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

Charles A. Cravotta III[2] and Carl S. Kirby[2]

Abstract. In this paper, we emphasize that the Standard Method hot peroxide treatment procedure for acidity determination (hot acidity) directly measures net acidity or net alkalinity, but that more than one water-quality measure can be useful as a measure of the severity of acid mine drainage. We demonstrate that the hot acidity is related to the pH, alkalinity, and dissolved concentrations of Fe, Mn, and Al in fresh mine drainage. We show that the hot acidity accurately indicates the potential for pH to decrease to acidic values after complete oxidation of Fe and Mn, and it indicates the excess alkalinity or that required for neutralization of the sample. We show that the hot acidity method gives consistent, interpretable results on fresh or aged samples.

Regional data for mine-drainage quality in Pennsylvania indicated the pH of fresh samples was predominantly acidic (pH 2.5 to 4) or near neutral (pH 6 to 7); approximately 25 percent of the samples had intermediate pH values. This bimodal frequency distribution of pH was distinctive for fully oxidized samples; oxidized samples had acidic or near-neutral pH, only. Samples that had near-neutral pH after oxidation had negative hot acidity; samples that had acidic pH after oxidation had positive hot acidity. Samples with comparable pH values had variable hot acidities owing to variations in their alkalinities and dissolved Fe, Mn, and Al concentrations. The hot acidity was comparable to net acidity computed on the basis of initial pH and concentrations of Fe, Mn, and Al minus the initial alkalinity. Acidity computed from the pH and dissolved metals concentrations, assuming equivalents of 2 per mole of Fe and Mn and 3 per mole of Al, was comparable to that computed on the basis of aqueous species and Fe^{II}/Fe^{III}. Despite changes in the pH, alkalinity, and metals concentrations, the hot acidities were comparable for fresh and aged samples. Thus, meaningful "net" acidity can be determined from a measured hot acidity or by calculation from the pH, alkalinity, and dissolved metals concentrations. Together, these water-quality data can be useful for evaluating the potential for toxicity, corrosion, or encrustation and can be helpful for determining the appropriate remediation. By demonstrating the measurements on fresh and aged samples, we hope to encourage (1) consistent use of the hot peroxide treatment procedure for acidity determination and (2) consistent reporting of negative acidity values.

---

[1]Paper was presented at the 2004 National Meeting of the American Society of Mining and Reclamation and the 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

[2]Charles A. Cravotta III is Research Hydrologist, U.S. Geological Survey, New Cumberland, PA 17070. Carl S. Kirby is Associate Professor, Department of Geology, Bucknell University, Lewisburg PA 17837.

Proceedings America Society of Mining and Reclamation, 2004 pp 334-365
DOI: 10.21000/JASMR04010334
https://doi.org/10.21000/JASMR04010334

Introduction

Acidic, 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). AMD ranges widely in quality from mildly alkaline to strongly acidic and corrosive, with dissolved solids ranging from about 200 to 10,000 mg/L (Hyman and Watzlaf, 1997; Rose and Cravotta, 1998; Nordstrom and Alpers, 1999). AMD characteristically has elevated concentrations of dissolved sulfate, iron, 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 iron (Fe), aluminum (Al), and manganese (Mn) in mine effluent and receiving water bodies commonly are measured to identify potential for environmental effects (Commonwealth of Pennsylvania, 1998a, 1998b, 2002; U.S. Environmental Protection Agency, 2000, 2002a, 2002b). These parameters also are measured 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 is soluble at low pH, and compared to Fe and Mn, relatively low concentrations of dissolved Al can be toxic (Elder, 1988). Accordingly, the U.S. Environmental Protection Agency (2000, 2002a, 2002b) recommends pH 6.5 to 8.5 for public drinking supplies and pH 6.5 to 9.0 for protection of freshwater aquatic life. Furthermore, the Commonwealth of Pennsylvania (1998a, 1998b, 2002) stipulates that effluent discharged from active mines must have pH 6.0 to 9.0 *and* alkalinity greater than acidity.

Different alternatives for treatment of AMD could be appropriate depending on the volume of the mine discharge, its alkalinity and acidity balance, and the available resources for construction and maintenance of a treatment system (Hedin *et al*., 1994; Skousen *et al*., 1998). if the effluent is “net alkaline,” the alkalinity exceeds the acidity and the pH will remain near neutral after complete oxidation of the effluent. Systems that facilitate aeration of the effluent and retention of precipitated solids are indicated. On the other hand, if the effluent is “net

acidic," the acidity exceeds the alkalinity and the pH will decline to acidic values after complete oxidation and precipitation of the dissolved metals. Systems that add alkalinity and that maintain or increase pH are indicated.

Although the correct determination of 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; U.S. Environmental Protection Agency, 1979a; American Public Health Association, 1998a; Desmier *et al*., in press). Furthermore, criteria for determination of net-acidic or net-alkaline solutions have been poorly defined by regulatory authorities and misapplied by many practitioners. Typically, the net acidity of AMD is computed by subtracting the alkalinity from the measured "hot" acidity, 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, 1998b). However, as argued by Kirby (2002), the difference between measured hot acidity and alkalinity can underestimate the alkalinity requirement and, consequently, result in incorrect identification of treatment alternatives and/or inadequate treatment. Recently, others have agreed with Kirby (2002) that hot acidity results should be interpreted as "net acidity." As will be shown in this paper, the correct interpretation of hot-acidity data is critical for solutions containing alkalinity and acidity in the form of dissolved metals. However, the hot acidity may not be analyzed or may be reported incorrectly as zero for such samples.

Purpose and Scope

This report examines the calculation and interpretation of the "net acidity" or "net alkalinity" on the basis of commonly measured water-quality data; it complements a companion report by Kirby and Cravotta (this volume) that explains the theoretical basis for the measurement and interpretation of acidity and alkalinity. First, background information on the geochemistry of AMD is presented. Second, field and laboratory data that were acquired during 1999-2003 for a wide variety of AMD sources in the Anthracite and Bituminous Coalfields in Pennsylvania are used to illustrate relations among the pH, alkalinity, acidity, and dissolved solute concentrations and to develop guidelines for their measurement and interpretation.

Background

AMD is characterized by elevated concentrations of dissolved sulfate (SO_4^{2-}), ferrous iron (Fe^{2+}), and ferric iron (Fe^{3+}) and colloidal or particulate Fe^{III} compounds that are produced by the microbial oxidation of reduced forms of sulfur and iron in pyrite (FeS_2):

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad (1)$$

$$Fe^{2+} + 0.25\ O_2 + 2.5\ H_2O \rightarrow Fe(OH)_3\,(s) + 2\ H^+ \quad (2)$$

The complete, stoichiometric oxidation of pyrite by oxygen (O_2) is indicated by combining Equations 1 and 2. Half the protons (H^+), or acid, produced by the complete oxidation of pyrite results from the oxidation of pyritic sulfur to SO_4^{2-} (Eqn. 1) and the other half results from the oxidation of Fe^{II} to Fe^{III} and its consequent precipitation as $Fe(OH)_3$ (Eqn. 2).

To avoid confusion between the identity of the aqueous ions and complexes shown in reactions and the analytical concentrations of chemical constituents, symbols for the total analytical concentration of chemical constituents are indicated without regard to valence, such as Fe and SO_4. Symbols with superscripted roman numerals are used to indicate the sum of aqueous species with a specific redox state, for example Fe^{II}, Fe^{III}, and Mn^{II}.

The "$Fe(OH)_3$" shown in Equation 2 is symbolic for the hydrous Fe^{III} oxide and sulfate minerals that together form ochres in AMD environments, including goethite (α–FeOOH), ferrihydrite (nominally $Fe_5HO_8{\cdot}4H_2O$), and schwertmannite ($Fe_8O_8(OH)_6SO_4$) (Bigham *et al*., 1996; Bigham and Nordstrom, 2000; Yu *et al*., 1999; Williams *et al*., 2002). Generally, ferrihydrite is the predominant precipitate from near-neutral AMD, whereas schwertmannite is predominant for low-pH AMD; however, both these minerals are metastable, ultimately recrystallizing to form goethite (Bigham *et al*., 1996; Yu *et al*., 1999; Williams *et al*., 2002). The transformation of schwertmannite to goethite can cause the associated solution pH to decrease and concentration of SO_4 to increase (Miller, 1980; Bigham *et al*., 1996).

Near-neutral AMD can form from rock that contains little pyrite or can originate as acidic AMD that has been neutralized by reaction with calcite ($CaCO_3$) and other minerals containing Ca, Mg, K, and Na. For example, dissolution of $CaCO_3$ neutralizes acid and can increase the pH and alkalinity of AMD:

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^- \quad (3)$$

The alkalinity of near-neutral AMD can be attributed almost entirely to bicarbonate (HCO_3^-) derived from the dissolution of carbonate minerals (Eqn. 3) and, to a lesser extent, the microbial reduction of SO_4 (Hedin *et al*., 1994; Rose and Cravotta, 1998). 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} generally will not be controlled by the precipitation of hydroxides (Cravotta and Trahan, 1999; Cravotta *et al*., 1999). However, 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).

As reported previously (Wood, 1976; Wood, 1996) and indicated with data presented later in this paper, the pH and alkalinity of AMD and other ground-water samples can be unstable. The pH, alkalinity, and associated properties potentially can change as the sample equilibrates to atmospheric conditions because of the exsolution of dissolved carbon dioxide (CO_2) and hydrogen sulfide (H_2S), the dissolution of O_2, and the consequent oxidation of Fe^{II} and Mn^{II} and the hydrolysis of Fe^{III} and Mn^{IV}. Sample instability results because the chemical reactions that establish equilibrium between the gaseous, aqueous, and solid phases in a system are not instantaneous but proceed at different rates. For example, aeration of AMD can rapidly saturate AMD with O_2 and promote the exsolution of CO_2 and H_2S. Although, the pH ultimately may decrease to acidic values because of the oxidation of Fe^{II} and the consequent precipitation of $Fe(OH)_3$ (Eqn. 2), initially, the Fe^{II} may persist in solution as dissolved CO_2 exsolves and pH increases:

$$HCO_3^- \leftrightarrow CO_2\,(g) + OH^- \qquad (4)$$

$$H_2CO_3^* \leftrightarrow CO_2\,(g) + H_2O \qquad (5)$$

where $[H_2CO_3^*] = [CO_2\,(aq)] + [H_2CO_3^o]$ (Stumm and Morgan, 1996). Ground water and coal-mine drainage commonly contain elevated concentrations of dissolved CO_2 in association with elevated partial pressure of gaseous CO_2 (Pco_2) of $10^{-1.5}$ to $10^{-0.5}$ 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_2 eventually will exsolve until concentrations of dissolved CO_2 equilibrate with atmospheric Pco_2 of $10^{-3.5}$ atm. The exsolution of CO_2 from the AMD (Eqns. 4 and 5 go to the right) can be accelerated by aggressive aeration

