

Net alkalinity and net acidity 1: Theoretical considerations

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Abstract

Net acidity and net alkalinity are widely used, poorly defined, and commonly misunderstood parameters for the characterization of mine drainage. The authors explain theoretical expressions of 3 types of alkalinity (caustic, phenolphthalein, and total) and acidity (mineral, CO₂, and total). Except for rarely-invoked negative alkalinity, theoretically defined total alkalinity is closely analogous to measured alkalinity and presents few practical interpretation problems. Theoretically defined “CO₂-acidity” is closely related to most standard titration methods with an endpoint pH of 8.3 used for determining acidity in mine drainage, but it is unfortunately named because CO₂ is intentionally driven off during titration of mine-drainage samples. Using the proton condition/mass-action approach and employing graphs to illustrate speciation with changes in pH, the authors explore the concept of principal components and how to assign acidity contributions to aqueous species commonly present in mine drainage. Acidity is defined in mine drainage based on aqueous speciation at the sample pH and on the capacity of these species to undergo hydrolysis to pH 8.3. Application of this definition shows that the computed acidity in mg L⁻¹ as CaCO₃ (based on pH and analytical concentrations of dissolved Fe^{II}, Fe^{III}, Mn, and Al in mg L⁻¹):

$$\text{acidity}_{\text{calculated}} = 50\{1000(10^{-\text{pH}}) + [2(\text{Fe}^{\text{II}}) + 3(\text{Fe}^{\text{III}})]/56 + 2(\text{Mn})/55 + 3(\text{Al})/27\}$$

underestimates contributions from HSO₄⁻ and H⁺, but overestimates the acidity due to Fe³⁺ and Al³⁺. However, these errors tend to approximately cancel each other.

It is demonstrated that “net alkalinity” is a valid mathematical construction based on theoretical definitions of alkalinity and acidity. Further, it is shown 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 minus calculated acidity, or (3) taking the negative of the value obtained in a standard method “hot peroxide” acidity titration, provided that labs report negative values. The authors recommend the third approach; i.e., net alkalinity = –Hot Acidity.

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1. Introduction

Acidic, metal-laden drainage from active and abandoned mines causes significant environmental and economic problems in coal and metal-mining districts worldwide (Nordstrom, 2000). The alkalinity and acidity

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of the mine effluent and receiving water bodies commonly are measured or calculated to identify potential environmental effects and to plan appropriate treatment methods to remove metals and produce near-neutral pH effluents (e.g., Skousen et al., 1998). Although these parameters may seem conceptually simple, they are often poorly understood. Water that initially has near-neutral pH (6–7) and contains dissolved metals can have both alkalinity and acidity and ultimately could have acidic pH (<4.5) after oxidation, hydrolysis, and precipitation of Fe, Mn, and other metals (Kirby and Cravotta, 2005). Morel and Hering (1993) refer to alkalinity as “one of the most central but perhaps not the best understood concepts in aquatic chemistry”. Acidity is less widely applied and commonly not well understood. The widely used derivative terms “net alkalinity” and “net acidity” have important practical applications but are poorly defined and commonly misunderstood. Incorrect interpretation of acidity, alkalinity, and terms derived from them can lead to inadequate design of treatment facilities or poor regulatory decisions.

Although many geochemical, chemical, and engineering texts discuss acidity in mine drainage waters, explanations: (1) vary in the example definitions of acidity, (2) do not provide adequate detail about how to assign the number of equivalents to aqueous species producing acidity, and (3) do not address net alkalinity or net acidity. Practitioners evaluating the environmental effects or treatment strategies for mine drainage or other metal-laden solutions need clarification that neither texts nor journal articles currently provide.

This paper: (1) investigates and compares theoretical definitions and laboratory practices for alkalinity and acidity determinations, (2) uses mathematical and graphical approaches to explain both positive and negative contributions of aqueous 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 (Kirby and Cravotta, 2005) examines more practical considerations of net alkalinity and net acidity.

2. Background on alkalinity and acidity

2.1. Verbal definitions based on the H_2O/CO_2 system

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 measures 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 some chosen pH endpoint. These endpoints are usually based on equivalence points at pH values of ≈ 4.5 , 8.3, and ≈ 11 , at which particular components in the H_2O/CO_2 system are at equal concentrations: $[H^+] = [HCO_3^-]$, $[H_2CO_3^*] = [CO_3^{2-}]$, and $[HCO_3^-] = [OH^-]$, respectively (see points x , y , and z in Fig. 1). Endpoints of titrations are ideally equal to these equivalence points. In practice, the pH of the $pH \approx 4.5$ and $pH \approx 11$ equivalence points could vary due to changing concentrations of dissolved CO_2 , organic acids, and other components.

2.2. Laboratory definitions of alkalinity and acidity

Table 1 gives a summary of alkalinity and acidity definitions from various sources. The single-endpoint standard methods for alkalinity titrations (USEPA, 1983a; ASTM, 1998; APHA, 1998) all use an endpoint near pH 4.5 and essentially agree on the laboratory protocols (see Table 1); the endpoint suggested by APHA (1998) varies as a function of the initial alkalinity (implying a system closed to gas exchange). For alkalinity, these titrations produce consistent, interpretable results. Only small negative numbers may be measured during some “Gran” titrations in low alkalinity samples (see Stumm and Morgan, 1996). In contrast, calculated theoretical alkalinites can be large negative numbers (Sections 2.2 and 2.3), illustrating that theoretical and laboratory definitions of alkalinity are conceptually and practically different. Because standard titration methods cannot return large negative values, they are inconsistent with the mathematically derived definitions of alkalinity.

The standard methods for acidity titration (ASTM, 1998; APHA, 1998; USEPA, 1983b) all use an endpoint near pH 8.3 and their laboratory protocols essentially agree (see Table 1). For samples containing hydrolyzable metals, the addition of H_2SO_4 acid serves to convert HCO_3^- into $H_2CO_3^*$, which allows CO_2 to degas rapidly upon boiling, so CO_2 -derived acidity is intentionally not measured. The addition of H_2O_2 causes oxidation of Fe^{II} and Mn^{II} so that they can be precipitated as oxides or hydroxides during the titration. Negative acidity values can be obtained for solutions containing alkalinity; however, many laboratories do not report these negative acidities, nor do they determine the acidity of samples with $pH > 6$. Negative values of acidity commonly are reported as zero. Indeed, only the most recent APHA (1998) 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”, but they do not specifically define net alkalinity. Laboratory practices for reporting negative numbers vary widely; examples of interpretation and misinterpretation are given by Kirby and Cravotta (2005).

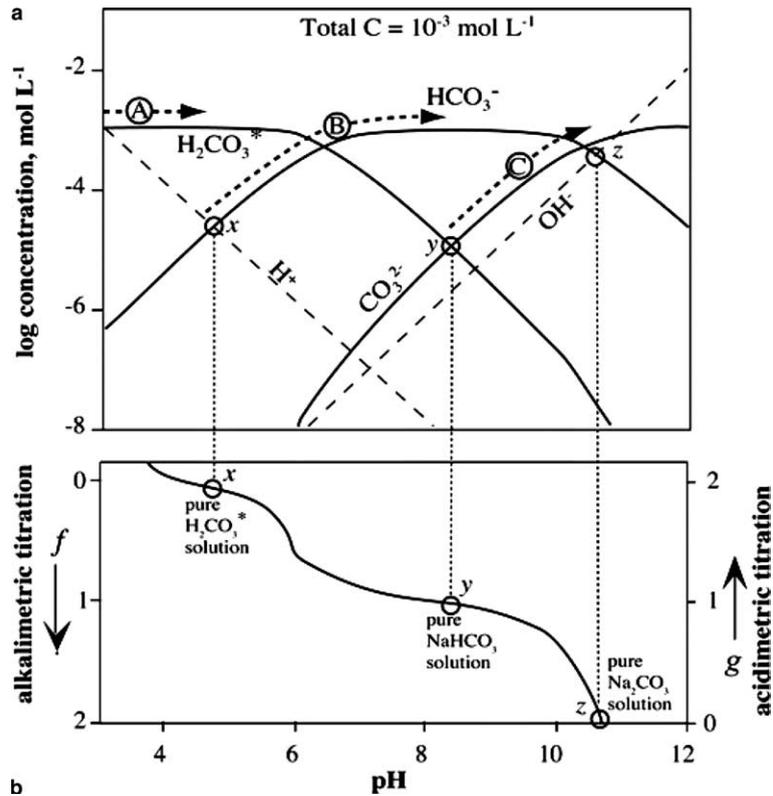


Fig. 1. (a) Distribution of CO_2 species and (b) titration curve for $\text{H}_2\text{O}/\text{CO}_2$ system illustrating principal components for acidity titrations (after Stumm and Morgan, 1996). Dashed arrows show concentration changes of principal components during titrations to equivalence points x , y , and z ; see Sections 2.1, 2.4, and 2.5 for more discussion.

2.3. Theoretical definitions of alkalinity based on charge balance

Alkalinity can be defined on the basis of solution electroneutrality, but Morel and Hering (1993) state that “the conceptualization of alkalinity as a charge balance is not strictly correct”, and this approach lacks the rigor of the proton condition-based definition (Section 2.4). A charge balance derivation (after Drever, 1997; in equivalents) of alkalinity for relatively dilute waters begins with an expression like

$$\begin{aligned}
 &[\text{H}^+] + [\text{K}^+] + [\text{Na}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] \\
 &+ \text{other cationic species} \\
 &= [\text{Cl}^-] + 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \\
 &+ [\text{OH}^-] + \text{other anionic species}, \quad (1)
 \end{aligned}$$

where for example $[\text{Ca}^{2+}] = \text{mol L}^{-1}$ of “free” Ca^{2+} plus associated species such as CaOH^+ , and $[\text{HCO}_3^-] = \text{free HCO}_3^-$ plus associated species such as CaHCO_3^+ . Because cations and anions are equally involved in ionic speciation, complex formation does not affect the charge balance. Eq. (1) above can be rearranged after Drever (1997) as

$$\begin{aligned}
 &\text{Sum (conservative cation species)} \\
 &- \text{sum (conservative anion species)} \\
 &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \\
 &= \text{alkalinity}, \quad (2)
 \end{aligned}$$

where both sides of Eq. (2) are *conservative* (unaffected by changes in pH, pressure, or temperature, and assuming no precipitation or dissolution of solids). In contrast to titration methods, if $[\text{H}^+]$ is greater than the sum of the other terms in Eq. (2), the alkalinity can be a negative value. In essence, a negative alkalinity value represents the amount of base needed to titrate a solution in a closed system up to the reference pH or endpoint, usually $\text{pH} \approx 4.5$. As discussed below, the computer speciation model PHREEQC (Parkhurst and Appelo, 1999) will return large negative alkalinity values for solutions with low pH values. Nevertheless, perhaps because alkalinity is frequently determined by titration or because $[\text{H}^+]$ and $[\text{OH}^-]$ are very small in most natural waters, many practitioners tend to consider only positive contributions to alkalinity (or acidity). In this work, positive alkalinity refers to any species that has a positive term in a mathematical alkalinity definition; this terminology

