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Water Treatment Rules of Thumb: Myths or Useful Tools?

By Robert J. Ferguson, French Creek Software, Inc.

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 article reviews common water treatment rules of thumb and their origins and compares them to ion association model saturation indices. 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 (AWT) Technical Reference and Training Manual.

Silica Rules of Thumb

120 mg/L (acid chromate); 150 mg/L (alkaline zinc/alkaline PO_4); 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 mg/L silica as SiO_2 . The alkaline treatments of the 1970s raised this value to 150 mg/L. All-organic treatment programs, with little or no pH control, further increased the control limits to 180 mg/L. This section reviews these limits in terms of program operating conditions.

Acid Chromate/and Phosphate Treatment: **Figure 1** depicts silica saturation levels at the 120 mg/L SiO_2 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. This 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 upward 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 mg/L 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. The limit is based on the solubility of amorphous silica at a typical lowest system temperature.

No pH Control Alkaline Treatment Range: **Figure 3** depicts silica saturation levels at the 180 mg/L SiO₂ limit common for alkaline treatment programs operate at the limit of calcium carbonate scale control. These programs typically operate in the 8.6 to 9.0 or greater 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. The 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.

Table 1: Rules of Thumb Combination Summary				
Program	Limit	pH Range	Temperature	Comments
Acid Chromate Acid Phosphate	120 mg/L 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 mg/L 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 mg/L 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 can form in a cooling system via two distinct mechanisms: through the formation of a stoichiometric MgSiO₃ and through interaction with precipitating magnesium hydroxide.

Figure 4 | Figure 5 | Figure 6 | Figure 7 | Figure 8 | Figure 9

Table 2: Magnesium Silicate Rules of Thumb		
Applicable pH Range	Ion Product Limit	Comments

Acid Chromate pH < 7.5	$[Mg][SiO_2] < 17,000$ Mg as mg/L Mg, SiO ₂ as mg/L SiO ₂	Stoichiometric magnesium silicate expected. Mg(OH) ₂ undersaturated.
pH 7.5 - 8.5	$[Mg][SiO_2] < 12,000$ Mg as mg/L Mg, SiO ₂ as mg/L SiO ₂	Stoichiometric magnesium silicate expected. Mg(OH) ₂ undersaturated except at extremes of pH, temperature and magnesium concentration.
pH > 8.5	$[Mg][SiO_2] < 6,000$ Mg as mg/L Mg, SiO ₂ as mg/L SiO ₂	May be supersaturated in Mg(OH) ₂ . Silica absorption/adsorption within/upon precipitating brucite {Mg(OH) ₂ mineral} expected.

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 3 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.

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.

Table 3: 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 •2H ₂ O	$[Ca][SO_4] < 50,000$ Ca as mg/L Ca, SO ₄ as mg/L SO ₄	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		0.99 (at 120 °F)		3.10 x Saturation (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 as shown in Table 4.

Table 4: 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 and 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:

$$[\text{Ca}][\text{CO}_3] = \text{Ksp at equilibrium}$$

where Ca is the calcium activity, CO_3 is the carbonate activity and Ksp is the solubility product.

The simple indices and saturation levels differ in how these properties are calculated. The biggest difference is in accounting for 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 10a** compares the limits in low sulfate

water. **Figure 11a** compares the Langelier Saturation Index and the calcite saturation level in 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, as shown in **Figure 10b** and **Figure 11b** respectively.

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

In general, rules of thumb were derived from simplified saturation level calculations. They provide quick and easy guidelines for troubleshooting and 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 pinpoint limits.

Although they can be useful tools, be leery of rules of thumb at extremes of pH, temperature and dissolved solids.

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AWT Recertification CEU Quiz

Based on the The Analyst Article from Summer 2004, Titled " Water Treatment Rules of Thumb: Myths or Useful Tools?" by: Robert J. Ferguson , French Creek Software, Inc.

- 1) Which of the following indices corrects for ion pairing, non-carbonate alkalinity and activity effects?
 - a) PSI (Practical Scaling Index)
 - b) LSI (Langelier Saturation Index)
 - c) CSI (Calcite Saturation Index)
 - d) RSI (Ryznar Stability Index)
- 2) Indices and Rules of Thumb are the most accurate methods to use in all circumstances to predict precipitation:
 - a) True
 - b) False
- 3) Which chemical program increases Silica saturation levels to 180 mg/L SiO_2 ?
 - a) Alkaline Zinc and Phosphate with pH 7.2 to 7.6
 - b) Phosphonates/Polymers and no pH control
 - c) Acid Chromate and Phosphate with pH 5.8 to 7.2
 - d) EDTA
- 4) What is the Magnesium Silicate Ion Product limit Rule of Thumb, when pH of the water is over 8.5 units?
 - a) < 12,000
 - b) <17,000
 - c) <16,000
 - d) <6,000
- 5) Which of the following inhibitors can increase the saturation limit by 5 times, when dealing with Calcium Sulfate Rules of Thumb?
 - a) Phosphino carboxylic acid
 - b) HEDP
 - c) AMP
 - d) PAA

- 6) Simple indices are commonly used for all of the following purposes, except:
- a) Establish cooling water pH control range
 - b) Determine the maximum Cycles of Concentration
 - c) Predict formation of Calcium Sulfate precipitate
 - d) Predict formation of Calcium Carbonate precipitate
- 7) A rise in LSI may indicate all but one of the following:
- a) Decrease in Calcium Carbonate precipitation likelihood
 - b) Increase in Magnesium Silicate precipitation likelihood
 - c) Increase in Calcium Carbonate precipitation likelihood
 - d) Rise in non-carbonate alkalinity in pairing
- 8) Examples of non-carbonate alkalinity include all except:
- a) Phosphate
 - b) Bicarbonate
 - c) Silica
 - d) Sulfate
- 9) To achieve maximum Cycles of Concentration without precipitating Calcium Carbonate where high levels of non-carbonate alkalinity are present, the best index to use would be:
- a) LSI
 - b) CSI
 - c) RSI
 - d) PSI
- 10) Rules of Thumb are reliable at all ranges of pH, Temperature, and dissolved solids:
- a) True
 - b) False