ACIDITY AND ALKALINITY IN MINE DRAINAGE: THEORETICAL CONSIDERATIONS[1]

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Abstract: Acidity, net acidity, and net alkalinity are widely used parameters for the characterization of mine drainage, but these terms are not well defined and are often misunderstood. Incorrect interpretation of acidity, alkalinity, and derivative terms can lead to inadequate treatment design or poor regulatory decisions. We briefly explain derivations of theoretical expressions of three types of alkalinities (caustic, phenolphthalein, and total) and acidities (mineral, CO_2, and total). Theoretically defined total alkalinity is closely analogous to measured alkalinity and presents few practical interpretation problems. Theoretically defined "CO_2-acidity" is closely related to most standard titration methods used for mine drainage with an endpoint pH of 8.3, but it presents numerous interpretation problems, and it is unfortunately named because CO_2 is intentionally driven off during titration of mine-drainage samples. Using the proton condition/mass-action approach and employing graphs for visualization, we explore the concept of principal components and how to assign acidity contributions to solution species, including aqueous complexes, commonly found in mine drainage. We define a comprehensive theoretical definition of acidity in mine drainage on the basis of aqueous speciation at the sample pH and the capacity of these species to undergo hydrolysis to pH 8.3. This definition indicates the computed acidity in milligrams per liter (mg L^{-1}) as $CaCO_3$ (based on pH and analytical concentrations of dissolved Fe^{III}, Fe^{II}, Mn, and Al in mg L^{-1}):

$$\text{Acidity}_{\text{computed}} = 50\cdot(10^{(3\text{-pH})} + 3\cdot C_{Fe^{III}}/55.8 + 2\cdot C_{Fe^{II}}/55.8 + 2\cdot C_{Mn}/54.9 + 3\cdot C_{Al}/27.0)$$

underestimates contributions from HSO_4^- and H^+, but overestimates the acidity due to Fe^{3+}. These errors tend to approximately cancel each other.

We demonstrate that "net alkalinity" is a valid mathematical construction based on theoretical definitions of alkalinity and acidity. We demonstrate that, for most mine-drainage solutions, a useful net alkalinity value can be derived from: 1) alkalinity and acidity values based on aqueous speciation, 2) measured alkalinity - computed acidity, or 3) taking the negative of the value obtained in a standard method "hot peroxide" acidity titration, *provided that labs report negative values*. We recommend the third approach; *i.e.*, Net alkalinity = - Hot Acidity.

Additional Key Words: calculated and measured acidity.

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Introduction

An aqueous solution with pH >4 can have both alkalinity and acidity. The computed difference between the alkalinity and acidity, commonly referred to as net alkalinity or net acidity, is widely used in mine-drainage characterization; however, the acidity and derivative terms are not well defined and often misunderstood. Incorrect interpretation can lead to poor treatment design or regulatory decisions.

Practitioners involved in the evaluation or design of mine-drainage treatment use alkalinity and acidity data to identify treatment alternatives and to determine the appropriate size and corresponding costs of treatment systems (*e.g.* Hedin *et al*., 1994; Skousen *et al*., 1998; U.S. Office of Surface Mining, 2002). Nevertheless, reference documents, text books, and other literature 1) vary significantly in the definitions of acidity, 2) do not provide adequate detail about contributions of specific aqueous species to acidity, and. 3) do not adequately address the computation of net alkalinity or net acidity.

This paper 1) compares theoretical definitions and laboratory practices for alkalinity and acidity, 2) explains both positive and negative contributions of species to alkalinity and acidity, 3) confirms that net alkalinity and net acidity are mathematically robust concepts, and 4) suggests methods that produce consistent and useful values for net alkalinity and net acidity. A companion paper (Cravotta and Kirby, this volume) examines the practical interpretations of the pH, alkalinity, and acidity for mine-drainage waters.

Verbal Definitions of Alkalinity and Acidity in the H_2O-CO_2 System

Alkalinity and acidity have various definitions. Stumm and Morgan (1996) define alkalinity as the "equivalent sum of the bases that are titratable with strong acid." They define acidity as the "equivalent sum of the acids that are titratable with strong base." Both titrations are defined in terms of the H_2O-CO_2 system. These verbal definitions imply that some reference points exist, *i.e*., that the titration must proceed from a starting pH to a chosen pH endpoint. These endpoints are based on equivalence points at pH values of ≈ 4.5, 8.3, and ≈ 11 (see points *x, y*, and *z* in Figure 1). Endpoints of titrations are ideally equal to these equivalence points. In practice, the pH 4.5 and 11 endpoints should be adjusted to match the pH of equivalence points, which shift due to changing solution CO_2 concentrations.

Dashed arrow A: The principal component H_2CO_3* does not contribute to “mineral acidity” because, although it can be deprotonated as pH increases, it is not deprotonated below the pH 4.5 equivalence point (pure H_2CO_3* solution). H^+ contributes 1 positive (+) equivalent per mole, HCO_3^- and OH^- contribute 1 negative (-) equivalent per mole, and CO_3^{2-} contributes 2 (-) negative equivalents per mole to “mineral acidity.”

Dashed arrow B: The principal component HCO_3^- does not contribute to “CO_2 acidity” because, although it can be deprotonated as pH increases, it is not deprotonated below the pH 8.3 equivalence point (pure $NaHCO_3$ solution). H_2CO_3* and H^+ contribute 1 positive (+) equivalent per mole, and CO_3^{2-} contributes 1 (-) negative equivalent per mole to “CO_2 acidity.”

Dashed arrow C: The principal component CO_3^{2-} does not contribute to “acidity” because it can not be deprotonated. H_2CO_3* contributes 2 positive (+) equivalents per mole, H^+ contributes 1 positive (+) equivalent per mole, and HCO_3^- and OH^- contribute 1 (-) negative equivalent per mole to “acidity.”

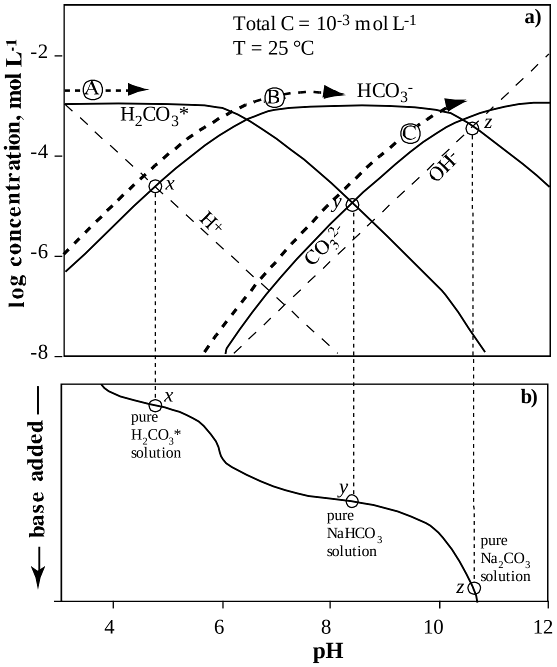

Figure 1. a) Distribution of CO_2 species and b) titration curve for H_2O-CO_2 system illustrating principal components for acidity titrations (after Stumm and Morgan, 1996).

