2.1 – Applicability of The Langelier Saturation Index to Swimming Pools

It is a common misconception that the Langelier Saturation Index applies only to closed systems because it was developed for water in distribution lines. Since it is based on calcium carbonate solubility equilibria, the Langelier Saturation Index is applicable to both open and closed systems containing dissolved calcium carbonate. The main difference is that in closed systems the alkalinity can vary at a given pH whereas in equilibrated open systems alkalinity is fixed at a given pH. In addition, since alkalinities are much lower in equilibrated open systems at comparable pH values, saturation hardness is much higher.

Another common misconception is that swimming pools are equilibrated open systems. Although swimming pools are open in a physical sense, they are not open in a thermodynamic (i.e., chemical equilibrium) sense. Swimming pools exhibit the characteristics of closed systems since they show the expected range and variability of alkalinity which is also typical of many public water supplies. If swimming pools were equilibrated open systems (i.e., in equilibrium with atmospheric carbon dioxide), they would contain only 4 to 18 ppm alkalinity over the 7.2 to 7.8 pH range.

At a given pH and alkalinity, swimming pools have the same concentration of dissolved CO_2 as a closed system. In order to attain equilibrium with the atmosphere, swimming pools would have to lose the excess carbon dioxide that they contain above the equilibrium value of 0.45 ppm. This will cause an increase in pH where higher alkalinities are allowed. However, although swimming pools are open to the atmosphere, they never achieve equilibrium with the atmosphere because of acid addition, which in combination with continual carbon dioxide loss causes the pH to vary with time resembling a sawtooth pattern.

Theory and Discussion

Closed Systems – Closed systems are characterized by the fact that no CO_2 is lost from solution (Stumm and Morgan 1996). The three equilibria (with concentration equilibrium constants of $^cK_{hydr}$, $^cK_1$, and $^cK_2$, respectively; see Chapter 1.1) can be represented as follows:

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$
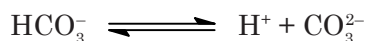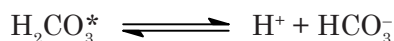
where: $H_2CO_3^* = CO_2(aq) + H_2CO_3$. The concentration of true carbonic acid (H_2CO_3) is negligible in comparison to dissolved carbon dioxide, e.g., only 0.15% of the latter is hydrated to carbonic acid at 25°C. The equilibrium expression for reaction 2 is:

$$^cK_1 = [H^+][HCO_3^-]/[H_2CO_3^*] = {^cK_{H_2CO_3}}/(1 + {^cK_{hydr}})$$

$$^cK_1 = 5.84 \cdot 10^{-7} \text{ at } 25°C \ (77°F) \text{ and } 1000 \text{ ppm TDS}$$

where: $^cK_1$ is a composite constant representing both the CO_2 hydration reaction ($^cK_{hydr}$) and ioniza-

tion of true H_2CO_3 ($^cK_{H_2CO_3}$). The equilibrium expression for reaction 3 is:

$$^cK_2 = [H^+][CO_3^{2-}]/[HCO_3^-]$$

$^cK_2 = 8.11 \cdot 10^{-11}$ at 25°C (77°F) and 1000 ppm TDS

The total concentration of species is given by:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

The concentration of individual species is given by:

$$[H_2CO_3^*] = C_T\alpha_0 \quad [HCO_3^-] = C_T\alpha_1 \quad [CO_3^{2-}] = C_T\alpha_2$$

where: α_0, α_1, and α_2 are the ionization fractions, i.e., the mol fraction of carbonic acid, bicarbonate ion, and carbonate ion, respectively. The ionization fractions can be expressed in terms of the hydrogen ion concentration (calculable from the pH) and applicable concentration equilibrium constants (see Chapter 1.1).

$$\alpha_0 = (1 + {}^cK_1/[H^+] + {}^cK_1{}^cK_2/[H^+]^2)^{-1}$$

$$\alpha_1 = ([H^+]/{}^cK_1 + 1 + {}^cK_2/[H^+])^{-1}$$

$$\alpha_2 = ([H^+]^2/{}^cK_1{}^cK_2 + [H^+]/{}^cK_2 + 1)^{-1}$$

Alkalinity is expressed by:

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] = C_T(\alpha_1 + 2\alpha_2)$$

Since C_T can vary at a given pH, alkalinities also can vary at a given pH. In stabilized water, the concentration of cyanurate ion must also be included in the total alkalinity (Wojtowicz 1995).

