

Water Treatment Rules of Thumb: Myths or Useful Tools

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ABSTRACT

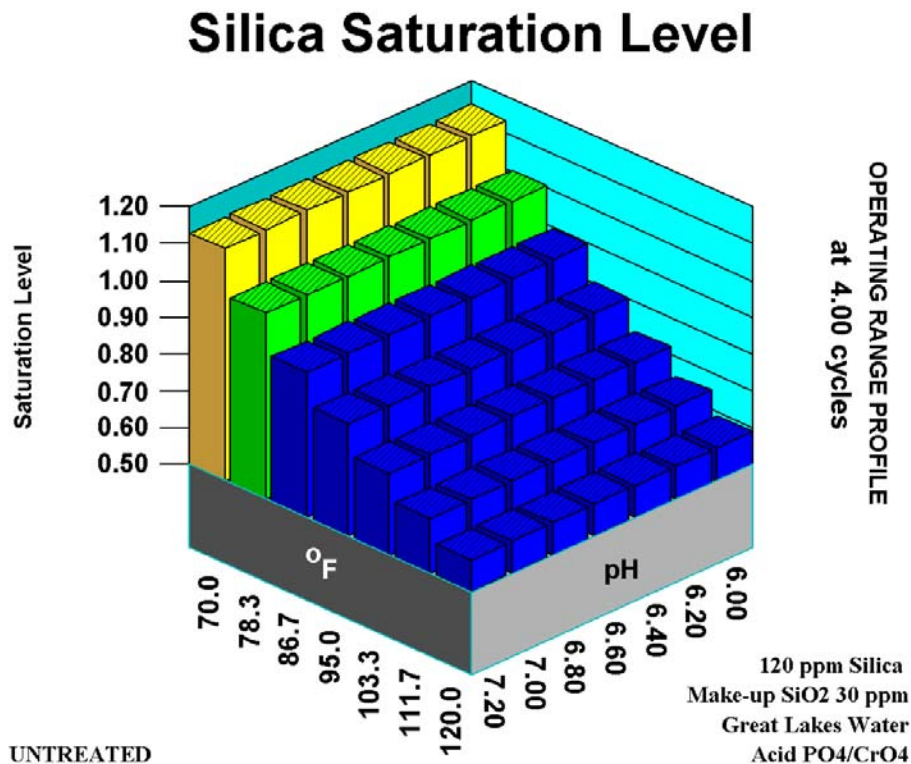
Water treatment chemists have used simple rules of thumb and indices since the early days of water treatment. The rules and indices are used to predict scale formation and in many cases, to determine the maximum concentration ratio for a tower's operation, and the control pH. Indices and rules of thumb are a way to estimate scale prediction when more rigorous, and accurate, methods are not available or practical. The availability of high powered Pentium class calculation power, and ion association model software for water chemistry modeling and prediction, have made more precise calculations economical for even the smallest water treater.

This paper reviews common water treatment rules of thumb, their origin, and compares them to ion association model saturation indices. Such a comparison reveals the general applicability and limitations of rules of thumb and simple indices. Where applicable, Rules of thumb are presented as summarized in the Association of Water Technologies Technical Reference and Training Manual.

SILICA RULES OF THUMB

120 mg/L (acid chromate) – 150 mg/L (alkaline zinc/alkaline PO4) - 180 mg/L (High pH)

