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Frequency Distribution of the pH of Coal-Mine Drainage in Pennsylvania

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ABSTRACT

The pH of coal-mine drainage in Pennsylvania has a bimodal frequency distribution, with modes at pH 2.5 to 4 (acidic) and pH 6 to 7 (near neutral). Although iron-disulfide and calcareous minerals comprise only a few percent, or less, of the coal-bearing rock, these minerals are highly reactive and are mainly responsible for the bimodal pH distribution. Field and laboratory studies and computer simulations indicate that pH will be driven toward one mode or the other depending on the relative abundance and extent of weathering of pyrite (FeS_2; acid-forming) and calcite ($CaCO_3$; acid-neutralizing). The pH values in the near-neutral mode result from carbonate buffering (HCO_3^- / H_2CO_3 and $HCO_3^- / CaCO_3$) and imply the presence of calcareous minerals; acid produced by pyrite oxidation is neutralized. The pH values in the acidic mode result from pyrite oxidation and imply a deficiency of calcareous minerals and the absence of carbonate buffering. The oxidation of only a small quantity of pyrite can acidify pure water ($0.012\ g\cdot L^{-1}$ FeS_2 produces pH~4 and $20\ mg\cdot L^{-1}$ SO_4^{2-}); however, because of the log scale for pH and ion complexation (SO_4^{2-} / HSO_4^- and $Fe^{3+}/FeOH^{2+}$), orders of magnitude greater oxidation is required to produce $pH < 3$. Laboratory leaching experiments showed that for a specific proportion of FeS_2:$CaCO_3$, effluents produced under variably saturated hydrologic conditions, in which oxygen availability and pyrite oxidation were enhanced, had lower pH and greater dissolved solids concentrations than effluents produced under continuously saturated conditions, in which oxygen availability and pyrite oxidation were diminished.

INTRODUCTION

In the northern Appalachian Plateau of the eastern United States, drainage from abandoned coal mines affects more than 8,000 km of streams and associated ground water (Boyer and Sarnoski, 1995). Most affected streams are in Pennsylvania, where contaminated mine runoff and mine discharges impair water quality in 45 of 67 counties (Pennsylvania Department of Environmental Protection, 1998). An understanding of factors affecting the chemistry of coal-mine drainage is needed for the effective planning and implementation of future mining and remediation of abandoned mine lands. This paper evaluates geochemical and hydrological factors affecting the pH of coal-mine drainage. Data for ground-water and discharge samples and laboratory leaching experiments are presented to explain regional water-quality trends for the northern Appalachian coalfields. Geochemical simulations demonstrate the range of effects on pH from different variables, including the amount of pyrite oxidized, buffering by carbonate minerals, and the formation of secondary minerals.

Geochemistry of Coal Mine Drainage

Ground water and associated mine discharges in the coalfields of Pennsylvania range widely in quality from near-neutral, or “alkaline” (alkalinity > acidity; $pH \geq 6$), to strongly acidic (Rose and Cravotta, 1998). The pH of coal-mine drainage in Pennsylvania has a bimodal frequency distribution (Brady and others, 1997, 1998); most samples are either near neutral (pH 6 to 7) or distinctly acidic (pH 2.5 to 4), with few samples having pH 4.5 to 5.5 (fig.1). The bimodal pH distribution is apparent for other regional compilations of water-quality data for coalfields in West Virginia (diPretoro, 1986), Ohio (Helsel and Hirsch, 1992, p. 61), and Germany (Klapper and Schultze, 1995). Whether near neutral or acidic, the drainage from most coal mines has elevated concentrations of dissolved solids, ranging from about $200\ mg\cdot L^{-1}$ to greater than $10{,}000\ mg\cdot L^{-1}$. In contrast, ground water and spring water from unmined areas typically are near neutral and are dilute compared to water from mined areas (Brady and others, 1996; Rose and Cravotta, 1998).

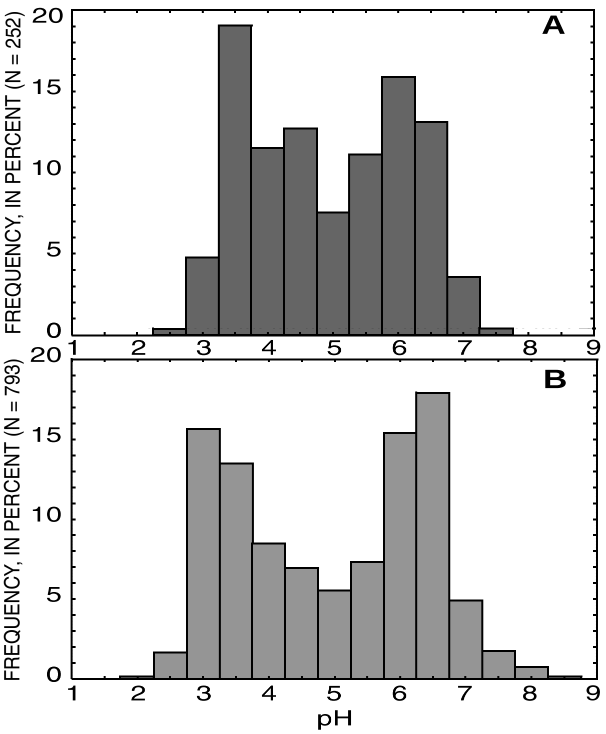

Figure 1. Frequency distribution of the pH of coal-mine discharges in Pennsylvania. *A,* Data for 252 coal-mine discharges in the anthracite coalfield (source: Growitz and others, 1985); *B*, Data for 793 surface coal-mine discharges in the bituminous coalfield (source: Hellier, 1994). Class intervals for pH ± 0.25.

