ACID/BASE ACCOUNT AND MINESOILS: A REVIEW[1]

by

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Abstract. Generation of acidity from the oxidation of iron sulfides (FeS_2) is a common feature of geological materials exposed to the atmosphere by mining activities. Acid/base accounting (ABA) has been the primary method to evaluate the acid- or alkaline-potential of geological materials and to predict if weathering of these materials will have an adverse effect on terrestrial and aquatic environments. The ABA procedure has also been used to evaluate minesoils at different stages of weathering and, in some cases, to estimate lime requirements. Conflicting assessments of the methodology have been reported in the literature. The ABA is the fastest and easiest way to evaluate the acid-forming characteristics of overburden materials; however, accurate evaluations sometimes require that ABA data be examined in conjunction with additional sample information and results from other analytical procedures. The end use of ABA data, whether it be for minesoil evaluation or water quality prediction, will dictate the method's interpretive criteria. Reaction kinetics and stoichiometry may vary and are not clearly defined for all situations. There is an increasing awareness of the potential for interfering compounds, particularly siderite ($FeCO_3$), to be present in geological materials associated with coal mines. Hardrock mines, with possible mixed sulfide mineralogy, offer a challenge to the ABA, since acid generation may be caused by minerals other than pyrite. A combination of methods, static and kinetic, is appropriate to properly evaluate the presence of acid-forming materials.

Additional key words: analytical method, minesoil acidity, pyrite, reclamation, siderite

Introduction

The term "acid/base account" means different things to different people. Some use the acid/base account (ABA) to evaluate the suitability of overburden materials for minesoils, while others use the ABA to predict post-mining water quality. The common theme to each function is that the ABA is a prediction tool. It is necessary to have the ability to predict whether earth-disturbing activities, such as mining, construction of pipelines and highways, or disposal of dredged materials, may produce acidity through the exposure of sulfide-containing minerals to the atmosphere (Fisher and Brown, 1994). This paper is a brief review of the ABA, documenting its creation, identifying its components, reviewing some of its applications, and discussing other procedures to evaluate potential production of acidity.

The ABA method was the first technology available to assess overburden material quality prior to disturbance (Skousen et al., 1987) and was initially developed in West Virginia (Smith et al., 1974a; Smith et al., 1974b; Smith et al., 1976). The concept for ABA arose from ideas based on the composition of the earth's crust (where there is generally a greater proportion of alkaline-producing elements than acid-producing ones). Early spoil classification systems were designed with revegetation in mind. Knabe (1964) as reported by Skousen et al (1990) added a designation of either negative or positive to minespoil, based on the presence or absence of unneutralized SO_4 (sulfides or pyrite were expressed as SO_4). Development of an

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overburden evaluation procedure became more important with passage of the Surface Mining Control and Reclamation Act (Public Law 95-87; U.S. Congress, 1977); whereby acid-forming materials were to be identified (30 CFR 780.22) and handled in a manner to control the impact on surface and groundwater and minimize adverse effects on plant growth (30 CFR 816.102). The ABA was proposed in 1976 and the final field and laboratory procedures for the method were published in 1978 (Sobek, et al., 1978). The ABA consisted of five components: acid potential, neutralization potential, pH, rock type, and depth below the land surface (Sobek et al., 1987). The method balances maximum potential acidity against total neutralizers and is defined as:

$$\text{A/B Account} = \text{NP} - \text{PA} \qquad (1)$$

where NP is the neutralization potential and PA is the potential acidity (either total or pyritic sulfur). The end use of the ABA data will influence its interpretation. Researchers have found that various ABA values may predict the potential for acid mine drainage; however, these threshold values are site dependent. Work is currently being conducted to obtain a better correlation between pre-mine ABA values and post-mine water quality. On the other hand, positive ABA values for overburden materials may indicate that adequate neutralizers (NP) are present in the material to counter any acidity produced through oxidation of FeS_2 or other sulfides (PA). If the overburden's ABA is negative, it is assumed that the material will eventually become acidic and will require remediation, commonly through liming or burial. The remaining components of the ABA (pH, rock type, and depth) are sometimes overshadowed by the importance placed on the ABA equation alone. It is essential to interpret the results of the ABA equation in the context offered by the other three variables.

