

THE KINETICS OF COOLING WATER SCALE FORMATION AND CONTROL

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ABSTRACT

The 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. 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 levels (degree of supersaturation) ^{1,2,3,4,5} and less rigorous methods such as the simple indices (Langelier Saturation Index ⁶, Ryznar Stability Index⁷, Practical Scaling Index ⁸, 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 ⁹ 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 CCP (calcium carbonate precipitation potential) ¹⁰ 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 ^{11,12,13} and growth rate. When inhibitors are added to the equation, their impact on induction time is critical to practical dosage calculation. ^{11,15}

A thorough cooling system evaluation would include system specific answers to these questions and include:

- 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.

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
$$\{Ca^{2+}\}\{CO_3^{2-}\} = K_{sp}$$

where $\{Ca^{2+}\}$ is the calcium activity in the water at the current conditions
 $\{CO_3\}$ 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 $\{Ca^{2+}\}$ and $\{CO_3^{2-}\}$ are used in ion association models to improve accuracy and account for phenomena such as common ion effects.^{1,2,3,4,14} 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 methods such as those derived by Pitzer¹⁵ and others.

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

Equation 2
$$\text{Saturation Ratio} = \frac{\{Ca^{2+}\}\{CO_3^{2-}\}}{K_{sp}}$$
 what we have
 what will be at $t = \infty$

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

Equation 3
$$\text{Saturation Ratio} = \frac{\{IAP\}}{K'_{sp}}$$
 what we have
 what will be at $t = \infty$

where $\{IAP\}$ is the ion activity product for the scale be evaluated
 K'_{sp} is the solubility product for the scale forming specie 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:

Equation 4 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 level calculated with some simplifications and assumptions.

Langelier Saturation Index Assumptions:

- 1) Total analytical values for Ca^{2+} and CO_3^{2-} are used rather than free ion concentrations
- 2) CO_3^{2-} 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-Hückel 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.^{11,15}

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_3 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^{+2} . 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 levels 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.^(1,6) 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 levels 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
$$[\text{Ca}^{2+} - \text{X}][\text{CO}_3^{2-} - \text{X}] = K_{\text{sp}}$$

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 level. 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
$$[\text{Ca}^{2+} - \text{X}][\text{SO}_4^{2-} - \text{X}] = K_{\text{sp}}$$

The solution becomes more complex for tricalcium phosphate:

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

The index provides a quantitative indicator of scale potential and has been used to correlate scale formation in a kinetic model.¹³ 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.^{10,12}

A PROPOSED 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). Some users in the geochemical world normalize these ratios by dividing the log10 of the saturation ratio by the order, to provide a common ground for interpreting indices.

Table 4 compares saturation ratios, momentary excess, and the "normalized" log₁₀ of saturation ratio at accepted limits for scale inhibitor performance; limits above which inhibitors are expected to fail at any dosage. A typical Great Lakes water was used for this example.

It can be seen that a "Power Index" on the close order of 1000 coincides with the failure points for barium sulfate, tricalcium phosphate, calcite, and reported failure point limits for silica. At this point the "Power Index" is under review as a normalized potential indicator of scale potential severity and failure point.

The Power Index shows promise for providing a numerical scale which indicates deposition potential on a comparable basis so that the upper limit for tricalcium phosphate could be indicated as a PI of approximately 1000 as would that of barium sulfate.

Laboratory studies will be conducted to validate and possibly refine the Power Index over a broad range of parameters, including values such as the ratio of reactants (e.g. calcium to carbonate ratio, barium to sulfate ratio).

It is of note that many kinetic models for crystallization include a driving force parameter, usually saturation ratio, and concentration component comparable to the momentary excess.

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 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 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 (BaSO_4) and calcite (CaCO_3).¹¹ 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 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 3 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 an open recirculating cooling water 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.