(Jageman *et al*., 1988) or heating of the solution (Langmuir, 1997; American Society for Testing and Materials, 2000). Note that if solids are not dissolved or precipitated as CO_2 exsolves, the acidity due to H_2CO_3* will decrease and the pH will increase while the alkalinity is conserved (Cravotta and Hilgar, 2000). In some cases, the increased pH could result in saturation with $CaCO_3$ (calcite or aragonite) and its precipitation by the reverse of Equation 3. The precipitation of $Fe(OH)_3$ and other solids, including $CaCO_3$, 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^+ as a product of oxidation, hydrolysis, and precipitation processes, can be measured or computed as the "acidity" of a solution. The acidity of AMD results mainly from the potential for hydrolysis of dissolved Fe^{II}, Fe^{III}, Al, and Mn^{II} and the precipitation of associated solid hydroxide compounds. Generally, except for extremely low-pH solutions, dissolved Fe in AMD is predominantly Fe^{II}. Because dissolved CO_2 tends to be minimized by aeration of water under atmospheric conditions, its acidity contribution is considered temporary and thus is not counted by methods used to measure or compute the acidity of AMD (Rose and Cravotta, 1998; Kirby and Cravotta, this volume). if a sample has acidity in excess of alkalinity (net acidic), the pH ultimately can decline to acidic values (pH < 4.5). For example, during 1999-2001, the streamwater in Shamokin Creek near Shamokin, Pa., as it exited the coal-mined part of the watershed was consistently near-neutral with pH 5.9 to 6.4, but it was net acidic with elevated concentrations of dissolved SO_4 and Fe^{II} ranging from 260 to 370 mg/L and 10 to 15 mg/L, respectively (Cravotta and Kirby, 2003). Despite dilution by "clean" tributaries that more than doubled the streamflow of Shamokin Creek at Sunbury, 32 km downstream from Shamokin, during 1999-2001, the streamwater at Sunbury had pH as low as 4.0 and dissolved SO_4 and Fe^{II} concentrations as high as 280 mg/L and 1.7 mg/L, respectively. Cravotta and Kirby (2003) attributed the decline in pH to the oxidation and hydrolysis of dissolved Fe^{II} and a corresponding deficiency of alkalinity necessary to buffer the acid generated by this process.

The rate of oxidation of dissolved Fe^{II} can be slow under environmental conditions, depending on the temperature, pH, concentrations of dissolved O_2 and Fe^{II}, and activities of biological and/or abiological catalysts (Nordstrom, 1985; Stumm and Morgan, 1996; Kirby *et al*., 1999). Although dissolved CO_2 may equilibrate with the atmosphere and Fe^{II} can be

oxidized in a timeframe 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 (U.S. Environmental Protection Agency, 1979a; American Public Health Association, 1998a; American Society for Testing and Materials, 2000) in which the sample is initially titrated with sulfuric acid (H_2SO_4) to pH ~ 4.0, unbuffered hydrogen peroxide (H_2O_2) is added, and then the sample is boiled and cooled prior to titration with sodium hydroxide (NaOH) to the endpoint pH of 8.2 or 8.3. The first two steps promote the exsolution of CO_2 and the oxidation of dissolved Fe^{II} and Mn^{II}. Except for the endpoint pH of 8.2 for the U.S. Environmental Protection Agency (1979a) and the endpoint pH of 8.3 for the American Public Health Association (1998a) and American Society for Testing and Materials (2000), these "hot peroxide treatment" procedures for measuring acidity are equivalent. Hereinafter, acidity measured by these methods is referred to as the "hot" acidity.

Methods of Data Collection and Analysis

Sample Site Selection

Field and laboratory data were acquired for the chemistry of nearly 200 abandoned coal-mine drainage sites in Pennsylvania that represented a wide range of solution compositions. In all these samples, dissolved iron, manganese, and/or aluminum 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 (Fig. 1) were sampled for analysis of chemical concentrations and loading (Cravotta *et al*., 2001). The 99 bituminous discharges previously had been studied by the Southern Alleghenies Conservancy (1998). The 41 anthracite discharges previously had been studied by the U.S. Geological Survey (USGS) (Growitz *et al*., 1985; Wood, 1996). Nevertheless, these prior reports did not include data on the "hot" acidity or the pH of oxidized samples.

In March 2000, discharges from 45 abandoned anthracite mines in the Shamokin Creek Basin, Western Middle Anthracite Field, Pa., were sampled to assess the effects of AMD on the

streamwater quality (Cravotta and Kirby, 2003). Most of these discharges were from underground mines, but seepage from spoil also was sampled. These data included values for "hot" acidities and dissolved metals, but they did not include the pH of oxidized samples. Lastly, in June 2003, discharges from eight abandoned, underground anthracite mines in the Wiconisco Creek, Swatara Creek and Schuylkill River Basins, Southern Anthracite Field, Pa., were sampled and analyzed by various methods for this study to evaluate differences among the methods for acidity determination, effects of sample storage, and associated relations among the acidities, pH, alkalinity, and metals concentrations.

Water-Quality Sampling and Analysis

In accordance with standard methods, field data for flow rate, temperature, specific conductance (SC), dissolved O_2, pH, and redox potential (Eh) were measured at each site when samples were collected (Rantz *et al*., 1982a, 1982b; Wood, 1976; U.S. Geological Survey, 1997 to present; Ficklin and Mosier, 1999). All meters were calibrated in the field using electrodes and standards that had been thermally equilibrated to sample temperatures. Field pH and Eh were determined using a combination Pt and Ag/AgCl electrode with a pH sensor. The electrode was calibrated in pH 2.0, 4.0, and 7.0 buffer solutions and in Zobell's solution (Wood, 1976; U.S. 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). Water samples were collected into sample-rinsed 3-L Teflon bottles and then split into sample-rinsed polyethylene bottles. An unfiltered subsample for analysis of acidity and alkalinity was capped leaving no head space and stored on ice. Two subsamples for analysis of "dissolved" anions and cations plus silica were filtered through a 0.45-µm pore-size nitrocellulose capsule filter. The subsample for cation analysis was preserved with nitric acid to pH < 2.

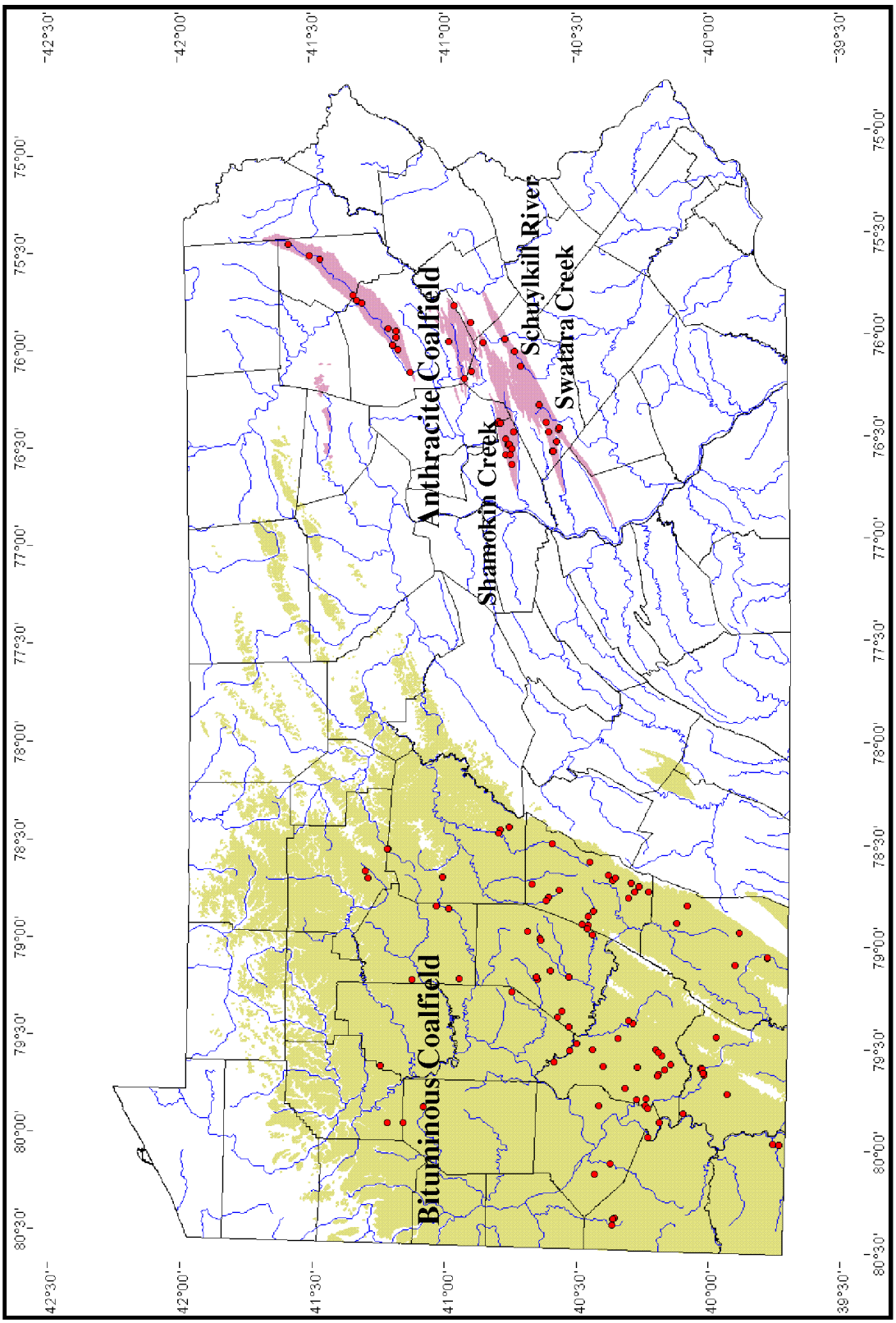

Figure 1. Map of Pennsylvania showing locations of 140 abandoned mine discharge sites in the Anthracite and Bituminous Coalfields that were sampled in 1999 by the USGS (Cravotta *et al.*, 2001) and locations of Shamokin Creek, Swatara Creek, and Schuylkill River Basins. Coalfield boundaries based on distribution of Pennsylvanian Age bedrock (Berg *et al.*, 1980).

All samples were processed using consistent, standard methods for analysis of alkalinity, anions, and cations. The unfiltered subsamples were analyzed for alkalinity in the laboratory within 48 hours of sampling by titration with H_2SO_4 to the endpoint pH of 4.5 (U.S. Environmental Protection Agency, 1979b; American Public Health Association, 1998b; American Society for Testing and Materials, 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 solution. Sulfate and chloride in the filtered, unpreserved samples were analyzed by ion chromatography (IC) (Fishman and Friedman, 1989; Crock *et al*., 1999). Concentrations of major cations, silica, and trace elements in the filtered, acidified samples were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma emission mass spectrometry (ICP-MS) (Fishman and Friedman, 1989; Crock *et al*., 1999). All samples collected in 1999 were analyzed in replicate by one or more of the methods and at two or more laboratories. Results for replicate analyses were averaged. Charge imbalances routinely were less than 5% relative to the mean of cation and anion equivalents.

