4.1 – The Effect of Cyanuric Acid and Other Interferences on Carbonate Alkalinity Measurement

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Proper water balance is essential not only for a corrosion–free pool but also for clear water. The calcium carbonate Saturation Index (SI) utilizes the pH, carbonate alkalinity, and calcium hardness to calculate a measure of the degree of calcium carbonate saturation of pool water (Langelier 1936; Larson 1942; Van Waters 1964). If the water contains other alkaline substances (e.g., cyanurate), the total alkalinity (as typically determined with a test kit) must be corrected to obtain the actual carbonate alkalinity (Snoeyink 1980; Stumm 1981) so that the correct SI will be obtained, otherwise serious corrosion problems can arise.

Part 2 of this article, to appear in a following issue, discusses the effect of cyanuric acid and other factors on the saturation index.

Water Chemistry

Carbonate Alkalinity – The carbonate alkalinity in swimming pool water is expressed as ppm of equivalent calcium carbonate. It consists primarily of bicarbonate ion (HCO_3^-) and minor amounts of carbonate ion (CO_3^{2-}), which along with carbonic acid forms a necessary buffer system against pH changes due to sanitizer addition.

$$CO_2(aq) \rightleftharpoons H_2CO_3 \underset{+H^+}{\overset{-H^-}{\rightleftharpoons}} HCO_3^- \underset{+H^+}{\overset{-H^-}{\rightleftharpoons}} CO_3^{2-}$$

(reaction sequence 1)

Actually, carbonic acid is a minor species, representing only about 0.15% of dissolved carbon dioxide ($CO_2(aq)$). The total molar concentration (C_T) of species in the carbonic acid system is represented by the following equation:

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

where $[H_2CO_3^*] = [CO_2(aq)] + [H_2CO_3]$. The molar concentrations of individual species as a function of ionization fraction (α) are given by:

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

where:

$$\alpha_0 = (\,1 + {}^cK_1 / [H^+] + {}^cK_1{}^cK_2 / [H^+]^2\,)^{-1}$$
$$\alpha_1 = (\,[H^+]/{}^cK_1 + 1 + {}^cK_2 / [H^+]\,)^{-1}$$
$$\alpha_2 = (\,[H^+]^2/({}^cK_1{}^cK_2) + [H^+]/{}^cK_2 + 1)^{-1}$$

${}^cK_1$ ($4.53\cdot10^{-7}$) and ${}^cK_2$ ($4.85\cdot10^{-11}$) are the first and second concentration ionization constants of carbonic acid at 80ºF and 0 TDS (Plummer 1982), and $[H^+]$ is the hydrogen ion concentration. Calculation of K values at TDS concentrations require use of activity coefficients (see Chapter 1.1).

The carbonate alkalinity (Alk_{carb}) is given by the following equation:

$$\begin{aligned} Alk_{carb} &= ([HCO_3^-] + 2\cdot[CO_3^{2-}])\cdot 50\cdot 10^3 \\ &= C_T(\alpha_1 + 2\alpha_2)\cdot 50\cdot 10^3 \text{ ppm } CaCO_3 \end{aligned}$$

A plot of ionization fractions vs. pH is shown in Figure 1. The plot shows that as the pH increases, carbonic acid is converted stepwise to bicarbonate and carbonate ions; the reverse being true when the pH decreases in accordance with the equilibria in reaction sequence 1. The ratio of carbonic acid to bicarbonate to carbonate is a function of pH only.

Cyanurate Alkalinity – Many outdoor pools

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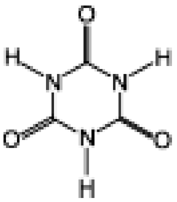
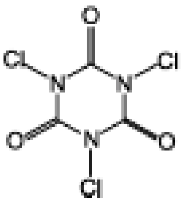
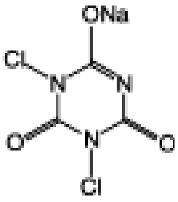
employ cyanuric acid (1, CA, H_3Cy) to stabilize free available chlorine (i.e.: HOCl and ClO^-) against excessive decomposition by sunlight. Many of these pools also use chloroisocyanurates (2, Trichlor: trichloroisocyanuric acid and 3, Dichlor: sodium dichloroisocyanurate) for disinfection, adding more cyanuric acid to the water.



