

APPENDIX D

COMPUTATIONAL PROCEDURES

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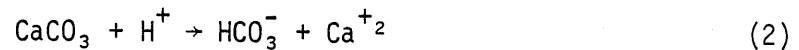
NEUTRALIZATION OF ACIDITY BY LIMESTONE - COMPUTATIONAL PROCEDURE

The alkalinity of an acidic or neutral water containing carbonate, sulfate, aluminum or iron is given by:

$$\begin{aligned}
 [Alk] = & [HCO_3^-] - [H^+] - [HSO_4^-] \\
 & - 3[Al^{+3}] - 2[Al(OH)^{+2}] - [Al(OH)_2^+] \\
 & - 3[Fe^{+2}] - 2[Fe(OH)^{+2}] - [Fe(OH)_2^+] \\
 & - 2[Fe^{+2}] - [Fe(OH)^+]
 \end{aligned} \tag{1}$$

where: brackets represent concentrations of the specified species. Hydroxy-bridged species of Al(III) and Fe(III) exist in addition to those shown here, but those shown in Eq. 1 appear adequate for describing the contributions of Fe(III) and Al(III) species to the alkalinity of a water.

Neutralization processes employing crushed limestone introduce alkalinity to a water at a rate directly proportional to the proton concentration in the water according to the first-order reaction:



As protons are removed by Eq. 2, the relative concentration of chemical species in Eq. 1 adjusts towards restoration of thermodynamic equilibrium between all species present in solution according to equations of the type:

$$\frac{[Z(OH)_{n+1}^{m-n-1}]}{[Z(OH)_n^{m-n}]} = K_n \quad (0 \leq n \leq m) \tag{3a}$$

or:

$$\frac{[M_{n+1} A^{n+1-m}][H^+]}{[H_n A^{n-m}]} = K_n \quad (0 \leq n \leq m) \tag{3b}$$

where Z^{+m} is a weak base-forming cation; A^{-m} is a weak acid-forming anion; and K_n is the n-th acidity constant.

For present purposes we assume total concentration of species of carbonates, sulfates and oxyhydrates of iron and aluminum to be conserved in the water, although the effects of removal of species from solution by precipitation as solids or exsolution as gases can be estimated. Then the total concentration of species of a particular cation Z^{+m} , or anion, A^{-m} can be written:

$$[Z_t] = [Z^{+m}] + [Z(OH)^{m-1}] + \dots + [Z(OH)_m] \tag{4a}$$

$$[A_t] = [A^{-m}] + [HA^{1-m}] + \dots + [H_m A] \tag{4b}$$

Amphoteric behavior, associated with a species of opposite sign to the parent cation or anion, is not considered in the expression for alkalinity, Eq. 1, nor

in Eq. 4, because this phenomenon usually contributes only slightly to the alkalinity of acidic or neutral waters.

Eqs. 3a and 4a combine as follows:

$$\begin{aligned}
 [Z_t] &= \frac{[H]}{K_1}[Z(OH)^{m-1}] + \frac{[H]}{K_2}[Z(OH)_2^{m-2}] + \frac{[H]}{K_n}[Z(OH)_m] + [Z(OH)_m] \\
 &= \frac{[H]^2}{K_1K_2}[Z(OH)_2^{m-2}] + \frac{[H]^2}{K_2K_3}[Z(OH)_3^{m-3}] + \dots + \frac{[H^+]^2}{K_{m-1}K_m}[Z(OH)_m] + \frac{[H^+]}{K_n}[Z(OH)_m] + [Z(OH)] \\
 &= \left\{ \frac{[H]^m}{K_1K_2K_3 \dots K_m} + \frac{[H]^{m-1}}{K_2K_3 \dots K_m} + \dots + \frac{[H]^2}{K_{m-1}K_m} + \frac{[H^+]}{K_m} + 1 \right\} [Z(OH)]_m \\
 &= 1 + \sum_{n=1}^m \sum_{j=1}^n \frac{[H^+]}{K_{m+1-j}} [Z(OH)]_m \quad (5)
 \end{aligned}$$

and similarly for $[A_t]$.

Réfer now to the contribution to alkalinity by each of the metals Al(III), Fe(II) and Fe(III), that can be written in the form:

$$\begin{aligned}
 -Alk_z &= m[Z^{+m}] + (m-1)[Z(OH)^{m-1}] + \dots + [Z(OH)_{m-1}^+] \\
 &= \sum_{n=1}^m m \sum_{j=1}^n \frac{[H^+]}{K_{m+1-j}} [Z(OH)]_m \quad (6)
 \end{aligned}$$

and similarly for alkalinity associated with anionic species.

