CHAPTER 4: STATIC TESTS FOR COAL MINING ACID MINE DRAINAGE PREDICTION IN THE EASTERN U.S.

by

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INTRODUCTION

Accurate prediction of post-reclamation water quality requires an understanding of many factors, including overburden geochemistry, the method and precision of overburden handling and its placement in the backfill, and site hydrology. Most of the work in prediction has focused on methods to quantify overburden geochemistry. Overburden analysis and characterization provide important information about which strata are acid-producing, potentially acid-producing, neutral, or alkaline. Identification of potential problem overburden aids in developing overburden handling and placement plans. It is then critical for each operator to carefully follow the overburden handling and placement prescription based on the site's overburden characterization.

Overburden analysis to predict overburden quality is not a new concept. Overburden characterization probably developed in Germany during the 1950's (Knabe, 1964), and researchers in the U.S. recognized the importance of overburden characterization for acid mine drainage prediction as early as 1960 (Cornwell, 1966; May and Berg, 1966). This chapter summarizes the laboratory procedures that are available to analyze overburden, as well as current overburden characterization practices in seven eastern mining states, and then provides some recommendations.

STATIC TESTS AVAILABLE FOR PREDICTING ACID MINE DRAINAGE

Acid-Base Accounting

Acid-base accounting (ABA) is an overburden analytical technique that evaluates the most important properties of a rock unit relative to its potential for immediate and future pollution. Early reclamationists realized that the reclamation potential of surface mined areas (relative to plant establishment and growth) was directly connected to the quality of the overburden material placed at the surface. Many early surface mine operators turned the overburden upside down, relative to its original position, as the overburden was removed to reach the coal. Such an operation left unweathered gray or black material associated with the coal bed on the surface. In many situations, the associated sulfur-bearing minerals produced acidic conditions in the minesoil and may have also caused an AMD problem (Greene and Raney, 1974).

Some of the earliest documented work on reclamation of surface mined areas was directed at revegetation efforts (Smith and Tyner, 1945; Tyner et al., 1948). These reports from West Virginia acknowledged the effects of minesoil quality on plant growth and identified three types of overburden material based on rock composition and degree of acidity. A minesoil classification system proved useful to reclamationists in determining lime and fertilizer rates and selecting plant species adapted to these specific minesoil conditions. Because minesoil classification systems proved useful for revegetation, similar systems were subsequently

developed for other coal mining areas including the mid-eastern coal region (Limstrom, 1948), Pennsylvania (Davis, 1965), and eastern Kentucky (Soil Conservation Service, 1973). Nevertheless, these systems were not initially used to predict drainage quality from disturbed sites.

Knabe (1964b) provided one of the earliest examples of characterizing alkaline versus acid materials. He refined overburden classification by placing a positive or negative number as a subscript. A positive subscript detailed the percent of $CaCO_3$ in the minesoil, while a negative number expressed the percent of potential unneutralized SO_4 (the sulfides or pyrite was expressed as SO_4). For example, A_{15} was a minesoil suitable for agriculture (A meaning alkaline, and 15 being the percent calcium carbonate in the material). A minesoil with the designation of T_{-10} was toxic with as much as 10 percent of the material being potentially unneutralized SO_4. Later, Knabe reported that he used a method called a "base-acid balance," which balanced the sum of all bases against all acids. The acids included acid-producing minerals (sulfides) and exchangeable acids like aluminum and iron (Knabe, 1973). His system accounted for the ultimate quantity of acidity or alkalinity that could be produced in the material upon weathering.

The early minesoil classification systems were useful but a premining method or technique was needed that could distinguish between materials that could be placed on the surface for revegetation and materials that should be buried beneath the rooting zone. Soon after Knabe reported on his work, researchers at West Virginia University (WVU) began developing a system for balancing the acid- and alkaline-producing potential of overburdens prior to disturbance. These WVU researchers first studied overburdens in Preston County, West Virginia and defined the acid-producing potential of rocks associated with the Freeport and Kittanning coal beds. Dr. Richard M. Smith recommended that sulfur (S) profiles and neutralization capacities should be determined for all stratigraphic sections from the surface down to and immediately underlying the coal bed before mining (West Virginia University, 1971). The West Virginia University researchers quantified acid-neutralizing materials in overburdens and developed the term neutralization potential (NP) (Smith et al., 1974).

The method of ABA was first described in 1973 (Grube et al., 1973). Logging of overburden cores and/or observations of a fresh highwall are used to distinguish geologic layers. Each of the layers are identified by: 1) color; 2) rock type; and 3) rock thickness. The chemical characteristics of each overburden layer (whether acid-producing, potentially acid-producing, or alkaline-producing) is determined by three measurements: 1) paste pH; 2) total or pyritic S; and 3) neutralization potential (NP). The most important part of the method balances maximum potential acidity (MPA) (from sulfuric acid produced during S oxidation) against total neutralizers (from alkaline carbonates, exchangeable bases, weatherable silicates, and phosphates) (Fig. 3.1). These dominant rock properties produce the most predictable response upon weathering. The MPA of a rock sample is calculated from the total S content. For each %S contained in the material, 31.25 metric tons of calcium carbonate are required for neutralizing the sulfuric acid produced from 1000 metric tons of the material. The NP is determined by reacting a pulverized, 2-gram sample of the rock with a known quantity and strength of acid. The solution is then back-titrated with a known strength of base to a predetermined end point to determine the sample's neutralizing component. Both NP and MPA are determined in parts per 1000 parts of overburden (metric tons per 1000 metric tons).

Further research in other areas in the Appalachian and Eastern Interior Coal Regions confirmed the usefulness and application of ABA (Smith et al., 1976), and final field and laboratory procedures for ABA were published in 1978 (Sobek et al., 1978). Problems with the approach have shown up over time, and various modifications have been suggested. The best are summarized later in this chapter.

Many states began passing laws in the early 1970's requiring prediction of the acid or alkaline nature of overburdens that were to be disturbed. For example, the 1971 West Virginia surface mining and reclamation law required the operator to show in the permit "the presence of any acid-producing materials which, when present in the overburden, may cause minesoils with a pH below 3.5 and prevent effective revegetation." Regulations promulgated to implement the law in succeeding years used acid-base accounting to determine the presence or absence of acid-producing materials in the overburden. Prior to the Surface Mining Control and Reclamation Act (SMCRA), "topsoiling" was seldom practiced. Therefore, ABA was particularly useful in selecting overburden layers that could be placed on the surface as topsoil. It was also used to select materials for special uses (e.g., hard sandstones for rock cores in valley fills, clayey materials for impermeable barriers, etc). ABA was the first technology available to assess the chemical quality of overburdens prior to disturbance. As a result, the concepts of pre-mine planning for reclamation and special handling procedures were formulated. ABA in its original and modified forms has been widely adopted in both the coal and mineral mining industries in the U.S., Canada, Australia and southeast Asia (British Columbia Acid Mine Drainage Task Force, 1989; Miller et al., 1991).

The components of ABA measurements are sometimes referred to by other terms since they have been adapted for use in metal mining and other applications (Miller and Murry, 1988). The term Acid Production Potential (APP) is equivalent to MPA, Acid Neutralizing Capacity (ANC) is equivalent to NP; and Net Acid-Producing Potential (NAPP) is the same as Net Neutralization Potential (NNP) and denoted with a positive or negative prefix.

The quality of drainage from a rock stratum is predicted by subtracting MPA from NP in the sample. If the number for MPA is higher (a deficiency of NP), the rock strata is predicted to produce acidic drainage upon weathering and leaching. If the number for NP is higher (an excess of NP), the rock is predicted to produce alkaline drainage. This 1:1 comparison of acid to base works well when dealing with individual rock units (Skousen et al., 1987). Assessing the quality of drainage that will come from a reclaimed mine site is much more difficult because MPA, NP, and volume in each rock unit in the overburden across the site must be taken into account. There are also many other factors and complex interactions that have an influence on the chemical production potential of rocks including microorganisms, trace elements, depositional environments, forms of pyrite, rare catalytic agents, uncommon compounds, and lithologic peculiarities. Nevertheless, ABA is the most common basis for post-mining water quality prediction (Perry, 1985).

The choice of which stoichiometry of pyrite oxidation most closely describes a mine spoil system directly affects the ABA calculation, alkaline addition rates, and prediction of expected post-mining water quality. Cravotta et al. (1990) noted that the stoichoimetry is based on the exsolution of carbon dioxide gas out of the spoil system. They suggested that in a closed spoil system, carbon dioxide is not exsolved, and additional acidity from carbonic acid is generated. Cravotta et al. (1990) proposed that up to four moles

of calcite (or about twice as much) might be needed for acid neutralization. On a mass basis, for each 1% S present, 62.5 metric tons of calcite would then be needed to neutralize the acid in 1000 metric tons of the material. Brady and Cravotta (1992), in analyzing ABA and water quality data from 74 mine sites, showed that correct prediction of post-mining net alkalinity in drainage was improved from 52% to 57% using a stoichiometric equivalence of 62.5. However, a later study (Brady et al., 1994) showed that the 31.25 equivalence factor was more accurate, correctly predicting post-mining net alkalinity in drainage on 31 of 38 mines (82%), while the 62.5 factor correctly predicted 22 of 38 (58%).