Laboratory Definitions of Alkalinity and Acidity

Laboratory methods for alkalinity and acidity measurement indicate the capacity of a solution to neutralize acid and base, respectively. The standard methods for (single endpoint) alkalinity titrations (USEPA, 1979b, APHA, 1998b; ASTM, 2000) all use titration with sulfuric acid (H_2SO_4) to an endpoint near pH 4.5 and essentially agree on the laboratory protocols. Alkalinity titrations produce consistent and easily interpretable results.

The single-endpoint standard methods for acidity measurement (USEPA, 1979a; APHA, 1998a; ASTM, 2000) all use titration with sodium hydroxide (NaOH) to an endpoint of pH 8.2 or 8.3 and essentially agree on the laboratory protocols described below. For samples containing hydrolyzable metals, CO_2 is degassed upon boiling, thus CO_2-derived acidity is intentionally not measured. The intent is to measure the “non-CO_2 acidity” associated with H^+ and dissolved metals in a solution.

Specifically, the first step of the hot peroxide treatment acidity measured by standard methods (USEPA, 1979a; APHA, 1998a; ASTM, 2000), hereinafter referred to as “Hot Acidity,” is to titrate the sample to pH <4.0 with standardized H_2SO_4. Next, an aliquot of H_2O_2 is added, the sample is heated to boiling, cooled, and then titrated with standardized NaOH to an endpoint pH of 8.2 to 8.3. The initial acidification of the sample to pH <4.0 with H_2SO_4 converts all HCO_3^- to $H_2CO_3^*$, which along with other dissolved CO_2 originally in the sample, is driven off on heating. According to standard methods (USEPA, 1979a; APHA, 1998a; ASTM, 2000), the Hot Acidity result is computed by subtracting the equivalents of H_2SO_4 added from the equivalents of NaOH added:

$$\text{Acidity (mg L}^{-1}\text{ as CaCO}_3) = 50{,}000\ (\text{A x B} - \text{C x D})/\text{S} \qquad (1)$$

where A and C are milliliters of standard NaOH and H_2SO_4, respectively, B and D are the normality of the acid and base, respectively, and S is the sample volume in milliliters. The acid added as H_2SO_4 (C x D) is comparable to the alkalinity titration with an endpoint pH of ≈ 4.5. If the acid added (C x D) exceeds the base added (A x B), negative Hot Acidity values can be obtained. Many laboratories do not report these negative numbers, but indicate a value of zero. Indeed, only the most recent APHA (1998a) method specifies what to do if a negative number is obtained. It states, "The absolute value of this negative value should be equivalent to the net alkalinity," and net alkalinity is not defined in the text.

As implied by APHA (1998a) and explained below, negative values for Hot Acidity are opposite in value to the net alkalinity, and positive values for Hot Acidity are equivalent to the net acidity (non-CO_2). The overall reaction representing the sample pretreatment steps for Hot Acidity prior to titration with NaOH can be represented as follows:

$$\begin{aligned} &H_2CO_3^* + 0.5\ H_2SO_4 + HCO_3^- + 0.5\ H_2O_2 + Fe^{2+} \\ &\qquad = 2\ H^+ + 0.5\ SO_4^{2-} + Fe(OH)_3\ (s) + 2\ CO_2\ (g). \end{aligned} \qquad (2)$$

Equation 2 shows only two protons as the product, which can be accounted for by the oxidation and precipitation of dissolved Fe in the sample. The exsolution of CO_2 during heating eliminates most of the acid that was added as H_2SO_4 plus the original $H_2CO_3^*$ acidity. Consequently, in the final step of the Hot Acidity method, titration with NaOH measures only the non-CO_2 acidity due to H^+ and hydrolyzable ions (Fe, Al, Mn). Thus, Equation 1 actually yields the net acidity. The subtraction of C x D from A x B is comparable to subtracting the alkalinity from the acidity, because the acid added as H_2SO_4 (C x D), which is equivalent to the alkalinity, was largely removed from the sample by boiling and the consequent exsolution of CO_2.

Theoretical (Proton Condition) Definitions - Assignment of Alkalinity - Acidity Contributions

Morel and Hering (1993) and Stumm and Morgan (1996) rigorously discuss alkalinity and acidity. They employ thermodynamic equilibrium constants (pK's) to indicate aqueous species distribution as a function of the pH, the electroneutrality condition, and a reference condition for defining alkalinity or acidity. These equivalent approaches express all pertinent dissolved species as the equivalent concentration of H^+. Dissolved species that occur in the highest concentration for a solution component (*e.g.*, Ca^{2+} in the highest concentration among all Ca species) at the pH of a reference point (titration endpoint) are referred to as “predominant species” by Stumm and Morgan (1996) and as "principal components” by Morel and Hering (1993). These predominant species or principal components do not contribute to the particular acidity or alkalinity in question (Eqns. 3-8).

The geochemical model PHREEQC (Parkhurst and Appelo, 1999) uses the proton condition to calculate alkalinity, and negative numbers are possible. PHREEQC does not calculate a value for acidity, but as shown in a later section, one can use PHREEQC output to calculate acidity by determining the distribution of aqueous species at the field pH and redox state and assigning the correct positive or negative contribution from each considered species.

Stumm and Morgan (1996) define acidities in equivalents per liter (eq L^{-1}) for the H_2O-CO_2 system (Fig. 1) with three different reference conditions as follows

$$\text{“mineral acidity”} = [\text{H-Acy}] = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \quad (3)$$

$$\text{“}CO_2\text{-acidity”} = [CO_2\text{-Acy}] = [H_2CO_3^*] + [H^+] - [CO_3^{2-}] - [OH^-] \quad (4)$$

$$\text{“acidity”} = [\text{Acy}] = 2[H_2CO_3^*] + [H^+] + [HCO_3^-] - [OH^-] \quad (5)$$

where [] indicates mol L^{-1}. Depending on total carbon concentrations, reference conditions for Equations 3-5 occur at pH ≈ 4.5, 8.3, and ≈ 11, respectively. Throughout the remainder of the text, we use Acidity, with an initial upper case letter, to refer to a pH 8.3 endpoint Acidity (Eqn. 4). We use “Hot Acidity” for the *Standard Methods* (APHA, 1998a) pH 8.3 endpoint Acidity that employs H_2SO_4, H_2O_2, and boiling; this titration method is most appropriate for characterizing mine drainage for treatment. We use acidity with an initial lower case letter as a more generic term.

