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Modeling Scale Formation and Optimizing Scale Inhibitor Dosages in Membrane Systems

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ABSTRACT

Water chemistry design and treatment software currently in use for membrane systems is not adequate for the rigors of high recovery systems in many cases due to reliance upon simple indices for scale prediction, inhibitor selection, and inhibitor dosage estimation. Simple indices use total analytical values for calculating the driving force for scale formation and do not account for common ion effects and ion association. Their applicability is limited to lower TDS systems. This paper discusses the application of an industry standard ion association model calculation engine to predicting scale in membrane systems and optimizing control. The ion association model engine calculates the most likely distribution of species for a brine, and uses the free ion concentrations to calculate the driving force for scale for minerals such as calcite, gypsum, barite, celestite, and silica. Calcium phosphate based scales can also be modeled using this method.

Models for optimizing scale inhibitor dosages, are also described, including the parameters critical to developing an effective dosage modulation model for scale inhibitors from laboratory data, field data, or a combination of both. The paper draws upon the concept of induction time as a basis for the mathematical models used to develop predictive models from actual data. The models are based upon the concept that threshold effect inhibitors do not prevent scale formation, they only delay the inevitable. The models are in agreement with current theories and practice and treat scale inhibitors as agents which extend the induction time before crystal formation and/or growth on existing active sites occurs in the case of calcium carbonate, calcium sulfate, and barium sulfate; and as dispersants which control particle size in the case of calcium phosphate and silica. Models presented are for commercially available inhibitors and have been used successfully to select treatments and optimize dosages in reverse osmosis systems, cooling water, and oil field applications.

INTRODUCTION

In the past, scale control in reverse osmosis was a straightforward process. Recovery rates were relatively low. Systems were operated with acid feed for pH control. And in many cases anti-scalants were fed to provide a safety factor in the event of loss of acid feed. The evaluation systems for modeling scale were adequate for low ionic strength systems. Characteristics of these systems, many of which are still in use today, include:

- scale predictions are based upon simple indices. [1,2,3,4]
- calculations always assume totally closed systems having no CO_2 exchange with the atmosphere.
- indices are calculated from total analytical values and do not account for the ion associations and common ion effects prevalent in higher dissolved solids brines.
- calculations estimate carbonate from uncorrected "M" alkalinity titrations and do not correct for non-carbonate alkalinity.
- ion activity estimations use methods appropriate for low ionic strength solutions.

Modeling of systems benefits from the incorporation of sophisticated calculation methods to improve accuracy and optimize treatment. This is of special applicability to those a) operating at higher recovery rates, b) using seawater and reuse brines for feedwater, and c) those operating in high ionic strengths. In this context, treatment optimization includes pH control and anti-scalant dosages.

The use of simple indices for modeling scale and its control in membrane systems can result in:

- pH prediction errors in excess of 0.5 pH units,
- acid requirement predictions off as much as 10X, and
- gross underestimates of sulfate contributed to the feedwater and brine from acid feed.

The Assumptions on which Historic RO Scale Evaluations are based can impact system operations by:

- Overestimation of $CaCO_3$ scale potential
- Overestimation of inhibitor requirement for $CaCO_3$
- Establishment of lower recovery when $CaCO_3$ limited
- Under estimation of sulfate salt scale potential ($CaSO_4$*$2H_2O$ $BaSO_4$ $SrSO_4$)
- Establishment of out-of-range recovery when sulfate scale limited

A further complication of using simple indices for scale prediction is errors in dosage requirements calculated from their use. Dosage models calculate the minimum effective anti-scalant dosage as a function of parameters such as scale indices, temperature, and time. The

errors in indices will be translated directly into the dosage recommendations. The same errors can effect limits for inhibitor performance. These errors can become significant when data from low TDS systems is extrapolated to high TDS brines using the simple indices.

The restrictions and limitations of historic modeling can be minimized or eliminated by their replacement with an ion association model engine. The use of such tools are commonplace in related water chemistry areas of cooling water, and oil field brine chemistry.

Scale Prediction and the Concept of Saturation

A majority of the indices used routinely by water treatment chemists are derived from the basic concept of saturation. A water is said to be saturated with a compound (e.g. calcium carbonate) if it will not precipitate the compound and it will not dissolve any of the solid phase of the compound when left undisturbed, under the same conditions, for an infinite period of time. A water which will not precipitate or dissolve a compound is at equilibrium for the particular compound.

By definition, the amount of a chemical compound which can be dissolved in a water and remain in solution for this infinite period of time is described by the solubility product (Ksp). In the case of calcium carbonate, solubility is defined by the relationship:

$$\mathbf{(Ca)(CO_3) = Ksp}$$

where

- (Ca) is the activity of calcium
- (CO_3) is the carbonate activity
- Ksp is the solubility product for calcium carbonate at the temperature under study.

In a more generalized sense, the term $(Ca)(CO_3)$ can be called the Ion Activity Product (IAP) and the equilibrium condition described by the relationship:

$$\mathbf{IAP = Ksp}$$

It can be shown that the Langelier Saturation Index is the base ten logarithm of calcite saturation level based upon total calcium in the water, an estimate of carbonate calculated from total alkalinity, and the solubility product for the calcite polymorph of calcium carbonate.[2,5]

The degree of saturation of a water is described by the relationship of the ion activity product (IAP) to the solubility product (Ksp) for the compound as follows:

- If a water is undersaturated with a compound: **IAP< Ksp**
  (It will tend to dissolve the compound).
- If a water is at equilibrium with a compound: **IAP= Ksp**
  (It will not tend to dissolve or precipitate the compound).

- If a water is supersaturated with a compound: **IAP>Ksp**
  (It will tend to precipitate the compound).

The index called Saturation Level, Degree of Supersaturation, or Saturation Index, describes the relative degree of saturation as a ratio of the ion activity product (IAP) to the solubility product (Ksp):

$$\textbf{Saturation Level} = \frac{\textbf{IAP}}{\textbf{Ksp}}$$

In actual practice, the saturation levels calculated by the various computer programs available differ in the method they use for estimating the activity coefficients used in the IAP; they differ in the choice of solubility products and their variation with temperature; and they differ in the dissociation constants used to estimate the concentration of reactants (e.g. CO_3 from analytical values for alkalinity, PO_4 from analytical orthophosphate). [5,6,7,8,9]

Table 1 defines the saturation level for common scale forming species and provides the basis for their discussion in this paper. Simple indices use analytical values for the ions, e.g. Ca. For example, by definition, the Langelier Saturation Index is the base ten logarithm of saturation level if calculated a) using analytical values rather than free ion concentrations, b) using an alkalinity which is not corrected for non-carbonate alkalinity, and c) using simple activity coefficients.

Ion Association in Brines

Ions in solution are not all present as the free species. For example, calcium in water is not all present as free $Ca.^{+2}$ 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 2 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 a 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 1).
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 levels based upon the free concentrations of ions estimated using the ion association model (ion pairing).