Components of the Acid/Base Account Equation

Neutralization Potential. The inherent base content of overburden material, including carbonates, other easily weatherable minerals, and exchangeable cations on clays, is included in the NP. The basic components in an unweathered overburden may be sufficient to equal or exceed the PA of the material. The methods commonly used to characterize this component are digestion with hot (Sobek et al., 1978) or cold (Caruccio and Caruccio, 1980) acid.

Potential Acidity. The PA is a measure of the maximum amount of acidity that may be generated by an overburden or minesoil sample. It is determined by a number of laboratory methods (ASTM, 1984; Sobek et al., 1978; O'Shay et al., 1990). The primary acid-producing compound in most geological samples and minesoils is FeS_2, although there are other acid-forming minerals that may be present; such as arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), and pyrrhotite ($Fe_{1-x}S$).

Uses of the Acid/Base Account Procedure

Acid/base account methodology was originally developed to identify overburden strata suitable for creation of minesoils. National and state reclamation regulations address the issue of acid forming-material (AFM) in essentially the same manner: AFM must be identified and handled or treated to control their impact on the environment. The ABA evolved into a predictive tool for a number of situations:

- determine the suitability of overburden strata and their potential to produce acid mine drainage;
- assess reclamation success in terms of complying with state and national regulations regarding AFM;
- predict the potential for release of acid drainage from mine wastes (Blowes et al., 1994); and
- to make lime recommendations. This use of the ABA is generally considered to be inappropriate; however, a modification of the ABA to obtain lime quantities for remediation of acidic materials has been employed.

Limitations of the Acid/ Account Method

Neutralization Potential

There are assumptions made regarding the NP determination that limit the procedure's validity. First, it is presumed that all neutralizing materials are consumed completely to release CO_2 (Day, 1994). Next, all of the alkalinity measured as NP is available to neutralize acidity. Finally, the reaction rates of alkaline materials are not considered. It should be understood that the NP is a measure of the maximum alkalinity available (Skousen et al., 1990), derived from a whole sample analysis, since complete reaction probably never occurs in situ. Problems that may occur with the neutralization of acidity can be placed in three classes: kinetic (timely delivery of base); physical (distribution of base within overburden or minesoil); and statistical (uncertainty in the estimation of the NP) (Donovan and Ziemkiewicz, 1994).

There are at least five points that should be considered when evaluating the NP of an overburden or minesoil material. The first three are related to the efficacy and reaction rates of the alkaline materials that are measured by the NP procedure. The last two indicate there is a potential for overestimating the NP value in certain materials. Possible amendments and alternatives to the NP procedure are presented later in this paper.

Reaction Rate of Carbonates. The particle size and type of carbonates in a sample is generally unknown. However, native carbonates can be present as large aggregates; and because of their relatively small surface area, will be inefficient in neutralizing the acidity produced by sulfide oxidation. Additionally, some carbonates will react more quickly than others (e.g., calcite reacts more quickly than dolomite). The data obtained from the NP analysis will no longer reflect actual conditions and will most likely be an overestimate, since the procedure requires a finely ground sample (Boon and Smith, 1985).

Iron Oxide Coatings. Iron oxide coatings can form on carbonates, preventing carbonate dissolution and reaction (Caruccio and Geidel, 1981). Acid neutralization will subsequently be inhibited. This component may be more relevant to treatment of acid mine drainage.

Availability of Neutralizing Materials. The reaction rate of bases and their ability to neutralize acidity is affected by dissolution of calcite, which is controlled by pH and the partial pressure of CO_2. Acidity will probably not be neutralized unless carbonates are in contact with acid-forming materials or an acidic minesoil solution (Ziemkiewicz and Skousen, 1992; Day, 1994). Additionally, the minesoil solution can become saturated with respect to calcite but undersaturated with respect to pyrite even though oxygen is present. This may lead to calcite leaching out of spoil materials before all sulfide-bearing materials are oxidized (Geidel, 1979; Doolittle, 1991; Brady et al., 1994).

