

Swimming Pool Water Buffer Chemistry

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Buffering is the resistance of water to pH change. Pure water has little buffering. Buffering is necessary to prevent severe pH fluctuations that would otherwise occur when acidic or basic sanitizers are added to pool water. The presence of alkalinity in the form of bicarbonate and cyanurate imparts buffering to swimming pool water. A buffer system consists of a weak acid and its anion (e.g., carbonic acid and bicarbonate or cyanuric acid and cyanurate). Since a buffer can react with either acidic or basic substances that are added to swimming pool water it resists pH changes in either direction. However, because of the relatively low concentrations of buffering alkalinity (carbonate, cyanurate, or borate) in swimming pool water, the acid or base neutralizing capacity without significant pH change is limited. Although the buffers in swimming pools can neutralize minor quantities of acidic or basic substances with only small pH changes, significant pH changes will occur if large quantities of sanitizers (especially acidic) are added or if sufficient acid is added (e.g., during pH adjustment). Maximum buffering occurs at a pH where the molar ratio of acid to anion is one. At 80°F and 1000 ppm TDS, maximum buffering occurs at pH 6.3 and 6.8 for the carbonic acid/bicarbonate and cyanuric acid/cyanurate systems, respectively. By contrast, maximum buffering in the boric acid/borate system occurs at pH 9.2. On a molar basis, the cyanuric acid/cyanurate system provides more effective swimming pool water buffering at pH 7.5, 80°F, and 1000 ppm TDS because its pH of maximum buffering is closer to pool pH. However, on an equivalent ppm basis, the buffer intensity of the carbonic acid/bicarbonate and cyanuric acid/cyanurate systems are roughly compa-

rable over the recommended pH range (7.2–7.8) and greater than that of borate at pH < 7.8. At pH 7.8, the buffering of the three systems are roughly comparable on a ppm basis. Borate significantly supplements swimming pool buffering at pH ≥ 7.8.

What is Buffering?

Buffering is the resistance to pH change when acidic or basic substances are added to water.

Why is Buffering Necessary?

Water without alkalinity has virtually no buffering in the 5 to 9 pH range because of the extremely low concentrations of hydrogen and hydroxyl ions. Indeed, addition of a small amount of pool acid to a swimming pool filled with alkalinity-free water would quickly lower the pH below 3. Therefore, a buffer is necessary to minimize pH changes when either acidic or basic substances are added to pool water.

What is a Buffer?

A buffer is a substance in solution that tends to stabilize the pH, by neutralizing any added acid or base. All buffers provide alkalinity. Actually, a buffer consists of two components, an acid and its ionized form, i.e., alkalinity. The acid is a base neutralizer and the alkalinity is an acid neutralizer. For example, carbonic acid and bicarbonate ion form a buffer system. In addition, cyanuric acid and cyanurate ion and boric acid and borate ion also form buffer systems.

The phenomenon of buffering can be illustrated by analyzing a titration curve for bicarbonate alkalinity, which is shown in Figure 1. This graph shows two plots, an s-shaped titration curve and a bell shaped buffer intensity curve. The titration curve shows the change in alkalinity as the pH is lowered

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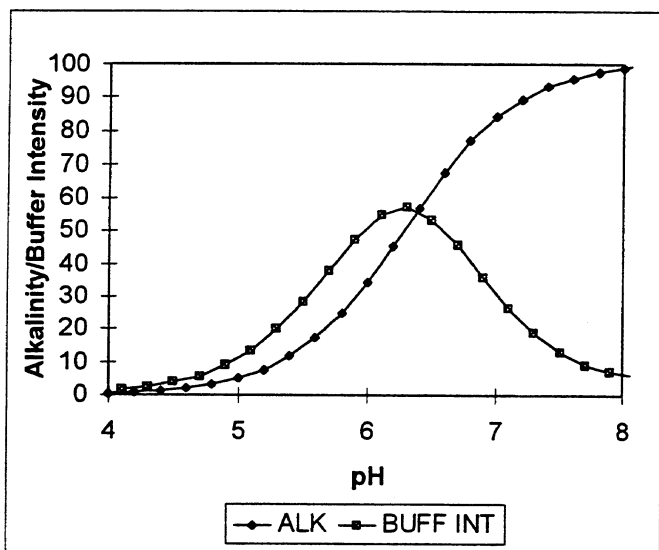


