The Chemistry of Strontium and Barium Scales

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Abstract

New 'mystery scales' are being encountered as cooling tower operators increase cycles to new highs, add 'reuse' water to the make-up, and utilize new make-up water sources as part of an overall water conservation strategy. Scales rarely, if ever, encountered in the past are emerging as potential problems. This threat of unexpected scale is compounded because most water treatment service companies do not include barium and strontium in their make-up water analyses. Water sources with even as little 0.01 mg/L of Ba (as Ba) can become very scale-forming with respect to barite ($BaSO_4$) when tower concentration ratios are increased and sulfuric acid used for pH control. Make-up waters incorporating reverse osmosis concentrate can also provide a strontium and barium source. In some cases, produced waters are also being used in an effort for greener water use. This paper discusses the chemistry of the barium and strontium based scales barite ($BaSO_4$), celestite ($SrSO_4$), witherite ($BaCO_3$) and strontianite ($SrCO_3$). Conditions for formation and control from a water treater's perspective are emphasized. Indices for prediction are discussed.

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:

$$(Ca)(CO_3) = Ksp$$

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:[1]

$$IAP = Ksp$$

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. [2,3]

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). [3,4,5,6,7]

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. [8,9,10,11] 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. [2] Other simple indices use the same approach to predict sulfate and other carbonate scales. The use of these simple indices is not recommended for high TDS water, high sulfate waters, or waters significantly above (or below) a neutral pH.

Ion Association Reduces Available Ion Concentration

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 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 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).

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.[3] 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.

TABLE 1 - SATURATION LEVEL FORMULAS

Calcium carbonate $\quad$ S.L. $= \dfrac{(Ca)(CO_3)}{K_{sp\ CaCO3}}$

Barium carbonate $\quad$ S.L. $= \dfrac{(Ba)(CO_3)}{K_{sp\ BaCO3}}$

Strontium carbonate $\quad$ S.L. $= \dfrac{(Sr)(CO_3)}{K_{sp\ SrCO3}}$

Calcium sulfate $\quad$ S.L. $= \dfrac{(Ca)(SO_4)}{K_{sp\ CaSO4}}$

Barium sulfate $\quad$ S.L. $= \dfrac{(Ba)(SO_4)}{K_{sp\ BaSO4}}$

Strontium sulfate $\quad$ S.L. $= \dfrac{(Sr)(SO_4)}{K_{sp\ SrSO4}}$

Tricalcium phosphate $\quad$ S.L. $= \dfrac{(Ca)^3(PO_4)^2}{K_{sp\ Ca3(PO4)2}}$

Amorphous silica $\quad$ S.L. $= \dfrac{H_4SiO_4}{(H_2O)^2 * K_{sp\ SiO2}}$

Calcium fluoride $\quad$ S.L. $= \dfrac{(Ca)(F)^2}{K_{sp\ CaF2}}$

Magnesium hydroxide $\quad$ S.L. $= \dfrac{(Mg)(OH)^2}{K_{sp\ Mg(OH)2}}$

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.

When indices are used to establish operating limits such as maximum cycles 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 concentration ratio 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: ION PAIRING REDUCES LSI
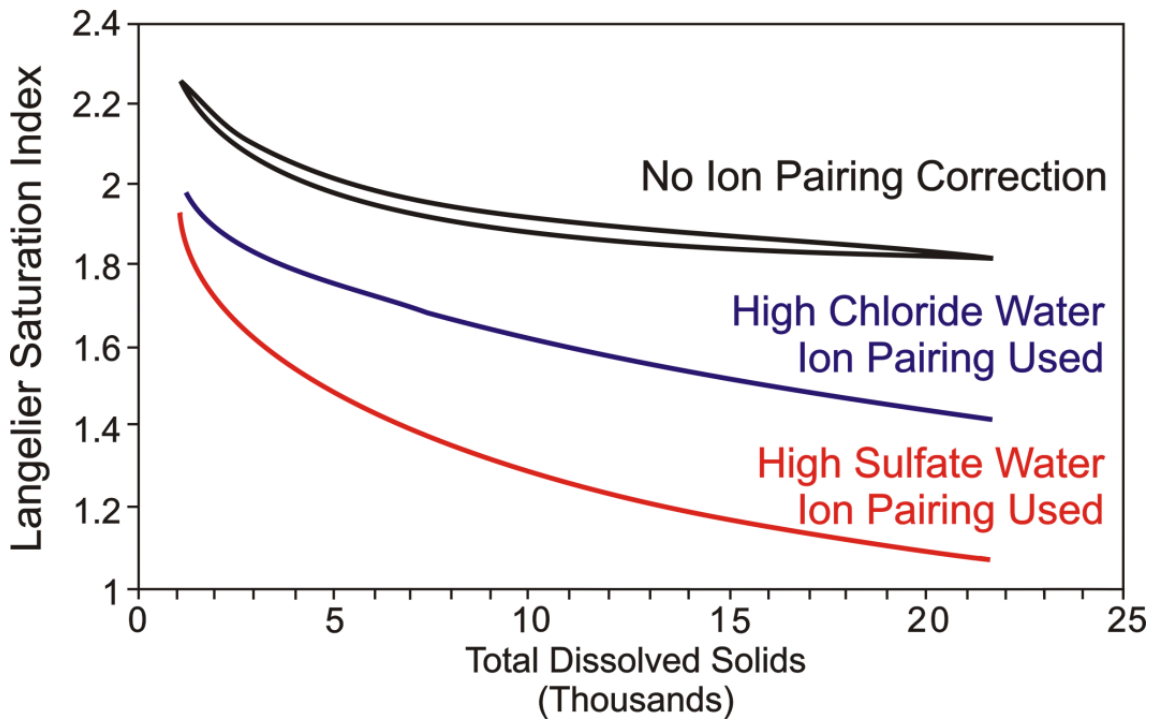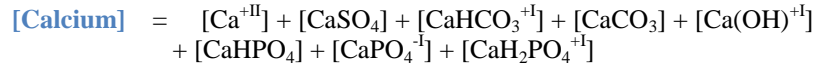## (Sulfate Effect Greater Than Chloride)

