3.2 – Calcium Carbonate Precipitation Potential

Although the calcium carbonate saturation index is applicable to swimming pool water balance calculations, it is only a qualitative indicator of calcium carbonate precipitation since it does not indicate the extent of precipitation that can occur at positive values of SI. Utilizing the mathematics of aqueous carbonate and cyanurate equilibria allows calculation of the quantitative calcium carbonate precipitation potential (CCPP), i.e., the equivalent calcium carbonate supersaturation. Precipitation of calcium carbonate is accompanied by a drop in pH and a reduction in hardness of 1 mol and in total alkalinity of 2 equivalents for each mol of calcium carbonate precipitated. The calcium carbonate precipitation potential increases with saturation index and buffer intensity. Buffer intensity in turn is a function of pH and total alkalinity. Because buffer intensity decreases with increasing pH, the CCPP also decreases as pH is increased. Cyanurate contributes to total alkalinity, thus it inreases the CCPP for a given carbonate alkalinity. At constant pH, carbonate alkalinity, and calcium hardness, the CCPP decreases with increasing TDS due to a decrease in SI. In Chapter 2.2 of this series, laboratory data on the precipitation of calcium carbonate under different conditions will be presented and interpreted.

Calcium Carbonate Precipitation Potential – Theory

Carbonate Equilibria – Dissociation of carbonic acid produces hydrogen and bicarbonate ions.

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

where $H_2CO_3^* \cong 0.997[CO_2] + 0.003[H_2CO_3]$. The activity ($K_1$) and concentration (${}^cK_1$) equilibrium constants are:

$$K_1 = [H^+]\gamma_{H^+}[HCO_3^-]\gamma_{HCO_3^-}/([H_2CO_3^*]\gamma_{H_2CO_3^*})$$

$$\begin{aligned} {}^cK_1 &= [H^+][HCO_3^-]/[H_2CO_3^*] \\ &= K_1\gamma_{H_2CO_3^*}/(\gamma_{H^+}\gamma_{HCO_3^-}) \end{aligned}$$

where the bracketed terms are molar concentrations and the γ's represent activity coefficients. The temperature dependent equation (T in Kelvin) for K_1 is given by (Plummer and Busenberg 1982):

$$\begin{aligned} \text{Log } K_1 = &-356.3094 - 0.06091964T + 21834.37/T \\ &+ 126.8339 \text{ Log } T - 1684915/T^2 \end{aligned}$$

Bicarbonate ion dissociates into hydrogen and carbonate ions.

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

The activity (K_2) and concentration (${}^cK_2$) equilibrium constants are given by the following expressions:

$$K_2 = [H^+]\gamma_{H^+}[CO_3^{2-}]\gamma_{CO_3^{2-}}/([HCO_3^-]\gamma_{HCO_3^-})$$

$$\begin{aligned} {}^cK_2 &= [H^+][CO_3^{2-}]/[HCO_3^-] \\ &= K_2(\gamma_{HCO_3^-})/(\gamma_{H^+}\gamma_{CO_3^{2-}}) \end{aligned}$$

The temperature dependent equation (T in kelvins) for K_2 is given by (Plummer and Busenberg 1982):

$$\begin{aligned} \text{Log } K_2 = &-107.8871 - 0.032528T \\ &+ 5151.79/T + 38.92561 \log T \\ &- 563713.9/T^2 \end{aligned}$$

The respective ionization fractions are calcu-

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lated as follows (where $\alpha_0 + \alpha_1 + \alpha_2 = 1$):

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

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

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

The total concentration of carbonate species (C_T) is given by:

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

The concentration of individual species is calculated from C_T and the ionization fractions.

