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## OPTIMIZING TREATMENT COST PERFORMANCE

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### ABSTRACT

Optimizing the cost performance of treatments in cooling systems requires the use of models that calculate the minimum effective dosage of scale and/or corrosion inhibitors and blends. This paper describes the theory, development, and applications of performance models to optimizing and comparing treatments in open recirculating cooling systems. The impact of blending inhibitors on dosage is described. Treatment and model limitations are also discussed.

### INTRODUCTION

The control and prediction of scale formation in cooling water systems is increasingly of economic significance, and is of special interest as chemists push the envelope of operation and control through water reuse, the utilization of less than desirable waters for makeup (including high TDS sources, high silica waters, and those with high levels of barium and strontium), and through concentrating the recirculating water to the mechanical limits of an open recirculating cooling system. Thermodynamic indices have been used traditionally to predict scale in these and other industrial water systems where mineral scale formation can be a costly problem. Dosage models for minimizing treatment dosages are derived from these thermodynamic indices. An understanding of the basis for the driving forces used for developing scale inhibitor dosage optimization models is essential for understanding their use in the dosage requirement kinetic models and in developing as universal a model as possible. Dosage models can only be as accurate and reproducible as the thermodynamic driving force indices used to develop them. Thermodynamics and kinetics answer several critical questions concerning projected water related problems and their solution:

WILL SCALE FORM? Thermodynamics only based indices tell only one part of the scale formation and control story. Indices such as ion association model free ion saturation ratios (degree of supersaturation)<sup>1,2,3,4,5</sup> and less rigorous methods such as the simple indices (Langelier Saturation Index<sup>6</sup>, Ryznar Stability Index<sup>7</sup>, Practical Scaling Index<sup>8</sup>, and other indices based upon total analytical values) indicate whether or not scale is likely to form. And the seasoned professional can interpret them to reach a usually reliable prediction of whether or not scale will form, how bad a problem it will cause, and whether or not inhibitors can control it.

HOW MUCH WILL DEPOSIT? Other thermodynamic derived indicators, such as free ion momentary excess<sup>9</sup> describe the instantaneous precipitation (or dissolution) required to bring a water to equilibrium. They are frequently used to estimate the quantity of scale that might form, as are their less rigorous counterparts such as the CCPP (calcium carbonate precipitation potential)<sup>10</sup> used in municipal water treatment.

WHEN WILL IT HAPPEN? WILL IT HAPPEN IN MY LIFETIME? Kinetic models add the element of time. Thermodynamic models tell you what will happen if a water is allowed to rest unperturbed for an infinite period of time. Kinetic models portray what will happen within the time constraints of your particular system, be it a twenty four (24) hour half life cooling tower, a six (6) second residence time utility once through condenser cooling system, or a three (3) week turnover fire water system in a nuclear power plant. Kinetic models add the parameters of induction time and growth rate. When inhibitors are added to the equation, their impact on induction time is critical to practical dosage calculation.<sup>11,12,13,14</sup>

A thorough evaluation would include all of these factors:

- the Thermodynamic Driving Force,
- the Quantity of Scale Forming,
- the Time before scale will form,
- the rate it will precipitate and form on surfaces,
- the inhibitor level required to safely get the water through the system, and
- the limit beyond which scale inhibitors will not be able to prevent scale at any dosage.

This paper summarizes the impact of both thermodynamic and kinetic considerations upon scale formation and control in cooling systems, and other industrial water processes. Where available, calculation methods are described. The relevance of the kinetic considerations is also emphasized where appropriate.

A similar approach is discussed for optimizing corrosion inhibitor dosages, including those where inhibitor solubility is the limiting factor for dosage.

#### **THERMODYNAMIC: DRIVING FORCE INDICES**

Thermodynamics tells us what to expect if a water sits unperturbed for an infinite period of time. In the case of predicting mineral scale formation, thermodynamic indices indicate whether or not a scale forming specie will tend to precipitate and whether or not the scale former will cause growth on existing deposits. All of the indices in use today, including the simplest and the most sophisticated, are derived from the basic relationship which defines the solubility product. For calcium carbonate this equates to:

Equation 1 
$$\{Ca\}\{CO_3\} = K_{sp}$$

where {Ca} is the calcium activity in the water at the current conditions  
{CO<sub>3</sub>} the carbonate activity at current conditions

$K_{sp}$  is the solubility product at the current conditions of temperature, ionic strength, and pressure.

The "free" ion activities for  $\{Ca\}$  and  $\{CO_3\}$  are used in ion association models to improve accuracy and account for phenomena such as common ion effects.<sup>1,2,3,4,9,14</sup> The activity of the individual ions can be estimated using simple techniques such as the Debye-Huckel equation or extensions of it, or using more rigorous, but less generalized, methods such as those derived by Pitzer<sup>1,2,11,15</sup> and others.

A simple arrangement of Equation 1 relates "what we have" to "what we can ultimately have":

$$\text{Equation 2} \quad \text{Saturation Ratio} = \frac{\{Ca\}\{CO_3\}}{K_{sp}} \quad \begin{array}{l} \text{what we have} \\ \text{what will be at } t = \infty \end{array}$$

Equation 2 can be generalized to cover any commonly encountered scales:

$$\text{Equation 3} \quad \text{Saturation Ratio} = \frac{\{IAP\}}{K_{sp}} \quad \begin{array}{l} \text{what we have} \\ \text{what will be at } t = \infty \end{array}$$

where  $\{IAP\}$  is the ion activity product for the scale to be evaluated  
 $K_{sp}$  is the solubility product for the scale forming species  
 under the conditions being evaluated.

Table 1 summarizes the Saturation Ratio relationship for common (and some not so common) mineral scales that might be expected in cooling water and other industrial aqueous systems.

Some water treatment chemists and engineers express the Saturation Ratio in the base ten logarithm form, and call it a Saturation Index:

$$\text{Equation 4} \quad \text{Saturation Index} = \log_{10}(\text{Saturation Ratio})$$

Simple indices, such as the Langelier Saturation Index, Ryznar Stability Index, and Practical Scaling Index are expressed in this manner. In fact, it can be shown that the Langelier Saturation Index is the base ten log of calcite saturation ratio calculated with some simplifications and assumptions:

Langelier Saturation Index Assumptions:

- 1) Total analytical values for Ca and  $CO_3$  are used rather than free ion concentrations
- 2)  $CO_3$  is estimated from "M" alkalinity with the assumption that all titrated alkalinity is in the  $HCO_3$  form. Although Langelier recommends correcting "M" alkalinity for non-carbonic acid system alkalinity, most users ignore the noncarbonate alkalinity correction when calculating the index. Example non-carbonate contributions include phosphates, silicates, borates, sulfides and cyanides.

3) A simplified activity coefficient is calculated using the basic Debye-Hueckel correlation.

As a result, the usefulness of the Langelier Saturation Index, and similar simple indices, is limited to neutral pH waters of low ionic strength, such as many potable waters.

Simple indices such as the Langelier Saturation Index should not be confused with more rigorous indices that express their results as the base ten logarithm. More sophisticated evaluations will also sometimes express the driving force as the base ten log.<sup>11,14</sup>

### **Interpreting Saturation Ratios and Indices**

Table 2 provides simple guidelines for interpreting indices derived from the solubility product relationship.

