

ACID-BASE ACCOUNTING: AN IMPROVED METHOD OF INTERPRETING OVERBURDEN CHEMISTRY TO PREDICT QUALITY OF COAL-MINE DRAINAGE¹

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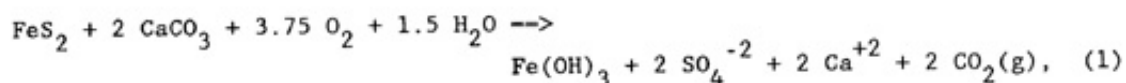
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and

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Introduction

Acidic mine drainage (AMD), which results from the accelerated oxidation of pyrite (FeS_2) in mined coal and overburden, has contaminated thousands of miles of streams in the Appalachian region of the United States. Acid-base accounting (ABA), which simplifies the complex hydrogeochemical system through use of a limited number of variables, commonly is used to predict the post-mining occurrence of AMD. ABA involves the measurement of sulfur (S) and carbonate (CO_3) concentrations in coal-bearing rocks and the computation of overburden net-neutralization potential (NNP) in units of tons of calcium carbonate per thousand tons of rock (tons CaCO_3 /1,000 ton) (Sobek and others, 1978). ABA was developed on the assumption that the stoichiometry of the following overall reaction of FeS_2 and CaCO_3 can be used to convert acid (H^+) into units of CaCO_3 :



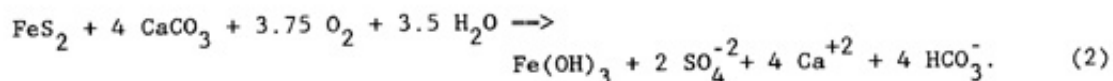
where the H^+ from 1 mol (mole) of FeS_2 [64 g (gram) of S] is neutralized by 2 mol of CaCO_3 (200 g). This method presumes that gaseous carbon dioxide (CO_2) will exsolve. Thus 3.125 g CaCO_3 will neutralize the acid from 1 g S; or 31.25 tons of CaCO_3 will neutralize the acid from 1,000 tons of rock that contains 1.0 percent pyritic S. The total S concentration, in percent, is multiplied by 31.25 and is assumed to be pyritic and acid-producing in order to compute maximum potential acidity (MPA) for comparison with neutralization potential (NP), in units of tons CaCO_3 /1,000 ton (Sobek and others, 1978). NNP is computed by subtracting mass-weighted MPA from NP (Smith and Brady, 1990). If the value of NNP is less than zero, the acid-producing potential of the rock exceeds its neutralization potential and if mined, therefore, would be expected to produce AMD.

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Many investigators have attempted to use overburden chemical data to predict the quality of coal-mine drainage, but with variable success. Several authors (Skousen and others, 1987; diPretoro and Rauch, 1988; Brady and Hornberger, 1989; Brady and others, 1990) have recognized an inconsistency between the overburden NNP computed by use of the conventional method of ABA and the corresponding post-mining water quality. These investigators pointed out that alkaline drainage rarely was observed until NP values were 2 or more times larger than MPA. Thus, despite being reported in "equivalent" units, NP values about 2 times MPA values appeared to be equivalent considering the corresponding alkalinity and acidity of post-mining drainage.

Cravotta and others (1990) suggested that ABA interpretations should consider the following net-neutral reaction to compute MPA, because CO₂ can dissolve to form a weak acid that can react with CaCO₃ :



Reaction 2 shows that H⁺ from 1 mol of FeS₂ (64 g of S) is neutralized by 4 mol of CaCO₃ (400 g), instead of 2 mol of CaCO₃ as assumed by the conventional ABA method, to produce bicarbonate (HCO₃) or alkalinity. Hence, total S, in percent, is multiplied by 62.5 instead of 31.25 to compute MPA.

Reactions 1 and 2 are "end-member" reactions; the hydrogeochemical relations in mine-spoil drainage or ground water probably lie somewhere in between. Nevertheless, use of total S and a factor of 62.5 should yield a conservative estimate of maximum potential acidity, because not all S will acid-producing nor will all CO₂ dissolve.