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.

This paper uses ion association model saturation levels to represent scale potential so that the limits described can be translated directly to both high and lower TDS waters, low and high
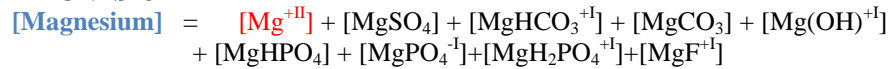
sulfate waters. Each chemistry evaluation accounts for over 120 ion pairs. Table 2 outlines some of the ion pairs used in the model.

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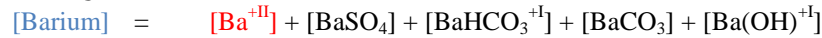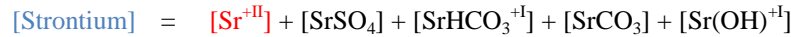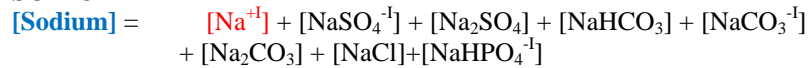
CALCIUM

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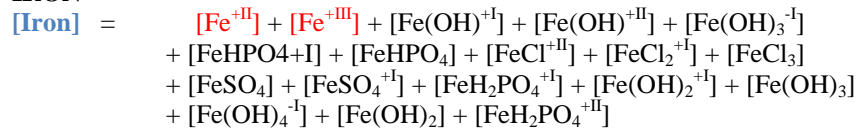$+ [AlF_3] + [AlF_4^{-I}] + [AlSO_4^{+I}] + [Al(SO_4)_2^{-I}]$

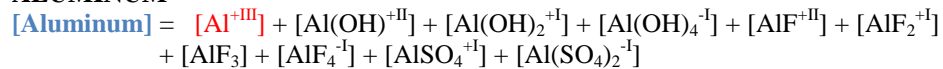**Total Analytical Value**   **Free Ion Concentration**

MYSTERY SCALES

Mystery scales are not so mysterious in other areas of water treatment. Both $BaSO_4$ and $SrSO_4$ are commonly evaluated in oil field and reverse osmosis applications. But Barium sulfate and strontium sulfate are not scales typically found in, or analyzed for, in cooling water systems. Their formation would not be expected in cooling systems operated in traditional concentration ratio ranges, using fresh water makeup. As concentration ratio increases, and/or less desirable waters are used for make-up, barium and strontium based scales can become troublesome.

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The chemistry of barite ($BaSO_4$) compares to calcite ($CaCO_3$) as follows:

- Barite solubility increases with temperature, as opposed to the inverse temperature solubility of calcium carbonate.
- Barite solubility is for the most part pH independent as opposed to the high pH dependence of calcium carbonate.
- Barite solubility is lower than calcium carbonate.

Celestite ($SrSO_4$) chemistry compares to calcite ($CaCO_3$):

- Celestite solubility decreases with temperature, like calcium carbonate.
- Celestite solubility, like that of barite, is for the most part pH independent as opposed to the high pH dependence of calcium carbonate.
- Celestite solubility is higher than calcium carbonate.

Pure barite or celestite scale is not typically encountered in operating systems. Most barite scales will contain strontium within the crystal lattice.[12]

Figures 2 and 3 show the impact of low levels of barium and strontium in a make-up water upon $BaSO_4$ and $SrSO_4$ scale potential. It is of interest that 0.007 mg/L of barium in a make-up water will not cause a problem, even in the absence of treatment, when present in a typical surface water and when concentrated in the range of 1 to 5 cycles. Pushing the concentration ratio above ten times can create a scale previously not encountered, if untreated. It is recommended that barium and strontium be included in the analysis of make-up waters for use in systems to be operated at high cycles, or when new water sources from reuse are to be concentrated.

Table 3 compares the solubility of common scales at 25°C and 50 °C, and provides a note on the general solubility trends as temperature increases. Please note that the solubilities are shown as solubility product and as the compound. The compound values are for reference only. Please note that solubility trends are more complicated than two points can demonstrate. Gypsum solubility, for example, increases with temperature to the 20°C to 30°C range and then decreases with further increase in temperature.