Figure 1 - Alkalinity Titration Curve

by acid. Acid converts alkalinity (i.e., bicarbonate ion) to carbonic acid. The shape of the titration curve is caused by a change in the strength of buffering with pH. Starting at pH 8, uniform addition of acid results in a gradual transition in the rate of pH change from high to low (i.e., pH 8 → 6) and then high again (i.e., pH 6.3 → 4) whereas the rate of alkalinity change goes in the opposite direction, i.e., from low to high to low again. This pattern is due to a change in the ratio of carbonic acid to bicarbonate ion. The incremental change in alkalinity divided by the incremental change in pH is equal to the buffer intensity which is a numerical measure of the strength of buffering. The bell-shaped curve of buffer intensity against pH in Figure 1 shows that maximum buffering occurs at pH 6.3. At this pH the rate of change of alkalinity is a maximum and the rate of change of pH is a minimum. This pH coincides with the presence of equal molar concentrations of carbonic acid and bicarbonate ion as shown in Figure 2.

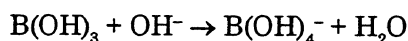
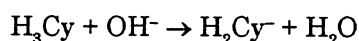
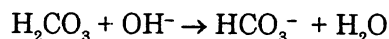
This plot shows the mol fraction of chemical species as a function of pH for the carbonic acid system. The pH of the carbonic acid/bicarbonate buffer system is simply determined by the ratio of carbonic acid to bicarbonate ion. Note that the carbonic acid system actually exhibits two buffer regions: the first, which consists of carbonic acid and bicarbonate ion, with maximum buffering at pH 6.3 and the second which consists of bicarbonate ion and carbonate ion with maximum buffering at pH 10.1. However, only the first is important in swimming pools.

A similar plot for the cyanuric acid system is shown in Figure 3. By contrast to the carbonic acid system, the cyanuric acid system exhibits three buffer regions at pH 6.8, 11.5, and 13.5 because it contains three ionizable hydrogen atoms. Only the first buffer

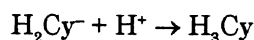
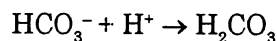
region is important in swimming pools. Boric acid also displays three buffer regions and again only the first is important in pools.

How Does a Buffer Work?

A buffer resists pH changes in either direction because: a) it contains an acid which can react with hydroxyl ions introduced into pool water by alkaline sanitizers (which tend to raise pH) and b) it contains the acid's anion (i.e., alkalinity) which reacts with hydrogen ions introduced into pool water by acidic sanitizers (which tend to lower pH). The reactions below show that carbonic, cyanuric, and boric acids react with hydroxyl ions to form bicarbonate, cyanurate, and borate ions, respectively.



Conversely, bicarbonate, cyanurate, and borate ions react with hydrogen ions to form carbonic, cyanuric, and boric acids, respectively.

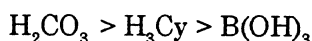


This neutralization of hydrogen and hydroxyl ions by the buffer system (i.e., weak acid and its anion) reduces pH changes which would otherwise occur in the absence of buffering.