In Fig 1, H^+, OH^-, $H_2CO_3^*$, HCO_3^-, and CO_3^{2-} are distributed as a function of pH by using equilibrium constants and the total CO_2 concentration. Fig. 1 illustrates the selection of principal components and the assignment of acidity equivalent contributions in this simple system considering the endpoint pH of different acidities.

Stumm and Morgan (1996) define alkalinities (in eq L^{-1}) in the H_2O-CO_2 system with three different reference conditions as follows

$$\text{“caustic alkalinity”} = [OH^- \text{-Alk}] = [OH^-] - 2[H_2CO_3^*] - [HCO_3^-] - [H^+] \quad (6)$$

$$\text{“p-alkalinity”} = [\text{p-Alk}] = [OH^-] + [CO_3^{2-}] - [H_2CO_3^*] - [H^+] \quad (7)$$

$$\text{“Alkalinity”} = [\text{Alk}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (8)$$

where [] indicates mol L^{-1}. Depending on total inorganic carbon concentrations, equivalence points occur at pH ≈ 11, 8.3, and ≈ 4.5, respectively. The selection of principal components and assignment of alkalinity equivalent contributions parallels those for acidities and thus are not discussed here. Stumm and Morgan's (1996) definition of "alkalinity" (Eqn. 8, pH ≈ 4.5 endpoint) is appropriate for titration of mine drainage. Throughout the remainder of the text, we use Alkalinity, with an initial upper case letter, to refer to an alkalinity with a pH ≈ 4.5 endpoint. We use alkalinity, with an initial lower case letter, as a more generic term.

If metals and SO_4 are added to the H_2O-CO_2 system, equivalence between CO_2 species and/or H^+ remains the criterion for a titration endpoint. Principal components now include the predominant SO_4 species (HSO_4^-, SO_4^{2-}) plus metal species including complexes with OH^-, HCO_3^-, CO_3^{2-}, HSO_4^-, and SO_4^{2-} ligands at the reference (endpoint) pH values. Predominance of species is established using pK's for metal and SO_4 reactions. For example, Fig. 2a illustrates that, for a simple Fe^{III}-SO_4 solution, $Fe(OH)_2^+$ predominates in solution and is the principal component for Fe^{III} for a pH 4.5 equivalence point (Alkalinity titration). SO_4^{2-} (not shown) would be the principal component for SO_4 species at pH 4.5. Figures 2b-d illustrate the selection of principal components and the assignment of Acidity equivalents per mole for an Acidity titration with a pH 8.3 endpoint. The concentrations of HCO_3^- and CO_3^{2-} and their metal complexes are too low to contribute significantly to Acidity. Metals contribute finitely, but negligibly to Alkalinity. For example, Fe^{III} contributes very little because concentrations are limited by solid Fe^{III} hydroxide solubility; Fe^{II} contributes very little because Fe^{2+} is a principal component at pH 4.5, and other Fe^{II} species are in very low concentration.

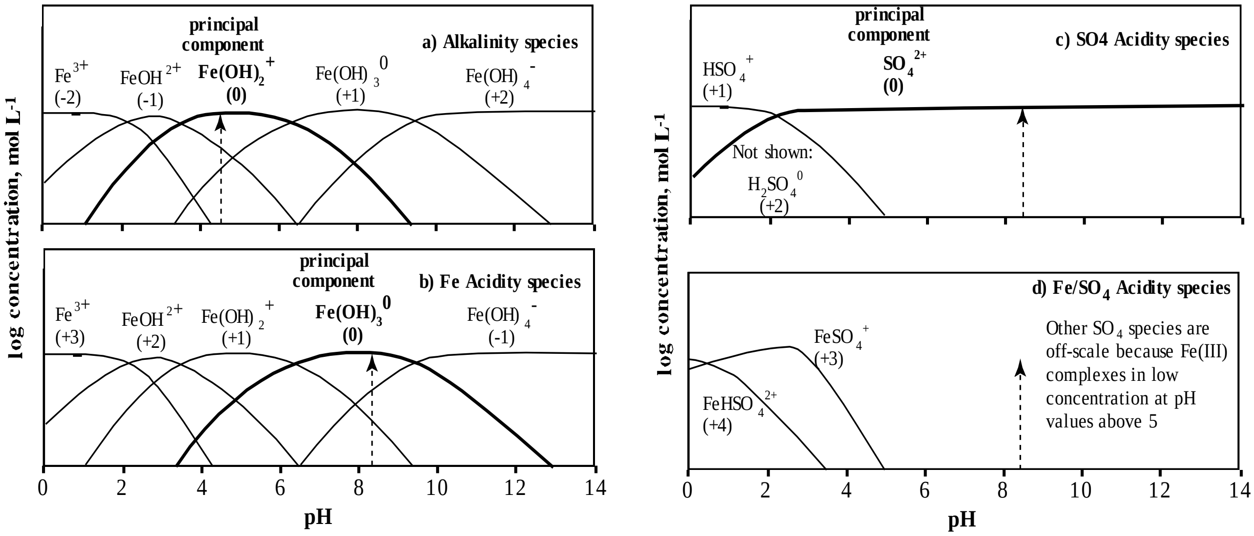

Figure 2. Schematic diagram (not to scale) of Fe^{III} and SO_4 speciation illustrating principal components (bold) and equivalents (in parentheses) of a) Alkalinity contributed, and b-d) Acidity contributed. Dashed arrows show the pH of the reference point.

Definitions of Net Alkalinity and Net Acidity in Use for Treatment of Mine Drainage

"Net alkalinity," is usually defined as (alkalinity - acidity). Such a definition is open to interpretation because of the different definitions of alkalinity and acidity. A common practice is to use the measured values ($\text{Alkalinity}_{\text{Std. Meth.}}$ – $\text{Hot Acidity}_{\text{Std. Meth.}}$). However, as explained above, the Hot Acidity reported by Equation 1 is actually the net acidity. Kirby (2002), Cravotta and Kirby (this volume), and Watzlaf *et al.* (in review) demonstrate that subtracting the Hot Acidity from the alkalinity gives a net alkalinity result that is incorrect and can result in inadequate addition of alkaline materials such as lime or limestone in mine-drainage treatment.

