Chapter 6

LABORATORY METHODS FOR ACID-BASE ACCOUNTING: AN UPDATE

Tim Kania
Pennsylvania Department of Environmental Protection
Ebensburg, PA 15931

Introduction

Laboratory methods for performing acid-base accounting overburden analysis (ABA) have been thoroughly detailed in previous publications. Sobek et al. (1978) formally presented a step-by-step laboratory protocol for performing ABA on mine overburden and is frequently cited as the source document. However, earlier publications described the application of ABA principals to mine overburden testing (West Virginia University, 1971; Grube et al., 1973; Smith et al., 1974; Smith et al., 1976). In 1988 Energy Center, Inc., under contract to the Department of Environmental Resources, Small Operator Assistance Program (SOAP), produced a detailed report on overburden sampling and testing (Noll et al., 1988). This latter document included a detailed description of considerations appropriate to planning an overburden analysis and to collecting the samples; it also added a boil step to the NP determination methodologies and provided a detailed description of methods for determining forms of sulfur.

This chapter focuses on aspects of the ABA procedures which have been somewhat controversial because of the effects that they can have on the reported results; it will not detail the laboratory protocols required to perform ABA.

Components of ABA

ABA is based on the premise that the propensity for a site to produce acid mine drainage can be predicted by quantitatively determining the total amount of acidity and alkalinity the strata on a site can potentially produce.

The maximum potential acidity (expressed as a negative) and total potential alkalinity (termed neutralization potential) are then summed. If the result is positive, the site should produce alkaline water, if it is negative, the site should produce acidic water. Sobek et al., (1978) defined any strata with a net potential deficiency of 5 tons per 1000 tons (ppt) or greater as being a potential acid producer. The maximum potential acidity (MPA) is stoichiometrically calculated from the percent sulfur in the overburden. The appropriate calculation factor is somewhat controversial. Sobek et al. (1978), noting that 3.125 g of $CaCO_3$ is theoretically capable of neutralizing the acid produced from 1 g of S (in the form of FeS_2), suggested that the amount of potential acidity in 1000 tons of overburden could be calculated by multiplying the percent S times 31.25. This factor is derived from the stoichiometric relationships in equation 6.1 and carries the assumption that the CO_2 exsolves as a gas.

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 2\ Ca^{+2} + CO_2(g) \qquad (6.1)$$

Cravotta et al., (1990) suggested that, in backfills where CO_2 cannot readily exsolve, the CO_2 dissolves and reacts with water to form carbonic acid and that the maximum potential acidity in 1000 tons of overburden should then be derived by multiplying the percent S times 62.50.

The neutralization potential (NP) is determined by digesting a portion of the prepared sample in hot acid, and then by titrating with a base to determine how much of the acid the sample consumed. NP represents carbonates and other acid neutralizers and is commonly expressed in terms of tons $CaCO_3$ per 1000 tons of overburden (ppt). Negative NP values are possible, and are sometimes derived from samples of weathered rock that contain residual weathering products which produce acidity upon dissolution.

Interpretation of ABA data involves the application of numerous assumptions; some of the more significant assumptions often used are:

- all sulfur in a sample will react to form acid;
- all material in the sample which consumes acid during digestion in the lab will generate alkalinity in the field;
- the reaction rate for the sulfur will be the same as the dissolution rate for the neutralizing material.
- NP and percent sulfur values below certain threshold levels do not influence water quality.

As these assumptions imply, interpretation of ABA data is far more complicated than simply summing the MPA and NP values. Chapter 11 titled "Interpretation of Acid-Base Accounting Data" discusses these assumptions in more detail.

In addition to the percent sulfur and NP determinations, two other measured parameters in an ABA overburden analysis are paste pH and fizz. Other derived values are calculated from one or more of the measured parameters and from other information such as the sample thickness, density and areal extent. The derived values used may vary somewhat but typically include calculations of maximum potential acidity, tons of neutralization potential, tons of potential acidity, and tons net neutralization potential for each sample, as well as for the entire bore hole. The derived values are also discussed in the chapter of this document which deals with the interpretation of ABA overburden analysis.