Actual induction times in cooling 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 recirculating cooling water systems is typically "second order" for bulk water precipitation. Once through systems, such as utility condenser cooling systems, tend to be closer to "first order" for growth on an existing substrate.^{12,13,16,17}

KINETICS: INDUCTION TIME EXTENSION BY INHIBITORS

Scale inhibitors do not prevent scale formation forever. they typically only delay the inevitable. Most threshold effect scale inhibitors function by interfering with the kinetics of crystal formation and growth, extending the induction time until the water has passed through the system without forming crystals or causing growth on existing substrates. Dosage models have been used successfully to prevent scale in cooling systems, reverse osmosis, oil field and mining applications. The impact of common scale inhibitors on induction time can be modeled by adding an inhibitor term to a classic model for induction time: ^{12,13}

$$\text{Equation 8} \quad \text{Time} = \frac{[\text{inhibitor}]^M}{k [\text{SR} - 1]^{P-1}}$$

where

- Time** is the induction time
- inhibitor** is the scale inhibitor molar concentration
- M** is s coefficient
- k** is a temperature dependent rate constant
- SR** is the saturation ratio
- P** is the number of molecules in a critical sized cluster

It must be noted that there is a maximum saturation level beyond which inhibitors will not prevent scale by this mechanism at any dosage. This is typically 150 x saturation for calcite, and 80 x saturation for barite, as outlined in Table 5.

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 level. This profile represents the dosage required to prevent growth on an existing substrate, as occurs in many low saturation ratio once through cooling systems. The critical saturation ratio for calcite is approximately 17 and decreases with temperature.

Figure 5 depicts the impact of saturation ratio increases on the dosage required at constant temperature and residence time when the critical saturation level 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. Figure 7 depicts the impact of temperature on dosage requirements, all other parameters being constant.

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

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.^{16,17,18}

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

Equation 9 deposit buildup = 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.
 N is a coefficient.
 t is time.

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 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.

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.