TABLE 1 - SATURATION LEVEL FORMULAS

Calcium carbonate	$S.L. = \frac{(Ca)(CO_3)}{K_{sp\ CaCO3}}$
Barium carbonate	$S.L. = \frac{(Ba)(CO_3)}{K_{sp\ BaCO3}}$
Strontium carbonate	$S.L. = \frac{(Sr)(CO_3)}{K_{sp\ SrCO3}}$
Calcium sulfate	$S.L. = \frac{(Ca)(SO_4)}{K_{sp\ CaSO4}}$
Barium sulfate	$S.L. = \frac{(Ba)(SO_4)}{K_{sp\ BaSO4}}$
Strontium sulfate	$S.L. = \frac{(Sr)(SO_4)}{K_{sp\ SrSO4}}$
Tricalcium phosphate	$S.L. = \frac{(Ca)^3(PO_4)^2}{K_{sp\ Ca3(PO4)2}}$
Amorphous silica	$S.L. = \frac{H_4SiO_4}{(H_2O)^2 * K_{sp\ SiO2}}$
Calcium fluoride	$S.L. = \frac{(Ca)(F)^2}{K_{sp\ CaF2}}$
Magnesium hydroxide	$S.L. = \frac{(Mg)(OH)^2}{K_{sp\ Mg(OH)2}}$

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.[5] 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.

When indices are used to establish operating limits such as maximum recovery or maximum pH, the differences between the use of indices calculated using ion pairing can be of extreme economic significance. In the best case, a system is not operated at as high a recovery as possible, because the use of indices based upon total analytical values resulted in high estimates of the driving force for a scalant. In the worst case, the use of indices based upon total ions present can result in the establishment of operating limits too high. This can occur when experience on a system with high TDS water is translated to a system operating with a lower TDS water. The high indices which were found acceptable in the high TDS water may be unrealistic when translated to a water where ion pairing is less significant in reducing the apparent driving force for scale formation.

Figure 1 compares the impact of sulfate and chloride on scale potential. The curves profile the calculation of the Langelier Saturation Index in the presence of high TDS. In one case the TDS is predominantly from a high chloride water. In the other case, a high sulfate water is profiled. Profiles for the index calculated based upon total analytical values are compared with those calculated with ion association model free ion activities.

Figure 1
ION PAIRING REDUCES LSI
(Sulfate Effect Greater Than Chloride)

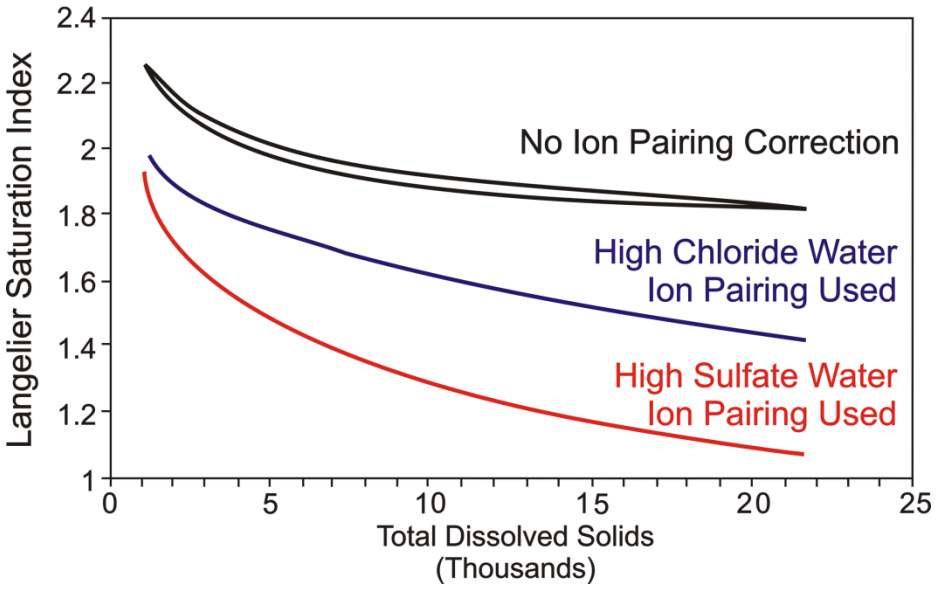


Table 2: Example Ion Pairs Used To Estimate Free Ion Concentrations

CALCIUM
[Calcium] = $[Ca^{+II}] + [CaSO_4] + [CaHCO_3^{+I}] + [CaCO_3] + [Ca(OH)^{+I}]$
$+ [CaHPO_4] + [CaPO_4^{-I}] + [CaH_2PO_4^{+I}]$

MAGNESIUM
[Magnesium] = $[Mg^{+II}] + [MgSO_4] + [MgHCO_3^{+I}] + [MgCO_3] + [Mg(OH)^{+I}]$
$+ [MgHPO_4] + [MgPO_4^{-I}] + [MgH_2PO_4^{+I}] + [MgF^{+I}]$

BARIUM
[Barium] = $[Ba^{+II}] + [BaSO_4] + [BaHCO_3^{+I}] + [BaCO_3] + [Ba(OH)^{+I}]$

STRONTIUM
[Strontium] = $[Sr^{+II}] + [SrSO_4] + [SrHCO_3^{+I}] + [SrCO_3] + [Sr(OH)^{+I}]$

SODIUM
[Sodium] = $[Na^{+I}] + [NaSO_4^{-I}] + [Na_2SO_4] + [NaHCO_3] + [NaCO_3^{-I}]$
$+ [Na_2CO_3] + [NaCl] + [NaHPO_4^{-I}]$

POTASSIUM
[Potassium] = $[K^{+I}] + [KSO_4^{-I}] + [KHPO_4^{-I}] + [KCl]$

IRON
[Iron] = $[Fe^{+II}] + [Fe^{+III}] + [Fe(OH)^{+I}] + [Fe(OH)^{+II}] + [Fe(OH)_3^{-I}]$
$+ [FeHPO4+I] + [FeHPO_4] + [FeCl^{+II}] + [FeCl_2^{+I}] + [FeCl_3]$
$+ [FeSO_4] + [FeSO_4^{+I}] + [FeH_2PO_4^{+I}] + [Fe(OH)_2^{+I}] + [Fe(OH)_3]$
$+ [Fe(OH)_4^{-I}] + [Fe(OH)_2] + [FeH_2PO_4^{+II}]$

ALUMINUM
[Aluminum] = $[Al^{+III}] + [Al(OH)^{+II}] + [Al(OH)_2^{+I}] + [Al(OH)_4^{-I}] + [AlF^{+II}] + [AlF_2^{+I}]$
$+ [AlF_3] + [AlF_4^{-I}] + [AlSO_4^{+I}] + [Al(SO_4)_2^{-I}]$

Total Analytical Value **Free Ion Concentration**

Alkalinity Correction for Non-carbonate Alkalinity

The use of simple indices can result in a much lower than required pH control point for the following reasons. The scale potential for calcium carbonate is over estimated in ammonia contaminated systems when simple indices are used to estimate scale potential and the alkalinity is not corrected for non carbonate alkalinity (e.g. ammonia). It is important to remember that a total "M" alkalinity titration measures the acid neutralizing capacity of the water, not just the carbonate and bicarbonate contributions.(10)

In neutral waters where carbonic acid equilibria is in complete control, simple indices such as the Langelier saturation index have their minimum error. In this case:

Formula 1: $ANC = 2.0 * [CO_3^{=}] + [HCO_3^{-}] + [OH^{-}] - [H^{+}]$

The contribution of hydroxide to the Acid Neutralizing Capacity is negligible near pH 7. Carbonate and bicarbonate concentrations can be estimated with reasonable accuracy.