Overburden analysis came into widespread use with the passage of SMCRA in 1977. The law requires that an operator must identify in the permit any potentially acid-producing materials in the overburden and determine the probable hydrologic consequences of such materials after disturbance and reclamation. Because little research had been conducted on water quality prediction from disturbed areas, the coal industry and regulatory authorities applied current overburden analytical methods and adapted the available methods to these purposes. ABA, already extensively used in the U.S. and several other countries by this time as an overburden selection tool, was adopted to predict post-mining drainage quality. Its popularity largely stems from its simplicity. However, there has been much controversy concerning the accuracy of such predictions (Erickson and Hedin, 1988; Miller et al., 1991).

One criticism is that the method does not account for the different reaction rates of acid- and alkaline-production in rocks. Other methods to evaluate reaction kinetics or rates include humidity cells or columns (Bradham and Caruccio, 1991; Caruccio et al., 1980; Ferguson and Morin, 1991), hydrogen peroxide (H_2O_2) digestion (Ammons and Shelton, 1988; O'Shay et al., 1990), or soxhlet reactors (Renton et al., 1988). Other options are mineralogical tests (Kwong, 1991), evolved gas analysis (EGA) (Hammack, 1987) and computer modeling (Ferguson and Robertson, 1994; Morin and Hutt, 1988; Rymer et al., 1991). Modifications in the way the acid potential is calculated have been recommended (Cravotta et al., 1990; Smith and Brady, 1990).

diPretoro and Rauch (1988) found that sites which had greater than 3% NP in overburden (or 30 metric tons $CaCO_3$ per 1000 metric tons of material) produced alkaline drainages, while acid drainage resulted at 1% or less NP. Brady et al. (1994) showed that 3% NNP in an overburden caused alkaline drainage while less than 1% NNP produced acidic drainage from 38 mines in PA. Perry and Brady (1995) stated that all sites with $\geq$2.1% NP (21 metric tons/1000 metric tons) produced net alkaline water, while 72% of sites with $\leq$1% NP produced net acid drainage. These values are summarized in Table 4.1.

Table 4.1. A generally accepted guideline for defining strata as either acid-generating or alkaline.

	Acid Tons / 1000 Tons	Undecided Tons / 1000 Tons	Alkaline Tons / 1000 Tons
NP	< 10	10 - 21	>21
NNP	< 0	0 - 12	>12

Brady and Hornberger (1990) suggest that NP from ABA shows the strongest relationship with actual post-mining water quality. This relationship is only qualitative (e.g. acid vs. non-acid), and NP must significantly

exceed MPA in order to produce alkaline water. If NP and MPA are similar, acid mine drainage will most likely result.

British Columbia Research Initial Test

The British Columbia Initial Test includes an assessment of the acid-generating potential of a sample compared to its neutralizing capability (Steffen Robertson Kirsten, 1989). In concept and technique, it is similar to ABA, but is sometimes followed by kinetic testing to confirm the initial interpretation. The acid-producing potential is estimated from either a total or sulfide S value. NP is measured by reacting the sample with sulfuric acid (rather than HCl) until a stable endpoint of pH 3.5 is reached. A pH endpoint of 3.5 is used because the bacteria, *Thiobacillus ferrooxidans*, which catalyzes the iron oxidation reaction, is considered to be less significant at pH values above this. The quantity of sulfuric acid consumed is interpreted to represent the neutralizing capability of the sample.

Potential acidity and NP, both expressed in $CaCO_3$ equivalent, are compared to estimate drainage quality. If NP exceeds potential acidity, the sample is considered non-acid or alkaline forming. When potential acidity is greater than NP, or the acid-base balance is nearly equal, the sample may be analyzed further with kinetic tests, such as the British Columbia Research Confirmation Test, or other weathering procedures.

ASTM Carbon/Sulfur Methods

These methods measure the total carbon and total S content by combusting coal, soil or rock materials. The overburden or rock sample is combusted under oxygen flow and converts any carbon or carbonaceous material to CO_2 and any S compounds (organic, sulfate, or sulfide) to SO_2. ASTM D 3177 describes the standard Eschka method for measuring total S in coal materials. ASTM D 4239 uses high temperature combustion methods to determine total S. SO_2 released during combustion is captured and measured in several ways. Method A in ASTM D 4239 uses an acid-base titration to determine the amount of SO_2 released. Method B in ASTM D 4239 uses a solution containing iodine to collect the combustion products and the solution is titrated to determine the amount of SO_2 released. Method C in ASTM D 4239 uses an infrared (IR) absorption detector with microcomputer capabilities to determine SO_2 released. ASTM D 5016 also describes measuring total S in ash and coal materials through combustion and IR absorption.

ACID POTENTIAL

Sulfur Forms

Sulfur in coal and associated strata can occur as organic S, sulfate S, and sulfide S. Organic S is complexed within the coal plant material and is organically bound within the coal. This form is only found in appreciable quantities in coal beds and in other carbonaceous rocks. Generally, the organic S component is not chemically reactive and has little or no effect on acid-producing potential. The organic S content of coal and other organic soils can be as high as 0.5% (w:w basis).

Sulfate S is usually only found in minor quantities in rocks of humid areas, but can be present in substantial amounts in more arid areas where leaching is limited. Sulfate is a reaction product of S oxidation. If gypsum ($CaSO_4$) is formed, no more acid is generated because gypsum is a neutral salt. If jarosite ($KFe_3(OH)_6(SO_4)_2$) is formed, then additional acid may be produced by the oxidation of this transient mineral. Acid generation from the oxidation of jarosite would not be large because of jarosite's low solubility ($K_{sp}= 10^{-98.6}$, Vlek et al., 1974). Carson et al. (1982) obtained jarosite (87% pure) from a soil and found that its titratable acidity was 18.7 cmol/kg compared to its theoretical acidity value of 522 cmol/kg.

Sulfide S is the predominant S species in the majority of overburdens and is the S form of greatest concern. Of all the sulfide minerals that may be present, the predominant sulfides are minerals containing iron such as pyrite or marcasite (FeS_2). In some areas, copper (chalcopyrite), lead (galena), and zinc (sphalerite) sulfides can also be found. These minerals are generally far less reactive than iron sulfides due to the greater stability of their crystal structures and the formation of low solubility products that encapsulate them, preventing further weathering (Knapp, 1987).

Iron disulfides are the major acid-producers, and variations in total S and MPA of overburden samples correlates closely with the pyritic S content (Caruccio and Geidel, 1978). Caruccio et al. (1988) provided an extensive review of the different forms and morphologies of pyritic materials.

The formation of acid from the oxidation of pyrites and other sulfide compounds is well known (Grim and Hill, 1974; Nordstrom, 1982). The equation of pyrite oxidation shows that 1000 metric tons of material containing 0.1% S, all as pyrite, would yield upon complete reaction 3.125 metric tons of acidity. 3.125 metric tons of $CaCO_3$ would have to be added to neutralize the acidity. The total S content of the rock accurately quantifies the acid-producing potential (APP) when S in the overburden rock is exclusively pyrite. However, in most cases, not all pyrite oxidizes, and when organic and/or sulfate S are present in significant amounts, total S measurements clearly overestimate the amount of acid that will be formed upon oxidation. However, the use of total S values to determine APP is generally accepted since intentional overestimation of the APP of rocks gives a margin of safety. Overestimation of the APP also helps deal with uncertainties such as rates of reaction (pyrite often reacts faster than carbonates in the system), poor mixing of overburden materials during backfilling, and inconsistent and random contact with water in the backfill. Therefore, maximum potential acidity (MPA) of a rock unit is calculated when the total S value is used. Removal of sulfates and organic S may be necessary to increase accuracy in predicting the APP of partially weathered materials containing mixed S species.

The rate of pyrite oxidation depends on numerous variables such as reactive surface area of pyrite (Singer and Stumm, 1968), ferric iron concentrations and other catalytic agents (Singer and Stumm, 1970), oxygen concentrations and solution pH (Smith and Shumate, 1970), forms of pyritic S (Caruccio et al., 1988), and presence of *Thiobacillus* bacteria (Leathen et al., 1953). The possibility of identifying and quantifying the effects of these and other controlling factors with all the various rock types in a field setting is unlikely. However, precise knowledge regarding the oxidation rates is generally not needed for most field situations.

Methods to Determine Acid Potential

Procedures to determine acid potential generally fall into one of two categories:
1) determination of total S content and use of a stoichiometric equation for pyrite oxidation to calculate MPA;
2) titration of acidity after oxidation of the sample by a strong chemical oxidant (hydrogen peroxide) or after a rigorous simulated weathering procedure (see Kinetic Test section).

