

## Net alkalinity and net acidity 2: Practical considerations

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### Abstract

The pH, alkalinity, and acidity of mine drainage and associated waters can be misinterpreted because of the chemical instability of samples and possible misunderstandings of standard analytical method results. Synthetic and field samples of mine drainage having various initial pH values and concentrations of dissolved metals and alkalinity were titrated by several methods, and the results were compared to alkalinity and acidity calculated based on dissolved solutes. The pH, alkalinity, and acidity were compared between fresh, unoxidized and aged, oxidized samples.

Data for Pennsylvania coal mine drainage indicates that the pH of fresh samples was predominantly acidic (pH 2.5–4) or near neutral (pH 6–7);  $\approx 25\%$  of the samples had pH values between 5 and 6. Following oxidation, no samples had pH values between 5 and 6.

The Standard Method Alkalinity titration is constrained to yield values  $>0$ . Most calculated and measured alkalinities for samples with positive alkalinities were in close agreement. However, for low-pH samples, the calculated alkalinity can be negative due to negative contributions by dissolved metals that may oxidize and hydrolyze.

The Standard Method hot peroxide treatment titration for acidity determination (Hot Acidity) accurately indicates the potential for pH to decrease to acidic values after complete degassing of  $\text{CO}_2$  and oxidation of Fe and Mn, and it indicates either the excess alkalinity or that required for neutralization of the sample. The Hot Acidity directly measures net acidity ( $= -\text{net alkalinity}$ ). Samples that had near-neutral pH after oxidation had negative Hot Acidity; samples that had  $\text{pH} < 6.3$  after oxidation had positive Hot Acidity. Samples with similar pH values before oxidation had dissimilar Hot Acidities due to variations in their alkalinities and dissolved Fe, Mn, and Al concentrations. Hot Acidity was approximately equal to net acidity calculated based on initial pH and dissolved concentrations of Fe, Mn, and Al minus the initial alkalinity. Acidity calculated from the pH and dissolved metals concentrations, assuming equivalents of 2 per mole of Fe and Mn and 3 per mole of Al, was equivalent to that calculated based on complete aqueous speciation of  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ . Despite changes in the pH, alkalinity, and metals concentrations, the Hot Acidities were comparable for fresh and most aged samples.

A meaningful “net” acidity can be determined from a measured Hot Acidity or by calculation from the pH, alkalinity, and dissolved metals concentrations. The use of net alkalinity  $= (\text{Alkalinity}_{\text{measured}} - \text{Hot Acidity}_{\text{measured}})$  to design mine drainage treatment can lead to systems with insufficient Alkalinity to neutralize metal and  $\text{H}^+$  acidity and is not recommended. The use of net alkalinity  $= -\text{Hot Acidity}$  titration is recommended for the planning of mine

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drainage treatment. The use of net alkalinity = (Alkalinity<sub>measured</sub> – Acidity<sub>calculated</sub>) is recommended with some cautions.

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## 1. Introduction

Acidic or abandoned mine drainage (AMD) affects the quality and potential uses of water supplies in coal and metal mining regions worldwide (Herlihy et al., 1990; Nordstrom, 2000). Although commonly referred to as “acid mine drainage,” AMD ranges widely in quality from alkaline (pH  $\approx$  10) to strongly acidic (pH  $\approx$  –3) and corrosive, with dissolved solids ranging from about 100 to 100,000 mg L<sup>–1</sup> (Hyman and Watzlaf, 1997; Rose and Cravotta, 1998; Nordstrom et al., 2000). AMD characteristically has elevated concentrations of dissolved SO<sub>4</sub>, Fe, and other metals. Dissolved metals and other constituents in AMD can be toxic to aquatic organisms and ultimately can precipitate forming ochreous encrustations that degrade the aquatic habitat (Winland et al., 1991; Bigham and Nordstrom, 2000).

The pH and concentrations and loadings of alkalinity, acidity, and metals such as Fe, Al, and Mn in mine effluent and receiving water bodies commonly are measured to identify potential for environmental effects (Commonwealth of Pennsylvania, 1998a,b, 2002; USEPA, 2000, 2002a,b). These parameters are used to identify appropriate treatment methods to remove the metals and maintain neutral pH (Hedin et al., 1994; Skousen et al., 1998). The pH of AMD is an important measure for evaluating chemical equilibrium, corrosiveness, and aquatic toxicity. The severity of toxicity or corrosion tends to be greater under low-pH conditions than under near-neutral conditions. For example, Al-bearing minerals are soluble at low pH, and relatively low concentrations of dissolved Al can be toxic (Elder, 1988). USEPA (2000, 2002a,b) recommends pH 6.5–8.5 for public drinking supplies and pH 6.5–9.0 for protection of freshwater aquatic life. Commonwealth of Pennsylvania (1998a,b, 2002) stipulates that effluent from active mines must have pH 6.0–9.0 and alkalinity > acidity.

Most geochemistry and environmental chemistry texts discuss only low pH, metal-laden mine water (e.g., Drever, 1997; Langmuir, 1997; Stumm and Morgan, 1996; Morel and Hering, 1993). However, near-neutral pH, metal-laden mine water that possesses considerable alkalinity and measurable acidity can be important because the pH can increase or decrease upon equilibration with the atmosphere (e.g., Cravotta et al., 1999). This latter type of water presents analytical and conceptual difficulties because of the instability of its pH, acidity, alkalinity, and CO<sub>2</sub> and metal concentrations.

The appropriateness of a particular treatment method for AMD depends on the flow rate, alkalinity and

acidity balance, and the available resources for construction and maintenance (Hedin et al., 1994; Skousen et al., 1998). The “net alkalinity” and “net acidity” are commonly calculated to determine whether a particular mine water requires the addition of alkalinity for treatment. The definition most commonly cited is

$$\text{net alkalinity} - \text{net acidity} = \text{alkalinity} - \text{acidity}, \quad (1)$$

without specifying whether the input values are based on measurement or on calculation. Similarly, net acidity is commonly defined as

$$\text{net acidity} = \text{acidity} - \text{alkalinity}. \quad (2)$$

Several flow diagrams for decision-making in the planning of mine drainage treatment employ net alkalinity as a critical decision parameter (e.g., Watzlaf et al., 2004; Hedin et al., 1994; Skousen et al., 1998, 2000; Bigatel et al., 1998). If treatment effluent is “net alkaline,” the alkalinity exceeds the acidity, and the pH will remain near neutral after complete degassing and oxidation of the effluent. Treatment systems that facilitate aeration of the effluent and retention of precipitated solids are indicated. If instead the effluent is “net acidic,” the acidity exceeds the alkalinity, and the pH will decline to acidic values after oxidation and precipitation of the dissolved metals. Systems that add alkalinity to maintain or increase pH are indicated.

Although the alkalinity and acidity balance is critical for selecting appropriate treatment alternatives or for predicting the outcome if mixing acidic and alkaline solutions, different methods of analysis and reporting of acidity are practiced (Ott, 1988; Fishman and Friedman, 1989; USEPA, 1983a; APHA, 1998a). Criteria for determination of net acidic or net alkaline solutions are poorly defined by regulatory authorities and misapplied by many practitioners. In many cases, the net acidity of AMD is calculated by subtracting the alkalinity from the measured “hot” acidity (APHA, 1998a), and vice versa for net alkalinity (e.g., Brady et al., 1990, 1994; Hedin et al., 1994; Skousen et al., 1998; Commonwealth of Pennsylvania, 1998a,b). Kirby (2002) showed that subtracting measured Hot Acidity from alkalinity can underestimate the alkalinity requirement and result in incorrect identification of treatment alternatives and/or inadequate treatment. Net alkalinity and net acidity only recently were rigorously defined in the literature (Kirby and Cravotta, 2005).

This study focuses on problems associated with the measurement of acidity in waters that also contain alkalinity, providing a brief review of standard titration prac-

tices. Using commonly measured water-quality data, this contribution examines (1) the measurement of alkalinity and acidity in synthetic and field mine drainage solutions, (2) the calculation of acidity based on metal and  $H^+$  concentrations ( $\pm$  aqueous speciation), and (3) the calculation and interpretation of “net acidity” or “net alkalinity.” Field and laboratory data for a wide variety of AMD sources in the Anthracite and Bituminous Coalfields of Pennsylvania are used to show relationships among the pH, alkalinity, acidity, and dissolved solute concentrations and to develop guidelines for their measurement and interpretation. This contribution complements a companion paper by Kirby and Cravotta (2005) that gives background information on the geochemistry of AMD and explains the theoretical basis for the measurement and interpretation of acidity and alkalinity.

One hypothesis tested by the present work is that the use of the calculation

$$\text{net alkalinity} = \text{alkalinity}_{\text{measured}} - \text{acidity}_{\text{measured}}, \quad (3)$$

can result in insufficient treatment of near-neutral pH, metal-laden mine water that possesses considerable alkalinity because net alkalinity values (Eq. (3)) for such waters are too high, and insufficient alkaline addition may be elected in the treatment design.

A second hypothesis is that the standard methods (APHA, 1998a; ASTM, 2000; USEPA, 1983a) for the determination of acidity in metal-laden water (“hot” acidity titrations) provide consistent results but underestimate the amount of non- $CO_2$  (i.e., metal, metal-complex, and  $H^+$ ) acidity in near-neutral pH, metal-laden mine water that possesses measurable alkalinity. The primary metals examined in this study are Fe, Al, and Mn, but the concepts presented herein apply to waters with other species that contribute acidity.

We argue that the correct interpretation of Hot Acidity data is critical for solutions containing both alkalinity and acidity and that Hot Acidity results should be interpreted as “net acidity”. We suggest a change in the text of the standard method “hot” acidity titrations and propose two practical definitions for net alkalinity and net acidity.

## 2. Background

### 2.1. Mine drainage without and with positive alkalinity

Kirby and Cravotta (2005) discuss the concept of and sources of positive (+) and negative (–) contributions to alkalinity and acidity in mine drainage in detail. Consistent with that paper, symbols for the total dissolved analytical concentration of chemical constituents are indicated herein without valence (e.g., Fe and  $SO_4$ ). Symbols with superscripted Roman numerals indicate the sum of aqueous species with a specific redox state, e.g.,  $Fe^{II}$ ,  $Fe^{III}$ , and  $Mn^{II}$ , and symbols with a charge (e.g.,  $Fe^{2+}$ ) re-

fer to a specific aqueous species. Dissolved metals, metal complexes,  $HSO_4^-$ ,  $H^+$ , and  $H_2CO_3^*$  ( $= H_2CO_3^0 +$  dissolved  $CO_2$ ) contribute positively to acidity. If dissolved oxygen (DO) is abundant, allowing iron oxidation and hydrolysis to go to completion, and there is no geological source of alkalinity, the resulting sulfuric acid solution is  $Fe^{III}$ -rich ( $\pm$  other metals) and has  $pH \leq 3.5$  (Cravotta et al., 1999). Such mine drainage typically has measurable DO, measurable positive “hot” acidity, and no positive alkalinity (measurable by standard methods). Such a solution would have a negative alkalinity as calculated by PHREEQC (Parkhurst and Appelo, 1999).

Near-neutral AMD with positive alkalinity can form from rock that contains little pyrite or can originate as acidic AMD that has been neutralized (Cravotta et al., 1999). Kirby and Cravotta (2005) discuss alkalinity sources and demonstrate that practically all of the positive alkalinity in near-neutral AMD is contributed by  $HCO_3^-$ ; negative contributions from metals are negligible. As the pH of initially acidic AMD increases to near-neutral values, concentrations of dissolved  $Fe^{III}$ , Al, and other metals can decline as  $Fe^{III}$  and Al hydroxides precipitate; concentrations of  $SO_4$ ,  $Fe^{II}$ , and  $Mn^{II}$  usually will not be controlled by the precipitation of hydroxides (Cravotta and Trahan, 1999; Cravotta et al., 1999). Under  $SO_4$ -reducing conditions, the formation of sulfide and carbonate minerals can limit concentrations of  $SO_4$ ,  $Fe^{II}$ , and  $Mn^{II}$  (Drever, 1997; Langmuir, 1997).

Water from continuously flooded coal mines commonly is anoxic or suboxic, has high  $Fe^{II}$  concentrations ( $\pm$  other metals), high  $CO_2$  concentrations, pH from 5.5 to 7, and measurable positive alkalinity (Rose and Cravotta, 1998; Cravotta et al., 1999). DO can be depleted due to chemical ( $Fe^{II}$  oxidation) and bacterial oxygen demand.  $Fe^{II}$  is predominant over  $Fe^{III}$  due to low concentrations of DO, incomplete pyrite oxidation, or dissimilatory  $Fe^{III}$  hydroxide reduction (Lovley, 1991; Chapelle et al., 1995; Rose and Cravotta, 1998). Alkalinity, high  $CO_2$ , and near-neutral pH may be explained by the presence of carbonate rocks and/or bacterial sulfate reduction. Although Fe concentrations are commonly lower than in low-pH mine waters, such mine water is common in flooded underground bituminous and anthracite coal mine waters in Pennsylvania, and such discharges can have very high volumetric flow rates ( $>0.5 \text{ m}^3/\text{s}$  or 8500 gal/min; Cravotta and Kirby, 2004a), imparting high metal and acidity loading to surface waters.