Paste pH

The paste pH test is described in the previously referenced manuals on ABA protocol (Sobek et al., 1978; Noll et al., 1988), however, in Pennsylvania, it has fallen into general disuse over the past several years. A portion of the prepared sample is mixed with deionized water, and then tested with a pH probe after one hour. The paste pH test may indicate the number of free hydrogen ions in the prepared sample, but, since pyrite oxidation reactions are time dependent, the paste pH results provide little indication of the propensity of a sample to produce acid mine drainage. In fact, the paste pH of a unweathered, high-sulfur sample is likely to be near that of the deionized water, while a weathered sample with relatively low percent sulfur, but which includes a small amount of residual weathering products, may have a significantly depressed paste pH. Because of its limited usefulness in helping predict the potential for acid mine drainage production, the paste pH test often is no longer performed, and for mine permit applications in Pennsylvania, it is not a required component of ABA.

Percent Sulfur

Since acid mine drainage results from accelerated weathering of sulfide minerals, the amount of sulfur in a sample, or in an overburden column, is obviously an important component of ABA. As noted above, ABA uses the percent sulfur to predict the "maximum potential acidity" or MPA that a particular overburden sample or column could produce if all the sulfur reacts.

Sulfur determinations for ABA are often performed for total sulfur only, however, determinations for forms of sulfur are sometimes included. Sulfur generally occurs in one of three forms in the rock strata associated with coals in Pennsylvania: sulfide sulfur, organic sulfur, and sulfate sulfur. Sulfide sulfur is the form which reacts with oxygen and water to form acid mine drainage. The sulfide minerals most commonly associated with coals in Pennsylvania are pyrite and marcasite, both of which are FeS_2, chemically. Other sulfide minerals such as chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS) may also be present in small amounts. Organic sulfur is that sulfur which occurs in carbon-based molecules in coal and other rocks with significant carbon content; since organic sulfur is tied up in compounds that are stable under surface conditions, it is not considered a contributor to acid mine drainage. Organic sulfur can represent a significant fraction of the total sulfur found in coal seams. Data from the Penn State Coal Data Base show that the average percent organic sulfur in several frequently mined coals in Pennsylvania ranges from a low of 0.55 % for the Upper Kittanning Coal to a high of 1.32 % for the Clarion Coal, with an overall average of 0.74%. Sulfate sulfur is often overlooked because in humid climates it generally is found in relatively small concentrations due to its high solubility. However, when present in Pennsylvania, sulfate sulfur often occurs in partially weathered samples as the reaction by-products of sulfide mineral oxidation. When solubilized, these weathering by-products are the source of the contaminants found in acid mine drainage, so when determinations for forms of sulfur are done, sulfate sulfur must be considered in the calculation of MPA. Alkaline earth sulfate minerals such as gypsum ($CaSO_4$) can also contribute to the sulfate sulfur fraction, but generally are not abundant in coal-bearing rocks in Pennsylvania. Where they are present, the alkaline earth sulfate minerals do not contribute to acidity.

Commonly used methods of performing total sulfur determinations are high temperature combustion methods (ASTM D4329), the Eschka Method (ASTM D3177) and the Bomb Washing Method (ASTM D3177). Of these methods, the high temperature combustion methods are the simplest and most frequently used and provide accurate, reproducible results.

Common methods used for determining forms of sulfur include ASTM D2492 and an EPA method. Noll et al., (1988) present an ASTM/EPA Combination method which the authors of that document felt combined the most desirable features of the other two methods.

Theoretically, the total of the sulfate and sulfide sulfur components should be a better indicator of the amount of reactive sulfur in a sample than should total sulfur. However, a laboratory study (Hedin and Erickson 1988) showed that total sulfur was related more strongly to leachate test results than was pyritic sulfur. Since pyritic sulfur is the form which contributes most significantly to acid mine drainage, these results indicate problems with pyritic sulfur determinations. A review of the methods for sulfur determinations described in Noll et al., (1988) reveals that the methods for total sulfur determinations have a relatively high degree of precision with few notable interferences and precautions, while the forms of sulfur determination methods described involve lesser degrees of precision and more numerous potential interferences and precautions. Stanton and Renton (1981) examined the nitric acid dissolution procedure, which is the cornerstone of the most frequently used methods for determining pyritic sulfur, including ASTM D2492; they found the procedure frequently does not succeed in digesting all the pyrite in a sample, thus underestimating the pyritic fraction of the sulfur in the sample. Brady and Smith (1990) compared total sulfur and forms of sulfur determinations performed by various laboratories. Their findings include:

- While the results generated by each laboratory were internally consistent in terms of the ratio of pyritic sulfur to total sulfur, there were significant differences between laboratories in the median percent pyritic sulfur/total sulfur. Where duplicate samples were available from different laboratories, differences were noted in the pyritic determinations, but total sulfur determinations were comparable.
- There was no significant difference in the percent pyritic sulfur/total sulfur between rock types (excluding coal). (This finding contradicts one of the primary reasons for doing determinations for forms of sulfur: that some rock types contain significant percentages of organic sulfur.)
- With one exception, all laboratories whose data was used in the study used a high temperature combustion method for determining weight percent total sulfur. The high temperature combustion results compared well on duplicate samples, while the pyritic results on the same samples did not.
- Standards are available from the National Institute of Standards for total sulfur but not for pyritic sulfur.
- A wide range of methods for determining pyritic sulfur were in use and individual laboratories had their own variations of the methods.
- One of the commonly used methods of pyritic sulfur determinations, ASTM D2492, was developed for use on coal and is probably not appropriate for determinations on rock overburden, according to ASTM Committee D-5 on Coal and Coke.

Figures 6.1 and 6.2 (data taken from Brady and Smith (1990)) compare total sulfur determinations and pyritic sulfur determinations of two different laboratories which performed analyses on duplicate samples. The high r^2 value for the total sulfur determinations indicate a strong correlation, and the low r^2 value for the pyritic determinations indicates a weak correlation.

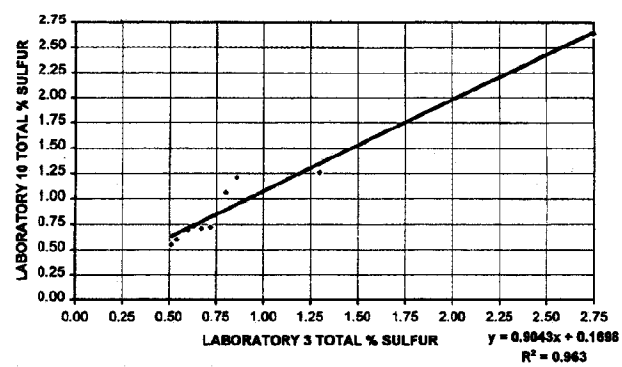

Figure 6.1 Comparison of percent total sulfur analysis results of duplicate samples analyzed by two different laboratories

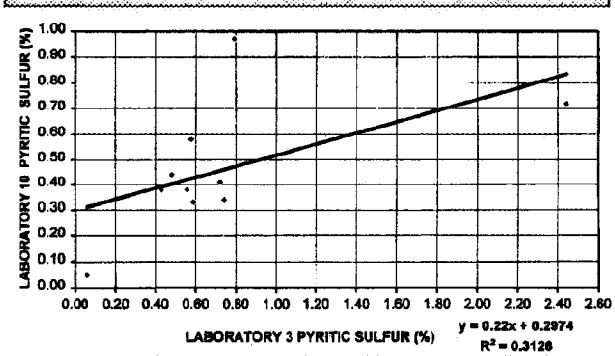

Figure 6.2 Comparison of percent pyritic sample analysis results for duplicate samples analyzed by two different laboratories

The above findings can be summarized as: Total sulfur determinations are typically simple to do, are reproducible, and can be calibrated and verified using available standards; pyritic sulfur determinations are done using a variety of methods (sometimes not standardized, and at least one of which is considered inappropriate for rock samples), produce results which are often not reproducible between laboratories, and cannot be calibrated and verified using available standards. Given these considerations, and that pyritic sulfur is the most abundant form in coal overburden (but not necessarily in the coal), total sulfur determinations currently provide the best basis for calculating MPA.