Furnace Combustion—The most popular and easiest methods are those that determine total S content. The analysis is usually accomplished using high-temperature furnace combustion. The sample is heated to approximately 1350^0C while a stream of oxygen is passed over the sample (ASTM D 4239). Sulfur dioxide released through combustion can be measured in several ways. Using a LECO Induction Furnace with Automatic Sulfur Titrator, the SO_2 is collected in a 0.2M hydrochloric acid (HCl) solution containing potassium iodide, starch, and a small amount of potassium iodate. The solution is then titrated with a standard potassium iodate solution to determine S content. Using infrared absorption, the resultant SO_2 gas is detected by infrared absorption and compared to a standard calibration.

Eschka Method—The Eschka method (ASTM D 3177 Method A) is a gravimetric procedure using wet chemistry and barium chloride precipitation. A portion of the overburden sample is heated with an Eschka mixture to convert all S to sulfate. The sulfate is then leached with hot water and precipitated as barium sulfate ($BaSO_4$). The total S content is calculated from the weight of $BaSO_4$. The Eschka method agrees closely with the LECO S Furnace for determining total S in coal but the mixed mineralogy of overburden complicates the technique and introduces error (Scholz and Rathleff, 1982). For routine S analysis of coals and overburden materials, the S furnace is recommended.

Bomb Washing—The Bomb Washing method determines total S by combusting an overburden sample in an oxygen bomb; the contents of the bomb are washed into a beaker, neutralized and filtered (Noll et al., 1988; ASTM D 3177 Method B). The S in the filtrate is precipitated as $BaSO_4$, filtered, and ashed. The ashed $BaSO_4$ residue is then weighed to determine the total S in the sample. Most samples will not sustain combustion so a combustion aid is required to quantitatively determine the S content.

X-Ray Diffraction—X-ray diffraction is the scattering of x-rays by mineral crystals, with accompanying variation in intensity due to interference effects. X-ray diffraction analysis evaluates the crystal structure of materials by passing x-rays through them and recording the diffraction (scattering) image of the rays. For inorganic, crystalline minerals, x-ray diffraction has been established as probably the most important, convenient and unambiguous technique applied to the study of soil and overburden mineralogical composition (Bish, 1994). Pyrite and other sulfide minerals, as well as calcite and dolomite can be determined by x-ray diffraction, but the analytical error associated with x-ray diffraction is relatively high, between 5 to 20% of the sample value.

X-Ray Fluorescence—X-ray fluorescence spectrometry, also called x-ray spectroscopy, x-ray emission spectrography and x-ray spectrochemical analysis, is a widely used analytical technique in laboratories

concerned with elemental analysis of soils and overburdens (ASTM D 4326). X-ray emission spectrography depends on the fact that when a beam of x-rays is directed onto the surface of a specimen, secondary (or fluorescent) radiation is emitted that contains wavelengths characteristic of each element present. The emitted radiation is collimated and directed to a detector in such a way that the spectral lines may be measured individually (Jones, 1982). X-ray spectrometers are capable of detecting more than 80 elements with atomic number >8, so S can be detected to determine potential acidity (the use of iron from analysis of the same sample may be used to calculate pyrite content and potential acidity). Calcium and magnesium may be used to estimate the carbonate content. However, the analytical error associated with x-ray fluorescence is between 2 to 10% of the sample value. Both x-ray diffraction and x-ray fluorescence are primarily used for confirmation of the presence and magnitude of minerals and elements in the sample, and are generally not used for determining exact values of minerals or elements (see Skousen et al., 1997).

Fractionation of S—Fractionation of S into its respective forms may be accomplished in three ways: 1) the ASTM Method D 2492, 2) a modified Environmental Protection Agency (EPA) method, and 3) a technique combining the use of both methods. In the ASTM D 2492 Method, a sample is mixed with 4.8M (40%) HCl and heated, then leached with barium chloride to remove sulfate S. The sulfate S content is calculated from the weight of $BaSO_4$ that is precipitated. Pyritic and organic S remain in the sample since neither are soluble in HCl. The sample, after HCl acid extraction, is then leached with 2M (12.5%) nitric acid to dissolve the iron sulfides. The iron in this nitric acid extract is quantified by titration or by atomic absorption spectrophotometry, and this value is used to calculate the amount of pyritic S in the sample. Organic S is calculated from the difference between the total S content measured by combustion and the sum of the sulfate and pyritic S contents.

The modified EPA method uses three portions of the overburden sample. One portion is combusted in a LECO Furnace and analyzed without any pretreatment to determine the total S content. A second portion is leached with 4.8M HCl (thereby removing the sulfate S) and then combusted giving pyritic and organic S. A third portion is leached with 4.8M HCl and 2M nitric acid (thereby removing sulfate and pyritic S) and then combusted giving organic S. The concentrations of each S form are then calculated.

The ASTM/EPA combination method tries to minimize the errors that are possible with the two other procedures. The sulfate S is determined as outlined in the ASTM method. The sample is treated with 40% HCl then leached with barium chloride to precipitate $BaSO_4$. Organic S is determined on a subsample that has been leached with 40% HCl (removing sulfate S) and 2M nitric acid (removing pyritic S), then combusted. The sulfide S content is calculated from the difference of the total S and the sum of the sulfate and organic S contents.

Fractionation of S into its respective forms is helpful in determining actual acid-producing potential. Removing sulfate and organic fractions (which are not typically acid producers) from total S and relying on pyritic S for MPA calculation gives more accurate estimates of acidity concentrations in drainage. However, as mentioned previously, total S values provide maximum potential acidity from a rock sample and intentionally overestimate the acid potential of the rock. Experience has shown that for unweathered material, it is generally preferable to be conservative and use total S values to predict acidity in drainage,

rather than pyritic S values. Table 4.2 compares the MPA values for several overburden samples calculated on total S vs pyritic S.

Table 4.2. Maximum potential acidity (MPA) from overburdens based on total S vs pyritic S (Frost, 1981; Johnson and Skousen, 1995; Tettenburn, 1980).

Overburden Type	Total S	Pyritic S	MPA Total S	MPA Pyritic S
	(%)	(%)	(Metric tons/1000 metric tons)	
Middle Kittanning Overburden	1.55	0.88	48.44	27.50
Middle Kittanning Overburden	0.79	0.62	24.69	19.38
Lower Kittanning Pavement	1.20	0.78	37.50	24.38
Lower Kittanning Overburden	0.34	0.33	10.63	10.31
Upper Freeport Overburden	1.01	0.88	31.56	27.50
Pittsburgh Overburden	0.58	0.32	18.13	10.00
Pittsburgh Overburden	0.97	0.04	30.31	1.25

Simulated Weathering Tests

Another way of measuring acid potential is by leaching the rock with a strong oxidant or with water for long time periods. H_2O_2 has been used as an oxidant to speed the reaction process, with mixed results. A modification of this approach by O'Shay et al. (1990) produced accurate and reproducible results in east Texas overburdens. More conventional simulated weathering tests produce good results, but almost all the techniques require long time periods in order to get sufficient data to develop acid potential determinations (see Chapter 5). There is also no standard leaching technique; the various methods have different flushing cycles, use different amounts of water per flushing cycle, use different particle size of the overburden material, etc.

A relatively short-term, standardized, accurate technique is needed to resolve questions concerning acid potential in situations where acid-base accounting fails to provide an adequate answer. The EGA method, which is discussed in more detail later in this chapter, may one day serve that purpose.

NEUTRALIZATION POTENTIAL METHODS

The natural base content of overburden materials, commonly present as carbonates or exchangeable cations on clays, is important in evaluating the future chemical producing potential of the overburden. The amount of alkaline material in unweathered overburden may be sufficient to counteract or overwhelm the acid produced from S oxidation in the material.

Neutralization Potential (NP) Procedure in Acid-Base Accounting

The NP procedure in ABA quantifies the neutralizing compounds in coal and overburden. Alkalinity production potential (APP) is equivalent to the term NP. Of the many types of basic compounds present,

carbonates and exchangeable bases are the only alkaline compounds that occur in sufficient quantity to effectively neutralize acid mine drainage. Siderite, a ferrous carbonate ($FeCO_3$), is not a desirable neutralizer because it does not yield an alkaline-producing material upon complete weathering and oxidation of iron.

The NP test involves treating the pulverized overburden sample with a known quantity of HCl, heating to ensure complete dissolution of bases, and back-titrating with sodium hydroxide (NaOH) (Sobek et al., 1978). The NP test relies on an initial subjective carbonate ranking procedure based on adding a few drops of dilute HCl to the sample and rating the observable fizz (Table 4.3). Based on the fizz rating, a quantity of HCl (either 20 or 40 ml of 0.1M or 0.5M) is added to a subsample of the overburden and heated for complete reaction with the sample. After the sample has cooled, it is back-titrated with 0.1M or 0.5M NaOH to determine the quantity of HCl that was neutralized by the sample. This value is then used to calculate the NP of the sample and is expressed as $CaCO_3$ equivalents in metric tons per 1000 metric tons of material. The NP procedure is simple, can be done quickly, and is very accurate in determining alkaline content of most overburden materials.