### 2.2. Instability of pH in initially near-neutral mine water

Wood (1976), Wood (1996), and our data (Section 4.1) indicate that the pH and alkalinity of AMD can be unstable. The pH, alkalinity, and associated properties can change as the sample equilibrates to atmospheric

conditions because of the degassing of dissolved carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S), dissolution of O<sub>2</sub>, oxidation of Fe<sup>II</sup> and Mn<sup>II</sup>, and hydrolysis of Fe<sup>III</sup> and Mn<sup>IV</sup>. Sample instability results because the chemical reactions that establish equilibrium among the gaseous, aqueous, and solid phases in a system proceed at different rates. For example, aeration of AMD can rapidly saturate AMD with O<sub>2</sub> and promote the degassing of CO<sub>2</sub> and H<sub>2</sub>S. Although, the pH ultimately may decrease to acidic values because of the oxidation of Fe<sup>II</sup> and the consequent precipitation of Fe(OH)<sub>3</sub>, initially, the Fe<sup>II</sup> may persist in solution as dissolved CO<sub>2</sub> degasses and pH increases:



where  $[\text{H}_2\text{CO}_3^*] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3^0]$  (Stumm and Morgan, 1996). Ground water and coal-mine drainage commonly contain elevated concentrations of dissolved CO<sub>2</sub> in association with elevated partial pressures of gaseous CO<sub>2</sub> ( $P_{\text{CO}_2}$ ) of  $10^{-1.5}$ – $10^{-0.5}$  atm in the vadose zone and/or underlying saturated zone (Cravotta et al., 1994; Langmuir, 1997; Rose and Cravotta, 1998). After the AMD emerges or has been sampled, the CO<sub>2</sub> eventually will degas until concentrations of dissolved CO<sub>2</sub> equilibrate with atmospheric  $P_{\text{CO}_2}$  of  $10^{-3.5}$  atm. The degassing of CO<sub>2</sub> from AMD (Eqs. (4) and (5)) can be accelerated by aggressive aeration (Jageman et al., 1988) or heating of the solution (Langmuir, 1997; ASTM, 2000). If solids are not dissolved or precipitated as CO<sub>2</sub> degasses, acidity due to H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> will decrease and pH will increase while the alkalinity is conserved (Eqs. (4) and (5)). The increased pH could result in saturation with and precipitation of CaCO<sub>3</sub> (calcite or aragonite). The precipitation of Fe(OH)<sub>3</sub> and other solids, including CaCO<sub>3</sub>, along flowpaths or while samples are in storage will consume some of the alkalinity in solution.

The potential for consumption of alkalinity, or the release of H<sup>+</sup> as a product of oxidation, hydrolysis, and precipitation processes, can be measured or computed as the “acidity” of a solution. The acidity of near-neutral AMD results mainly from the potential for hydrolysis of dissolved Fe<sup>II</sup>, Fe<sup>III</sup>, Al, and Mn<sup>II</sup> and the precipitation of associated solid hydroxide compounds. Except for low-pH solutions, dissolved Fe in AMD is predominantly Fe<sup>II</sup> (Rose and Cravotta, 1998; Nordstrom and Alpers, 1999; Yu et al., 1999). Because dissolved CO<sub>2</sub> tends to be degassed by aeration of water under atmospheric conditions, its acidity contribution is temporary and is not counted by methods used to measure or compute the acidity of AMD (Rose and Cravotta, 1998; Kirby and Cravotta, 2005). If a sample has acidity in excess of alkalinity (net acidic), the pH ultimately will decline to pH < 4.5. For example, Cravotta and Kirby (2004a) documented a drop in pH from 5.9–6.4 to 4.0 along a 32 km flowpath in Shamokin Creek near

Shamokin, Pennsylvania despite dilution by “clean” tributaries that doubled the flow rate. They attributed the decline in pH to the oxidation and hydrolysis of dissolved Fe<sup>II</sup> and a deficiency of alkalinity necessary to buffer the acid generated by this process.

The rate of dissolved Fe<sup>II</sup> oxidation can be slow under environmental conditions, depending on the temperature, pH, concentrations of dissolved O<sub>2</sub> and Fe<sup>II</sup>, and activities of biological and/or abiological catalysts (Nordstrom, 1985; Stumm and Morgan, 1996; Kirby et al., 1999). Although dissolved CO<sub>2</sub> may equilibrate with the atmosphere and Fe<sup>II</sup> can be oxidized in a time-frame of minutes to days, transformations of initially formed solids to more stable phases, such as the conversion of ferrihydrite or schwertmannite to goethite (Miller, 1980; Bigham et al., 1996), can require months or years. These kinetic factors are minimized with the standard “hot peroxide treatment” acidity method outlined in Section 2.4 (USEPA, 1983a; APHA, 1998a; ASTM, 2000).

### 2.3. Summary of theoretical definitions for alkalinity and acidity

For the CO<sub>2</sub>–H<sub>2</sub>O system, alkalinity (endpoint ≈ pH 4.5) is defined by Stumm and Morgan (1996) as

$$\text{alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]. \quad (6)$$

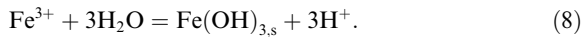
Kirby and Cravotta (2005) discuss other definitions but show that Eq. (6) is appropriate for AMD and that HCO<sub>3</sub><sup>-</sup> is responsible for essentially all positive alkalinity in AMD. Hereinafter, we refer to Alkalinity with an endpoint of pH ≈ 4.5 using an initial uppercase letter consistent (Kirby and Cravotta, 2005). Although other species (Stumm and Morgan, 1996) can contribute both positively and negatively to Alkalinity, these contributions are negligible in a titration (Kirby and Cravotta, 2005). If a solution has measurable Alkalinity, the negative contribution from H<sup>+</sup> to Alkalinity is negligible.

For the CO<sub>2</sub>–H<sub>2</sub>O system, “CO<sub>2</sub>-acidity” (endpoint = pH 8.3) is defined by Stumm and Morgan (1996) as

$$\text{CO}_2\text{-acidity} = [\text{H}_2\text{CO}_3^*] + [\text{H}^+] - [\text{CO}_3^{2-}] - [\text{OH}^-]. \quad (7)$$

Hereinafter, we refer to “CO<sub>2</sub>-acidity” as simply “Acidity” with an initial uppercase letter. Eq. (7) must be modified to incorporate the Acidity due to metal hydrolysis that occurs in mine water and associated ground or surface waters (Kirby and Cravotta, 2005). We also refer to the Standard Method Acidity titration (APHA, 1998a) that utilizes hydrogen peroxide and boiling/cooling steps as “Hot Acidity” (see Section 4.2 for details).

Metal hydrolysis can release H<sup>+</sup> to solution (Eq. (8)), and thus metals can be thought of as “potential H<sup>+</sup> Acidity” in mine water



Definitions of acidity for mine drainage in several texts (e.g., Drever, 1997; Langmuir, 1997) focus on *acid* mine drainage, which lacks measurable positive Alkalinity.

Hedin et al. (1994) and Watzlaf et al. (2004) give a widely cited definition of calculated Acidity in units of  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$

$$\begin{aligned} \text{Acidity}_{\text{calculated}} = & 50[(2\text{Fe}^{2+}/56) + (3\text{Fe}^{3+}/56) \\ & + (3\text{Al}/27) + 2\text{Mn}/55 \\ & + 1000(10^{-\text{pH}})], \end{aligned} \quad (9)$$

where metal concentrations are in  $\text{mg L}^{-1}$ ;  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in Eq. (9) actually refer to  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ , respectively. Eq. (9) includes only positive, non- $\text{CO}_2$  contributions to Acidity. Data from Hedin (2004) and Watzlaf et al. (2004), which is reproduced in Kirby and Cravotta (2005), found good agreement between measured Hot Acidity and calculated Acidity in large datasets with Acidities up to  $15000 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$  and with pH ranging from 1.6 to 8.5.

Kirby and Cravotta (2005) provide background on the theoretical definitions of several types of alkalinity and acidity, including the positive and negative contributions to each parameter. They consider metal hydrolysis and corresponding differences in the  $\text{OH}^-$  neutralizing capacities for all aqueous species in the PHREEQC (Parkhurst and Appelo, 1999) and WATEQ4F (Ball and Nordstrom, 1991) databases. They provide a rigorous theoretical definition of non- $\text{CO}_2$  Acidity that is applicable to mine drainage and is based on principal components and the proton condition:

$$\text{non-}\text{CO}_2 \text{ Acidity}_{\text{calculated, eq}} \text{ L}^{-1} = \sum_i^{\substack{\text{all species} \\ \text{less CO}_2}} \varepsilon_i M_i, \quad (10)$$

where  $\varepsilon_i$  is the number of equivalents per mole of the  $i$ th species that contributes either positive or negative Acidity, and  $M_i$  is the concentration in  $\text{mol L}^{-1}$  of the  $i$ th species. This approach is data intensive, requiring more solution chemistry information than is commonly available to the field practitioner. Although more theoretically satisfying, Eq. (10) does not increase the accuracy of an Acidity estimate over Eq. (9) above for samples in this study. Where Eq. (10) is used in this study, it is referred to as “complete aqueous speciation less  $\text{CO}_2$  contributions”.

#### 2.4. Titration methods for the measurement of alkalinity and acidity

Stumm and Morgan (1996) define alkalinity as the “equivalent sum of the bases that are titratable with strong acid” and acidity as the “equivalent sum of the acids that are titratable with strong base.” The authors define the titrations in terms of the  $\text{H}_2\text{O}$ – $\text{CO}_2$  system.

Equivalence points occur at pH values  $\approx 4.5$ , 8.3, and  $\approx 11$ , and these points correspond to pH values at which  $[\text{H}^+] \approx [\text{HCO}_3^-]$ ,  $[\text{H}_2\text{CO}_3^*] \approx [\text{CO}_3^{2-}]$ , and  $[\text{HCO}_3^-] \approx [\text{OH}^-]$ , respectively. Titration endpoints are ideally equal to these equivalence points. In practice, the pH 4.5 and 11 endpoints are only approximately equal to equivalence points because of changing solution  $\text{CO}_2$  concentrations and due to the presence of weak acids and bases with equilibrium constant (pK) values near equivalence points. Although theoretical Alkalinity definitions can be negative, Alkalinity titrations do not usually return negative values (Gran titrations can return small negative Alkalinity; see Stumm and Morgan, 1996).

Standard references for Alkalinity and Acidity measurements (USEPA, 1983b,a; ASTM, 2000; APHA, 1998b; APHA, 1998a) essentially agree on the major steps in laboratory protocols (Table 1). Adding  $\text{H}_2\text{O}_2$  before the Hot Acidity titration causes oxidation of metals.  $\text{H}_2\text{SO}_4$  addition aids in  $\text{CO}_2$  degassing. Boiling speeds reaction rates for oxidation and degassing. Samples must be cooled to room temperature before the addition of a base during titration to avoid interference from Mg (Payne and Yeates, 1970). Dramatic differences in Acidity titration results may be observed depending on titration methods (Payne and Yeates, 1970; Ott, 1988; Wood, 1996; Cravotta and Kirby, 2004a).

In Hot Acidity titrations for samples with hydrolyzable metals, unlike samples without hydrolyzable metals,  $\text{CO}_2$  is intentionally degassed, therefore the contribution of  $\text{CO}_2$  to positive Acidity is intentionally not counted. Not counting Acidity due to  $\text{CO}_2$  is appropriate when considering environmental effects of mine drainage and various methods of passive mine drainage treatment (see Section 4.2 and (Kirby and Cravotta, 2005)).

A small but important change was made in the Hot Acidity procedure between the 19th and 20th editions of *Standard Methods for the Examination of Water and Wastewater* (APHA, 1995; APHA, 1998a). The 19th edition reads, “If a negative value is obtained, determine the alkalinity according to Section 2320.” The 20th edition reads “If a negative value is obtained, report the value as negative. The absolute value of this negative value should be equivalent to the net alkalinity.” Net alkalinity is not specifically defined in the text. Other standard Acidity methods (ASTM, 2000; USEPA, 1983a) do not specify what should occur if a negative Acidity is obtained.

Watzlaf et al. (2004) state that many laboratories have not discovered the change between the 19th and 20th editions of *Standard Methods*. A commercial laboratory, using EPA Method 305.1 (USEPA, 1983a) for Acidity, reports negative values as  $< 1 \text{ mg/L}$  (Wilson, H., pers. commun., 2003). The state laboratory for the Pennsylvania Department of Environmental Protection reports negative values from EPA Method 305.1 for Hot Acidity as zero, and samples with  $\text{pH} > 6.5$  are

Table 1  
Major steps in standard method Alkalinity (A) and Hot Acidity (B) titrations

Step	If initial pH	
<b>(A)</b>		
1	≤4.5	Record Alkalinity equal to zero, or
2	>4.5	Titrate quickly with H <sub>2</sub> SO <sub>4</sub> solution to pH 4.5 (the exact endpoint varies depending on Alkalinity range). Use “low Alkalinity” method (a “Gran” titration approach) as necessary
Alkalinity as mg L <sup>-1</sup> CaCO <sub>3</sub> is calculated as $(A \cdot N \cdot 50,000)/\text{mL sample}$ , where $A$ = mL H <sub>2</sub> SO <sub>4</sub> titrant used, $N$ = normality of H <sub>2</sub> SO <sub>4</sub> titrant		
<b>(B)</b>		
1	≥4.5 (4.0; ASTM, 2000)	Titrate with H <sub>2</sub> SO <sub>4</sub> solution to pH ≤ 4; add five drops of 30% H <sub>2</sub> O <sub>2</sub> solution, boil for two to 5 min, cool to room temperature, and titrate with NaOH solution quickly to pH 8.3 (or 8.2; USEPA, 1983a), or
2	<4.5 (4.0; ASTM, 2000)	Add H <sub>2</sub> O <sub>2</sub> , boil, cool, and titrate quickly with NaOH solution to pH 8.3 (or 8.2; USEPA, 1983a)
Acidity as mg L <sup>-1</sup> CaCO <sub>3</sub> is calculated as $[(A \cdot B) \cdot (C \cdot D) \cdot 50,000]/\text{mL sample}$ , where $A$ = mL NaOH titrant used, $B$ = normality of NaOH titrant, $C$ = mL H <sub>2</sub> SO <sub>4</sub> titrant used, and $D$ = normality of H <sub>2</sub> SO <sub>4</sub> titrant		

also assigned an Acidity of zero based on historical data (PA DEP, written commun., 2003). Laboratories also commonly are constrained to follow a protocol other than *Standard Methods*, i.e., to report negative acidities as zero or below detection limit due to the laboratory's certification or policies.