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

Cyanurate Equilibria – Below pH 9, the only significant equilibrium in the cyanuric acid (CA) system is:

$$H_3Cy \rightleftharpoons H^+ + H_2Cy^-$$

$$K_{CA} = [H^+]\gamma_{H^+}[H_2Cy^-]\gamma_{H_2Cy^-}/([H_3Cy]\gamma_{H_3Cy})$$

$$\begin{aligned}{}^cK_{CA} &= [H^+][H_2Cy^-]/[H_3Cy] \\ &= K_{CA}\gamma_{H_3Cy}/(\gamma_{H^+}\gamma_{H_2Cy^-})\end{aligned}$$

The temperature dependent equation (T in kelvins) for K_{CA} is given by (Matte 1990):

$$\text{Log } K_{CA} = -\,31.08 + 0.154T - (2.441 \cdot 10^{-4})T^2$$

The total concentration of species is:

$$C_T' = [H_3Cy] + [H_2Cy^-]$$

The ionization fractions are (where $\alpha_0' + \alpha_1' = 1$):

$$\alpha_0' = (K_{CA}/[H^+] + 1)^{-1}$$

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

The concentration of individual species is calculated from C_T' and the ionization fractions.

$$[H_3Cy] = C_T'\alpha_0' \qquad [H_2Cy^-] = C_T'\alpha_1'$$

Calcium Carbonate Solubility – The solubility of calcium carbonate is controlled by the solubility product, which is the equilibrium constant for the reaction representing the dissolution of a solid to form its constituent ions.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

Since the activity of solids (e.g., $CaCO_3$) are equal to one, the activity solubility product (K_S) is given by:

$$K_S = \{Ca^{2+}\}\{CO_3^{2-}\} = [Ca^{2+}]\gamma_{Ca^{2+}}[CO_3^{2-}]\gamma_{CO_3^{2-}}$$

The concentration solubility product (${}^cK_S$) is given by:

$${}^cK_S = [Ca^{2+}][CO_3^{2-}] = K_S/(\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}})$$

Where the braces and brackets in the above two equations represent actual activities and concentrations, respectively, and $\gamma_{Ca^{2+}}$ and $\gamma_{CO_3^{2-}}$ are the activity coefficients of calcium and carbonate ions which were calculated using the Guntelberg approximation (Stumm and Morgan 1996). The temperature dependent equation for K_S for the calcite form of calcium carbonate is given by (Plummer and Busenberg 1982):

$$\begin{aligned}\text{Log } K_S = {} & -171.9065 - 0.077993T + 2839.319/T \\ & + 71.595 \text{ Log } T\end{aligned}$$

Where T is the temperature in kelvins.

The solubility (s) of calcium carbonate in CO_2–free distilled water can be calculated from aqueous equilibria. The mass balance is:

$$s = [Ca^{2+}] = C_T = {}^cK_S/[CO_3^{2-}] = {}^cK_S/C_T\alpha_2 = ({}^cK_S/\alpha_2)^{.5}$$

The charge balance is:

$$2[Ca^{2+}] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

Substituting the first equation into the second and rearranging gives the following equation; where $K_w = [OH^-][H^+]$ and $K_w = -\,4470.99/T + 6.0875 - 0.01706T$.

$$({}^cK_S/\alpha_2)^{.5}(2 - \alpha_1 - 2\alpha_2) + [H^+] - K_w/[H^+] = 0$$

This equation can be solved for $[H^+]$ by iteration. At 25°C the solubility is 0.012 g/L and the pH is 9.92. Table 1 shows calculated values of calcium carbonate solubility as a function of temperature and total dissolved solids.

	Solubility (mg/L)	
Temperature	TDS	
°F	1000 mg/L	5000 mg/L
32	12.1	21.5
80	10.7	19.0

Table 1 – Calculated Solubility of Calcium Carbonate

The solubility of calcium carbonate increases with decreasing pH due to the reactions:

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$$

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

Although the solubility of calcium carbonate increases as pH decreases, the solubility product remains unchanged. The lower the pH the lower the carbonate concentration. Therefore, in order to maintain saturated conditions, the calcium concentration must be increased.

Calcium Carbonate Supersaturation – Supersaturated solutions of calcium carbonate can be formed from saturated or undersaturated solutions when the calcium hardness, pH or alkalinity are increased. The degree of calcium carbonate saturation (S) is given by the ratio of the actual ion activity product (IAP) and the thermodynamic solubility product constant at infinite dilution (K_S):

$$\begin{aligned} S &= IAP/K_S = \{Ca^{2+}\}\{CO_3^{2-}\}/K_S \\ &= [Ca^{2+}]\gamma_{Ca^{2+}}[CO_3^{2-}]\gamma_{CO_3^{2-}}/K_S \end{aligned}$$

$$S = [Ca^{2+}][CO_3^{2-}]/{}^cK_S$$

S values of <1, 1, and >1 represent undersaturation, saturation, and oversaturation, respectively.