Fizz Rating

The importance of the fizz rating on ABA results is much underestimated and has often not received appropriate consideration. The fizz test is frequently presented as a minor part of the neutralization potential test; however the fizz test can have a large impact on the reliability and reproducibility of NP data, so it is discussed separately here. The fizz rating can be used as a check on the NP determination, since there should be a qualitative correlation between the two. More importantly, however, the fizz rating determines the volume and the strength of the acid which is used to digest the prepared sample, which in turn can affect the NP determination results (Evans and Skousen, 1995; Skousen et al., 1997). The NP result is then somewhat dependent on the fizz test results, and the fizz test results are a matter of human judgment.

The fizz test is performed by adding one to two drops of 25% HCl to a small amount of the prepared sample (Sobek et al., 1978). The degree of reaction is observed and recorded, according to a four-tiered system where the reaction is judged to be none or 0, slight or 1, moderate or 2, strong or 3. (Other systems with more levels have been used for reporting fizz results. However, given the obvious difficulties inherent to a test based on qualitative judgment, additional levels of judgment can only imply a precision which is not obtainable.)

There is an additional consideration which further complicates the subjective nature of the fizz test. Thresholds for NP and percent sulfur are often used in interpreting ABA. The theory behind using thresholds is that strata which produce NP or percent sulfur values below the thresholds are thought to have little impact on postmining water quality. However, these same strata often represent the greatest mass of the overburden and can "dilute" the effects of the strata with significant NP and percent sulfur if they are included in the calculations of total NP and MPA for the site. In Pennsylvania a threshold value of 30 is often used for NP. A threshold value of a 1 (slight fizz) is also often used. The fizz threshold tends to label a 0 or no fizz as being "bad" and higher fizz ratings as being "good." Strata identified as having a 0 fizz will not be counted as contributing potential alkalinity to postmining water quality which could result in a negative permitting decision. Even with the best intentions of the lab personnel performing the test, one cannot expect objective and reproducible results from a subjective test with a particular outcome pre-labeled as either good or bad. This is not to suggest that the use of thresholds is inappropriate, but to point out another precaution concerning reported fizz test results.

Evans and Skousen (1995) suggested a two-tiered fizz rating system which would combine the 0 and 1 fizz ratings into a single category and a 2 or 3 fizz rating into a second category. They reported that during a round robin sample testing study conducted by representatives of West Virginia University, Consolidation Coal Company (Consol), and the Pennsylvania DER (now DEP) on samples processed at the Penn State Materials Research Laboratories, the fizz ratings varied significantly between laboratories for certain samples. The laboratories then used different normalities and volumes of acid to perform the NP determinations on those samples, as dictated by the fizz ratings. The NP values varied considerably, and generally were higher when a larger volume of acid was used to digest the samples. When the Consol lab ran the NP determinations for each sample twice, with a different volume of acid each time, the determination that was made with the higher volume of acid produced a higher NP in each case. The differences were often great enough to change the interpretation one would make regarding the alkaline-producing potential of the sample. Table 6.1 displays fizz and NP data generated by the WVU and Consol laboratories during the round robin test and shows how fizz rating, acid volume and acid normality can affect NP results. Most of the samples included in Table 6.1 were selected for the study because visual observation suggested that they were siderite-rich; therefore, the differences in the fizz results and NP determinations between laboratories are probably more representative of what one would expect for siderite-

Table 6.1 Fizz test results and NP determinations for replicate overburden samples.

	West Virginia University*			Consol**		
SAMPLE NUMBER	FIZZ	SOBEK NP	GEOCHEM NP	FIZZ	NP1	NP2
NP-01	1	20	18	1	--	50
NP-02	1	8	8	3	--	445
NP-03	0	11	8	1	--	27
NP-04	3	926	930	3	--	936
NP-05	3	710	710	3		724
NP-07	1	25	30	0	20	6
NP-09	2	288	266	0	136	26
NP-10	1	13	13	0	58	22
NP-11	1	11	10	0	97	29
NP-13	0	17	14	0	51	23
NP-14	0	14	7	0	7	4
NP-15	1	11	11	0	85	14
NP-18	1	15	14	0	93	25

***Digested samples in accordance with both Sobek and Geochem recommendations; autotitrated to pH 7.0.**
****NP1 results based on digestion in 80 ml of 0.1N HCl. NP2 results based on digestion in 20 ml of 0.1N HCl for 0 fizz, 40 ml of 0.1N for 1 fizz, and 80 ml of 0.5N for 3 fizz. Manually titrated to pH 7.0.**

rich samples as opposed to samples with low siderite content. Skousen et al., (1997) reported that when three different laboratories performed fizz determinations on replicates of 31 samples, all three laboratories assigned the same fizz rating to only 13 of the 31 samples.