Siderite. The presence of siderite ($FeCO_3$) in samples results in elevated NP values when the standard NP procedure of Sobek et al., 1978 is used (Dixon et al., 1982; Frisbee and Hossner, 1989; Morrison et al., 1990; Doolittle et al., 1992; Lappako, 1994). Siderite weathering is normally a slow process, the rate of reaction being reduced by a thin layer of hematite that forms on the crystal surface (Seguin, 1966; Doolittle et al., 1992; Frisbee and Hossner, 1995). However, when siderite is exposed to aqueous, acid conditions (like those that exist in the NP procedure) it reacts and the reaction rate increases with increases in temperature (Fisher and Brown, 1994). The initial siderite reaction reduces the acidity of the sample, but the net reaction is probably acidic when the resulting ferrous iron is oxidized and the subsequent ferric iron is hydrolyzed (Dixon et al., 1982; Boon and Smith, 1985; Doolittle et al., 1992; Lappako, 1994). Siderite probably affects many NP results, since it appears to be a common constituent of overburden (Dixon et al., 1982; O'Shay, 1982; Morrison et al., 1990).

Fizz Rating. Incorrectly-assigned fizz rating values during the NP procedure may result in erroneous determinations (Morrison, et al., 1990; Evans and Skousen, 1995). A higher NP value can be obtained when a sample is subjectively assigned a higher rating because a higher volume of HCl will be added to the sample.

Potential Acidity

The PA of minesoils can be accurately quantified by the total sulfur (S) content when all S is present as FeS_2; however, this is commonly not the situation. Overburden and minesoils can have a mixed S system. Total -S, instead of pyritic-S, is used to estimate PA in areas where a more reliable correlation has been found between total sulfur and mine drainage quality.

Sulfur Forms. Laboratory methods for PA are based on the oxidation of sulfide compounds in overburden and minesoils. Normally, there is a mixed group of S compounds present in many of the samples when PA measurements are made. Knowledge of the materials being tested, their depositional origin and degree of weathering, is essential to correctly use and interpret ABA data. Organic and sulfate (SO_4^{2-}) forms of S are common. Oxidation of sulfides, upon exposure to the atmosphere, will produce SO_4^{2-}. Oxidized overburden and minesoils can contain substantial amounts of SO_4^- and organic-S. Sulfate minerals such as gypsum ($CaSO_4 \cdot 2H_2O$), jarosite [$KFe_3(SO_4)_2(OH)_6$], and barite ($BaSO_4$) are commonly found in weathered sulfidic materials (Carson et al., 1982). Iron sulfate salts, such as melanterite ($FeSO_4 \cdot 7H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$), and copiapite [$Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$] are also observed. Organic-S is usually not considered an acid-producer; however, iron and aluminum sulfates can undergo hydrolysis and produce acidity (Nordstrom, 1982). Jarosite is formed in acidic, oxidizing environments. In acid sulfate soils, jarosite is only slightly stable and can eventually hydrolyze to goethite (α-FeOOH), with the production of sulfuric acid.

$$2KFe_3(SO_4)_2(OH)_6 + 6H_2O = 6Fe(OH)_3$$

$$+K_2SO_4 + 3H_2SO_4 \qquad (2)$$

Stoichiometry. The stoichiometry for the reaction of pyrite with air and water is used for the calculation of H_2SO_4 produced by the following reaction:

$$FeS_2 + 7/2H_2O + 15/4O_2 = Fe(OH)_3 +$$

$$2H_2SO_4 \qquad (3)$$

The stoichiometry of this reaction for FeS_2 oxidation predicts that complete oxidation of a material containing 0.1 percent S (all as pyrite) will yield H_2SO_4 requiring 3.125 tons of $CaCO_3$ equivalence to neutralize 1,000 tons of the material. However, the quantitative determination of FeS_2 weathering stoichiometry can be complex. There can be a wide range in the amount of acidity produced, depending on the reaction environment and the morphology and size of the FeS_2. Additional uncertainty may be involved in hardrock mines, where significant amounts of other sulfide minerals may be present in the sample, such as chalcopyrite, arsenopyrite, or pyrrhotite, since these minerals will have different oxidation stoichiometries.