### **Ion Association Reduces Available Ion Concentration**

Simple indices assume that all ions are free. This can lead to an overstatement of scale potential by the use of higher than available values for the reactants (e.g. Analytical Values of Ca and CO<sub>3</sub> rather than free ion concentrations). Ions in solution are not all present as the free species. For example, calcium in water is not all present as free Ca.<sup>+2</sup> Barium and strontium in a water are also not present totally as free ions. Anions such as sulfate also become associated with other ions and are present as "bound" rather than "free" ions. Other species form which are not available as driving forces for scale formation. Examples include the soluble calcium sulfate species, hydroxide species, and bicarbonate - carbonates. Table 3 outlines example species that can be present in a typical water.

Speciation of a water is time prohibitive without the use of a computer for the iterative number crunching required. The process is iterative and involves:

1. Checking the water for electroneutrality via a cation-anion balance, and balancing with an appropriate ion (e.g sodium or potassium for cation deficient waters, sulfate, chloride, or nitrate for anion deficient waters).
2. Estimating ionic strength, calculating and correcting activity coefficients and dissociation constants for temperature, correcting alkalinity for non-carbonate alkalinity.
3. Iteratively calculating the distribution of species in the water from dissociation constants (a partial listing is outlined in Table 3).
4. Checking the water for balance and adjusting ion concentrations to agree with analytical values.
5. Repeating the process until corrections are insignificant.
6. Calculating saturation ratios based upon the free concentrations of ions estimated using the ion association model (ion pairing).

The use of ion pairing to estimate the free concentrations of reactants overcomes several of the major shortcomings of traditional indices. Indices such as the LSI correct activity coefficients for ionic strength based upon the total dissolved solids. They do not account for "common ion" effects.<sup>(1,6)</sup> Common ion effects increase the apparent solubility of a compound by reducing the concentration of reactants available. A common example is sulfate reducing the available

calcium in a water and increasing the apparent solubility of calcium carbonate. The use of indices which do not account for ion pairing can be misleading when comparing waters where the TDS is composed of ions which pair with the reactants versus ions which have less interaction with them. The indices will also not be transportable between waters of varying quality. For example, a high sulfate water will have lower free calcium concentrations than a water with the same ionic strength but derived from chloride. Both waters will have the same ionic strength. Both will have the same "simple" index.

The "No Ion Pairing Correction" lines in Figure 1 depict the Langelier Index based upon total analytical values. Note that the calculated index, and therefore predicted scale potential, are almost identical for the high sulfate and high chloride cases. The ion pairing lines plot the base ten log of saturation ratio when corrected for ion pairing, and using free ion concentrations.

Ion association model saturation ratios are used routinely in oil field, reverse osmosis, and mining applications for the prediction of barium and strontium based scales. This would be expected because barium and strontium derived scales are typically encountered in high TDS brackish water and brines.

#### **THERMODYNAMIC: QUANTITY OF SCALE PREDICTION**

Momentary Excess has been used to indicate the quantity of scale that might precipitate. This index describes the quantity of scalant which would have to precipitate (or dissolve) instantaneously to bring a water to equilibrium.

Precipitation to equilibrium assumes that one (1) mole of calcium will precipitate for every mole of carbonate that precipitates. On this basis, we can estimate a quantity X, the precipitation required to restore a water to equilibrium, as follows:

Equation 5 
$$[\text{Ca} - \text{X}][\text{CO}_3 - \text{X}] = K_{sp}$$

X is a quantitative indicator of precipitation reserve for a water. X will be a small value when either calcium is high and carbonate low, or when carbonate is high and calcium low. It will increase to a maximum when equal parts of calcium and carbonate are present. As a result, this index (Precipitation to Equilibrium) will provide vastly different values for waters with the same saturation ratio. Momentary Excess can also be used to estimate the maximum precipitation expected for other scale forming species.

In the case of sulfate, momentary excess is calculated by solving for "X" in the relationship:

Equation 6 
$$[\text{Ca} - \text{X}][\text{SO}_4 - \text{X}] = K_{sp}$$

The solution becomes more complex for tricalcium phosphate:

Equation 7 
$$[\text{Ca} - 3\text{X}]^3 [\text{PO}_4 - 2\text{X}]^2 = K_{sp}$$

The index provides a quantitative indicator of scale potential and has been used to correlate scale formation in a kinetic model.<sup>12</sup> The index does not account for two critical factors. The pH will change in some cases as precipitate forms by the precipitation of alkalinity contributors such as carbonate or phosphate. Secondly, the index does not account for changes in driving force as the reactant levels decrease due to precipitation. A rigorous model would decrease the reactants by a minute amount, and recalculate the driving force after each minute precipitation, until equilibrium was reached.

Momentary Excess does not represent a quantitative assessment of the amount of a fouling which will precipitate. It is an indicator of the capacity of a water to scale, and can be compared to the buffer capacity of a water. The calculation method is covered in more detail in the literature.<sup>10,12</sup>

Estimates of actual precipitation involve an iterative process., primarily due to the change in pH that occurs as some scales, including  $\text{CaCO}_3$ ,  $\text{Mg(OH)}_2$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , precipitate.

### **A POWER INDEX**

Saturation Ratio provides a measure of the driving force for scale formation. It is a potential for scale formation analogous to voltage in electrical calculations. Momentary Excess provides a measure of how much scale might be moved by the Saturation Ratio driving force, much like amperage being a measure of the number of electrons being moved by the voltage driving force.

The author is investigating the use of a Scale Power Index to normalize some of the confusing aspects of scale index calculations. For example, higher order scale such as tricalcium phosphates can have very high Saturation ratios (> 100,000) but very low Momentary Excess (<0.01 mg/L).

The Power Index is calculated from two other indices as outlined in Equation 8.

Equation 8: 
$$\text{PI} = \text{Saturation Ratio} \times \text{Momentary Excess}$$

This factor is seen in many kinetic models for crystalization and growth on existing substrates and has been found useful in developing models for some scale inhibitors.

### **KINETICS: INDUCTION TIME**

Thermodynamics tells you if a scale is likely to form. Thermo can also indicate how much scale is likely to form through indicators such as "free ion" momentary excess, which describes the instantaneous precipitation (or dissolution) required to bring a water to equilibrium. Kinetics can tell you when the scale is likely to form, and the rate at which it will form. As outlined in this section, the thermodynamic and kinetic models are intimately related.

Saturation ratio calculations, and even simple indices, indicate whether or not scale is likely to form, or dissolve, if left undisturbed for an infinite period of time. Residence times in cooling systems are significantly less than infinity. The thermodynamics based indices, such as ion

association model saturation ratios, tell you whether or not scale is likely to form. Kinetics tell you when it is likely to form, and if it will form before the water passes through the cooling system and is safely discharged. A criticism of thermodynamic based indices is that they only tell you what will happen at time equals infinity. This section discusses induction time, its relationship to thermodynamic based saturation ratios, and the relevance of thermodynamic indices under actual cooling water chemistry, temperature, and residence times.

**Induction Time:** When reactants are mixed, a solution is heated, cooled, undergoes a pressure change or is otherwise perturbed, the impact of the environmental changes is not immediate. A finite time passes before the perturbation affects any susceptible reaction. In the case of scale formation, induction time can be defined as the time before a measurable phase change (precipitation or growth) occurs after perturbation. In a pure system, with only the reactants present such as calcium and carbonate, or barium and sulfate, scale formation might proceed as follows:

- 1) Aqueous calcium carbonate molecules congregate, and form larger and larger clusters.
- 2) The clusters grow to a critical size and overcome the "activation energy" needed for the change from the "aqueous" to "solid" phase to occur.
- 3) The phase change is then observed. In the case of  $\text{CaCO}_3$ , pH drops as the salt changes phase, and the induction time can be defined.
- 4) Crystals will then grow.