1. CA, Cyanuric Acid



2. TCCA, Trichlor



3. SDCC, Dichlor

Cyanuric acid forms alkaline ionization products depending on pH, i.e., mono–, di–, and triisocyanurate ions, which also buffer the water.

$$H_3Cy \underset{+H^+}{\overset{-H^-}{\rightleftharpoons}} H_2Cy^- \underset{+H^+}{\overset{-H^-}{\rightleftharpoons}} HCy^{2-} \underset{+H^+}{\overset{-H^-}{\rightleftharpoons}} Cy^{3-}$$

(reaction sequence 2)

The total molar concentration of species is represented by the following equation:

$$C_T' = [H_3Cy] + [H_2Cy^-] + [HCy^{2-}] + [Cy^{3-}]$$

The molar concentration of individual species can be calculated as a function of ionization fraction.

$$\begin{aligned} [H_3Cy] &= C_T'\alpha_0' \\ [H_2Cy^-] &= C_T'\alpha_1' \\ [HCy^{2-}] &= C_T'\alpha_2' \\ [Cy^{3-}] &= C_T'\alpha_3' \end{aligned}$$

Where:

$$\alpha_0' = (1 + {}^{c}K_1'/[H^+] + {}^{c}K_1'\,{}^{c}K_2'/[H^+]^2 + {}^{c}K_1'\,{}^{c}K_2'\,{}^{c}K_3'/[H^+]^3)^{-1}$$
$$\alpha_1' = ([H^+]/{}^{c}K_1' + 1 + {}^{c}K_2'/[H^+] + {}^{c}K_2'\,{}^{c}K_3'/[H^+]^2)^{-1}$$
$$\alpha_2' = ([H^+]^2/({}^{c}K_1'\,{}^{c}K_2') + [H^+]/{}^{c}K_2' + 1 + {}^{c}K_3'/[H^+])^{-1}$$
$$\alpha_3' = H^+]^3/({}^{c}K_1'\,{}^{c}K_2'\,{}^{c}K_3') + [H^+]^2/({}^{c}K_2'\,{}^{c}K_3') + [H^+]/{}^{c}K_3' + 1)^{-1}$$

and ${}^{c}K_1'$ ($1.32 \cdot 10^{-7}$ at average ionic strength $5 \cdot 10^{-4}$ M), ${}^{c}K_2'$($3.98 \cdot 10^{-12}$), ${}^{c}K_3'$ ($3.16 \cdot 10^{-14}$) are the first, second, and third ionization constants of cyanuric acid at 20–25ºC, determined experimentally by spectrometric titration with base over the pH range 4.8 to 13.5 (O'Brien 1972). A plot of the ionization fractions for cyanuric acid as a function of pH (Figure 2) shows stepwise conversion of cyanuric acid to mono–, di–, and triisocyanurate ions as pH increases in accordance with the equilibria in reaction sequence 2; the reverse occurring when pH decreases. Cyanuric acid and cyanurate ion are the only significant species at normal pool pH (7.2 – 7.8), and thus only the first ionization is important. The ratio of cyanurate to cyanuric acid is a function of pH only.

Cyanuric acid lowers the pH when added to pool water by ionizing, forming cyanurate and hydrogen ions. This results in conversion of bicarbonate to carbonic acid and carbon dioxide.

$$H_3Cy \rightleftharpoons H_2Cy^- + H^+$$
$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3^*$$

The overall reaction is:

$$H_3Cy + HCO_3^- \rightleftharpoons H_2Cy^- + H_2CO_3^*$$

For example, at start–up, the addition of 50 ppm cyanuric acid to a pool at 80ºF, pH 7.4, 100 ppm alkalinity, and 1000 ppm TDS will lower the pH to 7.0. Although addition of cyanuric acid lowers the pH, it does not change the total alkalinity, it simply replaces a portion of carbonate alkalinity with cyanurate alkalinity. However, when the pH is restored to the original value, total alkalinity, both carbonate and cyanurate, will be increased.

