

EFFECT OF DIGESTION METHOD ON NEUTRALIZATION POTENTIAL OF OVERBURDEN SAMPLES CONTAINING SIDERITE¹

Phil Evans and Jeff Skousen²

Abstract: The method used to determine neutralization potential (NP) in the Acid-Base Accounting (ABA) procedure may have a significant influence on the result when siderite is present in the overburden. Siderite (FeCO_3) initially yields alkalinity upon digestion. With time as ferrous iron (Fe^{+2}) oxidizes to ferric iron (Fe^{+3}) and ferric hydroxide precipitates, acidity is released thereby yielding a neutral solution. Thirteen overburden samples containing varying amounts of siderite were analyzed by four NP digestion methods. The methods were: 1) standard Sobek et al. method (Sobek); 2) a method that initially boils the sample for 5 minutes (DER1); 3) a method similar to #2 but includes filtering and treating the sample with H_2O_2 (DER2); and 4) the same procedure as #3 except the sample is not filtered (MDER). Significant differences in NP values were found among digestion methods, but generally the differences were not consequential since the NP results did not change the classification of the overburden sample. The NP values from three laboratories analyzing the same samples showed large variations in NP when no H_2O_2 was used. But when 5 ml of 30% H_2O_2 was used during digestion, the variation in NP values among the laboratories decreased dramatically. Conflicting NP values were also found when the samples were assigned different fizz ratings by the technician thereby changing the volume of acid added in the digestion procedure. At higher fizz ratings (more acid added), the NP values increased. ABA values (using %S and NP) calculated from data provided by the four NP digestion methods were similar. In comparing our ABA values with leachate pH from Soxhlet extractors, all methods accurately predicted acidic or alkaline leachate in 12 out of 13 samples.

Additional Key Words: acid-base accounting, acid mine drainage, hydrogen peroxide, overburden analysis.

Introduction

The Acid-Base Account (ABA) is an overburden analytical method which measures the total amount of acidity and the total amount of alkalinity that may be produced upon weathering in a particular overburden sample. Maximum potential acidity (MPA) of a rock sample is calculated from the total sulfur (S) content (measured by S combustion and gas analysis). For a material containing 1% S, 31.25 tons of calcium carbonate is required for neutralization (Sobek et al., 1978). The neutralization potential (NP) is determined by reacting a 2-gram sample of the rock with a known quantity and strength of hydrochloric acid. The solution is then back titrated with a known strength of base (NaOH) to a predetermined end point to determine neutralizing content of the sample. Both NP and MPA are determined in tons per 1000 tons of overburden. Using ABA, the quality of drainage from that rock is predicted by subtracting the calcium carbonate equivalent needed to neutralize the MPA from the NP in the sample. If the number for MPA is higher for a particular rock sample (a deficiency of NP), the rock sample upon weathering and leaching is presumed to produce acidic drainage. If the number for NP is higher (an excess of NP), the rock is predicted to produce alkaline drainage. This 1:1 ratio of acid to base works well when dealing with single rock units. However, assessing the quality of drainage from a mined site is much more difficult. Evaluating the MPA and NP of each rock unit in the overburden column and judging the total volume in each rock unit across the site complicates the prediction. Nevertheless, this acid-base accounting method is the most common basis for predicting post-mining water quality (Perry, 1985).

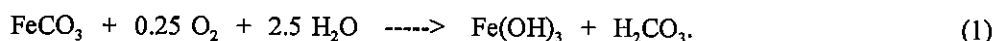
Lapakko (1994) suggested that NP determinations overestimate the amount of NP available from certain rock units especially when siderite, a ferrous carbonate, is present. Siderite forms in reducing environments of anaerobic sediments where S is deficient. In overburdens of the Appalachian coal fields, siderite is one of the most common carbonate minerals, along with calcite and dolomite (Geidel et al., 1986). It is also 14 times more soluble than pyrite (Meek, 1981) and more soluble than limestone (Geidel et al., 1986).

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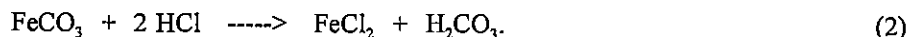
²Phil Evans, Laboratory Manager, Reic Laboratories, Beaver, WV 25813; Jeff Skousen, Associate Professor, Division of Plant and Soil Sciences, West Virginia University, Morgantown, WV 26506-6108.