Initially, for the 140 AMD samples collected in 1999, only the "cold" acidity was measured based on the first author's judgment that the "hot" acidity would be redundant with other available data for the computed acidity and alkalinity. The "cold" acidity was measured in the laboratory within 48 hours of sampling by titration at ambient temperature with NaOH to the endpoint pH of 8.3 after the addition of H_2O_2; samples containing alkalinity were not initially titrated with H_2SO_4, and samples were not boiled. In 2003, after discussion with A. W. Rose (2003, written commun.) and the second author about potential for the "hot" acidity of stored samples to be stable, 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 (American Public Health Association, 1998a, 1998b). These data were considered necessary to evaluate measured and computed acidity and the ultimate potential for pH to be acidic or neutral. In figures illustrating the data, these measurements on "aged" samples are identified accordingly.

For the Shamokin AMD samples collected in March 2000 and the Wiconisco-Swatara-Schuylkill AMD samples collected in June 2003, the standard method "hot" acidity (American Public Health Association, 1998a) was measured on unfiltered samples in the laboratory within

48 hours of sampling. For Shamokin AMD samples that had pH > 6.5, the "hot" acidity values were reported as "zero" when, if fact, titrations were not actually performed on these samples. As discussed later, some of these samples would have reported positive hot acidity titration values and others negative values.

To evaluate differences among the methods for acidity determination, effects of sample storage, and associated relations among the acidities, pH, alkalinity, and metals concentrations, various measurements of pH, alkalinity, and acidity were performed for the Swatara-Schuylkill AMD samples. In addition to its measurement in the field, the pH was measured on stored samples, with and without H_2O_2 added, within 24 hours of sampling, after 7 days, and after 5 months. Alkalinity, "hot" acidity, and "cold" acidity also were measured on the fresh and 5-month old samples by methods described above.

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^{II} and Fe^{III} species were computed on the basis of the Eh, temperature, and ionic strength of fresh samples. Nordstrom (1977) and Nordstrom *et al*. (1979) have shown there is good agreement between the measured Eh and that predicted by the Fe^{II}/Fe^{III} couple in acidic mine waters. Results expressed as molalities for selected species were used to compute the acidity due to H^+ and dissolved metals.

PHREEQC (Parkhurst and Appelo, 1999) also was used to simulate the acidimetric titration of the Swatara-Schuylkill samples with NaOH. Modeled solutions were oxidized by O_2 and equilibrated with atmospheric CO_2. The pH was decreased from the initial values by fixing pH to 4.0 with H_2SO_4, and then the pH was increased by adding aliquots of NaOH. Specific solid phases, including ferrihydrite and amorphous $Al(OH)_3$, were allowed to precipitate to maintain solubility equilibrium. Charge balance was established by adjusting sulfate concentration prior to speciation computations.

Computation of Acidity and Net alkalinity

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

$$\text{Acidity}_{\text{computed}}\ (\text{mg/L CaCO}_3) = 50\cdot(10^{(3\text{-pH})} + 2\cdot C_{Fe}/55.8 + 2\cdot C_{Mn}/54.9 + 3\cdot C_{Al}/27.0) \qquad (6)$$

Hedin *et al*. (1994) and Rose and Cravotta (1998) described a similar computation in which separate contributions from dissolved Fe^{II} and Fe^{III} are considered; this method also was evaluated. Nevertheless, owing to its relatively low solubility and 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 Equation 6, acid equivalents as H^+ (OH^- neutralizing capacity) of 2 per mole of Fe and Mn and 3 per mole of Al were assumed based on the relevant hydrolysis constants, pK_1 and pK_2, at 25 °C from 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, $Fe^{2+} \leftrightarrow Fe(OH)^+$; pK_1 = 10.6, $Mn^{2+} \leftrightarrow Mn(OH)^+$). 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, $Fe^{3+} \leftrightarrow Fe(OH)^{2+}$; pK_2 = 3.5, $Fe(OH)^{2+} \leftrightarrow Fe(OH)_2^+$). At pH < 5, uncomplexed Al^{3+} ions, with 3 equivalents per mole, tend to be dominant (pK_1 = 5.0, $Al^{3+} \leftrightarrow Al(OH)^{2+}$; pK_2 = 5.2, $Al(OH)^{2+} \leftrightarrow Al(OH)_2^+$). Because SO_4^{2-} is a principal component and is not involved in hydrolysis reactions at pH 8.3, the formation of metal-sulfate complexes does not affect the equivalent acidities of the dissolved metals.

Considering the different tendencies for metal hydrolysis and corresponding differences in the OH^- neutralizing capacities for various aqueous species, a more precise estimate of the acidity can be computed

$$\text{Acidity}_{\text{speciated}}\ (\text{mg/L CaCO}_3) = 50\cdot\Sigma\ (e_i \cdot mM_i) \qquad (7)$$

where the concentration for each species (mM_i) in millimoles is multiplied by its acid equivalents per millimole (e_i). Kirby and Cravotta (this volume) provide a detailed explanation of the acidity contributions due to different aqueous species. The acid equivalent values ranged from -1 to +4 on the basis of the principal aqueous components at the titration endpoint pH of

8.3. Because the titrated acidity measures base consumption by all hydrolyzable species, the acidity computed on the basis of aqueous speciation considered contributions from Fe^{II}, Fe^{III}, Mn^{II}, and Al species, plus bisulfate (HSO_4^-) and associated complexes. For example, values were assigned for equivalent acidity of -1 for $Al(OH)_4^-$, 0 for $Al(OH)_3^0$, 1 for $Al(OH)_2^+$, 2 for $Al(OH)^{2+}$, 3 for Al^{3+} and $AlSO_4^+$, and 4 for $AlHSO_4^{2+}$, with consistent values for other metal species (Kirby and Cravotta, this volume).

The "net alkalinity" was computed by subtracting the computed acidity from the measured, fresh alkalinity:

$$\text{Net alkalinity (mg/L } CaCO_3) = \text{Alkalinity - Acidity}_{\text{computed}} \quad (8)$$

The "net acidity" is simply the opposite of the net alkalinity:

$$\text{Net acidity (mg/L } CaCO_3) = \text{-Net alkalinity} = \text{Acidity}_{\text{computed}} - \text{Alkalinity} \quad (9)$$

According to Kirby and Cravotta (this volume), the net acidity computed by Equation 9 should be comparable in value to the "hot" acidity where the H_2SO_4 added to the sample is subtracted from the NaOH added.

Comparison of Measured and Computed Acidity with pH of Mine Drainage

Data on the pH, acidity, alkalinity, and selected solute concentrations for the 140 AMD samples collected in 1999 from abandoned coal mines in the Anthracite and Bituminous Coalfields of Pennsylvania are summarized in Table 1 and Fig. 2. Sampled flow rates at the 140 AMD sites ranged from 0.01 to 132 m^3/min. Median flow rates for the anthracite mine discharges generally exceeded those for the bituminous mines (Table 1, Fig. 2). The differences in median flow rates reflect differences in the physiographic and geologic settings between the two coalfields (Berg *et al*., 1989; Edmunds, 1999; Eggleston *et al*., 1999) and indicate that, on average, the anthracite mines have larger recharge areas and more extensive flooded volumes compared to the bituminous mines.

Table 1. Hydrochemical characteristics of discharges from 140 abandoned coal mines in Pennsylvania, 1999[a]
[median (minimum; maximum)]

Coalfield & Number of Samples	Field Measurements			Laboratory Measurements								
	Flow Rate (m^3/min)	Oxygen (mg/L)	pH, field (units)	pH, lab aged (units)	Alkalinity	Acidity, computed[b]	Acidity, hot [c]	Acidity, cold	Sulfate	Iron	Manganese	Aluminum
					(mg/L as $CaCO_3$)				(mg/L; 0.45-µm filtered)			
Anthracite N=41	3.84 (0.01; 132)	1.9 (0.3; 11.1)	5.1 (3.0; 6.3)	4.4 (2.4; 8.1)	3 (0; 120)	51 (0; 702)	12 (-79; 588)	91 (19; 673)	260 (34; 1300)	15 (0.046; 312)	2.9 (0.019; 19)	0.280 (0.007; 26)
Bituminous N=99	0.75 (0.01; 16.7)	0.6 (0.2; 11.5)	5.2 (2.7; 7.3)	3.4 (2.2; 8.6)	14 (0; 510)	119 (1; 1587)	60 (-326; 754)	210 (20; 2340)	580 (120; 2000)	43 (0.16; 512)	2.3 (0.12; 74)	1.5 (0.008; 108)

a. Data from U.S. Geological Survey (Cravotta *et al.*, 2001). Sample site locations shown in Figure 1.
b. Acidity computed on the basis of Equation 6, assuming equivalents of 2 per mole of Fe and Mn and 3 per mole of Al.
c. Hot acidity of "aged" samples was measured on only 38 of 41 anthracite samples and 88 of 99 bituminous samples; some of the original samples were not archived or were not available.

Table 2. Hydrochemical characteristics of discharges from abandoned coal mines in the Shamokin Creek Basin, Western Middle Anthracite Field, 2000, and the Wiconisco Creek, Swatara Creek, and Schuylkill River Basins, Southern Anthracite Field, 2003[a]
[median (minimum; maximum); "n.d." no data]

Basin & Number of Samples	Field Measurements			Laboratory Measurements								
	Flow Rate (m^3/min)	Oxygen (mg/L)	pH, field (units)	pH, lab aged (units)	Alkalinity	Acidity, computed[b]	Acidity, hot	Acidity, cold	Sulfate	Iron	Manganese	Aluminum
					(mg/L as $CaCO_3$)				(mg/L; 0.45-µm filtered)			
W.Middle N=45	0.32 (0.02; 32.3)	5.2 (0.1; 12.6)	4.9 (2.6; 6.7)	n.d. (n.d.; n.d.)	2 (0; 116)	51 (1; 305)	25 (0; 306)	n.d. (n.d.; n.d.)	233 (8.4; 802)	7.0 (0.04; 57.4)	2.4 (0.01; 7.1)	0.62 (<.20; 35.8)
Southern N=8	2.05 (0.04; 7.57)	6.5 (0.9; 12.0)	4.4 (3.4; 6.0)	6.2 (2.7; 6.7)	0.6 (0; 45)	40 (22; 402)	6.2 (-23; 486)	75 (28; 377)	188 (75; 1090)	7.8 (0.16; 200)	1.9 (1.0; 8.2)	3.0 (0.005; 11.4)

a. Data from U.S. Geological Survey (Cravotta and Kirby, 2003, this volume). Basin locations shown in Figure 1.
b. Acidity computed on the basis of Equation 6, assuming equivalents of 2 per mole of Fe and Mn and 3 per mole of Al.

