by a factor of 1.53 [$(92)(60)/(72)(50) = 1.53$], but is still more economical because of the reduced cost of \$0.77 for active PBTC replacing \$1.00 worth of active HEDP [$(1.53)/(2) = 0.77$].

If water conditions are too severe for PAA, HEDP, and PBTC, and consequentially their salts are prone to precipitation, crystal modifiers such as copolymers and terpolymers may be needed.

VIII. Developments From Vanderpool

Late in the twentieth century, many contributions to establishing guidelines for chemical usage were made. A number of reports described the quantitative determinations of phosphonate dosage for calcium carbonate inhibition. These efforts have been considerably extended by Dan Vanderpool. He says:

“The phenomenon of threshold inhibition of calcium carbonate and the discovery of stable threshold inhibitors in the 1970s has led to major innovations in water treatment. ... Yet after more than 30 years, attempts to understand the mechanism of threshold inhibition have failed to yield a quantitative theory that explains inhibitor dose requirement.”

Vanderpool, as a result, proposed a method for estimating the minimum effective concentrations of phosphonates. He combines theoretical concepts of nucleation with informed observations about crystal growth inhibition and surface chemistry.

The derived levels appear to be lower than most prevailing recommendations. Some cushion, however, should, in all cases, be allowed (especially at lower hardness) for the degradation of the phosphonates and for expected variations in temperature, and alkalinity. We provide the results of one set of calculations:

Table VIII
Minimum Phosphonate Dosage (100% Active Basis – mg/L)
(CSI 50, 40°C or 104°F, 1 mg/L Fe(OH)₃, 1mg/L Silt)

	AMP	HEDP	PBTC
DEACTIVATE NUCLEI – Calcium Carbonate	0.191	0.077	0.228
COVER SURFACE – Iron and Silt	0.723	0.498	0.085
MAINTAIN COVERAGE – Dispersed Matter	0.059	0.041	0.054
SUM OF THE ABOVE	0.973	0.616	0.367

Part of the reason for the higher dosage for AMP is its poor performance in the presence of iron.

IX. Contributions from Rob Ferguson

Programs developed by Ferguson provide treatment evaluation, and warn of conditions which may cause failure. Inhibitor addition is determined from a combination of water analysis reports, chemical profiles supplied by raw material suppliers, and laboratory and field test inputs. The “What If?” scenarios in WaterCycle® allow one to evaluate the scale potential of a cooling water over the temperature range expected and the pH ranges that may be encountered. No process for determining synergism among materials is provided in this computer model and its predicted intervention must be aggregated from field trials.

Ferguson believes that the parameters most critical to dosage are: “induction time”, temperature, and the degree of supersaturation. Threshold effect inhibitors do not prevent scale formation, but merely delay the inevitable by extending the time before growth begins. Because of cycling, the dosage for a once through system with a short residence time may be the same as that for a recirculating system with a longer residence time.

There are many ways to get to a CSI of 50 or interpret it, but, as a starting point, we take examples from the three writers to compare their recommendations in a very rough way:

Table IX
Minimum Phosphonate Concentrations (100% Active – mg/L)
(CSI ~ 50)

	HEDP	PBTC
Puckorius	0.5-1.0	0.3-0.5
Vanderpool	0.6	0.4
Ferguson	1.0	0.2-0.3

After examining these methods for determining and applying scaling indicators, it is easy to recognize the complexities we expect to encounter. While we see some general agreement in the three approaches, we will not attempt here to evaluate or reconcile the differing results.

One interesting aspect of Ferguson’s approach to scale abatement is that corrosion control dosages can also be determined. Corrosion inhibition and scale control models can then be integrated to arrive at a recommended formulation. The first step is to simulate the cycled water characteristics including the selection of an appropriate pH/alkalinity relationship. At each subsequent step (handling scale, preventing corrosion, solubilizing proposed additions, etc.), the simulation is repeated until a complete formula is established.

X. Concerns Beyond Calcium Carbonate

The relatively low calcium tolerance of phosphonates and polyacrylates causes them, at times, to complex with hardness salts before they can fulfill their dispersing functions. AA/AMPS copolymers, however, make a major improvement in the calcium tolerance of phosphonates, and even of homopolymers. Furthermore, the addition of a copolymer to a phosphonate does not adversely affect its dispersion of iron, manganese, and silt. These two materials are currently successfully combined in many proprietary products.

When greater quantities of metal are present, terpolymers are better able to disperse and transport them and prevent interference with scale and corrosion inhibition. In a process of treating for calcium carbonate, iron, and silt, we sometimes end up with insoluble complexes, which we have created and for which we expect to be held accountable.

A major concern relates to the phosphates found in agricultural run off, municipal water supplies, phosphonates introduced for scale prevention, and phosphorus compounds added for corrosion control. Happily, we have learned that certain AMPS-based copolymers can effectively prevent the precipitation of the resulting calcium phosphonate and phosphate salts.