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

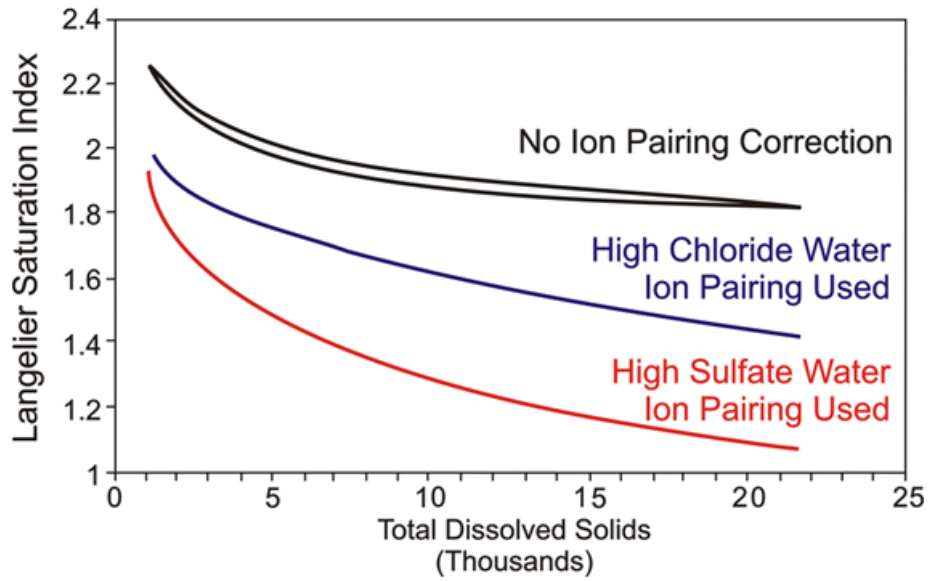


Figure 2: Induction Time vs Calcite Saturation Level

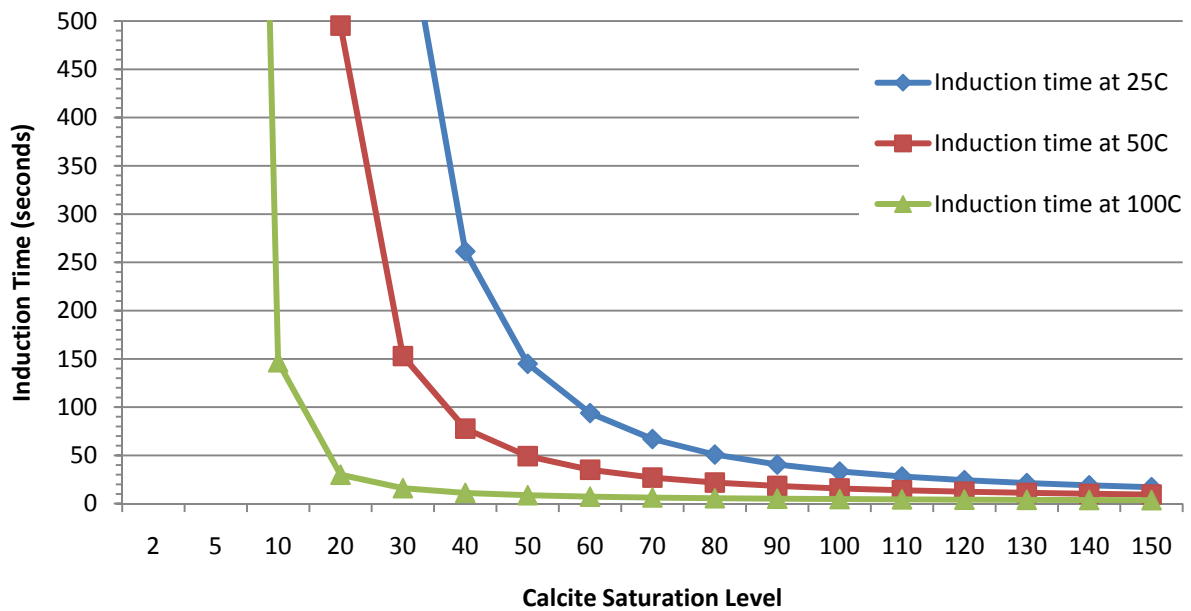


Figure 3: Induction Time vs Barite Saturation Level

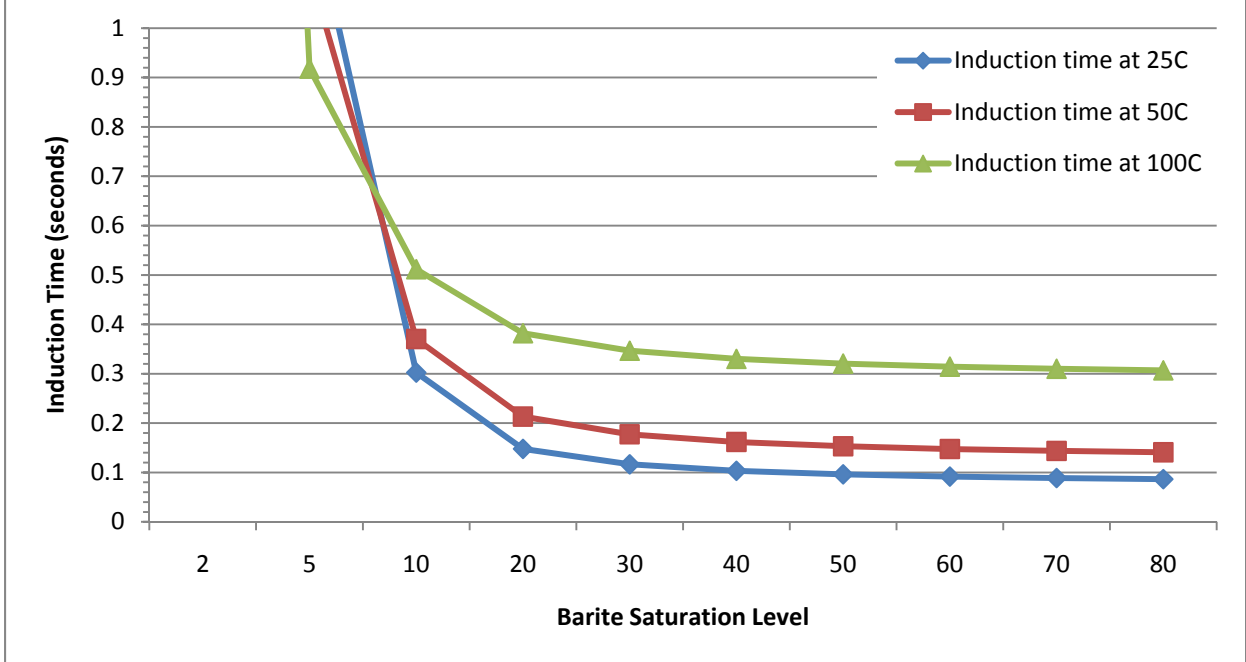


Figure 4: Phosphonate Dosage versus Calcite Saturation Ratio
(at constant temperature and induction time)

