EFFECT OF DIGESTION METHOD, SIDERITE CONTENT, AND FIZZ RATING ON NEUTRALIZATION POTENTIAL OF OVERBURDEN SAMPLES

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Abstract

When siderite ($FeCO_3$) is present in the overburden, the method used to determine neutralization potential (NP) in the Acid-Base Accounting (ABA) procedure may have a significant influence on the result. Siderite initially yields alkalinity upon digestion. With time, however, the alkalinity is neutralized by the acidity released as ferrous iron (Fe^{+2}) oxidizes to ferric iron (Fe^{+3}) and ferric hydroxide precipitates. Thirty-one overburden samples containing varying amounts of siderite, calcite, pyrite, and guartz were analyzed by four NP digestion methods and were titrated either by hand or by auto-titration. The methods were: 1) standard Sobek et al. method (Sobek); 2) a method developed by the Pennsylvania Department of Environment Protection (PADEP) that boils the sample for 5 minutes (PDEP); 3) a method similar to PDEP but it includes filtering and treating the sample with H_2O_2 before back-titrating developed by a Pennsylvania and West Virginia task force (PAWV); and 4) a modified Sobek method that adds H_2O_2 after the first hand titration (SobPer). For samples containing primarily calcite, guartz, or clays, the NP values for a particular sample were similar among digestion methods. For samples containing pyrite, the SobPer method (no filtering) and H₂O₂ addition produced the lowest NP values. Siderite-containing samples showed wide variation in NP values among methods. Increased boiling time alone (PDEP method) had little effect on NP values compared to the Sobek method. Filtering the samples and adding H₂O₂ before back-titration (PAWV method) decreased NP values of siderite samples compared to Sobek. Lower NP values were generally obtained with auto-titration vs hand titration because auto-titration can be set to add the base slowly, which allows for concurrent oxidation and hydrolysis of iron. Hand-titration of siderite samples especially requires H_2O_2 treatment to accelerate iron oxidation, and may require more H_2O_2 and retitration to reach a stable endpoint. The NP values from three laboratories analyzing the same samples by the Sobek hand titration method showed large variations. When the samples were filtered and 5 ml of 30% H₂O₂ were added before titration (PAWV hand titration method), the variation in NP values among the laboratories decreased by half (ave. difference of 54 to 25 tons/1000 tons). Variation in NP values were also found when the samples were assigned different fizz ratings by laboratory technicians, thereby changing the concentration of acid added in the digestion procedure. At higher fizz ratings (more acid added), the NP values increased, especially for siderite samples. A quantitative carbonate rating is proposed, which uses acid digestion and drying to determine the percent insoluble residue, which is then used to establish the acid strength and volume to add for NP digestion. ABA values of 13 samples calculated from % S and NP from different digestion methods gave the same sign (either positive or negative values) in 10 of 13 samples. In comparing ABA values with leachate pH and cumulative alkalinity from soxhlet extractors, the PAWV method with either hand or auto-titration accurately predicted acidic or alkaline leachate in 13 out of 13 samples. Based on these results, it is recommended that laboratories conducting NP for Acid-Base Accounting use the proposed carbonate rating and PAWV method. The use of auto-titration is recommended. If hand-titration is used, the solution after the first hand-titration may require additional H_2O_2 and re-titration.

Introduction

Acid-Base Accounting (ABA) is an overburden analytical method which calculates the total amount of acidity and the total amount of alkalinity that may be produced upon weathering of an overburden sample (Sobek et al., 1978). Maximum potential acidity (MPA) is calculated from the total sulfur (S) content as determined by S combustion and subsequent gas analysis. Stoichiometrically, a material containing 1% S will require 3 1.25 tons of calcium carbonate to neutralize the acid produced by 1000 tons of the material. The neutralization potential (NP) is determined by reacting a 2-g sample of rock with a known quantity and strength of hydrochloric acid. The solution is then back-titrated with a base (NaOH) of known strength to pH 7.0 to determine neutralizing content of the sample. Both NP and MPA are determined in tons of CaCO₃ equivalent per 1000 tons of overburden.

Using ABA, the quality of drainage from the weathering and leaching of a particular rock sample is predicted by subtracting MPA from NP. If the MPA value is higher for the sample (a deficiency of NP), the rock sample 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 single rock units (Skousen et al., 1987). However, assessing the quality of drainage from a reclaimed mined site where the MPA, NP, and volume of each rock unit in the overburden must be taken into account is much more difficult. Nevertheless, acid-base accounting is the most common basis for predicting post-mining water quality (Perry, 1985).

Lapakko (1994) suggested that the NP of certain rock units is overestimated, especially when siderite (FeCO₃) is present. Siderite, along with calcite and dolomite, is a common carbonate mineral in the overburden associated with Appalachian coal beds (Geidel et al., 1986). When present in an overburden sample, siderite reacts quickly with acid and contributes to the alkaline-producing potential of the rock (Morrison et al., 1990; Cargeid, 198 1; Meek, 1981; Wiram, 1992). Continued weathering of siderite, however, will produce a neutral (Shelton et al., 1984; Meek, 198 1) to slightly acid solution as indicated in the following reaction (Frisbee and Hossner, 1989; Cravotta, 1991; Doolittle et al., 1992):

$$FeCO_3 + 0.25 O_2 + 2.5 H_2O - Fe(OH)_3 + H_2CO_3^*$$
 (1)

where $H_2CO_3^* = H_2O + CO_2$ (aq). Equation 1 is an overall reaction that represents field conditions. However, in the laboratory determination of NP, many reaction steps during the titration can affect the pH. The first step in the reaction of siderite with hydrochloric acid (HCl) is:

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FeCO_3 + HCl - + Fe^{+2} + Cl^{-} + HCO_3^{-} (2)
FeCO_3 + HCl - + Fe^{+2} + Cl^{-} + HCO_3^{-} (2)
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Because excess HCl is added to the rock sample, bicarbonate (HCO_3^-) shown as a reaction product in reaction 2 is quickly consumed:

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HCl + HCO_3^- \dots > H_2O + CO_2(g) + Cl^- (3)
HCl + HCO_3^- \dots > H_3O + CO_2(g) + Cl^- (3)
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Because the solution is acidic, the CO_2 is exsolved as a gas. The ferrous iron (Fe⁺²) produced by reaction 2 also is unstable and will slowly oxidize to ferric iron (Fe³⁺) and consume additional HCl:

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Fe^{+2} + 0.25 O_2 + HCl - Fe^{+3} + Cl^{-} + 0.5 H_2O (4)
Fe^{+2} + 0.25 O_2 + HCl - Fe^{+3} + Cl^{-} + 0.5 H_2O (4)
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The ferric iron (Fe^{+3}) produced will consume base ions upon titration with sodium hydroxide (NaOH) and precipitate as a solid:

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Fe^{+3} + 3 NaOH ----- > Fe(OH)_3 + 3 Na^+. (5)
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 $Fe^{*3} + 3 NaOH ----> Fe(OH)_3 + 3 Na^*$. (5)

The overall combination of reactions 2-5 are essentially reaction I with the addition of sodium (Na^+) and chloride (Cl^-) :

 $FeCO_3 + 0.5 O_2 + 3 HCl + 3 NaOH ----- > Fe(OH)_3 + 3 Na^+ + 3Cl^- + 1.5 H_2O + CO_2 (g)$ (6)

 $FeCO_3 + 0.5 O_2 + 3 HCI + 3 NaOH ----> Fe(OH)_3 + 3 Na^* + 3CI^* + 1.5 H_2O + CO_2(g)$ (6)

Reaction 6, which represents the major reactants and products for the NP titration, shows that 3 moles of acidity (HCl) and 3 moles of base (NaOH) are consumed, and that CO_2 is exsolved. As a result, the overall reaction yields a zero NP for siderite (no net acidity or alkalinity). Because the standard NP procedure as outlined by Sobek et al. (1978) does not allow sufficient time for ferrous iron oxidation and subsequent precipitation of ferric

hydroxide, the procedure accounts for only the initial reaction, resulting in 2 moles of alkalinity (Equations 2 to 4). Therefore, erroneously high NP values can be generated with samples containing high amounts of siderite. Such an analytical oversight can lead to incorrect post-mining water quality predictions and produce costly, long-term reclamation liabilities (Wiram, 1992).

