AQUARIUS

Scaling Indices

Encrustation of tubing, boilers, coils, jets, sprinklers, cooling towers, and heat exchangers arise wherever hard water is used. Scale formation can greatly affect heat transfer performance. One mm thick scale, for example, can add **7.5% to energy costs**, while **1.5 mm adds 15%** and **7 mm can increase cost by over 70%**. Many factors can affect scaling. Scaling, which is basically the deposition of mineral solids on the interior surfaces of water lines and containers, most often occurs when water containing the carbonates or bicarbonates of calcium and magnesium is heated. The following sections will describe some indices that have gained wide acceptance in the corrosion community.

Langelier Saturation Index

The Langelier Index (LI), or Saturation Index (SI), is probably the most commonly used scale index. It is based on the chemical equilibrium equation for calcium carbonate ($CaCO_3$) and is an indicator of the tendency of water to deposit or dissolve $CaCO_3$. LI is given by:

$$\mathbf{LI = pH_a - pH_s}$$

Where: pH_a :actual (measured) pH

pH_s :equilibrium pH at CaCO3 saturation = A + B - log [Ca] - log [Alk]

Both [Ca^{2+}] and [Alk] (total alkalinity) are expressed as mg/L of equivalent $CaCO_3$

A and B are correction factors that relate, respectively, to the temperature and dissolved solids content of the water. (an equation to calculate pH_s is introduced at the end of this section)

- LI < -0.5: Under-saturation with $CaCO_3$ (dissolution of $CaCO_3$)
- -0.5 < LI< 0.5: Saturation with CaCO3 (equilibrium)
- LI > 0.5: Tendency toward CaCO3 deposition (scale formation)

It is assumed that when the value of LI is negative (LI < -0.5), it indicates corrosiveness

Ryznar Stability Index

The Ryznar stability index (RSI or RI) attempts to correlate an empirical database of scale thickness observed in municipal water systems to the water chemistry. Like LI, the RI has its basis in the concept of saturation level. Ryznar attempted to quantify the relationship between calcium carbonate saturation state and scale formation. The Ryznar index takes the form:

$$\mathbf{RSI = 2(pH_s) - pH_a}$$

Where: pH_a is the measured water pH

pH_s is the pH at saturation in calcite or calcium carbonate

The following indications to RI have been introduced by Ryznar and Carrier:

RI	Indication (Ryznar 1942)
RI < 5.5	Heavy scale will form
5.5 < RI < 6.2	Scale will form
6.2 < RI < 6.8	No difficulties
6.8 < RI < 8.5	Water is aggressive
RI > 8.5	Water is very aggressive

RI	Indication (Carrier 1965)
4.0 – 5.0	Heavy Scale
5.0 – 6.0	Light Scale
6.0 – 7.0	Little Scale or Corrosion
7.0 – 7.5	Significant Corrosion
7.5 – 9.0	Heavy Corrosion
> 9.0	Corrosion intolerable

Ryznar gives only an indication about the aggressiveness of the water but carrier gives an indication about the scale and corrosion potential of the water.

In general the empirical correlation of the Ryznar stability index can be summarized as follows:

- **RSI < 6** the scale tendency increases as the index decreases
- **RSI > 7** the calcium carbonate formation probably does not lead to a protective corrosion inhibitor film
- **RSI > 8** mild steel corrosion becomes an increasing problem.

Puckorius Scaling Index (PSI)

The PSI attempts to quantify the relationship between saturation state and scale formation by incorporating an estimate of buffering capacity of the water into the index.

Water high in calcium, but low in alkalinity and buffering capacity can have a high calcite saturation level. The high calcium level increases the ion activity product. A plot of ion activity product versus precipitate for the water would show a rapid decrease in pH as calcium precipitated due to the low buffering capacity. Even minuscule decreases in carbonate concentration in the water would drastically decrease the ion activity product due to the small quantity present prior to the initiation of precipitation.

Such water might have a high tendency to form scale due to the driving force, but scale formed might be of such a small quantity as to be unobservable. The water has the driving force but not the capacity and ability to maintain pH as precipitate matter forms.

The PSI index is calculated in a manner similar to the Ryznar stability index. Puckorius uses an equilibrium pH rather than the actual system pH to account for the buffering effects:

$$\mathbf{PSI = 2\,(pH_s) - pH_{eq}}$$

Where:

- pH_s is the pH at saturation in calcite or calcium carbonate
- pH_{eq} = 1.465 x log10[Alkalinity] + 4.54
- and [Alkalinity] = $[HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-]$

Larson-Skold Index and **Oddo-Tomson Index** are another two water quality indices which are not very popular in cooling towers systems.

It should be stated that all above indices are designed to indicate the tendency of given waters to deposit scales on metal substrates and surely not to predict the absolute corrosivity of specific waters. Generally speaking, scales precipitated onto metal surfaces can provide protection of the substrate from general corrosion. If on the other hand the scales are defective and contain voids and/or cracks, they could lead to localized corrosion. The assumption that water below saturation with respect to calcium carbonate is corrosive, while occasionally correct, is not reliable.

How to calculate pH_s :

$$pH_s = (9.3 + A + B) - (C + D)$$

$$A = \frac{(Log_{10}[TDS] - 1)}{10}$$

$$B = -13.12 \times Log_{10}(°C + 273) + 34.55$$

$$C = Log_{10}[Ca^{2+} as\ CaCO_3] - 0.4$$

$$D = Log_{10}[alkalinity\ as\ CaCO_3]$$

(from http://corrosion-doctors.org/Corrosion-by-Water/Scaling-indices.htm)