Now combining Eqs. 5 and 6:

$$\begin{aligned}
 Alk_z &= -[Z_t] \frac{\sum_{n=1}^m \sum_{j=1}^n \frac{[H^+]}{K_{m+1-j}}}{1 + \sum_{n=1}^m \sum_{j=1}^n \frac{[H^+]}{K_{m+1-j}}} \\
 \text{or } Alk_z &= -[Z_t] \frac{\mu_1}{1+\mu_0} \text{ and } Alk_A = [A_t] \frac{\mu}{1+\mu_0} \quad (7)
 \end{aligned}$$

where:

$$\mu_k = \sum_{n=1}^m n^k \sum_{j=1}^n \frac{[H^+]}{K_{m+1-j}} \quad (8)$$

Thus the total alkalinity of a water can be written as the sum of terms of the form of Eq. 7. Each of these terms is a function of three parameters:

- the total concentration of cationic or anionic species, Z_t or A
- the acidity dissociation constants for these species, K_n ; and
- the proton concentration of the water, $[H^+]$.

Such an expression would be sufficient to completely define the neutra-

lization history of a water (ie. $[H^+]$ or pH vs amount of neutralization agent added) if a hydroxide neutralizing agent such as lime or sodium hydroxide were used. However, in the case of limestone neutralization, account must be taken of the quantity of carbonate species introduced to the water as neutralization proceeds. For this accounting, we note that carbonate species added to the water during neutralization are equivalent to protons neutralized, both mineral acidity protons and those associated with protolyzed species formed from weak base-forming cations and weak acid-forming anions. That is, for $[H]_t$ defined by:

$$[H^+] = 2[H_2CO_3] + [HCO_3^-] + [H^+] - \sum Alk_Z - \sum Alk_A \quad (9a)$$

$[H^+]$ is constant throughout neutralization provided precipitation of metal oxyhydrates or exsolution of carbon dioxide does not occur.

The first two terms of Eq. 9a may be written:

$$2[H_2CO_3] + [HCO_3^-] = C_t \frac{2[H^+] + K_1}{[H^+] + K_1} \quad (9b)$$

where:

C_t = total concentration of carbonate species, and

K_1 is the first acidity dissociation constant for carbonic acid.

Combining Eqs. 9a and 9b, the concentration of carbonic species at any stage during neutralization is:

$$C_t = \left\{ C_{t_0} \frac{2[H^+]_0 + K_1}{[H^+]_0 + K_1} + [H^-]_0 - Alk_{Z_0} - Alk_{A_0} - [H^+] + Alk_Z + Alk_A \right\} \frac{[H^+] + K_1}{2[H^+] + K_1} \quad (9c)$$

where subscript zero represents pre-neutralization conditions for the water.

Consequently, the alkalinity of a water at any stage during neutralization is:

$$Alk_t = \frac{\left\{ C_{t_0} \frac{2[H]_0 + K_1}{[H]_0 + K_1} + [H]_0 - Alk_{Z_0} - Alk_{A_0} - [H^+] + Alk_Z + Alk_A \right\} \frac{[H^+] + K_1}{2[H^+] + K_1}}{1 + [H^+]/K_1} - [H^+] + Alk_Z + Alk_A$$

$$= \frac{\{[B] - [H^+] - [A]\}}{1 + 2[H^+]/K_1} - [H^+] - [A] \quad (10)$$

where $[B] = C_{t_0} (2[H^+]_0 + K_1) / ([H^+]_0 + K_1) + [H_0] - Alk_{Z_0} - Alk_{A_0}$ depends only on the chemical composition of the raw water and is constant during treatment; and $[A] = -Alk_Z - Alk_A$ measures the proton level of non-carbonic proton clotrating species in the water at a pH corresponding to $[H^+]$, and can be calculated given values of Z_t , A_t , K_n and $[H^+]$.

NEUTRALIZATION KINETICS

Neutralization according to Eq. 2 is measured by the rate of change of alkalinity, which is related to the chemical composition of the water by Eq. 1. Being controlled by the reactive surface of limestone per unit flow of acidic water to be neutralized, and by the rate of diffusion of protons from the acidic water to this surface; the first order reaction conforms to:

$$\frac{d[A]k}{dL} = k[H^+] \quad (11)$$

where L = Load factor = tons of limestone/cfs/inch, a measure of stone surface per unit flow; and k = a constant defining the rate of the reaction = 0.33238.