Effect of Other Water Constituents on Total Alkalinity – Total alkalinity (Alk_T) is given by the following expression:

$$\begin{aligned} Alk_T = {} & ([HCO_3^-] + 2 \cdot [CO_3^{2-}] + [H_2Cy^-] + [OH^-] \\ & - [H^+] + \Sigma[C_i]) \cdot 50 \cdot 10^3 \text{ ppm } CaCO_3 \end{aligned}$$

Where $\Sigma[C_i]$ is the sum of the equivalent concentrations of all other alkaline substances.

Although hydroxide ion contributes to alkalinity, its concentration below 9 is insignificant and thus it can be neglected. For example, at pH 7.5, the contribution of hydroxide to total alkalinity is only 0.02 ppm. Similarly, the effect of hydrogen ion is insignificant at normal pool pH.

Other source water and pool water constituents that can potentially affect total alkalinity measurement are: borate, silicate, phosphate, hydrosulfide, hypochlorous acid, hypochlorite, monochloramine, salts of organic acids, and organic bases. The potential effect of interfering substances depends on the ionization constants of the parent acid which determines the fraction (α) of the acid present as a titratable alkaline anion or base at a particular pH. For a monoprotic acid the ionization fraction (α_1) is given by:

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

For diprotic and triprotic acids, the equations for carbonic and cyanuric acids employed above can be used. The total effect of alkaline species is given by the difference between the ionization fraction of the titratable species at pool pH and pH 4 (i.e., the endpoint of the alkalinity titration). For example, in the case of phosphoric acid, the ionization fraction of HPO_4^{2-} is 0.80 at pH 7.8. On titration it is converted to $H_2PO_4^-$, increasing its ionization fraction from 0.20 to 1.00. Titration of $H_2PO_4^-$ to pH 4.0 reduces its ionization fraction to 0.99. Thus, the total titratable ionization fraction is: 0.80 + (1.00 – 0.99) = 0.81. Calculated ionization fractions at pH 4 and pH 7.8 (the maximum recommended value) for various acids and bases (no ionic strength correction) are given in Table 1.

Acid	Ionization Constant*	Titratable Species	Ionization Fractions pH 4.0/7.8
H_3BO_3	$5.8 \cdot 10^{-10}$	$B(OH)_4^-$	0/0.035
$H_2B_4O_7$	$1 \cdot 10^{-4}$	$HB_4O_7^-$	0.50/0.94
$HB_4O_7^-$	$1 \cdot 10^{-9}$	$B_4O_7^{2-}$	0/0.06
H_2SiO_3	$1.7 \cdot 10^{-10}$	$HSiO_3^-$	0/0.01
H_2S	$1.01 \cdot 10^{-7}$	HS^-	0/0.86
H_3PO_4	$7.08 \cdot 10^{-3}$	$H_2PO_4^-$	0.99/0.20
$H_2PO_4^-$	$6.3 \cdot 10^{-8}$	HPO_4^{2-}	0/0.80
NH_4^+	$5.75 \cdot 10^{-10}$	NH_3	0/0.035
Cl_3COOH	$4.6 \cdot 10^{-3}$	Cl_3COO^-	0.98/1.00

*From (Langes 1985)

Table 1 – Ionization Fractions of Potential Interfering Substances

Ortho boric acid (H_3BO_3) is used as a tabletting aid (<0.1%) and as an additive (5%) in trichloroisocyanuric acid tablets employed in swimming pool sanitation. Boric acid can also form by hydrolysis of tetraborate which is added to swimming pools as a buffering agent. Boric acid, a Lewis acid, is only slightly dissociated to orthoborate at pH 7.8: $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$. Even 100 ppm will increase alkalinity by only 3 ppm. However, continued use of tetraborate can lead to very high levels of boric acid, in which case the effect on alkalinity will become significant. The effect will also increase at pHs above 7.8. Use of boric acid in combination with sodium carbonate as a buffer system for spas has been patented (U.S. Patent 1994). At pH 7.8 and the maximum boric acid concentration of 1190 ppm, the borate concentration would correspond to about 34 ppm of equivalent carbonate alkalinity and represents a significant correction to total alkalinity.