Morrison (1990), Wiram (1992), and Meek (198 1) suggest adding a small quantity of 30% hydrogen peroxide (H_2O_2) to the filtrate of an overburden sample to oxidize ferrous iron to ferric iron before back-titration is initiated. Because the resulting ferric iron is precipitated as Fe(OH)₃ upon titration, the solution yields a more accurate NP value. The addition of H_2O_2 after the initial titration results in the formation of additional Fe(OH)₃ due to enhanced oxidation at higher pH values.

Another problem encountered in the NP determination when siderite is present deals with assigning fizz values. Fizz ratings are assigned by laboratory technicians to estimate the relative amount of carbonate present in a rock sample to determine the amount and strength of HCl to use in the digestion process (Sobek et al., 1978). The NP value is dependent on the acidity of the solution in which a sample is digested. In addition to greater dissolution of siderite, high strengths and volumes of added acid may react with non-carbonate minerals such as clay minerals, resulting in an NP value that is not solely dependent on the carbonate content of the sample.

Recognizing these problems, an overburden task force was assembled to address AMD prediction in Pennsylvania and West Virginia (Leavitt et al., 1995). This group consisted of representatives of the Pennsylvania Department of Environmental Protection (PADEP), Pennsylvania State University, CONSOL, Inc. (CONSOL), and West Virginia University (WVU). For evaluation purposes, the group collected 31 overburden samples of varying mineralogies and conducted standard and modified overburden analyses independently. This paper has the following objectives: 1) measure NP values using different digestion and titration techniques, 2) evaluate the differences in NP values determined on identical samples by different laboratories, 3) assess the use of fizz ratings in NP determinations, and 4) evaluate the accuracy of NP determinations by comparing NP values to acidity generated by artificial weathering.

Materials -- and Methods

Overburden samples were collected by PADEP from 31 locations in Pennsylvania and West Virginia as part of this laboratory testing study. The samples had variable contents of calcite $(CaCO_3)$, siderite, pyrite (FeS₂), quartz (SiO₂), and clay minerals. Each sample was analyzed at WVU by x-ray diffraction (XRD) to determine mineral components and by x-ray fluorescence (XRF) to determine elemental content. To prepare the samples for x-ray analysis, a small amount of each sample was crushed to less than 200 mesh and pressed into a wafer under 15-Mg total load. The wafer was analyzed by a Philips PW 1800 XRD unit to quantify the mineral content and a Philips PW 9550 Energy Dispersive unit for quantitative elemental analysis. Sulfur analyses were also performed using a Leco SC 432 Sulfur Analyzer.

Neutralization potentials (NP) were determined on each sample by four different digestion methods: 1) the standard Sobek et al. (1978) method (Sobek), 2) a method developed by the

PADEP (PDEP) (Noll et al., 1988), 3) a method using H_2O_2 treatment after filtering developed by the Pennsylvania and West Virginia Overburden Task Force and Morrison et al. (1990) (PAWV), and 4) a modified Sobek method developed by the authors using H_2O_2 treatment (no filtering) after the first hand titration and re-titrating (SobPer). The procedures for each method are outlined in Table I and described below. The original NP method outlined in Sobek et al. (1978) used hand titration with NaOH after digestion with HCl However, because many laboratories doing overburden analyses use automatic titrators, auto-titration was compared to hand titration of samples subjected to the Sobek and PAWV methods.

Fizz-Rating

Each of the digestion methods is contingent upon performing a fizz test to determine the appropriate amount and strength of acid that must be applied to dissolve carbonates. Fizz ratings were assigned according to the Sobek et al. (1978) guidelines (Table 2) by placing about 0.5 g of sample (less than 60 mesh) on aluminum foil, adding one or two drops of 1:3 (25% or 3M) HCl, and noting the reaction.

Digestion Procedure

The **Sobek** method was performed by adding a 2-g sample of overburden to each of three separate beakers with a fourth beaker serving as a blank (no sample). The amount and strength of HCl added to all beakers was based on the fizz rating assigned by the observed response of the sample to acid as outlined in Table 2. The beakers were then slowly heated to a maximum of $90-95^{0}$ C, care being taken not to allow the suspensions to boil. Reaction was complete when no bubbles were seen rising through the suspension and the sediment settled evenly over the bottom of the beakers when reduced to 80^{0} C. Distilled water was added to bring the volume in the beakers to 100 ml. The beakers were then heated and the suspension boiled for one minute, after which the beakers were removed from the heat and allowed to cool.

In the **PDEP** procedure, 2-g samples were placed in each of three beakers with a fourth beaker having no sample serving as a control. The proper amount and strength of HCl was added to each beaker based on the fizz rating. The suspensions in all beakers were brought to 100 ml volume prior to heating. Boiling chips were added to the suspension, beakers were covered with watch glasses, and the suspensions were boiled gently for 5 minutes. The beakers were then removed from the heat and allowed to cool.

The **PAWV samples** were treated as described for the PDEP samples except that the contents of the beakers were gravity filtered using Whatman #40 (0.45, m) filter paper after cooling. The filtered solution was then treated with 5 ml of 30% H₂O₂. The solution was then boiled for an additional 5 minutes (using boiling chips and watch glasses), and allowed to cool.

The **SobPer** method was the same as the **Sobek** method to step 5 in Table 1. After hand titration to pH 7.0, 5 ml of 30% H₂O₂ was added to the suspension and gently boiled for I minute, then cooled and re-titrated to pH 7.0. If a drop in pH or a black or green color was noted in the solution after the second titration, a second H₂O₂ treatment was used to ensure complete oxidation of ferrous iron, and re-titrated a third time. The total amount of NaOH

from all titrations was used in determining NP.

Once all the samples were prepared through the described digestions (Table 1), the solutions were hand titrated by the method of Sobek et al. (1978) with standard NaOH to achieve and hold an endpoint pH of 7.0 for 30 seconds. All overburden samples prepared by the Sobek and PAWV digestion methods were also titrated using a Fisher Computer-aided Titrimeter (Model 455 Burette, Model 489 Multi-sampler, Model 465 Printer) to determine the volume of NaOH needed to achieve and hold a pH 7.0 endpoint. Titration rate could be set from 1 (slowest) to 20 (fastest) and it was placed at 14 to achieve a relatively rapid determination.

Results of NP determinations performed at WVU were evaluated by ANOVA to identify the presence of significant differences among methods for each sample at the 0.05 level of significance. When significant differences were found, means were separated for each overburden sample by the Least Significant Difference (LSD) test (SAS Institute, 1985).

Laboratory Comparison

In addition to WVU conducting NP analyses, all overburden samples were analyzed for NP by laboratories at CONSOL of Pittsburgh, Pennsylvania, and **PADEP** in Harrisburg, Pennsylvania. These laboratories conducted the Sobek and PAWV methods using hand titration. Comparisons were made among the NP values obtained from the three laboratories.

Soxhlet Extraction

In order to evaluate the potential of each method to predict leachate quality, 13 of the 31 overburden samples were subjected to an artificial weathering process consisting of cyclic oven-oxidation followed by soxhlet leaching (Renton et al., 1988). One rotation of leaching and drying constituted one soxhlet cycle. Soxhlet analysis was chosen because the elevated temperatures and intensive leaching of the sample would allow complete oxidation of ferrous iron to ferric iron, subsequently allowing hydrolysis and precipitation of ferric hydroxide. In addition, any pyrite contained in a sample would also undergo oxidation. The pH value and cumulative alkalinity of the leachate after 6 cycles were used to determine whether the overburden sample would produce acidic or alkaline drainage.

Results - and - Discussion

Sample compositions

Based on their dominant mineral and elemental content, the samples were placed into one of four groups: iron (Fe group), calcium (Ca group), sulfur (S group), and silicon (Si group) (Tables 3 and 4). The x-ray spectrometer used in this study could only determine elements with atomic numbers 12 (magnesium) and greater. Except for the two high calcite samples (Ca1 and Ca2) and the high quartz sample (Si 1), all samples had >20% clay minerals (Table 3). Mineralogy data were unavailable for S3 and S5 due to insufficient sample for XRD analysis.

A few samples could have been placed in two groups. For example, sample Fe5 could have been put in the S group since it had 4.5% S (Table 4) and 9% pyrite (Table 3), but it also contained 40% iron in siderite and clay minerals. Other borderline samples were S4 and S5

where low S (2.7 to 2.8%) and high silicon (48 to 5 1%) contents could have qualified these two samples for the Si group. The Si 17 sample showed about equal amounts of iron, aluminum, and silicon in quartz, and clay minerals. Because only 8% siderite was found in Si17 (Table 3), it was placed in the Si group.