In overburden containing alkaline and pyritic material, the soluble bases may be sufficient to neutralize the acid at a rate equal to or exceeding the rate of acid production. Higher alkalinities also help control bacteria and restrict ferric iron activity, which can both accelerate acid generation (Leathen et al., 1953; U.S. EPA, 1971). Determining the MPA and NP of a sample will indicate the ultimate acidity or alkalinity that may be released from the material upon complete weathering.

Table 4.3. Description of fizz rating and amounts and strengths of HCl added to an overburden sample based on a fizz rating (Noll et al., 1988; Sobek et al., 1978).

Fizz Rating	Description	Amount of Acid	Strength of Acid
0 - None	No reaction.	20 ml	0.1 M
1 - Slight	Minimal reaction; a few bubbles per second to many fine bubbles.	40 ml	0.1 M
2 - Moderate	Active bubbling with only a small amount of splashing.	40 ml	0.5 M
3 - Strong	Very active bubbling that includes substantial splashing.	80 ml	0.5 M

The Modified Neutralization Potential Technique

Siderite ($FeCO_3$), when present in the overburden, reacts quickly with HCl in the standard NP procedure in ABA and falsely indicates that the rock will behave as a net alkaline contributor after weathering (Cargeid, 1981; Morrison et al., 1990; Wiram, 1992). Continued weathering of $FeCO_3$ actually produces a neutral (Meek, 1981; Shelton et al., 1984) to slightly acid solution (Cravotta, 1991; Doolittle et al., 1992; Frisbee and Hossner, 1989). If insufficient time is allowed for complete iron oxidation and precipitation of ferric hydroxide during back titration, erroneously high NP values can be generated on samples containing $FeCO_3$, yielding misleading NP information. Such an analytical oversight can lead to incorrect post-mining water quality predictions and produce costly, long-term reclamation liabilities (Wiram, 1992).

Meek (1981) and Morrison et al. (1990) suggested adding a small quantity of 30% H_2O_2 to the filtrate of an overburden sample to oxidize ferrous iron to ferric iron before back-titration is initiated. Leavitt et al. (1995) proposed a modified NP procedure that includes boiling a 2-gram overburden sample for 5 min after the acid is added, filtering the suspension, and adding 5 ml of 30% H_2O_2, then boiling for an additional 5 min. Significant reductions in NP values were found for $FeCO_3$ samples using the modified NP method compared to the standard Sobek et al. (1978) method (Table 4.4, Skousen et al., 1997). Variations in NP determinations among laboratories were also dramatically reduced by using this modified method compared to the standard NP method on $FeCO_3$ samples (Table 4.5).

Table 4.4. Neutralization potential (NP) values for the standard Sobek and the modified NP (H_2O_2) digestion methods on overburden samples. Prominent minerals are given for each sample (Skousen et al., 1997).

Sample Description	Sobek	H_2O_2
(Metric tons/1000 metric tons)		
49% Siderite	70 a[1]	16 b
65% Siderite	62 a	19 b
65% Siderite	63 a	17 b
61% Siderite	62 a	15 b
8% Siderite, 55% Clays	88 a	26 b
18% Siderite, 48% Clays	64	56
20% Siderite, 11% Calcite	367	322
90% Calcite	926	924
83% Calcite	835	847

[1]Values within rows without letters are not significantly different; values within rows with different letters are significantly different at $p < 0.05$.

Table 4.5. Neutralization potential values using the Sobek and modified NP (H_2O_2) digestion methods among three laboratories on overburden samples containing $FeCO_3$ and calcite (Skousen et al., 1997).

Sample Description	Sobek Method			H_2O_2 Method		
	Lab 1	Lab 2	Lab 3	Lab 1	Lab 2	Lab 3
----------(Metric tons/1000 metric tons)----------						
49% Siderite	70	89	29	16	14	20
65% Siderite	62	88	25	19	21	28
65% Siderite	63	87	14	17	16	25
61% Siderite	62	93	445	15	12	43
8% Siderite, 55% Clays	88	95	50	26	11	27
18% Siderite, 48% Clays	64	82	26	56	25	77
20% Siderite, 11% Calcite	367	607	363	322	301	277
90% Calcite	926	928	936	926	926	924
83% Calcite	835	828	837	847	844	851

Fizz ratings are done to assess the relative amount of carbonate present in a rock sample, which are then used to determine the amount and strength of acid to use in the NP digestion process. Conflicting NP values were found when overburden samples were assigned different fizz ratings and thereby digested in different amounts of acid (Table 4.6). At higher fizz ratings (more acid added), the NP values increased substantially. Since the subjective fizz rating was not found to be repeatable among laboratories and not reflective of the carbonate content of a rock, a quantitative and repeatable method to determine carbonate content was proposed (Skousen et al., 1997). The method uses the percent insoluble residue after acid digestion to assign a carbonate rating (Table 4.7), and has been found to accurately determine the amount and strength of acid to add for NP determination.

A 2-g sample of overburden is placed in a beaker. The appropriate amount and strength of HCl (Table 4.7) is added to the beaker. The suspension in the beaker is then brought to 100 ml volume prior to heating. Boiling chips are added to the suspension, the beaker is covered with a watchglass, and the suspension is boiled gently for 5 minutes. After cooling, the contents of the beaker are gravity filtered using a 0.45um (Whatman #40) filter. The filtered solution is then treated with 5 ml of 30% H_2O_2. The solution is then boiled for an additional 5 minutes (using boiling chips and watch glasses), and allowed to cool. The solution can then be hand-titrated using NaOH, to achieve and hold an endpoint pH of 7.0 for 30 seconds. However, since most analytical laboratories have auto-titrators, we recommend that auto-titration be used to determine the volume of NaOH needed to achieve and hold a pH 7.0 endpoint. The titration rate can be varied on most machines, so the middle setting is normally used for titrations.

CO_2 Coulometry

CO_2 Coulometry is an analytical technique that is routinely used to determine carbon (both total carbon and carbonate carbon). It is a two-step process in which total carbon is first determined by measuring the amount of CO_2 evolved when the sample is heated to 1000°C. Then, carbonate carbon is determined by digesting the sample in hot perchloric acid and measuring the amount of CO_2 evolved during the digestion. Organic carbon is then determined by difference (Morrison et al., 1990). Because calcite, dolomite, and siderite exhibit different rates of dissolution in acids (Evangelou et al., 1985), CO_2 coulometry can differentiate these carbonate sources with respect to time of CO_2 evolution. Morrison et al. (1990)

Table 4.6. Neutralization potential values of overburden when samples were digested according to standard fizz ratings compared to increasing the fizz rating and adding a corresponding higher amount of acid (Skousen et al., 1997).

Sample Description	Acid Added	Sobek	Acid Added	Sobek
49% Siderite	40 ml 0.1 M	70	40 ml 0.5 M	192
65% Siderite	40 ml 0.1 M	62	40 ml 0.5 M	155
65% Siderite	40 ml 0.1 M	63	40 ml 0.5 M	166
61% Siderite	40 ml 0.1 M	62	40 ml 0.5 M	192
18% Siderite, 48% Clays	40 ml 0.1 M	64	40 ml 0.5 M	234
20% Siderite, 11% Calcite	40 ml 0.5 M	367	80 ml 0.5 M	440
90% Calcite	80 ml 0.5 M	926	60 ml 1.0 M	919
83% Calcite	80 ml 0.5 M	835	60 ml 1.0 M	842

Table 4.7. Carbonate rating based on percent insoluble residue with corresponding acid volumes and acid strengths.

Carbonate Rating	Percent Insoluble Residue	Amount of Acid	Strength of Acid
	(%)	(ml)	(M)
0	95 - 100	20	0.1
1	90 - 94	40	0.1
2	75 - 89	40	0.5
3	< 75	80	0.5

concluded that CO_2 coulometry can be used to very accurately determine the carbonate carbon contents of overburdens containing calcite, dolomite, and siderite, and samples containing all three phases.

Calculations:

1. ml of acid consumed = (ml acid added) - (ml base added);
2. tons $CaCO_3$ equivalent/thousand tons of material = (ml of acid consumed) x (25.0) x (M of acid)

EVOLVED GAS ANALYSIS (EGA)

Evolved gas analysis (EGA) is a direct, one-step procedure that has been used for quantitatively evaluating the acid-producing and acid-neutralizing minerals in coal overburden samples. Hammack (1987) applied EGA to coal overburden analysis using a quadrapole mass spectrometer to detect carbon dioxide and sulfur dioxide evolution as samples were subjected to increasing temperatures.

This early work showed the potential of EGA for determining the amount and reactivity of pyrite as well as the amount of carbonate minerals in coal overburden samples. However, this EGA application was not quantitative because of problems associated with the quadrapole mass spectrometer.