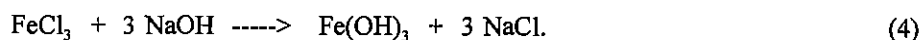
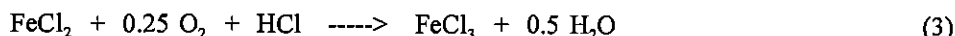
The NP laboratory procedure (Sobek et al., 1978) measures alkalinity by digestion of carbonates with HCl. When siderite is present, it reacts quickly with acid indicating that the rock is an alkaline contributor (Morrison et al., 1990; Cargeid, 1981; Meek, 1981; Wiram, 1992). However upon complete weathering, siderite is a neutral (Shelton et al., 1984; Meek, 1981) to slightly acid-producing rock (Frisbee and Hossner, 1989; Cravotta, 1991; Doolittle et al., 1992):



Because HCl is used for the digestion process in the NP determination, the acid rapidly reacts with the carbonate and neutralizes 2 moles of alkalinity:



The initial result is that siderite contributes 2 moles of alkalinity. However with time, ferrous iron (Fe^{2+}) oxidizes to ferric iron (Fe^{3+}), and ferric iron can hydrolyze, forming Fe(OH)_3 and precipitate:



The results of equations 2-4 are 3 moles of acidity (HCl) and 3 moles of alkalinity (NaOH) are consumed. This means that the acid and alkalinity effectively neutralize each other yielding a resultant NP for siderite of 0 with no net acidity or alkalinity produced. The standard NP procedure as stated in Sobek et al. (1978) does not allow sufficient time for ferrous iron oxidation and ferric hydroxide precipitation, and therefore this procedure accounts for only the initial reaction resulting in 2 moles of alkalinity (equation 2). When siderite is present in an overburden sample and insufficient time is given for complete iron oxidation and precipitation during back titration, erroneously high NP values can be generated providing inaccurate NP information. 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 (1981) suggest adding a small quantity of 30% hydrogen peroxide (H_2O_2) to the filtrate of an overburden sample prior to back titration in determining NP. Peroxide addition causes the ferrous iron to oxidize to ferric iron before back titrating. The resulting ferric iron is then precipitated as Fe(OH)_3 upon titration and the solution yields a more accurate NP value.

Another problem with siderite in the NP determination deals with assigning fizz values. Fizz ratings are done to assess the relative amount of carbonate present in a rock sample which helps in determining the amount and strength of HCl to use in the digestion process. Shelton et al. (1984) found that siderite reacts slowly with dilute acid at room temperature. Unlike the previous problem where NP is overestimated, siderite's slow reaction could result in a lower fizz rating which would result in too little acid being used in the digestion process (Morrison et al., 1990). If a weaker strength and lower amount of acid is used in the digestion process, the quantity of alkalinity in a rock may be underestimated.

Because of these problems, this study determined the NP of 13 overburden samples from Pennsylvania and West Virginia by four different methods of sample digestion. The results of different digestion methods were compared for each sample and then compared among samples that had similar elemental composition based on x-ray diffraction and x-ray fluorescence. The accuracy of the NP determinations was evaluated by comparing the ABA value (either excess or deficiency) of each overburden sample to the end pH achieved by weathering the sample in a soxhlet extractor. Soxhlet analysis was chosen because the elevated temperatures and intensive leaching of the soxhlet would allow the ferrous iron to oxidize to ferric iron, allowing hydrolysis and precipitation of ferric hydroxide and thereby generating acidity during soxhlet leaching.

To examine the effect of fizz rating on the NP determination, we used the standard Sobek et al. (1978) four-fizz rating system and a two-fizz rating system devised for this study. A two-fizz rating system reduces the number of classifications available and may eliminate variation in NP results by using fewer strengths and amounts of acid in the digestion process.