Different analyses. There are a number of procedures used to determine PA. These fall into three categories: (1) determination of S content and use of a stoichiometric equation for pyrite oxidation to calculate acidity; (2) determination of Fe and calculation of acidity from a stoichiometric equation for pyrite oxidation; and (3) titration of acidity after oxidation of the sample by a strong chemical oxidant, such as hydrogen peroxide (H_2O_2) or a simulated weathering procedure. The easiest methods are those that determine total S content. Sulfur forms (total, sulfate, pyritic, and organic) can be determined by sequential extraction of soluble S forms and determination of total residual (organic) S using wet chemistry or dry oxidation. There are two approaches (Sobek et al., 1978; Schafer, 1987) to S fractionation with extractions (Table 1). Recent research indicates the assumptions made in determining potential acidity with extraction methods may result in erroneous values, depending on the method used and the sample mineralogy (Table 2).

The ASTM method D2492-84 (ASTM, 1984; Sobek et al., 1978) is used to determine pyritic Fe. The procedure assumes that the total Fe remaining after digesting the sample with HCl is from pyrite, marcasite, or other iron sulfide minerals. The washed sample is digested in HNO_3 and the resulting solution analyzed for Fe. The acid potential is then calculated from the stoichiometric equation for FeS_2 oxidation, assuming all of the Fe is from FeS_2.

Direct titration of acidity produced by oxidation of a sample with hydrogen peroxide has been tested with mixed results. Potential acidity determinations of east Texas overburden sediments of Eocene Age, using a modification of the Sobek method (Sobek et al. 1978), were found to be accurate and reproducible (O'Shay et al., 1990). The stoichiometry for this

Table 1. Assumptions made in extraction of soluble S forms when estimating potential acidity, as defined by different methods.

Extraction Step	Material Identified by Each Extraction[†]	
	Sobek et al., (1987) Method	Schafer (1987) Method
Hot Water	Step not used	Non acid-producing (sulfates; gypsum, barite)
2:3 HCl	Non acid-producing (all sulfates)	Acid-producing (sulfates; jarosite)
1:7 HNO_3	Acid-Producing (pyrite)	Acid-Producing (pyrite)
Residual	Non acid-producing (organic S)	Acid-producing (non-extractable sulfides)

Note: Sobek method commonly used for samples from coal mines where organic S present; therefore, residual fraction is assumed to be non acid-forming. On the other hand, the Schafer method was designed to evaluate hardrock mine materials for potential acid production; therefore, the residual fraction is considered to be acid-forming (Jennings and Dollhopf, 1995).

Table 2. Mean percent mass removal of selected sample by sequential acid-base account extracts (from Jennings and Dollhopf, 1995)[†].

Sample	Is Sample an Acid-Forming Material?	Extracting Solutions			Residual Mass
		H_2O	HCl	HNO_3[‡]	
		mean % mass[†]			
$BaSO_4$ (Barite)	No	0.5	0.8	19.8	78.8
$CaSO_4.2H_2O$ (Gypsum)	No	40.6	56.5	3.3	-0.2[§]
$KFe_3(SO_4)_2(OH)_6$ (Jarosite)	Maybe	0.6	2.5	24.6	72.2
FeAsS (Arsenopyrite)	Yes	0.5	1.1	69.2	29.3
$CuFeS_2$ (chalcopyrite)	Yes	0.6	-0.7	27.1	73.0
FeS_2 (Ward's Pyrite)	Yes	0.7	-0.5	83.9	16.1
FeS_2 (marcasite)	Yes	0.8	-0.4	90.4	9.2
FeS_2 + Impurities (hardrock pyrite)	Yes	0.4	2.7	68.0	28.8
FeS_2 + Impurities (coal pyrite)	Yes	3.0	0.5	77.0	19.6