Reducing the number of tiers in the fizz test should reduce the amount of judgment required and consequently the subjectivity of the test. However, running the NP test with a reduced number of fizz test possibilities means that some samples would be digested in different volumes of acid than they would using the methods in Sobek et al. (1978) and Noll et al. (1988). Users of NP data need to be aware that changing the volume of acid used to digest a sample can change the NP results.

Skousen et al. (1997) described a protocol for a quantitative method of rating overburden samples based on the percent insoluble residue. Twenty ml of 10% HCl is added to 2.0 g of the prepared sample which has been dried in an oven. The solution is agitated until evolution of CO_2 is observed to cease. The solution is passed through a weighed filter, the filter plus residue are then dried and weighed, and the percent insoluble residue is calculated. The rating is then used to determine the volume and strength of acid used in the NP digestion; for that purpose the carbonate rating numbers are considered to be equivalent to the fizz rating values described in Sobek et al. (1978) and Noll et al., (1988). The NP and fizz determinations reported in Skousen et al., (1997) were run on replicates of the overburden samples, but the percent insoluble residue test was only run by one of the labs. As noted by the authors of that study, the method needs to be further tested to validate the proposed rating system and to provide a yardstick for comparing NPs based on the fizz test to those based on the percent insoluble test. One potential problem with the percent insoluble residue test is that, for some samples, the results may vary significantly when the percent HCl used in the digestion is changed (Keith Brady, personal communication). The samples studied by Skousen et al. (1997) were subjected to X-ray diffraction and characterized as belonging to one of four groups, based on their mineral and elemental content: Fe, Ca, S, and Si. When the percent insoluble residue test was performed on replicates of some of the samples using differing percents HCl, the results changed significantly for the iron-rich samples (Fe group) which included the samples with relatively high siderite content. (See Table 6.2.) The results for one of the carbonate-rich samples (Ca2) also changed significantly. These results raise questions concerning which % HCl should be used to achieve results which rate the carbonate in the samples in an accurate and reproducible way.

Given the difficulties which the current fizz rating system introduces into NP determinations, a reproducible, objective carbonate-rating test could significantly

Table 6.2 Comparison of percent insoluble residue to %HCl used to digest the sample.

(Samples which were digested with all three % HCl were tested at the DEP laboratory in Harrisburg, PA. For the samples digested in 10% and 50% HCl, the 10% digestion was done at West Virginia University and the 50% digestion was done at the PA Geologic Survey. Samples which were digested twice in the same percent HCl were duplicate samples.)

%HCl	Ca1	Ca2	Ca3	Fe1	Fe2	Fe3	Fe4	Fe6	Si1	Si13	Si15
10	13	39	34.1	97.5	97.7	97.8	99.2	77	99.2	85	96.8
10	-	-	-	-	-	-	-	69	-	86	-
25	-	13	-	-	-	-	-	54	-	86	-
25	-	-	-	-	-	-	-	45	-	85	-
50	4.7	13	25	26.4	17.9	22.5	23.8	32	80.9	85	89.5
50	-	-	-	-	-	-	-	33	-	86	-

improve the reproducibility of NP data. Until such a test is refined, individuals who generate and interpret ABA data need to be much more aware of the influence of the fizz test values on the NP determinations. Where fizz test results and NP values seem to be at odds, further testing would be prudent.

When a carbonate rating system other than the familiar four-tiered fizz test is used, data interpretation will have to be adjusted and interpretive rationales will have to be "recalibrated."

Neutralization Potential (NP)

The first step of the NP test is to conduct a qualitative fizz test on a small amount of the prepared sample as described earlier in this chapter. Based on the fizz test results, an appropriate volume and normality of HCl is selected then added to 2.0 grams of the prepared sample. (See Table 6.3.) Reagent water is added to bring the total volume to 100 ml (Noll et al., 1988). (Note that there are variations between the methods described in Noll et al. (1988) and in Sobek et al. (1978). This discussion is based on the methods described by Noll et al.) The solution is boiled for approximately 5 minutes, which is intended to dissolve potential neutralizers in the sample. After the solution is cooled, it is titrated with NaOH to a pH of 7.0; the end point is to be held for 30 seconds. The NP in terms of tons per thousand tons of rock (ppt) is then calculated from that amount of acid that was neutralized by the sample.