Comparison of Replicate NP Values Among Methods

A total of six digestion/titration combinations were tested: Sobek Hand, PDER Hand, Sobek Auto, PAWV Hand, PAWV Auto, and SobPer Hand (Table 5). All sample digestions were done in triplicate. The data showed very similar replicate results for each overburden sample. For example, triplicate runs for sample Fe 1 for Sobek Auto (average of 11 in Table 5) gave 9.9, 10.9, and 11. 5 (data not shown). The NP for the same sample determined by the PAWV Auto method averaged 7 with triplicate runs of 6.9, 8.0, and 5.8. The average NP for sample Ca3 determined by the Sobek Hand method was 711 with triplicate runs of 713.2, 7 10. 1, and 709.3; while the overall average NP generated by the SobPer Hand method was also 711 with triplicate runs of 712.4, 710.5, and 709.2. These examples show the overall consistency among replicates for each digestion method on a particular sample. Standard errors are given for the mean of each sample in Table 5.

Comparison of Methods by Sample Group

The first four samples in the **Fe group** (high siderite) showed very similar NP values within each method (Table 5). The Sobek and PDEP methods (no H_2O_2) titrated by hand gave high NP values (62 to 95). The PAWV method using both hand and auto-titration gave low NP values (9 to 19) for the same samples, an average reduction of at least 5 times from those generated without the use of H_2O_2 . The SobPer Hand method gave similar results as the Sobek Auto method. Evidently, auto-titration at the rate of deliverance with the standard Sobek digestion method allowed sufficient time for the oxidation of ferrous iron and subsequent ferric iron precipitation. Therefore, H_2O_2 treatment was not needed to oxidize ferrous iron when using auto-titration with these samples.

Sample Fe5 (9% pyrite and 18% siderite, Table 3) had very different NP values with different digestion methods. One would expect that auto-titration would allow the ferrous iron in siderite to oxidize and the sulfur in pyrite to also oxidize, both resulting in lower NP values. It is not clear why this sample gave such high NP values for Sobek Auto and PAWV Auto. A sample containing 4.5% S and little calcite and siderite should have a low NP, as was shown by the other methods. The Fe6 sample (11% calcite and 20% siderite) gave high NPs for all methods. Treatment with H_2O_2 (PAWV Auto and SobPer Hand) reduced the NP values by 30%.

As expected, **the Ca group showed** consistently high NPs with all methods and without regard to the titration technique. In fact, the values were generally within 1% of each other. Samples composed predominately of calcite and containing no pyrite or siderite result in similar NP values regardless of the NP method used or the titration technique.

In the S group, methods employing hand titration without the use of H_2O_2 treatment produced higher NP values than methods using H_2O_2 and auto-titration. The latter methods caused pyrite oxidation when the sample was not filtered and subsequent generation of

acidity that lowered NP values for this group. The only exception was sample S5 which exhibited similar NP values among methods.

The **Si group** showed variable results. Most of the samples (10 out of 17) did not show large differences in NP values among methods. Samples treated by Sobek Auto, PAWV Auto, and SobPer Hand methods often gave numerically lower NP values than methods using hand titration without H_2O_2 . Seven of the 17 samples showed significant differences among methods, and usually the SobPer Hand method gave the lowest NP value of all the methods.

Assuming that samples containing siderite with no calcite or dolomite will eventually produce low to neutral NP values, the data indicate that the use of H_2O_2 before titration reduces NP values. The reduction in NP values resulting from H_2O_2 treatment is due to enhanced oxidation of ferrous iron in siderite to ferric iron, and subsequent generation of acidity through ferric hydroxide formation. Filtering the sample before H_2O_2 treatment reduces the opportunity for oxidation of pyrite and the release of acidity. The acidity resulting from pyrite oxidation is accounted for in the potential acidity test (sulfur analysis), and should not be counted in the NP test. Compared to the Sobek method, the PAWV method incorporates: 1) increased boiling time, 2) filtering the suspension to remove pyritic material from the solution, and 3) H_2O_2 treatment to oxidize ferrous iron.

The PAWV method can be used with auto-titration. When hand titration is used, a green or black color in the solution after the first titration may indicate more ferrous iron that has not been oxidized. So, adding another 5 ml of H202 after the first hand titration and re-titrating would allow for complete iron oxidation and subsequent acidity generation. When high concentrations of ferrous iron exist in solution, as in the case of high siderite samples, the hand titration procedure becomes increasingly problematic. The base must be added slowly. Hand titration of such samples to pH 7.0 may take only a few minutes and even though pH 7.0 may be held for 30 seconds, all of the ferrous iron may not have oxidized. Because all of the iron acidity is not accounted for, erroneous titration data may be recorded. The addition of H202 after the initial hand titration followed by re-titration will eliminate the possibility of such errors.

Comparison of NP Among-Laboratorie

NP Determined By Hand Titration Without Adding H_2O_2

In addition to the WVU lab, the overburden samples were sent to analytical laboratories at PADEP and CONSOL for NP determinations (Table 6). The PADEP laboratory generally reported the highest NP results across all mineral groups than the CONSOL and WVU labs. NP values for the Ca group were very similar between WVU and CONSOL labs.

Large discrepancies in NP values among labs were apparent for a number of samples. In many cases the large variation resulted from different fizz ratings being assigned by the different laboratory technicians (Table 6). Only 13 of the 31 samples were given the same fizz rating by all three labs, and these samples generally gave the least variable NP values (note difference between high and low values for these samples). For example, all labs rated the S4 sample to have a 0 fizz and the NP results were identical. Samples Si I, Si2, and SO were also given the

same fizz rating and their results are very similar. From these data, it appears that much of the discrepancy between NP values among labs could be due to the assignment of a different fizz rating. CONSOL rated the fizz of sample Fe4 as a 3 while the other two labs rated the same sample as a 1. The much higher fizz rating assigned by CONSOL resulted in more acid being added to the sample, subsequently generating a high NP value (445). Although the other samples did not show as much variation among labs as did Fe4, the difference between the low NP and high NP value for each sample among the laboratories varied from 0 to 383, an average difference of 54 (Table 6). The different NP values obtained among the laboratories using Sobek Hand could change the classification of an overburden sample as to whether it would be predicted to be an acid-producer or an alkaline-producing rock in the Acid-Base Account evaluation.

NP Determined By Adding H_2O_2 .

The variation in NP values reported by the different labs for individual samples were significantly reduced when the samples were treated with H_2O_2 before titration (Table 7). In only one case (Ca2 which had a difference of 35 1) was the difference between high and low NP values among labs greater than 52. There were no clear trends between laboratories. PADEP gave the lowest NP values among laboratories for the Fe group, the opposite of what was reported in Table 6 when no H_2O_2 was used. The large variation in NP values for sample Fe4 was greatly decreased. Still, there were differences in NP values, but the average difference was reduced in half (from 54 to 25). The decrease in variation of NP values reported by these laboratories when H_2O_2 was used (especially in the Fe group samples) demonstrates the necessity of H_2O_2 addition in order to produce consistent results among laboratories.

Fizz <u>Ratings</u>

Strength and volume of HCl added during the NP digestion procedure is determined from a fizz rating system utilizing fizz values of 0, 1, 2, and 3 (Table 2). The values are derived from a visual response when acid is added to the sample. Assigning a fizz rating is a subjective evaluation which has been shown to introduce inconsistency into the eventual NP value.