Table 1
Summary of alkalinity and acidity definitions

Derivation of definition	Source	Definition	Endpoint pH	Negative values possible?	Comments
<i>Theoretical alkalinity</i>					
Charge balance (electroneutrality)	Drever (1997)	Sum (conservative cations) – sum (conservative anions) = $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$	≈4.5	Yes	Primarily H ₂ O–CO ₂ , can be extended to other species
Proton condition (charge and mass balance)	Parkhurst and Appelo (1999)	PHREEQC definition; metals are assigned alkalinity contributions based on reference conditions, e.g., $\text{Fe}^{2+} = 0 \text{ eq mol}^{-1}$, $\text{Fe}^{3+} = -2 \text{ eq mol}^{-1}$	≈4.5	Yes	Consistent with Morel and Hering (1993); Stumm and Morgan (1996)
<i>Laboratory (methyl orange) alkalinity</i>					
Titration	Stumm and Morgan (1996)	“Equivalent sum of the bases that are titratable with strong acid”; does not include H ⁺ or some other negative contributions to alkalinity	≈4.5	No*	Does not measure negative alkalinity
Titration	APHA (1998)	(1) If initial pH < 4.5, record alkalinity = 0, or (2) If initial pH > 4.5, titrate to a pH 4.5 endpoint using H ₂ SO ₄ . Use “low alkalinity” method (a “Gran” titration approach) as necessary.	≈4.5	No*	Standard method; Does not measure negative alkalinity*; endpoints should be adjusted for total carbon
<i>Theoretical acidity</i>					
Proton condition	Stumm and Morgan (1996)	Mineral acidity = $[\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-]$	≈4.5	Yes	Primarily H ₂ O–CO ₂ ; consistent with many texts
Proton condition	Stumm and Morgan (1996)	CO ₂ -acidity = $[\text{H}_2\text{CO}_3^*] + [\text{H}^+] - [\text{CO}_3^{2-}] - [\text{OH}^-]$	8.3	Yes	Primarily H ₂ O–CO ₂ ; consistent with many texts; applicable to mine drainage waters
Proton condition	Stumm and Morgan (1996)	Acidity = $2[\text{H}_2\text{CO}_3^*] + [\text{H}^+] + [\text{HCO}_3^-] - [\text{OH}^-]$	≈11	Yes	Primarily H ₂ O–CO ₂ ; consistent with many texts
Practical; based on charge balance	Hedin et al. (1994)	$50[(2\text{Fe}^{2+}/56) + (3\text{Fe}^{3+}/56) + (3\text{Al}/27) + 2\text{Mn}/55 + 1000(10^{-\text{pH}})]$; metals in mg L ⁻¹	Not specified	No	Widely used; suggested for pH < 4.5; may be applicable to higher pH's
Practical; based on speciation	Langmuir (1997)	Example total acidity for acid mine drainage : $[\text{H}^+] + [\text{HSO}_4^-] + 2[\text{Fe}^{2+}] + 3[\text{Fe}^{3+}] + 2[\text{FeOH}^{2+}] + 3[\text{Al}^{3+}]$	Not specified	No	Not for mine drainage with significant positive alkalinity (continued on next page)

Table 1 (continued)

Derivation of definition	Source	Definition	Endpoint pH	Negative values possible?	Comments
Practical; based on speciation	Drever (1997)	Example acidity for Al-rich water : $[H^+] - [HCO_3^-] + 3[Al^{3+}] + 2[Al(OH)^{2+}] + [Al(OH)_2^+] - [Al(OH)_4^-]$	Not specified	Yes	Ignores CO_3^{2-} and OH^- ; can be modified for Fe species
Laboratory CO_2 - or phenolphthalein-acidity Titration	Stumm and Morgan (1996)	“Equivalent sum of the acids that are titratable with strong base”; does not mention peroxide or hot titration	8.3	No	Can either include or exclude acidity due to CO_2 ;
Titration	APHA (1998)	(1) If pH is greater than 4.5, add H_2SO_4 to bring pH to approximately 4; add five drops of 30% H_2O_2 solution, boil, cool, and titrate using NaOH, or (2) If initial pH is less than pH 4.5, add H_2O_2 , boil, cool, and titrate quickly to a pH 8.3 endpoint using NaOH.	8.3	Yes, if lab reports negative values	Standard method; intentionally drives off acidity due to CO_2 , allows HCO_3^- to consume metal acidity (see Kirby and Cravotta, 2005)

applies similarly to a positive acidity contribution. Acidity is not typically defined based on charge balance.

2.4. Theoretical (proton condition) definitions and assignment of alkalinity/acidity contributions

Two of the more rigorous discussions of alkalinity and acidity are presented by Morel and Hering (1993) and Stumm and Morgan (1996). They use combinations of mass action (using equilibrium constants to distribute aqueous species), the electroneutrality condition, and a reference condition to define alkalinity or acidity. Morel and Hering (1993) refer to the “hydrogen ion conservation” (TOTh) approach, which Stumm and Morgan (1996) refer to as the “proton condition.” These equivalent approaches use slightly different terminology, but both approaches express all pertinent 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. Calcium, Mg, K, Na, and Cl are not typically thought to contribute to alkalinity or acidity. For example, as established by equilibrium constants, Ca^{2+} is the predominant dissolved Ca species at pH 4.5 and pH 8.3, so Ca^{2+} is a principal component and does not contribute to mineral acidity, CO_2 -acidity, alkalinity, or p-alkalinity (defined in Sections 2.5 and 2.6). However, $CaOH^+$ would be the principal component at pH 11, and thus Ca^{2+} would contribute 1 eq L^{-1} to acidity and -1 eq L^{-1} to caustic alkalinity. Principal components and the assignment of acidity and alkalinity contribution are explored for mine drainage solutions below.

PHREEQC (Parkhurst and Appelo, 1999) uses the proton condition to calculate alkalinity, and negative numbers are possible. Although PHREEQC does not calculate a value for acidity, one can use PHREEQC or another aqueous speciation code to calculate acidity (Section 4.4) by determining the distribution of aqueous species at the field pH and oxidation/reduction state and assigning the correct positive or negative contribution (base-consuming capacity) for each considered species.

In a pure water system, H_2O is the predominant species for alkalinity or acidity titration endpoints between pH 4.5 and 11. The solution always has ≈ 55.5 moles of H_2O L^{-1} , with much lower concentrations of H^+ and OH^- . Therefore, H_2O is a principal component and does not contribute to acidity or alkalinity. For all acidity and alkalinity definitions, H^+ contributes 1 positive (+1) equivalent per mole to acidity and 1 negative

(−1) equivalent per mole to alkalinity. Similarly, OH[−] contributes 1 negative (−1) equivalent per mole to acidity and 1 positive (+1) equivalent per mole to alkalinity.

2.5. Acidity based on the proton condition

Stumm and Morgan (1996) define acidities (in eq L^{−1}) in the CO₂/H₂O system (Fig. 1) with 3 different reference conditions, *f*, as follows:

$$\begin{aligned} \text{mineral acidity} &= [\text{H-Acy}]_{f=0} \\ &= [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \end{aligned} \quad (3)$$

$$\begin{aligned} \text{CO}_2\text{-acidity} &= [\text{CO}_2\text{-Acy}]_{f=1} \\ &= [\text{H}_2\text{CO}_3^*] + [\text{H}^+] - [\text{CO}_3^{2-}] - [\text{OH}^-] \end{aligned} \quad (4)$$

$$\begin{aligned} \text{acidity} &= [\text{Acy}]_{f=2} \\ &= 2[\text{H}_2\text{CO}_3^*] + [\text{H}^+] + [\text{HCO}_3^-] - [\text{OH}^-] \end{aligned} \quad (5)$$

where [] indicates mol L^{−1}. For the example diprotic acid-base titration, *f* = *g* − 2, where *f* is the ratio of the concentration of equivalent base added to the concentration of acid and *g* is the ratio of the concentration of equivalent acid added to the concentration of base (Stumm and Morgan, 1996). Depending on total inorganic C concentration, reference conditions (or equivalence points) for Eqs. (3)–(5) occur at pH ≈ 4.5, 8.3, and ≈ 11, respectively. Henceforth, Acidity is used, with an initial upper case letter, to refer to a pH 8.3 endpoint Acidity (Eq. (4)). Quotation marks are used for the 3 different acidities listed in Eqs. (3)–(5). Hot Acidity is used to refer to a *Standard Methods* (APHA, 1998) Acidity titration that employs H₂SO₄ and H₂O₂ addition and a boiling step before titration with base to a pH 8.3 endpoint; this titration method is most appropriate for characterizing mine drainage and other metal-laden solutions. (There are situations in which other endpoints may be considered: e.g., one might intentionally not titrate out Mn, and thus a pH lower than 8.3 might be employed.) The authors use CO₂-Acidity to refer to Acidity derived only from CO₂ species, and use acidity with an initial lower case letter as a more generic term.

Fig. 1 is based on diagrams from Stumm and Morgan (1996) and gives the distribution of species and a titration curve for a CO₂/H₂O system. The pH values at equivalence points *x*, *y*, and *z* correspond to equilibrium concentrations of pure solutions of H₂CO₃ (pH 4.5; [H⁺] = [HCO₃[−]]), NaHCO₃ (pH 8.3; [H₂CO₃^{*}] = [CO₃^{2−}]), and Na₂CO₃ (pH 11; [HCO₃[−]] = [OH[−]]), respectively. For an alkalimetric titration, *f* = 0 corresponds to the reference condition for a pure H₂CO₃ solution, which is equivalent to *g* = 2 for an acidimetric titration.

In Fig. 1, H⁺ and OH[−] are distributed using the 25 °C equilibrium dissociation constant, *K_w* (or p*K_w*) for water. The concentrations of H⁺ and OH[−] are equal

at pH = 0.5p*K_w* = 7. Dissolved CO₂ is distributed into the species H₂CO₃^{*}, HCO₃[−], and CO₃^{2−} by using the total CO₂ concentration and the first and second 25 °C dissociation constants for carbonic acid (*T*_{CO₂}; p*K*₁ ≈ 6.3; p*K*₂ ≈ 10.3). The equivalence points for H₂CO₃^{*} and HCO₃[−] and for HSO₃[−] and CO₃^{2−} are at pH = p*K*₁ and pH = p*K*₂, respectively. Fig. 1 and the text below illustrate the selection of principal components and assignment of acidity equivalent contributions for acidities in this simple system.

Dashed arrow A: In a “mineral acidity” titration (Eq. (3), pH ≈ 4.5), H₂CO₃^{*} is the predominant species at the pH 4.5 equivalence point and is the principal component. It does not contribute to “mineral acidity” because, although it can be deprotonated as pH increases, it is largely protonated below pH 4.5 (pure H₂CO₃ solution). H⁺ contributes 1 positive (+1) equivalent per mole, HCO₃[−] and OH[−] contribute 1 negative (−1) equivalent per mole, and CO₃^{2−} contributes 2 negative (−2) equivalents per mole to “mineral acidity.”