Materials and Methods

Overburden samples were collected from 13 locations in Pennsylvania and West Virginia. The samples were of variable composition from almost pure calcite (CaCO_3) to predominately siderite (FeCO_3). To identify the components contained in the samples, they were analyzed by x-ray diffraction (to determine compounds) and x-ray fluorescence (to determine elements) by the Department of Geology and Geography at West Virginia University. To perform x-ray diffraction (XRD), a small amount of each sample was crushed to less than 200 mesh and pressed into a wafer. The wafer was analyzed by a Phillips PW 1800 X-Ray Diffraction unit. The x-ray fluorescence (XRF) procedure used a Phillips PW 9550 Energy Dispersant Spectrometer to identify specific elements in the sample. Sulfur analysis was also done on each sample by a Leco SC 432 Sulfur Analyzer by the same department at WVU.

Neutralization potentials were determined by four different digestion methods: 1) Sobek et al. (1978) (Sobek), 2) Pennsylvania Department of Environmental Resources (DER) (DER1) (Noll et al., 1988), 3) Pennsylvania DER 2 (DER2) (Morrison et al., 1990), and 4) a modified Pennsylvania DER 2 (MDER) developed by the authors. The steps in each method are outlined in Table 1. Each of these methods is contingent upon performing a fizz test to determine the appropriate amount and strength of acid that must be applied to dissolve carbonates. This was done according to the Sobek et al. (1978) guidelines (Table 2). A fizz rating is done by placing about 0.5 g of sample (less than 60 mesh) on aluminum foil or a soil sample dish and adding one or two drops of 1:3 (25% or 3M) HCl. The fizz rating is determined by the following criteria:

0 None	-	No reaction;
1 Slight	-	Minimal reaction; a few bubbles per second to many fine bubbles;
2 Moderate	-	Active bubbling with only a small amount of splashing;
3 Strong	-	Very active bubbling that includes substantial splashing of the acid.

Digestion Procedures

The Sobek method was performed by adding a 2-gram sample of overburden to three separate beakers with a fourth beaker serving as a blank (no sample). The appropriate amount and strength of HCL (based on the fizz rating in Table 2) was added to all four beakers using a buret apparatus. The beakers were then placed on ring stands and gas burners were placed underneath to apply a controlled amount of heat. Thermometers were placed in the suspensions in the beakers to record the temperature. The samples were slowly heated to a maximum of 90-95°C to allow for complete reaction to occur, yet to ensure the samples did not boil. Reaction was determined to be completed when no bubbles were seen rising through the suspension and, when reduced to 80°C, the sediment settled evenly over the bottom of the beakers. Periodically, distilled water had to be added to some of the samples where evaporation of water was excessive. Once the suspensions cooled and the beakers were weighed, distilled water was added to each suspension to bring the volume in the beakers to 100 ml. The beakers were then placed over the heat once again and brought to a boil for one minute, then removed from the heat and allowed to cool.

In the DER1 procedure, 2-gram samples were placed in three beakers while no sample was put in the fourth. The proper amount and strength of HCl was added to each and then all beakers were brought to the 100 ml volume prior to heating. Boiling chips were added to the suspension, covered with a watch glass, and the suspension was then boiled gently for 5 minutes. The beakers were then removed from the heat and allowed to cool.

The DER2 samples were treated the same as the DER1 samples except that the contents of the beakers were gravity filtered using Whatman #40 filter paper after cooling. The filtered solution was then treated with 5 ml of 30% H_2O_2 added by an auto pipette. The solution was then boiled for an additional 5 minutes (using boiling chips and watch glasses). The MDER method was the same as the DER2 method except that samples were not filtered and peroxide was added to the suspension.

Once all the samples were prepared through the described digestions (Table 1), the solutions were placed on a Fisher Computer-aided Titrimeter to determine the volume of NaOH needed to achieve and hold a pH endpoint of 7. The speed of the titration could be set from 1 (slowest) to 20 (fastest) and was placed at 14 to achieve a relatively rapid determination.

Table 1. Steps used in determining NP by four digestion methods¹.

Steps	Sobek	DER1	DER2	MDER
1.	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.	Add water to 100 ml.
3.	Add water to 100 ml.	Boil 5 min.	Boil 5 min.	Boil 5 min.
4.	Boil 1 min.	Cool & titrate to pH 7.	Filter.	Add 5 ml of 30% H ₂ O ₂ .
5.	Cool & titrate to pH 7.		Add 5 ml of 30% H ₂ O ₂ .	Boil 5 min.
6.			Boil 5 min.	Cool & titrate to pH 7.
7.			Cool & titrate to pH 7.	