### 2.5. Definitions of net alkalinity in use

One common practice is to use

$$\text{net alkalinity} = (\text{Alkalinity}_{\text{measured}} - \text{Acidity}_{\text{measured}}), \quad (11)$$

while another common practice is to use

$$\text{net alkalinity} = (\text{Alkalinity}_{\text{measured}} - \text{Acidity}_{\text{calculated, Eq. (9)}}). \quad (12)$$

Hedin (2004) more recently presents

$$\begin{aligned} \text{net acidity}_{\text{calculated}} = & 50[1000(10^{-\text{pH}}) + 2(\text{Fe}^{2+})/56 \\ & + 3(\text{Fe}^{3+})/56 + 2(\text{Mn})/55 \\ & + 3(\text{Al})/27] - \text{Alkalinity}, \quad (13) \end{aligned}$$

where metals are in mg/L, and Alkalinity and net acidity are in mg L<sup>-1</sup> as CaCO<sub>3</sub>. The use of Eq. (13) is equivalent to the use of Eq. (12), but with the opposite sign.

Watzlaf et al. (2004) state that, “Net alkaline water contains enough alkalinity to neutralize the mineral acidity represented by dissolved ferrous iron and manganese” (see (Kirby and Cravotta, 2005), for more background on net alkalinity definitions and discussion of the imprecisely used term “mineral acidity”).

## 3. Methods

This investigation was initially based on a small dataset (5 field and 10 synthetic samples) analyzed at

Bucknell University. Subsequently, field and stored samples from two larger datasets ( $n = 140$  and  $n = 45$ ) originally collected by the US Geological Survey (USGS) for watershed or regional characterization studies were later re-examined as questions arose based on the Bucknell dataset.

### 3.1. Preparation of Bucknell synthetic mine drainage samples

Primary solutions to represent a wide range of mine waters were prepared as follows. Reagent grade FeSO<sub>4</sub> · 7H<sub>2</sub>O, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 17H<sub>2</sub>O, MnSO<sub>4</sub> · H<sub>2</sub>O, and NaHCO<sub>3</sub> were placed in a desiccator overnight before weighing. The Fe, Al, and Mn salts were dissolved in dilute H<sub>2</sub>SO<sub>4</sub> solution; NaHCO<sub>3</sub> was dissolved in distilled deionized water. N<sub>2</sub> gas was diffused into the solutions for anoxic samples until the DO concentration was less than 0.3 mg/L (by polarographic DO probe).

Oxygenated low-pH samples were prepared by mixing known volumes of the metal salt solutions above with distilled deionized water. The pH was adjusted by addition of dilute H<sub>2</sub>SO<sub>4</sub> solution. Five drops of 30% H<sub>2</sub>O<sub>2</sub> solution were added per 50 mL of sample, and solutions were stored open to the atmosphere for one week before titration.

Anoxic samples were prepared by slowly mixing known volumes of the low-DO solutions while bubbling N<sub>2</sub>. H<sub>2</sub>SO<sub>4</sub> or NaHCO<sub>3</sub> solution and/or water were added until the desired pH was achieved and no iron-oxide precipitate was observed. DO was monitored to ensure that oxygen did not enter the samples. Selected samples were charged with CO<sub>2</sub> by bubbling CO<sub>2</sub> was bubbled into the selected mixed solutions until immediately before titration.

Concentrations of dissolved Fe, Al, and Mn were checked using inductively coupled plasma atomic emission spectrometry (ICP-AES). Colorimetric Fe<sup>II</sup>

analyses using 1,10 phenanthroline were conducted with a spectrophotometer by Standard Methods (APHA, 1992). Sulfate was analyzed using ion chromatography with a conductivity detector. Dilutions were performed as necessary, and concentrations were calculated from daily working curves based on prepared standards. The Alkalinity of the  $\text{NaHCO}_3$  solution was checked using *Standard Methods* (APHA, 1998b).

### 3.2. Sample site selection

The 198 abandoned coal-mine drainage sites in Pennsylvania (plus 10 synthetic solutions) represented a wide range of solution compositions, ranging from samples with no measurable Alkalinity and low pH to samples with near-neutral pH and considerable Alkalinity. In all these samples, dissolved Fe, Mn, and/or Al were the predominant sources of acidity due to metals.

In 1999, discharges from 140 abandoned underground coal mines in the bituminous and anthracite coalfields of Pennsylvania were sampled for analysis of chemical concentrations and loading (Cravotta et al., 2001). The 99 bituminous discharges previously had been studied by Southern Alleghenies Conservancy (1998). The 41 anthracite discharges previously had been studied by the USGS (Growitz et al., 1985; Wood, 1996). These prior reports did not include data on the Hot Acidity or the pH of oxidized samples.

In 2000, discharges from five Pennsylvania underground mines and spoil piles in the anthracite coal region were sampled in the Bucknell dataset for comparison with the synthetic samples. Sample compositions varied widely.

In March 2000, discharges from 45 abandoned anthracite mines in the Shamokin Creek Basin in eastern Pennsylvania were sampled (Cravotta and Kirby, 2004a). Most of these discharges were from underground mines, but seepage from spoil also was sampled. These data included values for Hot Acidity and dissolved metals but not the pH of oxidized samples.

### 3.3. Water quality sampling and analysis for USGS samples

Field data for flow rate, temperature, specific conductance, dissolved  $\text{O}_2$ , pH, and redox potential (Eh) were measured using standard methods at each site when samples were collected (Rantz et al., 1982a,b; Wood, 1976; US Geological Survey, 1997 to present; Ficklin and Mosier, 1999). Meters were field-calibrated using electrodes and standards that had been thermally equilibrated to sample temperatures. The pH and Eh were determined using a combination Pt and Ag/AgCl electrode with a pH sensor. The pH electrode was calibrated in pH 2.0, 4.0, and 7.0 buffer solutions,

and the Pt electrode was calibrated in Zobell's solution (Wood, 1976; US Geological Survey, 1997 to present). Values for Eh were corrected to 25 °C relative to the standard hydrogen electrode in accordance with methods of Nordstrom (1977). An unfiltered subsample for analysis of Acidity and Alkalinity was collected in a sample-rinsed HDPE bottle leaving no head space and stored on ice. Two subsamples for analysis of "dissolved" anions and cations were filtered through a 0.45- $\mu\text{m}$  pore-size nitrocellulose capsule filter. The subsample for cation analysis was stored in an acid-rinsed HDPE bottle and preserved with nitric acid to  $\text{pH} < 2$ .

Within 48 h of sampling, the unfiltered subsamples were analyzed for Alkalinity by titration with  $\text{H}_2\text{SO}_4$  to the endpoint pH of 4.5 (USEPA, 1983b; APHA, 1998b; ASTM, 2000). The pH before and during titrations was measured using a liquid-filled combination Ag/AgCl pH electrode calibrated in pH 4.0, 7.0, and 10.0 buffer solutions. Within 1 month of sampling, sulfate and chloride in the filtered, unpreserved samples were analyzed by ion chromatography (Fishman and Friedman, 1989; Crock et al., 1999). Concentrations of major cations and trace elements in the filtered, acidified samples were determined using (ICP-AES and inductively coupled plasma mass spectrometry (Fishman and Friedman, 1989; Crock et al., 1999).

Initially, for the 140 AMD samples collected in 1999, only the "cold"  $\text{H}_2\text{O}_2$  Acidity was measured. Within 48 h of sampling, the "cold"  $\text{H}_2\text{O}_2$  Acidity was measured in the laboratory by titration at ambient temperature (Ott, 1988) with NaOH to the endpoint pH of 8.3 after the addition of  $\text{H}_2\text{O}_2$ ; the "cold"  $\text{H}_2\text{O}_2$  Acidity samples were not initially titrated with  $\text{H}_2\text{SO}_4$ , and samples were not boiled. In 2003, all available unpreserved subsamples (126 of 140) that had been collected in 1999 and archived at room temperature were analyzed for pH, Alkalinity, and Hot Acidity in accordance with standard methods (APHA, 1998a,b) to evaluate measured and computed Acidity and the ultimate potential for pH to be acidic or neutral.

For the Shamokin AMD samples collected in March 2000, the *Standard Method Hot Acidity* (APHA, 1998a) was measured on unfiltered samples in the laboratory within 48 h of sampling. For Shamokin AMD samples that had  $\text{pH} > 6.5$ , the Hot Acidity values were reported as "zero" when, in fact, titrations were not actually performed on these samples (Cravotta and Kirby, 2004a). Some of these samples would have reported positive Hot Acidity titration values and others negative values (Section 4.5).

### 3.4. Sampling and analysis for Bucknell samples

Field samples were collected in the same manner as the USGS samples with the following exceptions: (1)

three sets of 500-mL HDPE bottles were used, (2) to the third sample set, 40 drops of 30% H<sub>2</sub>O<sub>2</sub> solution were added upon collection; this third bottle was stored at room temperature, loosely capped to allow gas exchange, for at least seven days, (3) except for the stored sample, holding times for Alkalinity and Acidity analyses were less than 6 h, and (4) samples for Fe<sup>II</sup> analyses were collected by filtering (0.02 μm to prevent microbial iron oxidation) and acidifying (HCl) in 30-mL HDPE bottles.

### 3.5. Titration procedures for Bucknell samples

Standard and non-standard method titrations were conducted to elucidate the effects of different methods on solution chemistry and titration results. All titrations were performed with a digital titrator and 0.16 or 1.6 N NaOH or 0.16 N H<sub>2</sub>SO<sub>4</sub> solutions. Alkalinity and Acidity titrations used endpoints of pH 4.5 and pH 8.3, respectively. Field and laboratory pH was measured using a portable pH meter with a combination electrode calibrated with pH 4.00 and 7.00 buffers. Calculations for measured Alkalinities and Acidities in mg L<sup>-1</sup> as CaCO<sub>3</sub> were done according to *Standard Methods* (APHA, 1998b,a). If negative Acidity values were obtained, they were reported as such. Specific titrations are described in Table 2.

### 3.6. Aqueous speciation computations

Activities of aqueous species were calculated using the WATEQ4F data base with the WATEQ4F (Ball and Nordstrom, 1991; Drever, 1997) and PHREEQC (Parkhurst and Appelo, 1999) computer programs. The concentrations and activities of Fe<sup>II</sup> and Fe<sup>III</sup> species were computed on the basis of the measured

Eh, temperature, and ionic strength of fresh samples. Lindberg and Runnels (1984) explained that redox couples rarely attain equilibrium for dissolved species. However, Nordstrom (2000), based on several references therein, concludes that for dissolved Fe concentrations greater than 0.5 mg L<sup>-1</sup>, there is good agreement between the measured Eh and Eh based on analytical Fe<sup>II</sup>/Fe<sup>III</sup> determinations. Results expressed as molalities for selected species were used to compute the Acidity due to H<sup>+</sup> and dissolved metals.

PHREEQC (Parkhurst and Appelo, 1999) was used to model a Hot Standard Method Acidity titration (APHA, 1998a) of Bucknell samples SYN 3, SYN5, SYN7, and Site 49, all of which had near-neutral pH and contained considerable concentrations of metals, CO<sub>2</sub>, and alkalinity. Charge balance was maintained by adjusting SO<sub>4</sub><sup>2-</sup> concentrations. The simulations paralleled the steps in the titration, but allowed for the conceptual separation of chemical reactions that may actually take place simultaneously in the physical titration; stages modeled in order are given in Table 3.