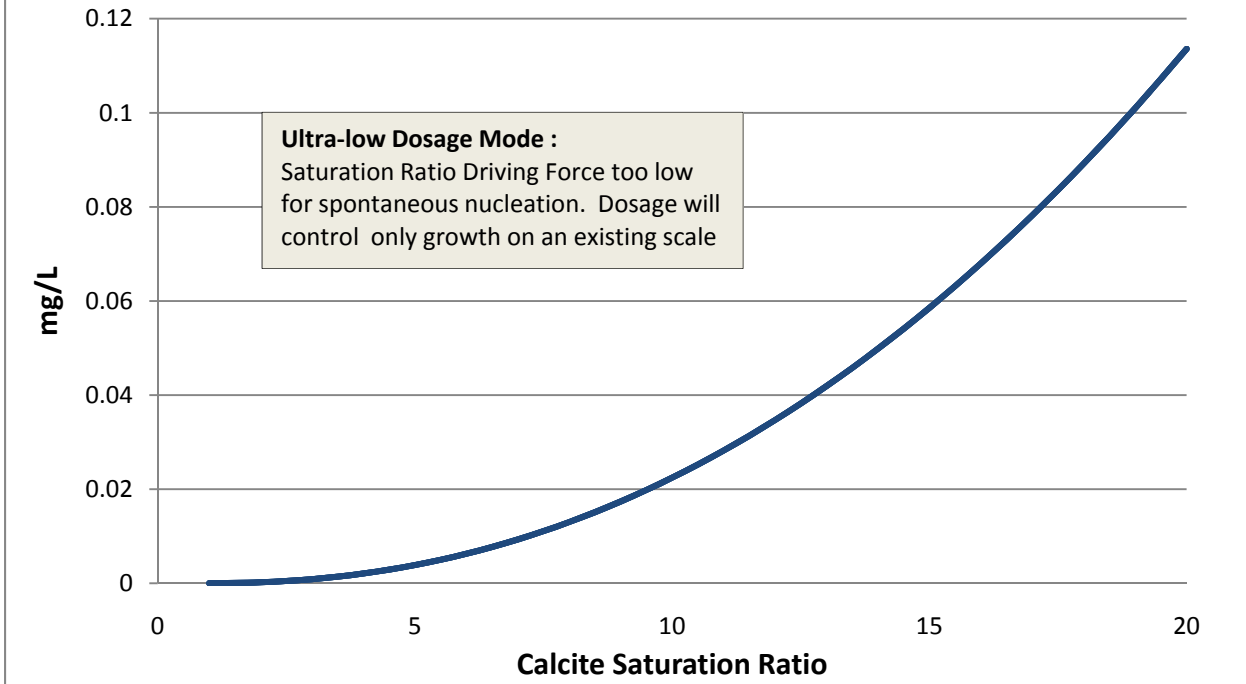


Figure 5: Phosphonate Dosage versus Calcite Saturation Ratio
(at constant temperature and induction time)