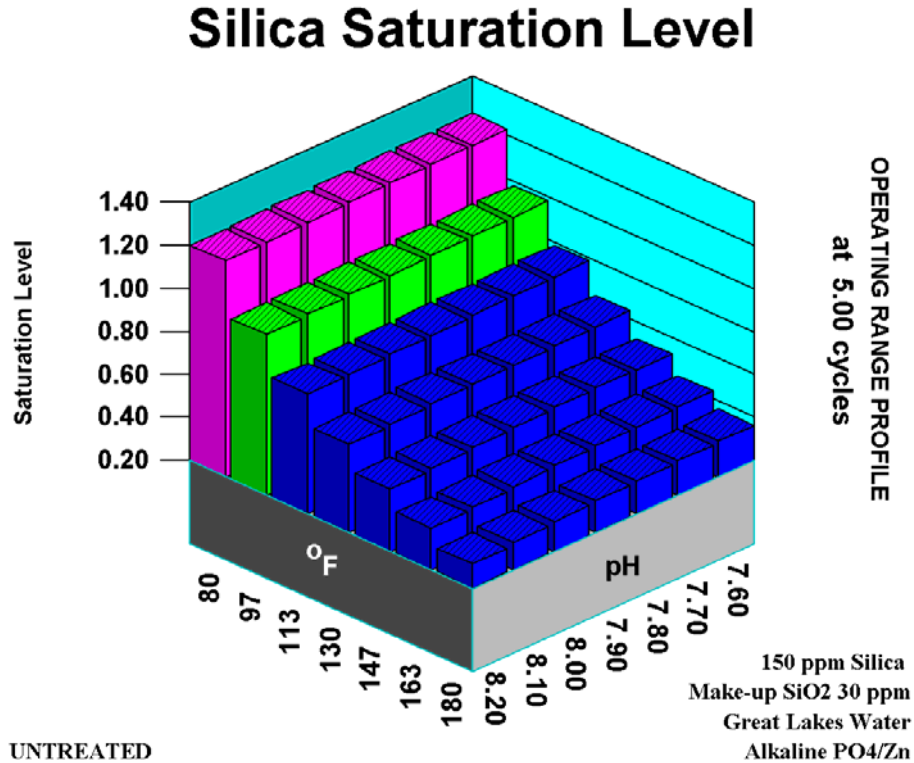
In the days of acid chromate and acid phosphate treatment programs many cooling water treatment programs were operated with a control limit of 120 ppm silica as SiO₂. The alkaline treatments of the 1970's raised the ante to 150 ppm. All organic treatment programs, with little or no pH control, further increased the control limits to 180 ppm. This section reviews these limits in terms of program operating conditions.



ACID CHROMATE/ACID PHOSPHATE TREATMENT: Figure 1 depicts silica saturation levels at the 120 ppm SiO₂ limit in an acid chromate or phosphate pH control range. It can be seen that the water becomes saturation with silica (1.0 x saturation) at ambient temperature (25 °C, 77 °F).

This early guideline equates to the solubility of silica in a slightly acidic pH range. Such a limit is based on the solubility of amorphous silica at a typical lowest system temperature. It should be noted that most published values for silica solubility are at 25 °C.

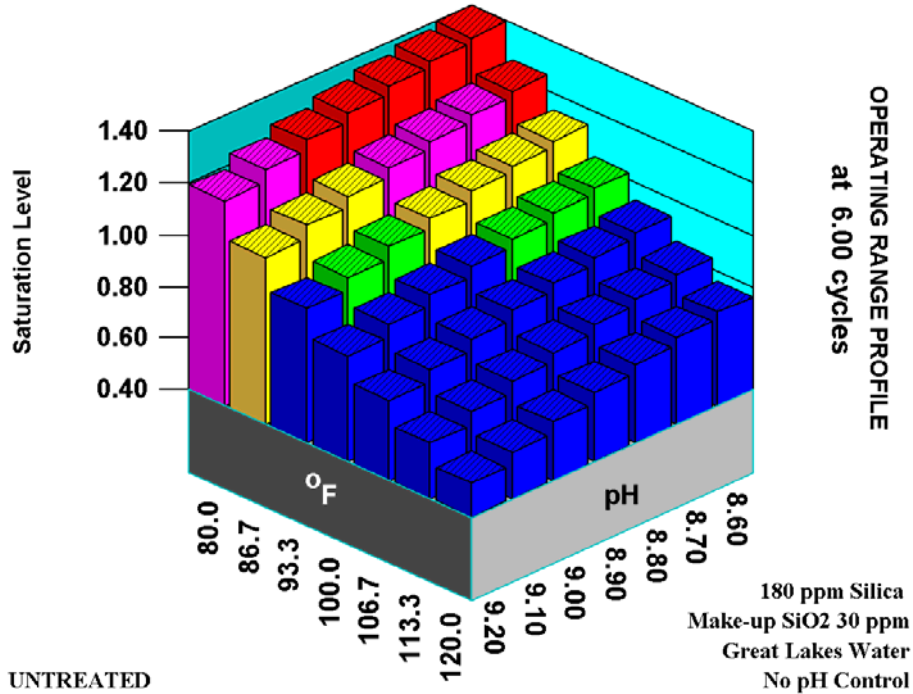
Acid control range programs relied upon pH control for calcium carbonate scale control. A slight upwards pH excursion could result in calcium carbonate precipitation. Silica limits were conservative in acid pH range programs to prevent silica precipitation for “hardening” calcium