### 3.7. Calculation of acidity and net alkalinity

The acidity due to metals was computed from pH and dissolved metals concentrations in milligrams per liter

$$\begin{aligned} \text{Acidity}_{\text{computed}}(\text{mg/L CaCO}_3) \\ = 50(10^{(3-\text{pH})}) + 2C_{\text{Fe}}/55.8 + 2C_{\text{Mn}}/54.9 + 3C_{\text{Al}}/27.0. \end{aligned} \quad (14)$$

Hedin et al. (1994; see Eq. (9)) and Rose and Cravotta (1998) described a similar computation in which separate contributions from dissolved Fe<sup>II</sup> and Fe<sup>III</sup> are con-

Table 2  
Titration procedures for Bucknell field and synthetic mine drainage samples; SM = Standard Method

Method	
H <sub>2</sub> O <sub>2</sub> Acidity	(Equivalent to “cold” H <sub>2</sub> O <sub>2</sub> Acidity used for some USGS samples): Gently stir sample. Record initial pH. Add 5 drops of 30% H <sub>2</sub> O <sub>2</sub> solution; wait 2 min; record pH. Titrate quickly to a pH 8.3 endpoint using NaOH
H <sub>2</sub> O <sub>2</sub> Alkalinity	Gently stir sample. If initial pH < 4.5, record Alkalinity equal to zero. If initial pH > 4.5, add 5 drops of 30% H <sub>2</sub> O <sub>2</sub> solution; wait 2 min; record pH. Titrate quickly to a pH 4.5 endpoint using H <sub>2</sub> SO <sub>4</sub> . If Alkalinity is less than 20 mg L <sup>-1</sup> as CaCO <sub>3</sub> , use “low Alkalinity” method (APHA, 1998b)
SM Alkalinity	See APHA (1998b) or Section 2.4
SM Hot Acidity	See APHA (1998a) or Section 2.4
N <sub>2</sub> -purge Acidity	Upon arrival to lab, purge CO <sub>2</sub> by diffusing N <sub>2</sub> gas into sample bottle (open to the atmosphere) before titration. Once dissolved oxygen concentration drops below 0.3 mg/L (as a proxy monitor for CO <sub>2</sub> gas removal), remove diffuser stone. Gently stir sample. Record initial pH. Add five drops of 30% H <sub>2</sub> O <sub>2</sub> solution; wait 2 min, and record pH. Titrate quickly to a pH 8.3 endpoint using NaOH
Stored H <sub>2</sub> O <sub>2</sub> Alkalinity	Add H <sub>2</sub> O <sub>2</sub> . Store open to the atmosphere for at least 7 days. Gently stir sample. Record initial pH. Titrate quickly to a pH 4.5 endpoint using H <sub>2</sub> SO <sub>4</sub> . Use APHA (1998b) “low Alkalinity” method as necessary
Stored H <sub>2</sub> O <sub>2</sub> Acidity	Add H <sub>2</sub> O <sub>2</sub> . Store open to the atmosphere for at least 7 days. Gently stir sample. Record initial pH. Titrate quickly to a pH 8.3 endpoint using NaOH



Table 3  
Modeling stages for simulation of Hot Standard Method Acidity titration

Stage	Modeling step
0	Solve initial solution and calculate initial $P_{CO_2}$
1	Add $H_2SO_4$ to decrease pH to 4
2	Equilibrate with atmospheric $P_{O_2}$ as a proxy for $H_2O_2$ addition
3	Equilibrate with atmospheric $P_{CO_2}$ as a proxy for boiling to drive off $CO_2$
4	Allow amorphous ferric iron hydroxide and pyrolusite ( $MnO_2$ ) to precipitate through remainder of simulation
5	Add NaOH to pH 8.3

sidered; this method also was evaluated. Nevertheless, due to the low solubility of  $Fe^{III}$  solids and the tendency to hydrolyze at low pH,  $Fe^{III}$  will not contribute much Acidity over a pH range from 2.5 to 8.3 as explained below. In Eq. (14), acid equivalents as  $H^+$  of 2 per mole of Fe and Mn and 3 per mole of Al were assumed based on the relevant 25 °C hydrolysis constants,  $pK_1$  and  $pK_2$  (Ball and Nordstrom, 1991), and the potential for the dissolved metals to hydrolyze over a pH range from 2.5 to 8.3. Uncomplexed  $Fe^{2+}$  and  $Mn^{2+}$  ions have 2 equivalents per mole and tend to predominate over  $Fe^{II}$  and  $Mn^{II}$  hydroxyl species in AMD with  $pH < 8.3$  ( $pK_1 = 9.5$  for  $Fe^{2+} \rightleftharpoons Fe(OH)^+$ ;  $pK_1 = 10.6$  for  $Mn^{2+} \rightleftharpoons Mn(OH)^+$ ). In contrast, the acid equivalence of  $Fe^{III}$  varies over the relevant pH range. At  $pH > 2.2$ , dissolved  $Fe^{III}$  has less than 3 equivalents per mole because of the tendency for  $Fe^{3+}$  to form hydroxyl complexes ( $pK_1 = 2.2$  for  $Fe^{3+} \rightleftharpoons Fe(OH)^{2+}$ ;  $pK_2 = 3.5$  for  $Fe(OH)^{2+} \rightleftharpoons Fe(OH)_2^+$ ). At  $pH < 5$ , uncomplexed  $Al^{3+}$  ions, with 3 equivalents per mole, tend to be dominant ( $pK_1 = 5.0$  for  $Al^{3+} \rightleftharpoons Al(OH)^{2+}$ ;  $pK_2 = 5.2$  for  $Al(OH)^{2+} \rightleftharpoons Al(OH)_2^+$ ). The formation of metal-sulfate complexes does not affect the equivalent Acidities of the dissolved metals (Kirby and Cravotta, 2005).

The “net alkalinity” was computed by subtracting the calculated Acidity from the measured, fresh Alkalinity

$$\begin{aligned} \text{Net alkalinity (mg/L CaCO}_3\text{)} \\ = \text{Alkalinity}_{\text{measured}} - \text{Acidity}_{\text{calculated,Eq.(14)}} \end{aligned} \quad (15)$$

The “net acidity” is simply the negative of the net alkalinity

$$\begin{aligned} \text{Net acidity (mg/L CaCO}_3\text{)} &= -\text{Net alkalinity} \\ &= \text{Acidity}_{\text{calculated,Eq.(14)}} - \text{Alkalinity} \end{aligned} \quad (16)$$

The net acidity computed by Eq. (16) should be comparable in value to the Hot Acidity where the  $H_2SO_4$  added to the sample is subtracted from the NaOH added (Kirby and Cravotta, 2005).

#### 4. Results and discussion

Characteristics, titration results, and calculated Alkalinity and Acidities of the Bucknell samples are presented in Tables 4–6. Cravotta and Kirby (2004b) gives summary data for the USGS datasets. The 193 USGS field samples had concentrations of dissolved  $SO_4$ , Fe, Al, and Mn that ranged from 8.4 to 2000, 0.04–512, 0.007–108, and 0.01–74  $mg L^{-1}$ , respectively. Values for pH, Alkalinity and Acidities for USGS samples are displayed in figures in later sections.

##### 4.1. Instability of pH values – USGS datasets

The pH of the 140 fresh Anthracite and Bituminous coal mine discharge samples collected in 1999 ranged from 2.7 to 7.3 (Fig. 1), with most either near neutral (pH 6–7) or acidic (pH 2.5–4). This result is similar to other regional data sets (e.g., Brady et al., 1997; Cravotta et al., 1999). Approximately 25% of the fresh AMD samples had pH values from 4.0 to 5.5. In contrast, the aged (fully oxidized) samples displayed a distinctively bimodal pH frequency distribution (Fig. 1),

Table 4  
Characteristics of Bucknell field samples from Western Middle Anthracite Field, PA

Site No.	pH	Concentration ( $mg L^{-1}$ )					Source	Measurable Alkalinity?
		Fe(II)	Fe(III)	Al	Mn	DO <sup>a</sup>		
8	3.6	0.4	0.6	17	2	9	Surface mine	No
23	3.6	7.2	3.3	7.6	6.9	<0.3	Deep mine	No
51	5.6	67	2.7	0.06	6.6	<0.3	Deep mine	Yes
20	5.7	23	1.4	0.04	3.5	0.9	Deep mine	Yes
49	5.9	19	1.2	0.03	3.0	<0.3	Deep mine	Yes

<sup>a</sup> DO, dissolved oxygen.

Table 5  
Characteristics of Bucknell synthetic samples

Sample	pH	Concentration (mg L <sup>-1</sup> )				Gasses	Measurable Alkalinity?
		Fe(II)	Fe(III)	Al	Mn		
SYN1	2.8	0	56	0	0	Oxic	No
SYN2	3.0	0	0	54	0	Oxic	No
SYN3	6.1	117	0	0	0	Anoxic	Yes
SYN4	6.0	91	0	0	0	Anoxic	Yes
SYN5	7.2	40	0	0	20	Anoxic	Yes
SYN6	6.6	0	0	0	19	Anoxic	Yes
SYN7	6.1 <sup>a</sup>	20	0	0	0	Anoxic, add CO <sub>2</sub>	Yes
SYN8	5.2 <sup>b</sup>	85	0	0	0	Anoxic, add CO <sub>2</sub>	Yes
SYN9	6.4	85	0	0	0	Anoxic	Yes
SYN10	4.1	0	0	0	18	Anoxic	No

<sup>a</sup> pH of SYN7 = 6.8 before CO<sub>2</sub> addition.

<sup>b</sup> pH of SYN8 = 7.3 before CO<sub>2</sub> addition.

Table 6  
Measured and calculated Alkalinity values for field and synthetic samples; nd indicates not determined

Sample	Alkalinity (mg L <sup>-1</sup> ) as CaCO <sub>3</sub>				Acidity (mg L <sup>-1</sup> ) as CaCO <sub>3</sub>				
	Standard method	H <sub>2</sub> O <sub>2</sub>	Stored H <sub>2</sub> O <sub>2</sub>	Calculated <sup>a</sup> Alkalinity	Standard method	H <sub>2</sub> O <sub>2</sub>	Stored H <sub>2</sub> O <sub>2</sub>	N <sub>2</sub> -purge H <sub>2</sub> O <sub>2</sub>	Calculated <sup>b</sup> Acidity
Site 8	0	0	0	-14	105	95	125	113	114
Site 23	0	0	0	-30	105	172	149	94	96
Site 51	37	0	0	37	128	283	223	138	139
Site 20	37	2	2	37	30	144	25	23	51
Site 49	66	32	29	66	-18	116	78	13	44
SYN1	0	0	0	-178	235	nd	249	nd	231
SYN2	0	0	0	-61	382	nd	379	nd	353
SYN3	3	0	0	3	217	225	214	nd	210
SYN4	20	0	0	20	103	118	87	nd	163
SYN5	43	6	4	43	36	61	34	nd	107
SYN6	2	3	3	2	27	32	38	nd	34
SYN7	147	113	112	147	-104	190	0	22	36
SYN8	69	0	0	69	79	737	75	130	152
SYN9	29	0	0	29	118	140	119	nd	151
SYN10	0	0	0	-4	33	34	41	nd	38

<sup>a</sup> Negative Alkalinities (calculated by PHREEQC for samples with Alkalinity less than zero) are primarily due to H<sup>+</sup> concentrations; other calculated Alkalinity values are equal to measured Standard Method Alkalinities.

<sup>b</sup> Acidity is calculated from Eq. (14).

with dominant modes at pH 2.5–4.5 and 6.0–8.5. The initially near-neutral samples exhibited the greatest change in pH with oxidation. None of the aged, oxidized samples had pH values between 5 and 6.

Fig. 2 compares field, fresh H<sub>2</sub>O<sub>2</sub> lab, and aged lab (four years) pH values from the 140 Anthracite and Bituminous discharges. The dark symbols (Fig. 2(a)) show the bimodal distribution of aged pH values. The differences between the pH of fresh, H<sub>2</sub>O<sub>2</sub>-treated samples and the aged samples (Fig. 2) could arise because the addition of H<sub>2</sub>O<sub>2</sub> without boiling: (1) does not promote CO<sub>2</sub> exsolution from high-pH samples, (2) does not result in complete oxidation of Fe<sup>II</sup> and Mn<sup>II</sup>, and (3) does not promote the formation of

thermodynamically stable phases such as goethite. The eventual recrystallization of schwertmannite to goethite as samples age will release SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> to solution (Bigam et al., 1996). Furthermore, because goethite is less soluble than ferrihydrite or schwertmannite, the pH of solutions in equilibrium with goethite will be lower than that for initial conditions with the precursor minerals. Hence, the pH of net-alkaline, near-neutral samples could increase with aging as CO<sub>2</sub> exsolves, and the pH of acidic samples that had initially precipitated schwertmannite could decrease as goethite forms. Ultimately, the pH will become stable when equilibrium among the gaseous, aqueous, and solid phases is achieved, as probably was the case for the 4-year-old

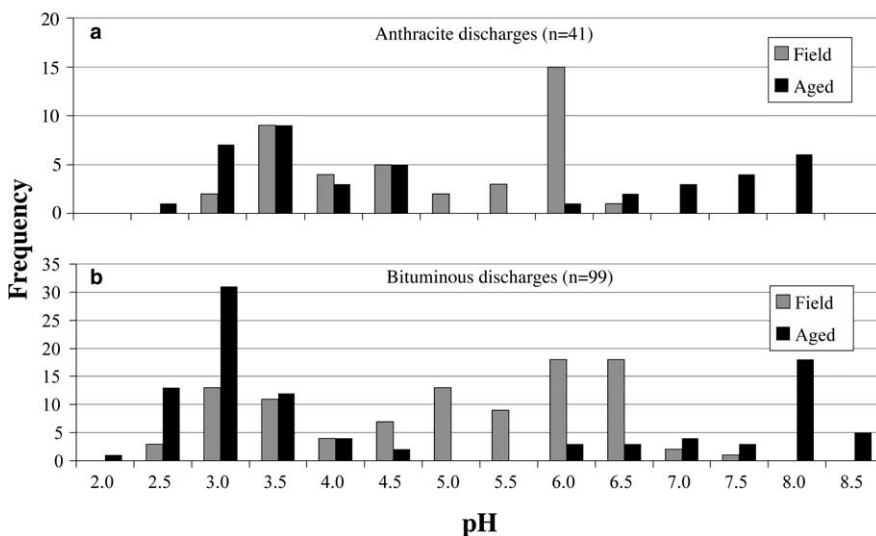


Fig. 1. Frequency distribution for pH of 140 abandoned mine discharges in Pennsylvania sampled in 1999: (a) anthracite discharges, (b) bituminous discharges.