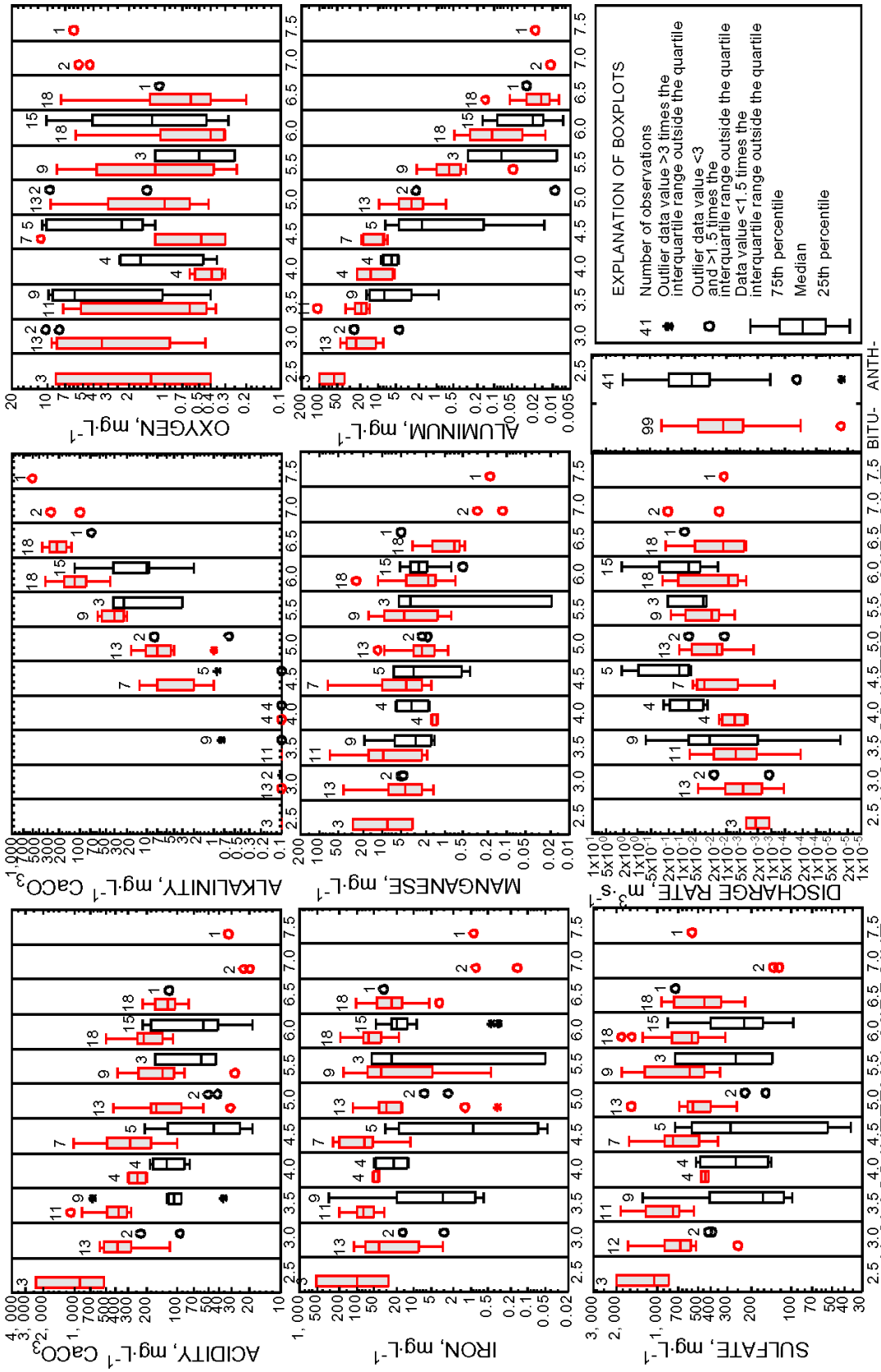

Figure 2. Boxplots showing concentrations of acidity, alkalinity, and dissolved solutes as a function of pH for 140 abandoned mine discharges in Pennsylvania sampled in 1999: *A*, computed acidity; *B*, alkalinity; *C*, oxygen; *D*, iron; *E*, manganese; *F*, aluminum; *G*, sulfate; *H*, flow rate.

The pH of the 140 fresh AMD samples ranged from 2.7 to 7.3 (Table 1). Concentrations of dissolved SO_4, Fe, Al, and Mn ranged from 34 to 2,000 mg/L, 0.046 to 512 mg/L, 0.007 to 108 mg/L, and 0.019 to 74 mg/L, respectively (Table 1). Although the median pH values for the anthracite and bituminous samples were similar, the minimum and maximum pH values were associated with bituminous mine discharges. The bituminous discharges also had greater median and maximum concentrations of alkalinity, acidity, SO_4, and other solutes than the anthracite discharges (Table 1, Fig. 2). The alkalinity was positively correlated with pH; acidity and dissolved Al concentrations were inversely correlated with pH; and SO_4, Fe, and Mn concentrations were not correlated with pH (Fig. 2). The general decline in dissolved Al concentration with increased pH is consistent with solubility control by Al hydroxide and hydroxysulfate minerals (e.g. Nordstrom and Ball, 1986; Bigham and Nordstrom, 2000). The lack of correlation between pH and concentrations of Fe and Mn implies these metals are not controlled by hydroxide mineral solubility. Median concentrations of dissolved O_2 generally were low (<2 mg/L) throughout the range of pH, consistent with the predominance of dissolved Fe^{II} and Mn^{II} species. The median SO_4, Fe, and acidity concentrations for bituminous discharges generally exceeded those for anthracite discharges at successive pH class intervals (Fig. 2). This implies that pyrite oxidation could be active in the bituminous mines and/or dilution with uncontaminated water is an important AMD attenuation mechanism for the anthracite mines. The elapsed time since mine flooding, access of air or oxygenated water, and remaining quantities of pyrite all could be important factors affecting SO_4, Fe, and acidity concentrations. Cravotta *et al*. (1999) discussed these and other environmental factors as they may affect the quality of effluents discharged from anthracite and bituminous mines.

The frequency distribution of pH of the 140 fresh AMD samples was bimodal (Figs. 2 and 3), with the majority either near neutral (pH 6 to 7) or acidic (pH 2.5 to 4), as documented for other regional data sets (e.g. Brady *et al*., 1997; Cravotta *et al*., 1999). Approximately 25 percent of the fresh AMD samples had pH values from 4.0 to 5.5. The bimodal pH frequency distribution was distinctive for the fully oxidized samples (Figs. 3, 4A, and 4B). The aged, oxidized samples had dominant modes at pH 2.5 to 4.5 and 6.0 to 8.5; none of the oxidized samples had intermediate pH values (Figs. 3 and 4B). The final oxidized pH for net acidic samples was approximated by the H_2O_2-treated samples (Fig. 4B). However, this method overestimated or

underestimated the ultimate pH for a large fraction of the acidic samples and all of the near-neutral samples, respectively. The range of pH for the aged, oxidized samples was nearly 2 units greater than that indicated by the H_2O_2-treated samples (Fig. 4B).

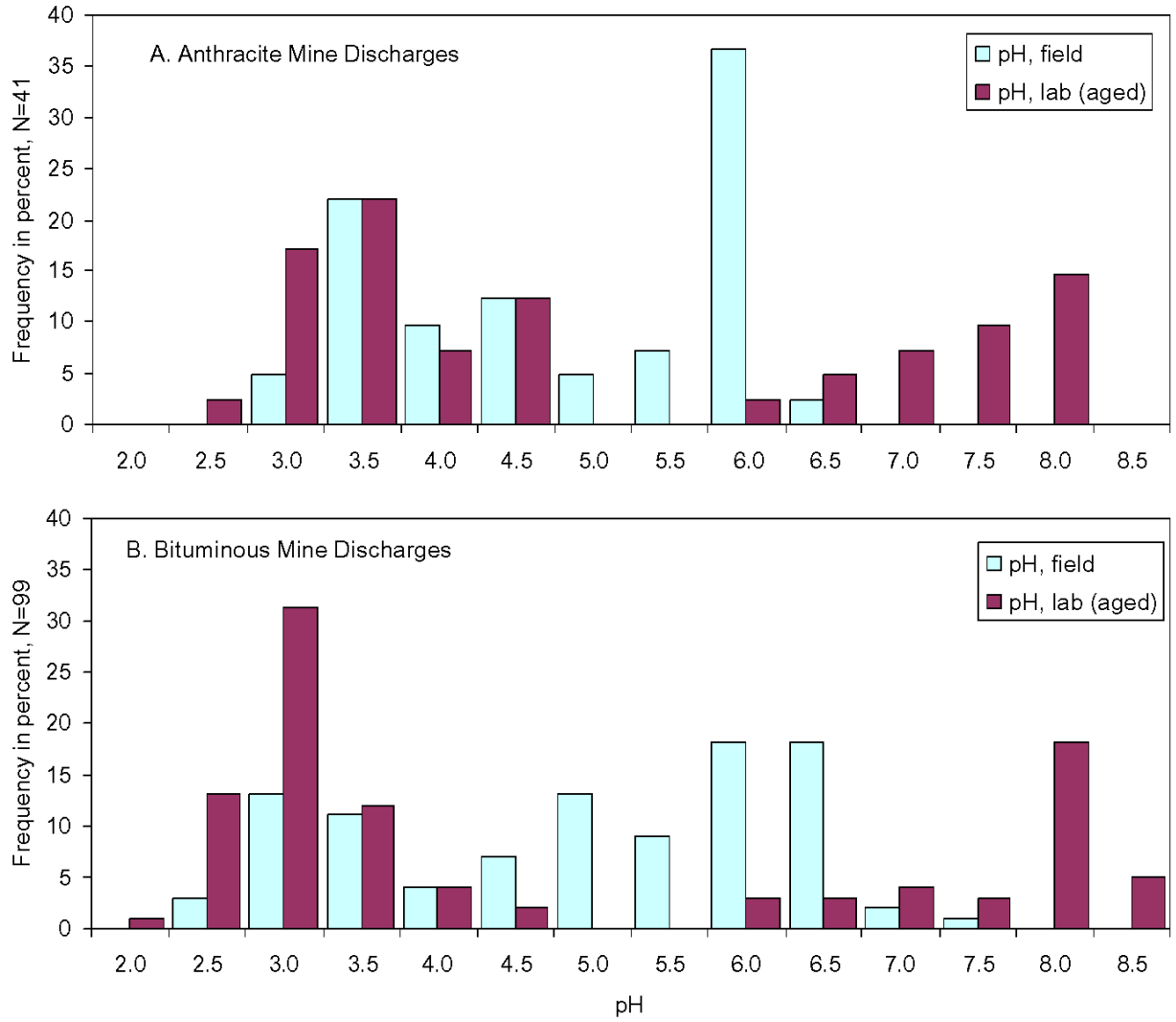

Figure 3. Frequency distribution for pH of 140 abandoned mine discharges in Pennsylvania sampled in 1999: *A*, Anthracite discharges; *B*, Bituminous discharges.