The WVU laboratory assigned fizz ratings to all samples within 5 minutes of each other in order to give them comparative values. To test whether different NP values would be generated with more acid, each sample was digested with acid corresponding to the next higher fizz rating and compared with the NP value from digestion with less acid. The NP values were higher for all the Fe group samples and variable for the other groups when using more acid as compared to less acid (Table 8). It is evident that NP results for samples containing siderite are more sensitive to the assigned fizz rating than samples that do not contain siderite. In fact, samples containing siderite showed two to three-fold differences in NP values between samples digested in different acid amounts. For example, sample Si14, a gray shale devoid of siderite, showed little variation in NP (7 to 8) when the fizz rating was increased from 1 to 2, while the NP values for sample Fe5, containing 18% siderite, increased from 64 to 234 when the fizz rating was increased from 2 to 3. Similar results were found when the CONSOL laboratory used different amounts of acid on eight of these samples (Table 9). When greater amounts of acid were used during sample digestion, the sample yielded a

An Alternative Procedure to Determine Carbonate Content of Rocks

Due to the discrepancies found in NP values resulting from different fizz ratings, an alternative procedure for determining the acid amount and strength was developed. Since the fizz rating does not seem to adequately reflect the amount of carbonate minerals in a rock, an easy, accurate, and repeatable procedure to quantify the carbonate content of a rock is desired. A procedure measuring the concentration of carbonate minerals in the sample will be inversely proportional to the concentration of acid-insoluble (non-carbonate) minerals contained within the sample. The following procedure was devised as an objective analytical process to determine the acid to be added in the NP test:

Procedure

- 1. Dry ground overburden sample (<60 mesh) in 1050 C oven, preferably overnight.
- 2. Dry and weigh a 0.45u filter and record weight.
- 3. Weigh 2.00 g of dried sample into 250-ml Erlenmeyer flask.
- 4. Add 20.0 ml of 10% (0. 1 M) HCl to flask.
- 5. Agitate flask until all CO, evolution ceases.
- 6. Mount the weighed 0.45u filter into vacuum filter assembly (gravity filtration can be used).
- 7. Quantitatively transfer suspension from Erlenmeyer flask to vacuum filter assembly.
- 8. Filter the suspension and wash the residue from the flask onto the filter paper with distilled, deionized water.
- 9. Remove the filter and place it into Petri dish; place Petri dish into 1051 C oven overnight.
- 10. Weigh the dried filter and residue.
- 11. Calculate the percent insoluble residue by dividing the weight (g) of the residue by the weight of the sample (2 g).

Comparison of Data

Percent insoluble residues were determined for most of the overburden samples used in this study for which fizz ratings had already been assigned (Table 10). Sixteen of the samples produced >95% insoluble residue and were all originally assigned either a 0 or 1 fizz rating. The samples with >95% insoluble residue should have been assigned a fizz rating of 0 (Table 11). The Ca group samples were predominantly composed of calcite having fizz ratings of 3. These Ca samples showed insoluble residues of 13 to 34% and should have been given a rating of 3. Many of the Si group samples also were judged to have a fizz of either 0 or 1 and varied between 84 to 99% insoluble residue. Based on these findings, a carbonate rating between 0 and 3 can be assigned fizz rating to the percent insoluble residue (Table 11). When comparing the original assigned fizz rating to the carbonate rating as defined by percent insoluble residue, 11 of 26 samples had a different rating (Table 10). Carbonate rating is an objective method for measuring carbonate content and it eliminates the subjectivity of assigning fizz ratings, and thereby reduces the variation in NP values due to this subjectivity.

Comparison to Leachate Quality from Soxhlets

To assess the prediction potential of NP values generated by various digestion procedures, ABA values (computed using the NP values from the various digestion methods and the %S value from Table 4) were compared to leachate pH and cumulative alkalinity after 6 cycles of soxhlet extraction (Table 12). If the ABA value gave excess NP (positive number), then the pH of the leachate should have been above 7.0 and the water would be expected to contain excess alkalinity. If the ABA value was a "Max Needed" or a deficiency of NP (negative number), then the leachate pH would be below 7.0 and the water would contain a negative alkalinity (Skousen et al., 1987). All methods accurately predicted alkaline leachate for 8 of 8 alkaline-producing samples (those with pH \geq 8.0). All methods also accurately predicted acidic leachate for samples S3 and S5.

Only three samples (Fe4, Fe5, and Si 15) gave positive and negative ABA values depending on the NP digestion method. Fe4 showed positive ABA values for Sobek Hand and PDEP Hand, and negativevalues for the others. The pH of the soxhlet leachate was 4.8 and the cumulative leachate alkalinity was -396 mg/l (acidic solution) indicating that this sample would be an acid-producer. The Sobek Auto and the H_2O_2 methods (PAWV and SobPer) all predicted this sample to be acid-producing. On the other hand, sample Fe5 gave very negative ABA results (-59 to -101) for all hand titration methods, a slightly negative value for PAWV auto-titration, but a high positive value for Sobek auto-titration. This sample containing siderite and pyrite showed a soxhlet leachate pH of 4.8 and very negative alkalinity values (-7807 mg/1). Sample Si15 showed slightly negative ABA values for all methods (-6 to -26) except for PDEP Hand. The soxhlet leachate pH was 2.3 and the water was highly acidic (- 1784 mg/1).

Based on the ABA value and the soxhlet leachate quality, PDEP Hand predicted 11 out of 13 samples. Sobek Hand and Auto methods predicted 12 of 13. PAWV Hand and Auto predicted 13 of 13 samples, while SobPer predicted 10 of 10 samples.

Summary and Conclusion

Overburden samples containing siderite gave very different NP values when using different digestion methods. Methods using auto-titration and H_2O_2 treatment (Sobek Auto, PAWV Hand, PAWV Auto, and SobPer Hand) gave lower NP values than the standard Sobek and PDEP hand titration methods. Samples containing calcite, quartz, or clay minerals gave similar NP values among methods. With samples containing pyrite, the SobPer Hand method gave the lowest NP values among methods due to pyritic material being oxidized by H_2O_2 treatment (not filtered). Compared to the Sobek method, the PAWV method incorporates: 1) increased boiling time, 2) filtered solutions for titration, and 3) H_2O_2 addition to oxidize ferrous iron. Auto-titration can be used for titrating when the machine is set to add the base slowly. If hand titration is used, adding more H_2O_2 after the first titration and re-titrating may be necessary if all the ferrous iron is to be oxidized.

The NP values determined by three different laboratories showed large variations with the Sobek Hand technique. The variations in NP were decreased substantially when the suspensions were filtered and 5 ml of $30\% \frac{H_2O_2}{D_2}$ were added to the solutions (PAWV method). Some of the variation in NP values was due to different fizz ratings being assigned to the

samples resulting in different amounts of acid being used in the digestion process. Results from separate studies by WVU and CONSOL indicated that higher fizz ratings, with subsequently greater amounts of acid being added during digestion, yielded higher NP values. An accurate fizz rating is critical for samples containing high concentrations of siderite. In such samples, an increase of I fizz rating can increase the NP four-fold. The subjectivity in assigning fizz classes can be eliminated by conducting a carbonate rating test. The test measures percent insoluble residue of the sample, which then can be used to determine the amount of acid to add for digestion.

Acid-base account values calculated from data provided by different NP digestion methods and percent S gave the same acid or alkaline prediction in 10 out of 13 samples. Only three samples (Fe4, Fe5, and Si 15) gave positive and negative ABA values due to differences in NP digestion methods. The PAWV method using either hand or auto-titration predicted the leachate quality from soxhlet reactors in 13 of 13 cases, and the SobPer Hand method predicted 10 of 10 cases.

The data indicate that laboratories conducting NP determinations for Acid-Base Accounting of overburden samples should use the PAWV method. The use of auto-titration is recommended. If hand titration is used (especially with high siderite samples), the solution after the first hand titration may require an additional H_2O_2 treatment and re-titration to ensure ferrous iron oxidation. Furthermore, it is recommended that a carbonate rating based on the percent insoluble residue replace the current subjective fizz rating.

Appendix: Modified NP Procedure

1. Principles

The NP procedure quantifies the amount of neutralizing compounds in overburden materials. It is based on a procedure for determining the calcium carbonate equivalent of limestones (Jackson, 1958). Of the many types of alkaline compounds present in overburden materials (carbonates, hydroxides and oxyhydroxides, and exchangeable cations on clays), only carbonates, specifically calcite and dolomite, are effective in supplying suitable quantities of alkalinity to control acid mine drainage. Siderite is a common carbonate in many areas, but it is not a neutralizer since it will produce both carbonate alkalinity and acidity from iron oxidation. This modified procedure is designed to eliminate siderite interference, and to provide an alternative procedure for determining the acid volume and strength to add for digestion, thereby reducing variability caused by subjective fizz ratings.

2. Summary of Procedure

The overburden sample is given a carbonate rating by quantitatively determining the percent insoluble residue. The carbonate rating dictates the amount and strength of HCl to be added to the sample for NP digestion. The modified NP digestion procedure heats the sample and acid for 5 minutes, then the suspension is cooled and filtered, then 5 ml of H_2O_2 is added and the solution is heated again. After the sample has cooled, it is back-titrated with a dilute solution of sodium hydroxide to determine the quantity of HCl that was neutralized by the sample, and (if titrating by hand) treated again with H_2O_2 and re-titrated. This value is then

used to calculate the NP of the sample and is expressed as tons/1000 tons $CaCO_3$ equivalent.