Different forms may also be expected in different temperature ranges. For example, gypsum is expected at lower temperatures, while anhydrite would form preferentially at higher temperatures.

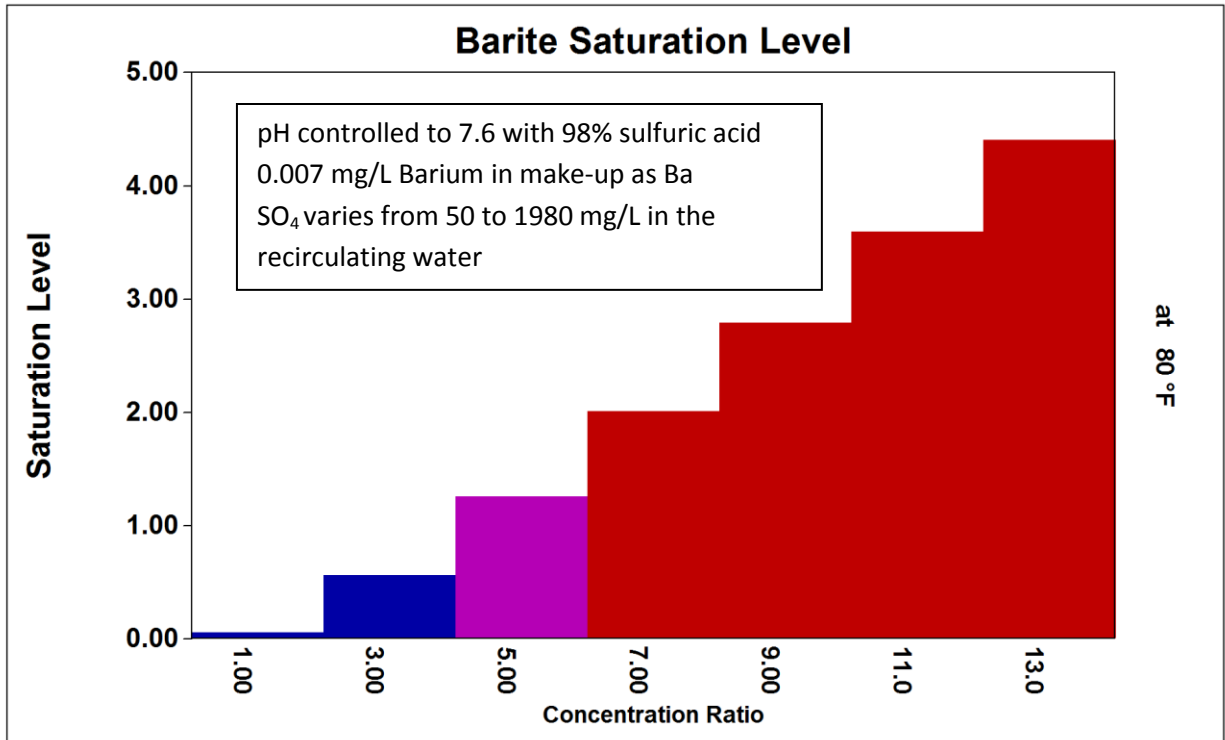## FIGURE 2: THE IMPACT OF EXTREMELY LOW BARIUM IN MAKE-UP

Barite Saturation Level

pH controlled to 7.6 with 98% sulfuric acid
0.007 mg/L Barium in make-up as Ba
SO_4 varies from 50 to 1980 mg/L in the
recirculating water

at 80 °F

FIGURE 3: THE IMPACT OF STRONTIUM IN MAKE-UP

Celestite Saturation Level

pH controlled to 7.6 with 98% sulfuric acid
2.2 mg/L Strontium in make-up as Sr
SO_4 varies from 50 to 1980 mg/L in the
recirculating water