Dashed arrow B: In a “CO₂-acidity” titration (Eq. (4); pH 8.3), HCO₃[−] is the predominant species at the pH 8.3 equivalence point and is the principal component. It does not contribute to “CO₂-acidity” because, although it can be deprotonated as pH increases, it is largely protonated below pH 8.3 (pure NaHCO₃ solution). H₂CO₃^{*} and H⁺ contribute 1 positive (+1) equivalent per mole, and CO₃^{2−} and OH[−] contribute 1 negative (−1) equivalent per mole to “CO₂-acidity.”

Dashed arrow C: In an “acidity” titration (Eq. (5); pH ≈ 11), CO₃^{2−} is the predominant species at the pH 11 equivalence point and is the principal component. It does not contribute to “acidity” because it cannot be deprotonated as pH increases. H₂CO₃^{*} contributes 2 positive (+2) equivalents per mole, H⁺ contributes 1 positive (+1) equivalent per mole, and HCO₃[−] and OH[−] contribute 1 negative (−1) equivalent per mole to “acidity.”

2.6. Alkalinity based on the proton condition

In parallel, Stumm and Morgan (1996) define alkalinities (in eq L^{−1}) in the CO₂/H₂O system with 3 different reference conditions, *f*, as follows:

$$\begin{aligned} \text{“caustic alkalinity”} &= [\text{OH}^- \text{-Alk}]_{f=2} \\ &= [\text{OH}^-] - 2[\text{H}_2\text{CO}_3^*] - [\text{HCO}_3^-] \\ &\quad - [\text{H}^+] \end{aligned} \quad (6)$$

$$\begin{aligned} \text{p-alkalinity} &= [\text{p-Alk}]_{f=1} \\ &= [\text{OH}^-] + [\text{CO}_3^{2-}] - [\text{H}_2\text{CO}_3^*] - [\text{H}^+] \end{aligned} \quad (7)$$

$$\begin{aligned} \text{alkalinity} &= [\text{Alk}]_{f=0} \\ &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \end{aligned} \quad (8)$$

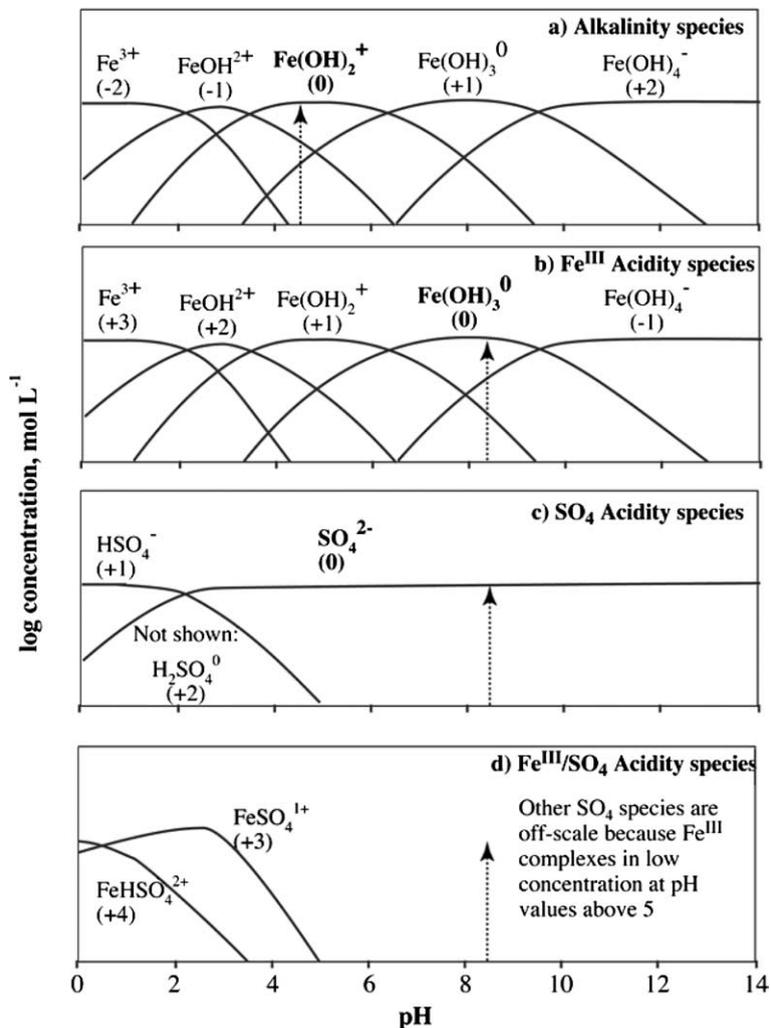


Fig. 2. Schematic diagram of major Fe^{III} and SO_4 speciation illustrating principal components (bold) and equivalents (in parentheses) of: (a) alkalinity contributed and (b–d) acidity contributed. Dashed arrow shows that principal component is the predominant species at the pH of the equivalence point.

where [] indicates mol L^{-1} . Depending on total C concentrations, equivalence points occur at $\text{pH} \approx 11$, 8.3, and ≈ 4.5 , respectively. The selection of principal components and assignment of alkalinity equivalent contributions parallel those for acidities and thus are not discussed here. Stumm and Morgan's (1996) definition of "alkalinity" (Eq. (8)) is appropriate for titration of mine drainage. The equivalence points for "caustic" (Eq. (6)) and "phenolphthalein or p-alkalinity" (Eq. (7)) occur at pH values higher than those in most mine drainage or fresh water (≈ 11 and ≈ 8.3 , respectively), thus they are not discussed further. Throughout the remainder of the text, Alkalinity is used, with an initial upper case letter, to refer to an Alkalinity with a $\text{pH} \approx 4.5$ endpoint. The authors use alkalinity, with an initial lower case letter, as a more generic term.

2.7. Alkalinity and acidity based on the proton condition in more complex systems

If metal and SO_4 species are added to the system, equivalence between CO_2 species and/or H^+ remains the criterion for the titration endpoint, and the pH values for the equivalence point remain the same. Some of the metal and SO_4 species will participate in protonation or hydrolysis reactions (e.g., $\text{HSO}_4^- = \text{SO}_4^{2-} + \text{H}^+$). Pre-dominance of these species at the reference pH is established and additional principal components are assigned using the corresponding dissociation constants for the metal and SO_4 complexation reactions analogous to the $\text{H}_2\text{O}/\text{CO}_2$ system. For example, in a simple $\text{Fe}^{\text{III}}/\text{SO}_4$ solution (Fig. 2(a)), $\text{Fe}(\text{OH})_2^+$ predominates and is the principal component for Fe^{III} for a pH 4.5 equiva-

lence point Alkalinity titration (or for a “mineral acidity” titration). The principal component for SO_4 species (not shown) at pH 4.5 would be SO_4^{2-} . Fig. 2(b)–(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. Some standard texts (Drever, 1997; Snoeyink and Jenkins, 1980; Langmuir, 1997) do not specifically include metal species in alkalinity definitions, but Morel and Hering (1993) and Stumm and Morgan (1996) indicate that metals can affect alkalinity. For solutions with $\text{pH} < 4.5$, PHREEQC (Parkhurst and Appelo, 1999) will return negative Alkalinity values. Both Drever (1997) and Langmuir (1997) provide brief practical definitions (without derivation) of acidity that include metal contributions. Although plots such as Fig. 2 typically are presented with log *activity* on the y -axis, Fig. 2 and subsequent similar plots have log *concentration* on the y -axis because concentrations rather than activities are the parameters of concern for alkalinity and acidity. The concentrations of HCO_3^- and CO_3^{2-} and their metal complexes are too low to contribute importantly to Acidity, and metals contribute little to Alkalinity (Section 4.2).

2.8. Terminology – points of potential confusion

Stumm and Morgan (1996) refer to “mineral acidity” (Eq. (3)) for solutions to which “mineral acid is added to a natural water beyond equivalence point x ” (i.e., to a pH lower than 4.5; see Fig. 1). The term “mineral acid” is an older chemistry term that developed because strong acids such as H_2SO_4 were produced from the dissolution of minerals. Because low-pH mine drainage contains metals from dissolved minerals, many workers refer to acidity contributed by metals as *mineral acidity*. In this paper, the authors refer to acidity contributed by metals as “metal acidity.” It is recommended that others adopt this terminology so as not to confuse acidity contributed by metals with the previously defined term “mineral acidity,” which has a different meaning.

Stumm and Morgan (1996) refer to acidity with an equivalence point of 8.3 as “ CO_2 -acidity” (Eq. (4)). Dissolved CO_2 can be a substantial source of acidity in uncontaminated or polluted ground waters. Nevertheless, the Acidity due to CO_2 is ephemeral because CO_2 -charged waters discharged to free-flowing streams or aerobic treatment ponds lose most of their CO_2 to the atmosphere, with a consequent increase in pH (e.g., Wood, 1976; Kirby and Cravotta, 2005). Therefore, in the Standard Method for waters containing hydrolyzable metals, CO_2 is degassed intentionally by boiling the sample before titrating with base (APHA, 1998). Thus, the Acidity determined by the standard Hot Acidity titration method does not measure Acidity due to CO_2 . For lack of an obvious alternative, the authors use Acidity to refer to a pH 8.3-endpoint acid-

metric calculation or titration. One could refer to “phenolphthalein-acidity” or “p-acidity” for a pH 8.3 endpoint, but this is not standard practice. No such confusion is associated with the standard method (APHA, 1998) Alkalinity with a pH 4.5 (methyl orange) endpoint.

Some confusion exists over the use of the terms acid- or base-neutralizing capacity (ANC or BNC). Stumm and Morgan (1996) and Morel and Hering (1993) use ANC as an “umbrella” term that includes “caustic alkalinity” (primarily due to bases stronger than Na_2CO_3), “p-alkalinity” (primarily due to CO_3^{2-}), and alkalinity (primarily due to HCO_3^-); see also Eqs. (6)–(8) for definitions. Stumm and Morgan (1996) also use BNC as an “umbrella” term for all acidities (Eqs. (3)–(5)). These authors refer only to dissolved species as sources of ANC. Consistent with Stumm and Morgan’s (1996) “Alkalinity” (Eq. (8)) or Langmuir’s (1997) *immediate alkalinity*, a US Geological Survey field manual (US Geological Survey, 1997 to present) defines Alkalinity in filtered samples only for dissolved species titrated to an equivalence point of approximately pH 4.5. However, the same report refers to ANC in an unfiltered sample as including both dissolved species and any suspended solids such as calcite or dolomite that may contribute Alkalinity upon dissolution. Langmuir (1997) uses the term *long-term alkalinity* to refer to the Alkalinity that can be imparted to a water from solids in a field setting, i.e., from a watershed or groundwater system. If such solids are ground finely for use in mine-drainage treatment, they could impart Alkalinity to unfiltered samples by their dissolution after sampling and/or during titration. Similarly, mine waters with suspended solids could have higher Acidities than those of filtered samples if they contain acid-storing sulfate minerals such as jarosite (Alpers et al., 1989). In practice, the distinction between filtered and unfiltered Alkalinity or Acidity usually is unnecessary because quantities of reactive suspended solids are negligible in most mine-drainage samples.