This procedure is different from those of Sobek et al. (1978) and Noll et al. (1988), but it is similar to a procedure presented by Morrison et al. (1990). This new procedure quantitatively measures carbonate content, increases the time of boiling, filters the suspension, and uses H_2O_2 to oxidize the sample (add before titration if using an auto-titrator, or add before the first hand titration and repeat if necessary). Accurate and repeatable results were obtained by this procedure on overburden samples of varying mineralogies.

3. Chemicals

- A. Distilled, deionized water (DD).
- B. Hydrochloric acid (HCl) solution, I part acid to 3 parts DD water (1:3). Dilute 250 ml of concentrated HCl (3 7% or 12. 1 M) with 750 ml of DD water.
- C. Sodium hydroxide (NaOH) solution, approximately 0.5M: Dissolve 20.0 g of NaOH pellets in DD water and fill to 1 liter. Standardize solution by placing 50 ml of certified 0.1 M HCl in a beaker and titrating with the prepared 0.5M NaOH until a pH of 7.0 is reached. Calculate the Molarity of the NaOH using equation 7:

 $M_2 = (M_1V_1) / V_2$ where: (7)

- V₁ Volume of HCl used;
- M₁ Molarity of HCl used;
- V₂ Volume of NaOH used;

M₂ Calculated Molarity of NaOH.

A. Distilled, deionized water (DD).

B. Hydrochloric acid (HCl) solution, 1 part acid to 3 parts DD water (1:3). Dilute 250 ml of concentrated HCl (37% or 12.1M) with 750 ml of DD water.

C. Sodium hydroxide (NaOH) solution, approximately 0.5M: Dissolve 20.0 g of NaOH pellets in DD water and fill to 1 liter. Standardize solution by placing 50 ml of certified 0.1M HCl in a beaker and titrating with the prepared 0.5M NaOH until a pH of 7.0 is reached. Calculate the Molarity of the NaOH using equation 7: $M_2 = (M_1V_1) / V_2$, where: (7)

V₁ = Volume of HCl used;

- M₁ = Molarity of HCl used;
- V₂ = Volume of NaOH used;
- M2 = Calculated Molarity of NaOH.

D. Sodium hydroxide (NaOH) solution, approximately 0.1M: Dilute 200 ml of 0.5M NaOH with DD water to a volume of 1 liter. Standardize solution by placing 20 ml of certified 0.1M HCl in a beaker and titrating with the prepared 0.1M NaOH until a pH of 7.0 is reached. Calculate the Molarity of the NaOH using equation 5.

E. Hydrochloric acid (HCl) solution, approximately 0.5M: certified grade, or dilute 42 ml of concentrated HCl (37% or 12.1M) with DD water and fill to a volume of 1 liter. Standardize solution by placing 20 ml of known 0.5M NaOH in a beaker and titrating with the prepared HCl until a pH of 7.0 is reached. Calculate the Molarity of the HCl solution using equation 8:

$$M_1 = (M_2V_2) / V_1$$
, where:

(7)

(8)

V₂ = Volume of NaOH used; M₂ = Normality of NaOH used;

M₂ = Normality of NaOH use V₁ = Volume of HCl used;

M₁ = Calculated Molarity of HCl.

F. Hydrochloric acid (HCl) solution (0.1M), certified grade, or dilute 200 ml 0.5M HCl solution to a volume of 1 liter with DD water. Standardize HCl solution by equation 6, and use 20 ml of the known NaOH Molarity.

G. Hydrogen Peroxide (30%).

D. Sodium hydroxide (NaOH) solution, approximately 0.1M: Dilute 200 ml of 0.5M NaOH with DD water to a volume of I liter. Standardize solution by placing 20 ml of certified 0. 1 M HCl in a beaker and titrating with the prepared 0. 1 M NaOH until a pH of 7.0 is

reached. Calculate the Molarity of the NaOH using equation 5.

- E. Hydrochloric acid (HCl) solution, approximately 0.5M: certified grade, or dilute 42 ml of concentrated HCl (37% or 12. 1 M) with DD water and fill to a volume of I liter. Standardize solution by placing 20 ml of known 0.5M NaOH in a beaker and titrating with the prepared HCl until a pH of 7.0 is reached. Calculate the Molarity of the HCl solution using equation 8:
- $M_1 = (M_2V_2) / V_1$ where: (8)
- V₂ = Volume of NaOH used;
- M₂ = Molarity of NaOH used;
- V₁ = Volume of HCl used;
- M_1 = Calculated Molarity of HCL
 - F. Hydrochloric acid (HCl) solution (0.1M), certified grade, or dilute 200 ml 0.5M HCl solution to a volume of I liter with DD water. Standardize HCl solution by equation 6, and use 20 ml of the known NaOH Molarity.
 - G. Hydrogen Peroxide (30%).

4. Materials

- A. Flasks (250-ml Erlenmeyer) or beakers.
- B. Buret, 100 in] (one for each acid strength and each base strength).
- C. Hotplate.
- D. pH meter with electrode, or automated titrator system.
- E. Balance with accuracy to 0.0 1 g.
- F. Vacuum filter assembly.
- G. Petri dishes.
- H. Air-forced drying oven, capable of 105^{0} C.
- I. Watchglasses.

5. Procedure

A. Carbonate Rating

- 1. Weigh 2.00 g of dried sample (<60 mesh) into a 250-ml Erlenmeyer flask.
- 2. Add 20.0 ml of 10% (0. IM) HCl to flask.
- 3. Agitate flask until all CO2 evolution ceases.
- 4. Mount a dried and weighed 0.45u filter into vacuum filter assembly.
- 5. Transfer suspension from Erlenmeyer flask to vacuum filter assembly.
- 6. Filter the suspension and wash the residue from the flask onto filter paper with DD water.
- 7. Remove the filter and place it into Petri dish; place Petri dish into 105⁰C oven overnight.
- 8. Weigh the dried filter and residue.

- 9. Calculate the percent insoluble residue by dividing the weight (g) of the residue by the original weight of the sample (2.0 g).
- 10. The carbonate rating is assigned based on Table 12 herein.

B. Digestion Procedure

- 1. Weigh 2.00 g of sample (<60 mesh) into a 250-ml Erlenmeyer flask or beaker.
- 2. Add the specified amount and strength of acid based on the carbonate rating.
- 3. Add DD water to make the total volume approximately 100 ml.
- 4. Cover the flask/beaker with a watchglass and boil the suspension gently for 5 minutes.
- 5. Cool and filter the suspension using Whatman #40 filter paper or equivalent. If a clear filtrate is not obtained, refilter using a finer grade filter.
- 6. Add 5 ml of 30% H₂O₂ to the filtrate.
- 7. Boil solution gently for an additional 5 minutes.
- 8. Cool and titrate the solution with 0.1M NaOH or 0.5M NaOH (strength corresponding to carbonate rating) to hold an endpoint pH of 7.0 for at least 30 seconds using an auto-titrator. If titrating by hand, titrate with appropriate NaOH solution to hold an endpoint pH of 7.0 for at least 30 seconds. If a green or black color forms during the titration, add an additional 5 ml of 30% H_2O_2 and re-titrate, and repeat if necessary.
- 9. Determine blanks (no sample) by following the same procedure. Boiling chips may be necessary to avoid loss of acid during boiling.

6. Calculations

A = (B - (C x (D / E))) x 25 x M, where: (9)

A = Tons of CaCO₃ equivalent per 1000 tons of material;

- B = ml of acid added to the sample;
- C = ml of base used to titrate the sample;
- D = ml of acid added to the blank;
- E = ml of base used to titrate the blank;
- M = Molarity of the acid.

6. Calculations

 $A = (B - (C \times (D/E))) \times 25 \times M$, where:

- A = Tons of CaCO3 equivalent per 1000 tons of material;
- B = ml of acid added to the sample;
- C = ml of base used to titrate the sample;
- D = ml of acid added to the blank;
- E = ml of base used to titrate the blank;
- M = Molarity of the acid.