Carbonate minerals, such as calcite and dolomite, are known to be the major contributors to groundwater alkalinity in the coal regions of Pennsylvania. The acid-digestion step of the NP test is suspected of dissolving various silicate minerals, which results in an NP determination that overstates the amount of carbonate minerals in a sample. Lapakko (1993), working with rock samples from metals ore in Minnesota, reported that silicate minerals such as plagioclase dissolve and neutralize acid at relatively low pH values such as those which occur in acid mine drainage or during a NP titration; however, he also noted that since this dissolution will only take place at low pH values, it is unlikely to help maintain a drainage pH of acceptable quality. His test results, based on leaching studies, also indicated that the rate of acid neutralization by silicate minerals was not adequate to maintain a drainage pH of 6.0 or above.

Siderite ($FeCO_3$) has long been suspected of interfering with the accuracy of NP determinations and of complicating the interpretation of the data (Meek, 1981; Morrison et al., 1990; Wiram, 1992; Leavitt et al., 1995). Siderite is common in Pennsylvania coal overburdens. Samples with significant amounts of siderite can make it difficult to hold the final end point

Table 6.3 Volume and Normality of HCl used to do NP digestion based on the sample fizz rating. (After Sobek and others (1978) and Noll and others (1988).)

FIZZ RATING	HCl VOLUME	HCl NORMALITY
None (0)	20 ml	0.1N
Slight (1)	40 ml	0.1N
Moderate (2)	40 ml	0.5N
Strong (3)	80 ml	0.5N

of the titration with NaOH (Noll et al., 1988). If iron in solution from the siderite is not completely oxidized when the titration is terminated, then the calculated NP value will be overstated, since complete oxidation of the iron would produce additional acidity. An uncertain titration end point can obviously affect the reproducibility of the NP results. Skousen et al. (1997) also found that laboratories tended to assign different fizz ratings to replicates of samples with high siderite content. As noted in the earlier section of this chapter which dealt with fizz ratings, assigning different fizz ratings to the same sample can change the acid volume and strength used in the NP digestion step, which will affect the NP results.

Meek (1981) and Morrison et al., (1990) proposed adding a hydrogen peroxide step to the NP determination procedures to eliminate the problems with the method caused by siderite. Morrison and Scheetz (1994) performed ABA tests on four samples using both the method described in Noll et al. (1988) and their modified approach. Under the modified method, after the sample was digested in acid, it was filtered into a vacuum flask. The filtering was done to ensure that the H_2O_2 did not oxidize pyrite or other solids in the undigested portion of the sample. The solution was then transferred to a 400 ml Pyrex beaker, and the vacuum flask was rinsed with 125 ml of deionized water. Five to 7.5 ml of 30 wt % H_2O_2 was added to the solution which was then boiled for three to five minutes. After cooling, the solution was then titrated to pH 7.0 with NaOH. The NP for each sample was lower when the modified method was used, and was significantly lower for the three samples known to contain a significant amount of siderite.

Evans and Skousen (1995) found that NP values were not appreciably different when samples were analyzed both with and without the hydrogen peroxide step; however they found that reproducibility between laboratories did improve when the hydrogen peroxide step was used. They also found that when the hydrogen peroxide step was performed without filtering the solution, the results sometimes did not compare well with other ABA methods, probably due to the oxidation of pyrite in the residue by H_2O_2. In fact, oxidation of pyrite with H_2O_2 has been used as a method of predicting the acid-producing potential of overburden (O'Shay, et al., 1990). Morrison and Scheetz (1994) used samples known to include a significant amount of siderite (determined by X-ray diffraction) in their comparative study, which may be why their results showed that the hydrogen peroxide step reduced NP.