Use of tetraborate (i.e., borax, $Na_2B_4O_7$ penta and decahydrate) as a swimming pool algaecide has been patented (U.S. Patent 1986). However, the extent of its use as an algaecide is unknown. Tetraborate is also used as a buffer in swimming pools. Although tetraborate can interfere to a greater extent than orthoborate on an equimolar basis, the effect will depend on the concentration employed. For example, at 40 ppm $Na_2B_4O_7$, the effect amounts to 5 ppm alkalinity. Tetraborate can revert to orthoborate in dilute alkaline solution (Cotton 1988), which significantly reduces its buffering capacity and its effect on alkalinity. Reversion of 40 ppm tetraborate to orthoborate would reduce the effect on alkalinity to only 1.4 ppm.

Silicic acid is present in source water, but due to its very small ionization constant, it will not interfere significantly.

Although hydrosulfide (HS^-) in source water will titrate to a significant extent, it is quickly oxidized by chlorine (either HOCl or ClO^-) to sulfate and will not interfere (e.g., $HS^- + 4ClO^- \rightarrow HSO_4^- + 4Cl^-$; $HSO_4^- + HCO_3^- \rightarrow SO^2{}_4{}^- + H_2CO_3{}^*$).

Phosphonates, which are added to pools for stain control, are converted by chlorine and sunlight to phosphates. Although dihydrogen phosphate ($H_2PO_4^-$) interferes to only a slight extent, monohydrogen phosphate (HPO_4^{2-}) can interfere significantly. Phosphate tends to precipitate as the highly insoluble calcium hydroxyapatite [$Ca_5OH(PO_4)_3$], limiting its concentration and lifetime. This precipitation can result in cloudy water, which can occur during shock treatment when the phosphate concentration reaches about 5 ppm. In addition, phosphate is also a vital nutrient for algae. Therefore, routine use of phosphorus–containing ancillary chemicals is not recommended.

Monochloramine is converted to ammonium ion and hydroxide ion on reaction with thiosulfate prior to alkalinity titration: $NH_2Cl + 2S_2O^2{}_3{}^- + H_2O + H^+ \rightarrow NH_4{}^+ + Cl^- + OH^- + S_4O^2{}_6{}^-$. Since ammonium ion dissociates to only a small extent at pH 7.8 it will not interfere significantly. Hydroxide will interfere if the monochloramine concentration is high (e.g., if combined available chlorine is >5 ppm), however, in a properly maintained pool, monochloramine will normally be low due to breakpoint chlorination: $2NH_2Cl + HOCl \rightarrow N_2 + 3Cl^- + 3H^+ + H_2O$.

Hypochlorite is reduced to chloride ion and two hydroxyl ions by thiosulfate prior to alkalinity titration and will interfere.

$$ClO^- + 2S_2O_3^{2-} + H_2O \rightarrow Cl^- + S_4O_6^{2-} + 2OH^-$$

Similarly, hypochlorous acid is reduced to equimolar amounts of chloride and hydroxide, increasing alkalinity.

$$HOCl + 2S_2O_3^{2-} \rightarrow Cl^- + S_4O_6^{2-} + OH^-$$

However, the total effect is small except under superchlorination or shock treatment conditions.

Organic acids from oxidation of organic matter yield chlorinated derivatives which are generally strong acids. For example, acetic acid forms trichloroacetic acid which is already 98% ionized at pH 4 (the end point of the alkalinity titration). Thus, because of this and the fact that the concentration of trichloacetate is typically quite low, the interference can be neglected. Organic bases, e.g. triethanolamine from copper algaecides, are not present in high concentrations because they are not routinely added to swimming pool water and furthermore are oxidized by chlorine.