(9)

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| Table 1. | Steps used | in determining | NP by | four digestion | methods'. |
|----------|------------|----------------|-------|----------------|-----------|
|----------|------------|----------------|-------|----------------|-----------|

| Steps | Sobek | PDEP | PAWV | SobPer |
|-------|--|----------------------------|--|---|
| I. | Add acid. | Add acid. | Add acid. | Add acid. |
| 2. | Heat (without boiling) until bubbling stops. | Add water to 100 ml. | Add water to 100 ml. | Heat (without) boiling) until bubbling stops. |
| 3. | Add water to 100 ml. | Boil 5 min. | Boil 5 min. | Add water to 100 ml. |
| 4. | Boil 1 min. | Cool & titrate to pH 7. | Filter. | Boil 1 min. |
| 5. | Cool & titrate to pH 7. | | Add 5 ml of 30% H ₂ O ₂ . | Cool & titrate to pH 7. |
| 6. | | | Boil 5 min. | Add 5 ml of 30% H ₂ O ₂ . |
| 7. | | | Cool & titrate to pH 7. | Boil 1 min. |
| 8. | | | | Cool & titrate to pH 7. Add more H_2O_2 and re-titrate if necessary. |

All analyses were determined on a 2-g sample of <60 mesh particle size.

| Table 2. | Description of | fizz rating and | amounts and | strengths of | HCI acid a | added to an | overburden sample bas | ed |
|-----------|-----------------|------------------|------------------|--------------|------------|-------------|-----------------------|----|
| on a fizz | rating (Sobek e | t al., 1978; Nol | l et al., 1988). | | | | | |
| | | | | | | | | |

| 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 |

| Table 3. Minerals (%) found in 31 overburden samples collected from Pennsylvania and West Virginia. Base | d |
|--|---|
| on their mineralogy and concentration of major elements (Table 4), the samples were divided into groups | |
| containing primarily iron (Fe group), calcium (Ca group), sulfur (S group), and silicon (Si group). | |
| | |

| | | | | | Clay | |
|------|----------|---------|--------|--------|----------|--|
| | Siderite | Calcite | Pyrite | Quartz | Minerals | |
| Fel | 49 | 0 | 0 | 2 | 35 | |
| 2 | 65 | 0 | 0 | 1 | 35 | |
| 3 | 65 | 0 | 1 | 1 | 34 | |
| 4 | 61 | 0 | 1 | 1 | 37 | |
| 5 | 18 | 1 | 9 | 24 | 48 | |
| 6 | 20 | 11 | 1 | 21 | 47 | |
| Cal | 0 | 90 | 1 | 1 | 6 | |
| 2 | 0 | 83 | 0 | 8 | 8 | |
| 3 | 0 | 23 | 2 | 14 | 21 | |
| S 1 | 0 | 0 | 63 | 18 | 20 | |
| 2 | 0 | 18 | 22 | 34 | 24 | |
| 31 | | | | | | |
| 4 | 0 | 0 | 13 | 26 | 61 | |
| 5' | | | | | | |
| Si 1 | 1 | 0 | 0 | 83 | 16 | |
| 2 | 1 | 0 | 1 | 76 | 23 | |
| 3 | 1 | 1 | 1 | 71 | 27 | |
| 4 | 1 | 2 | 0 | 69 | 28 | |
| 5 | 1 | 1 | 1 | 63 | 28 | |
| 6 | 1 | 0 | 0 | 52 | 47 | |
| 7 | 0 | 0 | 2 | 57 | 42 | |
| 8 | 1 | 0 | 0 | 42 | 55 | |
| 9 | 0 | 0 | 2 | 53 | 45 | |
| 10 | 1 | 0 | 0 | 50 | 48 | |
| 11 | 3 | 0 | 0 | 54 | 43 | |
| 12 | 3 | 0 | 1 | 46 | 50 | |
| 13 | 1 | 9 | 1 | 45 | 44 | |
| 14 | 1 | 0 | 1 | 42 | 56 | |
| 15 | 1 | 1 | 2 | 39 | 55 | |
| 16 | 3 | 1 | 1 | 43 | 51 | |
| 17 | 8 | 2 | 0 | 34 | 55 | |

Mineralogy data unavailable for S3 and S5.

Table 4. Elemental composition (%) of 31 overburden samples collected from Pennsylvania and West Virginia. Based on their mineralogy (Table 3) and concentrations of major elements, the samples were divided into groups of iron (Fe), calcium (Ca), sulfur (S), and silicon (Si).

| Sample | Fe | Al | Si | Ca | Mg & K | S |
|--------|----|----|----|----|--------|------|
| Fe 1 | 70 | 8 | 11 | 1 | 7 | 0.1 |
| 2 | 62 | 11 | 13 | 2 | 8 | 0.1 |
| 3 | 60 | 12 | 17 | 1 | 7 | 0.2 |
| 4 | 53 | 16 | 19 | 1 | 7 | 0.5 |
| 5 | 40 | 15 | 22 | 7 | 11 | 4.5 |
| 6 | 38 | 14 | 21 | 16 | 10 | 0.1 |
| Ca I | 1 | 6 | 8 | 68 | 16 | 0.1 |
| 2 | 1 | 8 | 18 | 58 | 15 | 0.1 |
| 3 | 1 | 11 | 32 | 29 | 27 | 0.1 |
| S 1 | 26 | 16 | 19 | 1 | 9 | 25.1 |
| 2 | 17 | 19 | 28 | 11 | 11 | 11.7 |
| 3 | 27 | 18 | 34 | 1 | 11 | 9.0 |
| 4 | 6 | 23 | 48 | 1 | 16 | 2.8 |
| 5 | 13 | 24 | 51 | 1 | 8 | 2.7 |
| Si I | 1 | 13 | 79 | 1 | 6 | 0.1 |
| 2 | 1 | 17 | 74 | 1 | 6 | 0.3 |
| 3 | 1 | 21 | 71 | 1 | 7 | 0.1 |
| 4 | 2 | 21 | 68 | 1 | 8 | 0.1 |
| 5 | 1 | 21 | 67 | 2 | 9 | 0.1 |
| 6 | 1 | 24 | 65 | 1 | 8 | 0.3 |
| 7 | 1 | 27 | 65 | 1 | 6 | 0.3 |
| 8 | 1 | 25 | 64 | 1 | 8 | 0.7 |
| 9 | 1 | 25 | 64 | 1 | 8 | 1.1 |
| 10 | 2 | 22 | 64 | 1 | 10 | 0.1 |
| 11 | 4 | 23 | 64 | 1 | 9 | 0.1 |
| 12 | 3 | 23 | 63 | 1 | 10 | 0.3 |
| 13 | 1 | 24 | 63 | 4 | 8 | 0.2 |
| 14 | 1 | 25 | 63 | 1 | 10 | 0.1 |
| 15 | 3 | 25 | 60 | 1 | 11 | 1.0 |
| 16 | 3 | 23 | 60 | 3 | 10 | 0.1 |
| 17 | 24 | 23 | 38 | 1 | 11 | 0.3 |

Table 5. Neutralization potential (NP) values (tons per 1000 tons) for four digestion methods and two titration techniques of 31 overburden samples. The samples were separated into four groups based on mineralogy and elemental composition.

| | Sobek | PDEP | Sobek | PAWV | PAWV | SobPer | Standard |
|---------|-------------------|-------|-------|--------|-------|--------|----------|
| Samples | Hand | Hand | Auto | Hand | Auto | Hand | Error |
| Fe 1 | 70 a ¹ | 89 a | 11 b | 16 b | 7 b | 14 b | 2.4 |
| 2 | 62 a | 88 a | 15 b | 19 b | 9 b | 21 b | 2.3 |
| 3 | 63 a | 87 a | 11 b | 17 b | 10 b | 15 b | 2.3 |
| 4 | 62 a | 95 a | 8 b | 15 b | 12 b | 5 b | 2.4 |
| 5 | 64 c | 82 c | 288 a | 56 c | 139 b | 25 c | 3.9 |
| 6 | 367 a | 356 a | 324 a | 322 a | 245 b | 250 b | 2.9 |
| Ca l | 926 | 936 | 926 | 924 | 928 | 926 | 0.8 |
| 2 | 835 | 843 | 834 | 847 | 841 | 840 | 0.9 |
| 3 | 711 | 724 | 710 | 728 | 708 | 711 | 1.2 |
| S 1 | -23 b | -26 b | -38 b | -74 ab | -35 b | -113 a | 2.4 |
| 2 | 78 a | 76 a | 75 a | 31 b | 75 a | -7 c | 2.2 |
| 3 | 79 a | 79 a | 17 b | 33 b | 16 b | | 2.3 |
| 4 | -1 b | -1 b | 1 b | -16 a | -1 b | -33 a | 1.5 |
| 5 | 23 | 23 | 14 | 18 | 12 | | 0.9 |
| Si 1 | 5 | 5 | 5 | 4 | 6 | 3 | 0.4 |
| 2 | 2 | 2 | 4 | 1 | 6 | -3 | 0.7 |
| 3 | 2 | 1 | 3 | 1 | 3 | -2 | 0.5 |
| 4 | 15 | 16 | 18 | 16 | 19 | 14 | 0.6 |
| 5 | 64 | 59 | 75 | 64 | 77 | 63 | 1.1 |
| 6 | -1 | -2 | 3 | -4 | 5 | -7 | 0.9 |
| 7 | -5 b | -5 b | -1 a | -6 b | 1 a | -11 b | 0.8 |
| 8 | -7 ab | -7 ab | -4 a | -9 b | -1 a | -14 b | 0.8 |
| 9 | -2 a | -11 a | -1 a | -25 b | -1 a | -25 b | 1.4 |
| 10 | 18 | 13 | 13 | 12 | | 7 | 0.7 |
| 11 | 40 b | 73 a | 13 c | 20 c | 15 c | 12 c | 2.0 |
| 12 | 23 | 19 | 11 | 15 | 14 | 8 | 0.9 |
| 13 | 113 | 109 | 114 | 112 | 131 | 110 | 1.1 |
| 14 | 7 | 7 | 13 | 9 | 15 | 6 | 0.8 |
| 15 | 23 b | 40 a | 25 b | 24 b | 25 b | 4 c | 1.4 |
| 16 | 17 b | 62 a | 11 b | 23 b | 12 b | 10 b | 1.8 |
| 17 | 88 a | 88 a | 20 b | 26 b | 19 b | | 2.4 |