at 160 °F
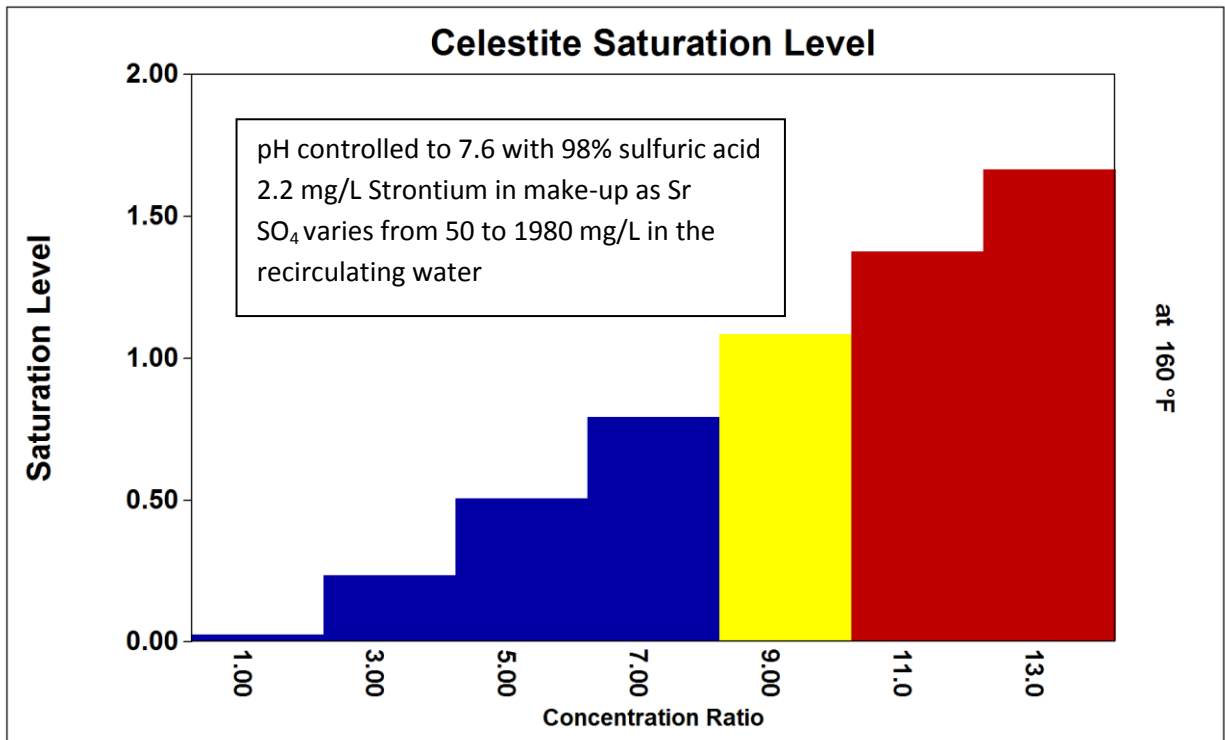
TABLE 3: SOLUBILITY PRODUCT COMPARISON					
SCALE FORMING SPECIE	FORMULA	MINERAL	Ksp 25°C (mg/L)	Ksp 50°C (mg/L)	Solubility Change As Temperature Increases
Calcium carbonate	$CaCO_3$	Calcite	4.27e-9 (6.84)	2.81e-9 (3.81)	Decreases
Calcium sulfate	$CaSO_4*2H_2O$	Gypsum	2.62e-5 (881)	2.42e-5 (778)	Increases then Decreases
Barium sulfate	$BaSO_4$	Barite	1.07e-10 (2.20)	2.16e-10 (5.75)	Increases
Strontium sulfate	$SrSO_4$	Celestite	2.23e-7 (89.6)	1.85e-7 (63.6)	Increases then Decreases
Silica	SiO_2	Amorphous silica	1.95e-3 (103)	3.48e-3 (209)	Increases
Tricalcium phosphate	$Ca_3(PO_4)_2$		2.00e-29 (0.56)	4.68e-30 (0.42)	Decreases

The same scale inhibitors that are effective against calcium carbonate and calcium sulfate are usually also effective in controlling strontium and barium derived scales. Limits are compared in Table 4. Scale inhibitors have not been observed to be effective above the upper limit, regardless of dosage. [13]

TABLE 4: 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

COOLING SYSTEM EVALUATION

The Nalco Handbook lists the barium concentration for Lake Michigan water at Chicago as 0.018 mg/L as Ba. This would be deemed insignificant by most water treatment chemists dealing with systems operating in the 1 to 4 cycle range. Even this low level of barium can create a scale problem at higher cycles, particularly with H_2SO_4 feed for pH control.

Table 5:   MAKE-UP WATER USED FOR SIMULATIONS

Lake Michigan   at Chicago

CATIONS		ANIONS	
Calcium (as $CaCO_3$)	80.00	Chloride (as $CaCO_3$)	5.00
Magnesium (as $CaCO_3$)	41.00	Sulfate (as $CaCO_3$)	1.00
Barium (as $CaCO_3$)	0.02	"M" Alkalinity (as $CaCO_3$)	113.0
Sodium (as $CaCO_3$)	19.00	"P" Alkalinity (as $CaCO_3$)	0.00
Potassium (as $CaCO_3$)	0.00	Oxalic acid (as C_2O_4)	0.00
Ammonia (as $CaCO_3$)	0.00	Cyanide (as HCN)	0.00
Aluminum (as $CaCO_3$)	0.00	Phosphate (as PO_4)	0.00
Zinc (as Zn)	0.00	Pyrophosphate(as PO_4)	0.00
Fluoride (as $CaCO_3$)	0.00	Boron (as $CaCO_3$)	0.00

PARAMETERS		COMMENTS
pH	8.20	
Temperature (°F)	77.00	
Calculated T.D.S.	222.19	
Calculated Cond.	263.92	

In a high cycle or zero blowdown scenario, a profile of Barite ($BaSO_4$) saturation level versus cycles and pH is a valuable tool for evaluating the need for treatment. Barite saturation ratio increases as pH decreases due to the sulfate added by the sulfuric acid used for pH control.

Figure 4 profiles the dosage requirements to control barite and celestite scale at higher cycles. Note that a dosage of 0.47 mg/L is recommended by the computer models at 13 cycles, pH 7.6, and 80 °F. The low temperature is used for the $BaSO_4$ evaluation because barite solubility increases with temperature. The dosage is significantly lower than would be fed for calcium carbonate scale control.

Figures 5 and 6 profile the $BaSO_4$ scale potential and dosage requirement over a broad range of pH and cycles to simulate the high cycles and drift limited cycles conditions.