¹All analyses were determined on a 2-gram sample of < 60 mesh particle size.

Table 2. Amounts and strengths of HCl acid added to an overburden sample based on a fizz rating.

<u>Fizz Rating</u>	<u>Amount of Acid</u>	<u>Strength of Acid</u>
0 - None	20 ml	0.1 M
1 - Slight	40 ml	0.1 M
2 - Moderate	40 ml	0.5 M
3 - Strong	80 ml	0.5 M

Soxhlet Extraction

In order to determine which method predicted leachate quality, soxhlet extractors were used to leach the overburden samples (Renton et al., 1988). The pH value of the leachate after 6 cycles was used to determine whether the overburden sample would produce acidic or alkaline drainage. The soxhlets were conducted by thoroughly wetting a 100-gram, 60-mesh particle size overburden sample, then transferring it to a 47-mm x 123-mm porous thimble. Cotton was placed on top of the thimble prior to placing it in the reactor to prevent channeling in the sample. Distilled water was added to the reservoir so that a total of 250 ml of water would leach the sample. The sample was then leached at a temperature of 85°C for a period of 20 to 24 hours. The thimble was removed and placed in a drying oven at a

temperature of 105°C for one week to allow for re-oxidation. After drying for one week, the leaching procedure was repeated. One rotation of leaching and drying constituted one Soxhlet cycle. The leachate pH value after 6 cycles was used for comparison.

Laboratory Comparison

These same overburden samples were analyzed for NP by laboratories at Consolidation Coal Company (Consol) of Pittsburgh, Pennsylvania, and also by the Pennsylvania Department of Environmental Resources (PADER) in Harrisburg, Pennsylvania. The digestion methods were similar to those outlined herein, except their samples after digestion were hand titrated.

Results of the NP determinations done at WVU were evaluated by ANOVA to determine significant differences among methods for each sample at the 0.05 level of significance. When significant differences were found, means were separated for each sample by the Duncan's New Range multiple comparison test (SAS Institute, 1985).

Results

The sample digestions for each method done in triplicate showed very similar results for each overburden sample. For example, triplicate runs for sample 1 for Sobek (average of 20 in Table 3) gave 20.0, 19.9, and 19.2. DER2 average for sample 1 was 19 with the triplicate runs being 19.9, 19.1, and 18.9. For sample 5, Sobek average was 710 with triplicate runs of 712.3, 708.1, and 709.8; while DER1 average was 710 with triplicate runs of 708.5, 711.5, and 710.6. These examples show the general trend and consistency among replicates for each NP digestion method on a particular sample.

Comparison of NP Among Methods

Examination of the NP results provided by the different digestion methods indicated no clear trends. Our assumption was that the Sobek and DER1 methods (also termed no peroxide methods) should have given higher NP results for siderite and other high iron samples than the H₂O₂ methods (DER2 and MDER) because no Fe²⁺ oxidation and ferric hydroxide precipitation occurred. It was also assumed that there would be very little difference in NP results for samples without significant iron content. Samples with high S would also show lower NP values with the peroxide methods due to pyrite weathering.

Samples 4 and 5 with high NP values showed very similar results among methods (Table 3). Although significant differences were found among methods for sample 4, the difference in values are inconsequential considering the extremely high NP. Sample 4 was primarily composed of calcite, while sample 5 was calcite with a small amount of dolomite (x-ray data not shown but the high calcite content can be verified by the high calcium contents in Table 4).

Samples with high iron contents (Table 4) showed variable results. Sample 2 had about 40% lower NPs by Sobek and DER1 methods than the H₂O₂ methods (Table 3). On the other hand, the H₂O₂ methods produced NP values almost 80% lower than the no peroxide methods for sample 9. Sample 9 contained about 45% iron and 7% calcium compared to 55% iron and 0% calcium for sample 2. This lower NP value by the peroxide methods could indicate iron oxidation. But, sample 9 also had a S content of 4.5% (Table 4) and oxidation of pyrite by H₂O₂ could have occurred causing the lower NP values. The difference among methods of 100 to 150 tons NP per 1000 tons for sample 9 was also very consequential.