NEUTRAL TO ALKALINE TREATMENT RANGE: Figure 2 depicts silica saturation levels at the 150 ppm SiO₂ limit common for alkaline chromate/zinc, alkaline phosphate, and alkaline zinc treatments. These programs typically operate in the 7.6 to 8.2 pH range. It can be seen that the water becomes saturation with silica (1.0 x saturation) at ambient temperature (25 °C, 77 °F).

This early guideline equates to the solubility of silica in a slightly alkaline pH range. Such a limit is based on the solubility of amorphous silica at a typical lowest system temperature.

Silica Saturation Level



NO pH CONTROL ALKALINE TREATMENT RANGE: Figure 3 depicts silica saturation levels at the 180 ppm SiO₂ limit common for alkaline treatment programs run at the limit of calcium carbonate scale control. These programs typically operate in the 8.6 to 9.0+ pH range. It can be seen that the water becomes saturation with silica (1.0 x saturation) at ambient temperature (25 °C, 77 °F).

This early guideline equates to the solubility of silica in an alkaline pH range. Such a limit is based on the solubility of amorphous silica at a typical lowest tube wall temperatures and the upper end of calcium carbonate scale control for common inhibitors.

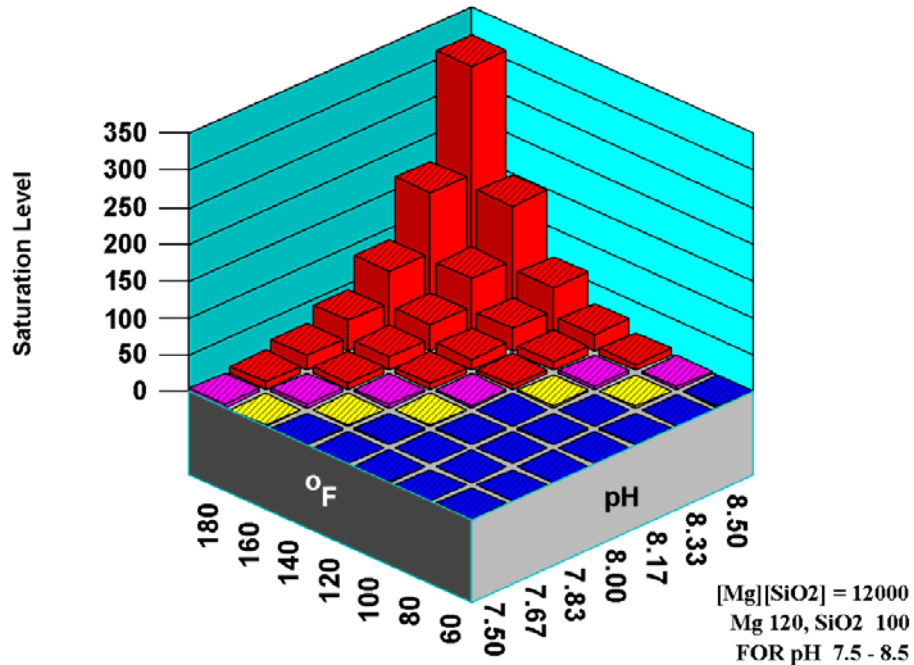
SILICA RULES OF THUMB COMAPRISON SUMMARY				
Program	Limit	pH Range	Temperature	Comments
Acid Chromate Acid Phosphate	120 ppm SiO ₂	5.8 – 7.2	1.0 x Saturation at 77 °F	pH adjustment for CaCO ₃ , Ca ₃ (PO ₄) ₂ control
Alkaline Zinc Alkaline PO ₄	150 ppm SiO ₂	7.2 – 7.6	1.0 x Saturation at 85 °F	Phosphonates/Polymers for CaCO ₃ , Ca ₃ (PO ₄) ₂ control
No pH Control	180 ppm SiO ₂	8.6 – 9.0+	1.0 x Saturation at 85 °F	Phosphonates/Polymers for CaCO ₃ , Ca ₃ (PO ₄) ₂ control