Induction time has been studied extensively for industrial processes. In the case of sucrose crystallization, the objective is to minimize induction time and maximize crystallization. In the case of scale control, the objective is to extend the induction time until a water has safely passed through the cooling system, or other process adversely affected by scale. The induction time, in the absence of scale inhibitors, has been modeled for common scales, including barite ( $\text{BaSO}_4$ ) and calcite ( $\text{CaCO}_3$ ).<sup>11</sup> Figures 2 and 3 are derived from this, and related works, by Mason Tomson, his staff and graduate students at Rice University.

Figure 2 profiles the untreated induction time for calcite in the practical operational range for calcite of 0 to 140x saturation. This range was chosen because it is the effective range for most scale inhibitors. The 140x saturation ratio limit is a commonly accepted upper limit for operation with common inhibitors such as phosphonates and polymers.<sup>14,16</sup> Figure 3 profiles the saturation ratio range for barite, 0 to 80x saturation.<sup>14,17</sup>

It should be noted that the induction times for both calcite and barite are several orders of magnitude below the typical residence time in an open recirculating cooling tower system. As a result, the use of the thermodynamic saturation ratios for predicting scale is accurate and an acceptable practice in typical cooling tower operating ranges.



Calculation of driving force requires a complete water analysis, and the temperature at which the driving force should be calculated. Figure 4 depicts the impact of saturation ratio increases on the dosage required at constant temperature and residence time at less than the critical saturation ratio. This profile represents the dosage required to prevent growth on an existing substrate.

Figure 5 depicts the impact of saturation ratio increases on the dosage required at constant temperature and residence time when the critical saturation ratio is achieved and spontaneous nucleation and crystal growth occurs. This profile represents the dosage required to prevent growth in a typical cooling system.

Figure 6 depicts the impact of dosage increases upon induction time at constant calcite saturation ratio and temperature.

**Temperature** Temperature affects the rate constant for the induction time relationship. As in any kinetic formula, the temperature has a great impact upon the collision frequency of the reactants. A common concept in basic chemistry is that reaction rates increase with temperature. The rule-of-thumb frequently referenced is that rates approximately double for every ten degrees centigrade increase in temperature. The temperature constant  $k$  in equation 9 and similar models was found to correlate well with the Arrhenius relationship, as outlined in formula 10.

Equation 10:

$$K = A e^{-Ea/RT}$$

**Where:**

$k$  is a temperature dependent constant;

$Ea$  is activation energy;

$R$  is the Gas Constant;

$T$  is absolute temperature.

This temperature effect is independent of the effect of temperature upon saturation ratio calculations. Figure 7 depicts the impact of temperature on dosage requirements, all other parameters being constant.

**pH** pH affects the saturation ratio calculations, but it also may affect the dissociation state and stereochemistry of the inhibitors<sup>11,15,23</sup>. Inhibitor effectiveness can be a function of pH due to its impact upon the charge and shape of an inhibitor molecule. This effect may not always be significant in the pH range of interest (e.g. 6.5 to 9.5 for cooling water).

**Active sites:** It is easier to keep a clean system clean than it is to keep a dirty system from getting dirtier. This rule of thumb may well be related to the number of active sites for growth in

a system. When active sites are available, scale forming species can skip the crystal formation stage and proceed directly to crystal growth.

Other factors can impact dosage such as suspended solids in the water. Suspended solids can act as sources of active sites, and can reduce the effective inhibitor concentration in a water by adsorption of the inhibitor.

It can be seen that the models follow what would be expected based upon common sense and experience. Dosage increases with increasing supersaturation. Induction time increases as dosage increases.

Models of this type have been developed for common scales and most commercial inhibitors. Application of the models to operating systems allows for the optimization of treatment levels and cost performance.

Table 5 summarizes some of the models available in the literature and from proprietary data bases.

## **SYNERGY AND INHIBITOR BLENDS**

Although many water treatment chemists and field personnel promote their products on the basis of "synergy," most blends of inhibitors are not quite as effective as either inhibitor alone. Inhibitor performance models demonstrate that inhibitors compete with each other for "active sites." Data for blends correlates to models used for competitive inhibition.

Inhibitors may have a particular operating range where they are most effective. A blend of the common scale control agents ATMP and HEDP demonstrates this effect. In this case, a blend of complementary inhibitors might seem to be synergistic. In actuality, the dosage for one of the inhibitors in a blend will have an optimum dosage lower than the dosage requirement for the blend. For example:

- a) HEDP (1-hydroxy ethylidene-1,1-diphosphonic acid) is typically most cost effective at lower temperatures and lower saturation ratios.
- b) ATMP(aminotris(methylenephosphonic acid)) is typically most cost effective at higher temperatures and higher saturation ratios.
- c) An HEDP/ATMP blend provides a smoothing effect over a broad application range of saturation ratio and temperature.

Table 6 summarizes dosage requirements for each phosphonate, and for a one-to-one blend, versus scale stress. Figure 7 presents the same data graphically.

HEDP dosages are lower at lower temperatures and saturation ratios. ATMP dosages gain

an advantage under conditions of increasing temperature and saturation ratio stress.

## **APPLICATION NICHES**

Inhibitors and their blends have specific application niches where they tend to be used.

As seen in Table 6 and Figure 8, application niches for the phosphonates compared can be identified based upon performance and mg/L dosage as follows:

HEDP tends to provide the lowest dosages at lower saturation ratios and lower temperatures.

ATMP tends to control scale at lower dosages at intermediate saturation ratios and temperatures. Of the three (3) phosphonates compared, PBTC (2-phosphonobutane-1,2,4-tricarboxylic acid) tends to provide the lowest dosage and highest upper limit at high saturation ratios.

Cost performance may vary based upon the actual cost per pound of the inhibitors (or blends).

For purposes of this paper three treatment niches will be defined:

### **The "Comfort Zone"**

The "Comfort Zone" is defined as a region where achieving scale and corrosion control is a relatively stress free operation. Calcium carbonate scale potential is well below the accepted limits for common phosphonates (Calcite x saturation 30 to 80, versus a limit of 135 to 140 x saturation).<sup>14,16</sup> Temperatures are below 120 °F. HEDP tends to be used with polymers and copolymers in the "comfort zone." Other treatments may be used due to treatment program constraints such as all polymer treatments where phosphate discharge is restrictive.

### **The "Stressed CaCO<sub>3</sub> Zone"**

The "Stressed CaCO<sub>3</sub> Zone" is defined as a region where achieving scale and corrosion control is difficult and requires excellent control. Calcium carbonate scale potential is approaching or above the accepted limits for common phosphonates (Calcite x saturation 120 to 200 versus a standard treatment limit of 135 to 140 x saturation). Stressed inhibitors such as PBTC and blends of PBTC with PMA (polymaleic anhydride) are required. Blends of HEDP and PMA are sometimes used. Skin temperatures are typically above 120 °F.

