This document contains comments offered on April 4, 2005 at CORROSION 2005. For more details, contact www.nace.org *to order a reprint of Paper No. 05063.*

SATURATION, STABILITY, AND SCALING INDICES

Robert R. Cavano – Scranton Associates, Incorporated

I. Introduction

Time is short so we will plunge right into this exciting saga of scaling indices, acknowledge their productive uses, uncover their severe limitations, and overlook their frequent mis-interpretations. We will present a drama filled with mystery and intrigue where scaling indicator break points are regularly published and tediously described, but where most practitioners use entirely different values. What is more, we must sadly recount a tale of treachery and favoritism where the speaker who discloses these improprieties is allotted less than twenty minutes while the one from Imperial Oil is given forty-five.

But these violations couldn’t possibly occur in Texas or at NACE, so we quickly move on. In doing so, we provide you with one of the best of the 623 papers scheduled for this conference --- one of only three not utilizing a Power Point presentation or requiring a sleep-inducing darkened room. There are no visuals at all. It’s all verbal, just as in the good old days!

We begin by asking if scale will form in a particular cooling water system and describe the extent of its accumulation by one or more reproducible and easily interpreted measures. Good Luck to you all and may the good Lord bless and help us!

One of my friends, possibly my only one, cancelled his dentist appointment to hear this paper. Originally, it was intended as a two semester college course but we don’t even have enough time today to cover the single spaced, nineteen page preprint let alone its 16 tables and 53 endnotes. I guess that a mere fifteen minutes of fame is better than none at all!

II. On to Stipulations

In Houston, or Hoeston as New Yorkers call it, lawyers sometimes stipulate. And to do so is perfectly legal, even in Texas. The contesting parties agree to agree on certain listed documents -- sort of a consensual, textual relationship.

Mr. Cunningham, your honor, we ask that you allow us to submit a preprint and to stipulate that:

A. Scale and fouling in cooling waters presents a complex and serious problem.
B. We should develop guidelines to predict the formation of deposits -- not
    wait until they form and the system fails.
C. Those predictions should assist us in selecting and applying treatment chemicals
    at optimal levels.

III. Let's Talk About Scale Formation

First we must learn whether reductions in heat transfer are likely to occur, and for what reasons. If we only recognize and deplore deposits in their totality, we need not name them. But if we hope to remove or prevent them, we need to determine both their nature and their origin.

To do this properly, we must obtain or develop an accurate definition of the water we will be treating, rather than the one we started with. Waters that are acceptable as we receive them become less so as they concentrate and as their temperatures increase.

We often evaluate a system by looking at a single water chemistry and only one set of operating conditions -- choosing the "worst case scenario". A more thorough understanding of scale potential can be had by evaluating the full range of possible outcomes. This can most conveniently be done with the WaterCycle® software program.

IV. Have You Ever Heard of Scaling Indicators?

The proclivity for calcium carbonate scale to form in a given water develops from many variables. Efforts to combine all of them into one meaningful number have engendered a multiplicity of indicators and very little consensus on interpretation.

The most commonly used indicators have been the Langelier Saturation Index (LSI), the Ryznar Stability Index (RSI), and the Puckorius Scaling Index (PSI). Methods for calculating these indices are well documented, and approximate values can be readily obtained from tables, nomographs, slide rules, and computer programs, including hand-held calculators.

LSI, RSI, and PSI are designed to be predictive tools for calcium carbonate scale and only that! They are **not** suitable for estimating calcium phosphate, calcium sulfate, silica or magnesium silicate scale. These indices can only be used accurately for untreated water or with treatments (phosphonates and acrylates) that "solubilize" calcium carbonate.

They are **not** useful for predicting calcium carbonate scale creation in waters already treated with "crystal modifiers" since such treatments (polymaleates, sulfonated styrene/maleic anhydride, or terpolymers) cause foulants to precipitate, but do not result in a true scale.

Each scaling index leads a non-linear life of its own, somewhat resistant to calculation and interpretation, especially by students from Texas Tech who haven't spent a lot of time on exponentials or logarithms. Don't worry though! We will try to use only "natural" logarithms so as to not offend any of you purists, and we'll try to warn you, usually in non-numerical terms, of the risks present in each and every one of these indicators.

Since the indices are non-arithmetic, estimates of the degree of scaling are not easily or immediately comprehended. For example, the quantity of scale added by a PSI change from 4.5 to 4.0 is much greater than one resulting from the same half unit change from 6.0 to 5.5.

Unfavorable experiences with early indices can be attributed, in part, to the fact that many important water characteristics had not been included in the calculations. Fortunately, tools to obtain and work with these additional sources of information are now available. The improved indicators are helpful in determining initial operating limits and treatment requirements, but they can never fully replace a complete water analysis and the careful monitoring of performance.

V. Saturation pH (pH_s)

Let us now speak of the Saturation pH (also known as pH_s). It describes the value attained when all of the various forms of alkalinity are adjusted to the point where the water is just saturated in calcium carbonate.