2.9. Definitions of net alkalinity and net acidity in use for treatment of mine drainage

Hedin et al. (1994) is a widely cited reference for “net alkalinity”, which they defined simply as (alkalinity–acidity). Similarly, “net acidity” is defined as (acidity–alkalinity). Such definitions are open to interpretation because of the different definitions of, and practices for measuring, alkalinity and acidity. For the overall characterization of mine-drainage quality, Brady et al. (1990, 1994) use “net alkalinity” defined on the basis of routinely measured values for alkalinity and acidity ($\text{Alkalinity}_{\text{Std. Meth.}} - \text{Hot Acidity}_{\text{Std. Meth.}}$). However, Kirby (2002), Kirby and Cravotta (2005), and Watzlaf et al. (2004) demonstrate that this computation gives an erroneous result if $\text{Alkalinity}_{\text{Std. Meth.}} > 0$,

and it can result in addition of inadequate amounts of alkaline materials such as lime or limestone in mine drainage treatment.

Hedin et al. (1994) and Rose and Cravotta (1998) showed that the measured Hot Acidity of mine drainage is comparable with calculated acidity in units of $\text{mg CaCO}_3 \text{ L}^{-1}$

$$\text{acidity}_{\text{calculated}} = 50[1000(10^{-\text{pH}}) + 2(\text{Fe}^{\text{II}})/56 + 3(\text{Fe}^{\text{III}})/56 + 2(\text{Mn})/55 + 3(\text{Al})/27], \quad (9)$$

where the total dissolved analytical concentrations of Fe^{II} , Fe^{III} , Mn, and Al are in mg L^{-1} . It should be noted that this computation method does not count negative contributions to acidity. Thus, another common practice is to calculate

$$\text{net alkalinity} = (\text{Alkalinity}_{\text{Std. Meth.}} - \text{acidity}_{\text{calculated}}, \text{ Eq. (9)}). \quad (10)$$

For example, Eq. (10) was applied by Cravotta and Kirby (2004) for evaluation of mine drainage characteristics and effects on a watershed scale. This application illustrated that the measured Hot Acidity is equal to the negative value of net alkalinity computed by Eq. (10). In a consistent interpretation, Hedin (2004) more recently presents

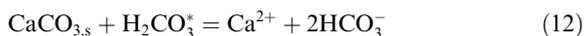
$$\text{net acidity}_{\text{calculated}} = 50[1000(10^{-\text{pH}}) + 2(\text{Fe}^{\text{II}})/56 + 3(\text{Fe}^{\text{III}})/56 + 2(\text{Mn})/55 + 3(\text{Al})/27] - \text{Alkalinity} \quad (11)$$

as a formula to calculate net acidity, where metals are in mg L^{-1} and Alkalinity and net acidity are reported as mg L^{-1} as CaCO_3 . The use of Eq. (11) is equivalent to the use of Eq. (10) (with the signs reversed).

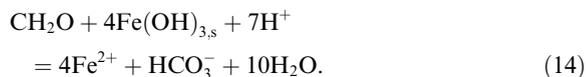
In Eqs. (9) and (11), Fe^{II} and Fe^{III} are shown instead of Fe^{2+} and Fe^{3+} used by the original authors because the iron concentrations employed are based on analytical techniques that distinguish between Fe^{II} and Fe^{III} , but not between actual species (e.g., “free” Fe^{2+} compared to hydroxyl or sulfate complexes). Hedin et al. (1994) state that Eq. (9) is appropriate for waters having $\text{pH} < 4.5$, but it is also commonly employed for higher-pH waters that contain alkalinity.

2.10. Positive alkalinity sources in mine drainage

Two main sources of positive (+) Alkalinity in mine drainage are the dissolution of carbonate rocks (Blowes and Ptacek, 1994; Cravotta, 1994) and SO_4 reduction/organic matter oxidation (Seal, 2003). Bicarbonate can be released to solution by the following reactions:



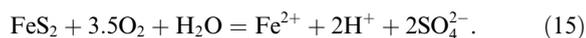
where CH_2O represents organic matter. Reductive dissolution of metal hydroxides may also contribute Alkalinity (Lovley, 1991), as in the reaction



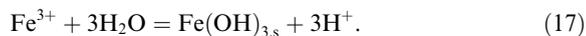
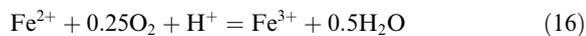
Although minor contributions to Alkalinity from hydroxyl, carbonate, phosphate, borate, silicate, and other species can be identified in some solutions (e.g., Stumm and Morgan, 1996), essentially all of the positive Alkalinity in mine drainage is due to HCO_3^- . The negative contributions of metals to Alkalinity are small (Section 4.2). Although it can cause a pH change, the ingassing or outgassing of CO_2 has no effect on solution Alkalinity (Stumm and Morgan, 1996; Cravotta and Hilgar, 2000).

2.11. Positive Acidity sources in mine drainage

Acidic mine drainage forms by the oxidation of Fe bearing sulfide minerals such as pyrite:



The Fe^{II} is subsequently oxidized, and Fe^{III} is precipitated:



The main sources of positive Acidity (Eq. (4)) in mine drainage are “free” H^+ , HSO_4^- , hydrolyzable metals and metal complexes, and CO_2 . Mine drainage waters can have a wide range of pH and $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ concentrations depending on dissolved O_2 (DO) concentrations, Fe^{II} oxidation rates, and the presence of Fe-oxidizing bacteria. Many low-DO waters have $\text{pH} > 6$ with dissolved Fe^{II} predominant, whereas many high-DO waters have $\text{pH} \approx 3.5$ with Fe^{III} predominant (Barnes and Clarke, 1964; Barnes et al., 1964; Langmuir, 1969, 1997; Rose and Cravotta, 1998). Mn and Al commonly are released by acid dissolution of silicate, carbonate, and oxide minerals associated with ore or coal deposits (Cravotta, 1991, 1994). Metals release acidity to solution (or consume base) by hydrolysis reactions such as



or successive hydrolysis reactions leading to precipitation of solids (e.g., Eq. (17)).

As result of microbial respiration and/or carbonate dissolution, many mine discharges also have dissolved CO_2 concentrations that are elevated compared to the surface water in equilibrium with the atmosphere (Blowes and Ptacek, 1994; Cravotta, 1994; Cravotta et al., 1994). The dissolved CO_2 temporarily depresses pH and contributes Acidity:

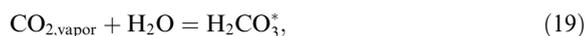


Table 2
Equivalents per mole positive and negative contributions to Acidity (pH 8.3 endpoint) by aqueous species of Fe^{II}, Fe^{III}, Al, Mn^{II}, CO₂, and S in the PHREEQC database

	Acidity due to species, eq/mol					
	+5	+4	+3	+2	+1	0
Fe ^{II} species			FeHSO ₄ ⁺	Fe ²⁺ , FeSO ₄ ⁰ , FeHCO ₃ ⁺	FeOH ⁺ , FeCO ₃ ⁰	Fe(OH) ₂ ⁰
Fe ^{III} species	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
Al species		AlHSO ₄ ²⁺	Al ³⁺ , AlSO ₄ ⁺ , Al(SO ₄) ₂ ⁻	AlOH ²⁺	Al(OH) ₂ ⁺	Al(OH) ₃ ⁰
Mn ^{II} species				Mn ²⁺ , MnSO ₄ ⁰	MnOH ⁺	Mn(OH) ₂ ⁰
H ₂ O/H ₂ S/CO ₂ species					H ⁺ , H ₂ CO ₃ [*] , H ₂ S	H ₂ O, HCO ₃ ⁻ , HS ⁻
Non metal-bound SO ₄				H ₂ SO ₄ ⁰	HSO ₄ ⁻	SO ₄ ²⁻

Principal components are shown as bold and do not contribute positively or negatively to Acidity. The total Acidity for this system is also given as an equation below the table. Acidity, eq L⁻¹ = 3[FeHSO₄⁺] + 2[Fe²⁺] + 2[FeCO₃⁰] + 2[FeHCO₃⁺] + [FeOH⁺] + [Fe(OH)₂⁰] + 5[Fe₃(OH)₄⁵⁺] + 4[FeHSO₄²⁺] + 4[Fe₂(OH)₂⁴⁺] + 3[Fe³⁺] + 3[FeSO₄⁺] + 2[FeOH²⁺] + [Fe(OH)₂⁺] - [Fe(OH)₃⁰] - [Fe(OH)₄⁵⁺] + 4[AlHSO₄²⁺] + 3[Al³⁺] + 3[AlSO₄⁺] + 3[Al(OH)₂⁺] - [Al(OH)₃⁰] + 2[Mn²⁺] + 2[MnSO₄⁰] + [MnOH⁺] + [H₂CO₃^{*}] + [H₂S] - [OH⁻] - [CO₃²⁻] - [S²⁻] + 2[H₂SO₄] + [HSO₄⁻] ± other metals and their complexes, with contributions determined by principals components and equilibrium constants. Brackets indicate mol L⁻¹.

where H₂CO₃^{*} refers to both dissolved CO₂ and H₂CO_{3,aq}. Stumm and Morgan (1996) state that the dissolution of carbonate minerals into a water has no effect on its acidity, but this statement is only true for the “acidity” referred to in Eq. (5) (endpoint pH ≈ 11). The “mineral acidity” and “CO₂-acidity” (Eqs. (3) and (4)) are affected by dissolution of carbonate minerals. These results are due to the presence of the CO₃²⁻ species in Eqs. (3) and (4), and its lack in Eq. (5).

3. Methods

3.1. Field and laboratory

In 1999, field and laboratory data were acquired for 140 coal-mine drainage sites from the bituminous and anthracite coalfields of Pennsylvania with solution compositions ranging from pH of 2.7 with no positive Alkalinity, to pH of 7.3 with positive Alkalinity (Cravotta et al., 2001). Concentrations of dissolved SO₄, Fe, Al, and Mn ranged from 36 to 2000, 0.046–512, 0.007–108, and 0.019–74 mg L⁻¹, respectively. Detailed descriptions of the methods of sampling and analysis and geochemical evaluation of these samples are provided in Kirby and Cravotta (2005). Activities of aqueous species, including Fe^{II} and Fe^{III}, were calculated with the WATEQ4F computer program (Ball and Nordstrom, 1991; Nordstrom, 2004) on the basis of the pH, Eh, temperature, analytical concentrations of anions and cations, and ionic strength of the fresh samples.

3.2. Geochemical modeling of the distribution of aqueous species

The geochemical computer code PHREEQC (Parkhurst and Appelo, 1999) was used to model 25 °C speciation in laboratory-synthesized mine drainage solutions (low-pH Fe^{III} and Al sulfate; see Kirby and Cravotta, 2005) and similar hypothetical solutions. The speciation allowed the calculation of theoretical Acidity as defined in Table 2 and discussed later in this paper. Calculated Alkalinities, including negative values, are from PHREEQC output. The pH was decreased in modeled solutions by adding H₂SO₄. Modeled solutions were oxidized by O₂. The pH was increased by adding aliquots of NaOH. Charge balance was established by making small adjustments in the SO₄ concentration of the initial solution before the simulation. The standard PHREEQC thermodynamic database was used in PHREEQC simulations and to draw the species distribution diagrams in this study.