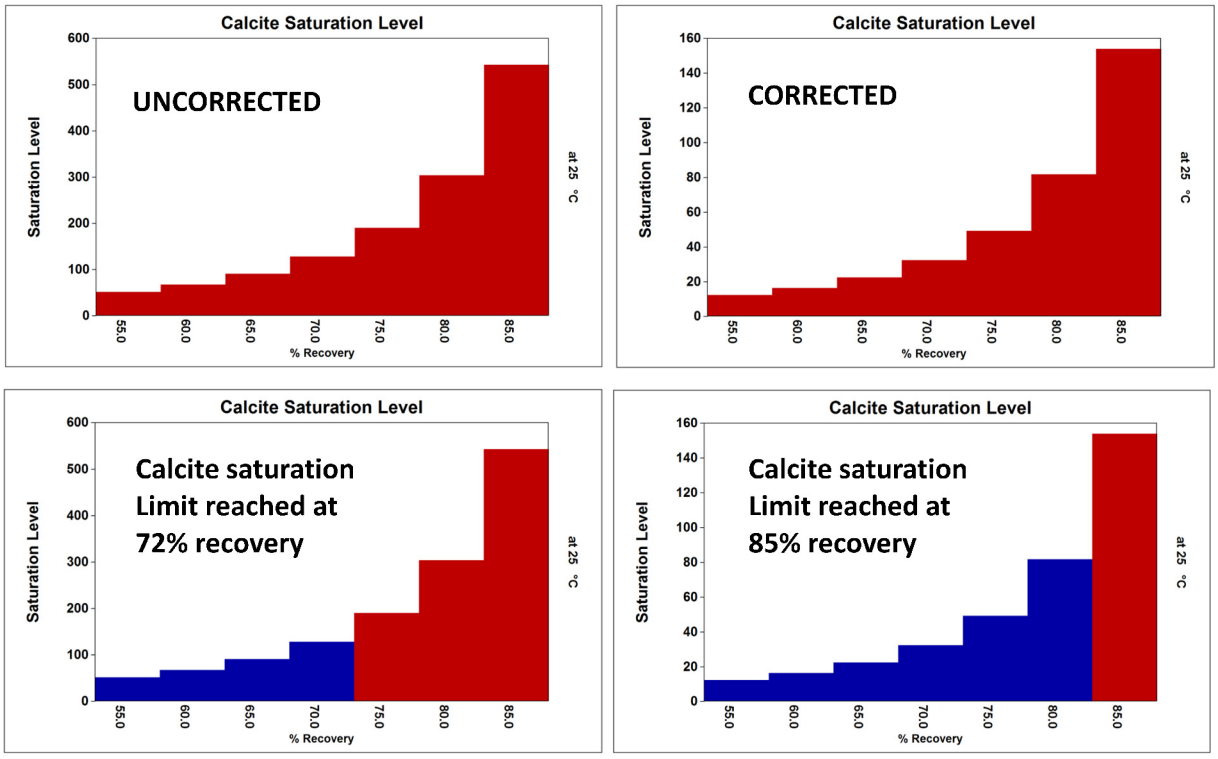
At higher pH, or when other alkalis such as ammonia are present:

Formula 2: $ANC = 2.0 * [CO_3^{=}] + [HCO_3^{-}] + [NH_3] + [PO_4] + [B(OH)_4] + [OH^{-}] - [H^{+}]$

Hydroxide becomes an increasing contributor to Acid Neutralization Capacity as water pH increases above 7.0 . Ammonia and other alkali contributions can lead to very high estimates of carbonate and bicarbonate if the alkalinity (ANC) is not corrected for them prior to use in simple index calculation. Langelier noted the necessity of correcting for non-carbonate alkalinity in his original paper.(1) He also pointed out the desirability of including the impact of ion association and common ion effects in all but low TDS waters. The graphs in Figure 1 compare models with and without correction for non-carbonate in an ammonia contaminated system.

Failure to correct for non-carbonate alkalinity when using simple indices can result in the establishment of a much lower pH control point than is really necessary to minimize calcium carbonate scale potential. The lower control point can increase the difficulty in maintaining control in poorly buffered waters, and increase the sulfate based scale potential of the water due to the higher sulfates in the feedwater and brine. Ion association model saturation levels corrects for the errors introduced by non-carbonate alkalinity and high TDS and should be employed when available.(5)

Figure 2: The Impact of Non-carbonate Alkalinity Correction Upon Maximum Recovery