Precipitation of Calcium Carbonate – Excess calcium carbonate is precipitated as follows:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

Bicarbonate ions dissociate to replenish the carbonate ions.

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

The result of the above reactions is:

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+$$

The hydrogen ions liberated in the above reaction can react with alkalinity, i.e., bicarbonate and cyanurate ions:

$$xH^+ + xHCO_3^- \rightarrow xH_2CO_3^*$$

$$(1-x)H^+ + (1-x)H_2Cy^- \rightarrow (1-x)H_3Cy$$

The overall reaction is:

$$\begin{aligned} &Ca^{2+} + (1+x)HCO_3^- + (1-x)H_2Cy^- \rightarrow \\ &\qquad CaCO_3 + xH_2CO_3^* + (1-x)H_3Cy \end{aligned}$$

The relative extents of neutralization of bicarbonate and cyanurate depend on pH (i.e., the first ionization fractions of carbonic and cyanuric acid) and the respective levels of bicarbonate and cyanurate alkalinity. Below pH 9, the reaction of hydrogen ions with hydroxyl ions is negligible. The precipitation of calcium carbonate results not only in a decrease in calcium hardness and alkalinity, but also in pH. One mol of hardness and two equivalents of alkalinity are consumed for each mol of calcium carbonate precipitated.

Calculation of Calcium Carbonate Precipitation Potential

Calculation Model – Total alkalinity (Alk_T, equivalents) is represented by:

$$Alk_T = [HCO_3^-] + 2[CO_3^{2-}] + [H_2Cy^-] + [OH^-] - [H^+]$$

Below pH 9 the concentrations of hydrogen and hydroxyl ions can be neglected. Substitution of appropriate terms for bicarbonate, carbonate, and cyanurate, gives the following equation, where i represents initial values of the various terms:

$$Alk_{T,i} = C_{T,i}(\alpha_{1,i} + 2\alpha_{2,i}) + C_T'\alpha_{1,i}'$$

After equilibration, i.e., after precipitation of calcium carbonate is completed (i.e., the saturation index is equal to 0), the following relationship holds:

$$Alk_{T,i} - 2x = (C_{T,i} - x)(\alpha_{1,f} + 2\alpha_{2,f}) + C_T'\alpha_{1,f}'$$

where: x is the concentration of calcium and carbonate ions precipitated as $CaCO_3$. Solving for x we have (where the subscripts i and f refer to initial and final conditions):

$$x = [C_{T,i}(\alpha_{1,f} + 2\alpha_{2,f}) + C_T'\alpha_{1,f}' - Alk_{T,i}]/(\alpha_{1,f} + 2\alpha_{2,f} - 2)$$

Substituting x into the equation for the degree of calcium carbonate saturation, $S_f = [Ca^{2+}][CO_3^{2-}]/{}^cK_S$, gives:

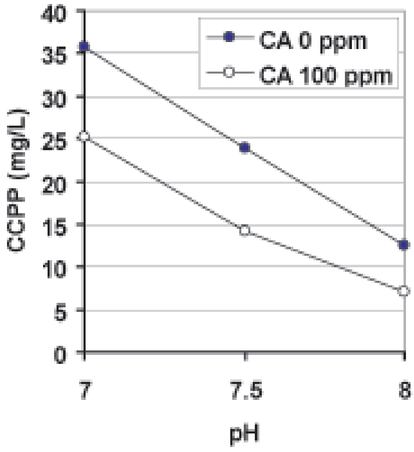

Figure 1 – CCPP as a Function of pH for Unstabilized and Stabilized Water

(SI = 0.50, C. Alkalinity = 100 mg/L, TDS = 5000 mg/L)

$$S_f = [Ca^{2+} - x][CO_3^{2-} - x]/{}^cK_S$$

This is one form of a working equation for calculation of CCPP. Another form is obtained by substituting ${}^cK_2[HCO_3^-]/[H^+]$ for the carbonate concentration and converting concentration equilibrium constants to activity equilibrium constants by introducing activity coefficients:

$$S = [Ca^{2+}]\gamma_{Ca^{2+}}K_2[HCO_3^-]\gamma_{HCO_3^-}/([H^+]\gamma_{H^+}K_S)$$