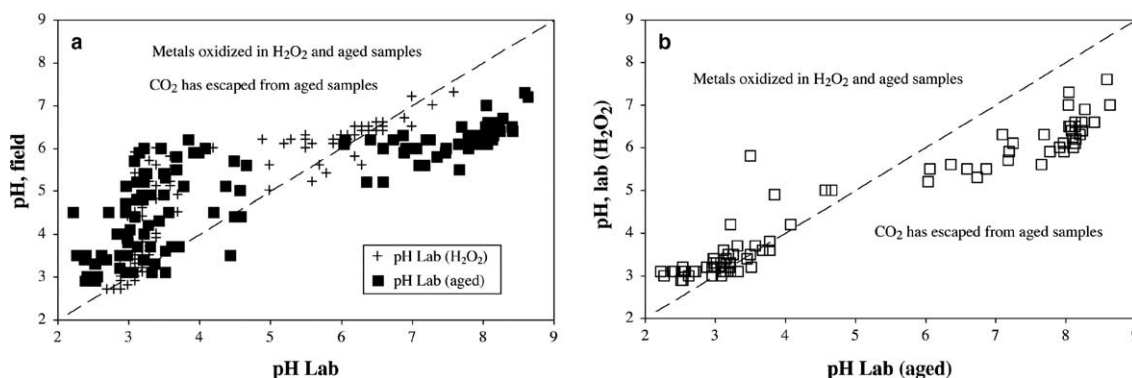


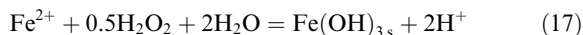
Fig. 2. Relations among pH values for 140 fresh, fresh H<sub>2</sub>O<sub>2</sub>, and aged sample pairs, Anthracite and Bituminous Coalfields, PA, 1999: (a) field-measured pH compared to lab pH values, (b) lab pH after H<sub>2</sub>O<sub>2</sub> treatment of fresh samples compared to lab pH of 4-year-old samples.

samples. Analysis of fresh and aged precipitates is needed to confirm the above hypothesis, and the length of time for equilibration is uncertain.

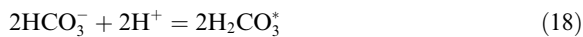
#### 4.2. Alkalinity results

Many of the AMD samples had near-neutral pH values and contained measurable Alkalinity under initial lab or initial field conditions but ultimately had acidic, oxidized pH values that were two or three units lower than initial conditions (Fig. 2). Initial Alkalinities of samples were greater than or, in few cases, equal to the Alkalinities of samples treated with H<sub>2</sub>O<sub>2</sub> or oxidized, aged samples (Fig. 3). The H<sub>2</sub>O<sub>2</sub> and stored H<sub>2</sub>O<sub>2</sub> Alkalinity methods give identical results within analytical uncertainty (Fig. 3(c)).

The initially colorless, near-neutral pH solutions develop orange turbidity due to the rapid formation of ferric hydroxide upon H<sub>2</sub>O<sub>2</sub> addition. H<sub>2</sub>O<sub>2</sub> addition or aging promotes iron oxidation and visible precipitation before titration, which causes a net production of H<sup>+</sup>



H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> are consumed by the reaction



which results in a lower pH at the end of the titration and a lower Alkalinity than the Standard Method.

The Site 49 and SYN 5 data (Tables 4–6) suggest that iron oxidation is not always completed during an H<sub>2</sub>O<sub>2</sub> or stored H<sub>2</sub>O<sub>2</sub> Alkalinity titration. The stoichiometry of Eqs. (17) and (18) implies that if all of the Fe<sup>II</sup> were

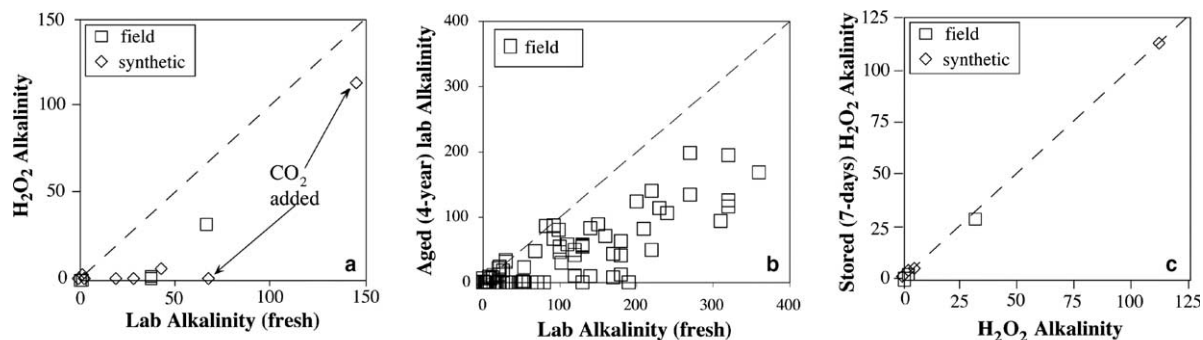


Fig. 3. Comparison of measured Alkalinity (as  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ ) methods: (a) Bucknell fresh  $\text{H}_2\text{O}_2$  Alkalinity vs. Standard Method Alkalinity, (b)  $n = 140$  USGS 4-year aged Alkalinity vs. fresh Standard Method Alkalinity, (c) Bucknell stored  $\text{H}_2\text{O}_2$  Alkalinity vs. fresh  $\text{H}_2\text{O}_2$  Alkalinity. Diagonal lines show where values on the  $x$ - and  $y$ -axes are equal.

oxidized, all sample alkalinity should be removed by the  $\text{H}_2\text{O}_2$  Alkalinity titration. However, the Site 49 and SYN 5 samples retain 32 and  $6 \text{ mg L}^{-1}$  of alkalinity as  $\text{CaCO}_3$ , respectively, in the  $\text{H}_2\text{O}_2$  Alkalinity titration.

The negative contribution of metal species to Alkalinity in near-neutral pH mine water is negligible (see (Kirby and Cravotta, 2005)). Aging or  $\text{H}_2\text{O}_2$  addition causes the consumption of some positive Alkalinity by  $\text{H}^+$  from metal Acidity (Eqs. (17) and (18)), and some of the Alkalinity originally present in the sample is "lost." Thus, some "real" Alkalinity is consumed before the titration takes place, thus the aging and  $\text{H}_2\text{O}_2$  methods underestimate the actual sample Alkalinity, which is measured correctly in the Standard Method. Although storage allows  $\text{CO}_2$  degassing, the loss of  $\text{CO}_2$  has no impact on Alkalinity (Stumm and Morgan, 1996).

The measured Alkalinity values are constrained to be zero or greater, but calculated Alkalinites may be negative for low pH samples. The interpretation of Standard Method Alkalinity values requires consideration of the potential for oxidation of dissolved  $\text{Fe}^{\text{II}}$  unless samples are analyzed within a short holding time.

#### 4.3. Acidity results for Bucknell samples and methods

Fig. 4(a) plots Hot Acidity against calculated Acidity (Eq. (14)). Similar comparisons in Hedin et al. (1994) and Watzlaf et al. (2004) showed that Hot and calculated Acidities (Eq. (9)) are nearly equal for samples with pH less than 4.5. Samples falling near the diagonal line (Hot Acidity = calculated Acidity; Fig. 4(a)) had no or very low Alkalinity, consistent with the results of Hedin et al. (1994) and Watzlaf et al. (2004). Samples that fall off of the diagonal line contain Alkalinity; the influence of initial Alkalinity on Acidity is discussed in Sections 4.5 and 4.6. The presence of  $\text{CO}_2$  has no influence on either Hot or calculated Acidity estimates because  $\text{CO}_2$  is driven off in the Standard Method and

because Eqs. (9) and (14) do not include contributions from  $\text{CO}_2$ .

In contrast to Hot Acidity, "cold" (i.e., sample or room temperature)  $\text{H}_2\text{O}_2$  Acidity has no boiling step, and the fact that "cold"  $\text{H}_2\text{O}_2$  Acidity is greater than Hot Acidity (Fig. 4(b)) shows that  $\text{CO}_2$  can contribute to the value of a "cold"  $\text{H}_2\text{O}_2$  Acidity titration. Although total carbon was not measured, PHREEQC modeling of the deep mine samples (see Sites 20, 23, 49, 51 in Table 4) returned higher than atmospheric  $P_{\text{CO}_2}$  values. SYN 7 and 8 were created with high  $\text{CO}_2$  concentrations. A "cold"  $\text{H}_2\text{O}_2$  Acidity titration allows the retention of  $\text{CO}_2$ , whereas a Hot Acidity titration intentionally drives off Acidity due to  $\text{CO}_2$  by lowering pH and boiling.

In addition to effects due to  $\text{CO}_2$  degassing, the reliability of a "cold"  $\text{H}_2\text{O}_2$  Acidity titration is negatively impacted by slow  $\text{Fe}^{\text{II}}$  (or  $\text{Mn}^{\text{II}}$ ) oxidation; as discussed in Section 4.2, Eqs. (17) and (18) do not go to completion when  $\text{H}_2\text{O}_2$  is added without a boiling/cooling step. Acidity due to metals can be underestimated in a "cold"  $\text{H}_2\text{O}_2$  Acidity titration, although this effect may not be recognized because it can be overwhelmed by the Acidity contributed by  $\text{CO}_2$  in some samples. Therefore, "cold"  $\text{H}_2\text{O}_2$  Acidity titrations should be avoided.

Fig. 4(c) shows stored (7-day)  $\text{H}_2\text{O}_2$  Acidity  $\geq$  Hot Acidity, but stored  $\text{H}_2\text{O}_2$  Acidity more closely approaches the Hot Acidity values than "cold"  $\text{H}_2\text{O}_2$  Acidity (Fig. 4(b)). In contrast to samples stored for four years (Section 4.5), apparently not all  $\text{CO}_2$  degasses during the 7-day storage period, and thus  $\text{CO}_2$  can contribute to the stored (7-day)  $\text{H}_2\text{O}_2$  Acidity measurement.

"Cold"  $\text{H}_2\text{O}_2$  Acidity is greater than stored  $\text{H}_2\text{O}_2$  Acidity (Fig. 4(d)) because storage allows  $\text{Fe}^{\text{II}}$  (or  $\text{Mn}^{\text{II}}$ ) oxidation and degassing of  $\text{CO}_2$  to go more nearly to completion: the result is a loss of metal- and  $\text{CO}_2$ -Acidity. Fig. 4(e) shows calculated Acidity  $\geq$   $\text{N}_2$ -purge Acidity.  $\text{CO}_2$  is not accounted for in the calculated Acidity,

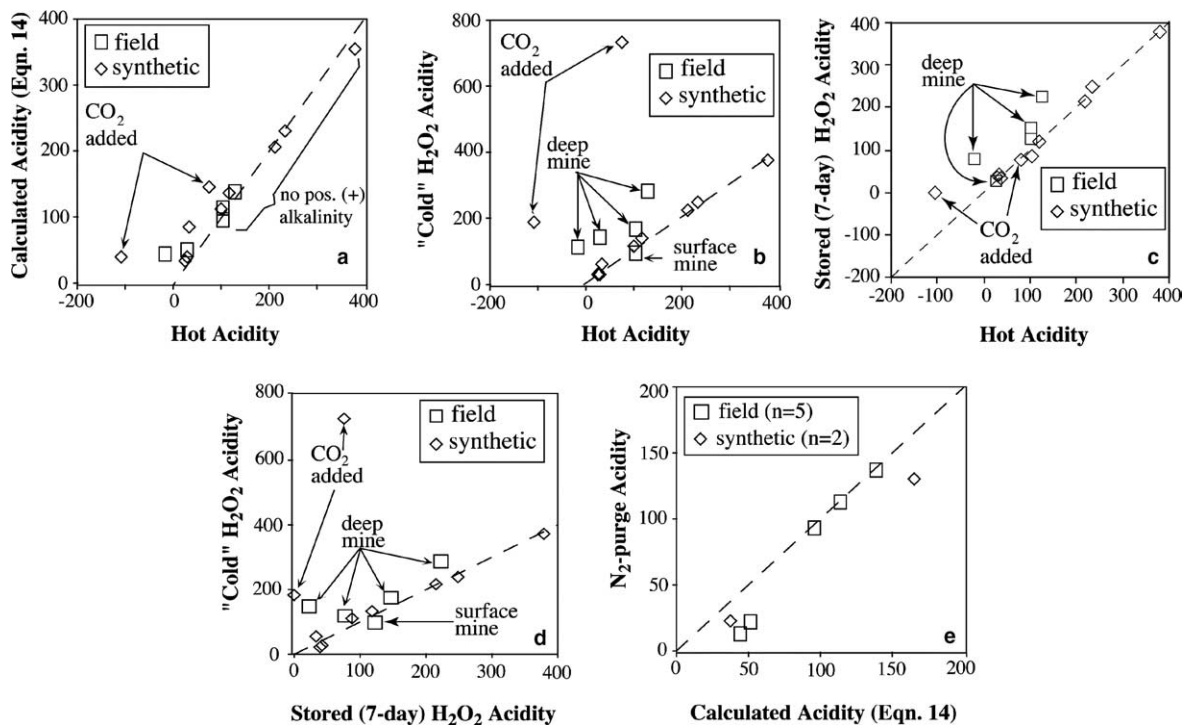


Fig. 4. Comparisons of Acidity (as  $\text{mg L}^{-1} \text{CaCO}_3$ ) methods for Bucknell samples. Diagonal lines show where values on the  $x$ - and  $y$ -axes are equal.

and it is driven off by the  $\text{N}_2$ -purge. Although the  $\text{N}_2$ -purge method uses  $\text{H}_2\text{O}_2$ , it does not include a boiling step, and thus slow  $\text{Fe}^{\text{II}}$  (or  $\text{Mn}^{\text{II}}$ ) oxidation rates prevent the completion of oxidation/hydrolysis reactions that can release  $\text{H}^+$  Acidity, thus lowering the Acidity estimate compared to Hot Acidity.

#### 4.4. Relation between Hot Acidity and pH

Fresh field pH values (square symbols, Fig. 5(a)) are scattered when plotted against fresh Hot Acidity. Plotting fresh lab  $\text{H}_2\text{O}_2$  pH values (cross symbols, Fig. 5(a)) against Hot Acidity reduces the scatter, but pH values are not bimodally distributed (see also Fig. 1). In contrast, when aged lab pH is plotted against either Hot Acidity or calculated net Alkalinity (Eq. (15)) for 140 USGS mine drainage samples (Fig. 5(b)), there is much less scatter, a distinct sinusoidal curve is evident in the data, and there is a pH gap that separates net acidic samples from net alkaline samples. Samples that had near-neutral pH after oxidation had negative values for Hot acidity; samples that had acidic pH after oxidation had positive Hot acidity. The aging permits complete  $\text{Fe}^{\text{II}}$  or  $\text{Mn}^{\text{II}}$  oxidation, permits  $\text{CO}_2$  degassing, and allows the sample to reach its ultimate pH. The pH gap in Fig. 5(b) corresponds to the bimodal pH distribution (Fig. 1). Fig. 5(b) also suggests that Hot Acid-

ity  $\approx$  calculated net Acidity = -calculated net Alkalinity; this relationship is also seen in later figures.