The DER2 method produced the lowest and MDER produced the highest NP values for samples 11, 15, and 18 (Table 3). Both DER2 and MDER are peroxide methods. These samples had high iron contents (62 to 87%) with varying amounts of silicon and aluminum (Table 4). Samples 1, 3, 7, 10, 13, and 14 had moderate amounts of iron (10 to 30%) and contained high amounts of silicon (35 to 52%) and aluminum (18 to 24%). Samples 7, 13, and 14 had greater than 1% S, while 1, 3, and 10 had much lower S amounts. Again, no clear trends were evident for NP on these samples. Samples 13 and 14 also had high S (Table 4) and the H₂O₂ methods should have given low NPs. On these two samples, MDER had low NP values as expected, but DER1, not DER2, had low NP values.

MDER yielded the highest NP values for samples 1, 2, 10, 11, 15, and 18. All these samples had 17 to 87% iron and little S. MDER also had a low NP value for sample 13 which had 29% iron and 9.0% S. NP of samples 9, 11, and 18 showed no significant difference between Sobek and DER1 methods, but gave 50 to 90% lower NP values

Table 3. Neutralization potential (NP) results for four digestion methods and titration to pH 7.0 of 13 overburden samples. NP values are in tons CaCO₃ equivalent per 1000 tons overburden. Each value is the mean of three replicates.

Sample	Digestion method ¹	NP		Sample	Digestion method	NP	
NP-01	1	20	b ²	NP-10	1	13	c
	2	18	c		2	13	c
	3	19	b		3	15	b
	4	30	a		4	17	a
NP-02	1	8	b	NP-11	1	11	b
	2	8	b		2	10	b
	3	12	a		3	7	c
	4	13	a		4	15	a
NP-03	1	11	b	NP-13	1	17	a
	2	8	c		2	14	b
	3	12	a		3	16	a
	4	12	ab		4	12	b
NP-04	1	926	b	NP-14	1	14	a
	2	930	a		2	7	c
	3	928	ab		3	12	b
	4	916	c		4	7	c
NP-05	1	710	a	NP-15	1	11	b
	2	710	a		2	11	b
	3	708	a		3	10	c
	4	707	a		4	18	a
NP-07	1	25	b	NP-18	1	15	b
	2	30	a		2	14	bc
	3	25	b		3	9	c
	4	27	b		4	26	a
NP-09	1	288	a				
	2	266	ab				
	3	145	c				
	4	165	bc				

¹Digestion Methods

- 1 = Sobek-heat till reaction complete, boil 1 min.
- 2 = DER1-boil 5 min.
- 3 = DER2-boil 5 min., filter, add 5 ml H₂O₂, boil 5 min.
- 4 = MDER-boil 5 min., add 5 ml H₂O₂, boil 5 min.

²NP values for each sample followed by the same letter are not significantly different at $p < 0.05$.

Table 4. X-ray fluorescence data showing the relative concentration (%) of elements in 13 overburden samples.

Sample	Fe	Al	Mn	Si	Mg	Ca	K	Ti	Cu	Zn	P	S ¹
----- % -----												
NP-01	29.1	21.6	1.1	41.7	0	0	5.5	1.0	0	0	0	0.34
NP-02	54.5	16.6	1.5	24.2	0	0	2.6	0.7	0	0	0	0.51
NP-03	14.9	23.6	0.4	51.7	0	0.8	7.6	1.5	0	0	0	0.07
NP-04	3.2	0	0	2.7	0	93.8	0	0	0	0	0	0.14
NP-05	4.0	6.5	0	18.6	9.8	57.7	2.8	0.4	0	0	0	0.09
NP-07	11.0	24.5	0.3	50.0	2.9	0.8	8.0	1.2	0.1	0.1	0.2	1.00
NP-09	45.0	13.6	1.9	24.3	0	6.9	2.6	0.6	0	0	1.8	4.53
NP-10	17.6	22.4	0.4	49.4	2.3	0.4	5.8	1.4	0.1	0	0	0.12
NP-11	87.2	0	1.5	11.1	0	0	0	0	0	0	0	0.11
NP-13	29.8	18.4	1.2	35.6	0	1.4	4.2	0.9	0	0	0	9.00
NP-14	10.5	23.7	0.3	50.9	2.8	0.7	0	1.5	0.1	0	0.3	2.68
NP-15	62.7	11.2	1.6	21.8	0	1.1	1.7	0	0	0	0	0.23
NP-18	72.0	9.0	2.0	13.8	0	1.9	1.4	0	0	0	0	0.12

¹S analyzed by Leco Sulfur Analyzer.

by the DER2 method. When comparing the Sobek, DER1 and DER2 digestion methods across all samples, the differences in NP values did not significantly alter the interpretation of these rock units for ABA, with the exception of sample 9.