MAGNESIUM SILICATE RULES OF THUMB

Stoichiometric, Adsorption on Mg(OH)₂

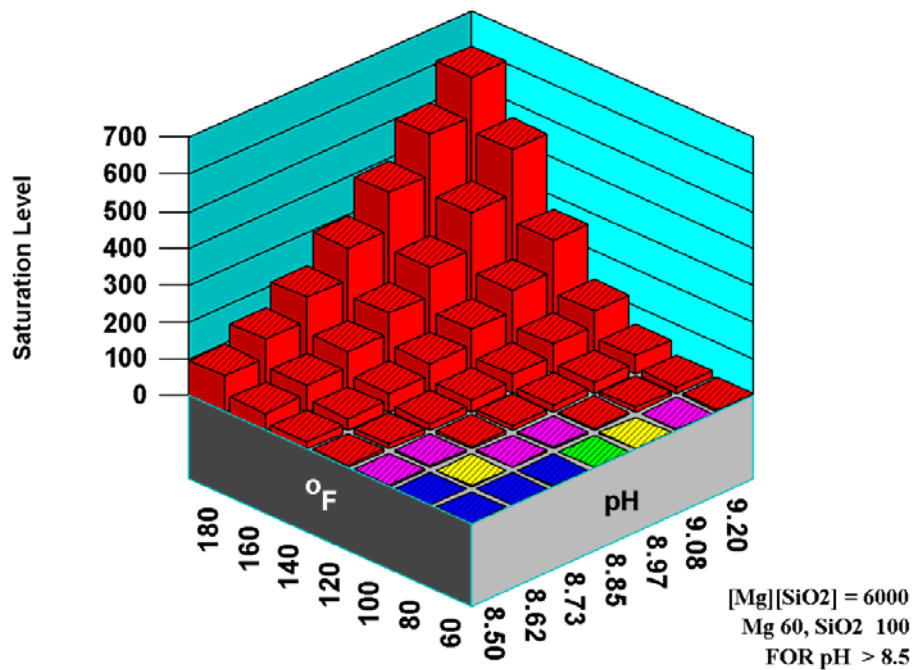
Rules of thumb for magnesium silicate are more complex than for other potential scales. They are divided into pH zones, as outlined in Table 2.