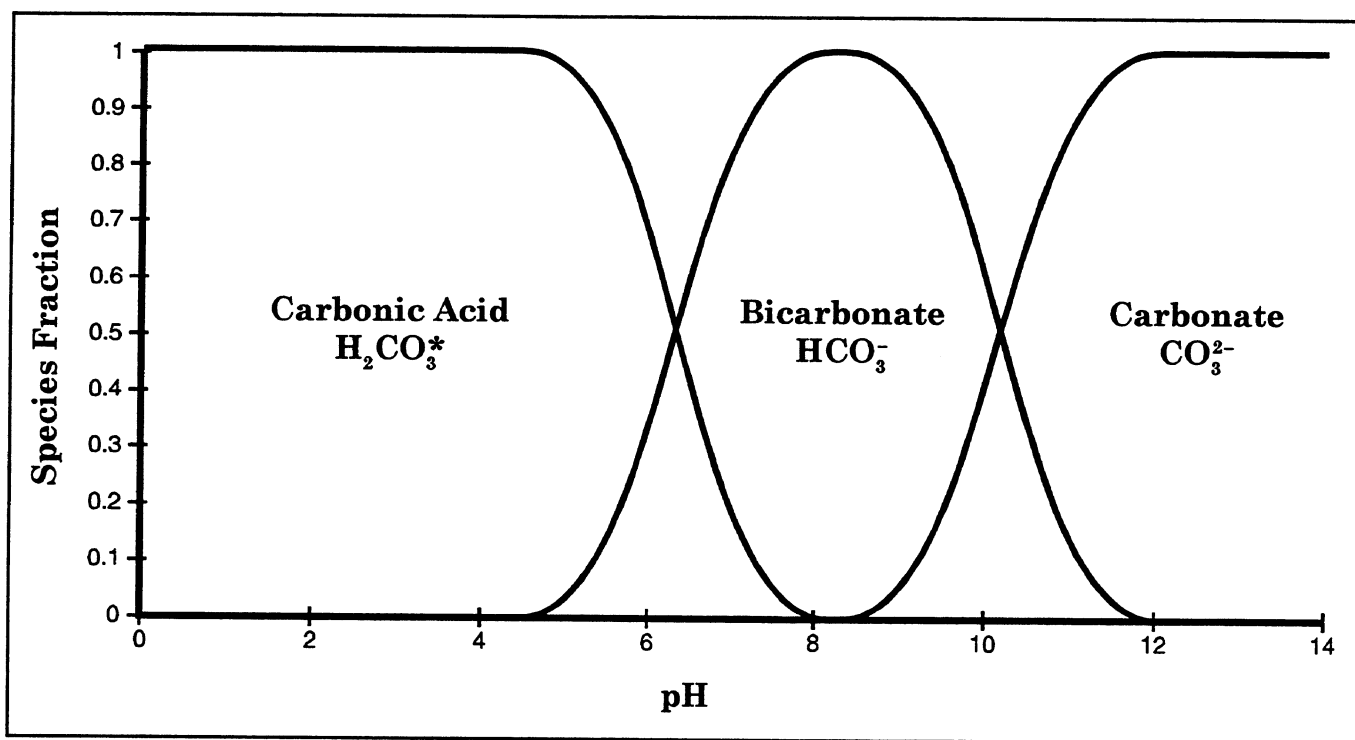
pH of Maximum Buffering

Maximum buffering occurs at different pHs which is determined by the strength of the respective acids. The stronger the acid, the greater the extent of ionization at a particular pH. The strength of carbonic, cyanuric and boric acids vary in the following order:

carbonic > cyanuric > boric



Carbonic acid is stronger than cyanuric acid which is stronger than boric acid. The stronger the acid the lower the pH of maximum buffering. Consequently,