The differences between the pH of fresh, H_2O_2-treated samples and the aged samples could arise because the addition of H_2O_2 without boiling (1) does not promote CO_2 exsolution from high-pH samples, (2) does not result in complete oxidation of Fe^{II} and Mn^{II}, 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_4^{2-} and H^+ to solution (Bigham *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 generally could increase with aging as CO_2 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-yr old samples. Analysis of fresh and aged precipitates is needed to confirm the above hypothesis, and the length of time for equilibration is uncertain.

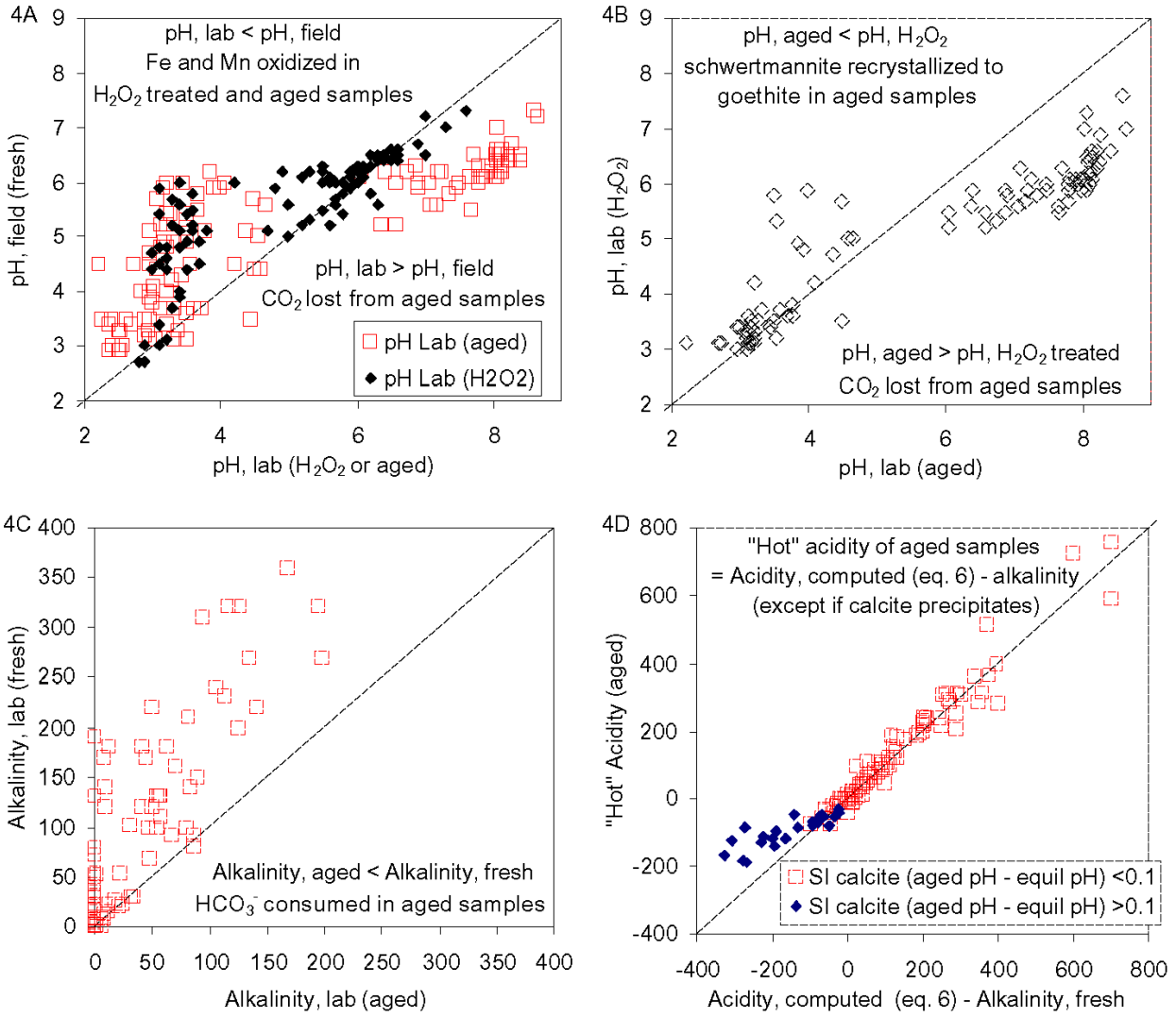

Figure 4. Relations among pH, alkalinity, and acidity for 140 fresh and aged sample pairs, Anthracite and Bituminous Coalfields, Pa., 1999: *A*, field-measured pH compared to lab-pH values; *B*, lab pH after H_2O_2 treatment of fresh samples compared to lab pH of 4-yr old samples; *C*, alkalinity of fresh samples compared to alkalinity of 4-yr old samples; *D*, "hot" acidity of 4-yr samples compared to computed acidity minus alkalinity (net acidity per Eqn. 8).

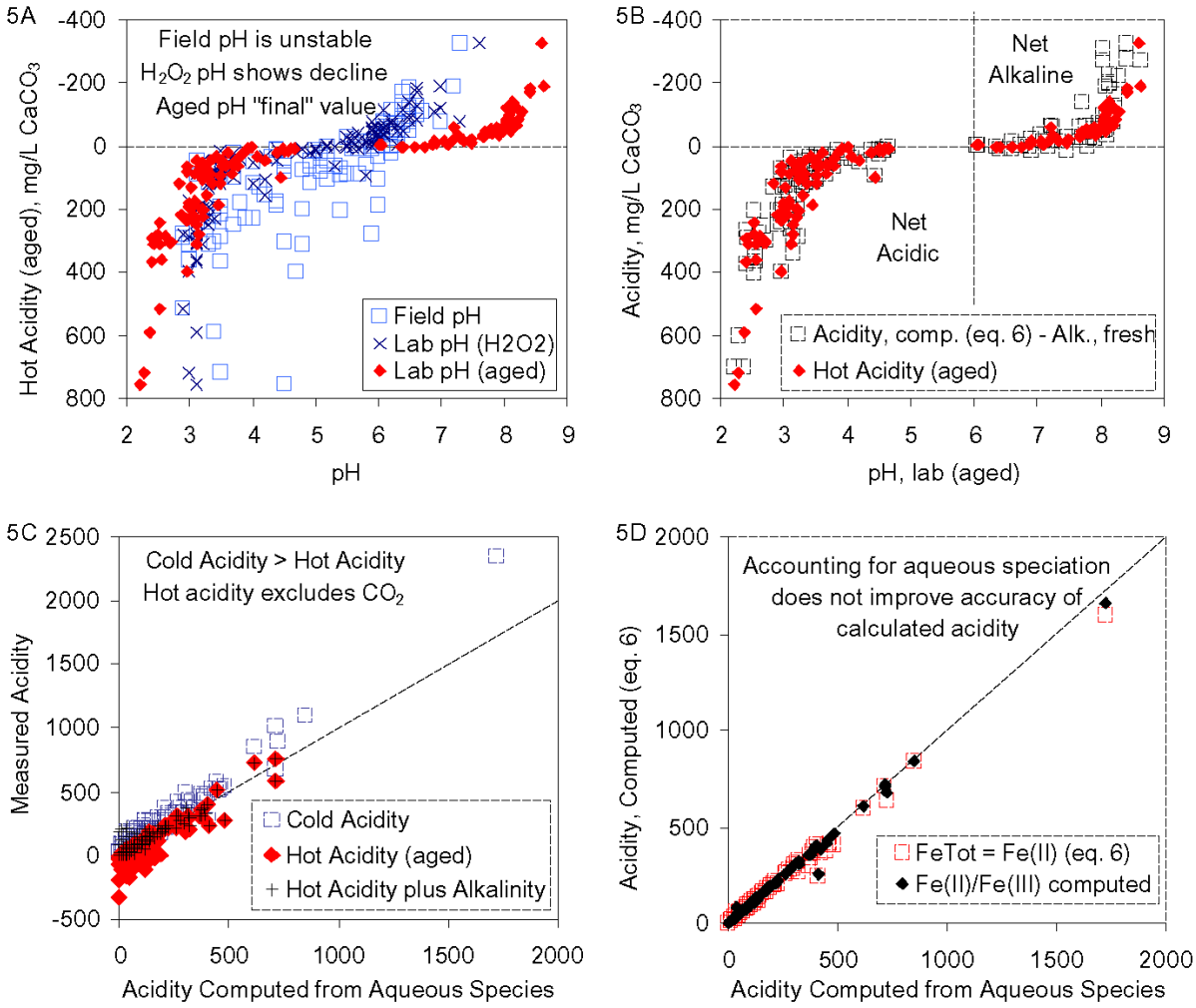

Figure 5. Relations among pH, alkalinity, and acidity for 140 fresh and aged sample pairs, Anthracite and Bituminous Coalfields, Pa., 1999: *A*, pH of fresh and aged samples compared to acidity; *B*, pH of aged samples compared to hot acidity and net acidity (computed acidity (Eqn. 6) minus alkalinity); *C*, measured hot and cold acidities compared to computed acidity based on aqueous speciation; *D*, computed acidity based on analytical concentrations compared to computed acidity based on aqueous speciation. In *B*, reference lines at pH of 6 and net alkalinity of 0 are shown to distinguish net acidic and net alkaline or near-neutral samples.

Many of the AMD samples had near-neutral or intermediate pH values and contained measurable alkalinity under field conditions but ultimately had acidic, oxidized pH values that were two or three units lower than initial conditions (Figs. 4A, 4B, 4C, 5A, and 5B). The alkalinities of samples under field conditions were greater than or, in few cases, equal to the alkalinities of oxidized, aged samples (Fig. 4C). The general decline in alkalinity of aged samples resulted from the reaction of HCO_3^- with H^+ produced as solid products precipitated from the sample such as $Fe(OH)_3$ per Equation 2 and/or $CaCO_3$ per the reverse of Equation 3.

The oxidized pH values were consistent with the measured "hot" acidity and the net acidity computed as the acidity due to dissolved metals (Eqn. 6) minus the fresh alkalinity (Eqn. 9). 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 (Figs. 4A, 4B, 5A, and 5B).