Figure 7 profiles the $CaCO_3$ scale potential over the operating range. Note that the simulation was run at 120 °F due to reverse temperature solubility relationship for calcite. Figure 8 depicts the dosage requirements for $CaCO_3$ inhibition.

It should be noted that the dosage for $CaCO_3$ control is higher than the dosage required for $BaSO_4$ control. This scenario can easily reverse for makeup waters with only a slightly higher barium concentration.

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 ($CaCO_3$). [14] Figures 9 and 10 are derived from this, and related works, by Mason Tomson and his graduate students at Rice University.

Figure 9 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 10 profiles the saturation level range for barite, 0 to 80x saturation.

Figure 9: Induction Time versus Calcite Saturation Level

Figure 10: Induction Time versus Barite Saturation Level
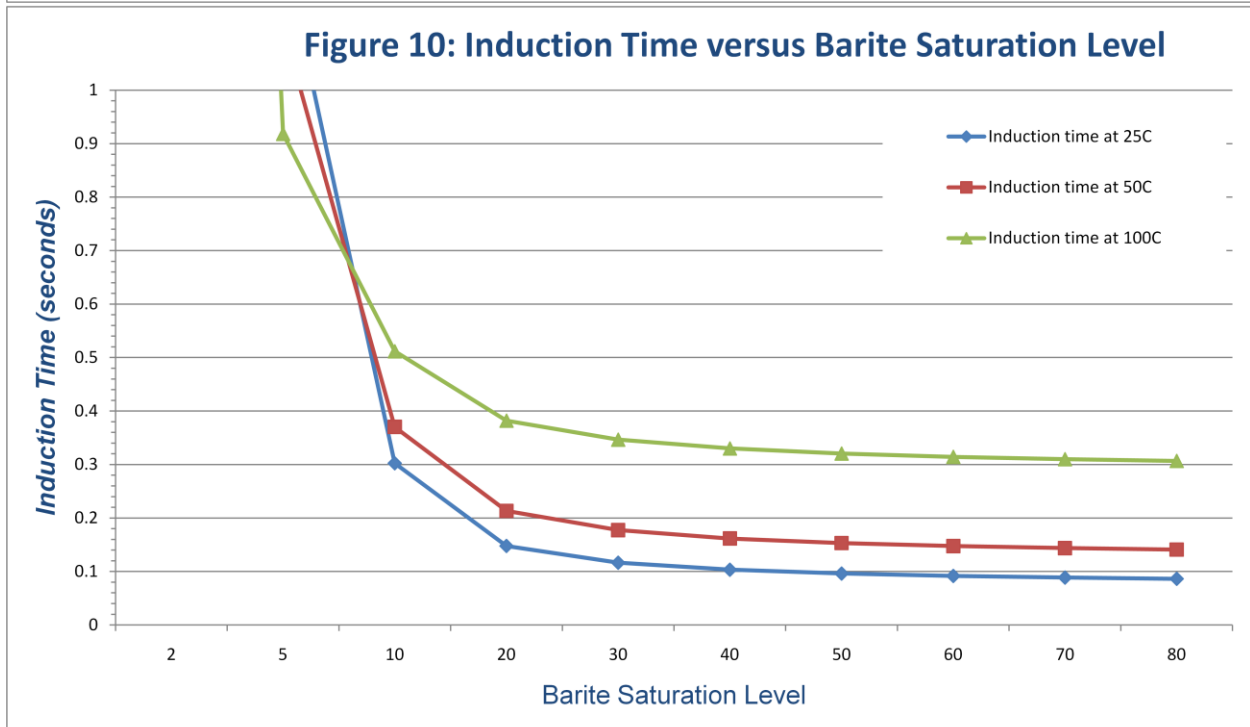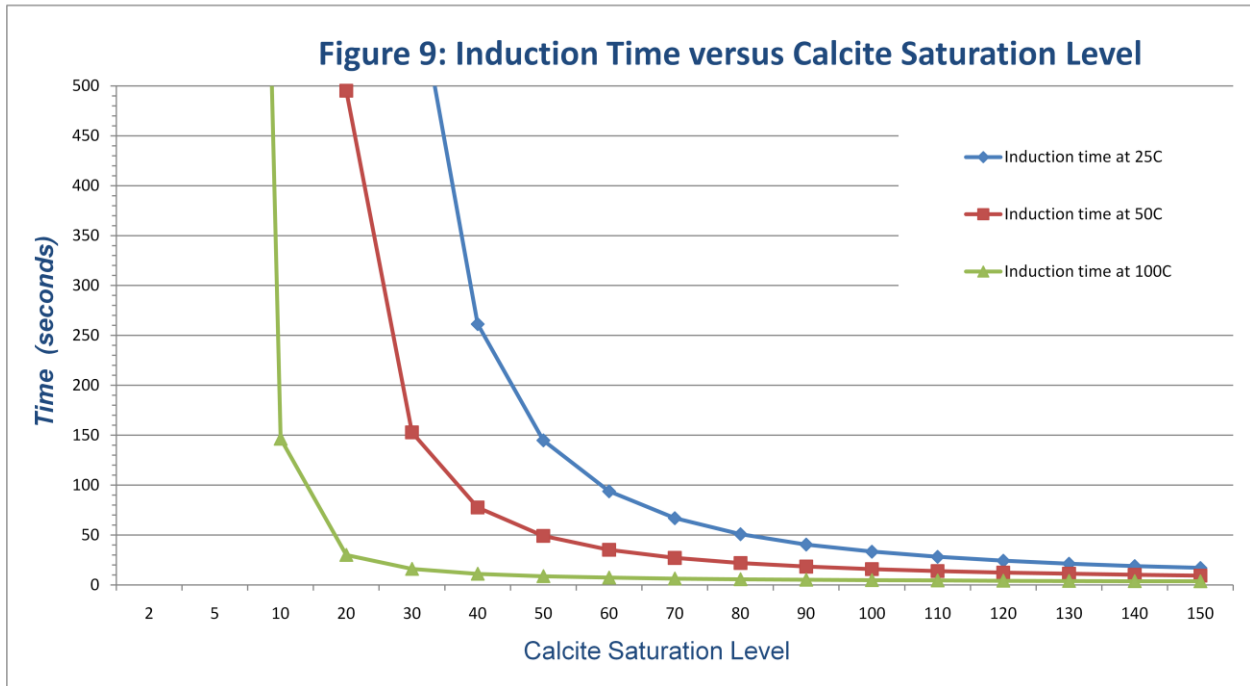
It should be noted that the induction times for both calcite and barite are several orders of magnitude below the typical residence time in an open recirculating cooling tower system. As a result, the use of the thermodynamic saturation ratios for predicting scale is accurate and an acceptable practice in typical cooling tower operating ranges.

