

# The Langelier Saturation Index: Overview and Update

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*The current saturation index equation is based on CaCO<sub>3</sub> solubility data published in 1929. This paper presents a brief historical review of the application of calcium carbonate saturation theory to water treatment and discusses revisions to the saturation index equation due to a more accurate value for the CaCO<sub>3</sub> solubility product constant and its temperature dependence and more realistic ionic strength corrections. The revised equation for the saturation index (SI) (Wojtowicz 1997b) is:*

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

*where both alkalinity [Alk] and hardness [Hard] are expressed in ppm CaCO<sub>3</sub>, TC is a temperature correction term, and the constant term C = -11.30 - 0.333 Log TDS. At 1000 ppm total dissolved solids (TDS), the value of C is -12.3. The revised equation gives lower SI values at ≥1000 ppm TDS than the current equation. In other words the current equation overestimates the value of SI for a given water. Although the difference is relatively small at 1000 ppm TDS, it increases and becomes significant above 1000 ppm TDS.*

## Introduction

There are numerous references in the literature stating that the Langelier saturation index was developed for concrete water lines or for boilers, cooling towers, heat exchangers, etc., or that it applies only to closed systems and therefore does not apply to swimming pools. Although it is generally applicable to aqueous systems, strictly speaking, Langelier's sole concern in developing the Saturation Index was corrosion protection for iron piping in municipal water distribution systems (Langelier 1936). In addition,

since it is based on calcium carbonate solubility equilibria it applies to both closed systems and open systems (including swimming pools) containing dissolved calcium carbonate (Wojtowicz 1997a).

In a closed system, aqueous CO<sub>2</sub> is not exchanged with the atmosphere and alkalinity can vary at constant pH. By contrast, in an open system aqueous CO<sub>2</sub> is exchanged with the atmosphere. An open system can exist in non-equilibrium or equilibrium states. At equilibrium with atmospheric CO<sub>2</sub>, alkalinity is fixed at a given pH and is much lower than in a closed system, varying from only 4 to 18 ppm from pH 7.2 to 7.8 (Wojtowicz 1997a). Consequently, saturation hardness at equilibrium is much higher than in a closed system, varying from ~11,400 to ~700 ppm at pH 7.2 to 7.8.

Although swimming pools continuously lose CO<sub>2</sub> to the atmosphere, they are not in equilibrium with atmospheric CO<sub>2</sub>. This is due to the fact that the typical upward pH drift caused by CO<sub>2</sub> loss is periodically interrupted by acid addition (Wojtowicz 1995b). At a given pH and alkalinity, swimming pools have the same aqueous CO<sub>2</sub> concentration as closed systems. In addition, the alkalinity can vary at constant pH as in a closed system. A swimming pool is an example of a non-equilibrated open system, i.e., it is a dynamic open system with species distribution patterns similar to a closed system. In spas, the rate of CO<sub>2</sub> loss is much greater than in pools due to higher temperatures, aeration, and turbulence. Aqueous CO<sub>2</sub> can equilibrate with atmospheric CO<sub>2</sub> if the duration of aeration is long enough.

## Background

The concept of a saturation index is rooted in thermodynamics and can be traced back to the nineteenth century with publication of the Reaction Isotherm (van't Hoff 1886) which states that the free energy change ( $\Delta G$  Joules) for a reaction is given by:

$$\Delta G = 2.3RT \text{Log } Q/K$$

where R is the gas constant (J/mol/deg) and Q and K

are functions of the actual and equilibrium compositions, respectively. Rearrangement of the above equation gives the following equation where the term  $\text{Log } Q/K$  is equal to what is commonly called the saturation index (SI) (Wojtowicz 1997c):

$$\Delta G/(2.3RT) = \text{Log } Q/K = \text{SI}$$

The thermodynamic saturation index is a general parameter which applies to any system capable of existing in an equilibrium state. Thus, the so-called Langelier saturation index is not a novel concept and should more appropriately be called the calcium carbonate saturation index.