Calculated net acidity generally was the same as the measured hot acidity, with the exception of high-pH samples that may have precipitated calcite (Figs. 4D and 5D). Assuming equivalents of 2 per mole of dissolved Fe and Mn and 3 per mole of dissolved Al per Equation 6, computed acidity and corresponding values of net acidity or net alkalinity generally compared well with the "hot" acidity measured for fresh or aged samples (Figs. 4D, 5B, 5D).

The data on pH, hot acidity, and net acidity for the Wiconisco-Swatara-Schuylkill AMD samples from the Southern Anthracite Field (Fig. 6) and the Shamokin AMD samples from the Western Middle Anthracite Field (Fig. 7) illustrated consistent relations as those described above. The pH of the Wiconisco-Swatara-Schuylkill AMD samples ranged from 3.4 to 6.0, and concentrations of dissolved SO_4, Fe, Al, and Mn ranged from 75 to 1,090 mg/ L, 0.16 to 200 mg/L, 0.005 to 11.4 mg/L, and 1.0 to 8.2 mg/L, respectively (Table 2). The pH of the Shamokin AMD samples ranged from 2.6 to 6.7, and concentrations of dissolved SO_4, Fe, Al, and Mn ranged from 8.4 to 802 mg/L, 0.04 to 57.4 mg/L, <0.20 to 35.8 mg/L, and 0.01 to 7.1 mg/L, respectively (Table 2).

Acidities measured on the fresh and 5-month aged Wiconisco-Swatara-Schuylkill AMD samples indicated that the hot acidity was stable, whereas the cold acidity was not (Fig. 6C). The cold acidity on fresh samples was greater than that for aged samples, and it was greater than or equal to the hot acidity (Figs. 5C and 6C). Larger values of cold acidity on fresh samples compared to aged samples and compared to the hot or computed acidity result from CO_2 and H_2S that is included in the cold acidity measurement but that largely will be eliminated by aeration and exsolution of these dissolved gases during hot acidity titration or under atmospheric conditions as samples aged.

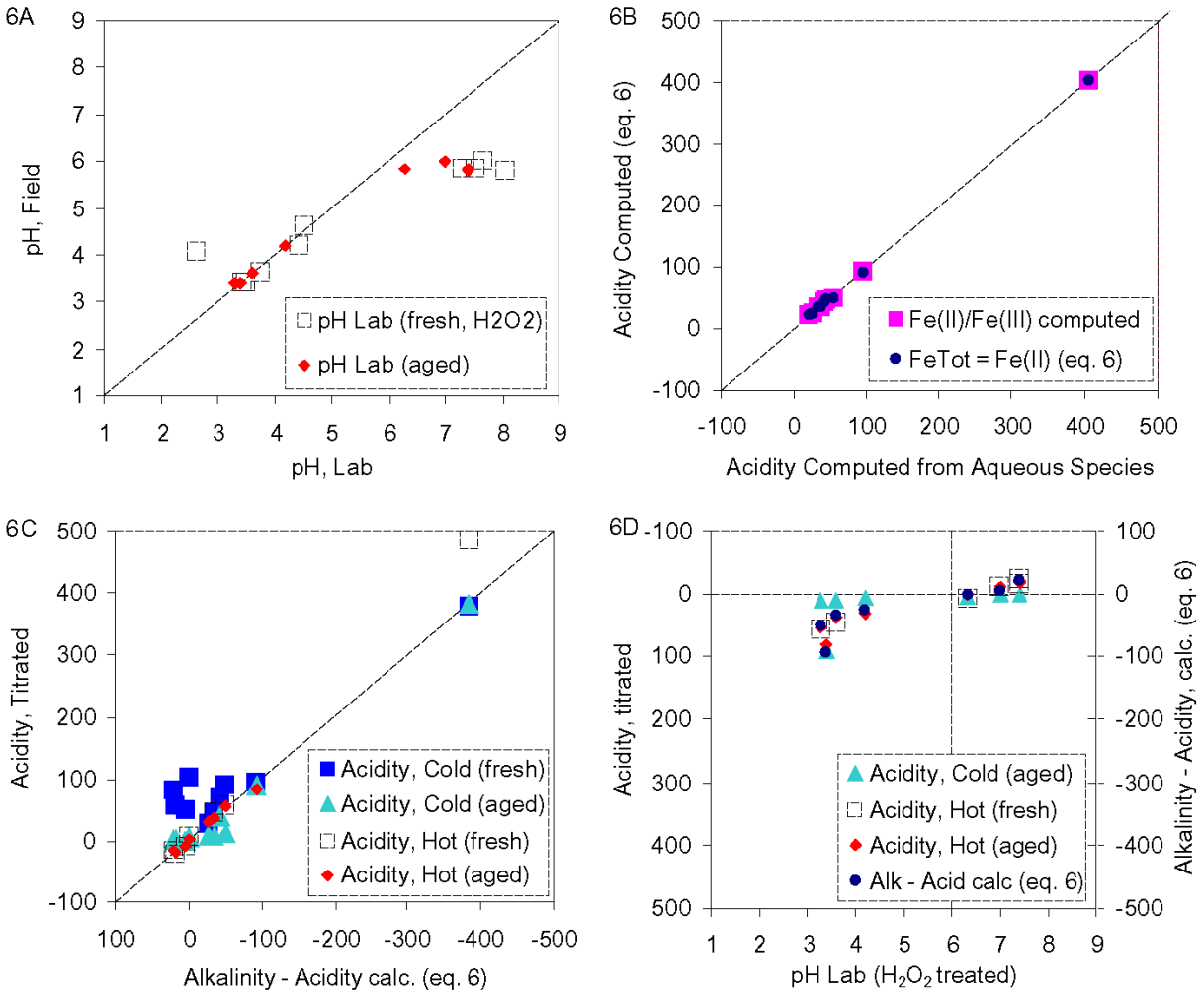

Figure 6. Relations among pH and acidities determined by various methods for 8 mine drainage samples, Wiconisco Creek, Swatara Creek, and Schuylkill River Basins, Southern Anthracite Coalfield, Pa., 2003: *A*, field-measured pH compared to lab-measured pH values; *B*, acidity computed from aqueous species compared to acidity computed from analytical concentrations; *C*, net alkalinity compared to various measured values for acidity; *D*, titrated acidity and computed net alkalinity compared to lab pH after H_2O_2 treatment of fresh samples. Reference lines at pH of 6 and net alkalinity of 0 are shown to distinguish net acidic and net alkaline or near-neutral samples.

Despite changes in pH as metals oxidize and their concentrations decline (Fig. 6A), the "hot" acidity was equivalent for the fresh and oxidized samples (Fig. 6C and 6D). As a metal-laden sample oxidizes, its electroneutrality will be maintained; an equivalent quantity of protons will be released into solution for each mole equivalent of metals oxidized and precipitated. Hence, hot acidity can be measured on fresh or aged samples; however, because it excludes contributions from CO_2, the hot acidity could underestimate the actual quantity of "caustic"

chemicals, such as NaOH or lime, needed to neutralize AMD without preaeration (e.g. Jageman *et al*., 1988; Means and Hilton, this volume). An evaluation of the difference between the cold acidity on fresh samples and the hot acidity could be useful to indicate the potential benefit of aeration before adding base chemicals to AMD.

The Shamokin AMD data represent typical results for "fresh" sample analyses at a non-research laboratory (Fig. 7). The oxidized pH was not recorded, and several samples with field pH > 5.6 were reported to have "hot" acidity concentration of zero. The acidity was not measured on those samples having laboratory pH > 6.4; however, the actual acidity could have been as much as 50 mg/L for several of these near-neutral samples (Figs. 7A and 7B). The hot acidity concentrations for samples that had field pH < 5.6 compared well with the computed acidity on the basis of dissolved metals (Eqn. 6). All the samples that had pH < 5.6 were net acidic. However, the relation between field pH and the computed net alkalinity is ambiguous for about a dozen samples that had pH of 5.8 to 6.3 (Fig. 7C). Although a majority of samples that had pH > 6 had positive net alkalinity, a few AMD samples with near-neutral pH had negative net alkalinity and corresponding positive values for hot acidity. The net acidic, high-pH samples had elevated concentrations of SO_4 and Fe^{II}, implying their origin as acidic AMD that had been partially neutralized.

For all three data sets, the measured hot acidities and the corresponding values for computed net acidities or net alkalinities on the basis of dissolved metals generally compared well with one another. The computed acidity avoids issues of different analytical methods, the lack of reporting negative values, or an assumed value of zero for near-neutral pH samples. However, it also involves assumptions regarding valence or speciation of the dissolved metals and requires that samples be filtered or free of suspended solids (Hedin, this volume). In Equation 6, acid equivalents of 2 per mole of Fe and Mn and 3 per mole of Al were assumed. The use of Equation 6 to compute acidity due to dissolved metals is warranted for filtered samples considering good agreement between the computed acidity and measured hot acidity.