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 cooling tower 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.[15, 16]

Induction Time Extension: 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: [17]

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

where **Time** is the induction time
     inhibitor is the scale inhibitor molar concentration
     k is a temperature dependent rate constant
     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 4.

SUMMARY

The greening of industry is pushing concentration ratios in cooling towers to new heights. Less desirable water sources are also increasingly being employed as make-up water as water re-use within plants increases. Even produced waters are being considered for industrial cooling applications. These factors can result in previously rare scales such as barite ($BaSO_4$) and celestite ($SrSO_4$). pH control of higher cycle systems also adds sulfate to the recirculating water, further aggravating the potential for barium and strontium based scales. Prudence dictates that barium and strontium should be added to routine analysis for cooling water make-up, at least during the survey phase. Deposit analysts should also be on the lookout for barium and strontium based scales. Fortunately, many of the phosphonates and polymers routinely used for calcium carbonate and calcium sulfate control are also effective in controlling barium and strontium based scales. Dosage requirements, however, may be different. The additional step of determining the minimum dosage requirement for barium and strontium based scales is recommended when barium is present in the make-up water.

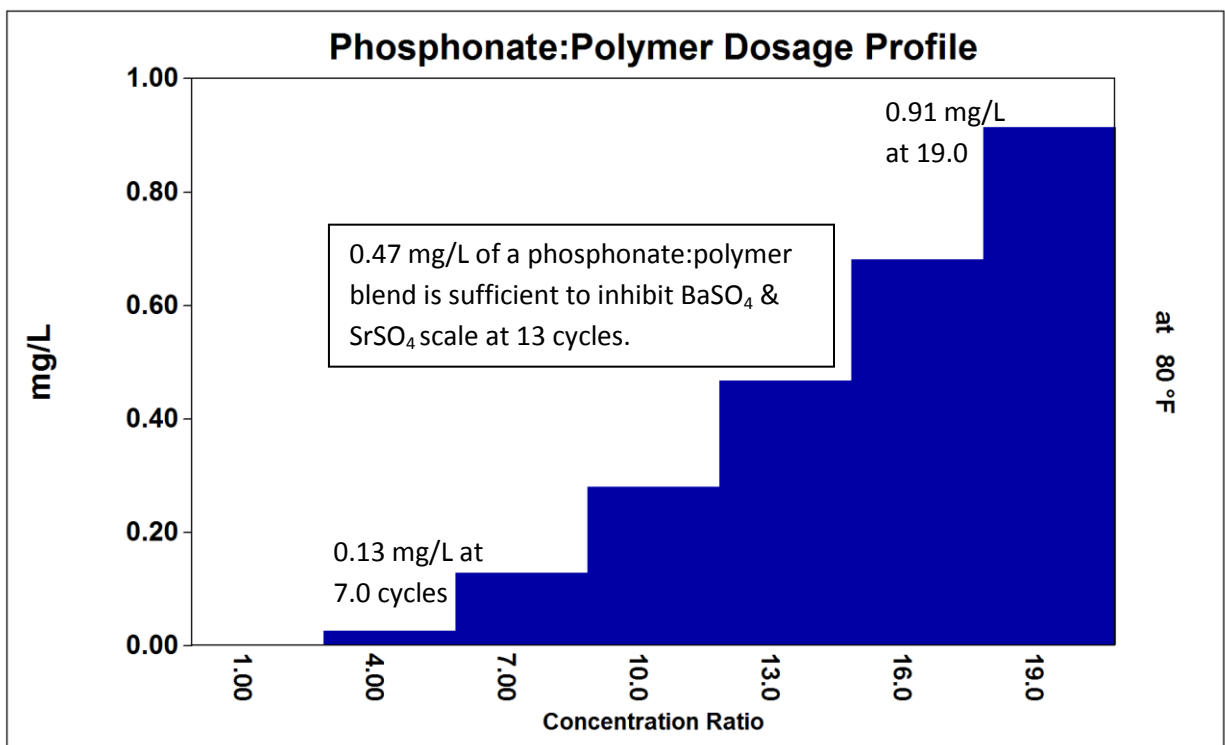**FIGURE 4: TREATMENT REQUIRED FOR $BaSO_4$ & $SrSO_4$ CONTROL**