This paper establishes a useful relation between the contents of sulfur and carbonate in coal-bearing rocks that can be used to predict whether post-mining discharge water will be acidic or alkaline. The above methods of ABA data interpretation, by use of stoichiometric equivalence factors of 31.25 (reaction 1) and 62.5 (reaction 2) to compute MPA and NNP, are compared with water-quality data from mine-site field studies. Net alkalinity, in units of milligrams CaCO₃ per liter of water (mg CaCO₃ /L), is calculated by subtracting acidity (base-neutralizing capacity) from alkalinity (acid-neutralizing capacity) and is used as an overall measure of post-mining water quality; the water is acidic if net alkalinity is less than zero, or alkaline if net alkalinity is greater than zero.

Comparison of Overburden Chemistry and Coal-Mine-Drainage Quality

Overburden NNP and associated net-alkalinity data for post-mining water were obtained from previous studies, principally by the U.S. Bureau of Mines (BOM) (Erickson and Hedin, 1988; P.M. Erickson, U.S. Bureau of Mines, written commun., 1990), West Virginia University (WVU) (diPretoro, 1986; diPretoro and Rauch, 1988), and Pennsylvania Department of Environmental Resources (PaDER) (Brady and others, 1990). These data, from a total of 74 coal mines in Pennsylvania, West Virginia, Maryland, Kentucky, and Illinois, have been combined in figure 1 to show the results of a comparison of observed net alkalinity and computed NNP (predicted net alkalinity). MPA (and ultimately NNP) was calculated from percent total S using a range of stoichiometric equivalence factors, including the multiplication factors 31.25 and 62.5. Matching signs on NNP and net alkalinity were counted as a correct prediction and mismatched signs as an incorrect prediction.

Figure 1 shows that the number of correct predictions of post-mining drainage quality was increased by using a factor of 62.5 (57 of 74 sites predicted correctly) instead of 31.25 (52 of 74 sites predicted correctly) to compute NNP. Just as importantly, when a factor of 62.5 was used, the errors in prediction became more balanced, or random. The error of predicting that a mine site would produce alkaline water when it actually produced acidic water was reduced from 20 of 22 wrong predictions when 31.25 was used to 10 of 17 wrong predictions when 62.5 was used. Therefore, the conventional ABA method of computing MPA by multiplying percent total S by 31.25 underestimates acid-producing potential, and a more conservative approach of using a factor of at least 62.5 to compute MPA as proposed by Cravotta and others (1990) is warranted.