### **The "Stressed Phosphate Zone"**

The "Stressed Phosphate Zone" is defined as a region where corrosion control is achieved by super-saturating the water with a solubility limited inhibitor such as orthophosphate, pyrophosphate, or zinc (in which case a purist would define the niche as a "Stressed Zinc Zone"). Calcium carbonate scale potential is typically controlled well below the accepted limits for common phosphonates. The solubility limited corrosion inhibitor is fed at a rate to assure the maximum presence of inhibitor without creating an inhibitor-based fouling problem.<sup>18, 19, 20</sup>

Typical saturation ratio and solubility based control ranges for the inhibitors are outlined in Table 7. Maximum solubilities shown are calculated using a computerized ion association model as follows. The limiting factor for an ion's solubility is determined (e.g.  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Zn}_3(\text{PO}_4)_2$ ). The concentrations of other species for this ion are back calculated from the limiting factor. The maximum solubility is calculated as the sum as all bound forms of the ion under study, plus the free ion concentration. Analytically, the maximum soluble zinc equates to the maximum filtered zinc in a water having a difference between the measured "total" (unfiltered) and "soluble" (filtered) values. The impact of zinc, orthophosphate, and pyrophosphate on each other's solubility is iteratively determined in the actual simulation model used. Figure 9 profiles the maximum solubility of a four to one (4:1) blend of orthophosphate and zinc, which parallels the maximum recommended dosage, beyond which fouling would be expected from precipitating inhibitor.

### KINETICS: RATE

Studies on operational surface condensers in the 1980's demonstrated that calcium carbonate build-up on condenser tubes could be modeled as a function of thermodynamic driving forces such as saturation ratios and momentary excess, when combined with the elements of temperature and time.<sup>21, 22, 23</sup>

At saturation ratios below the critical point, growth on an existing scale was found to correlate with a model in the format:

Equation 11                       $\text{deposit buildup} = \text{crystal growth} = K [\text{driving force}]^N t$

where                      **deposit buildup** is the measured increase in deposit.  
**K** is a temperature dependent rate constant correlating well with the Arrhenius relationship.  
**driving force** is momentary excess at lower saturation ratios and saturation ratio at higher saturation ratios. The "power" index combination of saturation ratio and momentary excess has also been used successfully.  
**t** is time.

### PUTTING IT ALL TOGETHER: COST PERFORMANCE

Several values are required to calculate and compare cost performance:

- 1) raw material/product cost.
- 2) models to calculate optimum dosage.
- 3) target operating concentration ratio and related values required for blowdown-leak-drift loss calculations.

Cost performance in its simplest form is based upon cost per million pounds of blowdown, or simply:

$$\text{Equation 12: } \text{cost/mm pounds blowdown} = \text{treatment dosage(ppm)} * \text{treatment cost/pound}$$

Comparisons based upon cost per million pounds of blowdown are valid only when comparing treatment costs at the same target concentration ratio. When comparing treatments under different operating conditions, the total treatment costs must be compared at the target concentration ratio for the treatment. For example, a treatment based upon the combination of PBTC and PMA (upper limit 225 x Calcite saturation) might operate at a target concentration ratio higher than a treatment based upon HEDP (upper limit 140 x Calcite saturation).

In the past five years, raw material costs for scale and corrosion inhibitors have increased rapidly and disparately,<sup>25</sup> necessitating a frequent review of treatment cost performance, and even reformulation.

## **SUMMARY**

Simple Indices and rigorous Ion Association Model Saturation Ratios have been used to predict scale and estimate its severity in cooling water systems. A criticism of their use is that they are thermodynamic based and represent what will be expected at  $t = \infty$ , and as result, that indices might not be representative of what will happen in a finite residence time cooling system or other aqueous industrial process. Induction time modeling validates the application of thermodynamic based indices to systems such as open recirculating cooling towers where the induction time for scale formation (or growth) from an untreated water is significantly shorter than the residence time of water in the system. The addition of inhibitor impact upon induction time provides a kinetic basis for scale inhibitor dosage models.

The same concept of induction time modeling can be used to determine inhibitor dosage required to extend the induction time for a given scale forming specie until a water has passed through the system. Models have been developed and used successfully using this method for over thirty years in cooling water systems ranging from low residence time utility once through condenser cooling systems, to long holding time index cooling towers.

It can be seen from the models developed that there is an intimate relationship between thermodynamic "indices" and kinetic aspects of the scale formation process and its inhibition.

The same thermodynamic solubility models can be used to calculate the maximum dosage for "solubility limited" corrosion inhibitors such as orthophosphate, polyphosphate, and zinc. Dosages are based upon maximum soluble inhibitor concentrations, and the concept that treatment levels above the maximum inhibitor solubility will not improve corrosion control and may result in the feed of another deposit control agent to prevent the solubility limited inhibitor from becoming a foulant.

Cost performance comparisons provide a useful tool for minimizing treatment costs and dosage. Computerized models allow optimization of formulations for target waters and operating ranges. This approach also provides a means for formulating replacement treatment programs for a given

water should raw material shortages or rapidly rising costs force a change in treatment approach. This treatment limits and optimum dosage approach also provides a product management tool for improving the consistency of treatment programs recommended and run by different field personnel.

Computer modeling provides a useful tool for predicting scale formation, estimating the water chemistry impact on scale formation and corrosion, and optimizing inhibitor dosages and overall treatment costs. Like all computer modeling tools, the results should be used as a tool for the water treatment professional, and not as a substitute for experience and judgment.

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<sup>19</sup>Ferguson, R.J., Optimizing Inhibitor Blends Using Computer Modeling, CORROSION/2007, Paper No. 07061, Houston, TX: NACE INTERNATIONAL, 2007.

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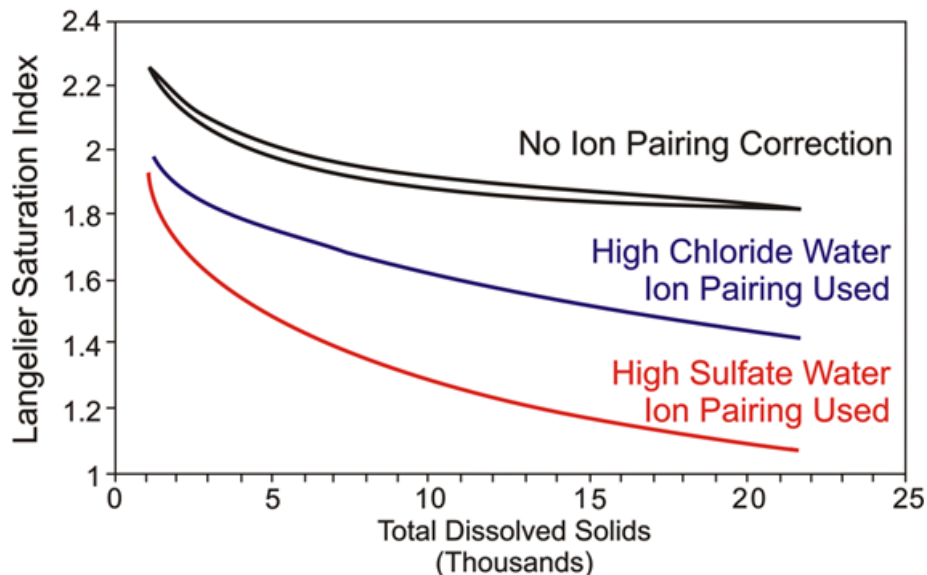
<sup>22</sup>Ferguson, R.J., Codina, O., Rule, W., Baebel, R., Real Time Control Of Scale Inhibitor Feed Rate, International Water Conference, 49th Annual Meeting, Pittsburgh, PA, IWC-88-57.

<sup>23</sup>Tomson, M.B., Kan, A.T., Fu, G., and M. Al-Thubaiti, NORM Scale Formation, Control, and Relation to Gas Hydrate Control, 10<sup>th</sup> International Petroleum Environmental Conference, Houston, TX, 2003.