[†] Arithmetic mean of three replications

[§] Minus sign (-) indicates mass gain during extraction reaction shows that the oxidation process liberates is two moles of sulfuric acid per mole of pyrite:

$$FeS_2 + 15/2H_2O_2 = Fe(OH)_3 + 2H_2SO_4 + 4H_2O \qquad (4)$$

Other Factors to Consider When Evaluating Materials

The other three components of ABA, pH, rock type, and depth below land surface, can provide important information that may influence the manner in which a minesoil or overburden sample is analyzed. A low pH will indicate acidity is already present in the sample. A sample containing shale would be more likely to contain acid-forming materials than a limestone. Lastly, a sample taken from a depth of 90 feet is unlikely to be weathered. Acid/base account data must always be interpreted in conjunction with the preceding variables.

Sample collection and handling can also be an important consideration in evaluating ABA status of overburden materials. Coarse fragments containing AFM may be discarded or they may be finely ground prior to overburden analysis. Consolidated materials may be considered as nonreactive as a coarse fragment but reactive when ground.

Active Acidity

Active acidity may be from natural weathering, applications of acid-forming fertilizers, or from prior oxidation of AFM. This type of acidity is relevant only to soils, weathered overburden, and minesoils and not to unweathered overburden. Active acidity is comprised of both exchangeable and non-exchangeable acidity. Exchangeable acidity is the sum of exchangeable H^+ and exchangeable Al^{3+} and is present in significant quantities only in samples with a pH less than about 5.5 (Thomas and Hargrove, 1984). Active acidity is routinely evaluated with a KCl extraction (Thomas, 1982). The ABA method used in Texas (Railroad Commission of Texas, 1988), unlike the standard A/B account procedure, includes a measurement of the KCl-exchangeable acidity:

$$A/B\ Account = NP - (PA + EA) \qquad (5)$$

Exchangeable acidity (EA) is usually composed of four types of acidity: acidity derived from the hydrolysis of exchangeable aluminum; acidity from the hydrolysis of partially hydrolyzed and non-exchangeable aluminum; weakly acidic groups (mostly from organic matter); and exchangeable H^+ (Thomas, 1982).

Soils may be highly buffered against changes in pH once acidification of the soil has occurred and substantial EA is present. In this case, the ABA would underestimate the amount of acidity requiring neutralization and thereby loses its value as a method to evaluate net alkalinity or acidity of the material. This is largely due to the dissolution of primary and secondary minerals, including the decomposition of clay minerals, and the release of Al^{3+} and Fe^{3+} into the system. These ions tend to hydrolyze, generate H^+, and buffer the system against an increase in pH.

$$Al^{3+} + 3H_2O = Al(OH)_3 + 3H^+ \qquad (6)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \qquad (7)$$

The acid/base calculation (Equation 5) only accounts for the exchangeable acidity ($Al^{3+} + H^+$) and does not take into account the buffering capacity (total or reserve acidity) of the soil. Use of the ABA to determine lime recommendations for both potential and current acidity has led to many ABA modifications. Regional needs and differences in materials being analyzed, have spurred the development of variations to the original ABA method. Interpretation of the ABA as a means to estimate lime recommendations is due, in part, to the units of expression (tons $CaCO_3$/1000 tons of material).

Other Potential Sources of Acidity

Inclusion of additional potential sources of acidity, other than pyrite, in the ABA calculation is advocated by several researchers. This appears to be a valid approach in acid sulfate minesoils and pyritic overburden materials that have undergone some weathering. Jarosite may produce acidity when it hydrolyzes (see Potential Acidity section). It is thought that the acid contribution of jarosite can be determined by modifying the sulfur fractionation (Schafer, 1987) to include a hot water extraction, that is supposed to leach non-acid-forming sulfates from the sample. The subsequent HCl extraction is intended to account for acid-forming sulfates such as jarosite (Table 1). A multiplier of 23.44 is suggested for the HCl-extraction S fraction, based on the stoichiometry of jarosite hydrolysis.

Soluble ferrous sulfate minerals (e.g., copiapite, rozenite, melanterite) may be a source of acidity that is not accounted for in some analytical schemes. These are transient minerals that dissolve and reform depending on climatic conditions yet can be important sources of acidity.