Equilibrated Open Systems – Equilibrated open systems possess one more equilibrium than closed systems, since they are in equilibrium with atmospheric carbon dioxide, a process which is governed by Henry's law (Stumm and Morgan 1996):

$$CO_2(g) \rightleftharpoons CO_2(aq)$$
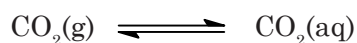
$$[CO_2(aq)] = P_{CO_2}K_H$$

where: $[CO_2(aq)]$ is the aqueous carbon dioxide concentration (mol/L), P_{CO_2} is the partial pressure of carbon dioxide ($3.16 \cdot 10^{-4}$ atm), and K_H is Henry's law constant [0.03405 mol L^{-1} atm^{-1} at 25°C (77°F)]. The concentration of species can be expressed in terms of K_H and P_{CO_2}.

$$[H_2CO_3^*] \cong [CO_2(aq)] = K_HP_{CO_2}$$

$$[HCO_3^-] = (\alpha_1/\alpha_0)K_HP_{CO_2} = {}^cK_1K_HP_{CO_2}/[H^+]$$

$$[CO_3^{2-}] = (\alpha_2/\alpha_0)K_HP_{CO_2} = {}^cK_1{}^cK_2K_HP_{CO_2}/[H^+]^2$$

The equilibrium dissolved CO_2 concentration is constant at 0.45 ppm regardless of pH. In addition, the total concentration of species is constant at a given pH, since K_H and P_{CO_2} are fixed at a given temperature and pressure, and is expressed by:

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = K_HP_{CO_2}/\alpha_0$$

Since C_T is constant at a given pH, alkalinity is also constant at a given pH.

$$\text{Alkalinity} = C_T(\alpha_1 + 2\alpha_2) = (\alpha_1 + 2\alpha_2)K_HP_{CO_2}/\alpha_0$$

where: the ionization fractions and equilibrium constants are as described for closed systems.

Application of the Phase Rule to Closed and Open Systems – The phase rule is a generalization used in analyzing equilibria in systems consisting of gas, liquid, and solid phases and is concerned with the number of variables involved in a system and the number of relationships between these variables. It is given by (Stumm and Morgan 1996):

$$f = c - p + 2$$

where: f is the number of degrees of freedom or independent variables, c is the minimum number of components necessary to describe the composition of the system, and p is the number of distinct phases. One degree of freedom is lost for each new phase. Table 1 lists the phase rule relationships for closed and equilibrated open systems containing dissolved calcium carbonate. The Table shows that

System	Components (c)	Phases (p)	Independent Variables (f)
Equilibrated Open	4 H_2O, CaO, CO_2, and H^+ or OH^-	2 Solution, CO_2(g)	4 T, P, pH, Ca^{2+}
Closed	4 H_2O, CaO, CO_2, and H^+ or OH^-	1 Solution	5 T, P, pH, Alk., Ca^{2+}

Table 1 – Phase Rule Relationships for Aqueous Carbonate Systems

at a fixed temperature and pressure, that an equilibrated open system has two degrees of freedom, i.e., pH and the concentration of calcium ions. By contrast, a closed system has three degrees of freedom, i.e., pH, alkalinity, and the concentration of calcium ions. If the systems are in equilibrium with solid calcium carbonate, then the Ca^{2+} concentration ceases to be a variable.

The Langelier Saturation Index in Open and Closed Systems – The Langelier Saturation Index (SI) for 1000 ppm TDS is given by:

SI = pH + Log Alk + Log Ca + TF − 12.1

where: Alk is the carbonate alkalinity in ppm $CaCO_3$, Ca is the calcium harness in ppm Ca, and TF is a temperature factor (0.6 at 76°F and 0.7 at 84°F). It is a common misconception that this equation is applicable only to closed systems since it was developed for water in distribution lines. The Langelier Saturation Index is not concerned whether a system is open or closed, i.e., how much dissolved CO_2 is present in the water. Instead, it is based on calcium carbonate solubility equilibria. Therefore, it applies to both open and closed aqueous systems containing dissolved calcium carbonate. The main difference is that in closed systems the alkalinity can vary at a given pH whereas in equilibrated open systems alkalinity is fixed at a given pH. In addition, since alkalinities are much lower in equilibrated open systems at comparable pH values, saturation hardness is much higher as shown in Table 2.

Equilibria in Swimming Pools – Swimming pools are not in equilibrium with atmospheric carbon dioxide because they are maintained (via chemical additions) in a supersaturated condition with respect to dissolved CO_2 and therefore can accommodate higher alkalinities than allowed in equilibrated open systems. At pH 7.5, 77°F, and 1000 ppm TDS, swimming pools contain ~4 to ~8 ppm of excess CO_2 (above the equilibrium value of 0.45 ppm) over the 80 to 160 ppm alkalinity range. Although swimming pools are open to the atmosphere and do evolve carbon dioxide, they never reach equilibrium with the atmospheric CO_2 because the resultant upward drift in pH is offset by periodic acid addition which restores pH and replenishes the dissolved CO_2 concentration. In addition, any neutralized alkalinity is replaced by periodic bicarbonate addition. At a given pH and alkalinity, swimming pools have the same concentration of dissolved CO_2 as a closed system. A swimming pool is a non–equilibrated open system, i.e., a dynamic open system with species distribution similar to a closed system.

pH	Carb. Alkalinity (ppm)	Calcium Hardness (ppm)
7.0	2.8	28,581
7.2	4.4	11,369
7.4	7.0	4,520
7.6	11.1	1,796
7.8	17.7	713
8.0	28.2	282

Table 2 – Saturation Alkalinity and Hardness in Equilibrated Open Systems
Temperature 77°F, TDS 1000 ppm

References

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

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.