Hedin *et al.* (1994) give a calculated acidity value in units of mg L^{-1} as $CaCO_3$

$$\text{acidity}_{\text{computed}} = 50\cdot(10^{(3\text{-pH})} + 3\cdot C_{Fe^{III}}/55.8 + 2\cdot C_{Fe^{II}}/55.8 + 2\cdot C_{Mn}/54.9 + 3\cdot C_{Al}/27.0) \qquad (9)$$

where metal concentrations are in mg L^{-1}. Another common practice is to calculate

$$\text{net alkalinity} = (\text{Alkalinity}_{\text{Std. Meth.}} - \text{acidity}_{\text{computed, Eqn. 9}}). \qquad (10)$$

Hedin (this volume) more recently presents

$$[\text{net}]\ \text{acidity}_{\text{computed}} = 50\cdot(10^{(3\text{-pH})} + 3\cdot C_{Fe^{III}}/55.8 + 2\cdot C_{Fe^{II}}/55.8 + 2\cdot C_{Mn}/54.9 + 3\cdot C_{Al}/27.0) - \text{Alk} \qquad (11)$$

as a formula to calculate net acidity, where metals concentrations are in mg L^{-1}, and alkalinity and net acidity are in mg L^{-1} as $CaCO_3$. The use of Equation 11 is equivalent to the use of Equation 10.

Methods

PHREEQC Modeling of the Distribution of Aqueous Species

The geochemical computer code PHREEQC (Parkhurst and Appelo, 1999) was used to model 25 °C speciation in lab-synthesized mine-drainage solutions (low-pH Fe^{III} and Al sulfate solution; see Kirby, 2002) and similar hypothetical solutions. The speciation allowed the calculation of theoretical Acidity as defined later in this paper. Calculated Alkalinities, including negative values, are from PHREEQC output. The standard PHREEQC thermodynamic database was used in PHREEQC simulations and to draw the species distribution diagrams. Modeled solutions were oxidized by O_2 rather than H_2O_2. CO_2 was degassed by allowing the solution to reach equilibrium with respect to atmospheric p_{CO2}. The pH was increased from the initial values by adding aliquots of sodium hydroxide. Charge balance was established before the simulation and then minor adjustments were made using H^+ concentrations.

Results and Discussion

Acidity Due to CO_2

Mine waters, especially those from deep mine sources, can have significant concentrations of CO_2, which is lost upon reaching the earth's surface, reaching equilibrium with atmospheric CO_2. Thus Acidity due to CO_2 is ephemeral and can be removed from mine drainage by preaeration prior to the addition of caustic chemicals for neutralization of acidity due to H^+ and metals (e.g. Jageman *et al*., 1988). Generally, CO_2 concentrations are non-zero but negligible when compared to H^+ and metals in most mine drainage. Considering these factors, standard Hot Acidity methods (USEPA, 1979a; APHA, 1998a; ASTM, 2000) intentionally drive off CO_2 and do not measure Acidity due to CO_2.

<u>Contribution of Metals to Positive (+) or Negative (-) Acidity</u>

Fig. 3 represents aqueous speciation during a Hot Acidity titration and illustrates why metals contribute positively to Acidity. Negative contributions from metals to Acidity are insignificant. This mine water represents an end-member composition. The water is pH 3, Fe^{III}-rich, and has no measurable (positive) Alkalinity. Dissolved Fe^{III} concentration can be high at the beginning of the titration because $Fe(OH)_3$ solubility, which controls the concentration of aqueous Fe^{III} species through equilibrium constants, is high at pH 2.8. At the pH 8.3 endpoint, $Fe(OH)_3^0$ is the predominant species and, thus, the principal component; it does not contribute to Acidity. Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$, and $Fe(OH)_4^-$ contribute 3, 2, 1, and –1 equivalents per mole, respectively, to Acidity. H^+ also contributes significantly to Acidity. Acidity from these sources decreases as the titration proceeds and total Fe decreases. Other significant sources of Acidity in mine drainage water can include HSO_4^-, Fe^{II}, Al, complexes, or other metals. Although the CO_2 concentration is initially high, the measured Acidity due to CO_2 (H_2CO_3*) is negligible due to intentional degassing of CO_2 before the titration begins.

Initial $Fe^{III} = 10^{-3}$ M = 56 mg L^{-1}. At pH 8.3 equivalence point, $Fe(OH)_3^0$ is principal Fe^{III} component and does not contribute to acidity. Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2^+$ contribute to positive acidity.

Fe^{III} acidity (eq L^{-1}) =
$3[Fe^{3+}] + 2[FeOH^{2+}] + [Fe(OH)_2^+] - [Fe(OH)_4^-]$
Positive contributions are significant due to high initial Fe^{III} concentrations (high solubility of $Fe(OH)_3$ at pH 3).

The H^+ acidity contribution is also significant at pH 3. Similar arguments can be made for Al, Mn, and other metal species that contribute to positive acidity.

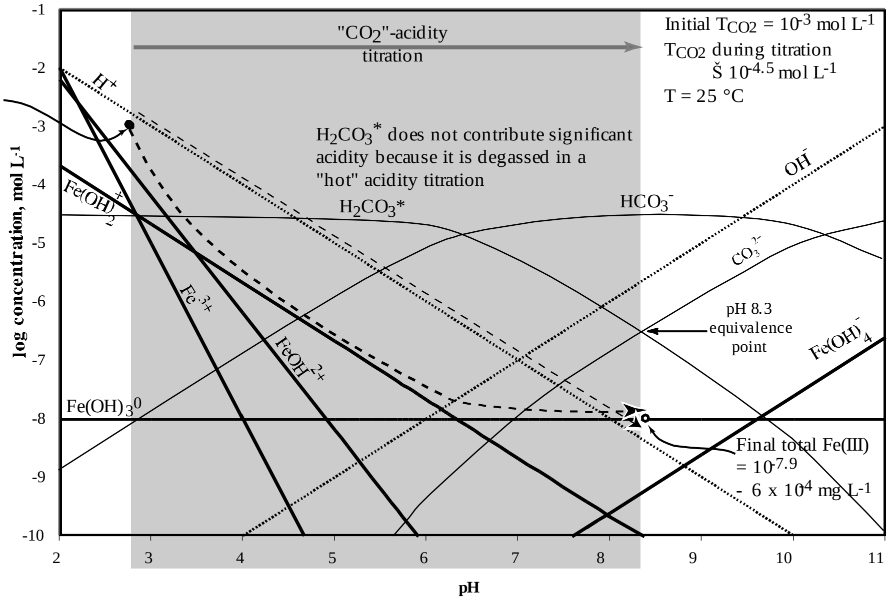

Figure 3. Speciation of H^+ and OH^- (dashed), carbonate (solid), and Fe^{III} (bold) species for a typical oxic, pH 3 mine discharge illustrating why metals contribute significantly to positive acidity. This diagram illustrates speciation changes during "CO_2-acidity" titration. Speciation for aqueous Fe^{III} complexes assumes amorphous $Fe(OH)_3$ is present and controls solubility of Fe^{III} throughout the range of pH as base is added. H^+ and SO_4^{2-} were used for charge balance, but SO_4 complexes are not shown to simplify the graph. Dashed arrows illustrate the consumption of Acidity species as the titration proceeds. Equilibrium constants are from Stumm and Morgan (1996).