Acidic mine drainage (AMD) is characterized by elevated concentrations of dissolved and particulate iron (Fe) and dissolved sulfate (SO_4^{2-}) produced by the oxidation of pyrite (FeS_2):

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

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

Half the acid (H^+) is produced by the oxidation of pyritic S (reaction 1), and half results from the oxidation and hydrolysis of pyritic Fe (reaction 2). Generally, mines that produce AMD feature interconnected underground "workings" (voids and rock rubble) or aboveground "spoil" (rubble and rejected coal) where pyrite has been exposed to oxygenated air and water and where the calcareous minerals, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), are absent or deficient relative to pyrite (Hornberger and others, 1990; Brady and others, 1994; Cravotta, 1994; Rose and Cravotta, 1998; Nordstrom and Alpers, 1999). Concentrations of manganese (Mn^{2+}), aluminum (Al^{3+}), and other solutes in AMD commonly are elevated due to aggressive dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water.

Near-neutral mine drainage can form from rock that lacks pyrite or can originate as AMD that has been neutralized by reaction with calcareous minerals (Cravotta and others, 1994; Blowes and Ptacek, 1994). In near-neutral mine waters, bicarbonate (HCO_3^-) is a significant anion along with SO_4^{2-}; concentrations of dissolved calcium (Ca^{2+}) and magnesium (Mg^{2+}) generally are elevated relative to dissolved Fe^{3+} and Al^{3+}, which precipitate as pH increases to above 4 to 5. For example, dissolution of calcite neutralizes acid and can increase the pH and alkalinity ($[OH^-] + [HCO_3^-] + 2\ [CO_3^{2-}]$) of mine water:

$$CaCO_3(s) + 2H^+ \leftrightarrow Ca^{2+} + H_2CO_3^* \quad (3)$$

$$CaCO_3(s) + H_2CO_3^* \leftrightarrow Ca^{2+} + 2\ HCO_3^- \quad (4)$$

where $[H_2CO_3^*] = [CO_2\ (aq)] + [H_2CO_3^o]$ (Stumm and Morgan, 1996). However, because the rate of pyrite oxidation can exceed the rate of calcite dissolution, particularly where oxygen is abundant, the pH and alkalinity of mine water will not necessarily increase in the presence of calcite.

Ion complexation, principally the protolysis of anions and the hydrolysis of cations (Stumm and Morgan, 1996), also can be a significant process that stabilizes, or "buffers," the pH of mine water. For example, pH can be buffered in the near-neutral range by the protolysis reaction involving bicarbonate and carbonic acid (pK=6.35; thermodynamic data from Ball and Nordstrom, 1991):

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3^* \quad (5)$$

Similarly, pH can be buffered in the acidic range by the protolysis reaction involving sulfate and bisulfate (pK=2.0)

$$SO_4^{2-} + H^+ \leftrightarrow HSO_4^-, \quad (6)$$

and by hydrolysis reactions involving ferric ions, such as the initial hydrolysis step (pK=2.2),

$$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+. \quad (7)$$

The importance of the above reactions will depend on the dissolved solute content of the water, the nature and abundance of acid-producing and neutralizing materials along flow paths, the sequence and intimacy of contact between the water and these materials, as well as the ability of the rock to transmit water and air.

Geologic and Hydrologic Framework

Bituminous coal deposits underlie western and north-central Pennsylvania, and anthracite deposits underlie east-central and northeastern Pennsylvania (fig. 2). The mineable coals, mostly of Pennsylvanian Age, are interbedded with shale, siltstone, sandstone, and occasional limestone (Brady and others, 1998). The bituminous coalfield lies within the Appalachian Plateaus Physiographic Province and is characterized by gently dipping strata; nearly horizontal coalbeds commonly crop out in the incised stream valleys. The anthracite coalfield lies within the adjacent Ridge and Valley Physiographic Province, which is characterized by complexly deformed strata. Mineable anthracite beds are present primarily in steeply folded and fractured synclinal troughs.

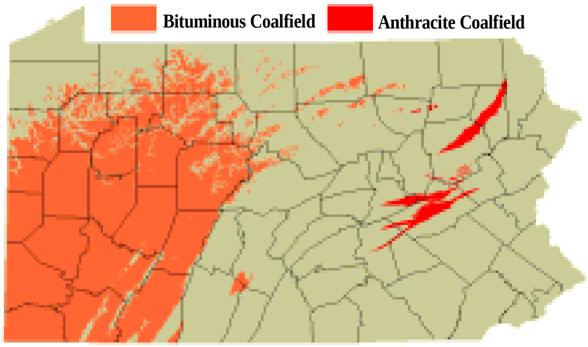

Figure 2. Locations of bituminous and anthracite coalfields in Pennsylvania (modified from Pennsylvania Geological Survey, 1964).

Coal-bearing rocks in the northern Appalachians have variable potential to produce AMD; the pyritic and calcareous contents of the rocks vary. Because weathering over many centuries has depleted reactive minerals from near-surface strata, the acid-forming and acid-neutralizing minerals generally are most abundant in rock deeper than about 10 m (Cravotta and others, 1994; Brady and others, 1996, 1998). Upon mining, however, pyrite in the deep-lying, unweathered strata is exposed to oxygenated air and water within underground workings or surface mine spoil. The spoil commonly consists of a heterogeneous mixture of rocks that are inverted stratigraphically relative to their original positions (Cravotta and others, 1994). Thus, although the relative abundance and vertical distribution of pyritic and calcareous materials at a proposed mine commonly are evaluated before mining to indicate the potential for AMD formation and to develop a materials handling plan (Brady and others, 1994), the quality and movement of water within the resultant mine spoil and backfill are difficult to predict.