* $H_2CO_3^* = CO_2(aq) + H_2CO_3$

Figure 2 – Distribution of Carbonic Acid, Bicarbonate, and Carbonate vs. pH

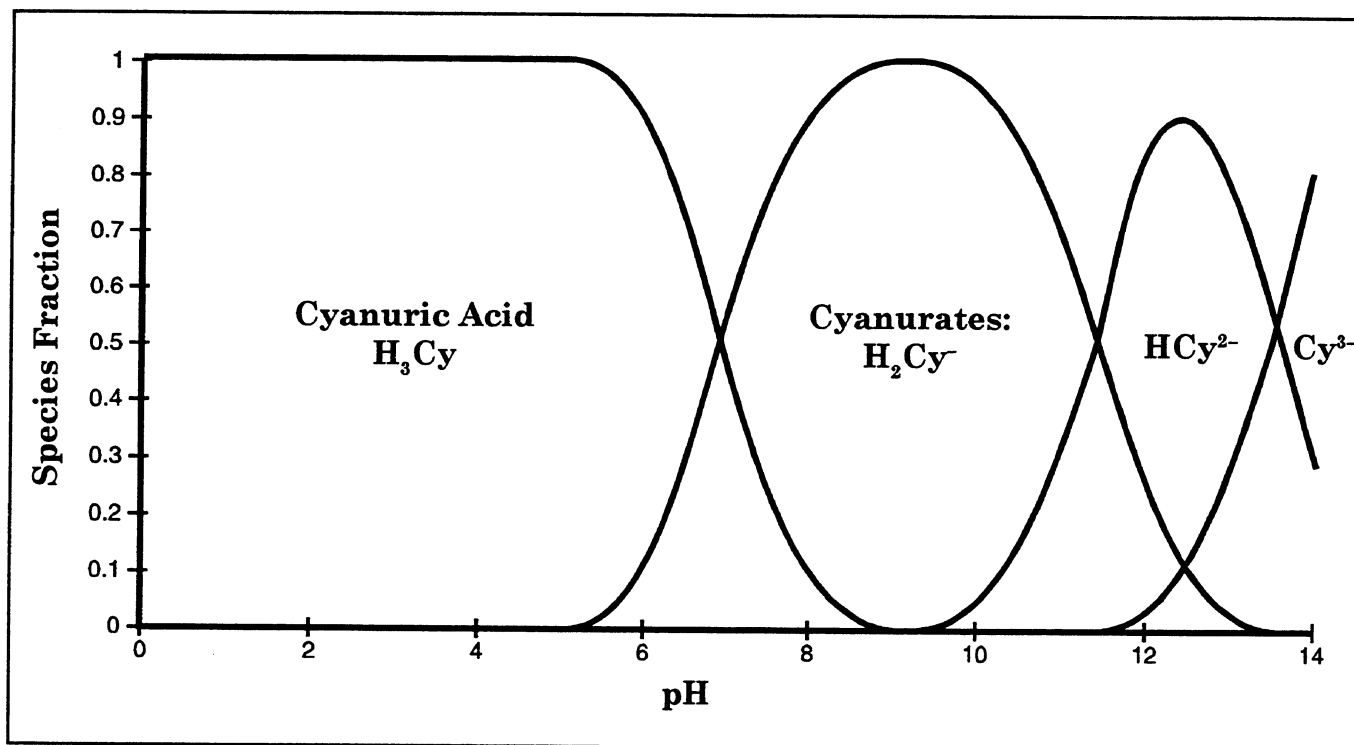


Figure 3 – Distribution of Cyanuric Acid and Cyanurates vs. pH

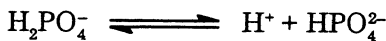
Acid	Alkaline Anion	pH of Maximum Buffering 80°F, 1000 ppm TDS
carbonic H ₂ CO ₃	bicarbonate HCO ₃ ⁻	6.3
cyanuric H ₃ Cy	cyanurate H ₂ Cy ⁻	6.8
boric B(OH) ₃	orthoborate B(OH) ₄ ⁻	9.2

Table 1 – Buffer Systems Important in Swimming Pools

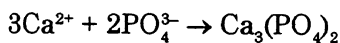
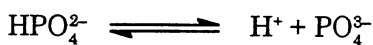
maximum buffering for carbonic, cyanuric, and boric acids occurs at pH 6.3, 6.8, and 9.2, respectively, as shown in Table 1.

Other Buffer Systems

Buffers have many practical applications and they also are very important in biological systems. For example, the pH of human blood is maintained at 7.4 by a mixture of bicarbonate and phosphate buffers. Phosphoric acid, with three ionizable hydrogen atoms, exhibits three buffer regions and is similar to cyanuric and boric acids in this regard. At first glance, the second phosphate buffer system, consisting of monophosphate (H₂PO₄⁻) and diphosphate (HPO₄²⁻) ions, appears potentially attractive for pools because it exhibits maximum buffering at pH 7.2 which is closer to pool pH than either the carbonate or cyanurate systems.



However, further examination reveals that phosphate promotes the growth of algae and it can also cause cloudy water because of precipitation of calcium phosphate which can occur at phosphate concentrations as low as 5 ppm.



Therefore, phosphates are not recommended for swimming pool use.

Buffer Intensity

Definition of Buffer Intensity – The strength of buffering is expressed numerically by the buffer intensity and for convenience is calculated in the same units as alkalinity, i.e., ppm calcium carbonate. Buffer

intensity is the change in alkalinity required to change pH by one unit. This is expressed mathematically by the equation stating that buffer intensity equals the change in alkalinity divided by the change in pH.

$$\text{Buffer Intensity (B)} = \Delta \text{Alkalinity} / \Delta \text{pH}$$

Calculation of Buffer Intensity – Buffer intensity varies with concentration and with pH. The greater the alkalinity the greater the buffer intensity. In other words, the greater the alkalinity, the greater the change in alkalinity required to change the pH by one unit. Buffer intensity for the carbonic acid system can be calculated by means of the following equation:

$$B = 2.3\{C_T[F_1(F_0 + F_2) + 4F_0F_2] + \text{OH}^- + \text{H}^+\} \cdot 50 \cdot 10^3 \text{ ppm CaCO}_3$$

where: C_T is the total molar concentration of carbonic acid, bicarbonate ion, and carbonate ion and F₀, F₁, and F₂ are their mol fractions or ionization fractions at a given pH and are calculated from a knowledge of the ionization constants of carbonic acid. In the pH range 5 to 9, the concentration of hydrogen and hy-