A variant of the EGA procedure, a method termed controlled-atmosphere programmed-temperature oxidation (CAPTO) (LaCount et al., 1983), has recently been applied to the analysis of coal overburden samples. The method employs a primary and secondary tube furnace design, slow linear temperature ramp and plug flow of an oxidizing or anoxic atmosphere through a sample diluted with an inert solid. Oxide gases evolved are measured with respect to temperature using a fast fourier transform infrared spectrometer (FTIR).

Transition metal carbonates (siderite and rhodochrosite) decompose to yield carbon dioxide under the above conditions at 300 to 600°C, depending on the oxygen concentration applied to the samples. At low oxygen concentrations, transition metal carbonates decompose at lower temperatures than the corresponding carbonates analyzed using higher oxygen concentrations. Alkaline earth metal carbonates (calcite and dolomite) evolve carbon dioxide at higher temperatures (600 to 830°C). The alkaline earth metal carbonates do not show the same oxygen concentration decomposition dependence exhibited by the transition metal carbonates.

Pyrite and marcasite oxidize under these same conditions, to yield sulfur dioxide, at temperatures ranging from 350 to 560°C. Marcasite and more reactive morphologies of pyrite oxidize in the range of 350 to 440°C, while more stable forms oxidize at temperatures from 450 to 550°C.

Using one analysis procedure, it is possible to determine the amount of acid-neutralizing carbonate (calcite and dolomite) present, to determine the amount of siderite, and to distinguish acid-producing minerals such as pyrite and marcasite from other sulfur forms that do not generate acidity, for example, calcium sulfate.

Recent work using mine overburden core samples has shown that the decomposition of alkaline earth metal and transition metal carbonates can be resolved to quantify the amount of each of the carbonate forms present. The acid-producing minerals are quantitatively determined from the same analysis. Additionally, this technique can predict the reactivity of pyrite morphologies under weathering conditions, since pyrites that weather more readily tend to oxidize at lower temperatures than pyrites that are more resistant to weathering. Otherwise this information can only be obtained using simulated weathering (kinetic) tests. Further work to compare these results with conventional and kinetic tests is planned.

Examples of two profiles are shown. The first example shows the oxidation of pyrite and the decomposition of sulfate from an overburden sample. The sulfur dioxide evolution at 412°C is produced from the oxidation of pyrite; 800 to 1000°C is the temperature range where various calcium sulfate morphologies decompose. The second profile shows the carbon dioxide evolution for a mine overburden sample. The evolution centered at 529°C is produced from the decomposition of transition metal carbonates and that at 751°C is derived from alkaline earth metal carbonates. With all of the variables analyzed, one can calculate an ABA that is based only on the active constituents.

ViRoLac Industries is currently evaluating the ability of this new ABA technique to identify sulfur forms and to distinguish transition metal carbonates from alkaline earth metal carbonates present in a wide range of mine overburden core samples. Currently, the estimated costs to perform an ABA analysis using CAPTO is about twice that of conventional ABA methods so, at this time, the method would be best reserved for problematic sites where conventional ABA methods cannot definitively predict water quality. However, this method is significantly less expensive than the more time-consuming simulated weathering tests and may prove to be an effective alternative to those methods.

ACID-BASE ACCOUNTING BY DOWN-HOLE PROMPT GAMMA RAY SPECTROSCOPY WIRELINE LOGGING

The U.S. Geological Survey, in cooperation with the West Virginia Geological and Economic Survey (WVGES), Schlumberger HydroGeological Technologies (HGT) and West Virginia University (WVU), are applying oil and gas industry well logging technology to the chemical characterization of coal-bearing strata. The methodology is based on chemical analyses of boreholes using prompt neutron gamma ray spectroscopy wireline logging, hereafter referred to as geochemical logging (GCL). Traditional methods generally involve coring, core sampling, and chemical analysis of selected core samples. In contrast, GCL consists of wireline logging of a drill hole. The logging provides continuous chemical analyses, top to bottom, of a 6.5 inch drill hole, thereby eliminating sampling bias and error as well as other analytical error

associated with sample preparation and analyses of a core. The GCL tool also interrogates a formation volume that is much larger than that analyzed by core. The data generated should be directly applicable to the chemical characterization of coal-bearing strata and the ABA of overburden.

Figure 1: Sulfur Dioxide Evolution Profile for Overburden Sample

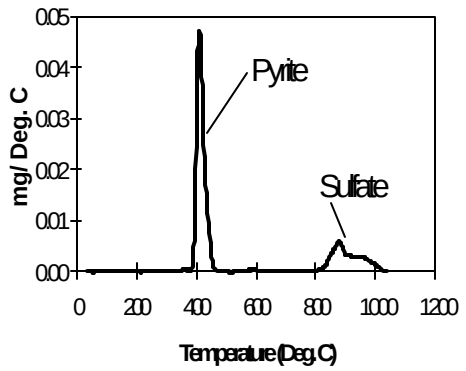
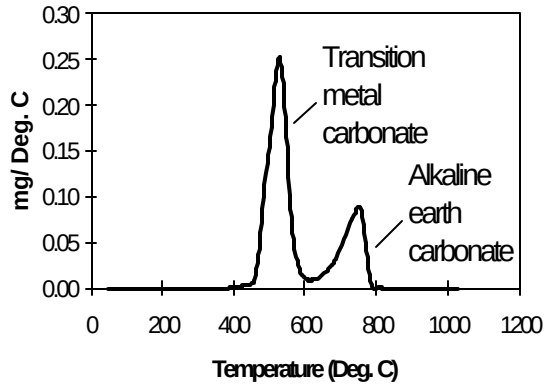


Figure 2: Carbon Dioxide Evolution Profile for Overburden Sample



In order to compare results from GCL with conventional analytical methods, two study sites were selected in an area known to have a variety of rock types and chemistries and histories of acid mine drainage, near the eastern edge of the bituminous coal field. The first site, in Tucker County, WV, was approximately 10 miles northeast of Davis, WV. The second site, in Mineral County, WV, was 5 miles west of Keyser, WV.

The core, minus core from coal beds, was boxed and transported to WVGES facilities. One complete set of quartered samples from each of the two cores was submitted to WVU analytical laboratories, where each sample was ground to -200 mesh and prepared for mineralogical and chemical analyses. Mineralogical analyses was conducted by X-ray diffraction (XRD); chemical analyses included major and minor element analyses by X-ray fluorescence (XRF), and ABA was conducted using standard wet chemical procedures. Sampling and analyses of the core in one-foot increments provided data for 650 samples from the first hole and 953 samples from the second.

The total suite of one-foot increment core samples was analyzed for total sulfur using a commercial analyzer. Calcium carbonate as calcite plus dolomite was determined by XRD, while calcium calculated as CaO was determined by XRF. MPA and NP were determined by standard wet chemical methods. The GCL analyses consist of continuous weight percent Si, Ca, Fe, Ti, K, and S determinations, for the entire length of the two test holes.

The chemical data from each of the two holes were compared in two ways. In the first case, data from only the Allegheny Formation were compared. Allegheny Formation samples were compared separately because these strata are known to consistently present problems in acid production when disturbed by surface mining. In the second case, data from the entire stratigraphic section penetrated by coring, which includes the Conemaugh and Allegheny Formations (minus the coal beds), were compared. The second case provided a wide range in lithologies and ABA variables. A comparison of the mean and standard deviation

for the geochemical wireline log data and chemical analyses of one-foot increment core data from Allegheny Formation strata is shown in Table 4.8.

Table 4.8. Comparison of borehole GCL data with chemical data of one-foot incremental samples of core from two bore holes for the Allegheny Formation. The means (m) and standard deviation (sd) values for GCL are based on a running average of direct borehole analyses in six inch increments by the neutron activation tool. The net neutralization potentials (NNP) were calculated for a number (n) of samples from calcium and sulfur values, using standard conversion procedures.

	Calcite		**Sulfur**		**NNP**	
	GCL	CORE	GCL	CORE	GCL	CORE
USGS/WVGES - 1, Allegheny Formation at the 95% confidence level						
m	0.64	1.28	0.16	0.17	1.5	7.7
sd	2.41	3.92	0.46	0.34	29	42
n	453	229	453	230	453	229
	unequal means		***equal means***		***unequal means***	
USGS/WVGES-3, Allegheny Formation at the 95% confidence level						
m	1.62	1.22	0.18	0.17	11	7.0
sd	4.03	3.06	0.26	0.24	39	36
N	425	212	425	212	425	212
	equal means		***equal means***		***equal means***	
USGS/WVGES-1 Conemaugh and Allegheny Formations total core analyses						
	Calcite		**Sulfur**		**NNP**	
	GCL	CORE	GCL	CORE	GCL	CORE
m	1.13	1.93	0.11	0.16	36	43
sd	3.14	4.91	0.35	0.33	34	51
n	1185	575	1185	575	1185	575
	unequal means		***unequal means***		***unequal means***	
USGS/WVGES-3 Conemaugh and Allegheny Formations total core analyses						
m	4.36	5.06	0.23	0.25	36	43
sd	8.81	10.2	0.46	0.80	86	105
n	1909	945	1909	945	1909	945
	equal means		***equal means***		***equal means***	

The numerical comparison of the results from GCL and core analyses indicates that there are some differences between the GCL data and the chemical data, particularly at the first site, where there was a twenty foot off-set between the core hole and the 6.5 inch air rotary hole. Although the mean values for sulfur were equal for the Allegheny Formation between the two methods, the mean values for calcite and NNP were not equal for either the entire core or the Allegheny Formation. A large part of the differences in data sets can be ascribed to differences in the amount of calcite within each of the two holes, as indicated

by differences in resistivity and density logs. These differences were sufficient to cause a noticeable difference in NNP values between the two holes.