#### 4.5. Comparison of Acidity and net acidity calculations to measured acidity

Fig. 6(a) shows the relationships between two different Acidity titrations and Acidity calculated using Eq. (10) (complete aqueous speciation less  $\text{CO}_2$  contributions). The “cold”  $\text{H}_2\text{O}_2$  Acidity is greater than or equal to aged (4-year) Hot Acidity. This result occurs because  $\text{CO}_2$  degasses in the Hot titration, but not in the “cold”  $\text{H}_2\text{O}_2$  titration. The Acidity calculated using aqueous speciation less  $\text{CO}_2$  contributions does not correspond to either the “cold”  $\text{H}_2\text{O}_2$  or the aged Hot Acidity (Fig. 6(a)). Either the “cold”  $\text{H}_2\text{O}_2$  or Hot Acidity can return negative values, but only the Hot Acidity (fresh or aged) returned negative values for samples in this study. In contrast, all calculated Acidities in this study are constrained to give only positive values. Kirby and Cravotta (2005) discuss calculation of Acidity in more detail.

Acidities calculated using Eq. (9) ( $\text{Fe}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Al}^{\text{III}}$ ,  $\text{H}^+$ ), Eq. (10) (complete aqueous speciation less  $\text{CO}_2$  contributions), and Eq. (14) (same as Eq. (9) except all  $\text{Fe} = \text{Fe}^{\text{II}}$ ), are essentially equivalent (Fig. 6(b)). Although Eq. (9) requires the speciation of iron into  $\text{Fe}^{\text{II}}$

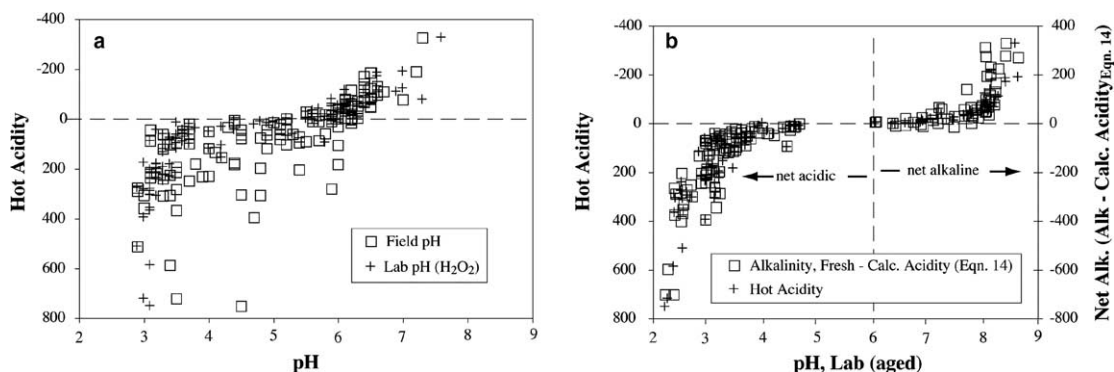


Fig. 5. Relationships between fresh field pH, 4-year aged lab pH, (fresh) Hot Acidity, and calculated net Alkalinity for 140 USGS mine drainage samples; all Acidities and Alkalinities are in  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ .

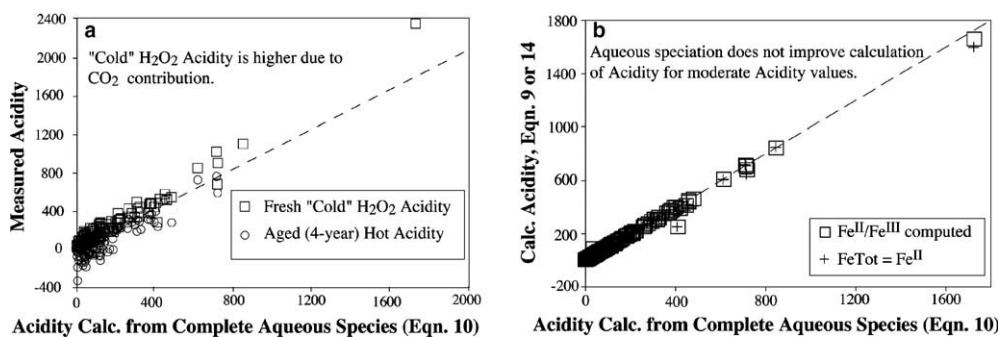


Fig. 6. Comparison of Acidity for 140 USGS mine drainage samples: (a) “cold”  $\text{H}_2\text{O}_2$  and Hot Acidity measurements vs. Acidity calculated with complete aqueous speciation less  $\text{CO}_2$  (Eq. (10)) and (b) Acidities calculated using Eqs. (9) and (14) vs. Acidity calculated with complete aqueous speciation less  $\text{CO}_2$  (Eq. (10)). All values are in  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ . Diagonal lines show where values on the x- and y-axis are equal.

and  $\text{Fe}^{\text{III}}$  species, distinguishing between  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  is not required in the calculation of Acidity, and this graphical evidence (Fig. 6(b)) supports the use of Eq. (14). This conclusion can save money and effort in planning for monitoring.

Many mine drainage monitoring schemes only collect data for total (rather than dissolved) iron. Dissolved rather than total iron concentrations are recommended for use in Eqs. (9), (10), and (14). If  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  are to be distinguished analytically, care must be taken to ensure that water samples for  $\text{Fe}^{\text{II}}$  are either analyzed very quickly or preserved ( $0.02 \mu\text{m}$  filters,  $\text{HCl}$ ) such that  $\text{Fe}^{\text{II}}$  does not oxidize before analysis.  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  may also be estimated based on total dissolved Fe and field redox potential (Nordstrom et al., 1979; Ball and Nordstrom, 1991). For samples with pH values greater than approximately 5, it is possible to use dissolved iron as a reasonable proxy for dissolved  $\text{Fe}^{\text{II}}$  concentrations in the absence of data for  $\text{Fe}^{\text{II}}$ .

Plotting Standard Method Hot Acidity (APHA, 1998a) vs. net acidity (Calculated Acidity<sub>Eq. (14)</sub> - Alkalinity<sub>Std.Meth.</sub>) (Fig. 7) clearly demonstrates that the

Standard Method Hot Acidity measurement returns a net acidity, as long as negative values are reported by the lab. Fig. 7(a) illustrates the problem associated with reporting negative Hot Acidity as zero; it shows data for 45 Shamokin Creek watershed samples for which the lab reported any negative values as “zero Acidity.” The “zero Acidity” values (Fig. 7(a); from samples with near-neutral pH and measurable Alkalinity) should have been reported as negative numbers, but the standard lab practice at the time of collection was to report negative values as zero. In the Bucknell dataset, all negative Hot Acidity values are reported as negative rather than as zero; in these samples, net acidity = Hot Acidity (Fig. 7(b)).

For most samples, aged Hot Acidities corresponded well to net Acidity calculated using Eq. (16) ( $\text{Fe} = \text{Fe}^{\text{II}}$ ) (Fig. 7(c)). However, the same was clearly not true for samples with high ( $>50 \text{ mg L}^{-1}$ ) fresh Alkalinities (circles in Fig. 7(c)). The samples with the lowest net acidity or aged Hot Acidity values (i.e., the most alkaline samples) were very near saturation with respect to calcite based on saturation indices. These samples appear more

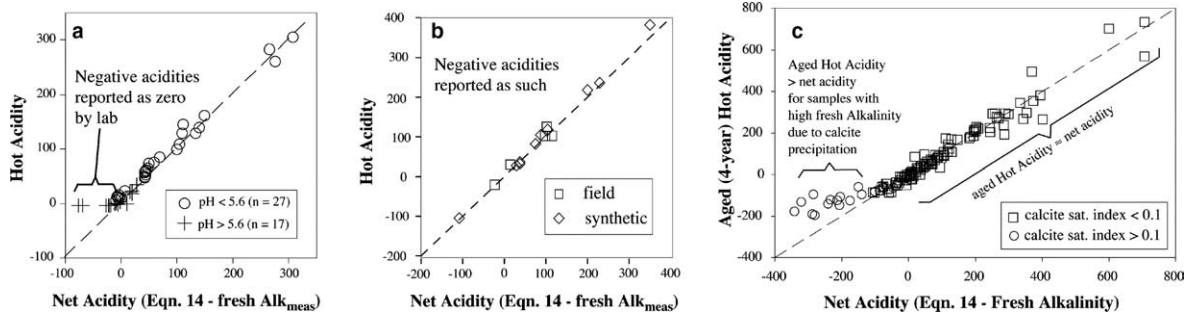


Fig. 7. Comparison of net Acidity estimates: (a) Standard Method Hot Acidity vs. net acidity for 44 Shamokin, PA USGS field samples; several samples should have had negative Hot Acidity values reported. (b) Same plot for Bucknell samples; negative Hot Acidity values are reported. (c) Aged (4-year) Hot Acidity for 140 USGS samples vs. net Acidity (calculated Acidity – measured Alkalinity); negative Hot Acidity values are reported. Diagonal line shows where values on  $x$ - and  $y$ -axes are equal. All values are in  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ .

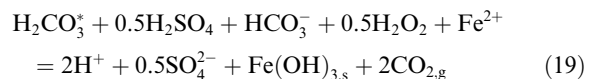
alkaline (i.e., have smaller negative Acidity) when considering the aged Hot Acidity than when considering the calculated net acidity.

We interpret the behavior in Fig. 7(c) as follows. Samples initially near calcite saturation became supersaturated with calcite as  $\text{CO}_2$  degassed during storage. Calcite, which should contribute negatively to sample Acidity (considering both solid and aqueous components) could precipitate on vessel walls during storage, but it could remain on vessel walls when the solution is transferred to another vessel for the aged Hot Acidity titration. The aged Hot Acidity value would thus be too small a negative number because of the removal of negative Acidity by calcite precipitation. This problem should not occur if the titration were carried out on a fresh sample or in the same vessel with the precipitated calcite. A fresh (unstored) Hot Acidity titration for such high alkalinity samples should equal the calculated net acidity (Eq. (16)), but we have not conducted this experiment for samples with fresh Alkalinities  $> 50 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$ . Although storage does not affect the Hot Acidity measurement of most samples, storage should be avoided due to this potential problem with calcite precipitation in samples with high initial alkalinity. Samples in this high net alkalinity range are clearly net alkaline and will not require alkaline addition for treatment. However, this issue would be of concern if one wished to calculate the Alkalinity loading of a discharge. More research on samples with very high Alkalinity is recommended.

#### 4.6. What occurs in the Standard Method Hot Acidity titration?

The greatest deviations between the several Acidity methods occur in samples of near-neutral pH, metal-laden mine water that possesses considerable Alkalinity as shown by the data in Table 6 and Figs. 4 and 7. Several

reactions take place in such a solution during a Standard Method Hot Acidity measurement (APHA, 1998a) (Table 7). Although it provides consistent and reproducible results, the Standard Method Hot Acidity titration underestimates the non- $\text{CO}_2$  Acidity initially present in a sample containing alkalinity. The overall reaction that results in the loss of non- $\text{CO}_2$  Acidity during the preparatory steps is given by

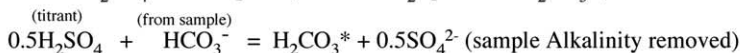
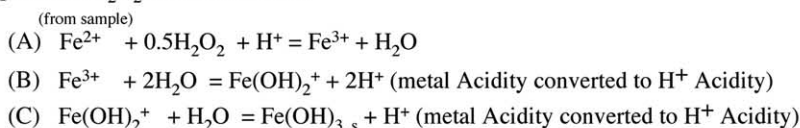
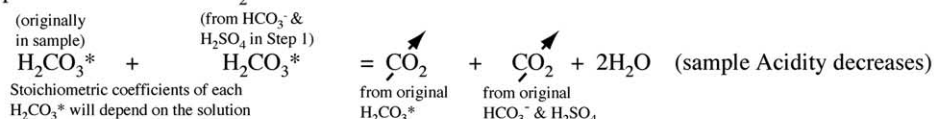


where all species are aqueous except for  $\text{Fe}(\text{OH})_3$  and  $\text{CO}_2$ .

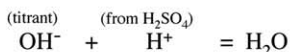
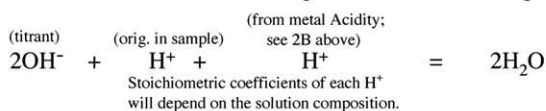
In an actual titration of such a sample, oxidation will unavoidably be accompanied by metal hydroxide precipitation, whereas a computer simulation allows the user to model reactions separately. Fig. 8 illustrates solution composition changes during a Hot Acidity titration as modeled by PHREEQC for the Site 49 sample (near-neutral pH, high  $P_{\text{CO}_2}$ , and has initial  $\text{Fe}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ , and alkalinity; Tables 4 and 6). The calculated Acidities consider contributions from all  $\text{H}^+$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Al}$ ,  $\text{SO}_4$ , and  $\text{CO}_3$  species in the PHREEQC database on the basis of the proton condition (Kirby and Cravotta, 2005) for an equivalence point of pH 8.3. The total Acidity includes the positive contribution of  $\text{H}_2\text{CO}_3^*$  to Acidity ( $1 \text{ eq L}^{-1}$ ); the non- $\text{CO}_2$  Acidity (Eq. (10)) ignores  $\text{H}_2\text{CO}_3^*$  contributions.