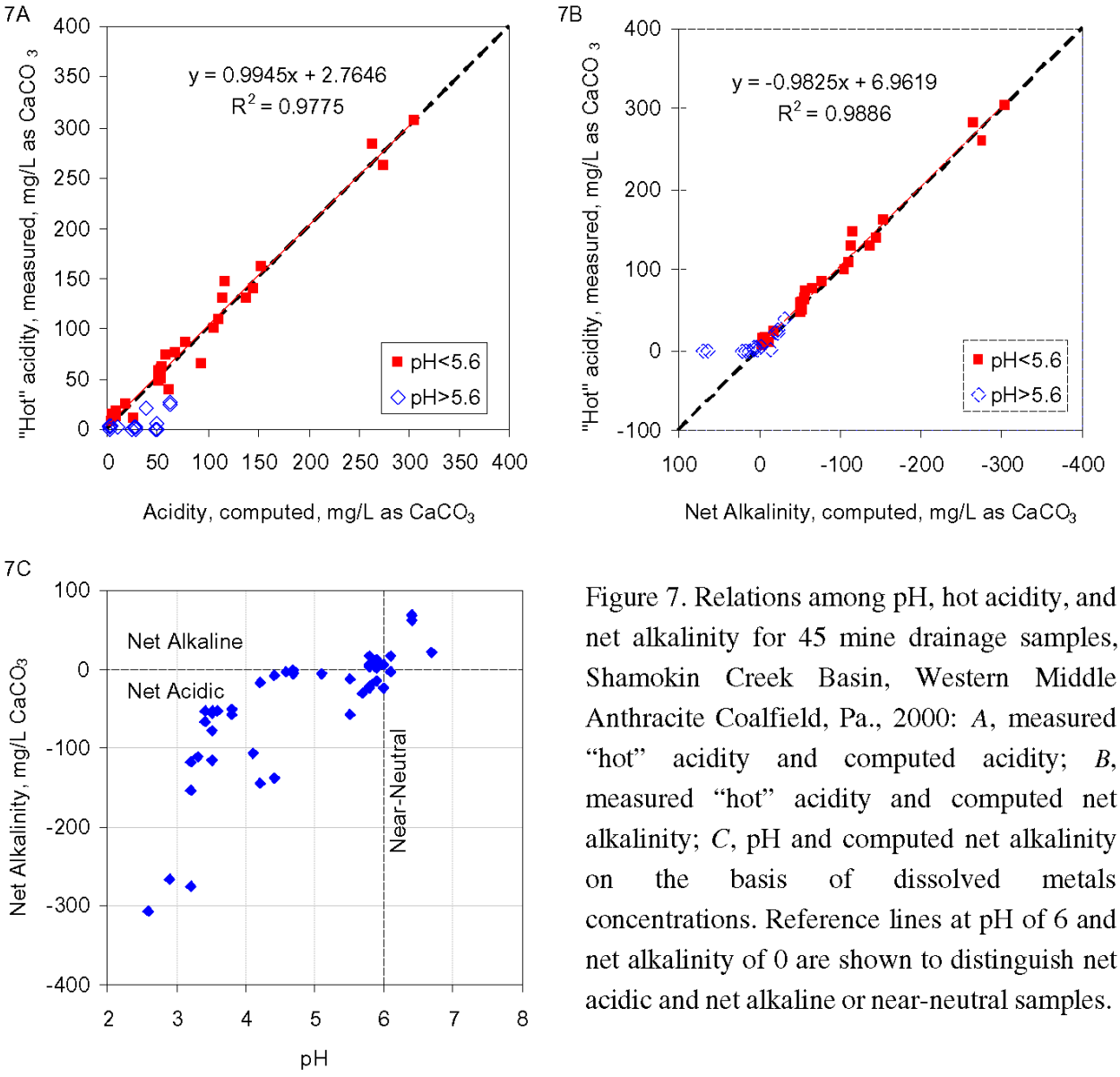

Figure 7. Relations among pH, hot acidity, and net alkalinity for 45 mine drainage samples, Shamokin Creek Basin, Western Middle Anthracite Coalfield, Pa., 2000: *A*, measured "hot" acidity and computed acidity; *B*, measured "hot" acidity and computed net alkalinity; *C*, pH and computed net alkalinity on the basis of dissolved metals concentrations. Reference lines at pH of 6 and net alkalinity of 0 are shown to distinguish net acidic and net alkaline or near-neutral samples.

Practical Considerations and Conclusions

Regional data for mine-drainage quality in Pennsylvania indicate that: (1) The pH of oxidized mine drainage has a distinctive bimodal frequency distribution, with modes at pH 2.5 to 4 (acidic) and pH 6 to 8.5 (near neutral); oxidized samples have acidic or near-neutral pH, only. (2) Samples that have near-neutral pH after oxidation have negative values for hot acidity indicating surplus alkalinity; samples that have acidic pH after oxidation have positive values for hot acidity indicating a deficiency of alkalinity. (3) Samples with comparable pH values could have substantially different concentrations of "hot acidity" owing to differences in their

concentrations of alkalinity and/or dissolved Fe and Mn. (4) The hot acidity is comparable to "net acidity" computed on the basis of initial pH and concentrations of Fe, Mn, and Al minus the initial alkalinity. (5) Acidity computed from the pH and dissolved metals concentrations, assuming a valence of 2 for iron and manganese and 3 for aluminum, is closely equivalent to that computed considering the Fe^{II}/Fe^{III} distribution or on the basis of aqueous species. (6) Despite changes in the pH, alkalinity, and metals concentrations, the hot acidities were comparable for fresh and oxidized samples. (7) The addition of H_2O_2 to a fresh sample will indicate if the ultimate pH after exposure to the atmosphere will be acidic; however, this method can overestimate or underestimate the ultimate pH for aged, acidic or near-neutral samples, respectively.

In conclusion, meaningful net acidity can be determined from a measured hot acidity or by calculation from the pH, alkalinity, and dissolved metals concentrations. Together, these water-quality data can be useful for evaluating the potential for toxicity, corrosion, or encrustation and can be helpful for determining the appropriate remediation. if the standard method hot acidity, using initial titration with H_2SO_4, addition of H_2O_2, and boiling prior to titration with NaOH to the endpoint pH of 8.3 (American Public Health Association, 1998a; American Society for Testing and Materials, 2000), is applied rigorously, consistent and interpretable results are obtained. Generally, the hot acidity is stable and gives consistent results for fresh and aged samples, whereas pH and alkalinity can be unstable as the sample ages. Thus, the hot acidity is a better overall measure than pH, alkalinity, or derivative terms for the severity of acid mine drainage. The hot acidity indicates both the required quantities of base needed for neutralization of aerated AMD and the potential for pH to decrease owing to the oxidation and hydrolysis of dissolved Fe and Mn. The measurement of hot acidity on fresh or aged samples will indicate a comparable "net acidity" result; therefore, sample refrigeration and immediate measurement should not be considered necessary unless measurements of pH, alkalinity, or other unstable constituents also are needed on the same sample. The hot acidity is not ambiguous compared to cold acidity or computed net acidity, where contributions from CO_2 and differences in sample preservation can affect the outcome. Nevertheless, the hot acidity could underestimate the quantity of "caustic" chemicals needed to neutralize AMD containing dissolved CO_2. In such cases, the cold acidity titration with addition of H_2O_2 prior to titration with NaOH to the

selected endpoint pH could be a useful measure and, compared with the hot acidity, could indicate potential benefits of aeration before the addition of chemicals to neutralize the AMD.

The results and conclusions of this report are consistent with the following paraphrased comments from Arthur W. Rose (2003, written commun.) sent as E-mail to the authors prior to our measurement of pH and hot acidity on aged samples: The standard method hot acidity involving initial titration with H_2SO_4 and addition of H_2O_2 is the preferable way to determine net acidity. The titration method alleviates a number of problems associated with sample collection and preservation. Also, it is widely used in industry and is a relatively accurate measurement, except for the inconsistent reporting of negative values. Obviously we need to get labs to report negative acidities. it gives the correct answer without filtration and without a determination of Fe^{II}/Fe^{III}, and it does not require refrigeration or immediate titration of samples. Despite internal changes in pH and consumption of alkalinity during sample storage, the "net" value measured by hot acidity is unchanged. In addition to determining if the solution ultimately will have acidic pH (positive net acidity) or near-neutral pH (positive net alkalinity), the hot acidity measurement is useful for sizing of passive systems, or for evaluating mixing of acidic and alkaline solutions.

Acknowledgments

This work evolved following discussions with Arthur W. Rose, Robert S. Hedin, Keith B. C. Brady, and Brent P. Means. The authors wish to acknowledge their input. The authors also wish to thank Donald R. Williams, Jeffrey B. Weitzel, James E. Welch, and Suzanne J. Ward of the USGS, and Harold Wilson of Wilson Testing Laboratories, Shamokin, Pa., for providing field or laboratory assistance with sampling and alkalinity and acidity measurements. The manuscript benefitted from reviews by Kevin J. Breen, Arthur W. Rose, and Eric F. Perry.

Literature Cited

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

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

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

Ball, J. W., and Nordstrom, D. K., 1991, User's manual for WATEQ4F with revised data base: U.S. Geological Survey Open-File Report 91-183, 189 p.

Berg, T. M., Barnes, J. H., Seven, W. D., Skema, V. K., Wilshusen, J. P., and Yannaci, D. S., 1989, Physiographic provinces of Pennsylvania: Pennsylvania Geological Survey, 4th Series, Map 13, scale 1:2,000,000.

———, *et al*., 1980, Geologic map of Pennsylvania: Pennsylvania Geological Survey, Fourth Series, Map # 1, scale 1:2,500,000, 3 sheets.

Bigham, J. M., and Nordstrom, D. K., 2000, Iron and aluminum hydroxysulfate minerals from acid sulfate waters, In Jambor, J. L., Alpers, C. N., and Nordstrom, D. K., (eds.), *Sulfate minerals, crystallography, geochemistry and environmental significance*: Mineralogical Society of America Reviews in Mineralogy and Geochemistry, v. 40, p. 351-403.

———, Schwertmann, U., Traina, S. J., Winland, R. L., and Wolf, M., 1996, Schwertmannite and the chemical modeling of iron in acid sulfate waters: Geochimica et Cosmochimica Acta, v. 60, p. 2111-2121. http://dx.doi.org/10.1016/0016-7037(96)00091-9.

Brady, K. B. C., Rose, A. W., Cravotta, C. A., III, and Hellier, W. W., 1997, Bimodal distribution of pH in coal-mine drainage (abs.): Geological Society of America, GSA Abstracts with Programs, v. 29, no. 1, p. 32.

———, Hornberger, R. J., and Fleeger, G., 1998, Influence of geology on post-mining water quality-Northern Appalachian Basin, In Brady, K. B. C., Smith, M. W., and Schueck, J. H., (eds.), *The prediction and prevention of acid drainage from surface coal mines in Pennsylvania*: Harrisburg, Pa., Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256, p. 8.1-8.92.

———, Smith, M. W., Beam, R. L., and Cravotta, C. A., III, 1990, Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage--Part 2. Mine site case studies, In *Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Charleston, West Virginia, April 23-26, 1990*: Morgantown, W.Va., West Virginia University, v. 1, p. 226-241.

https://doi.org/10.21000/JASMR90010227

———, Perry, E. F., Beam, R. L., Bisko, D. C., Gardner, M. D., and Tarantino, J. M., 1994, Evaluation of acid-base accounting to predict the quality of drainage at surface coal mines in Pennsylvania, U.S. A.: U.S. Bureau of Mines Special Publication SP 06A, p. 138-147.
https://doi.org/10.21000/JASMR94010138

Commonwealth of Pennsylvania, 1998a. Chapter 87. Surface mining of coal. *Pennsylvania Code, Title 25. Environmental Protection*: Harrisburg, Pa., Commonwealth of Pennsylvania, p. 87.1-87.122.

——— 1998b, Chapter 89. Underground mining of coal and coal preparation facilities. *Pennsylvania Code, Title 25. Environmental Protection*: Harrisburg, Pa., Commonwealth of Pennsylvania, p. 89.1-89.96.

——— 2002, Chapter 93. Water Quality Standards. *Pennsylvania Code, Title 25. Environmental Protection*: Harrisburg, Pa., Commonwealth of Pennsylvania, p. 93.1-93.226.

Cravotta, C. A., III, and Hilgar, G. M., 2000, Considerations for chemical monitoring at coal mines, In Kleinmann, R. L. P., (ed.), *Prediction of water quality at surface coal mines*: Acid Drainage Technology Initiative, Morgantown, W.Va., National Mine Land Reclamation Center, p. 195-218.

———, and Kirby, C. S., 2003, Effects of abandoned coal-mine drainage on streamflow and water quality in the Shamokin Creek Basin, Northumberland and Columbia Counties, Pennsylvania, 1999-2001: U.S. Geological Survey Water-Resources Investigations Report 03-4311.