Surface mines and underground mines in the bituminous coalfield generally can be categorized as “updip” or “downdip” depending on the direction that mining proceeded relative to the dip of the coal bed. In the past, most bituminous mines were mined updip so that water would drain freely and pumping costs would be minimized. Updip mines also provided greater access of oxygen to the subsurface, however, which facilitates the oxidation of pyrite and the formation of AMD (Hornberger, 1985). In contrast, downdip mines tend to fill with ground water, which requires pumping during active mining but also reduces the access of oxygen to pyritic rock. Upon mine closure, substantial parts of downdip mines can be permanently inundated thereby minimizing oxygen transport and pyrite oxidation. Hence, the downdip mines generally produce less acidic water than updip mines; however, unless calcareous strata are present, they may not produce near-neutral water.

Most anthracite mines were developed as large underground mine complexes, where shafts and tunnels connected mine workings within multiple coalbeds. Because anthracite mines commonly were developed hundreds of meters below the regional water table and because of the large size of most underground mine complexes, their discharge volumes (overflows or tunnels) tend to be substantially greater than those from surface mines. Upon closure, large volumes of the mine complexes flooded, as expected for downdip mines, producing underground “mine pools.” Discharges emanated where the mine pools overflowed from topographically low points overlying the mine complex.

During active mining, the potential for catastrophic flooding of anthracite mine complexes was a major concern. Partly due to the high cost of pumping as the mines were developed to greater and greater depths, most mines had closed by 1960. At some mines, the flooding problem was solved by the construction of extensive drainage tunnels. By promoting the circulation of water and air within the mine workings, the drainage tunnels promoted the formation of AMD where pyritic strata were present. For example, the Jeddo Tunnel, the largest drainage tunnel system in the anthracite coalfield, drains a 70-km^2 area in the Eastern Middle Anthracite Field (LeRigina, 1988). Acidic water from the Jeddo Tunnel (pH < 4; SO_4 > 400 $mg \cdot L^{-1}$) discharges at a rate of 175,000 to 270,000 $m^3 \cdot d^{-1}$ (Wood, 1996).

In addition to the mineralogical and hydrological factors described above, the age of the mine, the time elapsed since initial flooding, the origin and composition of the inflow water, the potential for stratification within the mine pool, and the location of the mine outflow can affect the mine-discharge composition. For example, water can be stratified in a mine pool, with generally older, poorer quality water at depth; overflows from the top of the pool generally will be better quality than outflows from boreholes, shafts, or tunnels tapping deeper zones (Ladwig and others, 1984). Regional data pertaining to all these factors are not generally available in digital format and, hence, their evaluation is beyond the scope of this paper.

STUDY METHODS

Available data for pH and concentrations of alkalinity, acidity, sulfate, and metals in groundwater and discharge samples from coal mines in Pennsylvania were compiled from several sources. Water-quality data for 793 bituminous surface mine discharges were obtained from the Mine Drainage Inventory data base (Hellier, 1994) maintained by the Pennsylvania Department of Environmental Protection (PaDEP). If multiple samples were reported for a discharge site, arithmetic means of concentration and discharge rate were used for that site. Data for 252 anthracite mine discharges reported by Growitz and others (1985) were obtained from the USGS National Water Information System (NWIS); the anthracite data are predominantly for underground mines. Additional water-chemistry data for selected large anthracite discharges reported by Wood (1996) and for recent USGS investigations at four surface mines in the bituminous field (Dugas and others, 1993; Cravotta and others, 1994; Cravotta, 1998) also were obtained from NWIS. Finally, data for laboratory leaching experiments were added to the compilation.

For the leaching experiments, reported in detail by Cravotta (1996), coaly shale that consisted mostly of quartz, kaolinite, and pyrite was obtained at a coal mine and taken to the laboratory to be crushed, and placed in vertical columns open to the atmosphere. The columns were leached biweekly with water simulating two different hydrologic conditions: variably saturated, aerobic (flooded for 2 days with 1.4 pore volumes, followed by 12-day drying period) or continuously saturated, stagnant (flooded continuously with 1.4 pore volumes). Powdered calcite was added on top of the shale to achieve molar ratios for $CaCO_3$:FeS_2 of 0:1, 1:1, and 2:1.

The pH data for the bituminous mines (fig. 1A) were determined in the laboratory on chilled samples. These laboratory pH values could be greater than field pH because of the exsolution of CO_2 or less than the field pH because of the oxidation and precipitation of Fe (reactions 2 and 3). Nevertheless, pH data for the anthracite mines (fig. 1B) and for the other field and laboratory data sets were determined at the time and location of sample collection. The similarity between field and laboratory pH values for the USGS mine-scale and laboratory leaching data compilations and the similarity between the pH frequency distributions for the bituminous and anthracite discharges (fig. 1) imply that the laboratory pH values are representative of field conditions. The USGS mine-scale and laboratory leaching data compilations also included values for redox potential (Eh). The Eh was determined on fresh samples using Pt and Ag/AgCl reference electrodes according to methods of Wood (1976) and Nordstrom (1977). The water-quality data were evaluated by use of computerized graphical, statistical, and geochemical routines.

The PHREEQC computer program (Parkhurst, 1995) was used to conduct “titration” simulations, where small increments of pyrite were added to a 1 L solution and oxidized. By adjusting different variables, these simulations evaluated the effects on pH, Eh, and sulfate concentrations as a function of the amount of pyrite reacted; oxygen availability; equilibrium with carbonate minerals; partial pressure of CO_2 (Pco_2); and precipitation of different hydrous iron oxide or sulfate minerals. A typical simulation involved 100 or more incremental steps with small additions of pyrite. After each of these steps, the pH, Eh, and dissolved species were calculated. The pH was plotted as a function of the total SO_4 concentration to indicate the resulting water quality for a given amount of pyrite oxidized.

