

EFFECTS OF SIDERITE ON THE NEUTRALIZATION POTENTIAL IN THE ACID- BASE ACCOUNT

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INTRODUCTION

Siderite has long been recognized as a potential source of error in the determination of neutralization potential within the acid base account procedure. Siderite is Iron Carbonate which will contribute alkalinity to the neutralization potential (NP) analysis, while the iron generated acidity is not measured by the acid potential (AP) analysis. While this interference has been recognized it has generally been assumed that there was not enough siderite present to influence the acid-base account result. In 1992, V. P. Wiram reported on effects of siderite masking at the Skyline Mine. Failure to recognize the presence of siderite in the overburden resulted in post mining seeps which were above discharge limits for iron. In 1990 J. Morison reported on the use of hydrogen peroxide in the AP test as a means of eliminating siderite masking. This report incorporates hydrogen peroxide addition along with a modification to the application of the fizz analysis in order to eliminate the effects of siderite and to reduce the subjectivity of the fizz test.

BACKGROUND

As the desire to reduce acid mine drainage from active mines has increased the reliance on predictive methodology has also increased. The most widely used predictive technique in the mining industry is the acid base account. Unfortunately, the acid base account has not always been a reliable predictor of the post closure water quality. This condition has created what has become known as the grey area. The grey area describes a range of values in which the post closure water quality cannot be reliably predicted.

Many factors can influence the accuracy of an acid-base account prediction. These factors include: the method of sample collection, the number of acres per sample, the amount of sample compositing, the spacial variability of the overburden, the degree of adherence to the reclamation plan, the presence of siderite, and the subjectivity of the acid-base account procedure.

In an effort to overcome these unknowns, and maintain a high degree of assurance of a non-acid outcome, the Pennsylvania DER published a guidance manual specifying a level of net alkalinity below which permits would not be issued. The Pennsylvania Coal Association took issue with this level and also with its method of implementation. In order to avoid litigation, a committee was established to try to resolve the outstanding issues. One of the sub-

committees of this group was charged with addressing prediction methodology.

Siderite and the subjectivity of the fizz test were identified as potential problems with the acid base amount. To test this hypothesis several samples some of which were known to contain siderite were subjected to acid-base amount analysis. The samples were prepared by Joel Morison at Pen State University, and were analyzed by the DER, West Virginia University, and CONSOL. This work confirmed that siderite and the fizz test could be significant problems in the acid-base account. Based on this work the acid-base account procedure, contained in Noll et. al. 1988, was modified to include a hydrogen peroxide step, and to reduce the number of acid volume/strength combination from four to two. This modified procedure is included in this report with the additions underlined.

METHOD COMPARISON

The results from this modified procedure were compared to acid-base account results using the Sobek method. A sample set was split in the field and the splits were sent to two independent labs. Each lab ran both the Sobek method and the modified method on each sample. The results were then compared lab to lab and method to method in order to determine the consistency of the reported value and the effect of siderite.

In comparing the NP of selected samples from lab 1 with lab 2 using the Sobek method a large difference in the reported value is apparent in samples "E" and "F". This difference is significantly reduced when the same samples are compared using the peroxide method. In samples with very little alkalinity, such as sample "A", the use of a larger acid volume in the modified method can result in a slight increase in reported alkalinity.

When the Sobek method is compared to the peroxide method within the same lab, we find that when siderite is absent, as in samples "A" and "G", the results of the two methods are nearly identical. However, when siderite is present the NP can be significantly overstated via the Sobek method.

In a effort to determine if the peroxide method improved the reproducibility of results lab to lab, lab 2 Sobek results were subtracted from lab 1 Sobek data. The standard deviation of this difference was computed for all of the samples. The same procedure was also applied to the peroxide data. The Sobek data had a standard deviation of 39.1 while the peroxide data had a standard deviation of 16.5. The smaller standard deviation of the peroxide results indicates that lab to lab variability is significantly reduced.

CONCLUSION

The modification of Noll et. al. contained in this report will eliminate the erroneous results obtained from the NP analysis when siderite is present. Further, the subjectivity of the fizz test is reduced. Additional testing of this procedure is planned in order to confirm these preliminary results, consequently, this method should be used with caution until this testing is completed.

OVERBURDEN SAMPLING AND TESTING

MANUAL

II. NEUTRALIZATION POTENTIAL

1. SCOPE AND APPLICATION

The neutralization potential test procedure quantifies the neutralizing compounds in coal and overburden. Of the many types of basic compounds present, carbonates are the only basic compounds that occur in sufficient quantity to be considered as-effective deterrents to the production of acid mine drainage. As always there are exceptions, siderite (FeCO_3) which is a carbonate, is not a desirable neutralizer since it will produce both carbonate alkalinity and acidity from iron oxidation. This modified procedure is designed to eliminate siderite interference, and to reduce variability caused-by subjective fizz interpretation.

2. SUMMARY OF METHOD

A portion of the laboratory sample is qualitatively ranked as to its carbonate concentration by means of the fizz rating. . A quantity of dilute hydrochloric acid, based on the fizz rating, is added to another portion of the laboratory sample which is then heated to insure complete reaction with.-the. sample. After the sample has cooled, it is filtered and hydrogen peroxide is added. The sample is then heated to remove any remaining hydrogen peroxide. 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. This value is then used to calculate the neutralization potential of the sample and is expressed as CaCO_3 .

