Swimming Pool Water Balance

Part 7: A Revised and Updated Saturation Index Equation

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At a given temperature, swimming pool water chemistry must be balanced by adjusting pH, carbonate alkalinity, and calcium hardness in order to maintain the proper saturation with respect to calcium carbonate to avoid etching of concrete, plaster, and tile grout, scaling, and cloudy water. Water balance is determined by means of the calcium carbonate saturation index (SI), which was originally proposed to provide corrosion control for iron pipes in public water distribution systems by means of deposition of thin films of $CaCO_3$ (Langelier 1936). The current saturation index equation is based on calcium carbonate solubility data published in 1929. This paper discusses revisions to the saturation index equation due to more accurate values for the calcium carbonate solubility product constant and its temperature dependence and more realistic ionic strength corrections. The revised equation is:

$$SI = pH + Log\ [Hard] + Log\ [Alk] + TC + C$$

where both hardness and alkalinity are expressed in ppm $CaCO_3$, TC is the temperature correction, and C = –11.30 – 0.333 Log TDS. The equation requires a reasonably accurate value of total dissolved solids (TDS). At 1000 ppm TDS, C is equal to 12.3. Above 1000 ppm TDS, this equation yields significantly lower values for SI than the current equation.

Derivation of the Calcium Carbonate Saturation Index Equation

The calcium carbonate saturation index equation is based on the calcium carbonate solubility product equilibrium constant (K_s), i.e., the product of the calcium $\{Ca^{2+}\}$ and carbonate $\{CO_3^{2-}\}$ ion activities (mol/L) at saturation.

$$1.\ CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad K_s = \{Ca^{2+}\}\{CO_3^{2-}\}$$

Since the activity of solids is taken as one, the concentration of calcium carbonate does not appear in the denominator of the equilibrium expression. The degree of saturation (S) of a solution is given by the ratio of the actual ion activity product and the solubility product constant:

$$2.\ S = \{Ca^{2+}\}\{CO_3^{2-}\}/K_s$$

The carbonate activity can be calculated from the bicarbonate and hydrogen ion activities based on the ionization reaction:

$$3.\ HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \quad K_2 = \{CO_3^{2-}\}\{H^+\}/\{HCO_3^-\}$$

$$4.\ \{CO_3^{2-}\} = K_2\{HCO_3^-\}/\{H^+\}$$

Where K_2 is the second ionization constant of carbonic acid. Substitution of equation 4 into equation 2 gives:

$$5.\ S = \{Ca^{2+}\}K_2\{HCO_3^-\}/\{H^+\}K_s$$

Taking logarithms, and noting that pH = Log 1/$\{H^+\}$, gives the saturation index (Log S = SI):

$$6.\ SI = pH + Log\{Ca^{2+}\} + Log\{HCO_3^-\} + Log\ K_2/K_s$$

Concentrations (mol/L) can be substituted for activities via the following relationships:

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7. $\{Ca^{2+}\} = [Ca^{2+}]\gamma Ca^{2+}$

8. $\{HCO_3^-\} = [HCO_3^-]\gamma HCO_3^-$

where $[Ca^{2+}]$ and $[HCO_3^-]$ are the concentrations (mol/L) and γCa^{2+} and γHCO_3^- the activity coefficients of calcium and bicarbonate ions, respectively. Activity coefficients of ionic species are typically less than one and approach one at high dilution. Substitution of equations 7 and 8 into equation 6 gives:

$$9.\ SI = pH + \text{Log}\,[Ca^{2+}] + \text{Log}\,[HCO_3^-] + \text{Log}\,K_2/K_s + \text{Log}\,\gamma Ca^{2+} + \text{Log}\,\gamma HCO_3^-$$

Total alkalinity is equal to $[HCO_3^-] + 2[CO_3^{2-}] + H_2Cy^- - [H^+] + [OH^-]$. For typical swimming pool water, the concentrations of H^+ and OH^- ions are negligible. In addition, the concentration of carbonate ion is very small. Therefore, alkalinity corrected for cyanurate ion (H_2Cy^-) can be substituted for bicarbonate without significant error.

$$10.\ SI = pH + \text{Log}\,[Ca^{2+}] + \text{Log}\,[Alk] + \text{Log}\,K_2/K_s + \text{Log}\,\gamma Ca^{2+} + \text{Log}\,\gamma HCO_3^-$$