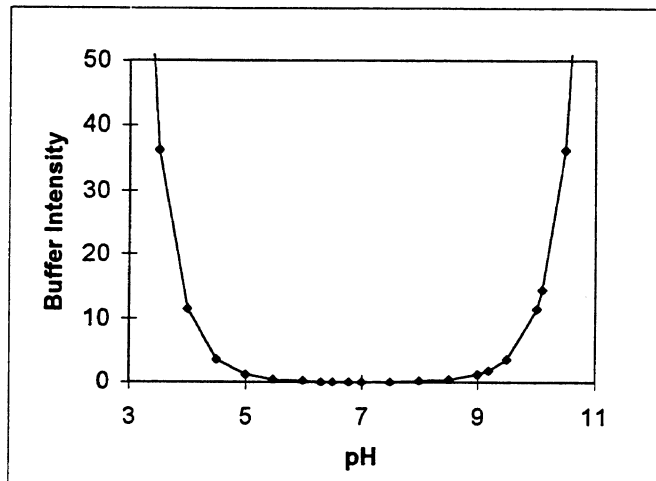


Figure 4 – Buffer Intensity of Water

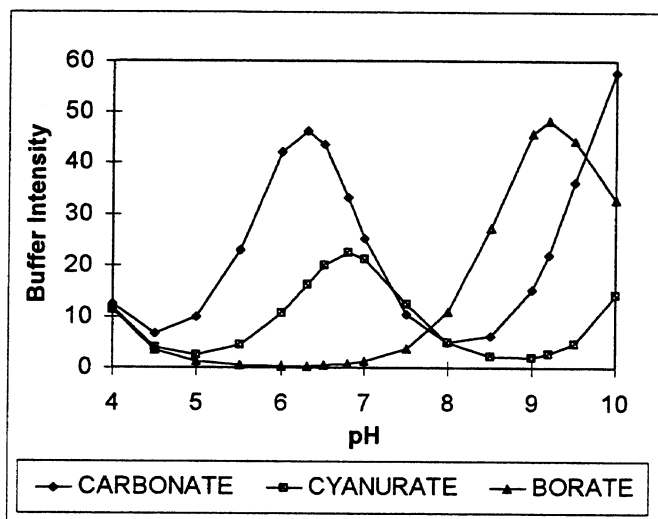


Figure 5 – Variation of Buffer Intensity with pH

droxyl ions is small, and therefore can be neglected.

Buffer Intensity of Water – As mentioned earlier, alkalinity-free water has little or no buffering in the 5–9 pH range. Figure 4 shows the buffer intensity of water vs. pH. Notice that water exhibits strong buffering only at very low or very high pH, i.e., below pH 4 and above pH 10 where appreciable concentrations of hydrogen and hydroxyl ions exist.

Buffer Intensity of Swimming Pool Alkalinity – Figure 5 shows a graph of buffer intensity vs. pH for the carbonate, cyanurate, and borate buffer systems at 100 ppm of total species concentration. Because cyanurate has a higher molecular weight, its maximum buffer intensity is lower than that of carbonate or borate alkalinity on a ppm basis. Nevertheless, the buffer intensity of cyanurate is compa-

rable to that of carbonate alkalinity in the usual swimming pool pH range of 7.2 to 7.8. However, the buffer intensities in the swimming pool pH range are much less than the maximum buffering intensities of these systems. The graph also shows that the buffer intensity of borate is less than that of carbonate or cyanurate alkalinity below pH 7.8, but greater above pH 7.8. Another point that needs to be made is that the concentration of buffers in swimming pool water is more than tenfold lower than that of typical laboratory buffers. Consequently, the buffer intensity is correspondingly lower and therefore pool pH will not be stabilized to the same degree as laboratory buffers.

Effect of Swimming Pool Sanitizers on Pool pH

Effect of Hypochlorite Sanitizers in Unbuffered Water – Table 2 below shows the calculated pH changes in alkalinity-free water due to the presence of the strong bases sodium and calcium hydroxide, present in sodium and calcium hypochlorite, respectively. It is seen that very large pH changes occur in unbuffered water when either sodium or calcium hypochlorite is added to pool water. The calculation assumes that all of the available chlorine has decomposed. This is a valid assumption since over time all available chlorine added to a pool decomposes to chloride ion which has no effect on pH.