Correcting Total Alkalinity for Cyanurate Concentration

The fraction (α_1') of cyanuric acid present as cyanurate ion as a function of pH can be calculated from the first ionization constant (K_1').

$$\alpha_1' = [H_2Cy^-] / C_T' = ([H^+] / K_1' + 1)^{-1}$$

Where $K_1' = 1.47 \cdot 10^{-7}$ is estimated at 80ºF and 0 TDS. The ionization fractions calculated from the experimentally determined first ionization constant represent the actual fraction of cyanuric acid present as titratable cyanurate ion at a given pH. At typical pool pH (7.2–7.8) the fraction of cyanuric acid present as cyanurate varies from 73 to 91%. Multiplying the fraction of cyanuric acid as cyanurate by 0.388 provides a factor (F) for converting ppm cyanuric acid to ppm equivalent carbonate alkalinity.

$$\begin{aligned} F &= (CaCO_3/2H_3Cy) \cdot \alpha_1' \\ &= (100.09/(2 \cdot 129.08)) \cdot \alpha_1' \\ &= 0.388 \cdot \alpha_1' \end{aligned}$$

Values of α_1' and F at 80ºF and 1000 ppm TDS and various pHs are tabulated in Table 2.

pH	α_1'	F
7.0	0.63	0.24
7.2	0.73	0.28
7.4	0.81	0.31
7.6	0.87	0.34
7.8	0.91	0.35
8.0	0.94	0.36
8.2	0.96	0.37

Table 2. Fraction (α_1') of CA Present as Cyanurate and Correction Factor (F) as a Function of pH

In the absence of other interferences, carbonate alkalinity is calculated from the total alkalinity (ppm) and cyanuric acid (ppm) as follows:

$$Alk_{carb} = Alk_T - CA \cdot F \text{ ppm } CaCO_3$$

For example at pH 7.4 and a total alkalinity of 100 ppm, the carbonate alkalinity at 50 and 100 ppm cyanuric acid, is 85 and 69 ppm, respectively. For convenience, an approximate factor of $^1/_3$ can be employed. Table 3 shows the error involved as a function of pH and CA concentration.

	ppm Cyanuric Acid		
pH	**100**	**200**	**300**
	Error: ppm Alkalinity		
7.0	+9	+19	+28
7.2	+5	+11	+16
7.4	+2	+5	+7
7.6	–1	–1	–2
7.8	–2	–3	–5
8.0	–3	–5	–8

Table 3 – Error in CA Correction vs. pH and CA Concentration

The above table shows that acceptable accuracy is obtained with the $^1/_3$ factor in the pH range 7.4 to 8.0 up to 200 ppm CA which will cover most conditions encountered in the field. Outside this range the actual factors in Table 2 should be used to adjust total alkalinity test kit results.

Demonstration of the Effect of Cyanuric Acid on Alkalinity

Lab Tests – Two series of tests were carried out in the laboratory to verify that cyanuric acid affects alkalinity as predicted by theory. In the first, three different solutions of cyanuric acid were prepared in distilled water and adjusted (using a pH meter) to pH 7.5 with 0.1N sodium hydroxide; no carbonate alkalinity was added. The solutions were analyzed with a swimming pool test kit (Taylor #2001). The results, tabulated in Table 4, show an average deviation of +4 ppm between calculated (F = 0.32) and measured alkalinity, which is within the accuracy of the test kit, i.e., ± 5–10 ppm. Although no carbonate alkalinity was present, the solutions showed the expected levels of alkalinity.

CA(ppm)	Alk_{carb}(ppm)	Alk_{T}(ppm)	
		calculated	measured
100	0	32	30
200	0	64	60
300	0	96	90

Table 4 – Effect of Cyanuric Acid on Alkalinity at pH 7.5

In the second series (Table 5), sodium bicarbonate was added along with cyanuric acid and the solution adjusted to pH 7.5, to provide both carbonate and cyanurate alkalinity. The total alkalinity was measured as above. After applying a correction for cyanuric acid (F = 0.333), the calculated carbonate alkalinity was in good agreement with the actual added carbonate alkalinity.

Spa Test – A 275–gallon spa with an initial pH of 7.8, no initial cyanuric acid, and an alkalinity of 78 ppm was maintained at 101–104°F during several–hour daily use periods. It was treated daily with 26 g of a 62:10:28 mixture of sodium dichloroisocyanurate/sodium bromide/sodium carbonate. The amount of sodium carbonate (soda ash) in the formulation was chosen so that cyanurate represented about 96% of potential cyanurate which is the equilibrium value at a pH of 8.2. The reaction sequence is shown below.