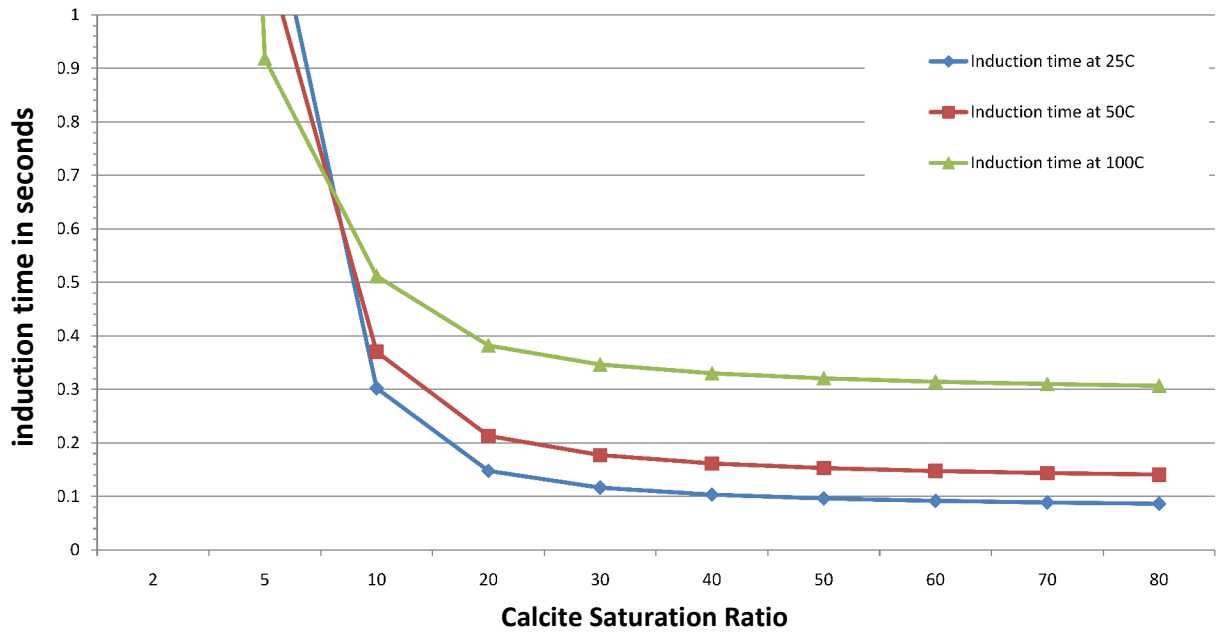
<sup>24</sup>Ferguson, R.J. and M.J. Smas, "Practical Application of Condenser Performance Monitoring to Water Treatment Decision Making," paper no. IWC-81-25 (Pittsburgh, PA: International Water Conference, 42nd Annual Meeting, 1981).

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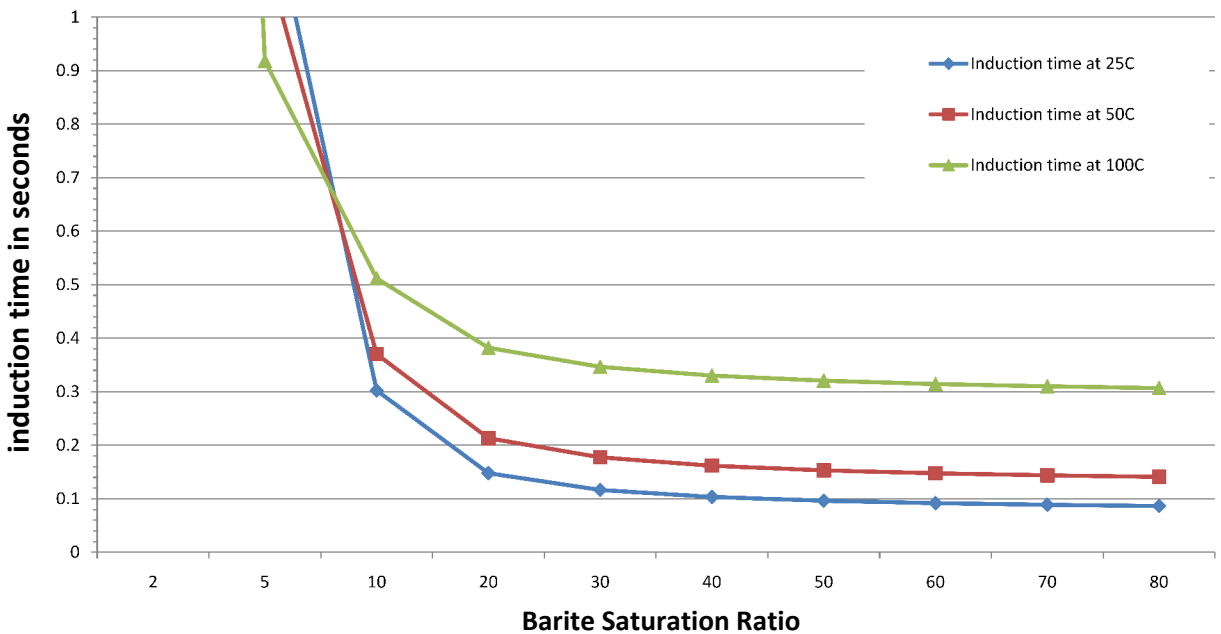
**Figure 1: ION PAIRING IMPROVES INDEX ACCURACY  
(Sulfate Effect Greater Than Chloride)**



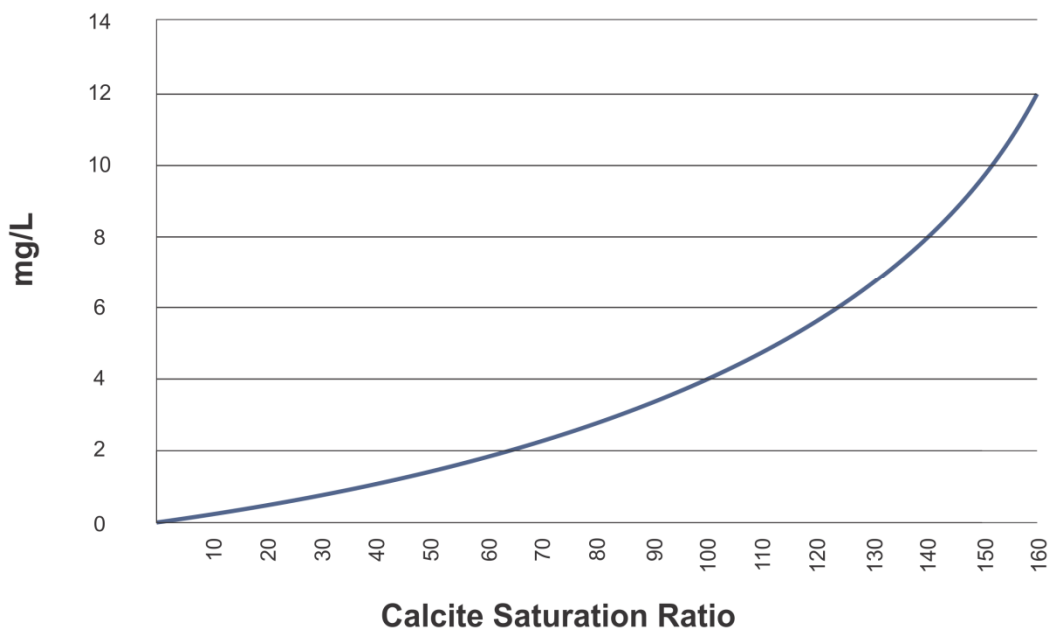
**Figure 2: Untreated Induction Time versus Calcite Saturation Ratio**