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

Table 6. NP values (tons per 1000 tons) using the Sobek Hand (without using H₂O₂) from three laboratories (WVU, PADEP, and CONSOL) on 31 overburden samples. Fizz ratings were determined independently by each laboratory¹.

| | WVU | | PADEP | | CONSOL | | Difference |
|--------|------|-----|-------|-----|--------|-----|------------------------|
| Sample | Fizz | NP | Fizz | NP | Fizz | NP | High - Low |
| Fe 1 | 1 | 70 | 1 | 89 | 0 | 29 | 60*2 |
| 2 | 1 | 62 | 1 | 88 | 0 | 25 | 63* |
| 3 | 1 | 63 | 1 | 87 | 0 | 14 | 73* |
| 4 | 1 | 62 | 1 | 93 | 3 | 445 | 383* |
| 5 | 1 | 64 | 1 | 82 | 0 | 26 | 56* |
| 6 | 2 | 367 | 3 | 607 | 3 | 363 | 244* |
| Ca I | 3 | 926 | | | 3 | 936 | 10 |
| 2 | 3 | 835 | 2 | 500 | 3 | 837 | 337* |
| 3 | 3 | 711 | - | - | 3 | 724 | 13 |
| \$ 1 | 0 | -23 | 0 | -39 | 0 | -27 | 16 |
| 2 | 1 | 78 | 0 | 44 | 0 | 77 | 34* |
| 3 | 0 | 17 | 1 | 80 | 0 | 23 | 63* |
| 4 | 0 | -1 | 0 | -1 | 0 | -1 | 0 |
| 5 | 0 | 23 | 1 | 25 | 0 | 4 | 21* |
| Si 1 | 0 | 5 | 0 | 11 | 0 | 7 | 6 |
| 2 | 0 | 2 | 0 | 6 | 0 | 4 | 4 |
| 3 | 0 | 2 | 0 | 5 | 0 | 3 | 3 |
| 4 | 0 | 15 | 1 | 32 | 0 | 17 | 15* |
| 5 | 2 | 64 | 1 | 61 | 0 | 54 | 10* |
| 6 | 0 | -1 | 0 | 5 | 0 | 0 | 6 |
| 7 | 0 | -5 | 0 | 1 | 0 | -3 | 6 |
| 8 | 0 | -7 | 0 | 1 | 0 | -5 | 8 |
| 9 | 0 | -2 | 0 | 1 | 0 | -4 | 5 |
| 10 | 0 | 18 | 0 | 14 | 0 | 20 | 6 |
| 11 | 1 | 40 | 1 | 73 | 0 | 22 | 51* |
| 12 | 0 | 23 | 0 | 36 | 0 | 15 | 21 |
| 13 | 2 | 113 | 3 | 155 | 0 | 122 | 42* |
| 14 | 0 | 7 | 0 | 12 | 0 | 7 | 5 |
| 15 | 1 | 23 | 1 | 40 | 0 | 6 | 34* |
| 16 | 0 | 17 | 1 | 62 | 1 | 27 | 45* |
| 17 | 1 | 88 | 1 | 95 | 1 | 50 | 45 |
| | | | | | | | mean difference = 54.4 |

¹All the labs digested samples according to fizz ratings and corresponding strengths and volumes of HCl (Table 2). ²Indicates that the laboratories assigned a different fizz rating to this sample.

| | WVU | | PADEP | | CO | SOL | Difference |
|--------|------|-----|-------|-----|------|-----|-----------------------|
| Sample | Fizz | NP | Fizz | NP | Fizz | NP | High - Low |
| Fe I | 1 | 16 | 1 | 14 | 0 | 20 | 6*2 |
| 2 | 1 | 19 | 1 | 21 | 0 | 28 | 9* |
| 3 | 1 | 17 | 1 | 16 | 0 | 25 | 9* |
| 4 | 1 | 15 | 1 | 12 | 3 | 43 | 31* |
| 5 | 1 | 56 | 1 | 25 | 0 | 77 | 52 * |
| 6 | 2 | 322 | 3 | 301 | 3 | 277 | 45* |
| Cal | 3 | 926 | 3 | 926 | 3 | 924 | 2 |
| 2 | 3 | 847 | 2 | 500 | 3 | 851 | 351* |
| 3 | 3 | 728 | - 3 | 711 | 3 | 728 | 17 |
| \$ 1 | 0 | -74 | 0 | -58 | 0 | -24 | 50 |
| 2 | 1 | 31 | 0 | 41 | 0 | 71 | 30* |
| 3 | 0 | 33 | | | 0 | 37 | 4 |
| 4 | 0 | -16 | 0 | -1 | 0 | -3 | 15 |
| 5 | 0 | 18 | | | 0 | 18 | 0 |
| Si 1 | 0 | 4 | 0 | 6 | 0 | 9 | 5 |
| 2 | 0 | 1 | 0 | 5 | 0 | 3 | 4 |
| 3 | 0 | 1 | 0 | 4 | 0 | 2 | 3 |
| 4 | 0 | 16 | 1 | 23 | 0 | 20 | 7* |
| 5 | 2 | 64 | 1 | 58 | 0 | 54 | 10* |
| 6 | 0 | -4 | 0 | 4 | 0 | 6 | 10 |
| 7 | 0 | -6 | 0 | 1 | 0 | 3 | 9 |
| 8 | 0 | -9 | 0 | 1 | 0 | 0 | 10 |
| 9 | 0 | -25 | 0 | 0 | 0 | -2 | 25 |
| 10 | 0 | 12 | 0 | 15 | 0 | 16 | 4 |
| 11 | 1 | 20 | 1 | 11 | 0 | 12 | 9* |
| 12 | 0 | 15 | 0 | 14 | 0 | 18 | 4 |
| 13 | 2 | 112 | 3 | 171 | 0 | 149 | 37* |
| 14 | 0 | 9 | 0 | 13 | 0 | 11 | 4 |
| 15 | 1 | 24 | 1 | 24 | 0 | 21 | 3* |
| 16 | 0 | 23 | 1 | 8 | 1 | 18 | 15* |
| 17 | 1 | 26 | 1 | 11 | 1 | 27 | 15 |
| | | | | | | | mean difference = 25. |

Table 7. NP values (tons per 1000 tons) using PAWV Hand (using H₂O₂) from three laboratories (WVU, PADEP, and CONSOL) on 31 overburden samples¹. Fizz ratings were determined independently by each laboratory.

¹All the labs digested samples according to fizz ratings and corresponding strengths and volumes of HCl (Table 2). All labs filtered the samples and added 5 ml of 30% H₂O₂ to the filtrates prior to titration and titrated to pH 7.0.