The PHREEQC-calculated Alkalinity values in Fig. 8 result from positive and negative contributions by various species on the basis of the proton condition (Stumm and Morgan, 1996) for an equivalence point of pH 4.5. For example, PHREEQC assigns  $\text{Fe}^{3+}$  an Alkalinity of  $-2 \text{ eq kg}^{-1}$ , whereas  $\text{Fe}^{2+}$  is assigned an Alkalinity of zero. For  $\text{pH} \leq 8.3$ , positive Alkalinity is due almost entirely to  $\text{HCO}_3^-$  ( $+1 \text{ eq kg}^{-1}$ ).

Table 7

Derivation of non-CO<sub>2</sub> Acidity loss during APHA (1998a) Hot Acidity titration for samples containing AlkalinityStep 1: Add H<sub>2</sub>SO<sub>4</sub> down to pH 4 (convert CO<sub>2</sub> species to H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>)Step 2: Add H<sub>2</sub>O<sub>2</sub> to oxidize metalsStep 3: Boil to drive off CO<sub>2</sub>

Step 4: Add NaOH to titrate Acidity

(A) Add sufficient OH<sup>-</sup> to titrate H<sup>+</sup> added as H<sub>2</sub>SO<sub>4</sub>; overcompensates because some H<sub>2</sub>SO<sub>4</sub> lost as CO<sub>2</sub> in Step 3(B) Add sufficient OH<sup>-</sup> to titrate original H<sup>+</sup> and metals to pH ≈ 8.3

Step 5: Standard Method Acidity calculation:

$$\text{Acidity, mg/L as CaCO}_3 = \frac{(X - Y) (50000 \text{ mg CaCO}_3 \text{ equiv}^{-1})}{\text{L sample}}$$

where

X = total equivalents of base added to pH 8.3

Y = equivalents of acid added to pH 4

Adding reaction in Steps 1 and 3 gives:

illustrating that some Acidity added as H<sub>2</sub>SO<sub>4</sub> is lost as CO<sub>2</sub> before the titration with base occurs.

The overall reaction resulting in loss of Acidity during the Steps 1-3 of the Hot Acidity titration is given by:

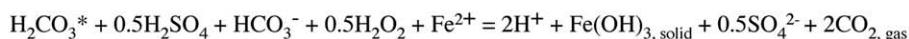


Figure 8 illustrates these effects graphically. Below are three equivalent statements of the effects of this procedure:

- (1) Some Acidity represented by the Y term (Step 5) is driven off as CO<sub>2</sub> in the Step 3, thus the Y term overcompensates for H<sub>2</sub>SO<sub>4</sub> addition (Step 1). It takes fewer equivalents of base to titrate back up to original sample pH than equivalents of acid required to lower original pH to 4.
- (2) Non-CO<sub>2</sub> Acidity originally in the sample are underestimated by the Standard Methods (1998a) Hot Acidity titration due to reaction with sample Alkalinity.
- (3) The Standard Methods (1998a) Hot Acidity measurement produces a value for *net* acidity rather than simply "Acidity" for all situations, *i.e.*, whether or not a negative value is obtained. This value is equal to (non-CO<sub>2</sub> Acidity - Alkalinity) and intentionally does not include CO<sub>2</sub> contributions.



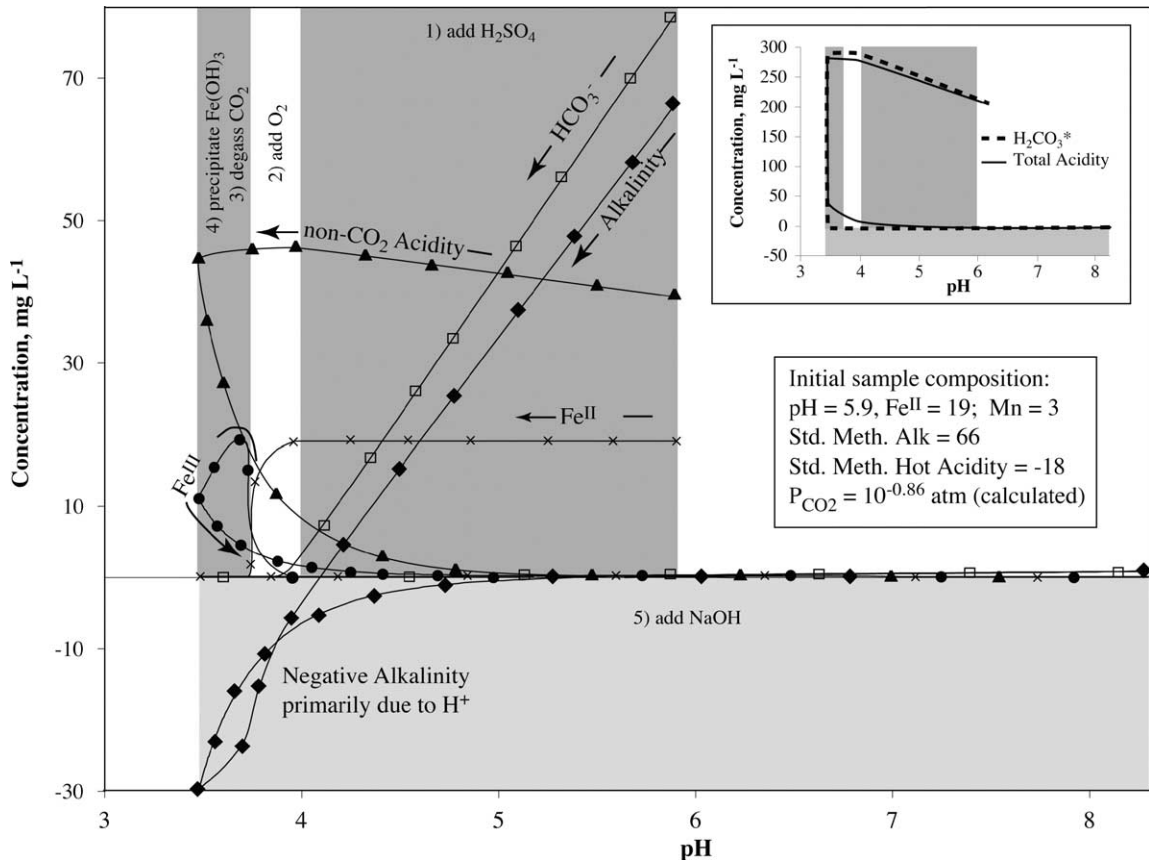


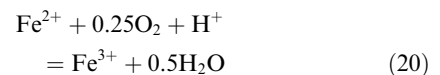
Fig. 8. Selected PHREEQC-modeled solution composition changes for the Site 49 Bucknell sample during a Standard Method (APHA, 1998a) Hot Acidity titration; see Section 4.6 for reactions associated with titration stages 1–5. All concentrations are in  $\text{mg L}^{-1}$  of the species indicated except Alkalinity and Acidity are in  $\text{mg L}^{-1} \text{CaCO}_3$ . Point symbols are present to guide the eye: the simulation generated 400 points for each concentration along the path of each line. Inset shows  $\text{H}_2\text{CO}_3^*$  and total Acidity changes for the same titration with a different y-axis scale.

During initial titration with  $\text{H}_2\text{SO}_4$ , the total Alkalinity decreases to negative values as  $\text{HCO}_3^-$  quantitatively converts to  $\text{H}_2\text{CO}_3^*$  (Eq. (18)). Where Alkalinity is negative, the concentration of  $\text{HCO}_3^-$  is lower than concentrations of  $\text{H}^+$ ,  $\text{HSO}_4^-$ , and negatively contributing metal species. These negative Alkalinity values are not measurable using the Standard Method Alkalinity titration to  $\text{pH} \approx 4.5$  endpoint (APHA, 1998b). See Kirby and Cravotta (2005) for further background on the assignment of Acidity contributions to metal species.

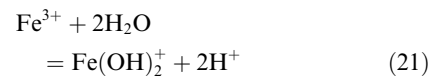
Sequential changes in solution composition during a simulated Hot Acidity titration as illustrated in Fig. 8 are as follows.

Stage 1: Due to the addition of  $\text{H}_2\text{SO}_4$  titrant, the pH,  $\text{HCO}_3^-$  and Alkalinity decrease, while  $\text{H}_2\text{CO}_3^*$ , non- $\text{CO}_2$  Acidity, and Acidity increase.

Stage 2: Due to the addition of  $\text{O}_2$  (as proxy for  $\text{H}_2\text{O}_2$ ),  $\text{Fe}^{\text{II}}$  oxidizes to  $\text{Fe}^{\text{III}}$



and then  $\text{Fe}^{\text{III}}$  hydrolyzes



causing pH and Alkalinity to decrease. Following oxidation,  $\text{Fe}(\text{OH})_2^+$  and  $\text{FeOH}^{2+}$  become the predominant aqueous Fe species.

Stage 3: Boiling and subsequent cooling steps are simulated by decreasing  $P_{\text{CO}_2}$  to atmospheric conditions.  $\text{CO}_2$  degasses, decreasing  $\text{H}_2\text{CO}_3^*$  and total Acidity and increasing pH very slightly (0.005 units).

Stages 4 and 5: Amorphous  $\text{Fe}(\text{OH})_3$  and pyrolusite ( $\text{MnO}_2$ ) solids are allowed to precipitate, causing  $\text{Fe}^{\text{III}}$ , Mn, total Acidity, non- $\text{CO}_2$  Acidity, and Alkalinity to decrease.

Stage 5: NaOH titrant is added incrementally, continuously increasing pH, and increasing Alkalinity to near zero; Alkalinity stays low due to lack of  $\text{CO}_2$  species until  $\text{OH}^-$  Alkalinity becomes important above pH 9. With the increase in pH to about 8.5,  $\text{Fe}^{\text{III}}$  decreases to its minimum concentration due to amorphous  $\text{Fe}(\text{OH})_3$  solid precipitation. If Al had been present in the sample, at pH about 6.5, dissolved Al also would decrease to its minimum concentration due to precipitation of amorphous  $\text{Al}(\text{OH})_3$ . As the NaOH is added and metals precipitate, Acidity decreases, becoming negative at pH > 9.

Although not shown, net alkalinity calculated as  $\text{Alkalinity}_{\text{PHREEQC}} - \text{Acidity}_{\text{Eq. (14)}}$  equals zero at pH 6.37; the theory behind this outcome is explained in Kirby and Cravotta (2005). One notable difference in a physical titration is that Mn precipitation tends to occur at pH > 7 due to slow kinetics rather than at the lower pH values suggested by the equilibrium titration simulation. Simulations of Hot Acidity titrations of three synthetic solutions (also with near-neutral pH, high  $P_{\text{CO}_2}$ , considerable  $\text{Fe}^{\text{II}}$  and/or  $\text{Mn}^{\text{II}}$ , and Alkalinity) gave very similar results to those shown in Fig. 8 and are thus not reported.

The most recent version of *Standard Methods* (APHA, 1998a) recognizes the underestimation of Acidity implicitly by stating that the absolute value of a negative Acidity titration result is equivalent to the net alkalinity. However, net alkalinity is not explicitly defined in the *Standard Methods* text. Although the term net alkalinity is in wide use among mine drainage workers, it has not been adequately defined in the literature until recently (Kirby and Cravotta, 2005). Further, many workers may not be aware of the recent change to the Standard Method, particularly because US EPA and ASTM methods (ASTM, 2000; USEPA, 1983a) do not now agree with the APHA (1998a) method.

The current study does not suggest that the Standard Method for Hot Acidity (APHA, 1998a) is wrong; it suggests that workers should be aware of exactly what the method measures. The results in Fig. 7 clearly demonstrate that the Standard Method Hot Acidity is actually a *net* acidity, as suggested implicitly by the most recent (APHA, 1998a) method. However, the instructions to the analyst only recognize the Standard Method

Hot Acidity result as a net Acidity *if* a negative result is obtained. In fact, the Standard Method Hot Acidity result is *always* a net Acidity, not only when a negative result is obtained. For all analyses in this study performed on fresh samples (i.e., with recommended storage times)

$$\begin{aligned} \text{net acidity} &= \text{Hot Acidity}_{\text{Std. Meth.}} \\ &= \text{Acidity}_{\text{calculated(Eq. (14))}} - \text{Alkalinity}_{\text{Std. Meth.}} \end{aligned} \quad (22)$$

and this value can be positive or negative (Fig. 7). Eq. (22) holds true for field and synthetic samples, with zero measured Alkalinity, with considerable measured Alkalinity, and with considerable  $\text{CO}_2$  concentrations. It is not certain that Eq. (22) holds true for sample with  $\text{Alkalinity}_{\text{Std. Meth.}} > 50 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$  (Section 4.5). Thus, the Standard Method Hot Acidity titration gives a good estimate for net acidity, as defined here, rather than Acidity, *provided that negative Acidities are reported*. Similarly

$$\text{net alkalinity} = \text{Alkalinity}_{\text{Std. Meth.}} - \text{Acidity}_{\text{calculated(Eq. (14))}} \quad (23)$$

and using the definitions above

$$\text{net alkalinity} = -\text{net acidity} \quad (24)$$

with the same caveat for high Alkalinity samples.

#### 4.7. Acidity due to $\text{CO}_2$

Mine drainage samples from flooded underground mines and reclaimed surface mines can have high  $\text{CO}_2$  concentrations (Rose and Cravotta, 1998). Most of the  $\text{CO}_2$  degasses after the ground water reaches the surface and attains equilibrium with atmospheric  $\text{CO}_2$ . Standard texts (Stumm and Morgan, 1996; Langmuir, 1997) state that a pH increase results due to  $\text{CO}_2$  degassing, whereas Alkalinity is unaffected. We (unpublished data) have noted that pH values of mine discharges commonly increase downstream, suggesting  $\text{CO}_2$  degassing is more rapid than oxidation and hydrolysis of Fe and/or Mn. Figs. 4 and 6 show the influence of Acidity due to  $\text{CO}_2$  on titration results for both field and synthetic samples.