Diagram illustrates speciation changes during an Alkalinity titration (to pH 4.5). Speciation for Fe^{II} and Fe^{III} is for aqueous complexes with no solid present. Fe^{II} concentration is well below the solubility limit for Fe(OH)₂. The initial Fe^{III} concentration is controlled by amorphous Fe(OH)_{3,s} solubility, but the Fe^{III} concentration remains constant and is no longer controlled by the solid as acid is added during the titration. SO₄ complexes are not shown. Dashed arrows illustrate the consumption of Alkalinity species as the titration proceeds. Equilibrium constants are from Stumm and Morgan (1996).

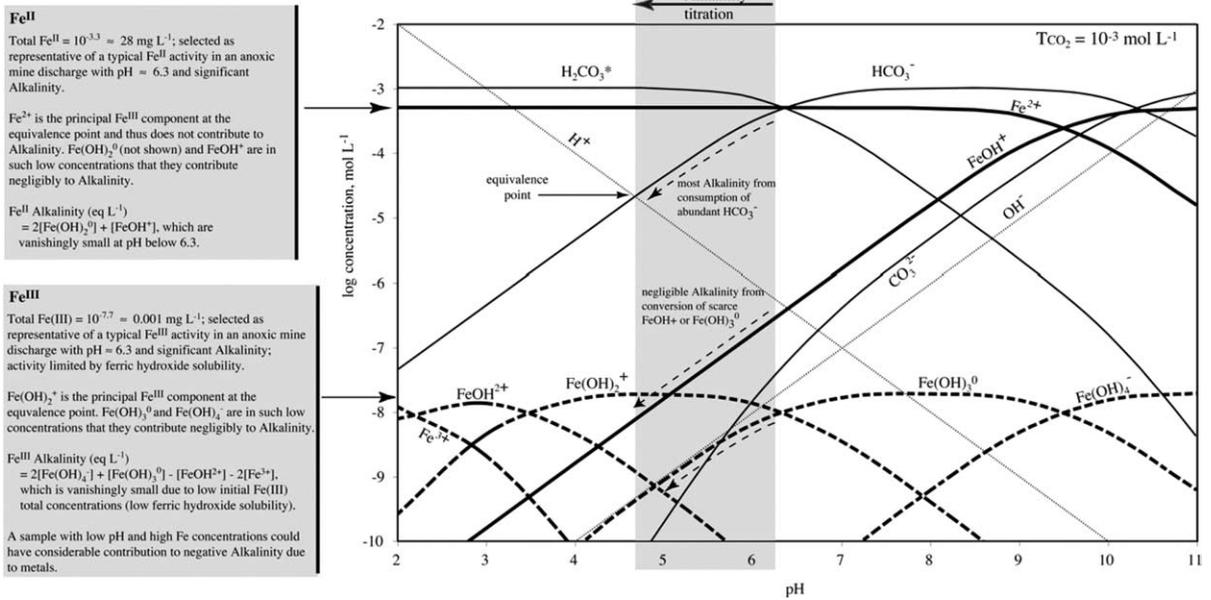


Fig. 3. Speciation of H⁺ and OH⁻ (dotted), dissolved CO₂ (solid), Fe^{II} (bold), and Fe^{III} (bold dashed) species for a typical anoxic, pH 6.3 mine discharge that contains significant Alkalinity; illustrates why metals contribute negligibly to positive or negative Alkalinity in samples with circumneutral pH.

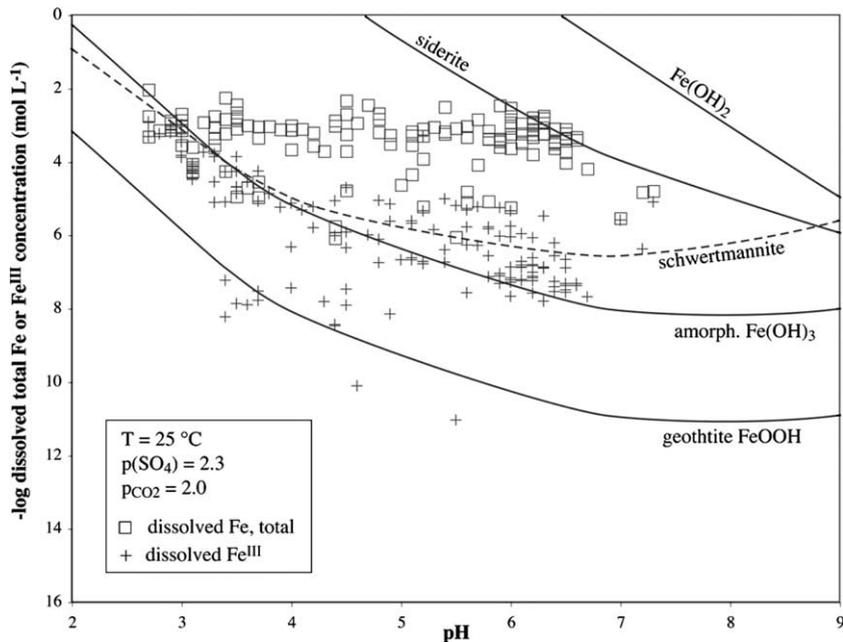


Fig. 4. Fe^{III} and Fe^{II} solid solubilities and corresponding concentrations of total dissolved Fe and Fe^{III} for 140 AMD samples. Equilibrium constants from Parkhurst and Appelo (1999) and Bigham et al. (1994).

4. Results and discussion

4.1. Acidity due to CO₂

Mine discharges, especially those from flooded underground mine sources, can have high concentrations of CO₂ before they are exposed to the atmosphere. After reaching the earth's surface, CO₂ degasses, reaching equilibrium with atmospheric CO₂ quickly, thus most Acidity due to CO₂ is ephemeral. This CO₂-derived Acidity does not need to be considered for mine drainage treatment due to its ephemeral nature; although CO₂ concentrations are non-zero, they are negligible when compared with H⁺ and metal concentrations. As mentioned previously, the standard method Hot Acidity titration (APHA, 1998) for mine water also intentionally drives off CO₂ when the solution is boiled and does not measure Acidity due to CO₂. See Kirby and Cravotta (2005) for further discussion.

4.2. Contribution of metals to positive (+) or negative (-) Alkalinity

Using Fe^{II} and Fe^{III} species as examples, Fig. 3 illustrates that although metals contribute to Alkalinity, their contributions are negligible compared to contributions from HCO₃⁻. Fig. 3 shows PHREEQC-calculated speciation for a water sample typical of a class of mine water with near-neutral pH, relatively high metal concentrations, and measurable Alkalinity. Mine water from deep mine sources that derives Alkalinity as well as metals from surrounding rocks is common. For

example, the coal mining regions of Pennsylvania have numerous large mine discharges with such water. Fig. 4 illustrates that concentrations of dissolved Fe, mostly present as Fe^{II}, can be up to tens of mg L⁻¹ due to the high solubility of siderite (FeCO₃). Dissolved Fe^{III} concentrations are typically low (<1.0 mg L⁻¹) due to the low solubility of Fe^{III} hydroxides and oxyhydroxysulfates (e.g., amorphous Fe^{III} hydroxide, goethite, and schwertmannite). This hypothetical near-neutral pH mine water represents an end member composition; real mine water compositions will have a variety of Fe^{II} and Fe^{III} concentrations and concentration ratios.

The hypothetical Alkalinity titration represented in Fig. 3 begins with an Fe^{II}-rich, CO₂-rich, Fe^{III}-poor water at pH 6.3; the titration proceeds to a pH 4.5 endpoint, at which the principal components are defined. As acid titrant is added, the relatively high concentration of HCO₃⁻ is converted to H₂CO₃^{*}, and HCO₃⁻ is measured as the predominant contribution to Alkalinity (1 eq mol⁻¹; see Eq. (8)). H₂CO₃^{*} is the principal component for CO₂ species, and thus does not contribute to Alkalinity. CO₃²⁻ contributes 2 equiv. per mole (Eq. (8)), but its concentration is so low as to be negligible.

Iron II is present in relatively high concentration as Fe²⁺, which is the principal component for the Fe^{II} species, and thus Fe²⁺ does not contribute to Alkalinity. The reaction



suggests that hydrolyzed Fe^{II} could accept H⁺ and thus act as a base. Indeed, the species FeOH⁺ and Fe(OH)₂⁰ (off scale to the right in Fig. 3) contribute positively to

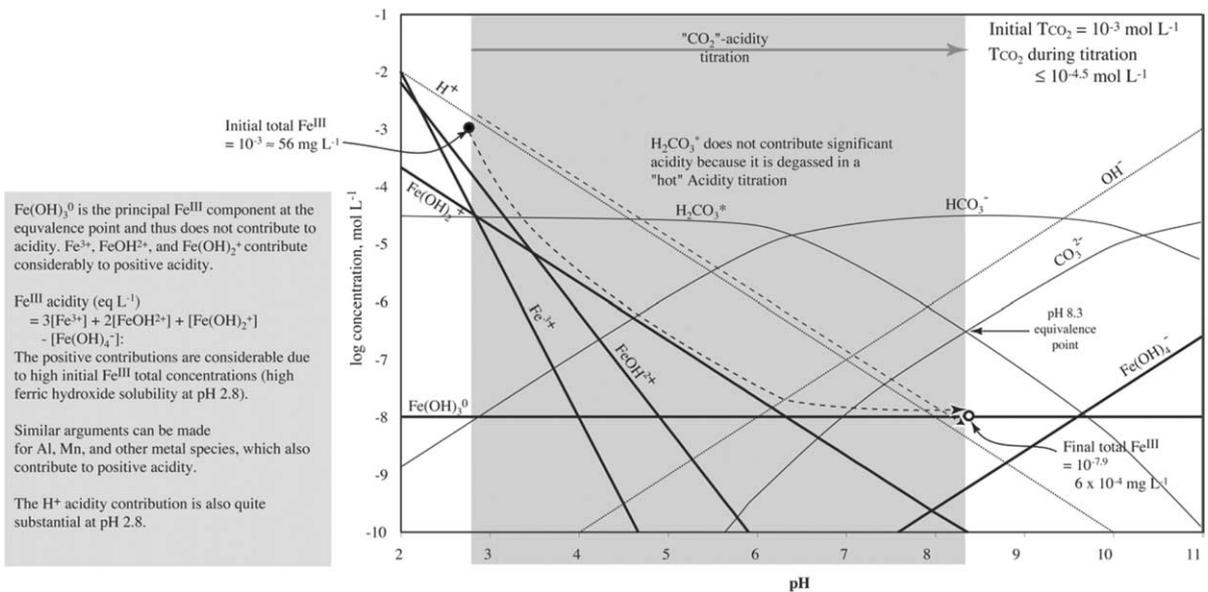


Fig. 5. Speciation of H⁺ and OH⁻ (dotted), carbonate (solid), and Fe^{III} (bold) species for a typical oxidic, pH 2.8 mine discharge illustrating why metals contribute significantly to positive Acidity.