² Indicates that the laboratories assigned a different fizz rating to this sample.

| | | Sobek | | Sobek | |
|--------|-------------|-------|-------------|-------|--|
| Sample | Acid Added | Hand | Acid Added | Hand | |
| Fe 1 | 40 ml 0.1 M | 70 | 40 ml 0.5 M | 192 | |
| 2 | 40 ml 0.1 M | 62 | 40 ml 0.5 M | 155 | |
| 3 | 40 ml 0.1 M | 63 | 40 ml 0.5 M | 166 | |
| 4 | 40 ml 0.1 M | 62 | 40 ml 0.5 M | 192 | |
| 5 | 40 ml 0.1 M | 64 | 40 ml 0.5 M | 234 | |
| 6 | 40 ml 0.5 M | 367 | 80 ml 0.5 M | 440 | |
| Ca 1 | 80 ml 0.5 M | 926 | 60 ml 1.0 M | 919 | |
| 2 | 80 ml 0.5 M | 835 | 60 ml 1.0 M | 842 | |
| 3 | 80 ml 0.5 M | 711 | 60 ml 1.0 M | 710 | |
| \$ 1 | 20 ml 0.1 M | -23 | 40 ml 0.1 M | -27 | |
| 2 | 40 ml 0.1 M | 78 | 40 ml 0.5 M | 86 | |
| 3 | 20 ml 0.1 M | 17 | 40 ml 0.1 M | 32 | |
| 4 | 20 ml 0.1 M | -1 | 40 ml 0.1 M | -2 | |
| 5 | 20 ml 0.1 M | 14 | 40 ml 0.1 M | 15 | |
| Si 1 | 20 ml 0.1 M | 5 | 40 ml 0.1 M | 2 | |
| 2 | 20 ml 0.1 M | 2 | 40 ml 0.1 M | 1 | |
| 3 | 20 ml 0.1 M | 2 | 40 ml 0.1 M | -1 | |
| 4 | 20 ml 0.1 M | 15 | 40 ml 0.1 M | 15 | |
| 5 | 40 ml 0.5 M | 64 | 80 ml 0.5 M | 74 | |
| 6 | 20 ml 0.1 M | -1 | 40 ml 0.1 M | -3 | |
| 7 | 20 ml 0.1 M | -5 | 40 ml 0.1 M | -4 | |
| 8 | 20 ml 0.1 M | -7 | 40 ml 0.1 M | -9 | |
| 9 | 20 ml 0.1 M | -2 | 40 ml 0.1 M | -4 | |
| 10 | 20 ml 0.1 M | 18 | 40 ml 0.1 M | 16 | |
| 11 | 40 ml 0.1 M | 40 | 40 ml 0.5 M | 28 | |
| 12 | 20 ml 0.1 M | 23 | 40 ml 0.1 M | 25 | |
| 13 | 40 ml 0.5 M | 113 | 80 ml 0.5 M | 124 | |
| 14 | 20 ml 0.1 M | 7 | 40 ml 0.1 M | 8 | |
| 15 | 40 ml 0.1 M | 23 | 40 ml 0.5 M | 25 | |
| 16 | 20 ml 0.1 M | 17 | 40 ml 0.1 M | 37 | |
| 17' | | | | | |

Table 8. NP values (tons per 1000 tons) of 31 overburden samples when samples were digested in acid according to standard fizz ratings compared to increasing the fizz rating and adding a corresponding higher acid amount.

'Insufficient sample available.

Table 9. NP values (tons per 1000 tons) of 8 overburden samples when samples were digested in different amounts of acid by the CONSOL lab.

| | | Acid Volume | and Strength | |
|----|--------|-------------------|-------------------|--|
| - | Sample | 20 ml of 0.1M HCl | 80 ml of 0.1M HCI | |
| _ | | tons per 1 | 000 tons | |
| Fe | 1 | 29 | 97 | |
| | 2 | 25 | 93 | |
| | 3 | 14 | 85 | |
| | 5 | 26 | 136 | |
| s | 3 | 23 | 51 | |
| | 5 | 4 | 7 | |
| Si | 11 | 22 | 58 | |
| | 15 | 6 | 20 | |

| | Percent | Calcium | 10.15 IV 10 | Original | | |
|--------|-----------|-----------|-------------|-------------|-----------|--|
| Sample | Insoluble | Carbonate | Carbonate | Fizz Rating | Different | |
| | Residue | Content | Rating | By WVU Lab | Rating | |
| Fe 1 | 97.5 | 2.5 | 0 | 1 | | |
| 2 | 97.7 | 2.3 | 0 | 1 | • | |
| 3 | 97.8 | 2.2 | 0 | i | | |
| 4 | 99.2 | 0.8 | 0 | 1 | | |
| 51 | | | | | | |
| 6 | 75.3 | 24.7 | 2 | 2 | | |
| Ca I | 13.0 | 87.0 | 3 | 3 | | |
| 2 | 13.3 | 86.7 | 3 | 3 | | |
| 3. | 34.1 | 65.9 | 3 | 3 | | |
| 5 1 | 92.9 | 7.1 | 1 | 0 | • | |
| 2 | 87.7 | 12.3 | 2 | 1 | | |
| 31 | | | | | | |
| 4 | 97.9 | 2.1 | 0 | 0 | | |
| 51 | | | | | | |
| Si I | 98.2 | 1.8 | 0 | 0 | | |
| 2 | 98.3 | 1.7 | 0 | 0 | | |
| 3 | 97.3 | 2.7 | 0 | 0 | | |
| 4 | 95.9 | 4.1 | 0 | 0 | | |
| 5 | 93.0 | 7.0 | 1 | 2 | | |
| 6 | 96.2 | 3.8 | 0 | 0 | | |
| 7 | 96.9 | 3.1 | 0 | 0 | | |
| 8 | 94.1 | 5.9 | 1 | 0 | | |
| 9 | 95.4 | 4.6 | 0 | 0 | | |
| 10 | 93.7 | 6.3 | 1 | 0 | • | |
| 11 | 99.2 | 0.8 | 0 | 1 | • | |
| 12 | 95.0 | 5.0 | 0 | 0 | | |
| 13 | 84.3 | 15.7 | 2 | 2 | | |
| 14 | 96.5 | 3.5 | 0 | 0 | | |
| 15 | 96.8 | 3.2 | 0 | 1 | • | |
| 161 | | | | | | |
| 17 | | | | | | |

Table 10. Percent insoluble residue and calcium carbonate content of 31 overburden samples containing various amounts of siderite, calcite, and quartz. A carbonate rating was devised based on Table 11 and compared to the original fizz rating assigned by the WVU laboratory technician.

¹Insufficient sample available to conduct analysis.

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Table 11. Carbonate rating based on percent insoluble residue or percent calcium carbonate content 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 | |
| | | | | |

Table 12. Acid-base account values (tons per 1000 tons) for 13 overburden samples compared to leachate pH and cumulative alkalinity (summed mg/l after each cycle) after 6 soxhlet cycles. Positive ABA values indicate an excess of NP suggesting the pH and alkalinity of the sample's leachate should be alkaline. If the ABA value is negative, the values represent a deficiency in NP and acidic leachate.

| | Acid-base Account Values | | | | | | | | |
|--------|--------------------------|-----------------------|-----------|------------------------|-----------|--------|---------------|------------|--|
| Sample | Sobek Hand | k PDEP Sol Hand Au | Sobek | obek PAWV auto Hand | PAWV | SobPer | Soxhlet pH | Cumulative | |
| | | | Auto | | Auto | Hand | | Alkalinity | |
| | | tons Ca | CO3 equiv | alent per 1 | 000 tons- | | | mg/l | |
| Fe I | 67 | 86 | 8 | 13 | 4 | 17 | 8.8 | 583 | |
| 2 | 59 | 87 | 12 | 16 | 6 | 18 | 8.2 | 606 | |
| 3 | 57 | 81 | 5 | 11 | 4 | 9 | 8.0 | 601 | |
| 4 | 46 | 79 ¹ | -8 | -1 | -4 | -11 | 4.8 | -396 | |
| 5 | -77 | -59 | 1471 | -85 | -2 | -116 | 4.8 | -7,807 | |
| Cal | 923 | 933 | 923 | 921 | 925 | 923 | 9.3 | 1,584 | |
| 3 | 708 | 721 | 707 | 725 | 705 | 708 | 9.5 | 2,591 | |
| S 3 | -202 | -202 | -264 | -248 | -265 | | 2.3 | -30,360 | |
| 5 | -61 | -61 | -70 | -66 | -72 | | 2.4 | -7,233 | |
| Si 11 | 37 | 70 | 10 | 17 | 12 | 9 | 9.0 | 905 | |
| 15 | -8 | 9 ¹ | -6 | -7 | -6 | -27 | 2.3 | -1,784 | |
| 16 | 14 | 59 | 8 | 20 | 9 | 7 | 8.8 | 828 | |
| 17 | 79 | 79 | 11 | 17 | 10 | | 8.4 | 519 | |

Indicate incorrect ABA predictions based on water quality for leaching test.