Langelier's Saturation Index Formulation

Langelier (1936) calculated the pH of saturation in unstabilized water using equation 5 (with S =1). He substituted alkalinity for bicarbonate and converted activities to concentrations by introducing ionic strength corrections.

$$11.\ pH_s = -\text{Log}\,[Ca^{2+}] - \text{Log}\,[Alk] - \text{Log}\,K_2/K_s$$

He calculated SI from the algebraic difference between the actual pH (pH_a) and the pH at saturation (pH_s), i.e., the pH that the water would have if it were at equilibrium at the existing alkalinity and hardness.

$$12.\ SI = pH_a - pH_s$$

Langelier overestimated the ionic strength correction because he utilized the less accurate Debye–Hückel limiting law (which applies to ionic strengths below 0.005), i.e., $\log\gamma = -0.5z^2\sqrt{\mu}$; where: γ is the ion activity coefficient, z is the ionic charge, and μ is the ionic strength of the water. Langelier calculated the ionic strength using the formula: $\mu = 0.5\Sigma c_i z_i^2$, where c is the concentration of an individial ion in mol/L. In the absence of a total ion analysis, he also indicated that ionic strength can be estimated by: $\mu = 2.5 \cdot 10^{-5} \cdot TDS$, where TDS is total dissolved solids in ppm. He included a Table of values for Log K_2/K_s as a function of temperature and TDS in his original paper based on older data for K_2 and K_s. A revised version of the Table is shown in Langelier's discussion at the end of the paper by Larson and Buswell (1942). At 32°F, his value of Log K_2/K_s is – 2.45.

Larson and Buswell Revision

Larson and Buswell (1942) modified Langelier's equation (equation 12) by inserting equation 11, and included appropriate factors for converting mol/L to ppm (–4.70 for alkalinity and –4.60 for calcium) and a term for ionic strength correction to give the following form of the saturation index equation:

$$13.\ SI = pH + \text{Log}\,[Ca^{2+}] + \text{Log}\,[Alk] + \text{Log}\,K_2/K_s + C$$

where: $C = -9.3 - 2.5\sqrt{\mu}/(1 + 5.3\sqrt{\mu} + 5.5\mu)$, K_s is the solubility product constant for the calcite form of calcium carbonate, and the ionic strength $\mu = 2.5 \cdot 10^{-5} \cdot$ (ppm TDS). Larson and Buswell list values of K_2 and K_s at different temperatures. Their value of LogK_2/K_s is –2.60 at 0°C.

Van Waters & Rogers Modification

A familiar and common form of the saturation index equation that is widely employed in swimming pool water balance is (Van Waters & Rogers 1964):

$$14.\ SI = pH + CF + AF + TF - 12.1$$

where: AF and CF represent logarithms of the alkalinity (ppm $CaCO_3$) and calcium hardness (ppm Ca). CF, AF, and TF are called calcium, alkalinity, and temperature factors, respectively. Actually these are not factors in the strict sense of the word, since they are additive rather than multiplicative terms.

Van Waters & Rogers (1964) published a Table of values of CF, AF, and TF for calculating SI (see also Wojtowicz 1995 for a Table of these factors). However, they do not cite the reference on which this Table or the value of the constant –12.1 is based. The temperature correction factors do not agree with those calculated from Langelier's data but are in good agreement with those calculated from Larson and Buswell's data and can be represented by the equation: TF = – 0.56 + 0.01827 • °F – 0.000041 • (°F)^2. In addition, no specific information on what value of TDS that equation 14 is valid for except that it applies to an average TDS. If a TDS of 1000 ppm is assumed, then a factor of –12.10 is obtained, based on Larson and Buswell's value for Log K_2/K_s at 32°F (–2.60) and the ionic strength correction of –0.20. Thus, it appears that the equation published by Van Waters and Rogers is based on the Larson and Buswell revision of Langelier's equation.

Revised and Updated Version of the Saturation Index Equation

The saturation index equation needs to be updated because the value of the calcium carbonate solubility product and its temperature dependence has changed significantly. In addition, more appropriate ionic strength corrections are necessary since the ionic strength corrections used by Langelier and by Larson and Buswell do not conform to modern practice.