Magnesium Silicate Saturation



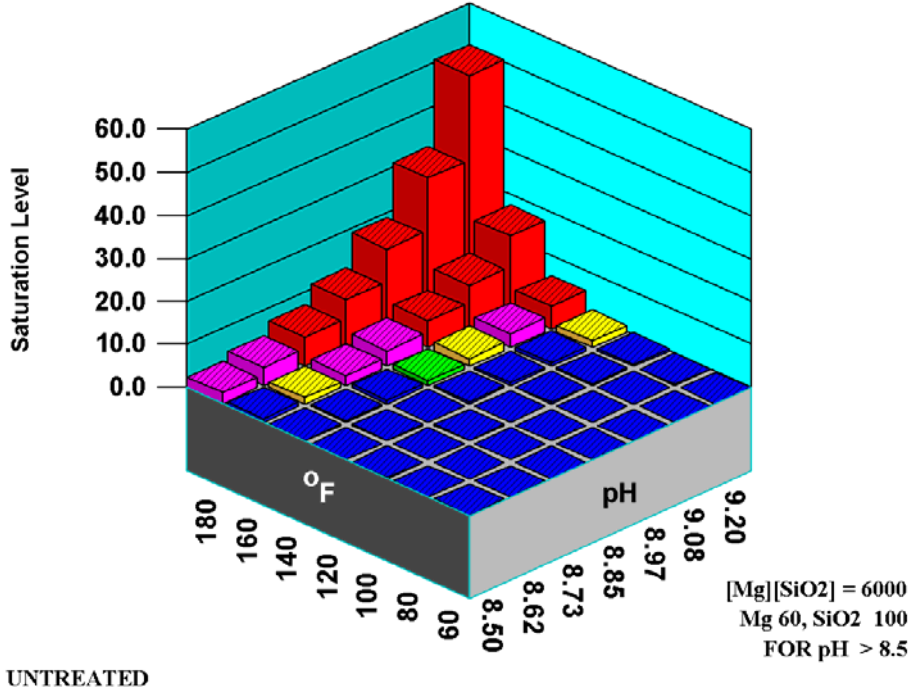
UNTREATED

Magnesium Silicate Saturation

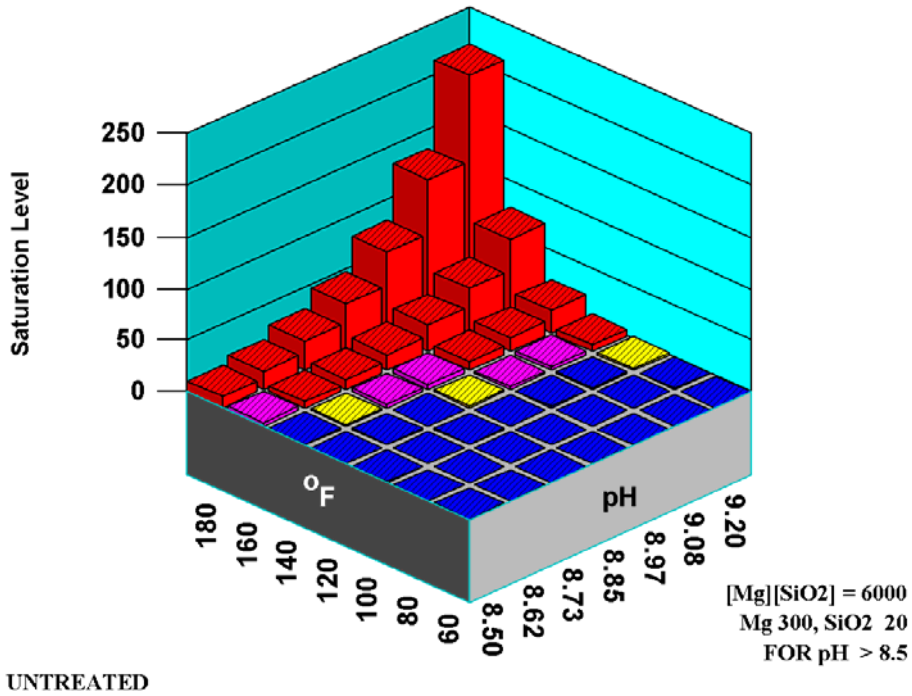


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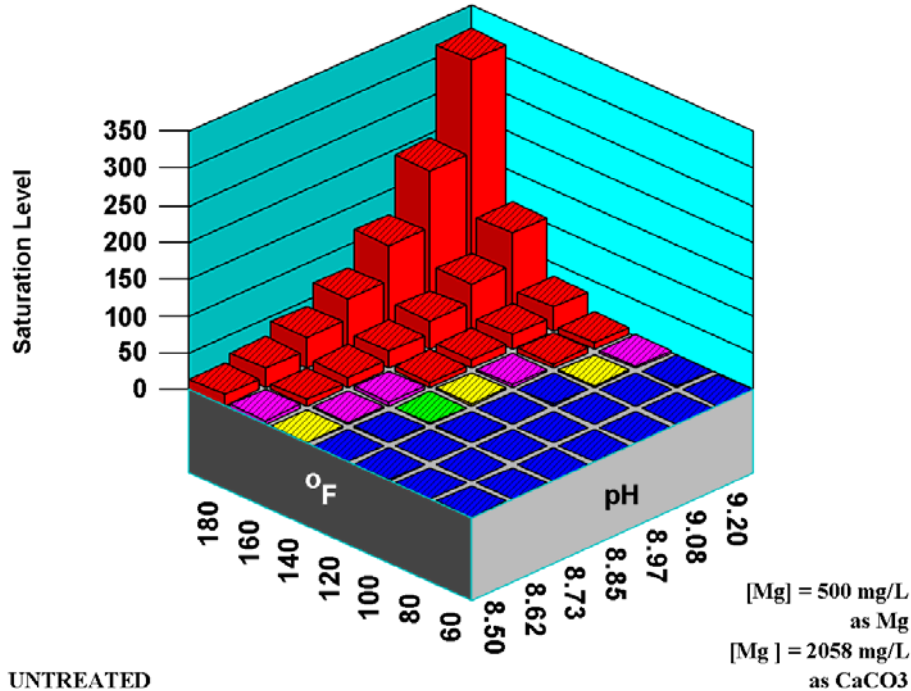
Brucite Saturation Level



Brucite Saturation Level



Brucite Saturation Level



CALCIUM SULFATE RULES OF THUMB

$[Ca][SO_4] < 500,000$ untreated, $[Ca][SO_4] < 10,000,000$ treated

Rules of thumb recommend carrying an ion product $[Ca][SO_4]$ of less than 500,000 in an untreated system, or up to 10,000,000 in a system treated with standard inhibitors. Table 2 compares these limits to ion association model saturation levels for gypsum and anhydrite. Gypsum is the expected form of calcium sulfate scale in cooling systems. Anhydrite is more prevalent at temperatures above those normally encountered in cooling water.

CALCIUM SULFATE RULES OF THUMB COMPARISON				
MINERAL FORM	UNTREATED RULE OF THUMB	ION ASSOCIATION MODEL SATURATION LEVEL AT LIMIT	TREATED RULE OF THUMB	ION ASSOCIATION MODEL SATURATION LEVEL AT LIMIT