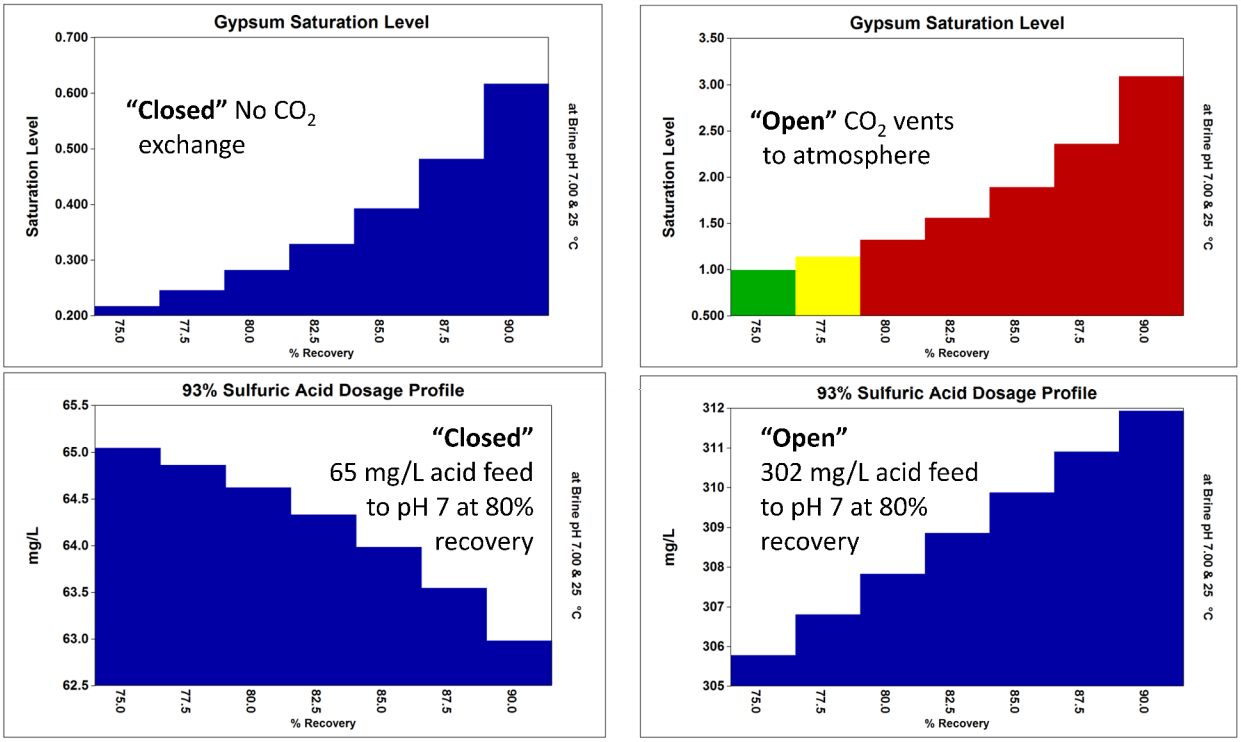


Raw Water 300 mg/L HCO_3, 50 mg/L NH_3

Acid Requirements in "Closed" versus "Open" Systems

Most RO modeling programs assume that the systems are unvented and totally closed with respect to carbon dioxide exchange with the atmosphere. Calculations performed for "closed" systems assume that CO_2 produced by acid addition builds up in the system. Calculations performed for "open" systems assume that CO_2 produced by acid addition is removed from the system. Figure 3 compares acid requirements, and the resultant sulfate contributions, for pH control in a "closed" versus "open" system.

Figure 3: pH Control in Closed versus Open Systems



In this case it can be seen that approximately five times as much acid is required for an "open" system rather than for a "closed" system. The difference is sufficient to create a calcium sulfate scale problem. Modeling software should be capable of treating a system as "closed" or "open" to assure that sulfate scale potential is evaluated accurately.

KINETIC ASPECTS

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.

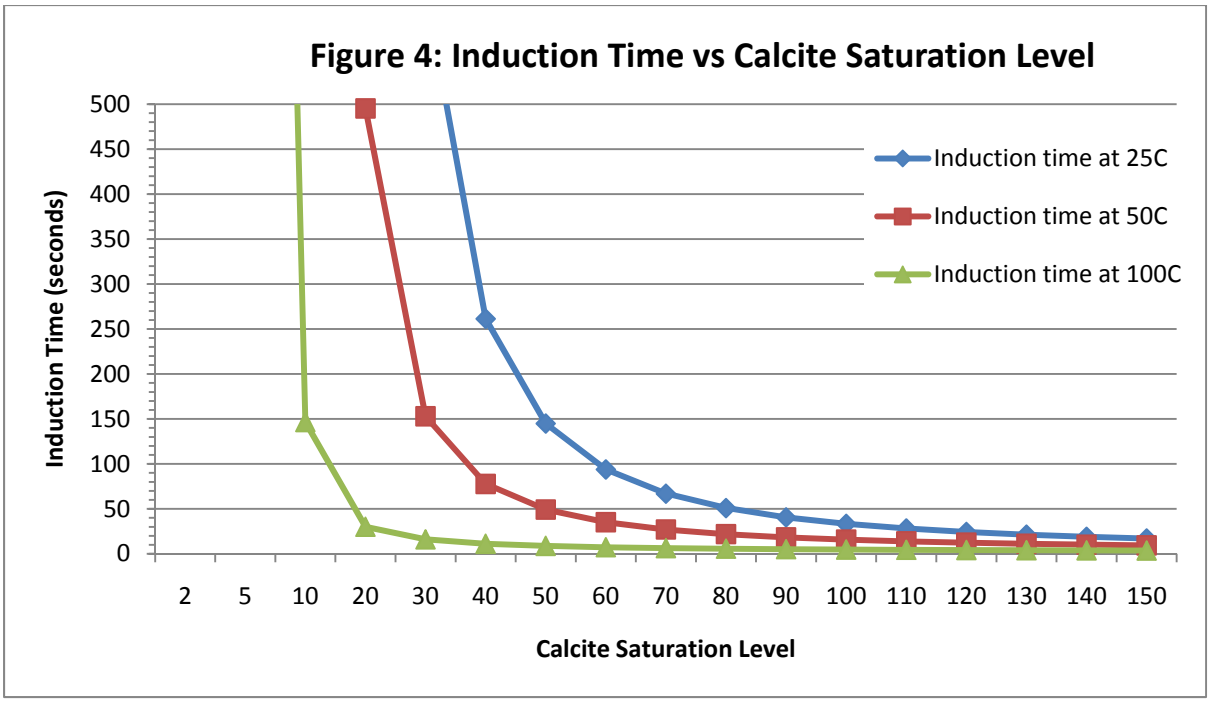
Saturation level calculations, and even simple indices, indicate whether or not scale is likely to form, or dissolve, if left undisturbed for an infinite period of time. Residence times in cooling systems are significantly less than infinity. The thermodynamics based indices, such as ion association 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 levels, and the relevance of thermodynamic indices under actual cooling water chemistry, temperature, and residence times.