RESULTS

Regional Studies

Although the bimodal frequency distribution of pH is similar for discharges from bituminous and anthracite mines (fig. 1), the relations between pH and SO_4 concentration or load differ between the two coalfields (fig. 3). The median SO_4 concentrations for bituminous discharges exceed those for anthracite discharges at each pH class interval and over the range of pH (fig. 3). Conversely, because discharge rates for most anthracite mines are significantly greater than those for the bituminous mines, the medians for SO_4 transport, or “loads,” for anthracite discharges exceed those for bituminous discharges at each pH class interval (fig. 3). The anthracite mine discharges are characterized by median SO_4 concentrations of 100 to 300 $mg{\cdot}L^{-1}$ and loads of 20 to 400 $kg{\cdot}day^{-1}$ that are independent of pH. In contrast, the median concentrations and loads for bituminous discharges increase with decreasing pH, from about 500 $mg{\cdot}L^{-1}$ and 10 $kg{\cdot}day^{-1}$, respectively, for pH > 5.5 to greater than 1,200 $mg{\cdot}L^{-1}$ and 40 $kg{\cdot}day^{-1}$, respectively, for pH ≤3.5 (fig. 3). The inversely correlated pH and SO_4 data (loads and concentrations) for bituminous mines imply that the extent of pyrite oxidation increases with decreasing pH, which is consistent with laboratory rate data (McKibben and Barnes, 1986; Moses and Herman, 1991; Cravotta, 1996). However, the lack of similar correlations between the pH and SO_4 data for anthracite mine discharges suggest other processes are important.

The anthracite mines generally were flooded for decades before most bituminous surface mines had been developed. Although discharges from the anthracite mines are primarily overflows from stagnant mine pools, historical data indicate that when the anthracite mines first flooded, the water chemistry was similar to that of present bituminous mine discharges, with lower pH and higher concentrations of SO_4 and Fe (Ladwig and others, 1984; Wood, 1996). Comparing data collected in 1975 and 1991 for selected anthracite discharges, pH increased from the acidic mode to the near-neutral mode while SO_4 concentrations decreased for most mines in the Southern and Western Middle Anthracite Fields (Wood, 1996). In contrast, pH data for the Eastern Middle Anthracite Field, which is largely drained by the Jeddo Tunnel, showed no

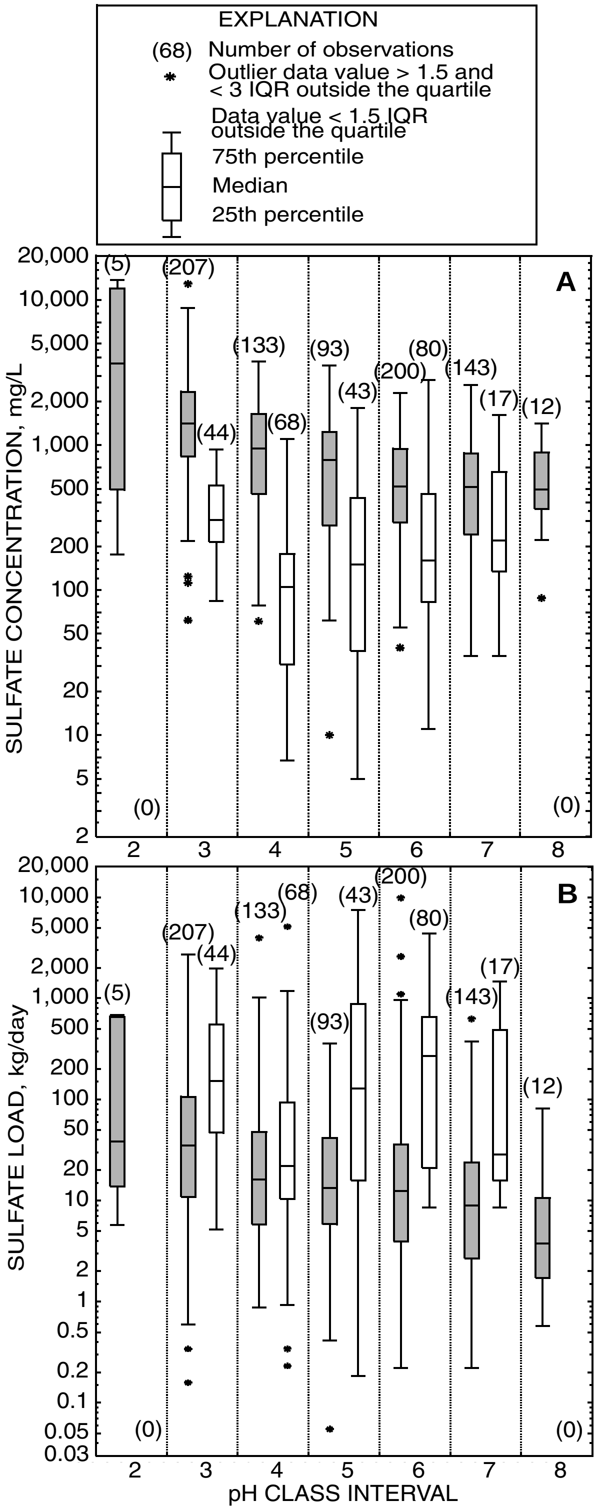

Figure 3. Boxplots showing sulfate data by pH class interval for 793 bituminous (shaded) and 252 anthracite coal-mine discharges in Pa. *A,* Sulfate concentration. *B,* Sulfate load. Class intervals for pH ± 0.5; interquartile range, IQR = 75th - 25th percentile.

change from the acidic pH mode. Hence, as pyrite and/or carbonate minerals are depleted and/or rates of reactions decrease, the pH and SO_4 frequency distributions and correlations are likely to change, but the time period for this change could span decades.