Taking logs of both sides, and noting that $pH = [H^+]\gamma H^+$, we have the saturation index equation with concentrations in mol/L.

$$SI = pH + Log\,[HCO_3^-] + Log\,[Ca^{2+}] + Log\,(K_2/K_S) + Log\,\gamma_{HCO_3^-} + Log\,\gamma_{Ca^{2+}}$$

This is further modified as follows:

$$SI = pH + Log\,[(C_T - x)\alpha_1] + Log\,([Ca^{2+}]_i - x) + Log\,(K_2/K_S) + Log\,\gamma_{HCO_3^-} + Log\,\gamma_{Ca^{2+}}$$

A computer program was written to perform the calculations using this working equation. The procedure involved inputting the initial pH, hardness, total alkalinity, and cyanuric acid and calculating the initial ionization fractions. The pH was then incremented and the new ionization fractions were calculated followed by calculation of the value of x which was inserted into the working equation. A test was made to determine if SI_f was equal to 0, i.e., the IAP was equal to K_S or the ratio $IAP/K_S = 1$. The iteration process (utilizing a Newton–Rhafson convergence algorithm) was continued until this test was satisfied to within the tolerance set. The model assumes no loss of carbon dioxide during the precipitation process, thus the acidity (Acy) remains constant:

$$Acy = 2[H_2CO_3^*] + [HCO_3^-] + [H_3Cy] + [H^+] - [OH^-]$$

Values of CCPP at 80°F for various conditions calculated using the above computer program are shown in Tables 1–6. For consistency, the TDS in most instances was set at 5000 ppm, although it is understood that this is

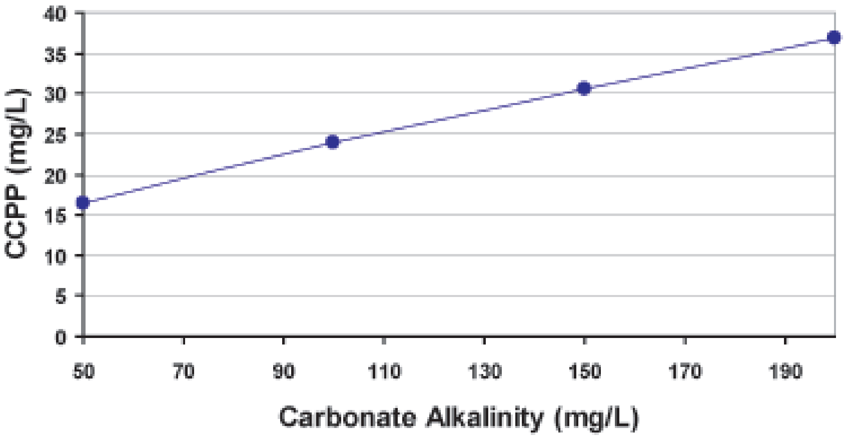

Figure 2 – Effect of Carbonate Alkalinity on CCPP

(pH = 7.5, SI = 0.50, CA = 100 mg/L, TDS = 5000 mg/L)

higher than for most swimming pool water. An analytical model for CCPP has been developed for cyanuric acid free water (Rossum 1983).

pH_i	Carb.Alk. mg/L	CA mg/L	Hard. mg/L	Buffer Intensity	pH_f	CCPP mg/L
7.0	100	0	4786	32.6	6.63	25.2
7.5	100	0	1514	12.2	7.07	14.1
8.0	100	0	479	6.3	7.54	7.1

Table 2 – Calcium Carbonate Precipitation Potential as a Function of pH: Unstabilized Water (TDS = 5000 mg/L, SI = 0.50)

Effect of pH (Stabilized Water) – The presence of cyanurate alkalinity increases the CCPP by increasing the buffer intensity (Table 3). A plot of CCPP against pH for unstabilized and stabilized water is shown in Figure 1.