Effect of Hypochlorite Sanitizers in Buffered Water – Table 3 below shows the pH changes in typical swimming pool water buffered with bicarbonate and cyanurate alkalinity. It is seen that by contrast with unbuffered water, very small pH changes occur in buffered water.

Hypochlorite	Treatment	oz/week	Δ pH/week
Sodium	maintenance	56.0	+1.5
Sodium	shock	106.5	+1.7
Calcium	maintenance	10.5	+1.2
Calcium	shock	20.0	+1.4

Table 2 – pH Changes Due to Alkaline Sanitizers in Unbuffered Water (pH 7.0, 80°F)

Hypochlorite	Treatment	oz/week	Δ pH/week
Sodium	maintenance	56.0	+0.02
Sodium	shock	106.5	+0.04
Calcium	maintenance	10.5	+0.01
Calcium	shock	20.0	+0.02

Table 3 – pH Changes due to Alkaline Sanitizers in typical pool water (pH 7.5, 80°F, Carbonate Alkalinity 100 ppm, Cyanuric Acid 100 ppm, TDS 1000 ppm)

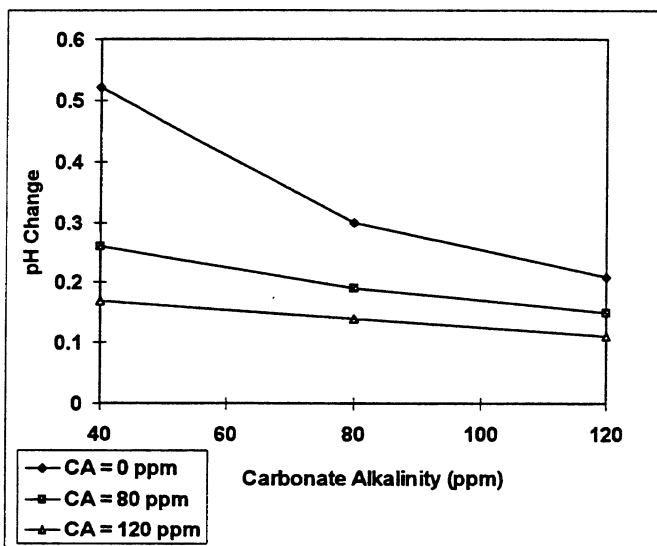


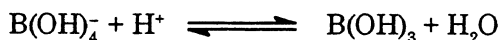
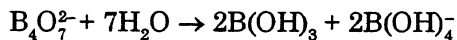
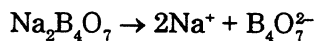
Figure 6 – Temporary pH Change Due To Hypochlorite Ion During Shock Treatment

Effect of Hypochlorite Ion in Buffered Water – Figure 6 shows the effect of hypochlorite ion on pool pH. In Tables 2 and 3, the calculation of the pH change assumed that all of the added available chlorine had decomposed. The plot in Figure 6 shows the effect of hypochlorite ion before it has decomposed. Although the low concentration of strong base present in hypochlorite sanitizers has a small effect on swimming pool pH as shown by Table 3, the hypochlorite ion provided by these sanitizers exerts a much greater initial effect on pH because of its higher concentration. Hypochlorite ion will increase pH by consuming hydrogen ions as shown by the reaction below.



The graph shows that the pH rise decreases with increasing carbonate and cyanurate alkalinity. This is however only a temporary pH rise which will disappear following decomposition of the added available chlorine.

Effect of Tetraborate Ion – Another alkaline ion, i.e., tetraborate ion, has a similar effect on pool pH. When sodium tetraborate (i.e., borax $\text{Na}_2\text{B}_4\text{O}_7$) is added to water it ionizes to sodium and tetraborate ions. The tetraborate ion, which is actually a complex, hydrolyzes to a mixture of boric acid and orthoborate ion.



Thus, tetraborate will raise pool pH because one of its hydrolysis products (i.e., borate ion) neutralizes hydrogen ions. The equilibrium for this reaction lies far to the right at pool pH. The pH change will depend on the concentration of tetraborate added. Addition of large quantities can have a large effect on pH. For example, addition of 100 ppm of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ to pool water at pH 7.5 and 80°F with 100 ppm carbonate alkalinity, 100 ppm cyanuric acid, and 1000 ppm TDS would raise the pH by 1.2 units, i.e. to 8.7.