GYPSUM $CaSO_4 \cdot 2H_2O$	$[Ca][SO_4] < 50,000$	0.96 (at 120 °F)	$[Ca][SO_4] < 10,000,000$ Ca as mg/L Ca, SO ₄ as mg/L SO ₄	4.98 X Saturation (at 120 °F)
ANHYDRITE $CaSO_4$	Ca as mg/L Ca, SO ₄ as mg/L SO ₄	0.99 (at 120 °F)		3.10 X Saturation (at 120 °F)

It can be seen that the untreated rule of thumb limit corresponds to an ion association model saturation level of approximately 1 at 120°F. The treated limit corresponds to a gypsum saturation level of 5 at 120°F.

Saturation level guidelines for treatment of calcium sulfate are commonly an upper limit of 2.5 X saturation for gypsum using common scale inhibitors such as AMP, HEDP, and PAA. This corresponds to a $[Ca][SO_4]$ product of 2,400,000. The recommended limit for specific Calcium sulfate inhibitors such as those in the phosphino carboxylic acid family is 5 X Saturation, and corresponds to the 10,000,000 $[Ca][SO_4]$ ion product limit.

The rules of thumb for calcium sulfate agree with ion association model saturation levels at 120°F. As with other rules of thumb, care should be taken in using them at temperatures other than 120°F. The rules of thumb become less reliable as the temperature deviates from 120°F.