Design of a neutralization process involves computing the Load Factor to produce a specified final pH for the water to be neutralized. To compute this Load Factor, Eqs. 10 and 11 are combined to obtain:

$$\begin{aligned} L &= \int dL = \int \frac{d[A]k}{k[H^+]} = \int \frac{1}{k[H^+]} d \left\{ \frac{([B]-[H^+]-[A])}{1+2[H^+]/K_1} - [H^+]-[A] \right\} \\ &= \int \frac{1}{k[H^+]} \frac{\{([B]-[H^+]-[A])-[H^+]-[A]\}}{1+2[H^+]/K_1} d[H^+] \\ &= - \frac{1}{k[H^+]} \left\{ \frac{2}{K_1} \cdot \frac{([B]-[H^+]-[A])}{(1+2[H^+]/K_1)} + \left(1 + \frac{d[A]}{d[H^+]}\right) \left(1 + \frac{1}{1+2[H^+]/K_1}\right) \right\} d[H^+] \quad (12) \end{aligned}$$

To evaluate $d[A]/d[H^+]$ in Eq. 12, note that [A] is the sum of terms of the form $[Z_t]_{\mu_1}/(1+\mu_0)$ and $[A_t]_{\mu_1}/(1+\mu_0)$, where μ_0 and μ_1 are defined by Eq. 8, ie.

$$[A] = \sum_{i=2}^{\mu_1} [X_t]_i \frac{\mu_1}{1+\mu_0} \quad (13)$$

where X_t = concentration of weak base-producing cation or weak acid-producing anion, and μ_0 = number of such cations and anions present. The lower limit of 2 in the summation in Eq. 13 indicates that carbonate species are excluded from the summation.

With μ_k defined by Eq. 8,

$$\frac{d\mu_k}{d[H^+]} = \sum_{n=1}^m n^k \cdot \frac{n}{[H^+]} \sum_{j=1}^n \frac{1}{K_{m+1-j}} \frac{[H^+]}{[H^+]} = \frac{1}{[H^+]} \sum_{n=1}^m n^{k+1} \sum_{j=1}^n \frac{[H^+]}{K_{m+1-j}} = \frac{\mu_{k+1}}{[H^+]} \quad (14)$$

so that:

$$\begin{aligned}
\frac{d[A]}{d[H^+]} &= \sum_{i=2}^{no} [X_t]_i \frac{d}{d[H^+]} \left(\frac{\mu_1}{1+\mu_0} \right) \\
&= \sum_{i=2}^{no} [X_t]_i \left\{ \frac{\mu_2}{[H^+](1+\mu_0)} - \frac{\mu_1 \mu_1}{(1+\mu_0)^2 [H^+]} \right. \\
&= \sum_{i=2}^{no} \frac{[X_t]_i}{[H^+]} \left\{ \frac{\mu_2}{1+\mu_0} - \left(\frac{\mu_1}{1+\mu_0} \right)^2 \right\} \quad (15)
\end{aligned}$$

By substituting Eqs. 13 and 15 in Eq. 12, the value of L to produce the required charge in $[H^+]$ from its initial value $[H^+]_0$ may be computed provided the initial concentrations of carbonate and other weak acid and weak base-forming ions are known, together with their acids dissociate constants.

COMPUTED TITRATION CURVES AND BUFFER INTENSITY CURVES

To compute an alkalinity titration curve for a water, Eq. 10 is evaluated for a final pH equal to the pH 4.5 endpoint of the titration curve and the resulting value deducted from the value of Alk_t by Eq. 10 at other pH values. For the acidity titration curve the value of Alk_t is computed at the pH 8.3 endpoint of the acidity titration, and from that value is subtracted the value of Alk_t at the pH at which acidity is required.

Buffer intensity, the derivative of alkalinity (or acidity) with respect to pH, measures the incremental alkalinity (or acidity) needed to produce unit change in pH, or the resistance of the water to neutralization at a particular pH.

LOAD FACTOR TO NEUTRALIZE WATER CONTAINING NON-CARBONATE pH BUFFERING SPECIES

eg. Al(III), Fe(III), $SO_4(II)$, Ca(II), Fe(II)

Rate of neutralization by limestone is:

$$\frac{d[Alk]}{dL} = 2ck [H^+]$$

where $[Alk]$ = alkalinity, L = Load Factor, c = units conversion factor, k = rate constant, $pH = \log[H^+]$.