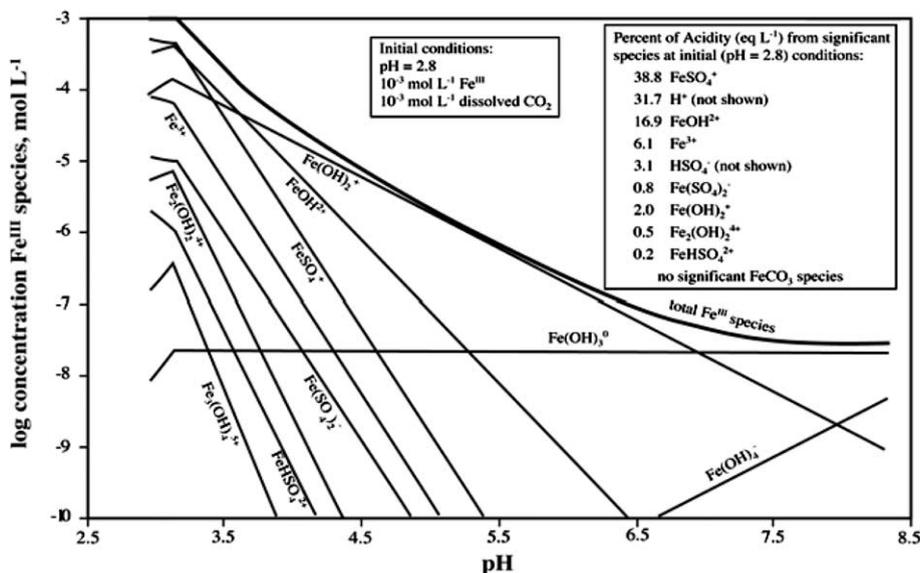
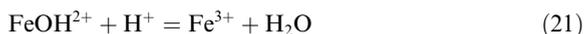


Fig. 6. PHREEQC-calculated speciation of major Acidity-contributing Fe^{III} species during an Acidity titration with NaOH titrant of a synthetic 56 mg L⁻¹ Fe^{III}/SO₄ solution. Total dissolved Fe^{III} concentration is controlled by Fe(OH)₃ solubility at pH > 3. Ephemeral H₂CO₃; Acidity was not included in calculation of Acidity percentages.

Alkalinity because they can lose OH⁻ (consume H⁺), but these contributions are vanishingly small because their concentrations are so low below pH 6.3.

Fe(OH)₂⁺ is the principal component for the Fe^{III} species and does not contribute to Alkalinity. The other Fe^{III} species can contribute either positively (+) or negatively (-) to Alkalinity as shown in the inset of Fig. 3. The reaction



suggests that hydrolyzed Fe^{III} could act as a base. However, due to low mineral solubility, the concentrations of hydrolyzed trivalent metal ion species (FeOH²⁺, AlOH²⁺) will be negligibly low in waters that contain Alkalinity and have pH values in the 5.5–7 range. Therefore, Alkalinity contributions by Fe^{III} species are vanishingly small. These concepts can be extended to examine the small contributions to Alkalinity of other metals and complexes such as HCO₄⁻. Manganese II behaves similarly to Fe^{II} because at pH 4.5 the predominant Mn^{II} species and principal component is Mn²⁺ (from PHREEQC database, Parkhurst and Appelo, 1999). Aluminium^{III} behaves similarly to Fe^{III}, contributing very little to Alkalinity.

4.3. Contributions of metals to positive (+) or negative (-) Acidity

Fig. 5 illustrates speciation during a Standard Method Hot Acidity titration (APHA, 1998; pH 8.3 endpoint) and demonstrates how metals contribute considerably and positively to Acidity, whereas negative contribu-

tions to Acidity from metals are low. This mine water represents another end member composition (cf. Fig. 3). The water has a pH of 3, is Fe^{III}-rich, and has no measurable (positive) Alkalinity. Iron^{III} concentration can be high at the beginning of the titration because Fe^{III} hydroxide solubility is high at pH 2.8. Fe(OH)₃⁰ is the predominant species and thus the principal component, so it does not contribute to Acidity. Fe³⁺, FeOH²⁺, Fe(OH)₂⁺, and Fe(OH)₄⁻ contribute 3, 2, 1, and -1 equivalents per mole, respectively, to Acidity. H⁺ also contributes considerably to Acidity at pH 2.8. Other important sources of Acidity in low pH mine water can include HSO₄⁻, Fe^{II}, Al, other metals, and metals complexed with ligands.

Complexation of metals with SO₄²⁻ and OH⁻ plays an important role in determining the Acidity contributions of mine drainage waters. Fig. 6 shows a modeled Acidity titration with important Fe^{III} and SO₄ species and total Fe^{III} concentrations illustrated. Fig. 6 also lists the percentage of Acidity equivalents for each species at the start of the titration. At pH 2.8, FeSO₄⁺, H⁺, and FeOH²⁺ contribute 87.4% of the Acidity, while Fe³⁺ contributes only 6.1% of the Acidity.

The contribution to Acidity from H⁺, metal complexes, and HSO₄⁻ varies as pH changes. Fig. 7 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 (Fig. 7(a) and (b)). As Acidity from H⁺ decreases, the percentages of the total Acidity from FeSO₄⁺ and AlSO₄⁺ both in-

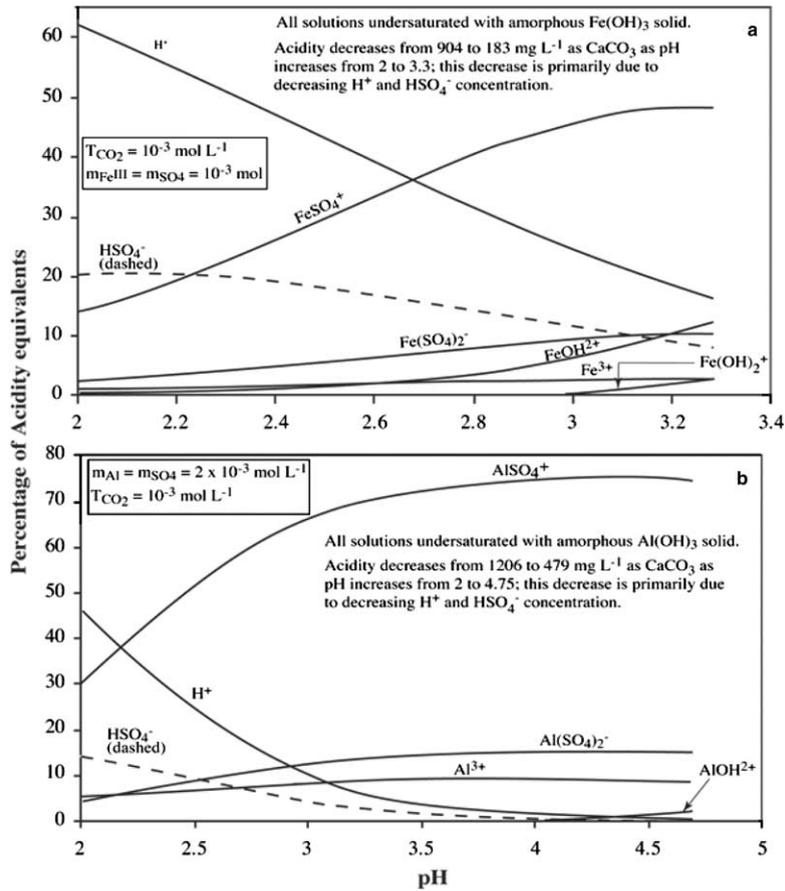


Fig. 7. PHREEQC-calculated percentage contributions to Acidity from major species in: (a) 56 mg L^{-1} $\text{Fe}^{\text{III}}/\text{SO}_4$ solution from pH 2 to pH 3.3, and (b) 54 mg L^{-1} Al/SO_4 solution from pH 2 to pH 4.75.

crease. Although Fe^{III} and Al hydroxyl complexes increase in importance as pH increases, they are not as important as metal- SO_4^{2-} complexes. Acidity from HSO_4^- also decreases with increasing pH as HSO_4^- is converted to SO_4^{2-} .

4.4. Calculation of theoretical acidity

The Acidities and percentage of Acidity contributions displayed in Figs. 5–7 are based on the rigorous proton condition approach (Stumm and Morgan, 1996). Table 2 shows the number of equivalents per mole contributions to Acidity with a pH 8.3 endpoint for mine drainage solutions containing H_2O , CO_2 , Fe^{II} , Fe^{III} , Al, Mn, SO_4^{2-} , and S^{2-} , for species in the PHREEQC database. This concept can be extended to other metals and complexes, and a similar table could be developed for Alkalinity. However, because almost all positive (i.e., measurable) Alkalinity in mine drainage is from HSO_3^- (see Section 4.3), such a table is not provided.

The calculated Acidity (for a pH 8.3 endpoint) is

$$\text{Acidity}_{\text{calculated}}, \text{ eq L}^{-1} = \sum_i^{\text{all species}} \varepsilon_i M_i, \quad (22)$$

where ε_i is the number of equivalents per mole of the i th species, and M_i is the concentration in mol L^{-1} of the i th species (Table 2). The concentrations of species are obtained from PHREEQC modeling results. In this study, Acidity due to CO_2 (as H_2CO_3^*) was not included because it is negligible compared to other Acidity contributions. Therefore, non- CO_2 Acidity is appropriate to consider for mine drainage treatment and is calculated as

$$\begin{aligned} \text{non-}\text{CO}_2 \text{ Acidity}_{\text{calculated}}, \text{ eq L}^{-1} \\ = \sum_i^{\text{all species less CO}_2} \varepsilon_i M_i. \end{aligned} \quad (23)$$

The inset (from Hedin et al., 1994) in Fig. 8 shows a strong linear relationship between measured Hot Acidity and calculated Acidity (Eq. (9)). Above $\approx 600 \text{ mg L}^{-1}$, measured Hot Acidities are slightly higher (>10%) than

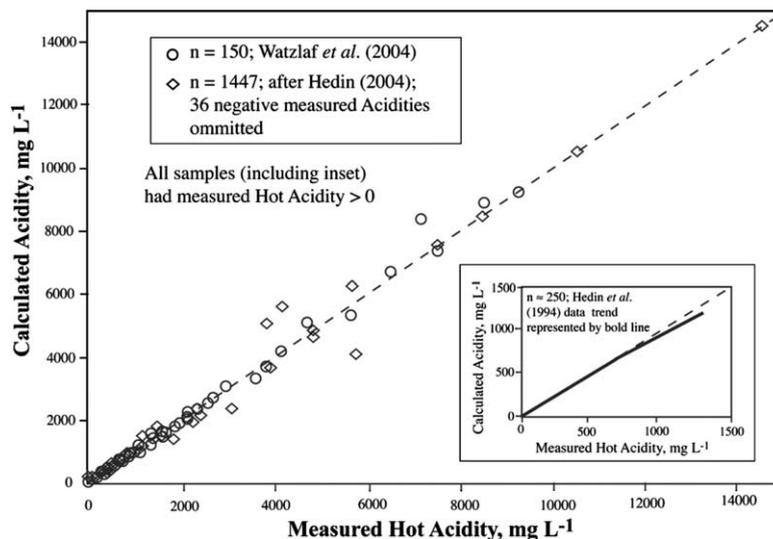


Fig. 8. Calculated acidity (Eq. (9)) versus measured Hot Acidity (Std. Meth.) for 3 large data sets. Diagonal dashed lines show where values on the x - and y -axis are equal. Inset data suggests systematic deviation of calculated acidity from Hot Acidity. More recent data sets do not show this deviation. Data used with permission of authors.

calculated Acidities. Fig. 8 also shows more recent large datasets (Hedin, 2004; Watzlaf et al., 2004) in which this deviation is not noted at high Acidities ($<15,000 \text{ mg L}^{-1}$ as CaCO_3); these later datasets suggest that the deviation noted in Hedin et al. (1994) may not be real.