Calcium Carbonate Solubility Product – The newer more accurate value of K_s for the calcite form of calcium carbonate (Plummer and Busenberg 1982) is given by the following temperature dependent equation:

$$15.\ \text{Log } K_s = -171.9065 - 0.077993T + 2839.319/T + 71.595 \text{ Log } T$$

where T is in kelvins.

Calcium carbonate crystalizes in three distinct forms, whose solubilities vary as follows:

Calcite < Aragonite < Vaterite

Calcite is the form commonly found in water distribution lines, and has also been found in swimming pools.

Second ionization Constant of Carbonic Acid – A new empirical expression (eq. 16) for the second ionization constant of carbonic acid has been developed by critical evaluation of previous data on CO_2 – H_2O equilibria (Plummer and Busenberg 1982).

$$16.\ \text{Log } K_2 = -107.8871 - 0.032528T + 5151.79/T + 38.92561 \text{ Log } T - 563713.9/T^2$$

where T is in kelvins.

Ionic Strength Correction – Equation 10 takes the following form after substitution of calcium hardness for calcium and converting concentrations from mol/L to ppm and introducing a factor of –9.7 (–4.70 for alkalinity and –5.00 for calcium hardness) to reflect this:

$$17.\ SI = pH + \text{Log [Hard]} + \text{Log [Alk]} + \text{Log } K_2/K_s - 9.7 + \text{Log } \gamma Ca^{2+} + \text{Log } \gamma HCO_3^-$$

Activity coefficients can be estimated by means of the Davies Approximation (Stumm and Morgan 1996):

$$18.\ \text{Log } \gamma = -Az^2 [\sqrt{\mu}/(1 + \sqrt{\mu}) - 0.3\mu]$$

where: A ≅ 0.5, z is the ionic charge, and μ is the ionic strength. Calculated values of A as a function of temperature are shown in Table 1.

Temperature °F	A*
32	0.49
50	0.50
68	0.51
86	0.52
104	0.53
122	0.54
140	0.55

*$A = 1.825 \cdot 10^6 d^{0.5}(\epsilon T)^{-1.5}$, d is the density, ϵ the dielectric constant: $\epsilon = 60{,}954/(T+116) - 68.937$, and T the temperature of water in kelvins. Calculation assumes d = 1.

Table 1 – Values of Constant A vs. Temperature

The Davies approximation applies to ionic strengths of <0.5. The following equations are obtained for Ca^{2+} and HCO_3^- ions using a value of A = 0.52 for a temperature of 85°F:

$$19.\ \text{Log } \gamma Ca^{2+} = -2.08[\sqrt{\mu}/(1 + \sqrt{\mu}) - 0.3\mu]$$

20. $\text{Log } \gamma HCO_3^- = -0.52[\sqrt{\mu}/(1 + \sqrt{\mu}) - 0.3\mu]$

The ionic strength can be calculated from a complete mineral analysis or lacking that from total dissolved solids (TDS) or conductivity measurements via the following relationships:

21. $\mu = 0.5\Sigma c_i z_i^2$

22. $\mu = 2.5 \cdot 10^{-5} TDS = 1.6 \cdot 10^{-5} \kappa$

where: c is the concentration and z the ionic charge of an individual ion in mol/L and κ is the conductivity (micro Siemens/cm). TDS is related to conductivity by the equation: TDS = 0.64κ. The total ionic strength corrections for various total dissolved solids concentrations are listed in Table 2.

		Log γ_{total}	
TDS	κ	Larson & Buswell	Revised
500	781.3	– 0.17	– 0.25
1000	1562.5	– 0.20	– 0.34
2000	3125.0	– 0.23	– 0.44
3000	4687.5	– 0.24	– 0.50
4000	6250.0	– 0.25	– 0.55
5000	7812.5	– 0.25	– 0.58

Table 2 – Ionic Strength Correction as a Function of TDS and Conductivity

The data show that Larson and Buswell not only underestimated the ionic strength correction, but their calculated values are rather insensitive to TDS concentrations above 2000 ppm, which is not normal.