There were fewer differences between the GCL and core data sets in the second site. At this site, the core hole was reamed to a 6.5-inch diameter. When the data were acquired from what was essentially the same hole, the means were equal for sulfur, calcite, and NNP for both the Allegheny Formation and the Conemaugh plus the Allegheny Formations.

The preliminary data indicate that GCL can provide a level of accuracy equivalent to chemical analyses of one-foot increment samples of core, and can be used for chemical characterization of coal-bearing strata and ABA of overburden. The logging has the advantage of providing accurate data at the well site in a matter of minutes for an individual drill hole or any number of holes. If further testing demonstrates that ECS logging is as accurate as conventional chemical methods of overburden characterization, then GCL of air rotary holes may eliminate the need for coring. The objectives of accuracy and rapid analysis appear to be met by GCL; now the industry will have to address the issue of cost effectiveness.

INTERPRETATION OF OVERBURDEN QUALITY BY ACID-BASE ACCOUNTING

ABA assesses the total amount of acidity or alkalinity that is contained in a specific rock unit. The assessment is based on the total S content and the carbonate content of the rock. The aim of ABA is to determine how much material is needed to neutralize all of the acid that could potentially form in coal overburden when pyrite is present. The use of total S provides a margin of neutralization safety against S percentages that may not all be pyritic and for pyritic S that may not all react.

Three basic assumptions should be understood when using ABA for overburden prediction (Perry, 1985). First, the values for MPA and NP represent maximum or ultimate quantities from pulverized, whole rock analysis. Complete reaction of all pyrite and bases probably does not occur in a mine backfill, thereby reducing the total amount of acidity or alkalinity produced in the ABA procedure. Second, S exists in three chemical forms in coal bearing rocks: sulfide, sulfate and organic, with sulfide S (pyrite) being the predominant acid producer. Third, pyrite may oxidize faster or slower than the dissolution of carbonate materials. Conventional ABA does not determine reaction rates of pyrite and carbonates, though the new EGA method can apparently indicate the reactivity of the pyrite.

Skousen et al. (1987) suggested that overburden with NNP values less than 5 metric tons per 1000 metric tons produce acid, while values greater than 20 metric tons per 1000 metric tons produce alkaline drainage. However, that was based on soil science and plant growth requirements. Today, the consensus view, based on field validation studies, is summarized in Table 4.1.

A common error when using ABA as a predictive method occurs when the Max Needed and Excess columns are summed together for the entire overburden above the coal bed (the Max Needed column representing a negative number and the Excess column representing a positive number). Summing the ABA values for an overburden column falsely assumes thorough mixing of all overburden in a backfill, uniform rates of weathering of all materials, and water contact throughout the backfill.

STATE PRACTICES

All the states interviewed practice overburden analysis using ABA; all use NP and all but Indiana use MPA based on total sulfur to arrive at an NNP value for all permits. Illinois will accept MPA values based on pyritic sulfur or total sulfur. Indiana uses MPA based on pyritic sulfur, though it also requires total sulfur analysis and fizz tests, and reserves the option of requiring additional tests, if warranted. Virginia gives applicants the option to do an organic/mineral sulfur speciation to alter MPA results. Tennessee adjusts total sulfur content of the overburden, and therefore MPA, by adding 10% to 15%, and Pennsylvania by adding 5% to 20%, of the coal mined as waste scatter into the spoil. West Virginia and Tennessee require NP to be adjusted for siderite when its presence is suspected.

Acid/base accounting (ABA), neutralization potential, and potential acidity (based on total or pyritic sulfur) are used to arrive at a net neutralization potential (referred to as *Calcium Carbonate Deficiency*) for each stratum in the overburden. Calcium Carbonate Deficiency is computed by subtracting neutralization potential (NP) from potential acidity (PA); therefore, negative numbers are desirable, since an NP larger than a PA would produce a negative number. A Calcium Carbonate Deficiency of five tons or more per one thousand tons of material is defined as *toxic forming*. Mass-weighted ABA for the entire overburden column is required if marginal values are observed for the individual strata. Additional information can be required if warranted. The applicant may request a waiver for overburden analysis prior to application submittal; the waiver must document that equivalent information is available.

Pennsylvania has a more rigorous requirement for siderite that they implement themselves: on properties with marginal NNP that contain units of high NP with low fizz, Pennsylvania will repeat the NP test with and without a modified H_2O_2 carbonate digestion method (Skousen et al, 1997). If there is a significant difference in the NP value based on the standard and modified H_2O_2 test methods, they will then determine the carbonate mineralogy in the sample by X-ray diffraction to differentiate the siderite and limestone/dolomite portions. ABA analysis is not a blanket requirement for Pennsylvania: ABA information is required for approximately 50% of new permit applications. No ABA analysis is requested if, in the reviewers' opinion, there is sufficient evidence from adjacent mining that any discharges will be alkaline and contain no problematic metal contaminants.

Only West Virginia and Alabama request kinetic tests if the previous history of predicting post-mining discharge quality in the permit area is not completely successful based solely on ABA. Alabama rarely requests leaching column tests, while West Virginia can opt for one or a combination of humidity cell, leaching column, and Soxhlet extraction tests. Kentucky, Maryland, Pennsylvania, and Tennessee do not request, but will accept and consider kinetic tests provided as supplemental information to permit applications. All of this information has been summarized in Table 4.7.

RECOMMENDATIONS AND FUTURE USE OF ACID-BASE ACCOUNTING

ABA has been applied to overburden characterization and water quality prediction on mined lands in many parts of the world for about 30 years. An extensive institutional knowledge base and "rules of thumb" have developed on interpreting ABA data, supplemented by a few published studies. ABA

Table 4.7. State Practices for Overburden Analysis

STATE	REQUIREMENTS	OPTIONS
AL	ABA, NP and MPA (based on total S) to arrive at an NNP value. Kinetic tests required if previous history of predicting post-mining discharge quality using ABA alone is not completely successful. Leaching tests rarely requested.	
IL	ABA, NP and MPA (based on total S) to arrive at an NNP value. Total S analysis may be substituted for MPA. Additional information or testing can be required.	
IN	ABA, NP and MPA (based on pyritic S) to arrive at an NNP value. Total S and fizz tests are required as supplemental information. Additional information or testing can be required.	
KY	ABA, NP and MPA (based on total S) to arrive at an NNP value.	Considers kinetic tests as supplemental information.
MD	ABA, NP and MPA (based on total S) to arrive at an NNP	Considers kinetic tests as supplemental information.
OH	ABA, NP and PA or MPA to determine a calcium carbonate deficiency (CCD). If CCD $\geq$ 5 tons per thousand tons, strata is defined as toxic forming. Mass weighted ABA required for entire overburden column if any marginal values are observed.	Applicants may request a waiver from overburden analysis if equivalent information is available.
PA	ABA, NP and MPA (based on total S) to arrive at an NNP value. ABA not needed if adjacent mines indicate that discharges will be acceptable. When ABA is required, PA tests for $FeCO_3$. At sites with marginal NNP that contain units of high NP with low fizz, PA will repeat NP test with and without modified H_20_2 carbonate digestion method. If NP values based on H_20_2 test methods differ, X-ray diffraction is used.	Adjusts total S content of overburden by adding 5-20% of coal mined as waste scatter in spoil. Considers kinetic tests as supplemental information.
TN	ABA, NP and MPA (based on total S) to arrive at an NNP value. Adjust NP for $FeCO_3$ when its presence is suspected.	Adjusts total S content of overburden by adding 10-15% of coal as waste in spoil. Considers kinetic tests as supplemental information.
VA	ABA, NP and MPA (based on total S) to arrive at an NNP value.	Organic/mineral S speciation to alter MPA.
WV	ABA, NP and MPA (based on total S) to arrive at an NNP value. Adjusts NP for $FeCO_3$ when its presence is suspected. Kinetic tests required if history of predicting discharge quality in the permit area using ABA alone is not completely successful.	

is a valuable assessment and prediction tool, and is the fastest and easiest way to begin evaluation of overburden materials for water quality prediction. Its application is most effective when used as part of a group of interpretive techniques for analyzing the interaction of geologic and hydrologic conditions, and mining and reclamation practices.