Complexation of metals with SO_4^{2-} and OH^- plays an important role in determining the Acidity contributions of various metals in mine-drainage waters. Although complexes with SO_4^{2-} have the same number of equivalents per mole as the uncomplexed metal ion (Table 1), the total concentration of dissolved metals in a system at equilibrium with solids such as $Fe(OH)_3$ or $Al(OH)_3$ can increase because of SO_4^{2-} complexes, with a corresponding increase in acidity.

Table 1. Positive and negative contributions to Acidity (pH 8.3 endpoint) in equivalents per mole by aqueous species of Fe^{II}, Fe^{III}, Al, Mn^{II}, CO_2, and S in the PHREEQC database. Principal components (bold) do not contribute positively or negatively to Acidity.

	Acidity due to species, eq mol^{-1}						
species	+5	+4	+3	+2	+1	0	-1
Fe^{II}			$FeHSO_4^+$	Fe^{2+}, $FeSO_4^0$, $FeHCO_3^+$	$FeOH^+$, $FeCO_3^0$	**$Fe(OH)_2^0$**	
Fe^{III}	$Fe_3(OH)_4^{5+}$	$FeHSO_4^{2+}$, $Fe_2(OH)_2^{4+}$	Fe^{3+}, $FeSO_4^+$, $Fe(SO_4)_2^-$	$FeOH^{2+}$	$Fe(OH)_2^+$	**$Fe(OH)_3^0$**	$Fe(OH)_4^-$
Al		$AlHSO_4^{2+}$	Al^{3+}, $AlSO_4^+$, $Al(SO_4)_2^-$	$AlOH^{2+}$	$Al(OH)_2^+$	**$Al(OH)_3^0$**	$Al(OH)_4^-$
Mn				Mn^{2+}, $MnSO_4^0$	$MnOH^+$	**$Mn(OH)_2^0$**	
H_2O-H_2S-CO_2					H^+, H_2CO_3*, H_2S	**H_2O,** **HCO_3^-,** **HS^-**	OH^-, CO_3^{2-}, S^{2-}
Non-metal-bound SO_4				$H_2SO_4^0$	HSO_4^-	**SO_4^{2-}**	

The contribution to Acidity from H^+, HSO_4^-, and metal complexes varies as the pH changes. Fig. 4 illustrates examples of these changes for Fe^{III} and Al-sulfate solutions that are undersaturated with respect to Fe and Al hydroxides. The total Acidity and the percentage of Acidity due to H^+ decrease as pH increases in Fig. 4a and 4b. As Acidity due to H^+ decreases, the percentages of the total Acidity due to $FeSO_4^+$ and $AlSO_4^+$ both increase. Both Fe^{III} and Al hydroxyl complexes increase in importance as pH increases, but they are not as important as metal-SO_4^{2-} complexes. Acidity due to HSO_4^- also decreases with increasing pH as HSO_4^- converts to SO_4^{2-}.

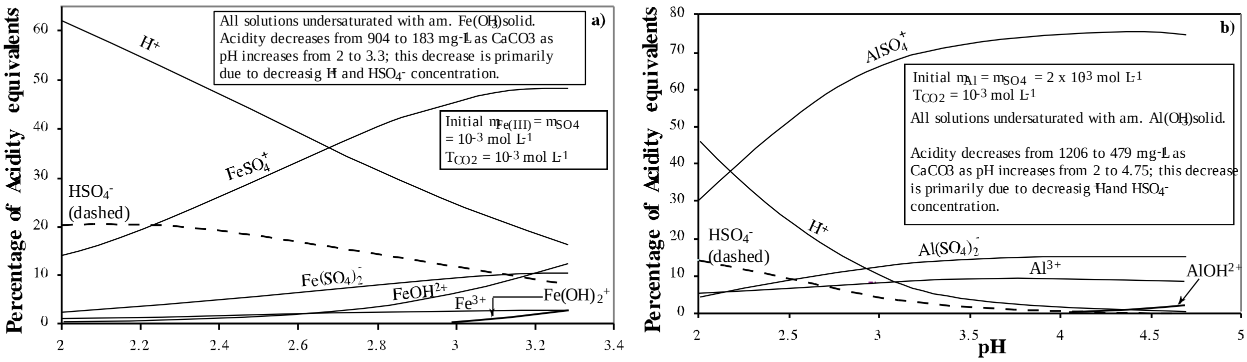

Figure 4. PHREEQC-calculated percentage contributions to Acidity at 25 °C from major species in a) 56 mg L^{-1} Fe^{III} solution from pH 2 to 3.3, and b) 54 mg L^{-1} Al solution from pH 2 to 4.75.

Calculation of Theoretical Acidity

The Acidity contributions displayed in Figure 4 are based on the proton condition approach (Stumm and Morgan, 1996) and were calculated considering values in Table 1 for the number of equivalents per mole contributions to Acidity with a pH 8.3 endpoint. Table 1 applies to solutions containing H_2O, CO_2, Fe^{II}, Fe^{III}, Al, Mn, and SO_4^{2-} and S^{2-} based on speciation by PHREEQC. The calculated Acidity (for a pH 8.3 endpoint) is thus given as

$$\text{Acidity}_{\text{computed}},\ \text{eq L}^{-1} = \sum_{\text{i}}^{\text{all species}} \varepsilon_i M_i \tag{12}$$

where ε_i = the number of equivalents per mole of the i^{th} species from Table 1, and M_i = the concentration in mol L^{-1} of the i^{th} species from Table 1. To express Acidity as mg L^{-1} as $CaCO_3$, multiply results of Equation 12 by 50,000 mg eq^{-1}. The concentrations of species can be obtained from PHREEQC modeling. In this study, Acidity due to CO_2 (as H_2CO_3*) was not included because, once CO_2 is degassed before a Hot Acidity titration begins, the H_2CO_3* concentration is negligible compared to other Acidity contributions. Because CO_2 is degassed during treatment, non-CO_2 Acidity is appropriate to consider for mine drainage treatment and is given by

$$\text{non-CO}_2\ \text{Acidity}_{\text{computed}},\ \text{eq L}^{-1} = \sum_{\text{i}}^{\substack{\text{all species}\\ \text{less CO}_2}} \varepsilon_i M_i . \tag{13}$$