The importance of calcium carbonate saturation in water treatment was already recognized in the nineteenth century as the following highlights show:

Heyer (1888):

- treated low alkalinity and low pH drinking water with granular  $\text{CaCO}_3$  (in a filter) to prevent corrosion of lead water distribution lines

Tillmans (1912):

- proposed carbonate saturation theory of pipe protection

Baylis (1935):

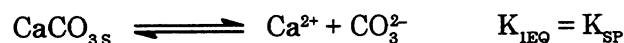
- published graphs of carbonate saturation in terms of pH and alkalinity

Langelier (1936):

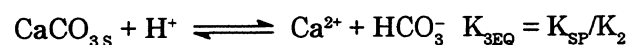
- derived equation for carbonate saturation in terms of pH, alkalinity, and Ca hardness

## Discussion

**Derivation Of The Calcium Carbonate Saturation Index** – The dissolution of calcium carbonate can be represented by the following reactions:



The overall reaction is:



where  $K_{\text{SP}}$  is the solubility product constant for the calcite form of calcium carbonate and  $K_2$  is the second ionization constant of carbonic acid. The quotient (Q) obtained by dividing the product of the product

activities by the product of the reactant activities is given by:

$$Q = \{\text{Ca}^{2+}\}\{\text{HCO}_3^-\}/(\{\text{H}^+\}\{\text{CaCO}_{3,s}\}) = \{\text{Ca}^{2+}\}\{\text{HCO}_3^-\}/\{\text{H}^+\}$$

where the braces represent activities (i.e., effective concentrations) and the activity of solid phases is assumed to be equal to one. Substituting the above equation into the saturation index expression gives:

$$\text{SI} = \text{Log } Q/K = \text{Log } \{\text{Ca}^{2+}\}\{\text{HCO}_3^-\}/(\{\text{H}^+\}K_{\text{3EQ}})$$

Expanding the left side of the above equation, and noting that  $\text{Log } 1/\{\text{H}^+\} = \text{pH}$  and  $1/K_{\text{3EQ}} = K_2/K_{\text{SP}}$  gives:

$$\text{SI} = \text{pH} + \text{Log } \{\text{Ca}^{2+}\} + \text{Log } \{\text{HCO}_3^-\} + \text{Log } K_2/K_{\text{SP}}$$

Activities can be converted to concentrations via the following relationships:

$$\text{Log } \{\text{Ca}^{2+}\} = \text{Log } [\text{Ca}^{2+}] + \text{Log } \gamma_{\text{Ca}^{2+}}$$

$$\text{Log } \{\text{HCO}_3^-\} = \text{Log } [\text{HCO}_3^-] + \text{Log } \gamma_{\text{HCO}_3^-}$$

where the terms in brackets represent actual concentrations and  $\gamma_{\text{Ca}^{2+}}$  and  $\gamma_{\text{HCO}_3^-}$  are the activity coefficients of calcium and bicarbonate ions which are a function of ionic strength which itself is a function of total dissolved solids (TDS). The total ionic strength correction (ISC) is given by:

$$\text{ISC} = \text{Log } \gamma_{\text{Ca}^{2+}} + \text{Log } \gamma_{\text{HCO}_3^-}$$

The saturation index equation with concentration units (mol/L) is:

$$\text{SI} = \text{pH} + \text{Log } [\text{Ca}^{2+}] + \text{Log } [\text{HCO}_3^-] + \text{Log } K_2/K_{\text{SP}} + \text{ISC}$$

Total alkalinity ( $\text{Alk}_T$ ) in stabilized swimming pool water is given by:

$$\text{Alk}_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{H}_2\text{C}_y^-] - [\text{H}^+] + [\text{OH}^-]$$

At swimming pool pH, bicarbonate ion represents ~99% of the carbonate alkalinity, therefore, carbonate alkalinity can be substituted for bicarbonate ion. This gives the following form of the saturation index equation:

$$\text{SI} = \text{pH} + \text{Log } [\text{Ca}^{2+}] + \text{Log } [\text{ALK}] + \text{Log } K_2/K_{\text{SP}} + \text{ISC}$$

Total alkalinity must be corrected for the cyanurate ion concentration  $[\text{H}_2\text{C}_y^-]$  before calculating the SI (Wojtowicz 1995a).