Mine-Scale and Laboratory Studies

Data for ground water and associated discharge samples from four surface mines in the bituminous coalfield, when combined so that each mine is represented equally (total frequency of 25 percent for each mine), also show a bimodal distribution of pH (fig. 4A). The pH of the ground water at each mine commonly ranges over several units, mainly caused by spatial variability or heterogeneity. Although acidic and near-neutral waters were sampled at three of the four mines, individual wells or discharges generally reflected locally acidic or near-neutral conditions. A few wells in mixed pyritic and calcareous spoil had water quality that varied temporally between acidic and alkaline (Cravotta and others, 1994; Rose and Cravotta, 1998). The effects of spoil composition and hydrology are indicated by the relations between pH and concentrations of SO_4^{2-} and Ca^{2+} (figs. 4B and 4C). Alkaline to weakly acidic water ($pH \geq 5$) that has relatively low SO_4^{2-} is characteristic of unmined bedrock and spoil that contain calcareous minerals and have low permeability (e.g. mine 1 in fig. 4). Strongly acidic water ($pH \leq 4$) that has high SO_4^{2-} is characteristic of high-permeability, well-drained, pyritic spoil (e.g. mines 2 and 3 in fig. 4). Moderately acidic water (pH 4 to 5) that has high SO_4^{2-} is characteristic of spoil or underlying bedrock that lacks dissolved oxygen (e.g. mines 2 and 4 in fig. 4). Although concentrations of Ca^{2+} and SO_4^{2-} are positively correlated, the linear relation between Ca^{2+} and SO_4^{2-} is evidently site specific with slopes differing among the mines. In general, calcareous strata produced water with the highest concentrations of Ca^{2+}, and noncalcareous, pyritic strata produced water with the highest concentrations of SO_4^{2-}. Lowest concentrations of Ca^{2+} and SO_4^{2-} were in water from unmined rock upgradient from the mines.

Laboratory leaching experiments demonstrate the bimodal pH distribution for water at coal mines generally results from the weathering of pyritic rocks that have a deficiency (low pH) or an abundance (near-neutral pH) of calcareous minerals necessary to buffer the pH (fig. 5A). Pyritic shale was subjected to leaching under continuously or variably saturated hydrologic conditions; calcite was added in different proportions to evaluate effects on the oxidation of pyrite and the transport of sulfate and metals (Cravotta, 1996). Without the addition of calcite, the leachate from the shale typically had pH 1.5 to 3.5 and high concentrations of sulfate and iron. However, with the addition of calcite, the leachate had pH 4.5 to 7 and lower concentrations of sulfate and iron. The dissolution of calcite not only neutralized acid but decreased pyrite oxidation rates, as indicated by higher pH and Ca^{2+} concentrations and lower SO_4^{2-} concentrations for leachate from shale with added calcite (figs. 5B and 5C). All the leachate samples were undersaturated with respect to gypsum; only leachate in continuously saturated columns with added calcite was saturated or supersaturated with respect to calcite.

The leaching tests also showed the hydrology of a mine has an important effect on pyrite oxidation. By maintaining stagnant, water-saturated conditions, which minimized the oxygen available for reactions, pyrite oxidation was minimized, as indicated by low SO_4^{2-} concentrations in leachate (figs. 5A and 5B). The leaching data can be summarized generally as follows:

- $pH < 3$ and $SO_4 > 1{,}500\ mg \cdot L^{-1}$ for variably saturated conditions without $CaCO_3$;
- pH 3.2-3.5 and $SO_4 < 1{,}000\ mg \cdot L^{-1}$ for continuously saturated conditions without $CaCO_3$;
- pH 4.5–6.5 and $SO_4 < 1{,}000\ mg \cdot L^{-1}$ for variably saturated conditions with $CaCO_3$ present; and
- $pH \geq 6.0$ and $SO_4 < 1{,}000\ mg \cdot L^{-1}$ for water-saturated conditions with $CaCO_3$ present.

For each $CaCO_3$:FeS_2 molar ratio, ranging from 0:1 to 2:1, lower pH and higher SO_4^{2-} and Ca^{2+} concentrations were produced under variably saturated, oxygenated conditions than under continuously water-saturated, stagnant conditions (figs. 5B and 5C) because of greater extent and rate of pyrite oxidation and the consequent dissolution of calcite and other minerals under oxygenated, acidic conditions.