Comparing Laboratory Results

NP Determined Without Adding Peroxide.

In 9 out of 11 samples (PADER did not analyze samples 4 and 5), the PADER lab achieved higher NP results than the WVU and Consol labs (Table 5). WVU gave the lowest NP results among laboratories for 8 of 11 samples. There are large discrepancies in NP values for all samples among laboratories. For example, sample 2 had an NP of 445 measured by Consol, 93 by PADER, and 8 by WVU. On the other hand, sample 9 had NP values of 26 by Consol, 82 by PADER, and 266 by WVU. The differences in NP values are large enough that it changes the interpretation of the overburden layer and alters the overburden handling and placement strategy during mining. Samples 4 and 5 (containing predominately calcite) showed very similar NP values by the WVU and Consol labs.

Table 5. NP results without using peroxide (H₂O₂) from three laboratories (WVU, PADER, and Consol) on 13 overburden samples. Fizz ratings were determined independently by each laboratory.

Sample	WVU ¹		PADER ²		Consol ³	
	Fizz	NP	Fizz	NP	Fizz	NP
NP-01	1	18	1	88	1	50
NP-02	1	8	1	93	3	445
NP-03	0	8	1	62	1	27
NP-04	3	930	-	-	3	936
NP-05	3	710	-	-	3	724
NP-07	1	30	1	40	0	6
NP-09	2	266	1	82	0	26
NP-10	1	13	1	73	0	22
NP-11	1	10	1	89	0	29
NP-13	0	14	1	79	0	23
NP-14	0	7	1	23	0	4
NP-15	1	11	1	87	0	14
NP-18	1	14	1	88	0	25

¹WVU digested samples according to fizz ratings and corresponding strengths and volumes of HCl (Table 2).

²PADER digested all samples in 40 ml of 0.1 M HCl (assumed 1 fizz).

³Consol digested samples according to fizz ratings and corresponding strengths and volumes of HCl (Table 2).

NP Determined By Adding Peroxide.

The NP differences among labs on these 13 samples were dramatically reduced by using a H_2O_2 method (Table 6). A large variation in the NP results occurred for samples 2 and 9, but the high fizz ratings given by the laboratory technician in each case and corresponding use of 0.5 M acid in those digestions probably caused the discrepancies. The dramatic decrease in variation of NP values among laboratories with peroxide demonstrates that H_2O_2 addition is necessary to produce consistent results among laboratories.

Table 6. NP results using peroxide (H_2O_2) from three laboratories (WVU, PADER, and Consol) on 13 overburden samples¹. Fizz ratings were determined independently by each laboratory. WVU used DER2 data.

Sample	WVU ²		PADER ³		Consol ⁴	
	Fizz	NP	Fizz	NP	Fizz	NP
NP-01	1	19	1	26	1	27
NP-02	1	12	1	15	3	43
NP-03	0	12	1	23	1	18
NP-04	3	928	-	-	3	924
NP-05	3	708	-	-	3	728
NP-07	1	25	1	24	0	21
NP-09	2	145	1	56	0	77
NP-10	1	15	1	20	0	12
NP-11	1	7	1	16	0	20
NP-13	0	16	1	33	0	37
NP-14	0	12	1	18	0	18
NP-15	1	10	1	17	0	25
NP-18	1	9	1	19	0	28

¹All labs added 5 ml of 30% H_2O_2 prior to titration and titrated to pH 7.0.

²WVU digested samples according to fizz ratings and corresponding strengths and volumes of acid (Table 2).

³PADER digested all samples in 40 ml of 0.1 M HCl (assumed 1 fizz).

⁴Consol 0 and 1 fizz samples were digested in 80 ml of 0.1 M HCl, and 80 ml of 0.5 M HCl for 2 and 3 fizz samples.