**The Langelier Saturation Index Equation –**

Langelier was not aware of the thermodynamic basis of the saturation index. However, he fortuitously arrived at the correct formulation for SI by arbitrarily defining it as follows (1936):

$$SI = pH_A - pH_S$$

where  $pH_A$  is the actual pH and  $pH_S$  is the pH of saturation. He derived the following equation with concentrations in mol/L for the pH of saturation of water containing calcium ions and carbonate alkalinity:

$$pH_S = -\text{Log} [Ca^{2+}] - \text{Log} [ALK] - \text{Log} K_2/K_{SP} + ISC$$

Langelier provided a Table of values of  $\text{Log} K_2/K_{SP}$  against temperature and TDS. He calculated activity coefficients using the Debye-Hückel Limiting Law:  $\text{Log} \gamma = -0.5Z^2\sqrt{IS}$ , where: Z is the ionic charge and  $IS = 2.5 \cdot 10^{-5}$  TDS. This law applies to ionic strengths (IS) <0.05 and will overestimate the ionic strength correction at higher ionic strengths.

**Modification Of The Saturation Index By Larson And Buswell –** Larson and Buswell (1942) combined Langelier's expressions for SI and  $pH_S$  to obtain the following form of the saturation index equation:

$$SI = pH + \text{Log} [Ca^{2+}] + \text{Log} [ALK] + \text{Log} K_2/K_{SP} + C$$

where the constant  $C = F + ISC$  and F is a factor for converting the concentrations of calcium and alkalinity from mol/L to ppm, i.e.:

$$F = -\text{Log} 40 \cdot 10^3 - \text{Log} 50 \cdot 10^3 = -4.6 - 4.7 = -9.3$$

Larson and Buswell used the following equation to calculate the total ionic strength correction:

$$ISC = -2.5\sqrt{IS}/(1 + 5.3\sqrt{IS} + 5.5 \cdot IS)$$

Their value of ISC at 1000 ppm TDS is -0.20 while their calculated value of  $\text{Log} K_2/K_{SP}$  at 32°F is equal to -2.60.

**Modification Of The Saturation Index Equation By Van Waters And Rogers –** Van Waters & Rogers (1964) modified the Larson and Buswell version of the saturation index equation as follows:

$$SI = pH + \text{Log} [Ca^{2+}] + \text{Log} [ALK] + TF + C$$

where the constant term C at 32°F and 1000 ppm TDS is given by:

$$\begin{aligned} C &= -9.3 + \text{Log} K_2/K_{SP} + ISC \\ &= -9.3 - 2.60 - 0.20 \\ &= -12.1 \end{aligned}$$

The temperature factor TF adjusts for the change in the value of  $\text{Log} K_2/K_{SP}$  above 32°F. The current familiar form of the saturation index proposed by Van Waters and Rogers is:

$$SI = pH + CF + AF + TF - 12.1$$

where CF and AF are so-called calcium and alkalinity factors which are logarithms of the calcium ion and carbonate alkalinity concentrations (in ppm), respectively. A list of values of CF, AF, and TF is given in Table 1.

T °F	TF	Hardness (ppm)	CF	Alkalinity (ppm)	AF
32	0.0	25	1.0	25	1.4
37	0.1	30	1.1	30	1.5
46	0.2	40	1.2	40	1.6
53	0.3	50	1.3	50	1.7
60	0.4	65	1.4	65	1.8
66	0.5	75	1.5	75	1.9
76	0.6	100	1.6	100	2.0
84	0.7	125	1.7	125	2.1
94	0.8	150	1.8	150	2.2
105	0.9	200	1.9	200	2.3
		250	2.0	250	2.4
		300	2.1	300	2.5
		400	2.2	400	2.6
		500	2.3	500	2.7
		600	2.4	600	2.8

\*Note that there is a difference of 0.4 between CF and AF which is due to the unnecessary step of converting calcium hardness in ppm  $CaCO_3$  to ppm Ca.