The definition of calculated acidity from Hedin *et al*. (1994) given in Equation 9 and the recent definition of net acidity given in Equation 11 (Hedin, this volume) require some clarification. In both Equations 9 and 11, metal concentrations are in mg L^{-1}. To be more precise, Fe^{2+} should be listed as Fe^{II}, and Fe^{3+} should be listed as Fe^{III} because the iron concentrations employed are based on analytical techniques that distinguish between Fe^{II} and Fe^{III}, but not between actual species (*e.g*., “free” Fe^{2+} compared to hydroxyl or sulfate complexes). The authors state that Equation 9 is appropriate for pH values less than 4.5, but it is also commonly employed in higher pH waters that contain Alkalinity. For samples with pH less than 4.5, Hedin *et al*. (1994) demonstrated a strong linear relation between measured Hot Acidity and calculated acidity. At acidities above approximately 300 mg L^{-1}, measured Hot Acidities are slightly higher than calculated acidities. Deviations were less than 10% up to 1,200 mg L^{-1} (Hedin *et al*., 1994). Hedin (2003, pers. commun.) and Watzlaf *et al*. (in review) recently found no significant deviation between calculated and measured hot Acidities.

Equation 9 is frequently employed in the calculation of net alkalinity or net acidity (see also Eqns. 10 and 11). Equation 9 cannot return negative numbers because it considers only positive contributions to Acidity and is not based on the proton condition approach. It intentionally does not include positive Acidity contributions from CO_2. While quite useful as noted later, Equation 9 does not correspond exactly with titrations or with other calculated acidities.

Even though metals were not speciated except to differentiate Fe^{II} from Fe^{III}, the calculated acidity produced by Equation 9 matched several hundred measured Hot Acidities reasonably well, although less well at higher acidities (Hedin *et al*., 1994). Hedin *et al*. (1994) suggest that even at low pH (2.7), H^+ acidity is only a minor component (compared to metals) of total acidity based on Equation 9. This statement conflicts with the results presented in Fig. 4 of this study, where Acidity due to H^+ accounts for 60 to 20% of total Acidity between pH 2 and pH 2.7. In addition, PHREEQC results in Fig. 4 assign significant Acidity contributions to HSO_4^-, $FeSO_4^+$, and $AlSO_4^+$, which are not included in Equation 9. Figure 4 suggests that the species Fe^{3+} only contributes a small percentage of the total Acidity in a sample compared to SO_4^{2-} complexes.

Fig. 5 illustrates the likely reason that, although speciation is not accounted for, Equation 9 matches Hot Acidity titrations for low-pH samples fairly well. Figure 5 provides calculated values of the average equivalents of Acidity per mole for all Fe^{III}, Al^{III}, H^+, and non-metal sulfate (primarily HSO_4^-) species for Fe and Al sulfate solutions at varying pH. Figure 5 includes saturation indices (log Q/K; see Drever, 1997) for amorphous Fe and Al hydroxides to show solubility limitation of these metals. It also plots calculated non-CO_2 Acidity based on Equation 13 and Table 1.

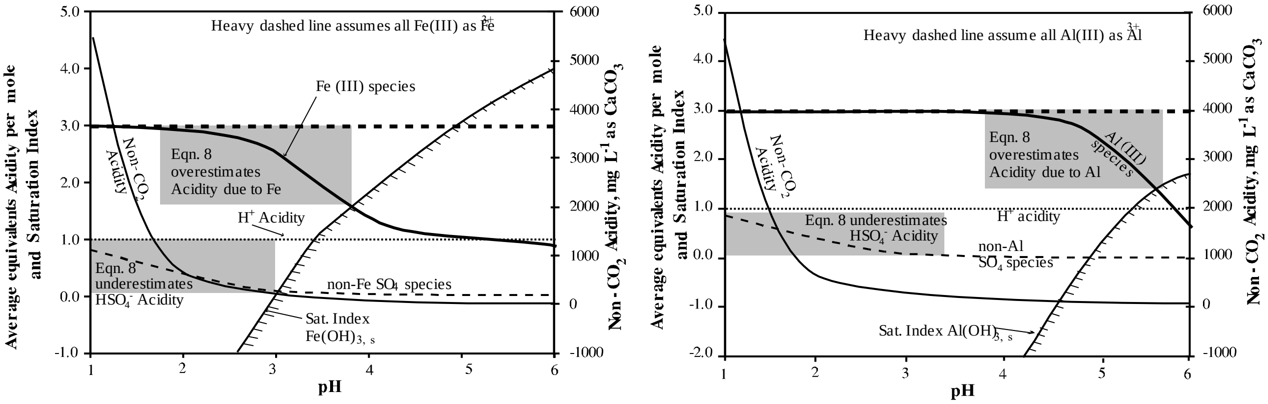

Figure 5. Plot of average equivalents Acidity per mole relative to pH for a) 10^{-3} mol L^{-1} Fe^{III} solution, and b) 10^{-3} mol L^{-1} Al^{III} solution based on PHREEQC speciation. Charge balance is by SO_4 species.

The value for the average Acidity equivalents per mole is calculated as

$$\text{average Fe, Al, or S equivalents Acidity mol}^{-1} = \left. \sum_{i}^{\text{all Fe species}} \varepsilon_i M_i \middle/ \sum_{i}^{\text{all Fe species}} M_i \right. \text{ or } = \left. \sum_{i}^{\text{all Al species}} \varepsilon_i M_i \middle/ \sum_{i}^{\text{all Al species}} M_i \right. \text{ or } = \left. \sum_{i}^{\text{all non-metal SO4 species}} \varepsilon_i M_i \middle/ \sum_{i}^{\text{all SO4 species}} M_i \right. \tag{14}$$

where the definitions are the same as in Equation 12.

In Figure 5, the average equivalents of Acidity per mole due to H^+ are always unity and appear as a solid horizontal line. Similarly, if Fe^{3+} is used as in Equation 9, the average equivalents of Acidity per mole due to Fe^{3+} is always +3 (dashed horizontal line in Fig. 5). However, if Fe^{III} is speciated into OH and SO_4 complexes shown in Table 1, the average equivalents of Acidity per mole due to Fe^{III} decreases significantly from +3 to +1.5 at pH values between 2 and 3.5 (the approximate solubility limit). This decrease occurs due to the relative increase in Fe^{III}-OH complexes compared to Fe^{3+} with increasing pH. Thus, Equation 9 overestimates the contribution of Fe^{III} to Acidity. However, because Equation 9 does not include SO_4 species, it underestimates Fe^{III}-SO_4 and HSO_4^- Acidity. These two effects essentially cancel each other out and, due to this fortunate circumstance, Equation 9 gives a reasonable estimate of non-CO_2 Acidity. There is still some concern that HSO_4^- Acidity could be underestimated in field solutions because SO_4 species may be much more predominant in real solutions that are complex mixtures compared to a synthetic solution in which Fe and SO_4 have molar ratios of 2:3.