———, and Trahan, M. K., 1999, Limestone drains to increase pH and remove dissolved metals from acidic mine drainage: Applied Geochemistry, v. 14, no. 5, p 581-606. http://dx.doi.org/10.1016/S0883-2927(98)00066-3.

———, Dugas, D. L., Brady, K. B. C., and Kovalchuk, T. E., 1994, Effects of selective handling of pyritic, acid-forming materials on the chemistry of pore gas and ground water at a reclaimed surface coal mine in Clarion County, PA, USA: U.S. Bureau of Mines Special Publication SP 06A, p. 365-374.
https://doi.org/10.21000/JASMR94010365

———, Brady, K. B. C., Rose, A. W., and Douds, J. B., 1999, Frequency distribution of the pH of coal-mine drainage in Pennsylvania, In Morganwalp, D. W., and Buxton, H., (eds.), U.S. *Geological Survey Toxic Substances Hydrology Program--Proceedings of the technical meeting*: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, p. 313-324.

———, Breen, K. J., and Seal, R., 2001, Arsenic is ubiquitous but not elevated in abandoned coal-mine discharges in Pennsylvania (abs.), In *U.S. Geological Survey Appalachian Region Integrated Science Workshop Proceedings, Gatlinburg, Tennessee, October 22-26, 2001*: U.S. Geological Survey Open-File Report 01-406, p. 105.

Crock, J. G., Arbogast, B. F., and Lamothe, P. J., 1999, Laboratory methods for the analysis of environmental samples, In Plumlee G. S., and Logsdon, M. J., (eds.), *The Environmental Geochemistry of Mineral Deposits--Part A. Processes, techniques, and health issues*: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, p. 265-287.

Desmier, R., Waite, T. D., Macdonald, B. C. T., and Melvillle, M. D., in press, Characteristics of the acidity in acid sulfate soil surface waters: *Applied Geochemistry*.

Drever, J. I., 1997, *The geochemistry of natural waters--Surface and groundwater environments* (3rd): Englewood Cliffs, N.J., Prentice-Hall, Inc., 436 p.

Edmunds, W. E., 1999, Bituminous coal, In Schultz, C. H., (ed.), *The geology of Pennsylvania*: Pennsylvania Geological Survey, 4th series, Special Publication 1, p. 470-481.

Eggleston, J. R., Kehn, T. M., and Wood, G. H., Jr., 1999, Anthracite, In Schultz, C. H., (ed.), *The geology of Pennsylvania*: Pennsylvania Geological Survey, 4th series, Special Publication 1, p. 458-469.

Elder, J. F., 1988, Metal biogeochemistry in surface-water systems--a review of principles and concepts: U.S. Geological Survey Circular 1013, 43 p.

Ficklin, W. H., and Mosier, E. L., 1999, Field methods for sampling and analysis of environmental samples for unstable and selected stable constituents, In Plumlee G.S., and Logsdon, M.J., (eds.), *The Environmental Geochemistry of Mineral Deposits--Part A. Processes, techniques, and health issues*: Society of Economic Geologists, Reviews in Economic Geology, v. 6A, p. 249-264.

Fishman, M. J., and Friedman, L. C., (eds.), 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 545 p.

Growitz, D. J., Reed, L. A., and Beard, M. M., 1985, Reconnaissance of mine drainage in the coal fields of eastern Pennsylvanian: U.S. Geological Survey Water Resources Investigations Report 83-4274, 54 p.

Hedin, R. S., this volume, The use of measured and calculated values to improve the quality of mine drainage data sets, In *Proceedings of the 2004 National Meeting of American Society of Mining & Reclamation and the 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004*: American Society of Mining & Reclamation.
https://doi.org/10.21000/JASMR04010879

———, Nairn, R. W., and Kleinmann, R. L. P., 1994, Passive treatment of coal mine drainage: U.S. Bureau of Mines Information Circular IC 9389, 35 p.

Herlihy, A. T., Kaufmann, P. R., Mitch, M. E., and Brown, D. D., 1990, Regional estimates of acid mine drainage impact on streams in the mid-Atlantic and southeastern United States: Water, Air, and Soil Pollution, v. 50, p. 91-107. http://dx.doi.org/10.1007/BF00284786.

Hyman, D. M., and Watzlaf, G. R., 1997, Metals and other components of coal mine drainage as related to aquatic life standards, In *Proceedings of the 1997 National Meeting of the American Society for Surface Mining and Reclamation, May 10-15, 1997, Austin, Texas*: American Society for Surface Mining and Reclamation, p. 531-545 https://doi.org/10.21000/JASMR97010531

Jageman, T. C., Yokley, R. A., and Heunisch, H. E., 1988, The use of preaeration to reduce the cost of neutralizing acid mine drainage: U.S. Bureau of Mines Information Circular IC 9183, p. 131-135. https://doi.org/10.21000/JASMR88010131

Kirby, C. S, 2002, Problems in alkalinity and acidity measurements in mine drainage, In *Proceedings of the 19th Annual Meeting of American Society of Mining & Reclamation, Lexington, Kentucky, June 9-13, 2002*: American Society of Mining & Reclamation, p 1068-1072.

———, and Cravotta, C. A., III, this volume, Acidity and alkalinity in mine drainage--Theoretical considerations, In *Proceedings of the 2004 National Meeting of American Society of Mining & Reclamation and the 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004*: American Society of Mining & Reclamation.
https://doi.org/10.21000/JASMR04011076

———, Thomas, H. M., Southam, G., and Donald, R., 1999, Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage: Applied Geochemistry, v. 14, p. 511-530. http://dx.doi.org/10.1016/S0883-2927(98)00071-7

Langmuir, Donald, 1997, *Aqueous environmental geochemistry*: New Jersey, Prentice-Hall, 600 p.

Means, B. P., and Hilton, T., this volume, Comparison of three methods to measure acidity of coal-mine drainage, In *Proceedings of the 2004 National Meeting of American Society of Mining & Reclamation and the 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004*: American Society of Mining & Reclamation.
https://doi.org/10.21000/JASMR0401249

Miller, S. D., 1980, Sulfur and hydrogen ion buffering in pyritic strip mine spoil, In Trudinger, P. A., and Walter, M. R., (eds.), Biogeochemistry of ancient and modern environments: New York, Springer-Verlag, p. 537-543. http://dx.doi.org/10.1007/978-3-662-26582-6_58 http://dx.doi.org/10.1007/978-3-642-48739-2_58.

Nordstrom, D. K., 1977, Thermochemical redox equilibria of Zobell's solution: Geochimica et Cosmochimica Acta, v. 41, p. 1835-1841. http://dx.doi.org/10.1016/0016-7037(77)90215-0.

———, 1985, The rate of ferrous iron oxidation in a stream receiving acid mine effluent, In Subitzky, Seymour, (ed.), *Selected papers in the hydrologic sciences 1985*: U.S. Geological Survey Water-Supply Paper 2270, p. 113-119.

———, 2000, Advances in the hydrochemistry and microbiology of acid mine waters: International Geology Review, v. 42, p. 499-515. http://dx.doi.org/10.1080/00206810009465095.

———, and Alpers, C. N., 1999, Geochemistry of acid mine waters, In Plumlee, G. S., and Logsdon, M. J., (eds.), *The Environmental Geochemistry of Mineral Deposits--Part A. Processes, methods, and health issues*: Reviews in Economic Geology, v. 6A, p. 133-160.

———, and Ball, J. W., 1986, The geochemical behavior of aluminum in acidified surface waters: Science, v. 232, p. 54-58. http://dx.doi.org/10.1126/science.232.4746.54 PMid:17773998.

———, Jenne, E. A., and Ball, J. W., 1979, Redox equilibria of iron in acid mine waters, In Jenne, E. A., (ed.), *Chemical modeling in aqueous systems--Speciation, sorption, solubility, and kinetics*: American Chemical Society Symposium Series 93, p. 51-79.

Ott, A. N., 1988, Dual acidity titration curves – Fingerprint, indicator of redox state, and estimator of iron and aluminum content of acid mine drainage and related waters: U.S. Geological Survey Water Supply Paper 2330, p. 19-33.

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

Rantz, S. E., and others, 1982a, Measurement and computation of streamflow--1. Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 284 p.

———, 1982b, Measurement and computation of streamflow--2. Computation of discharge: U.S. Geological Survey Water-Supply Paper 2175, 631 p.

Rose, A. W., and Cravotta, C. A., III, 1998, Geochemistry of coal-mine drainage, In Brady, K. B. C., Smith, M. W., and Schueck., J., (eds.), *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*: Harrisburg, Pa., Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256, p. 1.1-1.22

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

Southern Alleghenies Conservancy, 1998, Findings for the inventory and monitoring phase of the resource recovery program: Bedford, Pa., Southern Alleghenies Conservancy, unpublished report, 74 p.

Stumm, Werner, and Morgan, J. J., 1996, *Aquatic chemistry--Chemical equilibria and rates in natural waters* (3rd): New York, John Wiley and Sons, 1022 p.

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

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

———, 2000, Drinking water standards and health advisories (summer 2000): U.S. Environmental Protection Agency, 12 p. (http://www.epa.gov/OST).

———, 2002a, National primary drinking water standards: U.S. Environmental Protection Agency EPA/816-F-02-013, July 2002, 7 p. (http://www.epa.gov/safewater).

———, 2002b, National recommended water quality criteria--2002: U.S. Environmental Protection Agency EPA/822-R-02-047, 33 p.

U.S. Geological Survey, 1997 to present, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, 2 vols., variously paged (http://pubs. water. usgs. gov/twri9A).

Williams, D. J., Bigham, J. M., Cravotta, C. A., III, Traina, S. J., Anderson, J. E., and Lyon, G., 2002, Assessing mine drainage pH from the color and spectral reflectance of chemical precipitates: Applied Geochemistry, v. 17, p. 1273-1286. http://dx.doi.org/10.1016/S0883-2927(02)00019-7.

Winland, R. L., Traina, S. J., and Bigham, J. M., 1991, Chemical composition of ochreous precipitates from Ohio coal mine drainage: Journal of Environmental Quality, v. 20, p. 452-460. http://dx.doi.org/10.2134/jeq1991.202452x http://dx.doi.org/10.2134/jeq1991.00472425002000020019x

Wood, C. R., 1996, Water quality of large discharges from mines in the anthracite region of eastern Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 95-4243, 68 p.

Wood, W. W., 1976, Guidelines for the collection and field analysis of ground-water samples for selected unstable constituents: U.S. Geological Survey Techniques of Water Resources Investigations, Book 1, Chapter D2, 24 p.

Yu, J. -Y., Heo, B., Choi, I. -K., Cho, J. -P., and Change, H. -W., 1999, Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage: Geochimica et Cosmochimica Acta, v. 63, p. 3407-3416. http://dx.doi.org/10.1016/S0016-7037(99)00261-6.