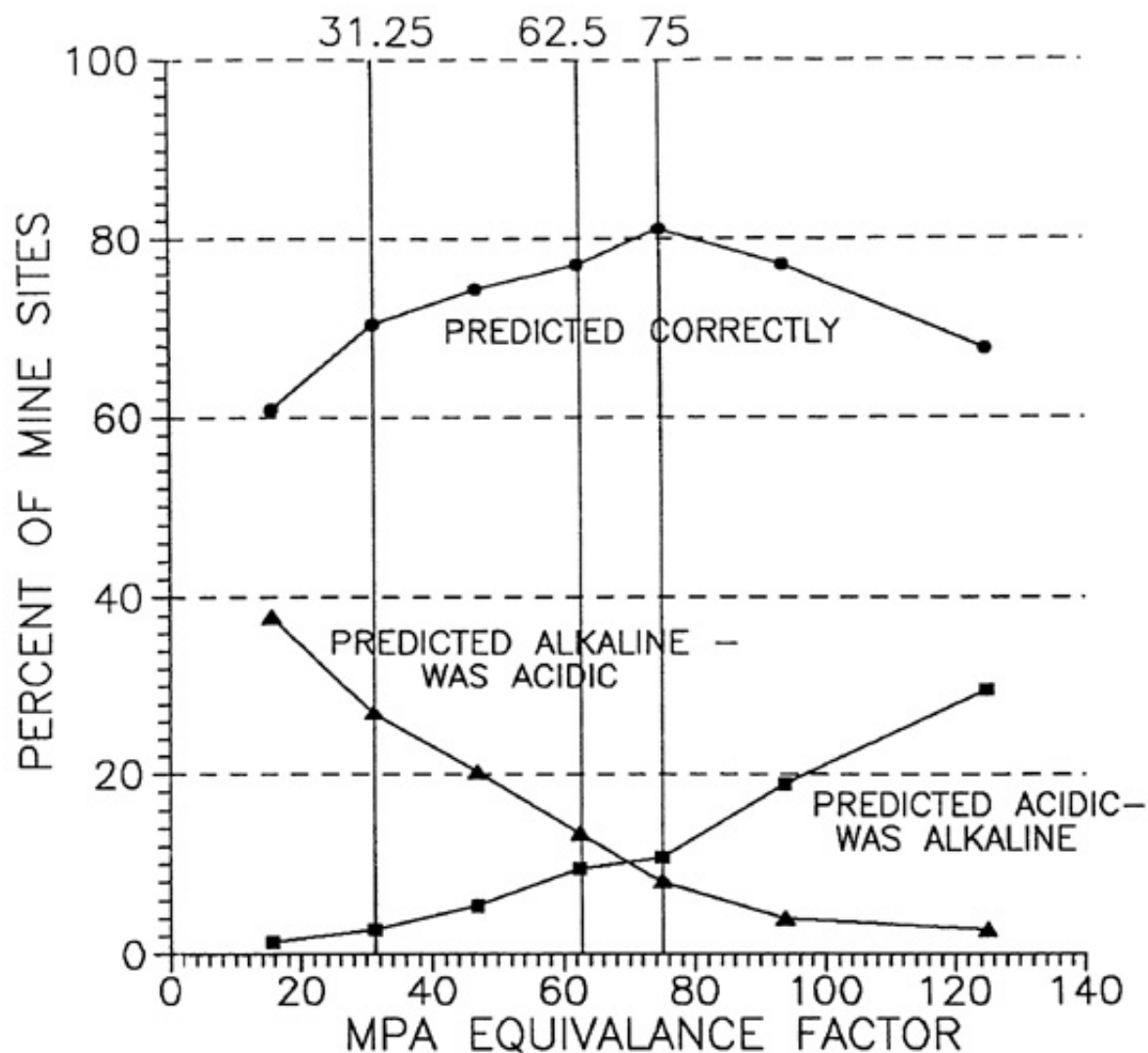


Figure 1.--Frequency of correct and incorrect predictions of net alkalinity of post-mining water based on overburden net-neutralization potential (NNP) for 74 mine sites. NNP was computed from measured neutralization potential (NP) and a range of multiplication factors to compute maximum potential acidity (MPA) from the total sulfur concentration in overburden: $NNP = NP - MPA$.

Errors in predicting the quality of mine drainage by use of NNP data can be addressed, in part, by noting concerns about the overburden and water-quality data used to create figure 1. The WVU and BOM data for 62 of the 74 mine sites include only one overburden log per site and assume a right-triangle approximation for volumetric adjustments to compute NNP (diPretoro, 1986; Erickson and Hedin, 1988). Multiple overburden logs commonly are needed to represent the geological and chemical variability at a site (Brady and others, 1988, 1992). Brady and others (1990) evaluated total S and NP data for multiple overburden logs for the remaining 12 of the 74 mine sites and used a computer program by Smith and Brady (1990) to

compute a cumulative mass-weighted NNP on the basis of improved estimates of the spatial distribution and mass of each unit mined. Nevertheless, all the investigators encountered difficulty in collecting representative post-mining water-quality samples. Errors in prediction also can result because the available water-quality data do not adequately represent a typical composition, or integrated net-alkalinity, for a mine site. A water sample, especially from a single discharge point or well, is not likely to be affected by the cumulative mass of strata at a site because of normal spatial and temporal hydrologic variations. As with overburden logs, multiple water samples commonly are needed to represent the site variability. For example, if alkaline and acid discharges occur on the same site, flow weighting, as done by Erickson and Hedin (1988), should be considered. The water-quality data thus are a potentially large source of error and partly explain why the use of ABA as a water-quality prediction tool is qualitative, whereby the sign, but not the magnitude, of net alkalinity is indicated.