Is Net Alkalinity a Rigorous Mathematical Construction?

Because net alkalinity has not been rigorously defined in the literature, derivations were constructed to check the mathematical validity of this concept. One concern is that Acidity and Alkalinity titration have different reference points (≈ pH 4.5 for Alkalinity; pH 8.3 for Acidity), and thus subtraction of Acidity from Alkalinity could potentially result in a definition of net alkalinity that does not have a unique solution for net alkalinity = zero. A partial derivation is given here for the H_2O-CO_2 system, but the concepts can be extended with the same result to the metal-laden water typical of mine drainage.

One way to check the validity of a complex mathematical function, *g(x)*, is to plot *f(x) = x* and *g(x)* on the same x-y plot. If the curves for each function intersect at a single point, then the function in question has a unique solution. The standard theoretical definitions for Alkalinity and Acidity consider both positive and negative contributions to Alkalinity and Acidity. Subtracting Acidity (Eqn. 4) from Alkalinity (Eqn. 8) and setting this value to zero gives

$$\text{NetAlk(1)} = g(x) = 0 \Rightarrow 2\left[OH^-\right] + \left[HCO_3^-\right] + 3\left[CO_3^{2-}\right] = 2\left[H^+\right] + \left[H_2CO_3{*}\right]. \qquad (15)$$

Putting this equation into the proton condition by solving for $[H^+]$ and making substitutions for CO_2 species and OH^- gives

$$g(x) = \left[H^+\right] = \frac{K_w}{\left[H^+\right]} + \frac{1}{2}\frac{K_1 C_T\left(1 + \frac{K_1}{\left[H^+\right]} + \frac{K_1K_2}{\left[H^+\right]^2}\right)}{\left[H^+\right]} + \frac{3}{2}\frac{K_1K_2C_T\left(1 + \frac{K_1}{\left[H^+\right]} + \frac{K_1K_2}{\left[H^+\right]^2}\right)}{\left[H^+\right]^2} - \frac{1}{2}C_T\left(1 + \frac{K_1}{\left[H^+\right]} + \frac{K_1K_2}{\left[H^+\right]^2}\right) \qquad (16)$$

where K_w is the dissociation constant for water, K_1 and K_2 are the first and second dissociation constants, respectively, for H_2CO_3*, and C_T is the total CO_2 concentration. The function *g(x)* intersects the line for *f(x) = x* at a single point, proving that *g(x)* has a unique solution; *i.e.*, net alkalinity makes mathematical sense. The pH defining net alkalinity = zero is 6.37.

Establishing a Formal Definition of Net Alkalinity

The use of the term net alkalinity arose because of the need to determine how much alkaline material should be added to a solution to remove metals and produce water ready to be released into a receiving stream. We argue that nearly metal-free water with pH ≥ 6.3 is desired. The requirement that the treated water be nearly metal-free means that metal concentrations are below effluent concentration limits in order to avoid negative impact on aquatic life or human health. The stipulation that pH must be ≥ 6.3 is based upon the derivation above, but also requires explanation using the buffer capacity of a solution.

The buffer capacity is a measure of the resistance of a solution to changes in pH. To illustrate the impact of various aqueous species, buffer capacities (β) for H_2O, and CO_2 were calculated as in Langmuir (1997) and are displayed in Figure 6. Changing CO_2 concentration would also change the buffer capacity, but the shapes of the curves in Figure 6 remain the same.

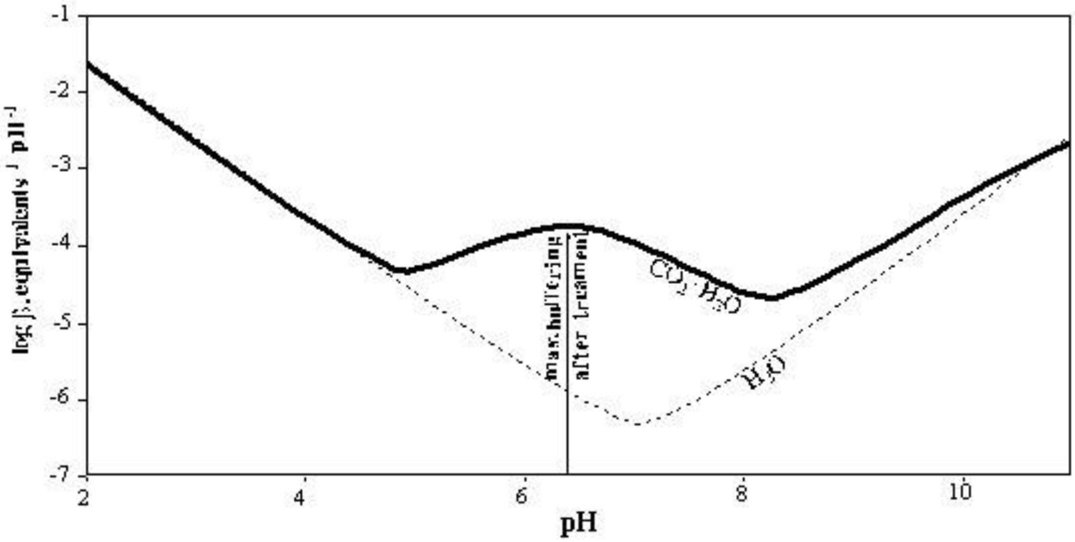

Figure 6. Plot of buffer capacity, β, relative to pH for the H_2O and the $CO_2 + H_2O$ systems. Maximum β after treatment = pH = $pK_{1,\text{ carbonic acid}}$ = 6.3.

Fig. 6 shows the individual and total buffer capacities due to 1) water alone, and 2) an aqueous solution containing 10^{-3} mol L^{-1} CO_2. Below pH 4, the total buffer capacity is due solely to H_2O. Above pH 4 to the pH 8.3 titration endpoint, the total buffer capacity is due to a combination of H_2O and CO_2. Metals also contribute to buffer capacity, but they are omitted for simplicity and because metal concentrations will be very low in a successfully treated water. The dark bold curve gives the total buffer capacity of post-treatment water in equilibrium with atmospheric CO_2 and with metals removed. An acceptable post-treatment water would thus be like most natural waters, having a pH ≥ 6.3 and retaining some Alkalinity to resist pH decrease due to further acid addition (*e.g.*, from acid mine drainage or acid precipitation).