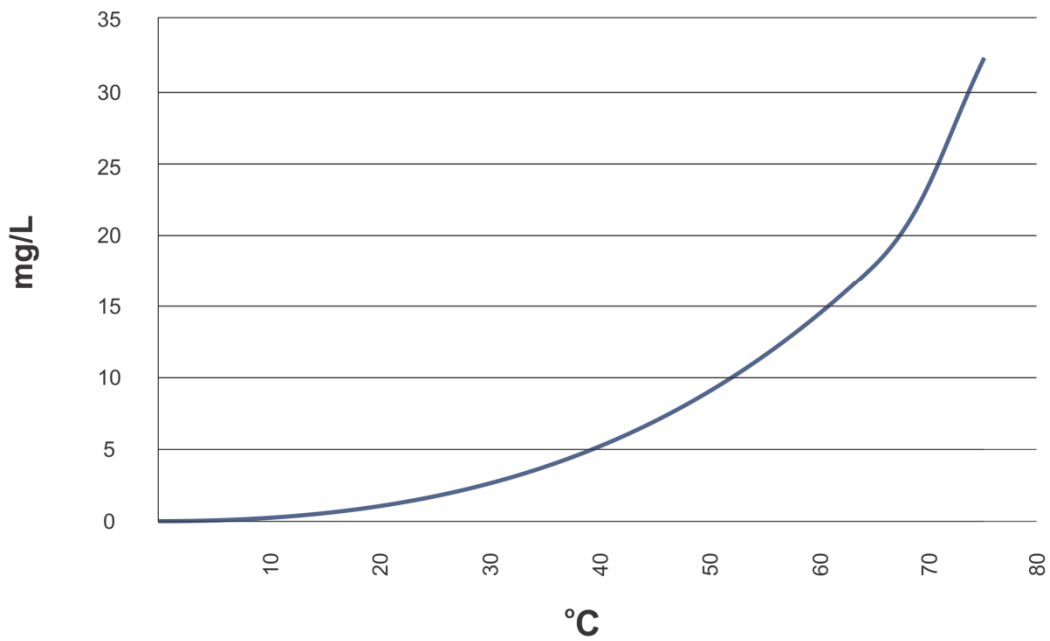
**Figure 3: Untreated Induction Time versus Barite Saturation Ratio**



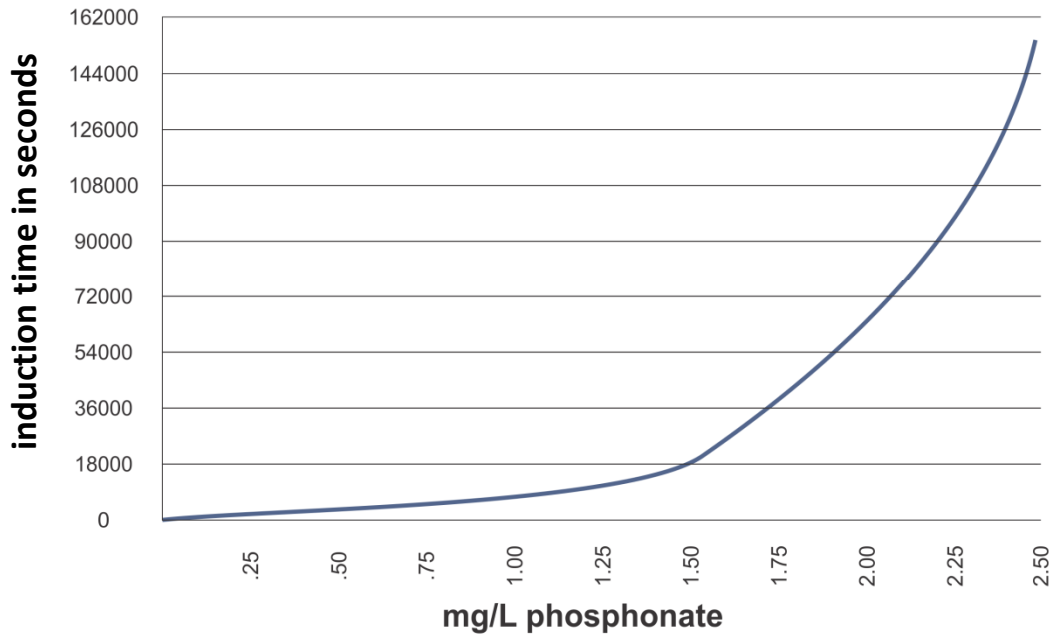
**Figure 4: Phosphonate Dosage versus Calcite Saturation Ratio**  
*(at constant temperature and induction time)*



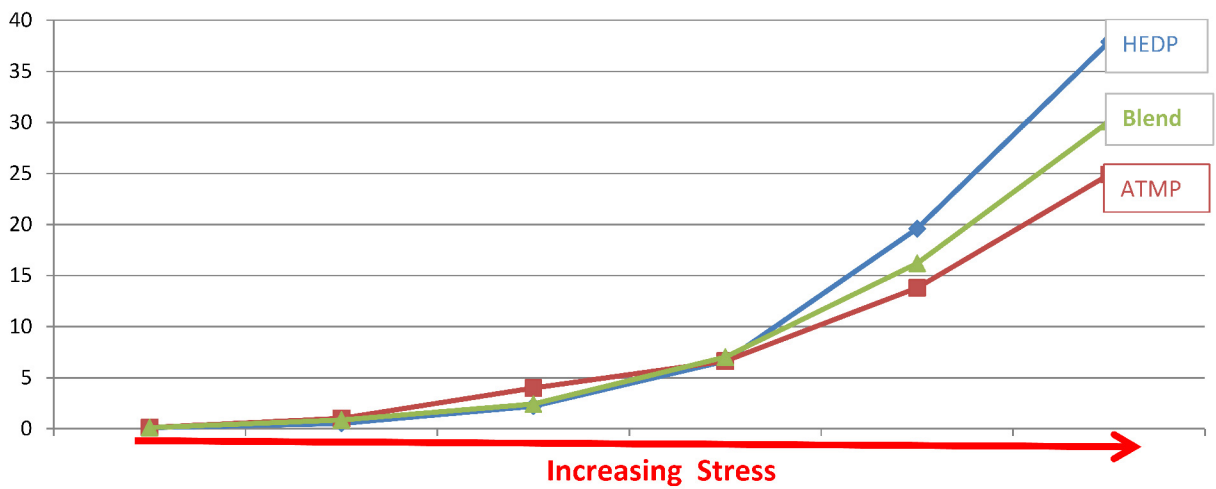
**Figure 5: Phosphonate Dosage versus Temperature**  
*(at constant calcite saturation ratio and induction time)*