Fizz Ratings

The standard system for determining the amount of acid to add during the NP procedure is a fizz rating system utilizing fizz values of 0, 1, 2, and 3 (Table 2). For each fizz rating, a corresponding strength and volume of HCl is used for sample digestion. Under a two-fizz rating system devised for this study, fizz ratings 0 and 1 were both considered a 1, and fizz ratings 2 and 3 were considered a 2 (Table 7).

Fizz rating is a subjective evaluation which may introduce inconsistency into the eventual NP value. In assigning fizz ratings for the WVU experiment, all samples were tested concurrently in a soil sample dish, allowing all the samples to be within a square foot of area. They were all assigned fizz values within 5 minutes in order to give them comparative values. For any sample that was not clearly in a distinct fizz rating class, the sample had the NP digestion methods performed using the acid strengths and amounts for both possible fizz classes. These values are given in Table 8.

Samples 3, 9, 13, and 14 were judged to have fizz ratings in two distinct fizz classes (Table 8). For example, sample 3 was rated a 0 and a 1. The sample was treated by all digestion methods using 20 and 40 ml of 0.1 M HCl. The NP results on sample 3 were strikingly higher for all digestion methods when using the higher amount of acid compared to the lower amount of acid (Table 9). Sobek, DER1 and DER2 were 70%, 210% and 149% higher respectively, using the higher fizz rating on sample 3.

Table 7. Fizz ratings and the corresponding amount of acid added for four-fizz and two-fizz procedures.

Procedure Fizz	Volume of HCl	M of HCl
Four-fizz System		
0 none	20 ml	0.1
1 slight	40 ml	0.1
2 moderate	40 ml	0.5
3 strong	80 ml	0.5
Two-fizz System		
1 none to slight	40 ml	0.1
2 moderate to strong	80 ml	0.5

Table 8. Fizz ratings and the corresponding volume (ml) and molarity (M) of HCl used for 13 overburden samples using the four-fizz and two-fizz rating systems. Asterisks (*) note differences.

Sample	Four-fizz system			Two-fizz system		
	Fizz	ml	M	Fizz	ml	M
NP-01	1	40	0.1	1	40	0.1
NP-02	1	40	0.1	1	40	0.1
NP-03	0	20*	0.1	1	40*	0.1
NP-04	3	80	0.5	2	80	0.5
NP-05	3	80	0.5	2	80	0.5
NP-07	1	40	0.1	1	40	0.1
NP-09	2	40*	0.5	2	80*	0.5
NP-10	1	40	0.1	1	40	0.1
NP-11	1	40	0.1	1	40	0.1
NP-13	0	20*	0.1	1	40*	0.1
NP-14	0	20*	0.1	1	40*	0.1
NP-15	1	40	0.1	1	40	0.1
NP-18	1	40	0.1	1	40	0.1

Table 9. NP values of four overburden samples that had different fizz ratings when using a four-fizz rating system (4F) compared to a two-fizz rating system (2F). NP values were determined for each sample at both fizz ratings and hence were digested in different acid volumes (ml).

Sample System	Fizz	ml	M	NP Values				
				Sobek	DER 1	DER 2	MDER	
-----tons per 1000 tons-----								
NP-03	4F	0	20	0.1	11	8	12	12
NP-03	2F	1	40	0.1	19	26	31	30
NP-09	4F	2	40	0.5	288	266	145	165
NP-09	2F	2	80	0.5	313	412	142	118
NP-13	4F	0	20	0.1	17	14	16	12
NP-13	2F	1	40	0.1	32	24	28	37
NP-14	4F	0	20	0.1	14	7	12	7
NP-14	2F	1	40	0.1	15	11	16	1

Sample 9 also gave higher NP results with Sobek and DER1, being 9% and 55% higher when using 80 ml of acid compared to 40 ml. The DER2 method showed similar results between the different acid volumes, but the NP value was about half that of the Sobek and DER1 methods. The MDER method, surprisingly, showed a decrease in NP with an increase in acid volume (Table 8). The reason for this result with MDER is unclear. It is possible that the unfiltered sediment containing 4.5% S in the sample may have been oxidized by a greater amount of the peroxide yielding a lower NP. Sample 13 had NP values for Sobek, DER1 and DER2 as being 94%, 75%, and 78% higher when using the two-fizz rating system (larger volume of acid), but it also had 9.0% S. Sample 14 yielded NP values 7%, 69%, and 30% higher for the same methods, respectively, when more acid was used for digestion. The MDER was not consistent. For samples 3 and 13 (0.1 and 9.0% S, respectively), the NP values increased with increasing acid amounts, while samples 9 and 14 (4.5 and 2.7% S, respectively) showed a decrease in NP with more acid.