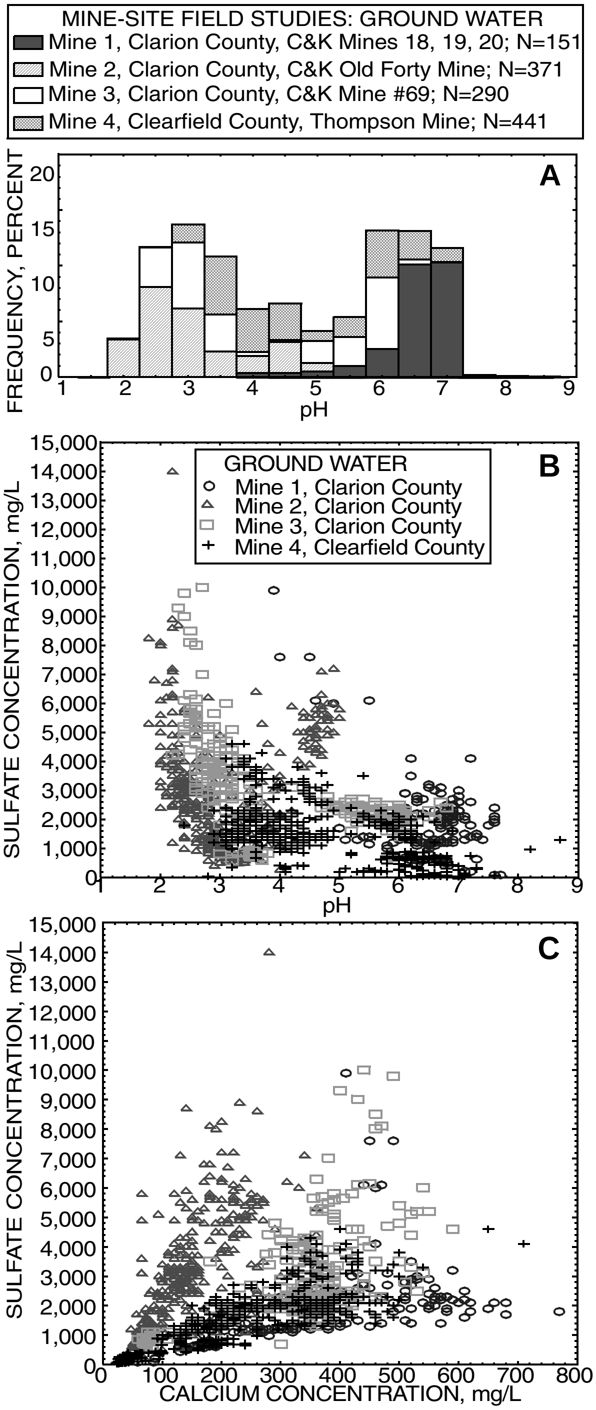

Figure 4. Chemistry data for 1,253 ground-water and discharge samples, collected monthly for 2 to 6 years, from four surface mines in the bituminous coalfield, Pa. (source: Dugas and others, 1993; Cravotta and others, 1994; Cravotta, 1996). *A,* Frequency distribution of pH; data for each mine weighted to represent 25% of the total. *B,* Relation between sulfate concentration and pH. *C,* Relation between sulfate and calcium concentrations.

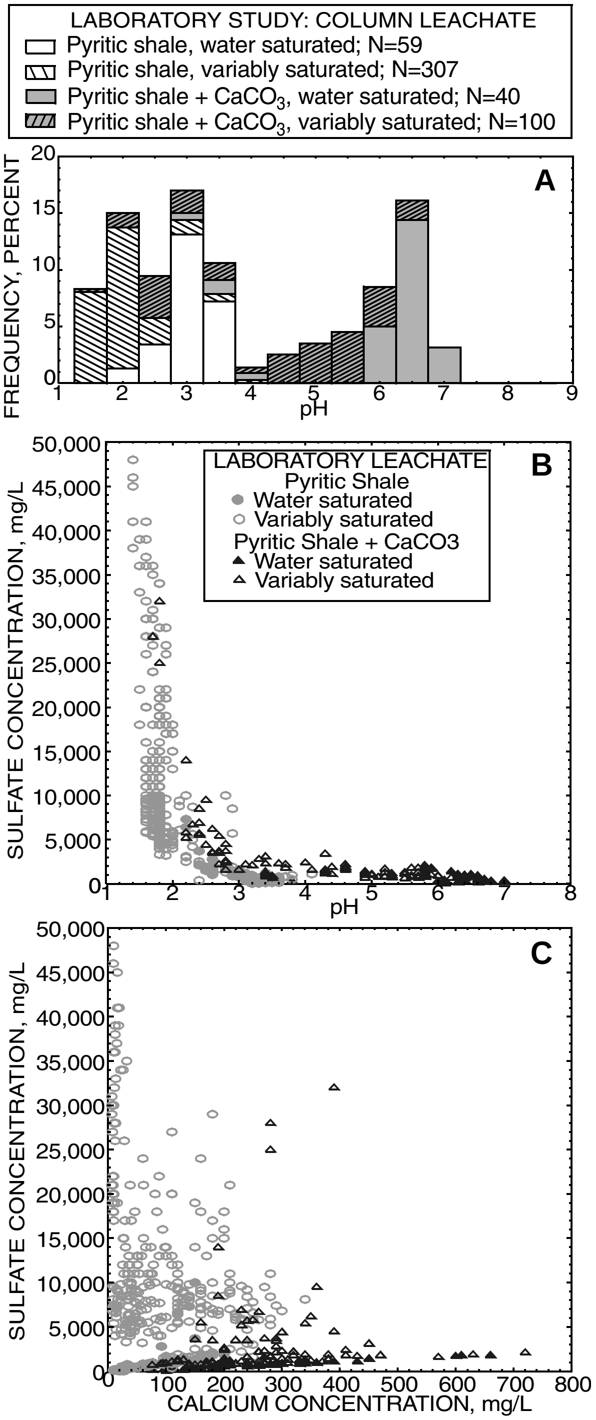

Figure 5. Chemistry data for 606 leachate samples from pyritic shale. Data for each of four leaching scenarios, collected biweekly over 3 to 9 months (source: Cravotta, 1996). *A,* Frequency distribution of pH; data for each treatment weighted to represent 25% of the total. *B,* Relation between sulfate concentration and pH. *C,* Relation between sulfate concentration and calcium concentration.

Geochemical Simulations

Geochemical simulations evaluated the effects on pH, Eh, and sulfate concentrations from pyrite oxidation over a range of conditions characteristic of the field conditions at coal mines. Although a wide range of conditions was considered, this paper evaluates only the most important variables affecting pH. A typical simulation involved 100 or more incremental steps with small additions of pyrite to 1 L solution. After each of these steps, the pH, Eh, and dissolved species were calculated. The pH was plotted as a function of the total concentration of sulfate species in solution (SO_4^{2-}, HSO_4^-, $FeHSO_4^{2+}$, etc.) which indicates the amount of pyrite oxidized (192 g SO_4 per 120 g FeS_2) if sulfate minerals do not precipitate.