We recommend the use of ABA as the first test for overburden quality and characterization. The combustion technique has been used extensively to determine total S and it has been shown to be an accurate and repeatable measurement. We also recommend the use of total S (rather than pyritic S) to represent MPA. This intentionally overestimates the acid potential to provide a margin of safety.

Since siderite is a common constituent in coal overburdens of the eastern U.S. and does not actually neutralize acidity, a change in the NP procedure has been recommended (Leavitt et al., 1995; Meek, 1981; Morrison et al., 1990; Skousen et al., 1997). We recommend the modified procedure described earlier in this chapter, which eliminates the subjectivity of the fizz test and accounts for siderite. By using this modified method, the ABA values (incorporating the modified NP values) of overburden samples were much closer to the actual water acidity or alkalinity values from intensive weathering tests. Widespread use of the modified NP procedure will likely improve the accuracy of water quality prediction. Alternatively, if it proves cost effective, then the wireline logging approach may one day supplant in-lab analysis.

In spite of increasingly accurate overburden characterization, further refinements are needed to predict the degree to which discharges will be acid or alkaline from a site. The new EGA techniques, selectively used, may help, once the methodology is field validated. However, there will still be many uncertainties in predicting the quality of water from surface and deep mines, and continued field validation of pre-mining overburden analyses to post-mining water quality is important in refining water quality prediction. The likely effect of mining and reclamation practices and hydrology of the reclaimed area is starting to be factored into predictions of post-mining water quality. Another good sign is that computers are being used to better model the volumes of overburden material in various categories on a site.

In summary, ABA balances maximum potential acidity against total neutralizers in each overburden sample. ABA satisfies the requirement to identify overburden layers that will or will not produce acid, and pinpoints those layers that should be analyzed further by other analytical methods. Borderline samples that give NNP values of 0 to +12 tons/1000 tons should be subjected to other tests to determine the acid-producing potential. Once the total overburden column has been assessed and proper interpretations have been made, practical mining and reclamation plans can be designed and implemented. Despite many criticisms, ABA has been and will continue to be the preferred first measure of overburden chemistry for both the industry and regulatory agencies as long as it remains the fastest and easiest way to evaluate overburden materials. It should be used within its limits, in conjunction with other methods of overburden analysis when necessary, and with good common sense.

REFERENCES

Ammons, J.T. and A.P. Shelton, 1988. Comparison of results from acid-base accounting versus potential acidity measured by the peroxide oxidation of weathered and unweathered soils containing pyrite. p. 206-209. In: Mine Drainage and Surface Mine Reclamation. USBM IC 9183. Pittsburgh, PA.

Bish, D.L, 1994. Quantitative x-ray diffraction analysis of soils. p. 267-295. In: Amonette, J.E, and L.W. Zelazny (Eds.), Quantitative Methods in Soil Mineralogy. Soil Science Soc.of America, Madison, WI.

Bradham, W.S. and F.T. Caruccio, 1991. A comparative study of tailings analysis using acid-base accounting, cells, columns and soxhlets. p. 157-174. In: Proc., 2nd International Conf. on the Abatement of Acidic Drainage, Montreal, Canada.

Brady, K., and C. Cravotta, 1992. Acid-Base Accounting: an improved method of interpreting overburden chemistry to predict quality of coal mine drainage. In: Proc., 13th WV Surface Mine Drainage Task Force Symp., April 8-9, 1992, Morgantown, WV.

Brady, K. and R.J. Hornberger, 1990. A manual for premining prediction of coal mine drainage quality. PA Dept. of Environmental Resources, Harrisburg, PA.

Brady, K., E. Perry, R. Beam, D Bisko, M. Gardner, and J. Tarantino, 1994. Evaluation of acid-base accounting to predict the quality of drainage at surface coal mines in Pennsylvania, USA. p. 138-147. In: International Land Reclamation and Mine Drainage Conf., Vol 1. USBM SP-06A-94, Pgh., PA.

British Columbia Acid Mine Drainage Task Force, 1989. Draft Acid Rock Drainage Guide. BiTech Publishers Ltd., Vancouver, British Columbia.

Cargeid, 1981. An evaluation of the proposed Holly Grove mine to impact the Little Kanawha River with acid water. Unpublished report to U.S. EPA, Columbia, SC.

Carson, C.D., D.S. Fanning, and J.B. Dixon, 1982. Alfisols and ultisols with acid sulfate weathering features in Texas. p. 127-146. In: Acid Sulfate Weathering. SSSA Spec. Publ. No. 10. SSSA, Madison, WI.

Caruccio, F. and G. Geidel, 1978. Geochemical factors affecting coal mine drainage quality. p. 129-148. In: Reclamation of Drastically Disturbed Lands. American Society of Agronomy, Madison, WI.

Caruccio, F.T., G. Geidel, and A. Pelletier, 1980. The assessment of a stratum's capability to produce acid drainage. p. 437-443. In: Proc., Symp. on Surface Mining Hydrology, Sedimentology, and Reclamation. University of Kentucky, Lexington, KY.

Caruccio, F., L.R. Hossner, and G. Geidel, 1988. Pyritic materials: acid drainage, soil acidity, and liming, In: L.R. Hossner (Ed.), Reclamation of Surface Mined Lands. Vol. 1. CRC Press, Boca Raton, FL, p. 159-190.

Cornwell, S.M., 1966. Anthracite mining spoils as media for plant growth. Ph.D. Thesis. Cornell University, Ithaca, NY.

Cravotta, C.A., 1991. Geochemical evaluation of acidic groundwater at a reclaimed surface coal mine in western Pennsylvania. p. 43-68. In: Proc., Meeting of the American Society of Surface Mining and Reclamation, Vol 1. Durango, CO.

Cravotta, C.A., K. Brady, M.W. Smith, and R.L. Beam, 1990. Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage: part 1, geochemical considerations. p. 221-225. In: Proc., Mining and Reclamation Conf., WVU, Morgantown, WV.

Davis, G., 1965. A guide for revegetating bituminous strip-mine spoils in Pennsylvania. Research Committee on Coal Mine Spoil Revegetation in Pennsylvania. NE Forest Experiment Station, Broomall, PA.

diPretoro, R.S. and H.W. Rauch, 1988. Use of acid-base accounts in premining prediction of acid drainage potential: a new approach from northern West Virginia. p. 2-10. In: Mine Drainage and Surface Mine Reclamation. USBM IC 9183. Pittsburgh, PA.

Doolittle, J.J., N. Frisbee, and L.R. Hossner, 1992. Evaluation of acid-base accounting techniques used in surface-mine reclamation. p. 68-76. In: Proc., Meeting of the American Society of Surface Mining and Reclamation. Duluth, MN.

Erickson, P.M. and R.S. Hedin, 1988. Evaluation of overburden analytical methods as means to predict post-mining coal mine drainage quality. p. 11-19. In: Mine Drainage and Surface Mine Reclamation. USBM IC 9183. Pittsburgh, PA.

Evangelou, V.P., K. Roberts, and G.W. Szekeres, 1985. The use of an automated apparatus for determining coal spoil carbonate types and reactivity. p. 163-165. In: Proc., National Symp. Surface Mining, Hydrology, Sedimentology, and Reclamation, December 8-13, 1985, Lexington, KY.

Ferguson, K.D. and K.A. Morin, 1991. The prediction of acid rock drainage - lessons from the database. p. 83-106. In: Proc., 2nd International Conf. on the Abatement of Acidic Drainage. Montreal, Canada.

Ferguson, K.D. and J.D. Robertson, 1994. Assessing the risk of acid rock drainage. p. 2-11. In: Proc., International Land Reclamation and Mine Drainage Conf., Vol 1. USBM SP-06A-94, Pgh., PA.

Frisbee, N.M. and L.R. Hossner, 1989. Weathering of siderite from lignite overburden. In: Proc., Meeting of the American Soc. for Surface Mining and Reclamation. Calgary, CN.

Frost, J, 1981. Variability of Kittanning coal overburden at a surface mine in Upshur County, West Virginia. M.S. Thesis, West Virginia University, Morgantown, WV.

Greene, B.C. and W.B. Raney, 1974. West Virginia's controlled placement, pp. 5-17 in: 2nd Research and Applied Technology Symp.on Mined Land Reclamation. NCA/BCR, Pittsburgh, PA.

Grim, E.C. and R.D. Hill, 1974. Environmental protection in surface mining of coal. EPA 670/2-74-093. National Environmental Research Center, U.S. EPA, Washington, DC.

Grube, W.E., R.M. Smith, R.N. Singh, and A.A. Sobek, 1973. Characterization of coal overburden materials and minesoils in advance of surface mining. p. 134-151. In: Research and Applied Technology Symposium on Mined-Land Reclamation, NCA/BCR, Pittsburgh, PA.

Hammack, R.W., 1987. Evolved gas analysis - A new method for determining pyrite, bicarbonate, and alkaline earth carbonates. In: Proc., 8th WV Surface Mine Drainage Task Force Symp., April 7-8, 1987, Morgantown, WV.