The possible presence of mixed mineral systems and the variable efficiencies of the extractants in solubilizing the various S forms (Table 2), require that care be taken when interpreting ABA results. For example, the presence of non acid-forming materials, such as glauconite, can result in elevated Fe levels in the HNO_3-extractable fraction (treated as entirely acid-forming). Also, there is the possibility that small grains of sulfide materials are included in the organic matrix of the sample (Boon and Smith, 1985). There are two ways to account for these additional potential acid producers. The first involves grinding the sample to a 300-mesh size instead of 60-mesh, as specified in the standard procedure from Sobek et al. (1978). Unfortunately, aggressive grinding introduces additional oxygen and heat, resulting in possible losses of pyrite through oxidation. Appreciable errors are probably eliminated by not grinding samples finer than 100-mesh. The second method is to include the residual-S (e.g., organic-S) as AFM, contributing the same amount of acidity as the HNO_3-extractable fraction (Harvey and Dollhopf, 1985). The pyritic-S and residual-S would be added and multiplied by 31.25.

Threshold Acid/Base Account Values

Attempts have been made to establish a range of threshold acid potential and neutralization potential values that will predict whether a system will produce net acidity. Additionally, there are other considerations to be made while examining the limitations of the acid/base account method.

Minesoils

Threshold values have been determined for overburden and mine conditions that may predict the potential for net acidity. The first established threshold value was an ABA of -5 tons $CaCO_3$/1000 tons (t/kt), derived from field and laboratory work conducted in West Virginia (Sobek et al., 1978). It was determined that an ABA less than -5 t/kt would probably result in an acidic minesoil (pH below 4.0).

Water Quality

Other threshold values and estimation methods have been used in an attempt to predict water quality. One value is obtained from the Neutralization Potential/Acid Potential (NP/AP) Ratio procedure, based on the results of NP and PA analyses. Other related procedures are MPA (maximum potential acidity = % total S X 31.25) and Net Neutralization Potential (N.N.P.). The MPA always uses a total S analysis. The N.N.P. is equal to NP (neutralization potential, carbonate or feldspar minerals) minus AP (acid potential = sulfide minerals). Morin and Hutt (1994) found that a NP/AP ratio greater than 4 was needed to prevent acid drainage from a site in Canada. They mention that NP/AP values between 2.5 and 3.0 have been reported to maintain a near-neutral pH. diPretoro and Rauch (1988) stated that an NP/MPA greater than 2.4 was needed to maintain an alkaline system. Other research reports that samples with an ABA less than 33 tons/1,000 tons should be considered as potential acid producers and be evaluated using kinetic tests (Sullivan and Essington; 1987). Morin and Hutt (1994) mention that predictions of acidity are more valid when kinetic tests (i.e.: humidity cells) are conducted along with the standard ABA (a static test). Independent work by several researchers has indicated that equal quantities of NP and MPA do not prevent acid mine drainage (Cravotta et al., 1990). Morin and Hutt (1994) state that it is necessary to determine NP/AP criteria on a site-specific basis; and therefore, the development of a "universal" threshold value for NP/AP ratios would probably not be valid.

Ways to Improve the Acid-Base Account Method as a Predictive Tool

Method Used Dependent on Sample Type

It appears that there are two types of samples that would require ABA; samples selected to determine overburden suitability and samples taken to evaluate reclaimed minesoils. A plausible approach to obtain valid ABA values for both kinds of samples would be to analyze each using different methods. Materials with a pH greater than 6 could be analyzed in the traditional manner:

$$ABA = NP - PA \qquad (1)$$

The NP procedure, however, should be amended to account for the presence of siderite (methodology is discussed below, under Improving Laboratory Procedures).

Minesoils, and sometimes undisturbed overburden, may contain pyritic materials that have undergone varying degrees of weathering. It probably would be necessary to estimate the lime requirement to neutralize current acidity and provide a means to evaluate other acid-forming materials, along with pyrite, that may be present. The ABA could be amended to include the following parameters: neutralization potential, lime requirement (LR), potential acidity (comprised of acid-forming sulfates, pyritic-S, and possibly residual-S--choice of fractions dependent on the degree of weathering and mineralogy), and a LR analysis. The ABA would be described as follows:

$$A/B\ Account = (NP - PA) - LR \qquad (8)$$

where a negative ABA would indicate the amount of $CaCO_3$ needed to neutralize both the PA and acidity currently present in the sample. Lime recommendation procedures are described below.