CA(ppm)	Alk_{carb}(ppm)[a]	Alk_{T} (ppm)	
		total calc.	measured[b]
0	100	100	100
50	100	116	100
100	100	132	100
		Average:	100

a) Added as sodium bicarbonate

b) Corrected for CA alkalinity

Table 5 – Effect of Cyanuric Acid on Alkalinity at pH 7.5

$$\text{NaCl}_2\text{Cy} + 2\text{H}_2\text{O} \rightarrow \text{NaH}_2\text{Cy} + 2\text{HOCl}$$

$$2\text{HOCl} + 2\text{NaBr} \rightarrow 2\text{HOBr} + 2\text{NaCl}$$

$$2\text{HOBr} \rightarrow 2\text{HBr} + \text{O}_2$$

$$1.96\text{HBr} + 0.98\text{Na}_2\text{CO}_3 \rightarrow 1.96\text{NaBr} + 0.98\text{CO}_2 + 0.98\text{H}_2\text{O}$$

$$0.04\text{NaH}_2\text{Cy} + 0.04\text{HBr} \rightarrow 0.04\text{H}_3\text{Cy} + 0.04\text{NaBr}$$

Overall:

$$\text{NaCl}_2\text{Cy} + 0.98\text{Na}_2\text{CO}_3 + 1.02\text{H}_2\text{O} \rightarrow 0.96\text{NaH}_2\text{Cy} + 0.04\text{H}_3\text{Cy} + 2\text{NaCl}$$

Some bromic acid (HBrO_3) is also formed in the decomposition of HOBr. Also small amounts of HOBr are consumed in formation of brominated organics.

Alkalinity was measured analytically (i.e., by titration with 0.02N H_2SO_4) rather than by test kit. During the 4–week test, pH ranged between 8.1 to 8.2, the carbonate alkalinity remained constant at 78 ppm, but the total alkalinity increased to 164 ppm. A total of 240 ppm of cyanuric acid (~8.6 ppm/day) was added to the spa water by the sanitizer. The carbonate alkalinity calculated from the total alkalinity and the cyanuric acid concentration is in excellent agreement with carbonate alkalinity determined by measuring the carbon dioxide concentration upon acidification (i.e., converting bicarbonate and carbonate to CO_2) as shown in Table 6.

Days	pH	Alk_{tot}[a]	Alk_{carb}[b]
0	7.8	78	78 (78)
7	8.2	103	81 (78)
14	8.1	128	84 (78)
21	8.1	147	81 (78)
28	8.1	164	76 (78)
		Average:	80 (78)