Although caution needs to be exercised to avoid overinterpreting the results in figure 1, some alternative explanations for errors can be considered. For example, errors noted as "predicted alkaline - was acidic" can result if neutralization is not instantaneous or if the native carbonate is calcite coated by iron oxyhydroxide compounds or is substantially siderite (FeCO_3). Errors noted as "predicted acidic -- was alkaline" can result if nonacid-forming S compounds, such as gypsum, are present or if pyrite oxidation is inhibited by alkaline conditions produced by recharge through calcitic strata overlying pyritic material.

The two factors that ABA considers, total S and NP, are assumed to represent FeS_2 and CaCO_3 ; however, other mineral forms contribute to the total S and NP quantities measured by the standard overburden analytical methods of Sobek and others (1978). Total S can consist of sulfide, sulfate, and organic sulfur components, and acid can be produced by each of these forms. Yet, because pyrite generally is considered to be the acid producer, some workers have suggested that MPA should be computed by considering sulfide S only. However, Brady and Smith (1990) have identified analytical problems associated with the determination of sulfide S, and the typical analytical method may not indicate the amount of pyrite present. Furthermore, Cravotta (1991) and Alpers and others (1991) have shown that the dissolution of iron- and aluminum-sulfate minerals and the subsequent hydrolysis of iron and aluminum can produce substantial quantities of acidity. Harvey and Dollhopf (1986) have suggested that some forms of organic S also may be acid-producing. Thus, consideration of pyritic S alone may underestimate acid production, and the use of total S to compute MPA will account for the total potential acidity.

The measurement of NP directly indicates the acid-neutralizing capacity of the rock, but it can be influenced by the presence of minerals other than CaCO_3 . Morrison and others (1990) demonstrated that siderite can appear as a neutralizer during the test for NP. On the other hand, Cravotta and others (1990) explained that the complete dissolution of FeCO_3 and subsequent hydrolysis of iron can produce acid. Hence, NNP can be overestimated (an overly high measured NP) because of the presence of siderite.

Limitations of the data and analytical methods only partly explain the error in predicting net alkalinity from NNP, because many environmental factors complicate the prediction of acidic drainage (Rose and others, 1983; diPretoro and Rauch, 1987). No attempt has been made in our evaluation of ABA and associated water-quality data to account for the combined effects of differences in spatial distribution of acid-forming and neutralizing minerals, differences in

mineral solubilities, relative rates and temporal variability of acid-production and neutralization reactions, effects of mining methods (such as selective handling of acidic spoil), and surface-water and groundwater hydrology. ABA interpretations would benefit from additional study of the effects of these factors.

Conclusions

Although an improved method of interpreting overburden chemistry to predict the quality of coal-mine drainage has been demonstrated, additional work is needed to perfect ABA methods and interpretations. ABA is only one of many useful tools to assess the hydrologic effects of coal mining (Rose and others, 1983; diPretoro and Rauch, 1987; Brady and Hornberger, 1989). An understanding of sampling and analytical methods and of hydrogeochemical processes that can affect mineral weathering enhances the interpretation of ABA and water-quality data. Generally, various mine-drainage-prediction methods, including ABA, will indicate consistent predictions. If different methods indicate inconsistent predictions, they also may indicate such problems as nonrepresentative samples or rapid lateral lithologic and chemical changes between the proposed mine and adjacent mines. The use of multiple tools and the computation of MPA by multiplying percent total S by a factor of 62.5 as proposed by Cravotta and others (1990) improve the accuracy of predicting the quality of mine-drainage water, primarily as a result of reducing the error "predicted alkaline -- was acidic."

Acknowledgments

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