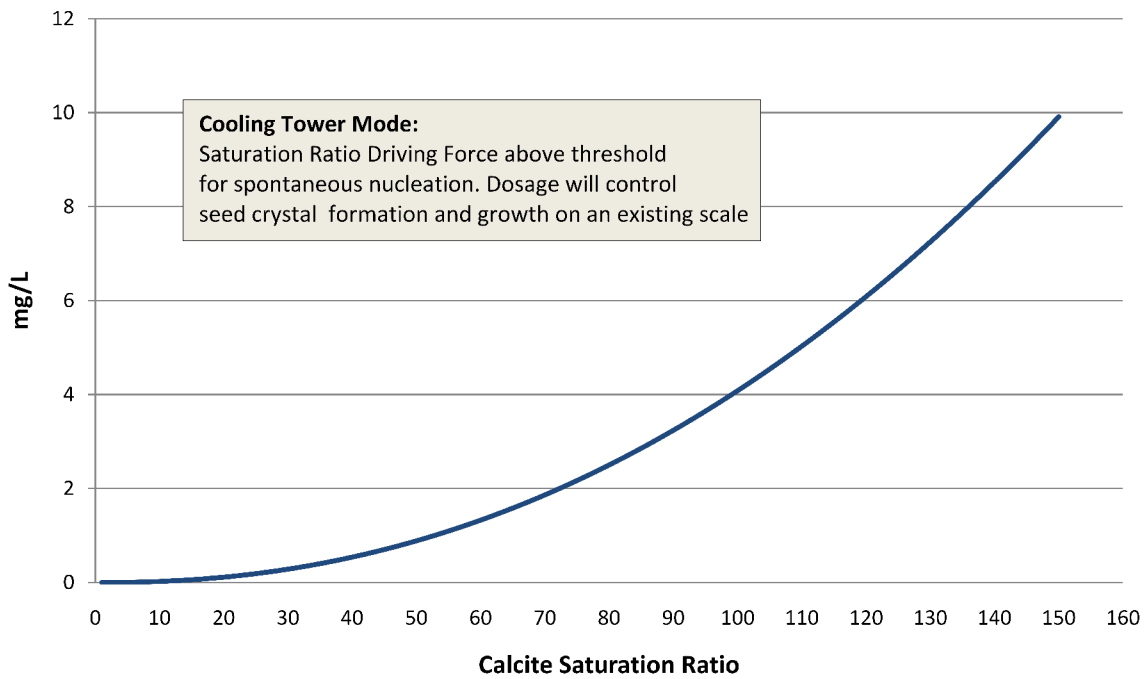


Figure 6: Induction Time versus Phosphonate Dosage
(at constant temperature and calcite saturation ratio)

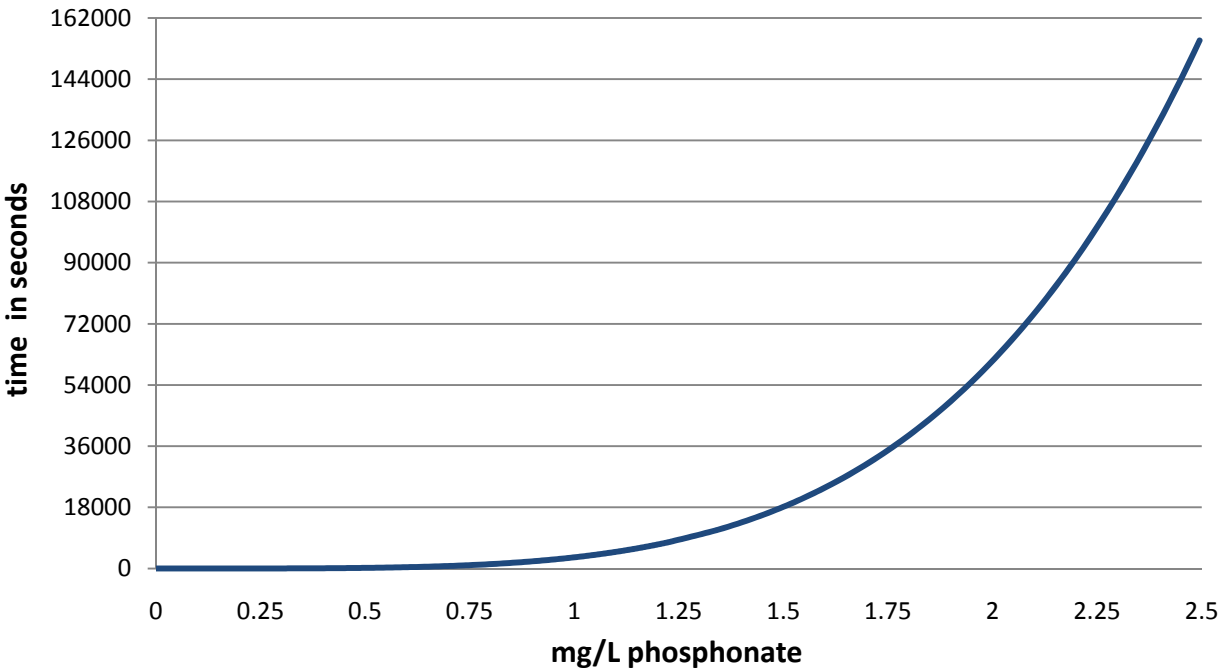


Figure 7: Phosphonate Dosage versus Temperature
(at constant calcite saturation ratio and induction time)