CALCIUM CARBONATE RULES OF THUMB

Simple Indices, Ion Association Saturation level, Treated, Untreated

Simple indices are frequently used to predict the formation of Calcium carbonate scale, to determine maximum cycles of concentration, and to establish a pH control range. Rules of thumb have also been established for upper limits of common scale inhibitors based upon simple indices. The most frequently used indices in cooling water treatment are those developed by Langelier, Ryznar and Brookes. This section discusses the advantages and disadvantage of each index and compares them to more rigorous calculated indices such as ion association model saturation indices.

CALCIUM CARBONATE RULES OF THUMB				
Index	Untreated Limit	Treated Limit	Stressed Inhibitor Limit	Comments
Langelier Saturation Level	0.0 – 0.2	2.5	3.0	Use alkalinity corrected for noncarbonate (e.g. NH ₃ , CN, PO ₄ , Si) alkalinity.
Ryznar Stability Index	6.0 – 5.8	4.0	3.5	Empirical rearrangement of pH and pHs used to calculate Langelier Saturation Index.
Practical Scaling Index	6.0 – 5.8	4.0	3.5	Interpretation similar to Ryznar. Index applicable to NH ₃ or other alkali contaminated waters. Calculates a pH as if only carbonic acid based alkalinity present.
Calcite Saturation Level	1.2 – 2.5	135 – 150	200 - 225	Index corrects for ion pairing, noncarbonate alkalinity, activity effects. Reproducible results at the same index.

Simple indices and the more rigorous ion association model saturation levels are both derived from the basic solubility equation

$$\{Ca\} \{CO_3\} = K_{sp} \text{ at equilibrium}$$

where Ca is the calcium activity
 CO₃ is the carbonate activity
 K_{sp} is the solubility product.

The simple indices and saturation levels differ in how these properties are calculated. The biggest difference is in the handling of ion pairs, or bound ions.

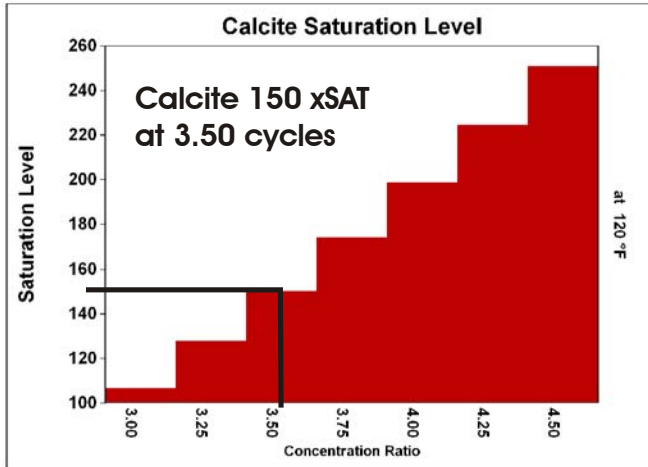
Sulfate, for example, readily forms calcium sulfate aqueous, making some of the calcium unavailable to participate in the formation of calcium carbonate scale. Simple indices, like the Langelier Saturation Index, ignore the formation of aqueous calcium sulfate and similar species. As a result, the simple indices tend to exaggerate the scale potential in high sulfate waters. Rigorously calculated ion association saturation levels are not affected. This phenomena is covered extensively in the literature.^{1,3}

Practically, the use of simple indices can lead to operation at lower than optimum cycle of concentration in high sulfate waters. Common inhibitors, for example, can prevent calcium carbonate scale formation up to a calcite saturation level of 150, which equates to a Langelier Saturation Index of 2.5 in low sulfate waters. Scale control is lost above these limits. Figure compares the limits in a low sulfate water. Figure compares the Langelier Saturation Index and the calcite saturation level in a high sulfate water. The bound ion effect becomes extremely significant in the high sulfate example.

Reliance on the Langelier Saturation Index limit of 2.5, rather than the ion association model calcite saturation level limit of 150, would result in operation at 3.5 rather than actual limit of 4.2 cycles, in this case.