Improve Laboratory Procedures

The main objective of the chemical characterization of a minesoil is to determine whether or not a parameter or element exceeds a threshold value (Askenasy and Severson, 1988). The two components of an acceptable laboratory analysis are to 1) obtain a representative sample for analysis, and 2) analyze the sample using an acceptable, reproducible method that accurately depicts the desired component in the field. Procedures used for ABA are reasonably accurate and reproducible, however, major errors in interpretation may occur if there are interfering substances in the sample. Additionally, the ABA method is a static test; it characterizes the sample at that point in time - there is no information on what may actually happen with time, since there are variations in the kinetics between acid and alkaline production (Harvey and Dollhopf, 1985; Morin and Hutt, 1994). Kinetic tests, involving simulated weathering methods, have been developed (Caruccio, 1968; Geidel, 1979; Smith et al., 1974b) in an attempt to obtain more practical information. Samples are placed into humidity cells and periodically flushed with water. The leachate is analyzed to determine trends in acidity production. These methods may require long periods of time to obtain a trend line and data interpretation remains difficult.

Neutralization Potential. There are several ways to improve the reliability of the NP determination. The first is very simple and only involves reporting the fizz rating results for each sample, along with the NP data. The fizz ratings are sometimes not included in laboratory reports. Samples having a positive NP value should have a corresponding fizz rating. A fizz rating of 0, along with an appreciable NP value, would indicate that siderite may be present in the sample. Another way to improve the NP procedure, and minimize the effect of siderite, consists of the addition of hydrogen peroxide to the sample after treatment with HCl (Morin and Hutt, 1994; Evans and Skousen, 1995).

Potential Acidity. A second area of concern is in the measurement of PA. There are several places where significant errors can occur. In the analytical methods, assumptions are sometimes made that all of the S present in the sample is present as FeS_2. This is not a sound assumption as organic-S and SO_4-S are commonly present. Unweathered overburden materials that are sampled and allowed to oxidize before analyses are conducted, may have a decreased amount of pyrite, increased acidity, and presence of various pyrite oxidation by-products. There is uncertainty in how to handle different S forms and whether the residual fraction is acid-forming.

Determination of pyritic S using the ASTM method (ASTM, 1984) assumes that a hot HCl wash will remove all of the Fe in the sample except that associated with FeS_2, which may not be correct.

Lime Requirements. The KCl-exchangeable acidity is related to the immediate need for limestone and an existing cation exchange capacity (Thomas, 1982). It is generally agreed that the value obtained as KCl-exchangeable acidity is not synonymous with a lime/limestone requirement (see Active Acidity section). The actual LR is probably in between the values obtained by KCl-exchangeable acidity (unbuffered salt solution) and the total active acidity obtained by the $BaCl_2$-TEA method (buffered at pH 8.2) (McLean, 1982).

Lime requirement procedures fall into three categories: soil-lime incubations (equilibrations); soil-base titrations; and soil-buffer equilibrations (McLean, 1982). The first type is time-consuming and would not be practical in a reclamation scenario. The second category involves adding progressively larger increments of a standard base, such as $Ca(OH)_2$, to aliquots of a given sample, and measuring the resulting pH (Sobek et al., 1978). The last type of LR method consists of adding a buffer solution to a sample and measuring the resulting pH of the suspension. The SMP single-buffer method (McLean, 1982) is commonly used. There is another buffer method that has been proposed (Improved Woodruff Buffer) as an alternative to the SMP single-buffer method, for its ease of use (Brown and Cisco, 1984). The choice of method to use is uncertain and may be site- and material-dependent. Field trials and/or bench tests are necessary to select the appropriate procedure.