Skousen et al. (1997) subjected 31 overburden samples of known mineralogy (determined by X-ray diffraction) to four variations of the NP test. The variations were defined by the authors of that paper as: 1) **(Sobek)**, the standard Sobek method (Sobek et al., 1978); 2) **(Boil)**, a method that includes boiling of the sample for five minutes during the digestion step (Noll et al., 1988); 3) **(H_2O_2)**, the same as the boil method except that after digestion the sample is filtered and treated with H_2O_2 before titration; 4) **(SobPer)**, the same as the Sobek method except that H_2O_2 is added to the sample (no filtration) after the first titration. Among their findings the authors concluded:

- The four variations on the NP test produced similar results for samples containing little pyrite or siderite.
- The SobPer method gave lower NP values than the other methods for samples which included significant amounts of pyrite, due to oxidation of the pyrite by H_2O_2 in the unfiltered samples.
- Compared to the other three methods, the H_2O_2 method provided: The lowest NP values for samples with significant siderite content; the best reproducibility between the laboratories which participated in the study; results which were the most consistent with soxhlet leachate results.
- Autotitration at a slow setting is preferable to hand titration, especially for samples with significant siderite content.

Skousen et al. (1997) briefly describe a method to perform NP determinations with the H_2O_2 step. If the hydrogen peroxide step performs according to its intent, it should generally decrease the NP's of strata with a significant siderite content, but should not appreciably affect the NP values of strata that do not include significant amounts of siderite. It should also lead to better reproducibility of NP data between laboratories, especially for samples with significant siderite content.

Other Methods of Determining Carbonate Content

The NP test has been adapted and widely used to approximate the carbonate content of mine overburdens largely because it is relatively quick, inexpensive, and easy to perform. However, as noted in this chapter, it may not always provide results which are accu-

rate and reproducible. Other methods of determining carbonate content have occasionally been used in Pennsylvania on high risk-sites or on sites where the NP test provided questionable results.

Morrison et al. (1990) suggested CO_2 coulometry as an alternative method for determining carbonate content of overburden samples and reported promising results, however, the method has not been widely adopted for characterizing overburden samples to date.

X-ray diffraction, which can give detailed information on the overburden mineralogy, has been used on a few sites in Pennsylvania. In cases where X-ray diffraction has been used and where fizz test ratings and NP results seemed in conflict and suggested the presence of siderite (results which showed significant NP values for samples which did not fizz), the X-ray diffraction results verified the presence of the siderite.

In situations where NP data provide ambiguous results and/or where mining presents a risk to significant uses of nearby groundwater or surface water sources, tools such as X-ray diffraction and CO_2 coulometry are available and should be considered to verify the NP results.

Conclusions

Three aspects of ABA overburden analysis laboratory techniques create problems with reproducibility and accuracy of data.

Difficulties in performing forms of sulfur determinations can lead to unreliable results if pyritic sulfur determinations are used to calculate MPA instead of total sulfur determinations. Since pyritic sulfur is typically the largest component of total sulfur in coal overburdens, and since total sulfur determinations can be done more reliably, MPA calculations should be based on total sulfur and not pyritic sulfur.

The importance of the qualitative fizz rating in ABA has often been overlooked. The fizz rating can significantly affect the outcome of NP determinations. Since the fizz rating is a qualitative test, reproducible results can be elusive, and where multiple labs performed fizz tests on replicates of samples reproducibility was poor (Evans and Skousen, 1995; Skousen et al., 1997). The fizz rating determines the normality and volume of acid which is used to digest the sample; when the normality and volume of acid changes, so does the NP result. Reducing the subjectivity of the fizz test by reducing the number of choices in the rating system from 4 to 2 as suggested by Evans and Skousen (1995) could result in more consistent NP determinations. However, when the number of fizz rating possibilities are reduced, some samples are digested in a larger volume of acid than they would under the traditional way of performing the tests, resulting in higher NP determinations. The interpretive rationale applied to ABA data will have to be "recalibrated" if a carbonate rating system other than the traditionally used four-tiered system is ultimately adopted

The quantitative method of rating carbonate content of overburden samples by determining the percent insoluble residue, as described by Skousen et al. (1997), requires additional testing to determine if it could be used as a more objective option than the fizz test for rating carbonate content. The percent HCl used to digest the samples may significantly affect the percent insoluble residue for siderite-rich samples.