**Table 1 – Current factors for SI calculation (Van Waters & Rogers 1964)**

**Updated Version Of The Saturation Index Equation**

**Revised Equation –** The revised form of the saturation index equation is:

$$SI = pH + \text{Log} [\text{HARD}] + \text{Log} [\text{ALK}] + TC + C$$

where the calcium hardness [HARD] in ppm CaCO<sub>3</sub> is substituted for ppm [Ca<sup>2+</sup>] and TC is a temperature correction term that adjusts for the change in Log K<sub>2</sub>/K<sub>sp</sub> from its new value of -2.25 at 32°F (Plummer and Busenberg 1982) to higher temperatures, C = F + Log K<sub>2</sub>/K<sub>sp</sub> + ISC, ISC = Log γCa<sup>2+</sup> + Log γHCO<sub>3</sub><sup>-</sup> and F is given by:

$$F = -\text{Log} 100 \cdot 10^3 - \text{Log} 50 \cdot 10^3 = -5.0 - 4.7 = -9.7$$

Activity coefficients are calculated by means of the Davies approximation (Stumm and Morgan 1996).

$$\text{Log } \gamma = -0.52Z^2[\sqrt{IS}/(1 + \sqrt{IS}) - 0.3 \cdot IS]$$

Ionic strength (IS) can be calculated from a complete mineral analysis, TDS, or conductivity (κ micro Siemens/cm or μS/cm) measurement.

$$IS = 0.5 \sum C_i Z_i^2 = 2.5 \cdot 10^{-5} \text{TDS} = 1.6 \cdot 10^{-5} \kappa$$

where C and Z are the concentration (mol/L) and ionic charge of an individual ion. At 1000 ppm TDS, the value of C is:

$$C = -9.7 - 2.25 - 0.34 = -12.29$$

**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<sub>2</sub>/K<sub>sp</sub> against temperature in °F:

$$TC = -0.25 + 0.00825^\circ\text{F}$$

**Values of Parameters** – Values of the parameters in the revised saturation index equation are given in Table 2. Note that the Logs of alkalinity and hardness have the same value at the same ppm level in contrast to the current Table (#1).

**Ionic Strength Correction** – A comparison of the revised ionic strength corrections with those of Larson and Buswell is shown in Table 3. The Larson and Buswell ionic strength corrections uncharacteristically show little variation with concentration.

**Values of the Constant Term (C)** – Values of the constant term (C) as a function of TDS and conductivity are tabulated in Table 4. The constant term can be calculated to ±0.01 by the equation:

$$C = -11.3 - 0.333 \text{Log TDS} = -11.23 - 0.333 \text{Log } \kappa$$

Temp. °F	TC	[ALK] or [HARD] ppm	Log[ALK] or Log[HARD]
32	0.0	25	1.4
42	0.1	30	1.5
55	0.2	40	1.6
67	0.3	50	1.7
79	0.4	65	1.8
91	0.5	75	1.9
103	0.6	100	2.0
115	0.7	125	2.1
		150	2.2
		200	2.3
		250	2.4
		300	2.5
		400	2.6
		500	2.7
		600	2.8

**Table 2 – Values of parameters in revised SI equation**

TDS ppm	Conductivity μS/cm	Ionic strength correction (ISC)	
		Larson & Buswell (1942)	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 3 – Comparison of the revised ionic strength corrections with those of Larson and Buswell**

TDS ppm	Conductivity mS/cm	Constant Term C
500	781.3	12.20
1000	1562.5	12.29
2000	3125.0	12.39
3000	4687.5	12.45
4000	6250.0	12.50
5000	7812.5	12.53

**Table 4 – Values of the constant term (C) as a function of TDS and conductivity**

**Comparison of Calculated Values of SI –** 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 and the revised equation are given in Table 5.

TDS ppm	Conductivity mS/cm	Larson & Buswell (1942)	Revised	Difference: Larson & Buswell - Revised
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 Saturation Index (pH 7.5, Alkalinity 100 ppm, Hardness 300 ppm, Temperature 84°F)**

The revised equation gives lower SI values at  $\geq 1000$  ppm TDS than the Larson and Buswell equation. In other words, the current equation predicts higher values of SI than the revised equation for the same water. Although the difference 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, i.e., although the ionic strength correction is higher, the temperature correction and the value of  $\text{Log } K_2/K_{sp}$  are lower in the updated equation.

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