pH_i	Carb.Alk. mg/L	CA mg/L	Hard. mg/L	Buffer Intensity	pH_f	CCPP mg/L
7.0	100	100	4786	52.7	6.65	35.8
7.5	100	100	1514	23.1	7.09	23.9
8.0	100	100	479	10.6	7.56	12.5

Table 3 – Calcium Carbonate Precipitation Potential as a Function of pH: Stabilized Water (TDS = 5000 mg/L, SI = 0.50)

Effect of Alkalinity – At constant SI, pH, TDS, and cyanuric acid concentration, the CCPP increases with increasing carbonate alkalinity due to increasing buffer intensity (Table 4). A plot of CCPP vs. alkalinity is shown in Figure 2.

pH_i	Carb.Alk. mg/L	CA mg/L	Hard. mg/L	Buffer Intensity	pH_f	CCPP mg/L
7.5	50	100	3027	17.0	7.11	16.5
7.5	100	100	1513	23.1	7.09	23.9
7.5	150	100	1009	29.1	7.09	30.6
7.5	200	100	757	35.2	7.09	36.8

Table 4 – Calcium Carbonate Precipitation Potential: Effect of Alkalinity (TDS = 5000 mg/L, SI = 0.50)

Effect of Varying Cyanuric Acid Concentration – The data in Table 5 show that at constant SI, pH, carbonate alkalinity, and TDS, the CCPP increases with increasing cyanuric acid concentration due to increasing buffer intensity. A plot of CCPP as a function of CA concentration is shown in Figure 3.

pH_i	Carb.Alk. mg/L	CA mg/L	Hard. mg/L	Buffer Intensity	pH_f	CCPP mg/L
7.5	100	50	1514	17.6	7.08	19.2
7.5	100	100	1514	23.1	7.09	23.9
7.5	100	150	1514	28.5	7.10	28.4
7.5	100	200	1514	34.0	7.11	32.6

Table 5 – Calcium Carbonate Precipitation Potential: Effect of Varying Cyanuric Acid Concentration (TDS = 5000 mg/L, SI = 0.50)

Effect of Saturation Index – At constant pH, TDS, carbonate alkalinity, cyanuric acid concentration, and buffer intensity, the CCPP increases with increasing SI (Table 6). A plot of CCPP against SI is shown in Figure 4.

SI_i	Carb.Alk. mg/L	CA mg/L	Hard. mg/L	Buffer Intensity	pH_f	CCPP mg/L
0.25	100	100	851	23.1	7.29	10.7
0.50	100	100	1514	23.1	7.09	23.9
0.75	100	100	2692	23.1	6.91	38.8
1.00	100	100	4786	23.1	6.73	54.1

Table 6 – Calcium Carbonate Precipitation Potential: Effect of Saturation Index at pH 7.5 (TDS 5000 mg/L)

Effect of Total Dissolved Solids – At constant pH, carbonate alkalinity, cyanuric acid, and calcium hardness. The CCPP decreases with increasing TDS due to a decreasing saturation index (Table 7). A plot of CCPP against TDS is shown in Figure 5.

TDS mg/L	Carb.Alk. mg/L	CA mg/L	SI	Buffer Intensity	pH_f	CCPP mg/L
1000	100	100	0.50	25.6	7.10	25.1
2000	100	100	0.38	24.6	7.19	18.2
3000	100	100	0.30	23.9	7.25	13.8
4000	100	100	0.24	23.5	7.30	10.4
5000	100	100	0.19	23.1	7.34	7.9

Table 7 – Calcium Carbonate Precipitation Potential: Effect of Total Dissolved Solids at pH 7.5 and Hardness 740 mg/L