Combining the theoretical definitions of net alkalinity and the above argument based on the desirability of having significant buffering capacity (pH ≥ 6.3) in post-treatment water suggests that

$$\text{Net alkalinity} = \text{Alkalinity (PHREEQC)} - \text{non-}CO_2\text{ Acidity (Eqn. 13)} \qquad (17)$$

be used as the formal definition of net alkalinity because this definition results in a net alkalinity of zero for samples with a pH of 6.37 and that do not contain dissolved metals. Waters that are net alkaline would have $[HCO_3^-] > [H_2CO_3^*]$. Waters that are net acidic would have some combination of metal, $H_2CO_3^*$, and H^+ concentrations > $[HCO_3^-]$ and pH values < 6.37 after hydrolysis and precipitation of metals.

One may also calculate

$$\text{Net alkalinity} = (\text{Alkalinity}_{\text{Std. Meth.}} - \text{non-}CO_2\text{ acidity}_{\text{computed, Eqn. 13}}). \qquad (18)$$

Alternatively, one may use Equation 10 ($\text{Alkalinity}_{\text{Std Meth.}}$ - $\text{acidity}_{\text{computed, Eqn. 9}}$). Cravotta and Kirby (this volume) show that using Equation 9 or 14 returns very similar results for computed acidity, even though Equation 9 does not account for speciation rigorously. Hence, either Equation 10 or 18 is useful to indicate the net alkalinity of mine drainage. However, Cravotta and Kirby (this volume) also found that net alkalinity calculated in these ways *does not* return the same negative value of a Standard Method Hot Acidity titration (APHA, 1998a) for solutions with high alkalinities that are saturated with respect to calcite. For this reason, we recommend that net alkalinities be obtained by

$$\text{Net alkalinity} = -\text{ Hot Acidity}, \qquad (19)$$

where “Hot Acidity” = value of a Standard Method Hot Acidity titration *provided that negative numbers are reported by the lab*. For example, if a lab reports Standard Method Acidity = -50, the net alkalinity = 50 mg L^{-1} as $CaCO_3$, and no alkaline addition is needed for treatment. If a lab reports Standard Method Acidity = 50, the net alkalinity = -50 mg L^{-1} as $CaCO_3$, and 50 mg L^{-1} alkalinity as $CaCO_3$ addition is needed for treatment. Equation 19 provides consistent and easily interpretable net alkalinity for use in mine drainage treatment.

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Literature Cited

American Public Health Association (APHA), 1998a. Acidity (2310)/Titration method, p. 2.24-2.26, In Clesceri, L. S., Greenberg, A. E., and Eaton, A. D. (eds), *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Assoc., Washington, DC.

———, 1998b, Alkalinity (2320)/Titration method, p. 2.26-2.29, In Clesceri, L. S., Greenberg, A. E., and Eaton, A. D. (eds), *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Assoc., Washington, DC.

American Society for Testing and Materials (ASTM), 2000. Standard test methods for acidity or alkalinity of water: D 1067-92, in *Annual Book of ASTM Standards*, Sect. 11.01, p. 65-71, Water and Environmental Technology, ASTM, West Conshocken PA.

Cravotta, C.A., III, and Kirby, C. S., this volume, Acidity and alkalinity of mine drainage--Practical considerations. 2004 National Meeting of the American Society of Mining and Reclamation and the 25th West Virginia Surface Mine Drainage Task Force, April 18 – 24, Morgantown WV.

https://doi.org/10.21000/JASMR04010334

Drever, J. I., 1997. *The Geochemistry of Natural Waters*, 3rd ed., Prentice Hall, Upper Saddle River, NJ.

Jageman, T. C., Yokley, R. A., and Heunisch, H. E., 1988. The use of preaeration to reduce the cost of neutralizing acid mine drainage. US Bur. Mines Info. Circ. IC 9183, p. 131-135.

https://doi.org/10.21000/JASMR88010131

Hedin, R. S., Nairn, R. W., and Kleinmann, R. L. P., 1994. *Passive Treatment of Coal Mine Drainage*, US Bur. Mines Info. Circ. IC 9389, US Dept. Interior: Washington, DC.

———, this volume. The use of measured and calculated acidity values to improve the quality of AMD data sets, presented at 2004 National Meeting of the American Society of Mining and Reclamation and The 25th West Virginia Surface Mine Drainage Task Force, April 18 – 24, Morgantown WV. https://doi.org/10.21000/JASMR04010879

———, 2003. personal communication, Hedin Environmental, Inc., Pittsburgh PA.

Kirby, C. S, 2002. Problems in alkalinity and acidity measurements in mine drainage, presented at American Society for Surface Mining & Reclamation, Lexington KY, June 9-13, 2002.
https://doi.org/10.21000/JASMR02011068

Langmuir, D., 1997. *Aqueous Environmental Geochemistry*; Prentice Hall, Upper Saddle River, NJ.

Morel, F. M. M., and Hering, J. G., 1993. *Principles and Applications of Aquatic Chemistry*, John Wiley & Sons, Inc., New York, 588 p.

Parkhurst, D. L., and Appelo, C. A. J., 1999, User's guide to PHREEQC (Version 2)--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.

Skousen, J. G., Rose, A. W., Geidel, G., Foreman, J., Evans, R., Hellier, W., and others, 1998. Handbook of technologies for avoidance and remediation of acid mine drainage. Morgantown, W.V., National Mine Land Reclamation Center, 131 p.

Stumm, W., and Morgan, J. J., 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed., John Wiley & Sons, New York, 1022 p.

U.S. Environmental Protection Agency (USEPA), 1979a. Method 305.1, Acidity (Titrimetric), In Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency EPA/600/4-79-020, n.p. (http://www.nemi.gov).

———, 1979b. Method 310.1, Alkalinity (Titrimetric, pH 4.5), In Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency EPA/600/4-79-020, n.p. (http://www.nemi.gov).

U.S. Office of Surface Mining Reclamation and Enforcement (OSM), 2002. AMDTreat 3.1: Washington, D.C., US Office Surface Mining Reclamation and Enforcement (accessed June 15, 2003, on the World Wide Web at http://amd.osmre.gov).

Watzlaf, G. R., Schroeder, K. T., Kleinmann, R. L. P., Kairies, C. L., Nairn, R. W., in review. *The Passive Treatment of Coal Mine Drainage*, U.S. Department of Energy, accessed November 2003 at ftp://ftp.netl.doe.gov/pub/Watzlaf/.