The data in Table 2 for total ionic strength correction can be represented to ± 0.01 by the following equations:

23. $\text{Log } \gamma_{total} = 0.654 - 0.333 \cdot \text{Log TDS}$

24. $\text{Log } \gamma_{total} = 0.719 - 0.333 \cdot \text{Log } \kappa$

Revised Saturation Index Equation – A general form of the saturation index equation is:

25. SI = pH + Log [Hard] + Log [Alk] + TC + C

This can be simplified to:

26. SI = pH + LH + LA + TC + C

where TC is the temperature correction for the term Log K_2/K_s, C = Log $K_2/K_s - 9.7 + \text{Log } \gamma Ca^{2+} + \text{Log } \gamma HCO_3^-$, and LH and LA represent logarithms of the calcium hardness and alkalinity, respectively, in ppm $CaCO_3$. Note that carbonate alkalinity and calcium hardness are expressed in the same units in contrast to previous versions of the saturation index in which hardness was expressed as ppm Ca rather than $CaCO_3$. Substitution of the value of Log K_2/K_s at 32°F (–2.25) and the total ionic strength correction (–0.34) gives the following revised equation for the saturation index for 1000 ppm TDS:

27. SI = pH + LH + LA + TC – 12.29

No correction has been made for the concentration of ion pairs such as $CaHCO_3^+$, $CaCO_3^\circ$, and $CaSO_4^\circ$. Since ion pairs are not fully ionized, they do not participate in the equilibria responsible for calcium carbonate solubility. Ion pair formation will affect both alkalinity and hardness. While the ionic strength is also affected, the effect is negligible. The effect of ion pair formation will be discussed in Part 9 of this series.

Temperature Correction – The temperature correction (TC) is calculated to ±0.01 using the following equation which was obtained by linear regression analysis of Log K_2/K_s against temperature:

28. TC = – 0.25 + 0.00825 • °F

For temperatures in °C, the following equation can be used:

29. TC = 0.02 + 0.01485 • °C

A plot of the temperature correction as a function of temperature in °F is shown in Figure 1.

Values of TC, LA, and LH – Values of TC as a function of temperature and LA and LH for various alkalinities and hardness are presented in Table 3, where hardness and alkalinity are both expressed as ppm $CaCO_3$.