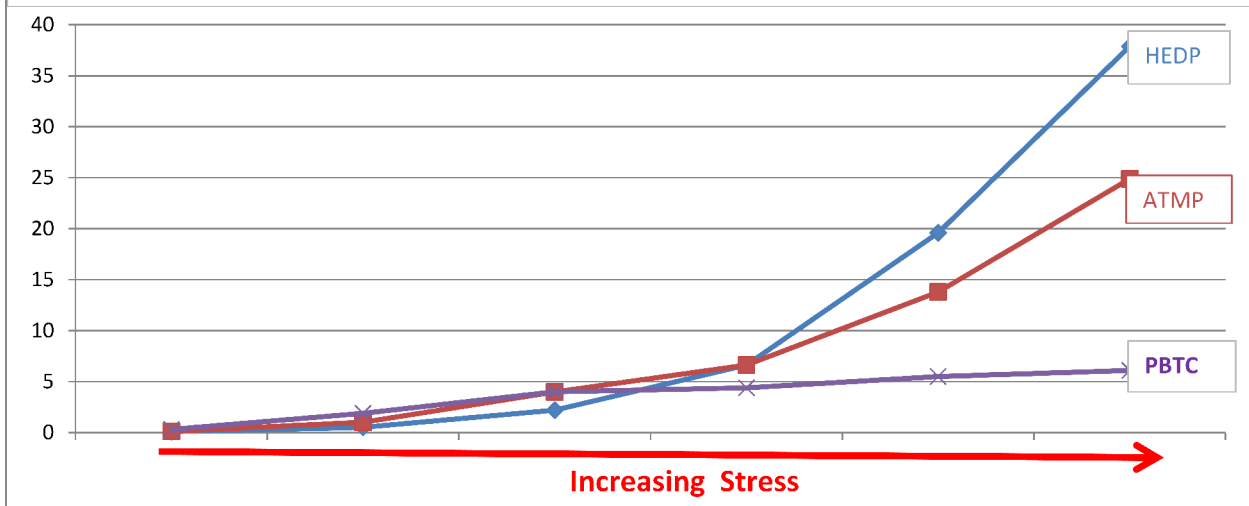
**Figure 6: Induction Time versus Phosphonate Dosage**  
*(at constant temperature and calcite saturation ratio)*



**Figure 7: Minimum Effective Dosages Comparison**  
**Individual Inhibitor Dosages versus Blend**

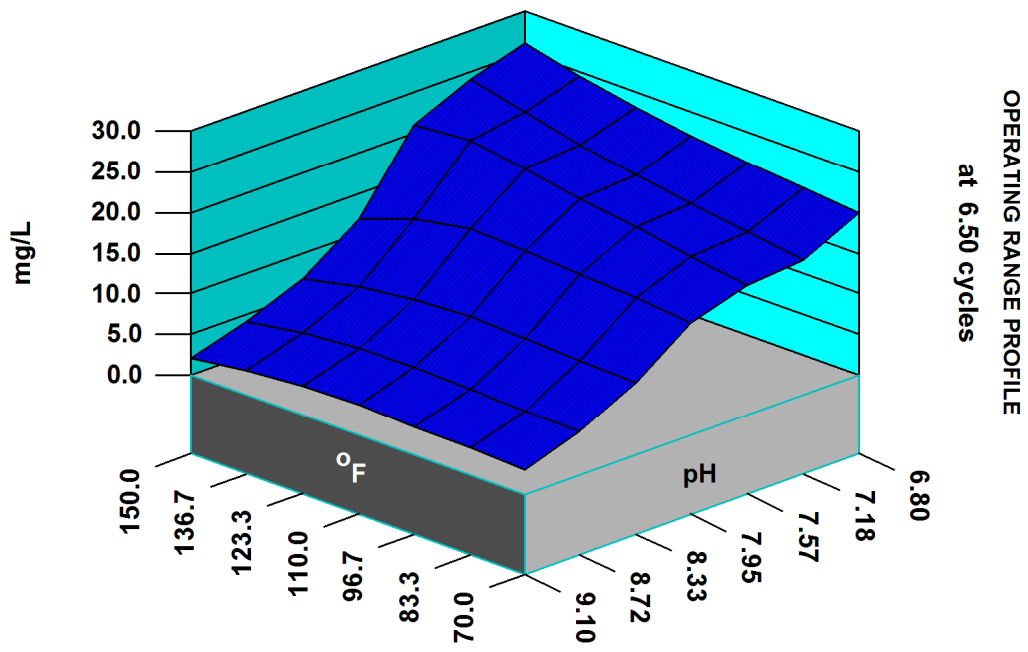


**Figure 8: Minimum Effective Dosages for Common Phosphonates versus Temperature and CaCO<sub>3</sub> Saturation Stress**



**Figure 9**

**4:1 Ortho PO<sub>4</sub>:Zn Dosage Profile**



**TABLE 1 - SATURATION RATIO FORMULAS**

<b>Calcium carbonate</b>	$\text{S.L.} = \frac{(\text{Ca})(\text{CO}_3)}{K_{\text{sp CaCO}_3}}$
<b>Barium carbonate</b>	$\text{S.L.} = \frac{(\text{Ba})(\text{CO}_3)}{K_{\text{sp BaCO}_3}}$
<b>Strontium carbonate</b>	$\text{S.L.} = \frac{(\text{Sr})(\text{CO}_3)}{K_{\text{sp SrCO}_3}}$
<b>Calcium sulfate</b>	$\text{S.L.} = \frac{(\text{Ca})(\text{SO}_4)}{K_{\text{sp CaSO}_4}}$
<b>Barium sulfate</b>	$\text{S.L.} = \frac{(\text{Ba})(\text{SO}_4)}{K_{\text{sp BaSO}_4}}$
<b>Strontium sulfate</b>	$\text{S.L.} = \frac{(\text{Sr})(\text{SO}_4)}{K_{\text{sp SrSO}_4}}$
<b>Tricalcium phosphate</b>	$\text{S.L.} = \frac{(\text{Ca})^3(\text{PO}_4)^2}{K_{\text{sp Ca}_3(\text{PO}_4)_2}}$
<b>Amorphous silica</b>	$\text{S.L.} = \frac{\text{H}_4\text{SiO}_4}{(\text{H}_2\text{O})^2 * K_{\text{sp SiO}_2}}$
<b>Calcium fluoride</b>	$\text{S.L.} = \frac{(\text{Ca})(\text{F})^2}{K_{\text{sp CaF}_2}}$
<b>Magnesium hydroxide</b>	$\text{S.L.} = \frac{(\text{Mg})(\text{OH})^2}{K_{\text{sp Mg}(\text{OH})_2}}$
<b>Trizinc phosphate</b>	$\text{S.L.} = \frac{(\text{Zn})^3(\text{PO}_4)^2}{K_{\text{sp Zn}_3(\text{PO}_4)_2}}$
<b>Zinc hydroxide</b>	$\text{S.L.} = \frac{(\text{Zn})(\text{OH})^2}{K_{\text{sp Zn}(\text{OH})_2}}$
<b>Calcium pyrophosphate</b>	$\text{S.L.} = \frac{(\text{Ca})(\text{P}_2\text{O}_7)}{K_{\text{sp Ca}(\text{P}_2\text{O}_7)}}$

Table 2: Interpreting Saturation Ratios and Log Indices				
	Using Calcite Example	Saturation Ratio	Log <sub>10</sub> Indices	Saturation State
{IAP} < K <sub>sp</sub>	{Ca}{CO <sub>3</sub> } < K <sub>sp</sub>	< 1.0	< 0.0	Undersaturated: scale will not tend to form.
{IAP} = K <sub>sp</sub>	{Ca}{CO <sub>3</sub> } = K <sub>sp</sub>	= 1.0	= 0.0	At saturation: Scale will not be expected to form or dissolve.
{IAP} > K <sub>sp</sub>	{Ca}{CO <sub>3</sub> } > K <sub>sp</sub>	> 1.0	> 0.0	Supersaturated: Scale is expected to form or grow on existing substrates.
Note: Log 10 indices refers to those that express the Saturation Ratio in Log 10 form. Interpretation of Ryznar and Practical Indices differs. See the references for specifics.				