Alkalinity is related to $[H^+]$ and concentrations of pH buffering species by:

$$[Alk] = \frac{c}{1 + \frac{[H^+]}{K_1}} = [H^+] - \sum_{m=2}^n [Z]_m \frac{\mu_{1,m}}{1+\mu_{0,m}}$$

$$\text{where } \mu_{k,m} = \sum_{i=1}^k \prod_{l=1}^i \frac{[H^+]}{K_{j+1-i,m}} \quad j = \text{number of species}$$

$$= c/(1+[H^+]/K_1) - [H^+] - f[H^+] \text{ where } c = \text{inorganic carbon concentration}$$

During neutralization, protons are conserved, i.e. $2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{H}^+] + f[\text{H}^+] =$ constant. This provides a basis for computing the inorganic carbon concentration at any time provided limestone is used for neutralization and CO_2 is not lost from the system.

$$c = \left[C_0 \frac{(2+K_1/[\text{H}^+]_0)}{(1+K_1/[\text{H}^+]_0)} + [\text{H}^+]_0 + f[\text{H}^+]_0 - [\text{H}^+] - f[\text{H}^+] \right] \frac{1+K_1/[\text{H}^+]}{2+K_1/[\text{H}^+]}$$

$$= [a - [\text{H}^+] - f[\text{H}^+]] \frac{1+K_1/[\text{H}^+]}{2+K_1/[\text{H}^+]}$$

where $a = \text{total protons} = 2[\text{H}_2\text{CO}_3]_0 + [\text{HCO}_3^-]_0 + [\text{H}^+]_0 + f[\text{H}^+]_0$

$$[A1k] = \frac{a}{1 + \frac{2[\text{H}^+]}{K_1}} - ([\text{H}^+] + f[\text{H}^+]) \left[1 + \frac{1}{1 + \frac{2[\text{H}^+]}{K_1}} \right]$$

$$\frac{d[A1k]}{d[\text{H}^+]} = - \left\{ \frac{2K_1(a - [\text{H}^+] - f[\text{H}^+])}{(K_1 + 2[\text{H}^+]^2)} + \left[1 + \frac{df[\text{H}^+]}{d[\text{H}^+]} \right] \left[1 + \frac{K_1}{K_1 + 2[\text{H}^+]} \right] \right\} \frac{df[\text{H}^+]}{d[\text{H}^+]} = \sum_{m=2}^n \frac{[Z]_m}{[\text{H}^+]} \left\{ \frac{\mu_{2m}}{H\mu_{0,m}} - \left(\frac{\mu_{1m}}{H\mu_{0,m}} \right)^2 \right\}$$

$$L = \int dL = \int \frac{d[A1k]}{2ck_1[\text{H}^+]} = \int \frac{d[A1k]}{d[\text{H}^+]} \cdot \frac{d[\text{H}^+]}{2ck_1[\text{H}^+]} = - \int \frac{\frac{2K_1(a - [\text{H}^+] - f[\text{H}^+])}{(K_1 + 2[\text{H}^+]^2)} + \left[1 + \frac{df[\text{H}^+]}{d[\text{H}^+]} \right] \left[1 + \frac{K_1}{K_1 + 2[\text{H}^+]} \right]}{2ck_1[\text{H}^+]}$$

$$d[\text{H}^+] = - \int 1/[\text{H}^+] d[\text{H}^+]$$

Runge-Kutta solution of integral for load factor:

$$\Delta x = \{e([\text{H}^+]) + 4e([\text{H}^+] + [\Delta\text{H}^+]/2) + e([\text{H}^+] + [\Delta\text{H}^+])\} / 6$$

TITRATION CURVE FOR ALUMINUM SULFATE + CARBON DIOXIDE EXSOLUTION

$$[N_x^+] + [\text{H}^+] + 3[\text{Al}^{+3}] + 2[\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_2^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + 2[\text{SO}_4^{2-}]$$

$$3[\text{SO}_4^{2-}] = 2[\text{Al}_t]$$

$$C_{t_0} = \frac{[\text{H}_2\text{CO}_3]_0}{1 + \frac{K_{1c}}{[\text{H}^+]_0} + \frac{K_{1c}K_{2c}}{[\text{H}^+]_0^2}}$$