Similar results were found when the Consol laboratory used different amounts of acid on these samples (Table 10). When greater amounts of acid were used during NP sample digestion, the sample yielded a higher NP value.

Table 10. NP values determined by different amounts of acid on eight samples digested by the Consol lab.

Sample	Acid Volume and Strength	
	80 ml of 0.1 M HCl	20 ml of 0.1 M HCl
	-----tons per 1000 tons-----	
NP-07	20	6
NP-09	136	26
NP-10	58	22
NP-11	97	29
NP-13	51	23
NP-14	7	4
NP-15	85	14
NP-18	93	25

Comparison to Leachate pH from Soxhlet

To assess the prediction made by the NP digestion procedures, ABA values (using the NP values from the NP digestion methods and %S value) were compared to the leachate pH after 6 cycles of soxhlet extraction (Table 11). If the ABA value gave excess NP (positive number), then the pH of the leachate should have been above 7.0. If the ABA value was a Max Needed or a deficiency of NP (negative number), then the leachate pH was predicted to be below 7.0.

All the methods accurately predicted alkaline leachate for samples 1, 3, 4, 5, 10, 11, 15, and 18. All methods also accurately predicted acidic leachate for samples 2, 7, 13, and 14. So, 12 out of 13 samples were predicted accurately regardless of the NP digestion method. For sample 9, all methods predicted excess NP, but the soxhlet leachate was 4.8. All samples with 0.5% S or greater produced acidic leachate.

Summary and Conclusions

When comparing Sobek, DER1 and DER2 NP digestion methods, few consequential differences were found in the NP value (differences were less than 6 tons per 1000 tons). The MDER method, in a few cases, produced significantly different NP values than the other three methods.

The NP values determined by three different labs showed dramatic variations in the results when no H₂O₂ was used. Some of the variation was due to the different fizz ratings and therefore different amounts of acid were used in the digestion. The variations in NP were decreased substantially when 5 ml of 30% H₂O₂ were added in the digestion process. The use of different laboratories also showed trends. WVU consistently having lower NP values and PADER consistently giving higher values. Results from separate studies by WVU and Consol indicate that higher fizz ratings

Table 11. Acid-base account values for 13 overburden samples compared to resultant leachate pH after 6 soxhlet cycles. Excess NP results if the ABA values are positive. If negative, the values represent a deficiency in NP.

Sample	Acid-base Account Values				Soxhlet pH
	Sobek	DER1	DER2	MDER	
NP-01	9	7	9	19	8.4
NP-02	-8	-8	-4	-3	4.8
NP-03	7	6	10	7	8.8
NP-04	921	926	924	912	9.3
NP-05	707	707	705	705	9.5
NP-07	-6	-1	-6	-4	2.3
NP-09	147	124	4	23	4.8
NP-10	9	9	-12	13	9.0
NP-11	7	7	3	12	8.8
NP-13	-265	-268	-265	-269	2.3
NP-14	-69	-77	-72	-76	2.4
NP-15	4	4	3	10	8.0
NP-18	11	10	6	22	8.2

(thereby causing greater volumes of acid to be added during digestion) yielded higher NP values. Some of the variation in assigning fizz classes can be reduced by using a two-fizz rating system rather than the standard four-fizz rating system.

Acid-base accounts calculated from the data provided by the four different NP digestion methods generally showed no appreciable difference and did not change the overall classification of the overburden sample. All methods accurately predicted alkaline soxhlet leachate for samples 1, 3, 4, 5, 10, 11, 15, and 18, and acidic leachate for samples 2, 7, 13, and 14. All samples with 0.5% S or greater produced acidic leachate in the soxhlet. Samples 4 and 5, each having 0.1% S, had extremely high alkalinity values. Sample 2 had 0.5% S and 55% iron, and the leachate turned slightly acidic (pH 4.8). Sample 9, with 4.5% S, had excess NP values, but the leachate was slightly acidic (pH 4.8). Other high iron, high siderite samples (samples 11, 15, and 18) did not have acidic soxhlet leachate.

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