Johnson, C.D. and J.G. Skousen, 1995. Minesoil properties of 15 abandoned mine land sites in West Virginia. J. Environ. Qual. 24:635-643.

Jones, A.A., 1982. X-ray fluorescence spectrometry. p. 85-121. In: Page et al. (Editors), Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, 2nd Edition. American Society of Agronomy, Madison, WI.

Knabe, W., 1964. Methods and results of strip-mine reclamation in Germany. Ohio J. Sci., 64(2):75-105

Knabe, W., 1973. Development and application of the Domsdorf Ameliorative Treatment on toxic spoil banks of lignite opencast mines in Germany. p. 273-294. In: R.J. Hutnik and G. Davis (Eds.), Ecology and Reclamation of Devastated Land, Vol. 2. Gordon and Breach Sci. Publ. Inc., NY.

Knapp, R. 1987. The biogeochemistry of acid generation in sulfide tailings and waste rock. In: Proc., Acid Mine Drainage Seminar. Environment Canada En 40-11-7/1987. Halifax, Nova Scotia.

Kwong, Y.J., 1991. Acidic generation in waste rock as exemplified by the Mount Washington minesite, British Columbia, Canada. p. 175-190. In: Proc., 2nd International Conf. on the Abatement of Acidic Drainage, Montreal, Canada.

LaCount, R.B., R.P. Anderson, C.A. Helms, S. Friedman, and W.B.Romine, 1983. Construction and Operation of a Controlled-Atmosphere Programmed-Temperature Reaction Apparatus, DOE/PETC/TR-8315, April, 1983, 115 pages.

Leathen, W.W., S. Braley, and L.D. McIntyre, 1953. The role of bacteria in the formation of acid from certain sulfuritic constituents associated with bituminous coal. Part 2. Ferrous iron oxidizing bacteria. Appl. Microbiol 1:65-68.

Leavitt, B., J. Skousen, and P. Ziemkiewicz, 1995. Effects of siderite on the neutralization potential in the acid-base account. In: Proc., WV Surface Mine Drainage Task Force Symp., Morgantown, WV.

Limstrom, G.A., 1948. Extent, character, and forestation possibilities of land stripped for coal in the central states. Technical Paper 109, Central States Forest Experiment Station, Columbus, OH.

May, R.F. and W.A. Berg, 1966. Overburden and bank acidity—Eastern Kentucky strip mines. Coal Age 71:74-75.

Meek, F.A., 1981. Development of a procedure to accurately account for the presence of siderite during mining overburden analysis. In: Proc., WV Surface Mine Drainage Task Force Symp. Morgantown, WV.

Miller, S.D., J.J Jeffery, and J.W.C. Wong, 1991. Use and misuse of the acid-base account for AMD prediction. p. 489-506. In: Proc., 2nd International Conf. on the Abatement of Acidic Drainage, Vol. 3, CANMET, Ottawa, Ontario.

Miller, S.D., and G.S. Murray, 1988. Application of acid-base analysis to wastes from base metal and precious metal mines. p. 29-32. In: Mine Drainage and Surface Mine Reclamation, Vol. 1, USBM IC 9183, Pittsburgh, PA.

Morin, K.A. and N.M. Hutt, 1988. An empirical technique for predicting the chemistry of water seeping from mine rock piles. p. 12-19. In: Mine Drainage and Surface Mine Reclamation. USBM IC 9183, Pittsburgh, PA.

Morrison, J.L., S.D. Atkinson, A. Davis, and B.E. Sheetz, 1990. The use of CO_2 coulimetry in differentiating and quantifying the carbonate phases in coal-bearing strata of western Pennsylvania: its applicability in interpreting and modifying neutralization potential (NP) measurements. p. 243-247. In: Proc., Mining and Reclamation Conf., WVU, Morgantown, WV.

Noll, D.A., T.W. Bergstresser, and J. Woodcock, 1988. Overburden sampling and testing manual. PA Dept. of Environmental Resources. Harrisburg, PA.

Nordstrom, D.K., 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. p. 37-56. In: Acid Sulfate Weathering. SSSA Special Publication 10. Madison, WI.

O'Shay, T., L.R. Hossner, and J.B. Dixon, 1990. A modified hydrogen peroxide oxidation method for determination of potential acidity in pyritic overburden. J. Environ. Qual. 19:778-782.

Perry, E., 1985. Overburden analysis: an evaluation of methods. p. 365-375. In: Proc., Symp.on Surface Mining, Hydrology, Sedimentology, and Reclamation. U.KY, Lexington, KY.

Perry, E.F. and K.B. Brady, 1995. Influence of neutralization potential on surface mine drainage quality in Pennsylvania. In: Proc., WV Surface Mine Drainage Task Force Symp., Morgantown, WV.

Renton, J.J., T.E. Rymer, and A.H. Stiller, 1988. A laboratory procedure to evaluate the acid producing potential of coal associated rocks. Mining Science and Technology 7:227-235.

Rymer, T.E., J.J. Renton, and P.F. Ziemkiewicz, 1991. Isolation of critical predictive acid-producing parameters from variable field data using advanced computer technology. In: Proc., 2nd International Conference on the Abatement of Acidic Drainage, Montreal, Canada.

Scholz, A.G. and D. Rathleff, 1982. A rapid method to determine total sulphur. J. Coal Quality 2(1):16-19.

Shelton, P.A., J.T. Ammons, and J.R. Freeman, 1984. NPs: a closer look. Green Lands 13(4):35-37.

Singer, P.C. and W. Stumm, 1968. Kinetics of the oxidation of ferrous iron. p. 12-34. In: Proc., 2nd Symp. on Coal Mine Drainage Research. NCA/BCR, Pittsburgh, PA.

Singer, P.C. and W. Stumm, 1970. Acid mine drainage: the rate determining step. Science 167:1121-1123.

Skousen, J.G., J. Renton, H. Brown, P. Evans, B. Leavitt, K. Brady, L. Cohen, and P. Ziemkiewicz, 1997. Neutralization potential of overburden samples containing siderite. J. Environ. Qual. 26(3): 673-681.

Skousen, J.G., J.C. Sencindiver, and R.M. Smith, 1987. A review of procedures for surface mining and reclamation in areas with acid-producing materials. WVU Energy and Water Research Center, Publication No. EWRC 871, Morgantown, WV.

Smith, E.E. and K.S. Shumate, 1970. Sulfide to sulfate reaction mechanism. Water Pollution Control Research Series 14010 FPS. USDI, FWQA. Washington, DC.

Smith, M.W. and K. Brady, 1990. Evaluation of acid base accounting data using computer spreadsheets. p. 213-219. In: Proc., 1990 Mining and Reclamation Conf., WVU, Morgantown, WV.

Smith, R.M., W.E. Grube, T.A. Arkle, and A.A. Sobek, 1974. Mine spoil potentials for soil and water quality. U.S. EPA 670/2-74-070. Washington, DC.

Smith, R.M., A.A. Sobek, T. Arkle, Jr., J.C. Sencindiver, and J.R. Freeman, 1976. Extensive overburden potentials for soil and water quality. U.S. EPA 600/1-76-184. Washington, DC.

Smith, R.M. and E.H. Tyner, 1945. Reclaiming strip-mine spoil banks. WVU Agricultural Experiment Station, Circular 53. WVU, Morgantown, WV.

Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith, 1978. Field and laboratory methods applicable to overburdens and minesoils. U.S. EPA 600/2-78-054. Washington, DC.

Soil Conservation Service, 1973. Kentucky guide for classification, use, and vegetative treatment of surface mine spoil. USDA, SCS, Lexington, KY.

Steffen Robertson Kirsten, 1989. Draft acid rock technical guide. Prepared for the British Columbia Acid Mine Drainage Task Force in conjunction with Norecol Environmental Consultants and Gormley Process Engineers. Bitech Publishers, Vancouver, Canada.

Tettenburn, F., 1980. Overburden characterization and its role in premine planning of two West Virginia surface mines. M.S. Thesis, WVU, Morgantown, WV.

Tyner, E.H., R.M. Smith, and S.L. Galpin, 1948. Reclamation of strip-mined areas in West Virginia. J. American Society of Agronomy 40:313-323.

U.S. Environmental Protection Agency, 1971. Inorganic sulfur oxidation by iron-oxidizing bacteria. Water Pollution Control Res. Series 14010 DAY. USDI, FWQA. Washington, DC.

Vlek, P.L.G., T.J.M. Blom, J. Beek, and W.L. Lindsay, 1974. Determination of solubility product of various iron hydroxides and jarosite by the chelation method. Soil Sci. Soc. Am. Proc. 38:429-432.

West Virginia University, 1971. Mine spoil potentials for water quality and controlled erosion. U.S. EPA, OWP, Project No. 14010, EJE. Washington, DC.

Wiram, V.P., 1992. Siderite masking: a factor to consider in overburden acid-base balancing. In: Proc., WV Surface Mine Drainage Task Force Symp. Morgantown, WV.