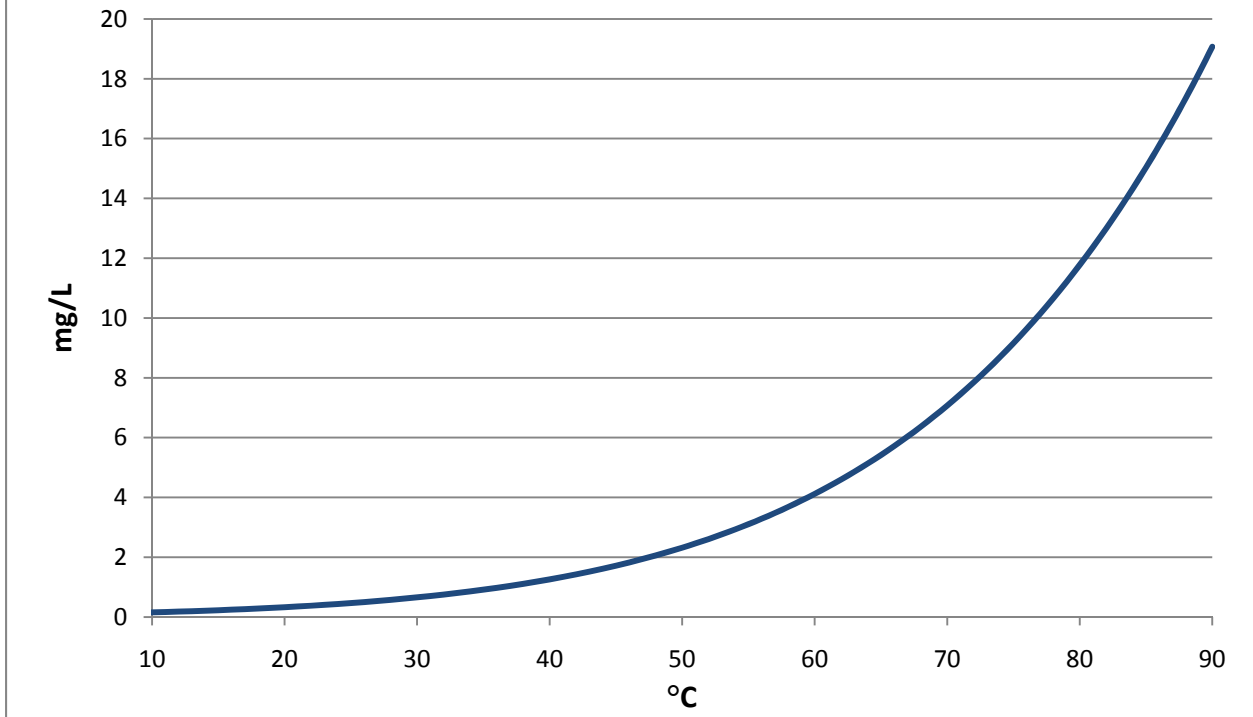


TABLE 1 - SATURATION LEVEL FORMULAS

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

Table 2: Interpreting Saturation Ratios and Log Indices				
	Using Calcite Example	Saturation Ratio	Log ₁₀ Indices	Saturation State
{IAP} < K _{sp}	{Ca}{CO ₃ } < K _{sp}	< 1.0	< 0.0	Undersaturated: scale will not tend to form.
{IAP} = K _{sp}	{Ca}{CO ₃ } = K _{sp}	= 1.0	= 0.0	At saturation: Scale will not be expected to form or dissolve.
{IAP} > K _{sp}	{Ca}{CO ₃ } > K _{sp}	> 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

$$[\text{Calcium}] = [\text{Ca}^{+2}] + [\text{CaSO}_4] + [\text{CaHCO}_3^{+1}] + [\text{CaCO}_3] + [\text{Ca(OH)}^{+1}] + [\text{CaHPO}_4] + [\text{CaPO}_4^{-1}] + [\text{CaH}_2\text{PO}_4^{+1}]$$