Phosphonate:Polymer Dosage Profile

FIGURE 5: BaSO$_4$ SCALE POTENTIAL PROFILE WITH pH CONTROL

Barite Saturation Level
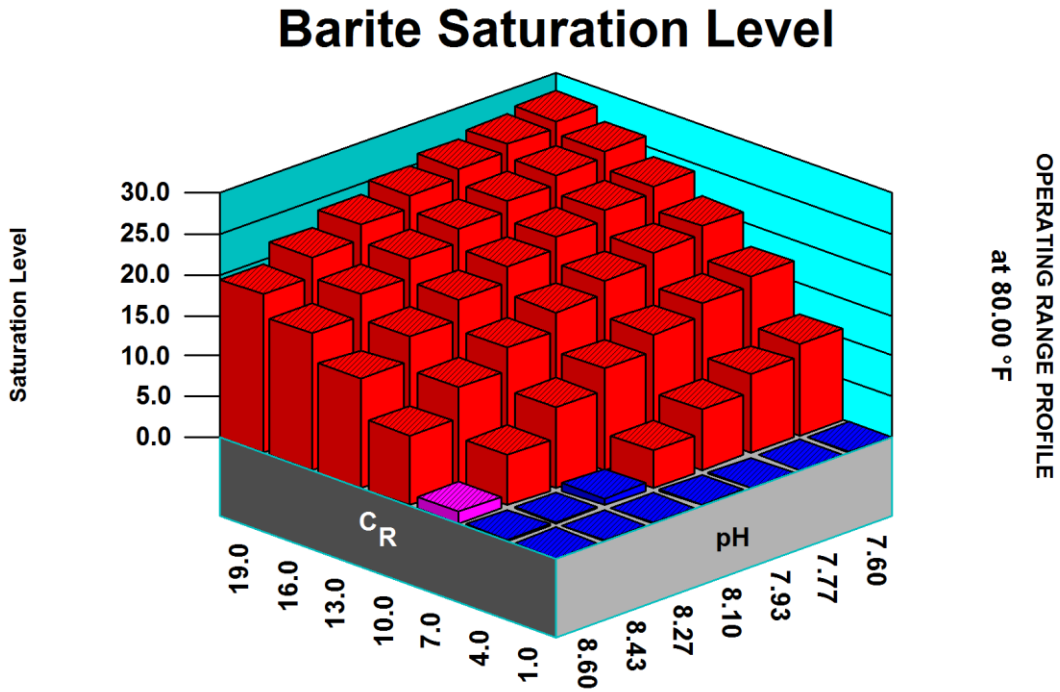
FIGURE 6: TREATMENT REQUIREMENT FOR BaSO$_4$ and SrSO$_4$