Eq. (9) is frequently employed for calculating net alkalinity or net acidity (see also Eq. (10)). Eq. (9) cannot return negative numbers because it considers only positive contributions to Acidity; Eq. (10) includes a negative contribution from Alkalinity and thus can return negative numbers. Eqs. (9)–(11) intentionally do not include positive Acidity contributions from CO_2 .

In Fig. 8, metals were not speciated except to differentiate Fe^{II} from Fe^{III} , but the calculated Acidities (Eq. (9)) matched several hundred measured Hot Acidities reasonably well (Hedin et al., 1994) or very well (Hedin, 2004; Watzlaf et al., 2004). Hedin et al. (1994) state that even at fairly low pH (2.7), H^+ acidity is only a minor component of total Acidity (compared to metals) based on Eq. (9). This statement conflicts with the results presented in Figs. 6 and 7 of this study, where Acidity due to H^+ accounts for 60% to 20% of total acidity from pH 2 to pH 2.7. In addition, PHREEQC results in Fig. 7 assign Acidity contributions to HSO_4^- , FeSO_4^+ , and AlSO_4^+ , which are not included in Eq. (9). Figs. 6 and 7 suggest that the aqueous species Fe^{3+} contributes only a small percentage of the total Acidity compared to SO_4^{2-} complexes.

Another potential concern with Eqs. (9) and (11) lies in the pH term. The pH is defined as the negative \log_{10} of the activity of H^+ (a_{H^+}). All other terms in Eqs. (9) and (11) are in concentrations rather than activities,

which is appropriate for calculating Acidity. Strictly, these equations should employ H^+ concentration, not H^+ activity, in the calculation of Acidity. The relationship between concentration and activity for H^+ is

$$m_{\text{H}^+} = a_{\text{H}^+} / \gamma_{\text{H}^+} \quad (24)$$

where γ_{H^+} is the activity coefficient, which is a function of ionic strength, and m_{H^+} is the concentration in mol kg^{-1} of water. The effect of using m_{H^+} ($\approx M_{\text{H}^+}$ in mol L^{-1} of solution in dilute solutions) instead of a_{H^+} in Eq. (9) or (11) is to increase the value of the calculated Acidity. Using H^+ concentration (from PHREEQC results) instead of H^+ activity for solutions modeled in this paper, the “correction” to calculated Acidity is very small. The “correction” is probably negligible for mine drainage solutions except those with $\text{pH} < 2$. The activity coefficient effect is usually small at $\text{pH} > 2$ because: (1) the activity correction only amounts to an $\approx 10\%$ increase in the H^+ acidity term (for $\gamma_{\text{H}^+} \approx 0.9$ and $m_{\text{H}^+}/a_{\text{H}^+} \approx 1.1$), and (2) there are many other Acidity-contributing species. These other species swamp the effect of the “correction,” which appears not to be needed for any but the most concentrated and acidic mine waters.

Fig. 9 illustrates the likely reason that, although complete aqueous speciation is not accounted for, Eq. (9) matches Hot Acidity titrations for low-pH samples well. Fig. 9 provides calculated values of the average equivalents of Acidity per mole for all Fe^{III} , Al^{III} , H^+ , and non-metal SO_4 (primarily HSO_4^-) species for synthetic Fe and Al sulfate solutions at varying pH. Fig. 9 includes saturation indices ($\log Q/K$; see Drever, 1997)

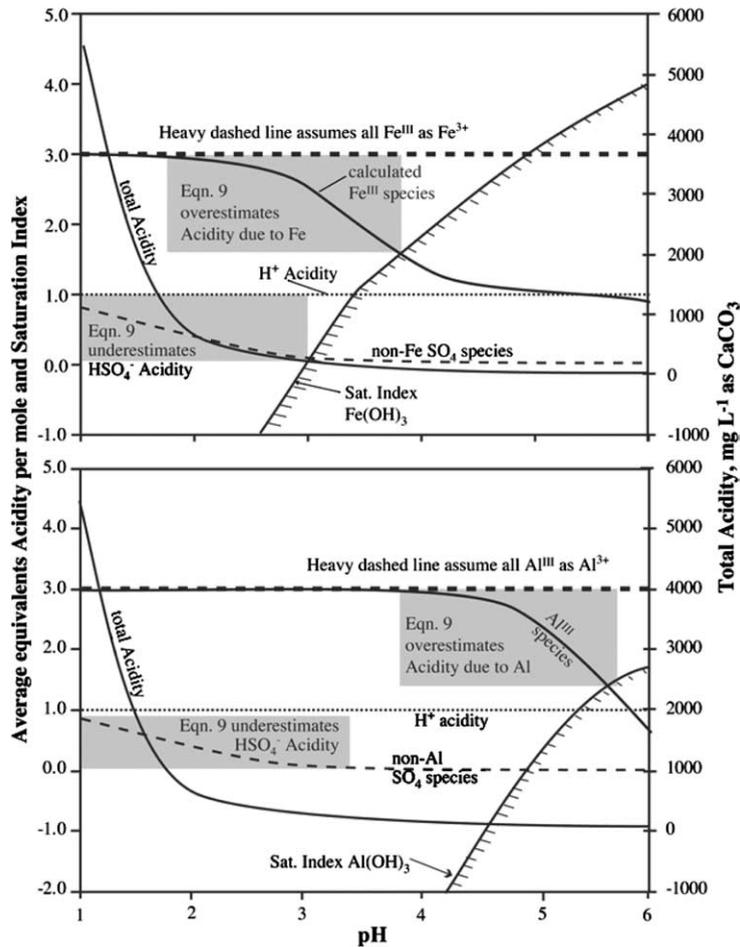


Fig. 9. Plot of average equivalents Acidity per mole versus pH for: (a) 10^{-3} mol L⁻¹ Fe^{III} solution, and (b) 10^{-3} mol L⁻¹ Al^{III} solution based on PHREEQC speciation.

for amorphous Fe and Al hydroxides to show solubility limitations for these metals. Fig. 9 also shows calculated non-CO₂ acidity based on Eq. (23) and Table 2. The value for the average metal Acidity equivalents per mole is calculated as

$$\begin{aligned} & \text{average Fe, Al, or S equivalents Acidity, mol}^{-1} \\ &= \frac{\sum_i^{\text{all Fe species}} \varepsilon_i M_i}{\sum_i^{\text{all Fe species}} M_i} \quad \text{OR} = \frac{\sum_i^{\text{all Al species}} \varepsilon_i M_i}{\sum_i^{\text{all Al species}} M_i} \quad \text{OR} \\ &= \frac{\sum_i^{\text{all non-metal S species}} \varepsilon_i M_i}{\sum_i^{\text{all S species}} M_i} \end{aligned} \quad (25)$$

where the definitions are the same as in Eq. (22).

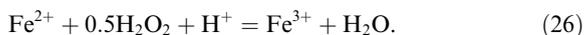
In Fig. 9, the average number of equivalents of Acidity per mole due to H⁺ is always unity and appears as a

dashed horizontal line. Similarly, if Fe³⁺ is used as in Eq. (9), the average equivalents of Acidity per mole due to Fe³⁺ is always +3 and appears as a dashed horizontal line. However, if Fe^{III} is speciated into the OH and SO₄ complexes shown in Table 2, the average equivalents of Acidity per mole due to Fe^{III} decreases from +3 to +1.5 at pH values between 2 and 3.5 (the approximate solubility limit). This decrease occurs because of the increases in Fe^{III}-OH complexes relative to Fe³⁺ with increasing pH. Thus, Eq. (9) overestimates the contribution of Fe^{III} to Acidity. However, because Eq. (9) does not include SO₄ species, it underestimates Fe^{III}-SO₄ and HSO₄⁻ Acidity. Fig. 9b shows similar behavior for an Al/SO₄ solution. Because these two effects tend to cancel each other out, Eq. (9) gives a reasonable estimate of non-H⁺ Acidity. There is some concern that HSO₄⁻ Acidity could be underestimated by Eq. (9) in “real world” solutions because SO₄ species may be much more predominant in real solutions that are much more complex mixtures compared with synthetic solutions in

which Fe or Al and SO_4 are in equivalence. However, the data in Fig. 8 suggest that this concern is unwarranted up to $\approx 15,000 \text{ mg L}^{-1}$ Acidity as CaCO_3 .

4.5. Contribution of Fe^{III} and Mn^{II} species to Acidity

The choice of the principal component for determining the Acidity contribution of Fe^{II} species is complicated by the oxidation step in the standard method Hot Acidity titration. Examining Fe^{II} speciation in Fig. 3, one might initially conclude that Fe^{2+} is the principal component in a titration with a pH 8.3 endpoint and would therefore contribute zero equivalents of Acidity per mole. However, the standard method titration is always conducted by adding H_2O_2 to oxidize any Fe^{II} present to Fe^{III} as shown in Eq. (26):



The Fe^{III} then contributes Acidity as illustrated in Figs. 2 and 5. However, the oxidation of Fe^{2+} to Fe^{3+} consumes one equivalent of H^+ , thus each Fe^{2+} contributes only 2 equiv. of Acidity per mole overall (consistent with its coefficient of 2 in Eqs. (9) and (11)). Similarly, FeOH^+ contributes 1 equivalent acidity per mole overall. Similar arguments can be made for Acidity due to Mn^{2+} or for other metals that undergo oxidation during titration.

4.6. 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 ($\approx \text{pH } 4.5$ for Alkalinity; $\text{pH } 8.3$ for Acidity), and this fact could result in a definition of net alkalinity that does not have a unique solution for net alkalinity = zero. These derivations are shown for the $\text{H}_2\text{O}-\text{CO}_2$ system, but the concepts can be extended to metal-laden water typical of mine drainage.

One way to check the validity of a complicated 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 has a unique solution (Schweinsberg, A, pers. comm., 2004) We also solved for a unique solution iteratively using a spreadsheet, which is an equivalent approach.