$$[\text{Na}^+] = \frac{50}{27} [\text{Al}_t] \left\{ \frac{2}{3} - \frac{3[\text{Al}^{+3}] + 2[\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_2^+]}{[\text{Al}^{+3}] + [\text{Al}(\text{OH})^{+2}] + [\text{Al}(\text{OH})_2^+] + [\text{Al}(\text{OH})_3]} \right\} + [C_t] \frac{2[\text{CO}_3^{2-}] + [\text{HCO}_3^-]}{[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]} - [\text{H}^+] + [\text{OH}^-]$$

$$K_1 = \frac{[Al(OH)^{+2}][H^+]}{[Al^{+3}]} = 10^{-3.8} \quad K_2 = \frac{[Al(OH)_2^+][H^+]}{[Al(OH)^{+2}]} = 10^{-4.5} \quad K = \frac{[Al(OH)_3][H^+]}{[Al(OH)_2^+]} = 10^{-6.8}$$

$$K_{1c} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} = 10^{-6.37} \quad K_{2c} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 10^{-10.25}$$

$$[Al_t] = [Al(OH)_3] \left\{ 1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_2 K_3} + \frac{[H^+]^3}{K_1 K_2 K_3} \right\}$$

$$[Al(OH)_2^+] = \frac{[H^+]}{K_3} [Al(OH)_3] = \frac{\frac{[H^+]}{K_3} [Al_t]}{1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_2 K_3} + \frac{[H^+]^3}{K_1 K_2 K_3}} [Al(OH)^{+2}] = \frac{[H^+]}{K_2} [Al(OH)_2^+]$$

$$[Al^{+3}] = \frac{[H^+]}{K_1} [Al(OH)^{+2}]$$

$$\frac{[Al_t] (3[Al^{+3}] + 2[Al(OH)^{+2}] + [Al(OH)_2^+])}{[Al^{+3}] + [Al(OH)^{+2}] + [Al(OH)_2^+] + [Al(OH)_3]} = \frac{\left\{ \frac{3[H^+]^3}{K_1 K_2 K_3} + \frac{2[H^+]^2}{K_2 K_3} + \frac{[H^+]^3}{K_3} \right\} [Al(OH)_3]}{\left\{ \frac{[H^+]^3}{K_1 K_2 K_3} + \frac{[H^+]^2}{K_2 K_3} + \frac{[H^+]}{K_3} + 1 \right\} [Al(OH)_3]}$$

$$[Al_t] = [Al_t] \frac{\frac{3[H^+]^3}{K_1 K_2 K_3} + \frac{2[H^+]^2}{K_2 K_3} + \frac{[H^+]}{K_3}}{\frac{[H^+]^3}{K_1 K_2 K_3} + \frac{[H^+]^2}{K_2 K_3} + \frac{[H^+]}{K_3} + 1}$$

$$\frac{[C_t] (2[CO_3^{2-}] + [HCO_3^-])}{[CO_3^{2-}] + [HCO_3^-] + [H_2CO_3]} = [C_t] \frac{\left\{ 2 + \frac{[H^+]}{K_2} \right\} [CO_3^{2-}]}{\left\{ \frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1 \right\} [CO_3^{2-}]} = [C_t] \frac{2 + \frac{[H^+]}{K_2}}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}$$

$$[Na^+] = \frac{50}{27} [Al_t] \left\{ \frac{2}{3} - \frac{\frac{3[H^+]^3}{K_1 K_2 K_3} + \frac{2[H^+]^2}{K_2 K_3} + \frac{[H^+]}{K_3}}{\frac{[H^+]^3}{K_1 K_2 K_3} + \frac{[H^+]^2}{K_2 K_3} + \frac{[H^+]}{K_3} + 1} \right\} + [C_t] \left\{ \frac{2 + \frac{[H^+]}{K_2}}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1} \right\} - [H^+] + \frac{K_w}{[H^+]}$$

$$\text{where: } K_1 = 10^{(pK_3 - pH)} = 10^{(6.8 - pH)} = \frac{[H^+]}{K_3}$$

$$K_2 = 10^{(pK_2 - pH)} = 10^{4.5 - pH} = \frac{[H^+]}{K_2}$$

$$K_3 = 10^{(pK_1 - pH)} = 10^{3.8 - pH}$$

$$K_4 = 10^{5 - pH} = 10^5 [H^+]$$

$$K_5 = 10^{pH - 9} = 10^5 [OH^-]$$

$$K_6 = 10^{(pK_{1c} - pH)} = 10^{(6.37 - pH)} = \frac{[H^+]}{K_{1c}}$$

$$K_7 = 10^{(pK_{2c} - pH)} = 10^{10.25 - pH} = \frac{[H^+]}{K_{2c}}$$