The ABA methodology is expected to be most quantitative for unoxidized overburden and minesoils; however, there still are problems when estimating lime recommendations to neutralize PA. Harvey and Dollhopf (1985), state that lime quantities may be overestimated when using PA values. Kinetic tests may provide more realistic values for estimating lime recommendations from PA, as the ABA method may include a portion of the PA that comes from non-reactive FeS_2 that would probably not weather under field conditions. On the other hand, the amount of lime needed to neutralize PA may be underestimated (Doolittle, 1991).

Doolittle (1991) reported that FeS_2 oxidation followed two different rate laws depending on the pH of the system. Oxidation followed zero-order kinetics with respect to FeS_2 concentration at pH values above 4 and first-order kinetics below 4. The dissolution of applied $CaCO_3$ was faster than the oxidation of FeS_2. Based on reaction rates, it was projected that the applied lime would dissolve before all the FeS_2 would oxidize leaving the potential for acid minesoil formation. Morphology of the pyrite, soil pH, temperature, oxygen concentration, water partial pressure, pCO_2, bacterial population, flushing frequency, and particle size, purity, and distribution of the limestone would modify the reaction rate in natural systems (Caruccio et al., 1988).

General Considerations. Instrumental error is also a potential source of laboratory error, but is normally small relative to the larger sources of error. The amount of acidity generated from FeS_2 oxidation is always calculated based on the stoichiometry shown in equation 4. The stoichiometry of oxidation of FeS_2 to H_2SO_4 has been shown to vary widely in laboratory trials and similar variation is expected in the field.

Selection of a specific approach to analyzing materials for their acid potential requires that the methods be operationally defined. The end use of PA data (reclamation planning, regulatory action, or mitigation) will dictate, to an extent, which analytical procedures are employed (Munk et al., 1996). Reliability of current PA methods increases if analytical data are interpreted in relation to the degree of sample weathering and mineralogy.

There is currently no definitive way to handle the PA component when estimating lime requirements. It is important to know, though, that a kinetic test may provide more realistic values and that additional limestone may be needed in the long run since there is evidence that FeS_2 may persist past the time when applied lime has dissolved.

Acid/base account data cannot be taken at face value, as seen above. It is necessary to have supplementary data on hand when evaluating

ABA results. Additional information (general awareness of the mineralogy and degree of weathering and knowledge of material color, fizz rating, and pH) is integral to proper interpretation.

Summary and Conclusions

The ABA is the fastest and easiest way to evaluate the acid-forming characteristics of overburden materials. However, accurate evaluations require that ABA data be examined in conjunction with additional sample information (mineralogy, pH, color, etc.) and results from other analytical procedures. Each component of the ABA has its limitations, and knowledge of these limitations is essential for the proper use of the ABA.

The NP and PA are both measures of a material's maximum potential to produce either alkalinity or acidity; neither procedure takes reaction rates into account. The results are always obtained under artificial conditions and may not reflect what will ultimately occur in the field, regardless of the analytical procedure used. Therefore, the ABA probably should be viewed only as a predictive indicator. Utility of the ABA will increase as field results are correlated with specific versions of the method.

The conclusions of this review are: 1) the ABA is expected to be most quantitative for unweathered overburden and minesoils; 2) an understanding of the potential interferences in methodology is necessary; 3) ABA alone is inadequate to determine lime requirements for oxidized materials; 4) reaction kinetics and stoichiometry can vary widely and are not clearly defined for all situations; 5) the variety of materials tested by the ABA method probably requires that two separate procedures be developed - one for samples with a pH above a threshold value (say pH 6, where the amount of exchangeable acidity is minimized) and one for samples below that threshold pH. The traditional method, where ABA = NP-PA, would be used for high pH samples. A modified method, where ABA = (NP-PA)-LR, would include a lime requirement determination and be used for lower pH samples; 6) correct interpretation of ABA values requires that acid/base account data be evaluated in conjunction with other information (pH, rock type, fizz value, and knowledge of sample mineralogy and degree of weathering); 7) proper evaluation of ABA data requires that the specific analytical procedures used be known; and 8) a combination of methods (static and kinetic tests) is appropriate for the evaluation of AFM and minespoil reactivity.

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