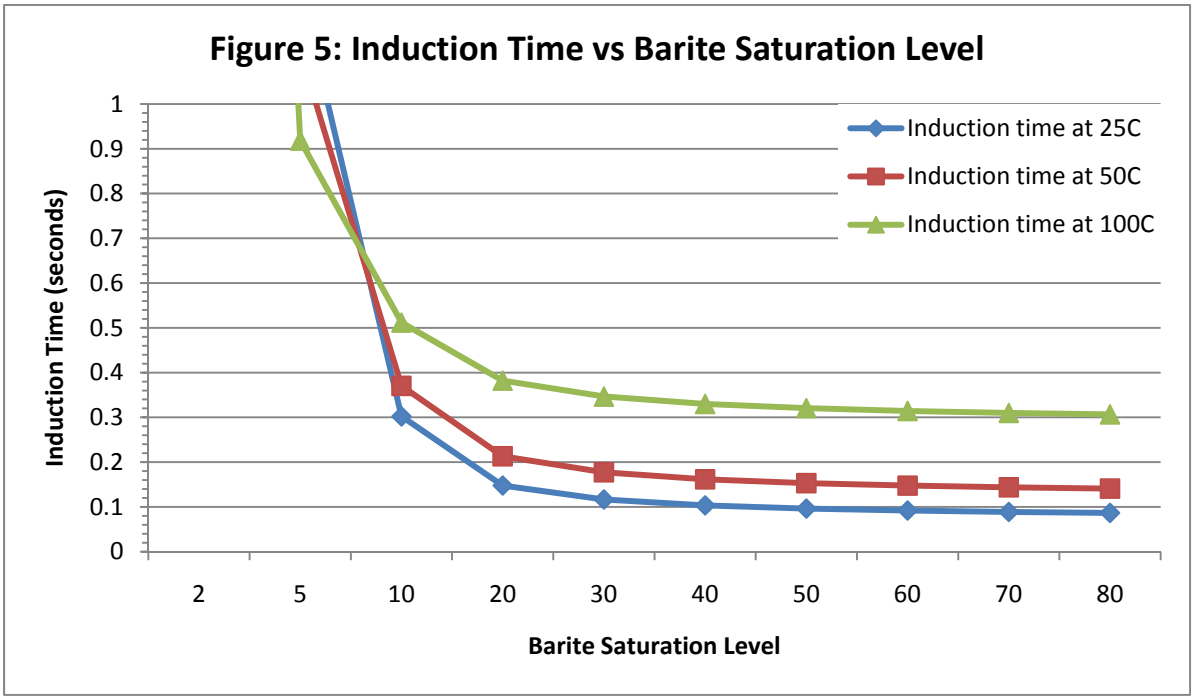
Induction Time: When reactants are mixed, a solution is heated, cooled, undergoes a pressure change or is otherwise perturbed, the impact of the environmental changes is not immediate. A finite time passes before the perturbation affects any susceptible reaction. In the case of scale formation, induction 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 CaCO3, 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 ($BaSO_4$) and calcite ($CaCO_3$). [15] Figures 4 and 5 are derived from this, and related works, by Mason Tomson and his graduate students at Rice University.

Figure 4 profiles the untreated induction time for calcite in the practical operational range for calcite of 0 to 150x saturation. This range was chosen because it is the effective range for most scale inhibitors. The 150x saturation level limit is a commonly accepted upper limit for operation with common inhibitors such as phosphonates and polymers. Figure 5 profiles the saturation level range for barite, 0 to 80x saturation.





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

Actual induction times in industrial systems will typically be lower than those of a pure system. Existing "seed" crystals and deposits provide a substrate for crystal growth without the necessity for achieving the "activation energy" for the initial phase change. In other words, it is easier to keep a clean system clean than to keep a dirty system from getting dirtier. Other factors can also decrease induction time.

Although beyond the scope of this paper, it should be noted that scale formation in membrane systems is typically "second order" for bulk water precipitation. Once through systems, such as potable water and utility condenser cooling systems, tend to be closer to "first order" for growth on an existing substrate.[16, 17]

DOSAGE OPTIMIZATION

Induction Time: The Key To The Models

Reactions do not occur instantaneously. A time delay occurs once all of the reactants have been added together. They must come together in the reaction media to allow the reaction to happen. The time required before a reaction begins is termed the induction time.

Thermodynamic evaluations of a water scale potential predict what will happen if a water is allowed to sit undisturbed under the same conditions for an infinite period of time. Even simplified indices of scale potential such as the ion association model saturation index can be interpreted in terms of the kinetics of scale formation. For example, calcium carbonate scale formation would not be expected in an operating system when the saturation index for the system only slightly above 1.0 x saturation. The driving force for scale formation is too low for scale formation to occur in finite, practical system residence times. Scale would be expected if the same system operated with a saturation index of 50. The driving force for scale formation in this case is high enough, and induction time short enough, to allow scale formation in even the longest residence time systems. [12] Scale inhibitors don't prevent precipitation, they delay the inevitable by extending induction time.[10,11,12]

Formula 3:

$$\text{Induction Time} = \frac{1}{k\,[\text{Saturation Ratio} - 1]^{P-1}}$$

Where:

Induction Time is the time before crystal formation and growth occurs;
k is a temperature dependent constant**;**
Saturation Ratio is the degree of super-saturation;
P is the critical number of molecules in a cluster prior to phase change

Temperature is a second parameter affecting dosage and is represented by the temperature dependent constant k in formula 3. 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 above was found to correlate well with the Arrhenius relationship, as outlined in formula 4.

Formula 4:

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

Where:

k is a temperature dependent constant;

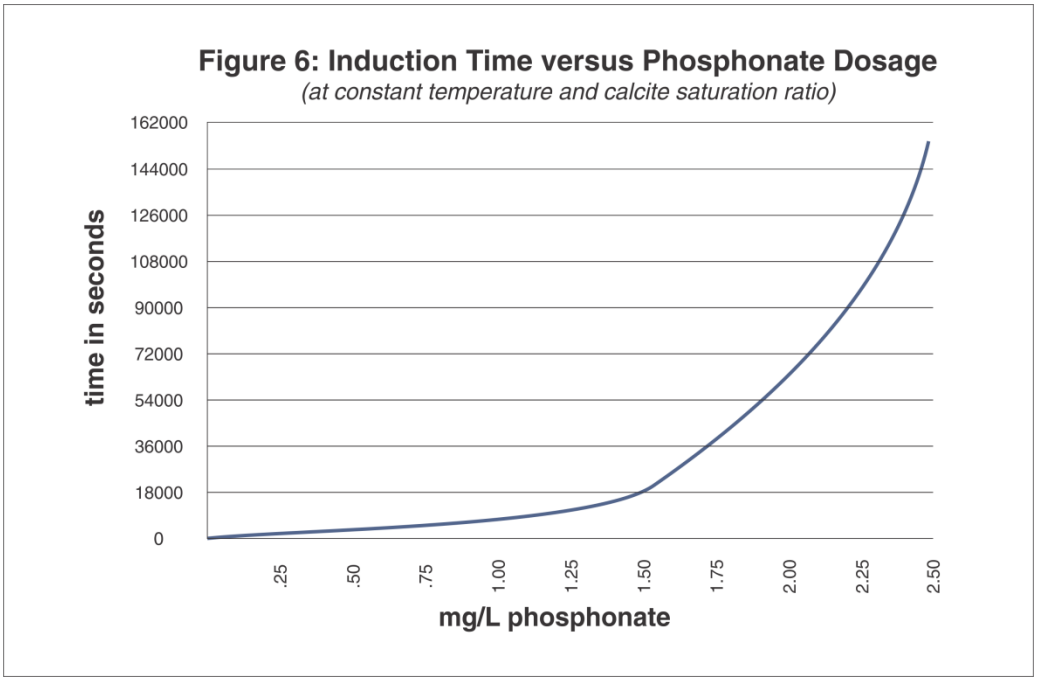
Ea is activation energy;

R is the Gas Constant;

T is absolute temperature.