**Table 3: Example Ion Pairs Used To Estimate Free Ion Concentrations**

**CALCIUM**

$$[\text{Calcium}] = [\text{Ca}^{+II}] + [\text{CaSO}_4] + [\text{CaHCO}_3^{+I}] + [\text{CaCO}_3] + [\text{Ca(OH)}^{+I}] + [\text{CaHPO}_4] + [\text{CaPO}_4^{-I}] + [\text{CaH}_2\text{PO}_4^{+I}]$$

**MAGNESIUM**

$$[\text{Magnesium}] = [\text{Mg}^{+II}] + [\text{MgSO}_4] + [\text{MgHCO}_3^{+I}] + [\text{MgCO}_3] + [\text{Mg(OH)}^{+I}] + [\text{MgHPO}_4] + [\text{MgPO}_4^{-I}] + [\text{MgH}_2\text{PO}_4^{+I}] + [\text{MgF}^{+I}]$$

**BARIUM**

$$[\text{Barium}] = [\text{Ba}^{+II}] + [\text{BaSO}_4] + [\text{BaHCO}_3^{+I}] + [\text{BaCO}_3] + [\text{Ba(OH)}^{+I}]$$

**STRONTIUM**

$$[\text{Strontium}] = [\text{Sr}^{+II}] + [\text{SrSO}_4] + [\text{SrHCO}_3^{+I}] + [\text{SrCO}_3] + [\text{Sr(OH)}^{+I}]$$

**SODIUM**

$$[\text{Sodium}] = [\text{Na}^{+I}] + [\text{NaSO}_4^{-I}] + [\text{Na}_2\text{SO}_4] + [\text{NaHCO}_3] + [\text{NaCO}_3^{-I}] + [\text{Na}_2\text{CO}_3] + [\text{NaCl}] + [\text{NaHPO}_4^{-I}]$$

**POTASSIUM**

$$[\text{Potassium}] = [\text{K}^{+I}] + [\text{KSO}_4^{-I}] + [\text{KHPO}_4^{-I}] + [\text{KCl}]$$

**IRON**

$$[\text{Iron}] = [\text{Fe}^{+II}] + [\text{Fe}^{+III}] + [\text{Fe(OH)}^{+I}] + [\text{Fe(OH)}^{+II}] + [\text{Fe(OH)}_3^{-I}] + [\text{FeHPO}_4^{+I}] + [\text{FeHPO}_4] + [\text{FeCl}^{+II}] + [\text{FeCl}_2^{+I}] + [\text{FeCl}_3] + [\text{FeSO}_4] + [\text{FeSO}_4^{+I}] + [\text{FeH}_2\text{PO}_4^{+I}] + [\text{Fe(OH)}_2^{+I}] + [\text{Fe(OH)}_3] + [\text{Fe(OH)}_4^{-I}] + [\text{Fe(OH)}_2] + [\text{FeH}_2\text{PO}_4^{+II}]$$

**ALUMINUM**

$$[\text{Aluminum}] = [\text{Al}^{+III}] + [\text{Al(OH)}^{+II}] + [\text{Al(OH)}_2^{+I}] + [\text{Al(OH)}_4^{-I}] + [\text{AlF}^{+II}] + [\text{AlF}_2^{+I}] + [\text{AlF}_3] + [\text{AlF}_4^{-I}] + [\text{AlSO}_4^{+I}] + [\text{Al(SO}_4)_2^{-I}]$$

**Total Analytical Value**

**Free Ion Concentration**

**TABLE 4: TREATED LIMITS COMPARISON**

SCALE FORMING SPECIE	FORMULA	MINERAL NAME	TYPICAL TREATED SATURATION RATIO LIMIT	STRESSED TREATMENT LIMIT
Calcium carbonate	CaCO <sub>3</sub>	Calcite	135 - 140	200 - 225
Calcium sulfate	CaSO <sub>4</sub> *2H <sub>2</sub> O	Gypsum	2.5 - 4.0	4.0 +
Barium sulfate	BaSO <sub>4</sub>	Barite	80	80+
Strontium sulfate	SrSO <sub>4</sub>	Celestite	12	12
Silica	SiO <sub>2</sub>	Amorphous silica	1.2	2.5
Tricalcium phosphate	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>		1400 - 2500	125,000

**Table 5: Typical Scale Inhibitor Models Available**

Inhibitor		Scales Modeled
ATMP	amino tris (methylene phosphonic acid)	CaCO <sub>3</sub> , CaSO <sub>4</sub> , BaSO <sub>4</sub>
HEDP	1-hydroxy ethylidene-1,1-diphosphonic acid	CaCO <sub>3</sub> , CaSO <sub>4</sub> , BaSO <sub>4</sub>
PBTC	2-phosphonobutane-1,2,4-tricarboxylic acid	CaCO <sub>3</sub> , CaSO <sub>4</sub> , BaSO <sub>4</sub>
HDTMP	hexamethylenediamine tetra(methylene phosphonic acid)	CaCO <sub>3</sub> , CaSO <sub>4</sub> , BaSO <sub>4</sub>
DTPMPA	diethylene triamine penta (methylene phosphonic acid)	CaCO <sub>3</sub> , CaSO <sub>4</sub> , BaSO <sub>4</sub>
PAA	polyacrylic acid	CaCO <sub>3</sub> , CaSO <sub>4</sub> , BaSO <sub>4</sub>
PMA	polymaleic anhydride	CaCO <sub>3</sub> , CaSO <sub>4</sub>
AA-AMPS	acrylic acid-2-acrylamido-2-methylpropane sulfonic acid	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , CaCO <sub>3</sub>
Proprietary copolymers, terpolymers	Various	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>
Proprietary polymers	Unknown	SiO <sub>2</sub> , MgSiO <sub>3</sub> , Mg:SiO <sub>3</sub>

**Table 6: Dosage Requirements for ATMP, HEDP, and a 1:1 BLEND**

	pH 7.9 70 °F	pH 8.1 123 °F	pH 8.5 123 °F	pH 8.7 137 °F	pH 8.9 140 °F	LEGEND HIGH DOSAGE MID DOSAGE LOW DOSAGE
HEDP	0.10	0.52	2.21	8.70	19.6	
ATMP	0.13	1.02	3.99	10.6	13.8	
BLEND	0.11	0.86	2.42	10.2	16.2	
AVERAGE	0.12	0.77	3.10	9.65	16.7	
X SAT	10.3	35.3	70.6	102	131	
Treatments are 20% active, Dosages are at 24 hours						


Table 7: Dosage Requirements for ATMP, HEDP, and PBTC						
	pH 7.9 70 °F	pH 8.1 123 °F	pH 8.5 123 °F	pH 8.7 137 °F	pH 8.9 140 °F	LEGEND  HIGH DOSAGE MID DOSAGE LOW DOSAGE
HEDP	0.10	0.52	2.21	8.70	19.6	
ATMP	0.13	1.02	3.99	10.6	13.8	
PBTC	0.32	1.90	4.00	4.4	5.5	
X SAT	10.3	35.3	70.6	102	131	
 <i>increasing CaCO<sub>3</sub> stress</i>						

Table 8: Solubility Limited Inhibitor Saturation Ratio Control Range		
Inhibitor	Low Level	Upper End
Orthophosphate	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> 500 x Sat	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> 1,500 x Sat
Pyrophosphate	1.0 x Maximum Soluble Pyro	1.2 x Maximum Soluble Pyro
Zinc	1.0 x Maximum Soluble Zn	2.0 x Maximum Soluble Zn