Earlier calculations of this pH did not take into account the many competing equilibria – again mostly because of major computational difficulties. Sulfate, for example, readily becomes calcium sulfate, leaving less calcium available to form calcium carbonate. A more precise way to calculate saturation pH was lacking but later found. This saturation level (however determined) then became the foundation for the three leading indices, utilizing relationships between the actual pH, the saturation pH (pH_s) and the equilibrium pH (pH_{eq}).

VI. Langelier Saturation Index (LSI)

First we come to that old household favorite, the lan-je-leer or longe-lee-ay Saturation Index, the LSI. The concept and formulas for this legendary standard and its essential component the saturation pH (pH_s) were introduced by Dr. Langelier way back in 1936 in order to predict the tendencies of a water to precipitate (or dissolve) calcium carbonate.

The LSI was designed to measure calcite formation in municipal distribution lines at ambient temperatures, but subsequently (and questionably) was adapted for cooling towers and later (erroneously) used as a measure of corrosion. Further enlightenment about the deficiencies of the LSI caused many of us to become increasingly more skeptical about in its interpretation.

In spite of many valid reasons for moving away from LSI and over to RSI and PSI, we now see a strong but puzzling return. One possible reason for this resurgence is that the LSI approximates the common logarithm of the calcite saturation, thereby becoming a convenient tool for conversion between indices.

The LSI index ($LSI = pH - pH_s$) may be positive, negative, or neutral. Rather than using the published value of LSI = 0 as a break point, many experienced observers show a preference for values greater than 1.5 or 1.7 (even as high as 2.5) as warning of scale formation --- and those less than negative 1.5 as indications of aggressive water.

VII. What is the Ryznar Stability Index (RSI)?

In 1944, John Ryznar proposed substantial modification of the Langelier index. He had seen that it was, surprisingly, possible for low hardness and high hardness waters to both have the same LSI. Ryznar named his creation the Stability Index ($RSI = 2pH_s - pH$) to differentiate it from Langelier's Saturation Index and he justified this re-statement with experimental data.

By changing the placement of the two variables (pH and pH_s), Ryznar obtained values which better estimated the severity of scaling tendencies and, in addition, were always positive. It is important that they be positive --- because if some of you can't handle logarithms, how in the hell can you be expected to cope with negative numbers?

Rather than worshiping the usual value of RSI = 6 as a break point, we might better use RSI values at < 5 or > 7 as the regions of most concern -- though some experts consider that only waters at < 4.5 are definitely scale forming and only those > 8.5 are clearly aggressive.

VIII. Should You Use the Puckorius Scaling Index (PSI)?

Another major adjustment to the scaling index took place when the actual pH used in the LSI and RSI was replaced by the equilibrium pH (pH_{eq}). pH_{eq} is defined as 1.465log(M Alk) + 4.54, a good estimate of the alkalinity of cycled water. The resulting indicator, the PSI ($PSI = 2pH_s - pH_{eq}$), was developed by Paul Puckorius and Maxey Brooke in about 1980 in response to difficulties they had encountered with existing measures.

Conveniently, the PSI uses the same numbering systems and descriptions (and general interpretation) as does the RSI, and, thank goodness, it is also always positive. While the PSI appears to be an improvement over the other indicators for many applications, it is not completely free of the imprecisions described earlier.

IX. The Last Indicator We Discuss Is the Calcium Saturation Index (CSI)

Limitations for all of the earlier approaches were well recognized and widely lamented. Due to the many complex pairings possible, the standard analytical methods designed for total calcium and total carbonates, did not tell the full story of a system and were not sufficiently reproducible among systems.

What was needed was a more rigorous assessment of the potential for calcium carbonate scale to form under the various conditions of heat transfer – an in-depth profile for a cooling system over its entire operating range.

Eventually, an improved indicator became available and is known as the Calcium Saturation Index (CSI), the relative degree of saturation of calcium carbonate. Advanced software made the many separate calculations possible and allowed a rapid evaluation of scale potential for waters of differing compositions. Software such as WaterCycle® permits the rapid calculation of CSI and of many other water parameters.

X. Several Observations About Corrosion

Scaling indicators were never intended to measure corrosive tendencies towards mild steel or other metals, but rather to describe the degree of aggressiveness towards calcium carbonate scale. In fact, they give little or no attention to chloride and sulfate content, among the most widely recognized contributors to corrosion.

Paul Puckorius suggested that " … cooling water … is always corrosive, mainly because of the presence of dissolved oxygen and dissolved solids." This is true even when the water is scale-forming, and particularly true if it is not scale-forming.

XI. What Does All of This Mean and Where Does This Leave Us?

With many apologies, most of us continue to use one or more of these old indices. If a practitioner selects, becomes familiar with, and uses them with suitable restraint, they can be helpful. The ultimate choice will most likely be made on the basis of previous conditions of servitude or because of identification with French, Polish, or Lithuanian antecedents.

Predicting scale formation is as much an art as a science. So we pursue our art -- recognizing that an indicator or product which has worked for us should continue to be used -- until such time as it can be replaced with something demonstrably better. But let's not wait too long!

Your Honor! The court having earlier accepted our stipulations, we now ask that it grant a continuance until there has been further comments and questions.