For many purposes associated with the treatment of mine drainage waters, it is not important to know the amount of Acidity due to  $\text{CO}_2$  in a water sample. If a solution to be treated reaches the surface laden with  $\text{CO}_2$ , the  $\text{CO}_2$  will degas sufficiently rapidly and lose most of this  $\text{CO}_2$ -derived Acidity within treatment systems open to the atmosphere. In this way, the  $\text{CO}_2$ -derived Acidity is ephemeral, and it does not require treatment.

Limestone is commonly used in passive mine drainage treatment. Calcite dissolves more completely and more rapidly at higher  $\text{CO}_2$  partial pressures; this fact

Table 8

Correct interpretation of alkalinity and acidity values ( $\text{mg L}^{-1} \text{CaCO}_3$ )

Water	pH	Acidity <sub>calc</sub> (Eq. (14))	Alk <sub>meas</sub> (Std. Meth.)	Acidity <sub>meas</sub> (Std. Meth.)	True net acidity <sup>a</sup>	True net alkalinity <sup>b</sup>	Requires additional alkalinity for treatment?
A	6.2	100	105	−5	−5	5	No
B	6.1	150	100	50	50	−50	Yes, 50 mg/L

<sup>a</sup> Negative numbers denote net alkaline water.<sup>b</sup> Negative numbers denote net acid water.

Table 9

Incorrect interpretation of Alkalinity and Acidity values ( $\text{mg L}^{-1} \text{CaCO}_3$ )

Water	pH	Alk <sub>meas</sub> (Std. Meth.)	Acidity <sub>meas</sub> (Std. Meth.)	Incorrect net acidity <sup>a</sup> (Alk <sub>meas</sub> − Acid <sub>meas</sub> )	Incorrect net alkalinity <sup>b</sup> (Acid <sub>meas</sub> − Alk <sub>meas</sub> )	Apparently requires additional alkalinity for treatment?
A	6.2	105	−5 (or 0)	−110 (or −105)	110 (or 105)	No
B	6.1	100	50	−50	50	No ( <i>incorrect</i> , needs 50 mg/L)

<sup>a</sup> Negative numbers denote apparently net alkaline water.<sup>b</sup> Negative numbers denote apparently net acid water.

may be one reason to attempt to measure CO<sub>2</sub>-derived Acidity. Anoxic limestone drains are components of passive mine drainage treatment systems that depend upon high CO<sub>2</sub> partial pressures to ensure adequate treatment (Hedin and Watzlaf, 1994). If the measurement of CO<sub>2</sub>-derived Acidity is required, then the standard methods are not appropriate because they intentionally degas CO<sub>2</sub> before the titration. The measurement of CO<sub>2</sub> Acidity in mine water is difficult (Langmuir, 1997). If desired, one could estimate the Acidity due to CO<sub>2</sub> using the calculated acidities based on PHREEQC simulations as demonstrated in Kirby and Cravotta (2005).

#### 4.8. Formal practical net alkalinity definition 1 – calculated

A formal, widely accepted definition of net alkalinity (or net acidity) is not available, but there is a clear need for guidance to workers designing passive mine drainage treatment. Theoretical mathematical definitions of Alkalinity and Acidity and their use to define and calculate net alkalinity are examined in Kirby and Cravotta (2005). Alkalinity and Acidity are not useful as solely theoretical concepts (Morel and Hering, 1993). In their mathematical definitions, Alkalinity and Acidity each have both positive and negative contributions. As defined by laboratory practices, an Alkalinity titration measures (in most cases) only positive contributions, primarily HCO<sub>3</sub><sup>-</sup> in mine waters. In contrast, Hot Acidity titrations can be said to either (1) provide a net acidity value that includes neutralization of some original sample Acidity by original sample HCO<sub>3</sub><sup>-</sup> or (2) underestimate the positive contributions from non-CO<sub>2</sub> Acidity.

Based on these observations and on other arguments in this paper, we propose the use of

$$\begin{aligned} \text{net alkalinity} &= -\text{net acidity} \\ &= \text{positive Alkalinity contributions} \\ &\quad - \text{positive non-CO}_2 \\ &\quad \text{Acidity contributions.} \end{aligned} \quad (25)$$

The Standard Method for Alkalinity (APHA, 1998b) provides a value for the positive Alkalinity contributions. Positive non-CO<sub>2</sub> Acidity as mg L<sup>-1</sup> as CaCO<sub>3</sub> can be calculated using Eq. (9) (Hedin et al., 1994 or by using Eq. (10), which requires complete speciation of dissolved species. Thus, the first formal practical definition is given in Eq. (15), which is closely equivalent to calculating net alkalinity using

$$\begin{aligned} \text{net alkalinity} &= \text{Alkalinity}_{\text{measured}} \\ &\quad - \text{Acidity}_{\text{calculated}}, \text{ Eq. (10).} \end{aligned} \quad (26)$$

If a positive value for Eqs. (15) or (26) is obtained, no alkaline addition is required for treatment. If a negative value is obtained, the absolute value of Eqs. (15) or (26)

provides the quantity of alkaline addition required to produce a pH ≈ 6.3 solution with Fe, Mn, and Al essentially removed. Some environmental consultants and mine drainage researchers have used this approach for years, but no published justification is found in the literature.

A mine water that has been treated such that it can be released harmlessly to the environment would have net alkalinity ≥ 0. A sample with zero net alkalinity or acidity should have a pH of approximately 6.3 (=pK<sub>1</sub> for carbonic acid) where [H<sub>2</sub>CO<sub>3</sub>\*] ≈ [HCO<sub>3</sub><sup>-</sup>]. A pH of 6.3 also corresponds to the maximum buffering capacity for the H<sub>2</sub>O–CO<sub>2</sub> system (see (Kirby and Cravotta, 2005)). Solutions that are net alkaline would have [HCO<sub>3</sub><sup>-</sup>] > [H<sub>2</sub>CO<sub>3</sub>\*] + [metals] and pH values >6.3 after the solution has stabilized following metal reactions and CO<sub>2</sub> degassing. Stable solutions that are net acidic would have some combination of metal, H<sub>2</sub>CO<sub>3</sub>\*<sup>+</sup>, and H<sup>+</sup> concentrations > [HCO<sub>3</sub><sup>-</sup>] and pH values < 6.3.

The above discussion leaves aside some complications of the effect of speciation of metals and HSO<sub>4</sub><sup>-</sup> on Acidity and therefore net alkalinity. Kirby and Cravotta (2005) discuss these issues at greater length. Using the species calculated by PHREEQC and using the concentration rather than activity of H<sup>+</sup> to calculate Acidity is more rigorously correct than using Eq. (9) or (14), but the improvement in an Acidity estimate using the more rigorous approach is small in most cases (see Fig. 6(b)). Further research is needed to determine which approach is best for samples with Alkalinity > 50 mg L<sup>-1</sup> as CaCO<sub>3</sub>.

#### 4.9. Formal practical net alkalinity Definition 2 – measured

If negative values are reported by the lab, the Standard Method Hot Acidity (APHA, 1998a) value is equal to a consistent and useful net acidity value. An alternative equivalent approach to the use of Eq. (15) or (26) for calculating net alkalinity is suggested by the data in Fig. 7

$$\begin{aligned} \text{net alkalinity} &= -\text{measured Hot Acidity}_{(\text{APHA}, 1998a)}, \\ & \end{aligned} \quad (27)$$

and

$$\text{net acidity} = \text{measured Hot Acidity}_{(\text{APHA}, 1998a)}. \quad (28)$$

In addition, Eq. (13) also gives a reliable net acidity value.

#### 4.10. Examples of correct and incorrect interpretations of net alkalinity/net acidity

In Table 8, Alkalinity and Acidity values for two solutions have been correctly interpreted to give meaningful net alkalinity and net acidity values. The true net acidity

value is obtained by either (1) calculating ( $\text{Acidity}_{\text{Eq. (14)}} - \text{Alkalinity}_{\text{measured}}$ ) or (2) using the Standard Method Hot Acidity titration value (*with negative values* reported if obtained). The true net alkalinity is equal to the negative of the true net Acidity. Water A *does not* require the addition of alkalinity for treatment; Water B *does* require the addition of alkalinity for treatment.

In Table 9, Alkalinity and Acidity values for the same two solutions have been incorrectly interpreted to give erroneous net alkalinity and net acidity values. The incorrect net acidity value is obtained by ( $\text{Acidity}_{\text{measured}} - \text{Alkalinity}_{\text{measured}}$ ). Water A is net alkaline, but not by as much as indicated in Table 9. Importantly, Water B is incorrectly shown to be net alkaline; suggesting that no additional alkalinity is required for treatment; Water B *does indeed* require the addition of alkalinity for treatment.

## 5. Conclusions and recommendations

- (1) The Standard Method Hot Acidity (APHA, 1998a) titration result is actually a net acidity, and the text should be changed to recognize that this method always returns a net acidity, regardless of whether a negative value is obtained. The text should also recognize that changing the sign of this net acidity value gives net alkalinity, again regardless of whether the Hot Acidity value is positive or negative. EPA, ASTM, and other standard references should be made consistent with a revised Standard Method text; changes should require the reporting of negative Acidity values and a statement to the effect that net acidity rather than acidity is obtained. State regulatory agencies should ensure that their laboratories report negative acidity values.
- (2) Eqs. (3) or (11) should *not be used* to calculate net alkalinity. Their use will result in a falsely positive value and can thus result in the incorrect conclusion that a water is net alkaline and can “treat itself” with no alkaline addition, given aeration and adequate retention time in a pond or wetland (see Table 9 for a hypothetical example). From this study, the Site 20 sample (Tables 4 and 6) has a Standard Method Alkalinity of  $37 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$  and a Standard Method Acidity of  $30 \text{ mg L}^{-1}$ , giving an apparent net alkalinity of  $+7 \text{ mg L}^{-1}$ , suggesting that no alkaline addition is needed for treatment. However, following oxidation, precipitation of metals, and  $\text{CO}_2$  degassing during storage, this water has a pH of 5.0. Iron oxidation at this pH would be  $\approx 100$  times slower than at pH 6.5, (Kirby et al., 1999), further complicating passive treatment. Calculation of net alkalinity using Eqs. (15) or (26) correctly gives a net alkalinity of  $-14 \text{ mg L}^{-1}$ , demonstrating that this water indeed requires alkaline addition for successful treatment.
- (3) The use of Eq. (10) for calculation of non- $\text{CO}_2$  Acidity (see also (Kirby and Cravotta, 2005)) is recommended for practitioners familiar with geochemical modeling because the results are rigorously correct for a wide range of solutions. A limitation with this approach is that it requires complete water chemistry data for filtered samples that commonly are not available. Furthermore, because of the steep learning curves associated with geochemical modeling, such an approach is not recommended for those unfamiliar with the concepts of aqueous speciation and mineral equilibria.
- (4) Positive (+) Acidity contributions can be calculated using data for pH and dissolved metals concentrations in Eq. (14). Data from Watzlaf et al. (2004) and Hedin (2004) for samples with  $< 15000 \text{ mg L}^{-1}$  Acidity as  $\text{CaCO}_3$  support this approach. Distinguishing between  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  in Eq. (9) does not appear to be critical for most waters, although it is likely that  $\text{Fe}^{\text{III}}$  predominates for most solutions with  $\text{pH} < 3$  and  $\text{Fe}^{\text{II}}$  predominates at higher pH.
- (5) In order to treat borderline net alkaline water with high initial calculated Acidity, it would be best to add more alkalinity than the calculated need if technically and financially feasible.
- (6) *If negative values are reported* by the lab, the Standard Method Hot Acidity titration (APHA, 1998a) returns a consistent net Acidity that can be reliably used to determine the amount of alkalinity required for adequate treatment. Using Hot Acidity results has a distinct advantage over other methods – it requires minimal sampling effort (no filtration or preservation) and only a single titration – although the titration is labor-intensive due to the boiling and cooling steps. Eqs. (13), (15) or (26), which require more data, may be used as quality control checks for the Hot Acidity titration.
- (7) There are some questions about the behavior of Mn, Ca, and Mg in Hot Acidity titrations and in active and passive mine drainage treatment. We observed that Mn solid precipitation occurred at considerably higher pH than predicted by PHREEQC. Means and Tilton (2004) suggested that not all Mn is oxidized in Acidity titrations, and thus Mn-Acidity may be underestimated. In many passive treatment scenarios, Mn is not successfully oxidized because virtually all Fe must be removed before Mn oxidation can occur (Hedin et al., 1994). The lack of Mn oxidation/removal

may be deemed acceptable for some abandoned mine discharges where there are no specific regulatory requirements for Mn removal. Means and Tilton (2004) suggest that Ca and Mg can be counted as Hot Acidity for some high-Ca and high-Mg solutions.

The interpretation of Alkalinity and Acidity is most problematic for near-neutral pH, metal-laden mine water discharges that contain Alkalinity. Such discharges can have very high flow rates and can contribute considerably to the total metal loading of a watershed (Cravotta and Kirby, 2004a; Cravotta, 2005). A decision not to use supplemental alkalinity sources such as limestone (or to use too little limestone) in treatment design for a mine discharge can result in inadequate treatment, perhaps in a very high-cost treatment system. Such a result is clearly undesirable because the treated effluent could remain net acidic. A clear understanding of the meaning of the net alkalinity and appropriate methods for its determination are needed to avoid the construction of a poorly functioning and/or inadequate treatment system.

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