Effect of Gaseous Chlorine – Table 4 shows calculated pH changes when maintenance doses of an acidic sanitizer such as chlorine gas is added to water. Note that a very large pH change occurs in unbuffered water. As expected, it is seen that the pH change is very much lower in buffered water and decreases with increasing carbonate and cyanurate alkalinity.

Effect of Chlorine and Chloroisocyanurates – Table 5 shows calculated weekly pH changes due to maintenance doses of three acidic sanitizers: chlorine gas, Trichlor, and Dichlor. The calculated data show that gaseous chlorine exerts the greatest effect on pH followed by Trichlor and then Dichlor. Chlorine gas has a much greater effect on pH than chloroisocyanurates because it produces much more strong acid per mol of sanitizer.

Carbonate Alkalinity, ppm	Total Cyanurate, ppm	$\Delta\text{pH}/\text{week}$
0	0	-3.7
50	0	-0.55
50	50	-0.38
100	0	-0.33
100	100	-0.22

Table 4 – Calculated pH Changes for Maintenance Doses of Chlorine (pH 7.5, 80°F, Cl_2 6.8 oz/week, TDS 1000 ppm)

Sanitizer	oz/week	$\Delta\text{pH}/\text{week}$
chlorine gas	6.8	-0.22
Trichlor	7	-0.14
Dichlor	10.5	-0.09

Table 5 – Calculated pH Changes Due to Acidic Sanitizers (pH 7.5, 80°F, Carbonate Alkalinity 100 ppm, Cyanuric Acid 100 ppm, TDS 1000 ppm)

Effect of Carbon Dioxide Loss on Pool pH

Figure 7 shows the effect of carbon dioxide loss on pool pH under different degrees of buffering (pH 7.5, 80°F, and TDS 1000 ppm). Since swimming pool water is oversaturated with carbon dioxide there is a continual evolution of carbon dioxide into the atmosphere from the surface of the water. This results in an increase in pH with time. The graph shows that the weekly pH change at constant carbonate alkalinity as expected decreases with increasing cyanuric acid concentration. However, by contrast, the weekly pH change at constant cyanuric acid increases with increasing carbonate alkalinity. This seems to contradict the known buffering effect of carbonate alkalinity. This apparent paradox is due to the fact that the rate of carbon dioxide loss varies with the square of the alkalinity concentration whereas buffering varies only with the first power of the alkalinity concentration.

About the Author

Now retired, **John A. 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 3266 N 151st Street, Goodyear, AZ 85338, phone #602-473-3576. 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, com-

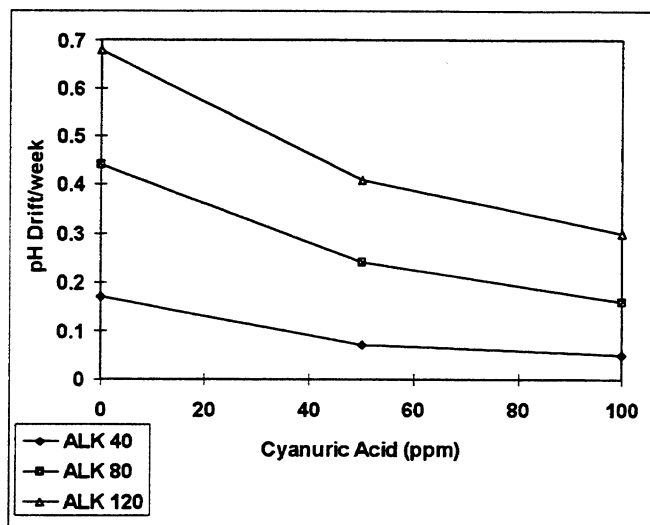


Figure 7 – Effect of Alkalinity and CA on pH Drift Due to CO₂ Loss

puter programming, and expert witnessing.

About the Presenter

Note: Mr. Wojtowicz was unable to attend the symposium as originally planned, and therefore Dr. Charles F. Sikorski agreed to present the paper for Mr. Wojtowicz. Dr. Sikorski is the Technical Service Manager for the Alkali Chemicals Division of FMC Corporation. For the last 18 years he has worked in numerous technical capacities at FMC, involved with product applications, new product development, commercial development, and technical service in support of a variety of FMC's sodium carbonate and phosphate products. He earned his undergraduate and graduate degrees (B.S., M.S., and Ph.D.) in ceramic science at Rutgers University in New Jersey. He holds 2 US Patents and has published and/or presented more than a dozen technical works.