MAGNESIUM

$$[\text{Magnesium}] = [\text{Mg}^{+2}] + [\text{MgSO}_4] + [\text{MgHCO}_3^{+1}] + [\text{MgCO}_3] + [\text{Mg(OH)}^{+1}] + [\text{MgHPO}_4] + [\text{MgPO}_4^{-1}] + [\text{MgH}_2\text{PO}_4^{+1}] + [\text{MgF}^{+1}]$$

BARIUM

$$[\text{Barium}] = [\text{Ba}^{+2}] + [\text{BaSO}_4] + [\text{BaHCO}_3^{+1}] + [\text{BaCO}_3] + [\text{Ba(OH)}^{+1}]$$

STRONTIUM

$$[\text{Strontium}] = [\text{Sr}^{+2}] + [\text{SrSO}_4] + [\text{SrHCO}_3^{+1}] + [\text{SrCO}_3] + [\text{Sr(OH)}^{+1}]$$

SODIUM

$$[\text{Sodium}] = [\text{Na}^{+1}] + [\text{NaSO}_4^{-1}] + [\text{Na}_2\text{SO}_4] + [\text{NaHCO}_3] + [\text{NaCO}_3^{-1}] + [\text{Na}_2\text{CO}_3] + [\text{NaCl}] + [\text{NaHPO}_4^{-1}]$$

POTASSIUM

$$[\text{Potassium}] = [\text{K}^{+1}] + [\text{KSO}_4^{-1}] + [\text{KHPO}_4^{-1}] + [\text{KCl}]$$

IRON

$$[\text{Iron}] = [\text{Fe}^{+2}] + [\text{Fe}^{+3}] + [\text{Fe(OH)}^{+1}] + [\text{Fe(OH)}^{+2}] + [\text{Fe(OH)}_3^{-1}] + [\text{FeHPO}_4^{+1}] + [\text{FeHPO}_4] + [\text{FeCl}^{+2}] + [\text{FeCl}_2^{+1}] + [\text{FeCl}_3] + [\text{FeSO}_4] + [\text{FeSO}_4^{+1}] + [\text{FeH}_2\text{PO}_4^{+1}] + [\text{Fe(OH)}_2^{+1}] + [\text{Fe(OH)}_3] + [\text{Fe(OH)}_4^{-1}] + [\text{Fe(OH)}_2] + [\text{FeH}_2\text{PO}_4^{+2}]$$

ALUMINUM

$$[\text{Aluminum}] = [\text{Al}^{+3}] + [\text{Al(OH)}^{+2}] + [\text{Al(OH)}_2^{+1}] + [\text{Al(OH)}_4^{-1}] + [\text{AlF}^{+2}] + [\text{AlF}_2^{+1}] + [\text{AlF}_3] + [\text{AlF}_4^{-1}] + [\text{AlSO}_4^{+1}] + [\text{Al(SO}_4)_2^{-1}]$$

Total Analytical Value

Free Ion Concentration

Scale	Saturation Ratio Limit	Momentary Excess at Limit	Power Index At Limit	Order	Log10(SR) ÷ Order
Calcite	125 - 150	28.5 - 32.6	3550 - 4870	2	1.05 - 1.09
Tricalcium phosphate	125000 - 150000	0.00793 - 0.00862	991 - 1300	5	1.02 - 1.04
Barium sulfate	80	12.5	1006	2	0.952
Silica	2.2 - 2.8	252 - 360	567 - 1000	1	0.301 - 0.447

SCALE FORMING SPECIE	FORMULA	MINERAL NAME	TYPICAL TREATED SATURATION RATIO LIMIT	STRESSED TREATMENT LIMIT
Calcium carbonate	CaCO ₃	Calcite	125 - 150	200 - 225
Calcium sulfate	CaSO ₄ *2H ₂ O	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

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