Firstly, the oxidation of pyrite, in the absence of calcite, is considered for different Pco_2 and Po_2 (fig. 6A). Except for depressing the pH of initially pure water, varying Pco_2 from $10^{-3.5}$ to 10^{-1} atm has little effect on the pH after pyrite oxidation has begun. In contrast, limiting the availability of oxygen has a significant effect on the pH as simulated for an “open system” (air equilibrium, Po_2=0.2 atm, for complete oxidation of S and Fe in FeS_2 by reactions 1 and 2) or a “closed system” (3.5 mol O_2 per mol FeS_2 for oxidation of only S by reaction 1). Starting with pure water in equilibrium with ambient Pco_2, pH declines from 5.5 to 4 with the oxidation of only a small quantity of pyrite (0.012 $g{\cdot}L^{-1}$ FeS_2 produces pH~4 and 20 $mg{\cdot}L^{-1}$ SO_4^{2-}); continued pyrite oxidation decreases pH to about 3 at the point where total SO_4 concentration is 100 $mg{\cdot}L^{-1}$. As SO_4 concentration increases from 100 to 1,200 $mg{\cdot}L^{-1}$ the pH declines asymptotically approaching 2. For an open system, where oxygen is unlimited, the oxidation of pyritic S and Fe^{2+} and the precipitation of amorphous $Fe(OH)_3$ (reactions 1 and 2) results in pH about 0.3 units *greater than* that for the closed system where oxygen is limited to only the stoichiometric amount needed to produce SO_4^{2-} (reaction 1). The pH decreases about 0.5 units if a phase such as goethite (FeOOH) precipitates instead of higher solubility amorphous $Fe(OH)_3$, resulting in pH under air equilibrium that is *less than* that under oxygen limited conditions (fig. 6A). The narrow range of pH results mainly from the logarithmic scale for pH, plus buffering by ionic complexation $Fe(OH)^{2+}/Fe^{3+}$ and SO_4^{2-}/HSO_4^- (reactions 6 and 7) and dissolution of previously formed iron minerals. The simulations illustrate that for a specific SO_4 concentration, a lower pH cannot be achieved simply from pyrite oxidation; however, most mine water samples have greater pH at a given SO_4 concentration because of neutralization reactions with other minerals that increase pH and add other solutes.

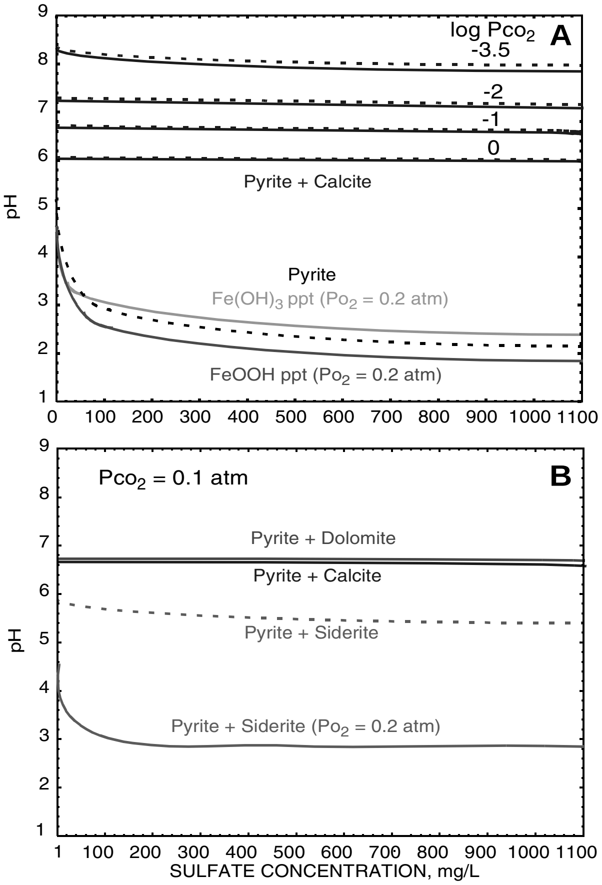

FIGURE 6. Simulated pH and sulfate concentration resulting from pyrite oxidation under different conditions (dashed line O_2 limited; solid line Po_2= 0.2 atm). Simulations conducted using PHREEQC (Parkhurst, 1995); temperature = 10°C, Pco_2 = 0.1 atm, and amorphous $Fe(OH)_3$ allowed to precipitate, unless specified. *A*, Effects of Po_2 and Pco_2 and equilibrium with calcite. *B*, Equilibrium with var ious carbonate minerals.

Secondly, the oxidation of pyrite in equilibrium with various carbonate minerals including calcite, dolomite, or siderite ($FeCO_3$) is considered (figs. 6A and 6B). For example, if calcite equilibrium is maintained, the pH remains relatively constant at a particular Pco_2 despite the oxidation of pyrite (fig. 6A); however, the pH can range widely as a function of Pco_2 from a relatively constant pH value of 6 (P_{CO_2} = 1 atm) to pH values of 8.0 to 8.4 ($P_{CO_2} = 10^{-3.5}$ atm). For calcite equilibrium at P_{CO_2} = 0.1 atm, pH is 6.6±0.1 over the entire range of SO_4^{2-}. Little difference results if equilibrium with dolomite (pKsp = 16.5) is maintained instead of with calcite (pKsp = 8.5) (fig. 6B); for P_{CO_2} = 0.1 atm, these calcareous minerals buffer pH at about 6.6. However, if siderite (pKsp = 10.5) is the available carbonate mineral, the pH generally will be much lower at equilibrium. For a closed system, where oxygen is limited to only the stoichiometric amount needed to produce SO_4^{2-}, siderite buffers pH at about 5.5, because H^+ is consumed by the reaction:

$$FeCO_3 + 2\,H^+ \leftrightarrow Fe^{2+} + H_2O + CO_2(aq). \qquad (8)$$

However, if oxygen is available to oxidize Fe^{2+}, siderite has little buffering effect, because all Fe is oxidized by the reaction:

$$FeCO_3 + 0.25\,O_2 + 1.5\,H_2O \rightarrow Fe(OH)_3 + CO_2(aq) \qquad (9)$$

An increase in the dissolved CO_2 by reaction 9 will produce a corresponding decrease in the ratio of $HCO_3^-/H_2CO_3^*$ and hence decrease the pH (per reaction 5).