a) Initial CA = 0 ppm

b) Values in parenthesis by CO_2 analysis

Table 6 – Spa Test on the Effect of Cyanuric Acid on Alkalinity

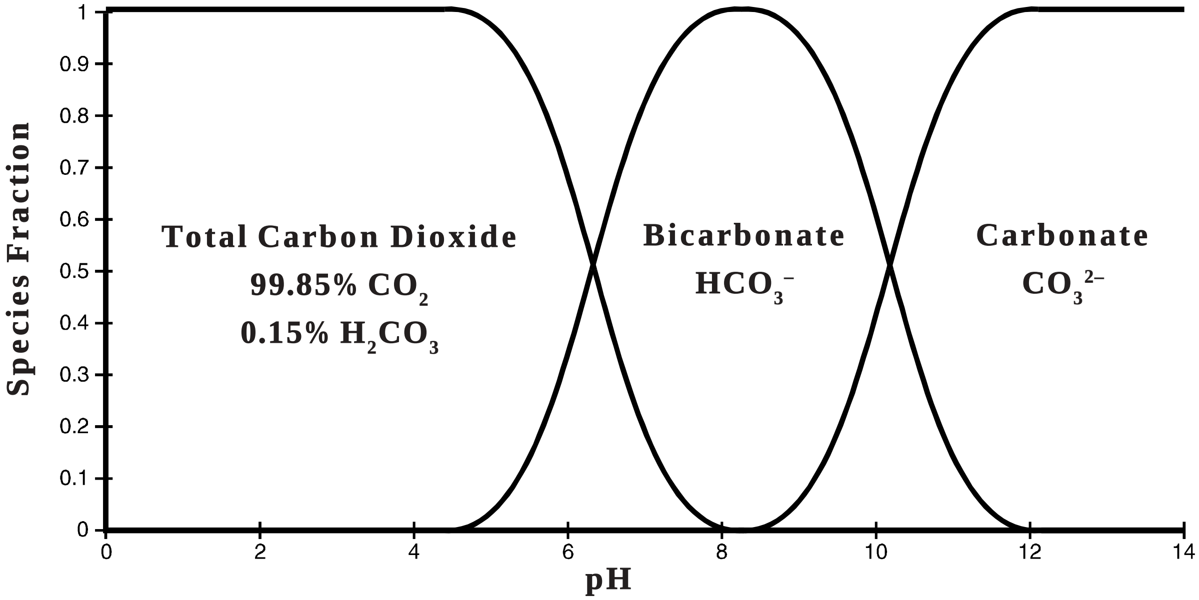


Figure 1. Distribution of Total CO_2, Bicarbonate, and Carbonate vs. pH

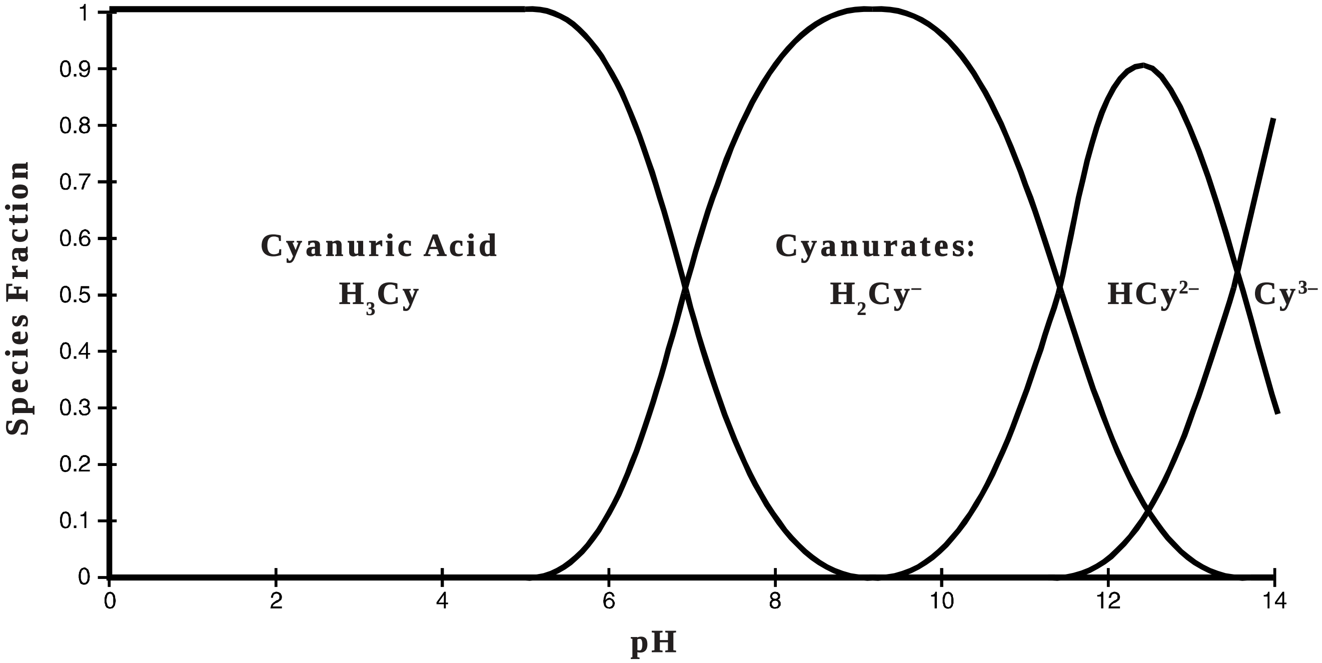


Figure 2. Distribution of Cyanuric Acid and Cyanurates vs. pH

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