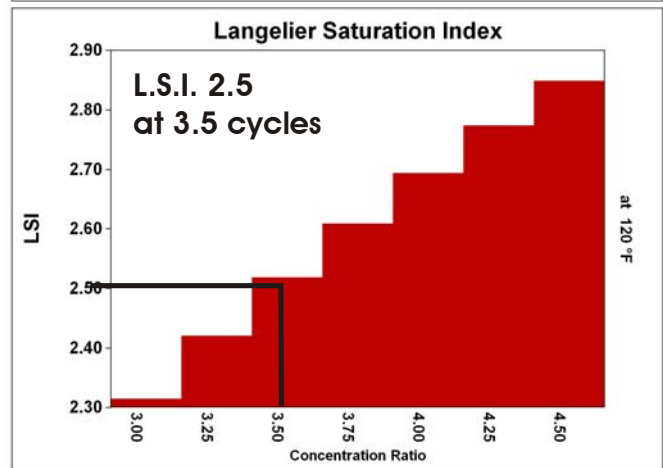
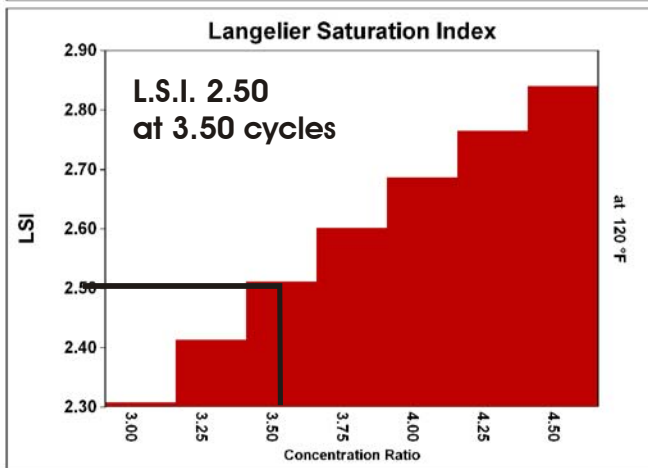
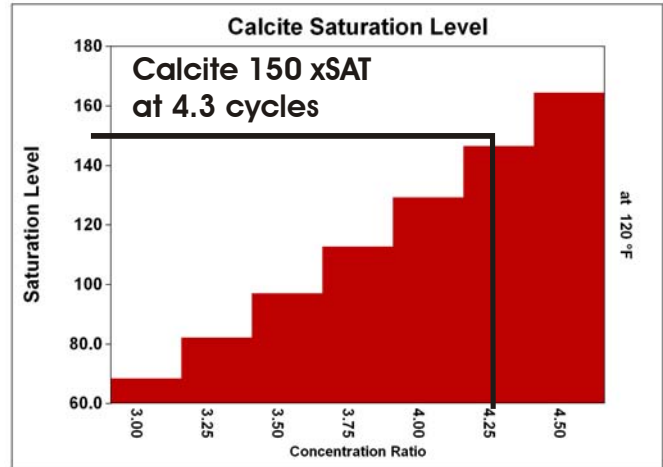
High Chloride Makeup

LSI 2.5 cycles = Calcite 150 xSAT cycles



High Sulfate Makeup

LSI 2.5 cycles << Calcite 150 xSAT cycles



Similar effects are encountered when comparing calcite saturation level limits to other simple indices such as the Ryznar Stability Index, and Practical Scaling Index.

SUMMARY

Rules of Thumb, in general, were derived from simplified saturation level calculations. They provide quick-and-dirty guidelines for troubleshooting, evaluating a system. In most cases, they are applicable to a single temperature and become less effective as predictive tools the further an operating system is from the temperature at which the Rule of Thumb was meant to apply.

Ion Association model saturation levels are the preferred method for evaluating scale potential, and establishing control limits. Computerized systems allow the evaluation of scale potential over a broad operating range and can more accurately pin point limits.

Although they can be useful tools, Be leery of Rules of Thumb at extremes of pH, temperature, dissolved solids.

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