The standard theoretical definitions for Alkalinity (Eq. (8); $\text{pH } 4.5$) and Acidity (Eq. (4); $\text{pH } 8.3$) consider both positive and negative contributions to Alkalinity and Acidity and are repeated here for reference:

$$\text{Alkalinity} = -[\text{H}^+] + [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (27)$$

and

$$\text{Acidity} = [\text{H}^+] + [\text{H}_2\text{CO}_3^*] - [\text{OH}^-] - [\text{CO}_3^{2-}] \quad (28)$$

Subtracting Acidity from Alkalinity and setting this value to zero gives

$$\begin{aligned} \text{Net Alkalinity} = g(x) &= 0 \\ &\Rightarrow 2[\text{OH}^-] + [\text{HCO}_3^-] + 3[\text{CO}_3^{2-}] \\ &= 2[\text{H}^+] + [\text{H}_2\text{CO}_3^*]. \end{aligned} \quad (29)$$

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

$$\begin{aligned} g(x) &\approx [\text{H}^+] \\ &\approx \frac{K_w}{a_{\text{H}^+}} + \frac{1}{2} \frac{K_1 C_T \left(1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_1 K_2}{a_{\text{H}^+}^2}\right)}{a_{\text{H}^+}} \\ &\quad + \frac{3}{2} \frac{K_1 K_2 C_T \left(1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_1 K_2}{a_{\text{H}^+}^2}\right)}{a_{\text{H}^+}^2} \\ &\quad - \frac{1}{2} C_T \left(1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_1 K_2}{a_{\text{H}^+}^2}\right) \end{aligned} \quad (30)$$

where a is activity, 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; a plot of $g(x)$ is shown in Fig. 10. Eq. (30) as shown is not an equality, but a close approximation because concentrations rather than activities are used; the validity of this approximation was confirmed by PHREEQC modeling as discussed below.

Derivations for two other potential definitions of net alkalinity were similarly checked for mathematical validity. The second potential definition for net alkalinity considered only positive (+) contributions to Alkalinity and Acidity because measured Alkalinity returns only positive values and because Eq. (9) considers only positive contributions to Acidity. The third potential definition used a single endpoint of $\text{pH } 5.65$ (pH of a pure CO_2 solution; $[\text{H}_2\text{CO}_3^*] = [\text{HSO}_3^-]$). Although both of these alternative definitions proved mathematically valid, producing unique values for net alkalinity = zero, there are conceptual and practical obstacles to their use, and these derivations are not shown or considered further.

The function $f(x) = x$ (or $[\text{H}^+] = [\text{H}^+]$) gives a straight line with a slope of unity; this slope is not obvious in Fig. 10 due to unavoidable awkward scaling. The curve for the net alkalinity = zero function, $g(x)$, monotonically decreases and intersects the line for $f(x) = x$ at a single point, proving that $g(x)$ has a unique solution. Therefore, the definition of net alkalinity given in Eq. (29) makes mathematical sense.

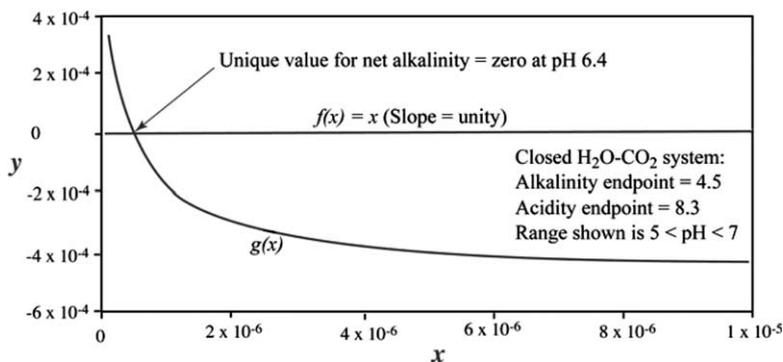


Fig. 10. Plot illustrating that a unique value for net Alkalinity = calculated Alkalinity – calculated Acidity = zero exists for an open H₂O–CO₂ system considering positive and negative contributions to Alkalinity and Acidity, confirming that net alkalinity is mathematically reasonable.

The pH defining net alkalinity = zero for this function is approximately 6.37 based on Eq. (29). For brevity, the above discussion does not include the contribution of metals to Alkalinity or Acidity. These contributions could be included, but once a mine water has been treated or has undergone reactions (oxidation, hydrolysis, precipitation) such that it can be released harmlessly to the environment, metal contributions to either Alkalinity or Acidity will be vanishingly small. The pH for Alkalinity (PHREEQC-calculated) – non-CO₂ Acidity (Eq. (23); PHREEQC speciation) = zero was found to be 6.4 in modeled titrations of a field sample and of synthetic samples. Thus, even in more complex solutions containing metals, net alkalinity = zero occurs at pH 6.4 for samples that have been allowed to react to reach equilibrium.

4.7. Establishing a formal definition of net alkalinity

The above discussion confirms that net alkalinity is a rigorous theoretical mathematical construction. However, the use of the term net alkalinity arose because of the need for a means to determine how much alkaline material should be added to a water to remove metals and produce water ready to be released into a receiving stream. A practical choice must be made as to what definition is most meaningful for the water quality practitioner. It is argued that a nearly metal-free water with pH ≥ 6.3 is desired. Treated water must be nearly metal-free, with metal concentrations below appropriate effluent concentration limits, in order to avoid negative impact on aquatic life or human health. The stipulation that pH must be greater than or equal to 6.3 requires explanation using the buffer capacity of water.

The buffer capacity (Langmuir, 1997) or the equivalent buffer intensity (Stumm and Morgan, 1996), a measure of the resistance of a solution to changes in pH (Δ concentration base/ Δ pH), is illustrated in Fig. 11 for water and applicable aqueous species. Buffer capacities

(β) for H₂O and H₂O/CO₂ were calculated as in Langmuir (1997). The buffer capacity for a solution initially containing 10^{-3} mol L⁻¹ CO₂, Fe^{III}, and Al (balanced by SO₄) was derived from the Δ concentration base/ Δ pH in a PHREEQC Acidity titration simulation which allowed precipitation and dissolution of amorphous Fe(OH)₃ and Al(OH)₃ solids. The dotted curve shows buffering by water alone. The heavy dashed curve shows buffering by water and CO₂, with a maximum β at pH 6.3 (=pK₁ for carbonic acid). The solid curve shows buffering by water, CO₂, Fe^{III}, and Al.

In Fig. 11, the H₂O/CO₂/Fe^{III}/Al/SO₄ system represents the pre-treatment buffer capacity of an example low-pH mine drainage water. Below pH 3, most of the total buffer capacity is due to water alone. Above pH 3, buffering increases due to Fe^{III} hydrolysis and precipitation until Fe^{III} is exhausted, then buffering decreases. At pH ≈ 5 , buffering increases due to Al hydrolysis and precipitation until Al is exhausted, then buffering decreases. Above pH 7, buffering increases due to Al solid dissolution until all Al reenters the solution due to the amphoteric nature of Al hydrolysis. Above pH 9, buffering is due to water and CO₂, with water predominant above pH 10. Changing CO₂ or metal concentrations would change the buffer capacities, but the shapes of the curves in Fig. 11 would remain the same.

The CO₂/H₂O curve in Fig. 11 gives the total buffer capacity of a post-treatment water 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). After metals are removed, water with pH < 6.3 is net acidic, and water with pH > 6.3 is net alkaline.

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

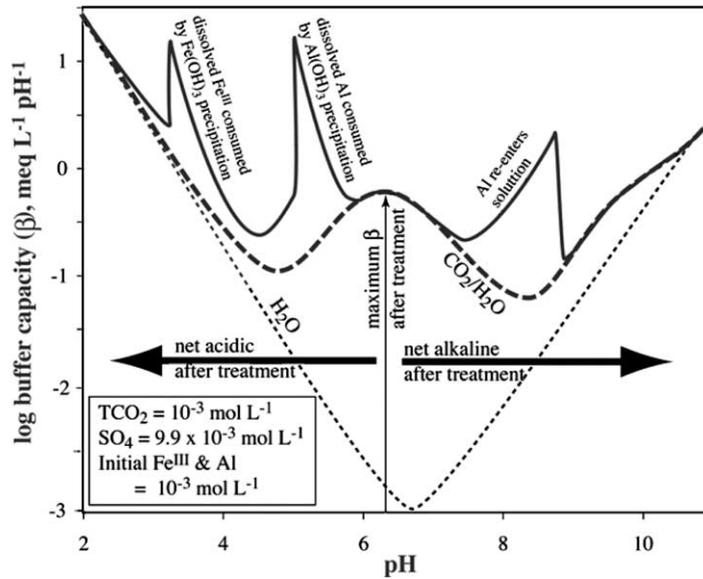


Fig. 11. A plot of buffer capacity, β , versus pH for the H_2O , $\text{CO}_2/\text{H}_2\text{O}$, and $\text{Fe}^{\text{III}}/\text{Al}/\text{SO}_4/\text{CO}_2/\text{H}_2\text{O}$ systems. Fe and Al concentrations contribute to β and change due to precipitation and dissolution. Maximum β after treatment ($\text{CO}_2/\text{H}_2\text{O}$ system) $\approx \text{pH} = \text{p}K_1$, carbonic acid ≈ 6.3 .

$$\text{Net alkalinity} = \text{Alkalinity (from PHREEQC)} \\ - \text{non-}\text{CO}_2 \text{ Acidity (Eq. (23))} \quad (31)$$

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 that do not contain dissolved metals. Pre-treatment waters that are net alkaline would have $[\text{HCO}_3^-] > [\text{H}_2\text{CO}_3^*] + [\text{H}^+] + \text{metals} + \text{sulfur} + \text{acid complexes}$. Waters that are net acidic would have $[\text{H}_2\text{CO}_3^*] + [\text{H}^+] + \text{metals} + \text{sulfur} + \text{acid complexes} > [\text{HSO}_3^-]$ and pH values < 6.37 after hydrolysis and precipitation of metals.

One may also calculate:

$$\text{Net alkalinity} = (\text{Alkalinity}_{\text{Std. Meth.}} \\ - \text{non-}\text{CO}_2 \text{ Acidity}_{\text{computed, Eq. (23)}}) \quad (32)$$

Alternatively, one may use Eq. (10) ($\text{Alkalinity}_{\text{Std. Meth.}} - \text{acidity}_{\text{computed, Eqn. (9)}}$) or Eq. (11) to calculate net acidity. Kirby and Cravotta (2005) show that Eqs. (9) and (23) return similar results for computed acidity, even though Eq. (9) does not account for speciation rigorously. Hence, Eqs. (10), (11), (31), and (32) all can be useful to give the net alkalinity of mine drainage and as a quality control check (Hedin, 2004) on Hot Acidity titrations. However, Kirby and Cravotta (2005) also found that net alkalinity calculated in these ways *does not* return the same negative value of a Standard Method Hot Acidity titration (APHA, 1998) for solutions with high alkalinities that are satu-

rated with respect to calcite and allowed to degas CO_2 ; Hot Acidity of these samples exceeded calculated net acidity due to consumption of Alkalinity during calcite precipitation. For this reason, the authors recommend that net alkalinities be obtained by:

$$\text{Net alkalinity} = -\text{Hot Acidity}, \quad (33)$$

where “Hot Acidity” is the 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 Hot 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 Hot 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. Eq. (33) provides consistent and easily interpretable net alkalinity for use in mine drainage treatment.

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