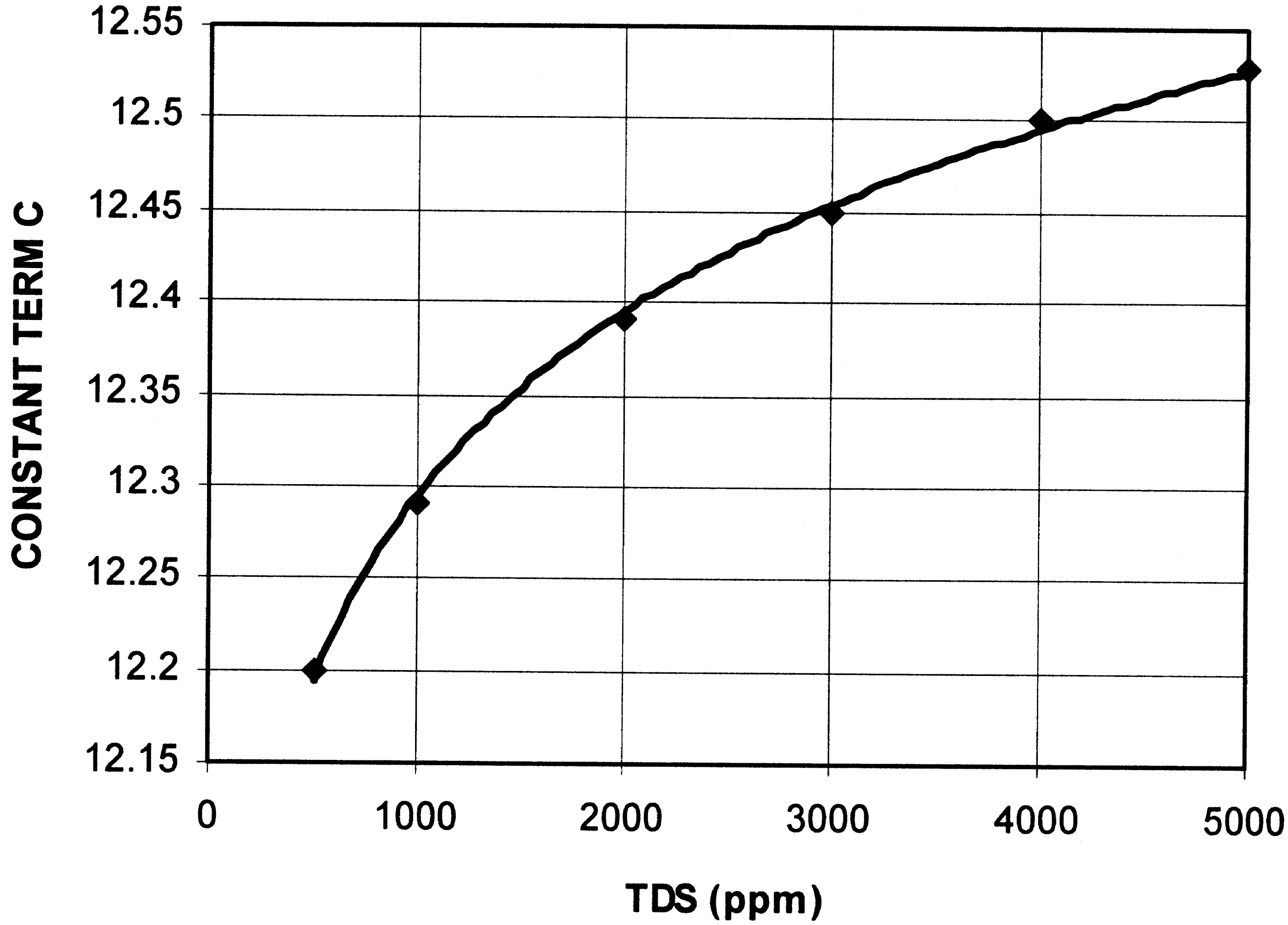

Figure 2 – Constant Term C as a Function of TDS

Comparison of Calculated SI Values – The calculated values of SI at 84°F for pH 7.5, 100 ppm carbonate alkalinity, and 300 ppm calcium hardness at various values of TDS and conductivity using the Larson and Buswell equation 13 and the revised equation 25 are given in Table 5.

		Calculated Saturation Index		
TDS	**κ**	**L&B Equation 13**	**Revised Equation 25**	**Difference Eq. 13 - Eq. 25**
500	781.3	0.21	0.22	–0.01
1000	1562.5	0.18	0.13	0.05
2000	3125.0	0.16	0.03	0.13
3000	4687.5	0.14	–0.03	0.17
4000	6250.0	0.13	–0.08	0.21
5000	7812.5	0.13	–0.11	0.24

Table 5 – Calculated SI Values as a Function of TDS

The revised equation gives lower SI values at ≥1000ppm TDS than the Larson and Buswell equation. Although the diffference is relatively small at 1000 ppm TDS, it increases and becomes significant above 1000 ppm TDS. The fact that the difference is not greater at 1000 ppm TDS is due to compensating errors. Although the ionic strength correction is higher, the temperature correction and the value of Log K_2/K_s are lower in the updated equation. Above 1000 ppm TDS the current equation predicts a greater degree of saturation than actual. Thus, the current equation may indicate a positive SI for a water with an actual negative SI.

References

Langlier, W. F. "The Analytical Control of Anti—Corrosion Water Treatment", *Journal of the American Water Works Association* 28 (1936): 1500–1521.

Larson, T. E. and Buswell, A. M. "Calcium Carbonate

Saturation Index and Alkalinity Interpretations." *Journal of the American Water Works Association* 34 (1942): 1667–1684.

Stumm, W. and Morgan, J. J. *Aquatic Chemistry*, New York, NY: John Wiley & Sons, 3rd edition 1996.

Van Waters & Rogers Technical Information Bulletin FK 41464 "Scale Formation and pH Control in Swimming Pools." 1964.

Wojtowicz, J. A. "Swimming Pool Water Balance Part 1: Effect of Cyanuric Acid and Other Interferences on Carbonate Alkalinity Measurement." *Journal of the Swimming Pool and Spa Industry* 1 (1995): 6–12.

About the Author

Now retired, **Mr. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. He holds over 55 U. S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 60 Philson Court, Cheshire, CT 06410, phone no. 203–272–1479. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide–UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.