Siderite, a common mineral in Pennsylvania coal overburdens, can interfere with NP determinations, generally resulting in values that are high relative to the amount of calcium carbonate in the sample. Adding a hydrogen peroxide step (such as described by Skousen et al., (1997)) to the NP determinations reduces the interference of siderite and does not appreciably affect NP determinations for samples without significant amounts of siderite. NP determinations run with the hydrogen peroxide step provide better reproducibility between laboratories and produce results which better represent the true carbonate content of the rock.

Literature Cited

Brady, K.B.C., and M. W. Smith, 1990. Pyritic sulfur analyses for coal overburden: Differences between laboratories. In: Proceedings 1990 National Symposium on Mining, University of Kentucky, Lexington, Kentucky, pp. 53-58.

Cravotta, C. A. III, K. B. C. Brady, and R.L. Beam, 1990. Effectiveness of the addition of alkaline materials at surface mines in preventing or abating acid mine drainage: Part 1. Theoretical considerations. In: Proceedings: 1990 Mining and Reclamation Conference and Exhibition, Charleston, WV, pp. 221-225.

Evans, P. and J. Skousen, 1995. Effect of digestion method on neutralization potential of overburden samples containing siderite. In Proceedings: 1995 National Meeting of the American Society for Surface Mining and Reclamation, Gillette, Wyoming, pp. 696-707.

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. In: Research and Applied Technology Symposium on Mined-Land Reclamation, Pittsburgh, PA, pp. 134-151.

Hedin, R.S. and P. M. Erickson, 1988. Relationships between the initial geochemistry and leachate chemistry of weathering of overburden samples. In: Proceedings Mine Drainage and Surface Mine Reclamation, Vol. 1 Mine Water and Mine Waste. 19-21 April, 1988, Pittsburgh, PA, U.S. Bureau of Mines Information Circular 9183, pp. 21-28.

Lapakko, Kim, 1993. Evaluation of tests for predicting mine waste drainage pH. Report to the western governors' association, 76 p.

Leavitt, B., J. Skousen, and P. Ziemkiewicz, 1995. Effects of siderite on the neutralization potential in the acid-base account. In: Proceedings, 17th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Meek, F. A., 1981. Development of a procedure to accurately account for the presence of siderite during mining overburden analysis. In: Proceedings, 2nd Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Morrison, J.L., S.D. Atkinson, and B.E. Scheetz, 1990. The use of CO_2 coulometry in differentiating and quantifying the carbonate phases in the coal-bearing strata of western Pennsylvania: Its applicability in interpreting and modifying neutralization potential (NP) measurements. In: Skousen, J., J. Sencindiver, and D. Samuel, eds, Proceedings of the 1990 mining and reclamation conference and exhibition, Charleston, West Virginia, pp. 243-248.

Morrison, J.L., B.E. Scheetz, 1994. Overburden characterization: An examination of the neutralization potential determination and identifying potential sources of manganese. Final Report: July 1, 1987-April 12, 1994, PFDAFR-486-043, 68 p.

Noll, D.A., T.W. Bergstresser, and J. Woodcock, 1988. Overburden sampling and testing manual. Contract No. ME 86120, Pennsylvania Department of Environmental Resources, 78 p.

O'Shay, Tracey, L. R. Hossner, and J. B. Dixon, 1990. A modified hydrogen peroxide oxidation method for determination of potential acidity in pyritic overburden. Journal of Environmental Quality, v.19, p778-782.

Skousen, J., J. Renton, H. Brown, P. Evans, B. Leavitt, K. Brady, L. Cohen, and P. Ziemkiewicz, 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, v. 26, p. 673-681.

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

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. EPA-600/1-76-184.

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

Stanton, R.W., and J.J. Renton, 1981. Organic and pyritic sulfur in coal: Potential errors in determinations. West Virginia Geological and Economic Survey, Circular number C-22.

West Virginia University, 1971. Mine spoil potentials for water quality and controlled erosion. USEPA, OWP, Project No. 1410, EJE.

Wiram, V. P., 1992. "Siderite masking" a factor to consider in overburden acid-base balancing. In Proceedings: 13th annual West Virginia surface mine drainage task force symposium, Morgantown, WV.