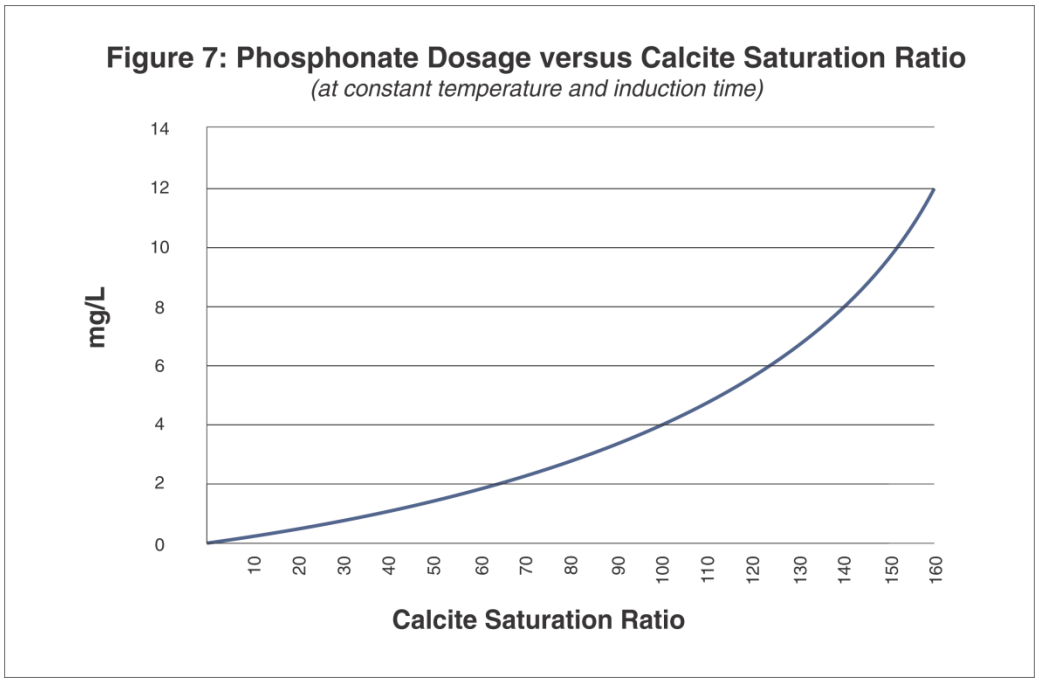
Models for optimizing dosage demonstrate the impact of dosage on increasing induction time. An example is profiled in Figure 3. Saturation level and temperature impacts upon the dosage requirement to extend induction time are depicted in figures 4 and 5. Factors impacting the anti-scalant dosage required to prevent precipitation are summarized as follows:

Time The time selected is the residence time the inhibited water will be in the cooling system. The inhibitor must prevent scale formation or growth until the water has passed through the system and been discharged. Figure 6 profiles the impact of induction time upon dosage with all other parameters held constant.

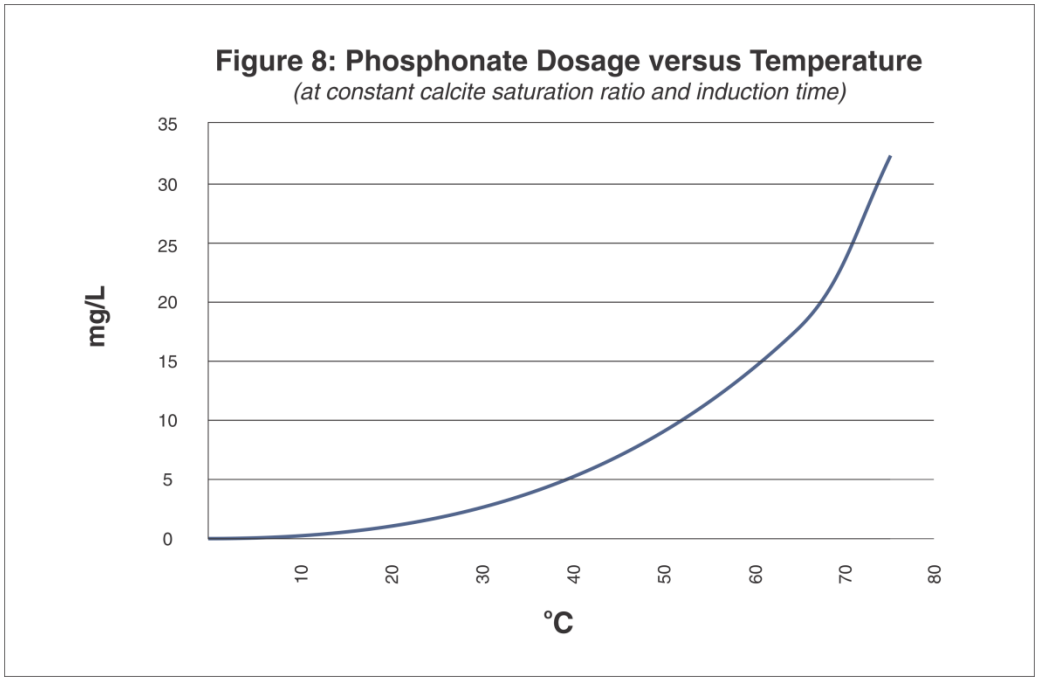


Degree of Supersaturation An ion association model saturation level is the driving force for the model outlined in this paper, although other, similar driving forces have been used. Calculation of driving force requires a complete water analysis, and the temperature at which the

driving force should be calculated. Figure 7 profiles the impact of saturation level upon dosage, all other parameters being constant.



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. This temperature effect is independent of the effect of temperature upon saturation level calculations. Figure 8 profiles the impact of temperature upon dosage with other critical parameters held constant.



pH pH affects the saturation level calculations, but it also may affect the dissociation state and stereochemistry of the inhibitors[8]. 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.

Formula 5 adds the impact of inhibitor dosage on extending induction time to formula 3. The goal of the inhibitor dosage is to extend the time before precipitation until the treated water has passed through the system and precipitation will no longer be a threat to membrane life.

Formula 5:

$$\text{Induction Time} = \frac{[\text{inhibitor}]^{M}}{k\,[\text{Saturation Ratio} - 1]^{P-1}}$$

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.

State-of-the-art RO modeling software should incorporate the ability to optimize dosages for all of the scales expected.

Scale inhibitors have upper limits and are not effective above saturation level driving force, regardless of the inhibitor dosage. Table 3 outlines generally accepted limits for inhibition of scales by standard commercially available inhibitors. Limits are provided for both standard inhibitors and for those formulated for extreme, "stressed" conditions.