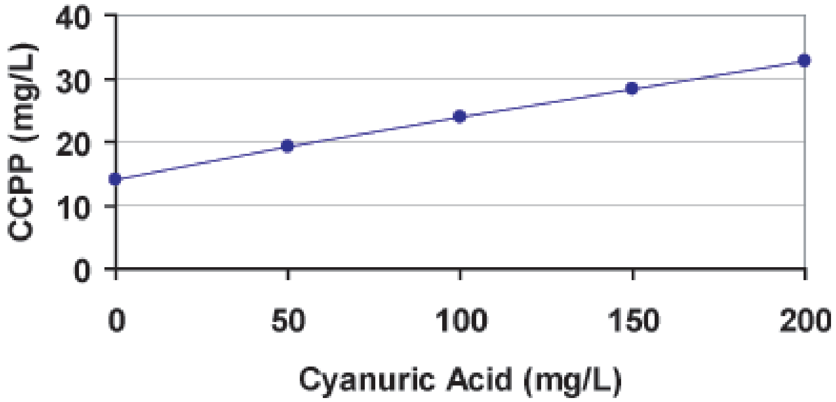

Figure 3 – Effect of Cyanuric Acid on CCPP

(pH = 7.5, SI = 0.50, C. Alkalinity = 100 mg/L, TDS = 5000 mg/L)

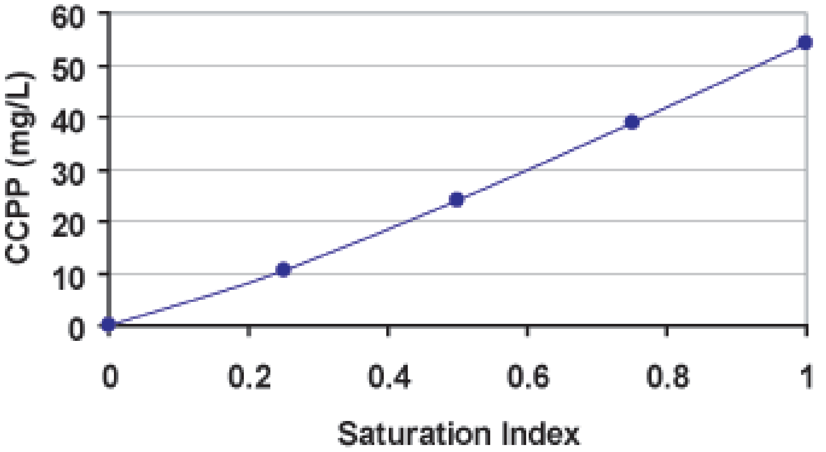

Figure 4 – Effect of Saturation Index on CCPP

(pH = 7.5, C. Alkalinity = 100 mg/L, CA = 100 mg/L, TDS = 5000 mg/L)

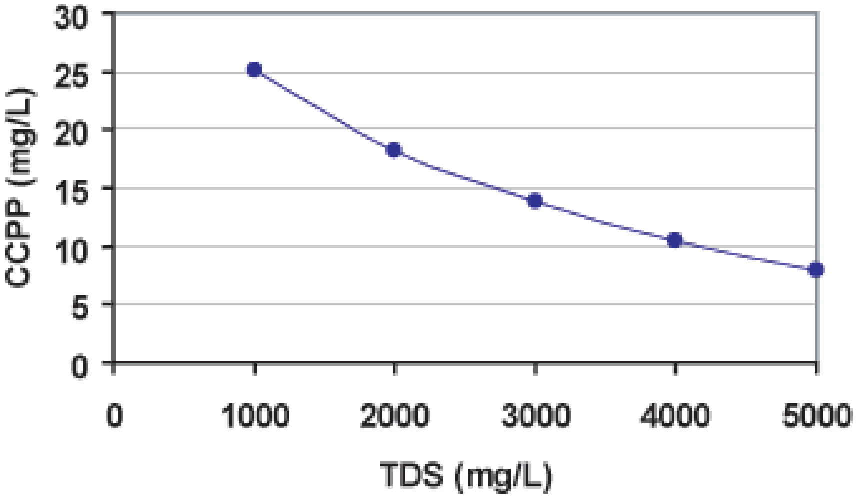

Figure 5 – CCPP as a Function of TDS

(pH = 7.5, C. Alkalinity = 100 mg/L, Hardness = 740 mg/L, CA = 100 mg/L)

Effect of pH (Unstabilized Water) – The effect of pH on CCPP is shown in Table 2. The CCPP decreases with increasing pH at constant alkalinity. This is due entirely to the decreasing initial buffer intensity.

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