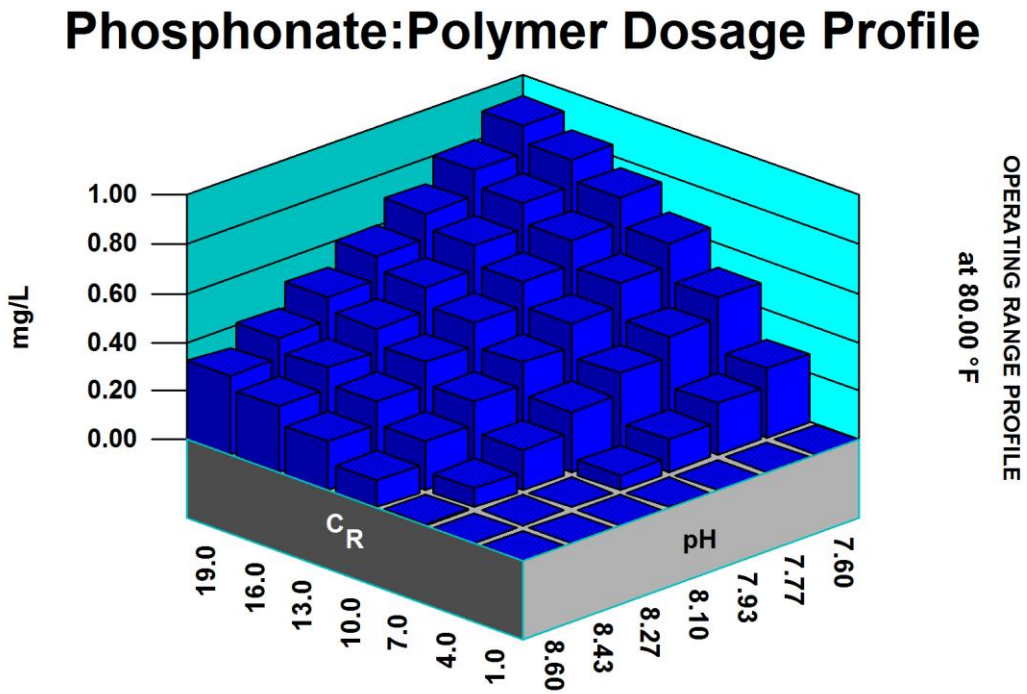Phosphonate:Polymer Dosage Profile

FIGURE 7: CaCO₃ SCALE POTENTIAL PROFILE
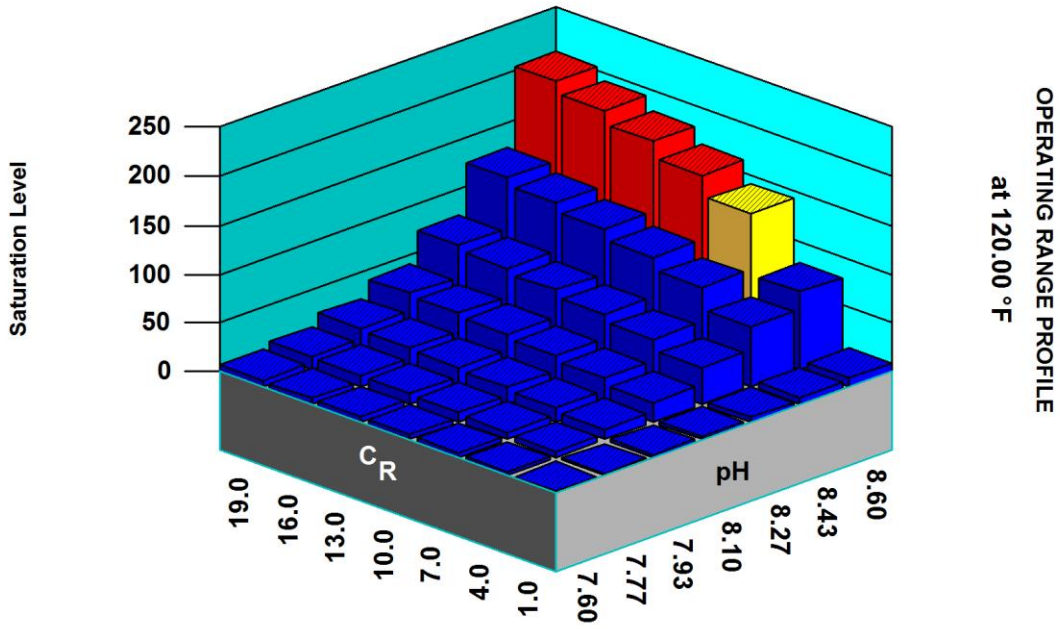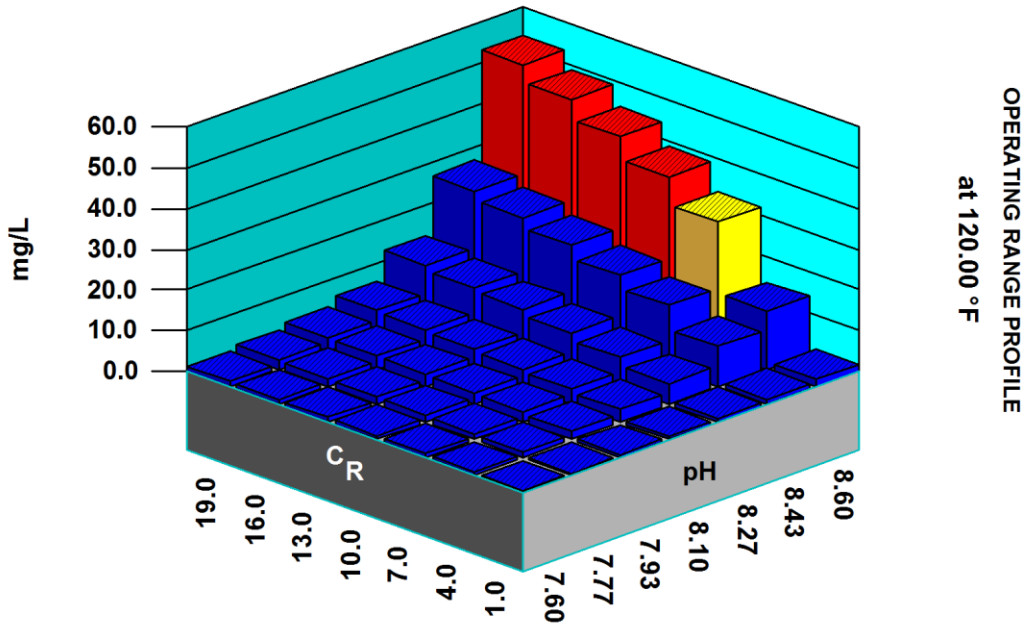

Calcite Saturation Level

FIGURE 8: TREATMENT REQUIRED FOR CaCO₃ CONTROL

Phosphonate:Polymer Dosage Profile

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