TABLE 3: TREATED LIMITS COMPARISON

SCALE FORMING SPECIE	FORMULA	MINERAL NAME	TYPICAL SATURATION RATIO LIMIT	STRESSED TREATMENT LIMIT
Calcium carbonate	$CaCO_3$	Calcite	135 - 150	200 - 225
Calcium sulfate	$CaSO_4*2H_2O$	Gypsum	2.5 - 4.0	4.0 +
Barium sulfate	$BaSO_4$	Barite	80	80+
Strontium sulfate	$SrSO_4$	Celestite	12	12
Silica	SiO_2	Amorphous silica	1.2	2.5
Tricalcium phosphate	$Ca_3(PO_4)_2$		1500 - 2500	125,000

CONCENTRATION POLARIZATION

Concentration polarization is a phenomena whereby ion concentrations in the boundary layer at the membrane are projected to be higher than those of the bulk water. Estimates vary for the amount of concentration expected but vary from 1.12 times to 1.4 times that of the bulk water. Values between 1.12 and 1.2 are typically cited. [14]

Concentration polarization can, in theory, affect all concentration dependent calculations including:

- pH;
- brine ion concentrations;
- recovery limits for treated and untreated conditions;
- maximum recovery based upon antiscalant saturation level maximum;
- dosage.

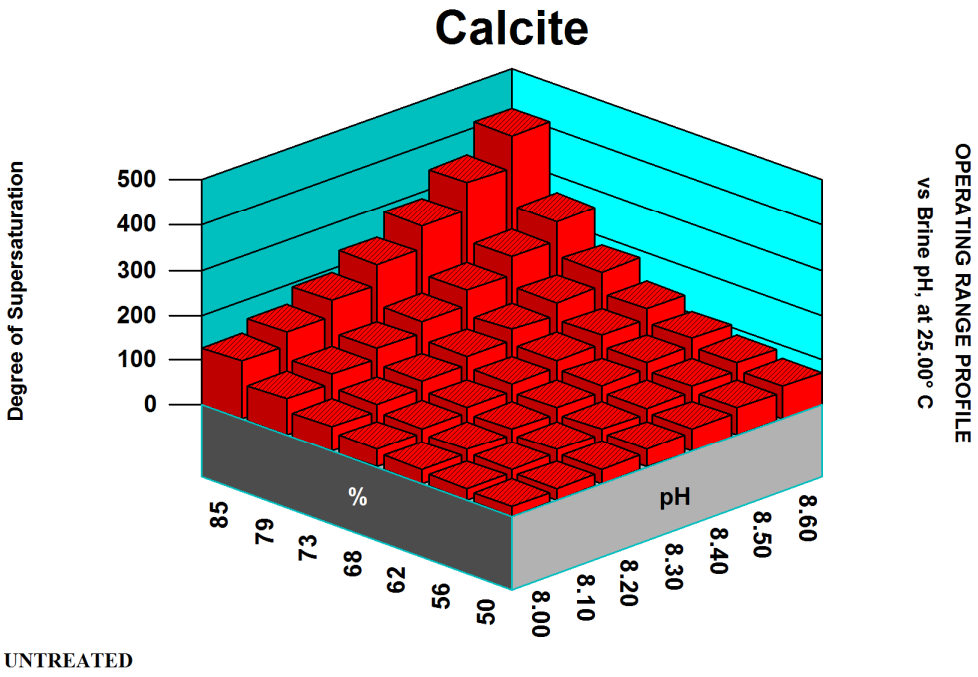
In practice, the residence time of water in the boundary layer is insignificant with respect to the overall residence time in a system, and therefore has a minimal impact on dosage calculations. Dosage calculated for the longer residence time bulk water provide a dosage sufficient to prevent scale in the shorter residence time in the boundary layer.

The exception to this observation is the case where the saturation level in the boundary layer will exceed the antiscalant maximum saturation level limit. For example if a calcite inhibitor has a saturation level upper limit of 150x saturation, and the projected boundary layer saturation level is 175x, recovery should be decreased, and/or pH decreased so that the projected boundary layer saturation level is under 150x saturation. Concentration polarization calculations and checks are recommended as an additional safety refinements in reverse osmosis modeling software.

APPLICATION OF THE MODELS

Figures 9 and 10 profile calcite scale potential and dosage requirements for a common commercial inhibitor, 30% active polyacrylic acid. The model incorporates cut-off limits beyond where the inhibitor is unable to prevent scale. Limit summaries assist in assuring that a treatment scheme will handle all potential scales at the target operating pH and recovery. Table 4 summarizes the status for the treatment at 73% recovery and a pH of 8.4

Figure 9: $CaCO_3$ Scale Potential



UNTREATED

Figure 10: Inhibitor Dosage Profile

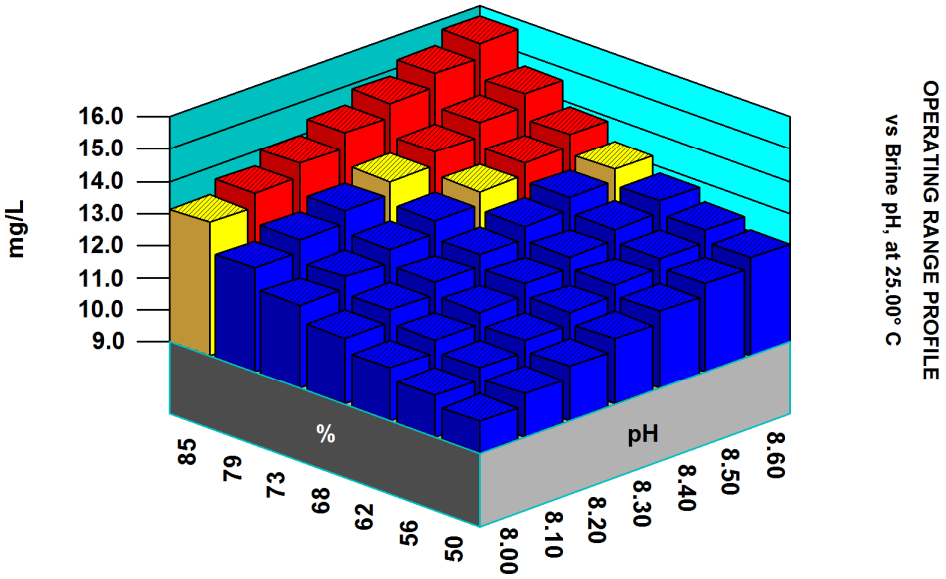
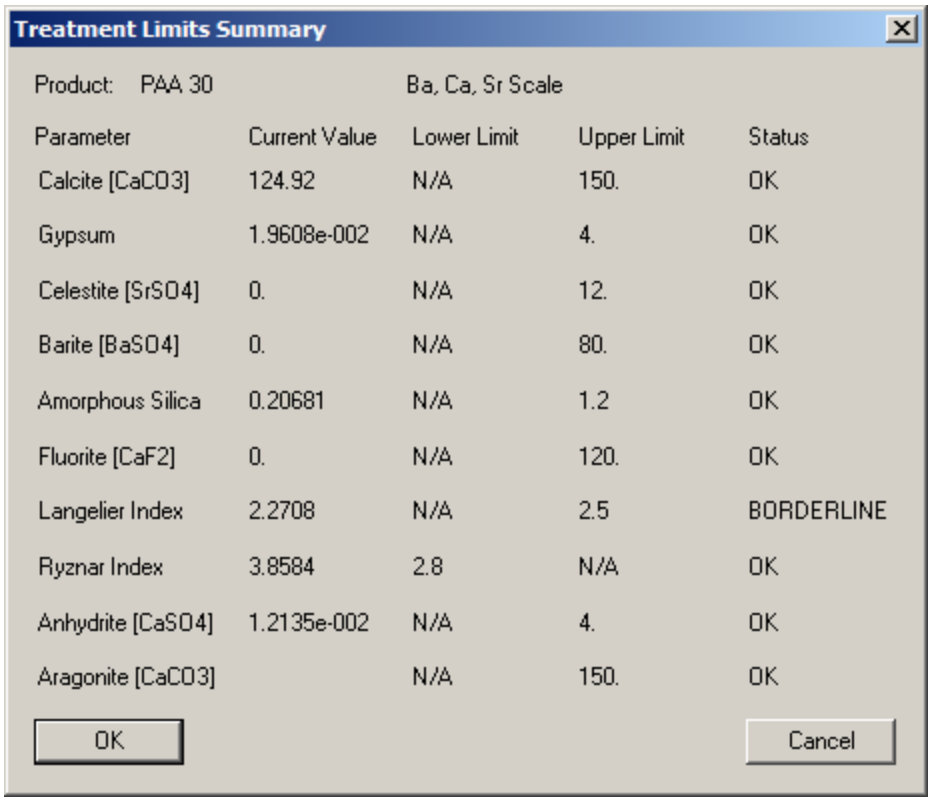