DISCUSSION AND CONCLUSIONS

The bimodal distribution of pH for coal-mine drainage, with modes at pH 2.5 to 4 (acidic) and pH 6 to 7 (near neutral), is a regional phenomenon controlled by the mineralogy and hydrology of the mines. Although iron disulfide (pyrite) and calcareous minerals (calcite and dolomite) comprise only a few percent, or less, of the coal-bearing rock, these acid-forming and acid-neutralizing minerals are highly reactive and are mainly responsible for the bimodal pH distribution. The acidic mode, classified as AMD, is produced by the oxidation of pyrite in the absence of carbonate buffering. The field and laboratory studies indicate that, where calcite and dolomite are absent, extensive pyrite oxidation can result under variably saturated conditions, producing severe AMD (pH < 3 and SO_4 > 2,000 mg·L^{-1}); these conditions can be found at some well-drained underground mines and surface mines (e.g. bituminous mines, fig. 3). The studies also indicate that, where calcareous minerals are absent or deficient, the oxidation of only small amounts of pyrite under stagnant water-saturated conditions can produce AMD (pH < 4 and SO_4 > 200 mg·L^{-1}); these conditions commonly are found at flooded underground mines (e.g. anthracite mines, fig. 3). In contrast, where calcareous minerals are abundant, the pH can be buffered to be near neutral. Some near-neutral water contains high concentrations of SO_4 (median > 200 mg·L^{-1}), suggesting an origin as AMD that had been neutralized by reactions with calcareous minerals after, or downflow from the location of, pyrite oxidation.

The geochemical simulations confirm the interpretations of the field and laboratory data. The simulations clearly illustrate the effect of pyrite oxidation on lowering pH and of calcite and dolomite dissolution on increasing pH. Specific conclusions from the simulations are as follows:

- The near-neutral pH mode results from the dissolution of calcite and dolomite and by resultant carbonate buffering ($HCO_3^-/H_2CO_3^*$; $HCO_3^-/CaCO_3$; $HCO_3^-/CaMg(CO_3)_2$). As long as carbonate equilibrium is maintained or approximated, near-neutral pH can be maintained despite continued amounts of pyrite oxidation.
- In the absence of carbonate buffering, only a small amount of pyrite oxidation produces dilute AMD (0.012 g·L^{-1} FeS_2 produces pH~4 and 20 mg·L^{-1} SO_4^{2-}). However, because of the logarithmic scale for pH and ion speciation, unit decreases in pH require greater than 1 order of magnitude increases in the amount of pyrite oxidation.
- Buffering in the acidic mode is due to ion speciation (SO_4^{2-}/HSO_4^-; $Fe(OH)^{2+}/Fe^{3+}$) and to precipitation and dissolution of $Fe(OH)_3$.
- The least frequent pH range of pH 4.5 - 5.5 indicates a poorly buffered condition and could result from limited reactions with calcareous minerals (undersaturated) or limited availability of O_2 resulting in the incomplete oxidation of Fe^{2+} from pyrite or siderite.

The results of this evaluation have several implications. Firstly, the bimodal distribution for pH and the tendency for calcareous minerals to buffer pH in the near-neutral range support the approach of using “acid-base” accounting, where only pyritic and calcareous minerals are evaluated, as a basis for predicting post-mining water quality (e.g. Brady and others, 1994). Generally, “net alkaline” mine water has pH $\geq$ 6 (Rose and Cravotta, 1998), and near-neutral pH is desirable to limit the mobility of iron and associated metals (Stumm and Morgan, 1996). The calcareous minerals not only neutralize acid, but their dissolution tends to slow or inhibit pyrite oxidation. Furthermore, although siderite may temporarily buffer pH in the near-neutral range, the presence of siderite should be considered as a negative factor with regard to the prediction of mine-drainage quality, because once the iron precipitates any benefits of siderite as a neutralizing agent will be negated (Skousen and others, 1997).

Secondly, the laboratory experiments indicate that addition of calcite can increase pH and reduce the transport of iron and other metals; however, equilibrium with calcite, hence buffering by the carbonate minerals, is not achieved except under conditions of water saturation. On the other hand, pyrite oxidation tends to be diminished under continuously saturated conditions, in which oxygen availability is limited, compared to variably saturated hydrologic conditions, in which oxygen availability is enhanced. Thus, for those mines where the importation and addition of alkaline materials is needed to achieve a net-neutral acid-base account, the placement of alkaline and pyritic materials in continuously wet zones would be prudent. In practice, however, a permanently wet zone in spoil generally will not be realized immediately and may be difficult to sustain (Cravotta and others, 1994).

Thirdly, recent field and laboratory work indicates iron hydroxysulfate minerals, which tend to be yellowish colored, form dominantly under acidic conditions whereas relatively pure iron hydroxide, which tends to be reddish colored, tends to form dominantly under near-neutral conditions (e.g. Bigham and others, 1996a, 1996b). Because these minerals have different coloration and related spectral properties, new approaches to characterizing mine drainage by use of remote sensing may have merit. For example, preliminary testing of aerial and ground-based spectral reflectance techniques has demonstrated the potential for differentiating between acidic and near-neutral drainages (Robbins and others, 1996). These techniques may be useful for locating and characterizing water quality where access is restricted.

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