Table 4: Treatment Limits Summary



Treatment Limits Summary

Product: PAA 30 Ba, Ca, Sr Scale

Parameter	Current Value	Lower Limit	Upper Limit	Status
Calcite [CaCO3]	124.92	N/A	150.	OK
Gypsum	1.9608e-002	N/A	4.	OK
Celestite [SrSO4]	0.	N/A	12.	OK
Barite [BaSO4]	0.	N/A	80.	OK
Amorphous Silica	0.20681	N/A	1.2	OK
Fluorite [CaF2]	0.	N/A	120.	OK
Langelier Index	2.2708	N/A	2.5	BORDERLINE
Ryznar Index	3.8584	2.8	N/A	OK
Anhydrite [CaSO4]	1.2135e-002	N/A	4.	OK
Aragonite [CaCO3]		N/A	150.	OK

OK Cancel

SUMMARY

Classic RO predictions lack accuracy as TDS, pH, and alkalinity increase due to the use of simple indices that are accurate only at low TDS and near neutral pH.

State-of-the-art calculations include calculation methods which overcome the limitations of prior art and allow accurate modeling in high TDS brines. Refinements provided include corrections for non-carbonate alkalinity, the use of free ion concentrations and activities for driving force calculations. They also provide options for treating systems "Closed" or "Open" with respect to carbon dioxide equilibrium with the atmosphere to improve the accuracy of carbonate equilibria and pH adjustment calculations.

Dosage models are available or can be developed for new inhibitors, that allow accurate prediction of dosage requirements and treatment failure points.

REFERENCES

[1] Langelier, W.F., The Analytical Control Of Anti-Corrosion Water Treatment, JAWWA, Vol. 28, No. 10, p. 1500-1521, 1936.

[2] Ryznar, J.W., A New Index For Determining The Amount Of Calcium Carbonate Scale Formed By Water, JAWWA, Vol. 36, p. 472, 1944.

[3] Stiff, Jr., H.A., Davis, L.E., A Method For Predicting The Tendency of Oil Field Water to Deposit Calcium Carbonate, Pet. Trans. AIME 195;213 (1952).

[4] Oddo,J.E., Tomson, M.B.,Scale Control, Prediction and Treatment Or How Companies Evaluate A Scaling Problem and What They Do Wrong, CORROSION/92, Paper No. 34, (Houston, TX:NACE INTERNATIONAL 1992).

[5] Ferguson, R.J., Computerized Ion Association Model Profiles Complete Range of Cooling System Parameters, International Water Conference, 52nd Annual Meeting, Pittsburgh, PA, IWC-91-47.

[6] W. Chow, J.T. Aronson, W.C. Micheletti, Calculations Of Cooling Water Systems: Computer Modeling Of Recirculating Cooling Water Chemistry, International Water Conference, 41rst Annual Meeting, Pittsburgh, PA, IWC-80-41.

[7] Johnson, D.A., Fulks, K.E.,Computerized Water Modeling In The Design And Operation of Industrial Cooling Systems, International Water Conference, 41rst Annual Meeting, Pittsburgh, PA, IWC-80-42.

[8] Truesdell, A.H., Jones, B.F., WATEQ - A Computer Program For Calculating Chemical Equilibria Of Natural Waters, J. Research, U.S. Geological Survey, Volume 2, No. 2, p. 233-248, 1974.

[9] Musil, R.R., Nielsen, H.J., Computer Modeling Of Cooling Water Chemistry, International Water Conference, 45th Annual Meeting, Pittsburgh, PA, IWC-84-104.

[10] Werner Stumm and James J. Morgan, Aquatic Chemistry, John Wiley & Sons, Inc,, New York, 1996, pp 138 - 140.

[11] Gill, J.S., Anderson, C.D., Varsanik, R.G., Mechanism Of Scale Inhibition By Phosphonates, International Water Conference, 44th Annual Meeting, Pittsburgh, PA, IWC-83-4.

[12] Amjad, Z., Masler,III, W.F., The Inhibition Of Calcium Sulfate Dihydrate Crystal Growth By Polyacrylates And The Influence Of Molecular Weight, CORROSION/85, Paper No. 357, Houston, TX: NACE INTERNATIONAL, 1985).

[13] Ferguson, R.J., Developing Scale Inhibitor Models, WATERTECH, Houston, TX, 1992.

[14] Byrne, Wes, Reverse Osmosis A Practical Guide For Industrial Users, Tall Oaks Publishing, Inc., Littleton, CO, 2002, pp 158, 457 - 458.

[15] Tomson, M.B., Fu, G., Watson, M.A. and A.T. Kan, "Mechanisms of Mineral Scale Inhibition, Society of Petroleum Engineers, Oilfield Scale Symposium, Aberdeen, UK, 2002.

[16] Ferguson, R.J., A Kinetic Model for Calcium Carbonate Scale, CORROSION/84,Paper No. 46, (Houston, TX:NACE INTERNATIONAL 1984).

[17] Ferguson, R.J., Thirty Years of Ultra Low Dosage Scale Control , CORROSION/2003,Paper No. 063, (Houston, TX:NACE INTERNATIONAL 2003).