The procedure that is presented is a modification of -the procedure presented -by Noll et. al. 1988 which is a modification of Sobek et. al. offered in Field and Laboratory Methods Applicable to Overburdens and Mine soil. The first change is in the acid digestion procedure which has been simplified by reducing the number of acid concentrations and volumes from four to two. This change may marginally-affect the results; but the change in results will be minor compared-to errors which have resulted from the variability of the-fizz test. The second chancre involves the addition of hydrogen peroxide after digestion and-before-titration. This change will eliminate erroneous results caused by siderite interference- and does not alter the results obtained by the Sobek procedure in non-siderite bearing samples.

3. INTERFERENCES AND PRECAUTIONS

3.1 Many interactions take place in the course of this test that effect the precision which can be obtained but they do not affect the usefulness of the results.

- I. Certain iron complexes which can be dissolved in the HCl digestion, consume NaOH in the back titration with the formation of iron hydroxide. This tends to lower the calculated neutralization potential. The addition of the hydrogen Peroxide step provides a more stable end point, and assures that acidity associated with ferrous iron is expressed at pH 7.0.

- II. Pyrite will not dissolve appreciably under the conditions of this test.

4. APPARATUS AND MATERIALS

4.1 pH METER and ELECTRODE: Automated systems will improve, the precision of the test as well as remove the tedium of the titration, but manual systems are adequate.

4.2. BURET: automatic or standard

4.3 HOT PLATE:

4.4 BEAKERS or ERLLENMYER FLASKS:

4.5 BALANCE:

4.6 FILTER PAPER

4.7 WATCHGLASSES:

5. REAGENTS

5.1 All chemicals shall be reagent grade and the water shall be Type III reagent water or better. Commercially available standardized hydrochloric acid and sodium hydroxide solutions may be used.

5.2 HYDROCHLORIC ACID (0.1N): Dilute 8.3 ml of concentrated HC1 in 1 liter of water, mix well. Standardize as follows: (refer to ASTM E 200)

- a. Dry 2 g of anhydrous sodium carbonate at 250 C for 4 hours. Cool in a desiccator.
- b. Weigh .22 g of Na₂CO₃ to the nearest 0.1 mg. Dilute with 50 ml of water.
- c. Titrate with the 0.1N HC1 solution to the methyl red end point, or potentiometricly to a pH of 4.5.
- d. Calculate the normality:

$$A = B / (.053 * C)$$

A = normality of the HC1 solution

B = grams of Na₂CO₃ used

C = milliliters of HC1 solution used in the titration

- e. Use the average of three standardizations for all subsequent calculations.

5.3 HYDROCHLORIC ACID (0.5N): Dilute 41.5 ml of concentrated HC1 in 1 liter of water, mix

well. Standardize as follows: (refer to ASTM E 200)

- a. Dry 5 g of anhydrous sodium carbonate at 250 C for 4 hours. Cool in a desiccator.
- b. Weigh 1.10 g of Na_2CO_3 and record the weight to the nearest-.1 mg. Dilute with 50 ml of water.
- c. Titrate with the 0.5N HCl solution to the methyl red end point, or potentiometricly to a pH of 4.5.
- d. Calculate the normality:

$$A = B / (.053 * C)$$

A = normality of the HCl solution

B = grams of Na_2CO_3 used

C = milliliters of HCl solution used in the filtration

- e. Use the average of three standardizations for all subsequent calculations.

5.4 HYDROCHLORIC ACID (25%): Dilute one volume of concentrated HCl in three volumes of water.

5.5 HYDROGEN PEROXIDE (30%):

5.6 SODIUM HYDROXIDE (0.1N): Dilute 5.45 ml 50% NaOH to 1 liter with water. Mix well. The concentration will not be determined but is a part of the blank data.

5.7 SODIUM HYDROXIDE (0.5N): Dilute 27.25 ml of 50% NaOH to 1 liter with water. Mix well. The exact concentration will not be determined but is a part of the blank data.

5.8 SODIUM CARBONATE (anhydrous):

5.9 ASCARITE:

5.10 CALCIUM CARBONATE:

6. SAMPLE CONSIDERATIONS

This procedure does not require any special sample handling considerations. The normal -60m sample is all that is required.

7. PROCEDURE

7.1 Determine the fizz rating of the samples as follows

- a. Place a small amount of sample on a watchglass and make a

depression in the center. Add one or two drops of 25V HCL to the depression. Determine the fizz rating based on the following criteria:

0. FIZZ (NONE): No reaction or an occasional bubble caused by trapped air.
1. FIZZ (SLIGHT): Minimal reaction, the reaction ranges from a few bubbles per second to many fine bubbles that cover the entire sample/acid interface.
2. FIZZ (MODERATE): Active bubbling with only a small amount of splashing.
3. FIZZ (STRONG) Very active bubbling that includes substantial splashing of the acid.

Proper identification of the fizz rating will minimize the number of neutralization potential determinations that will have to be rerun due to insufficient-addition of acid and will serve as a qualitative check of the neutralization potential.

7.2 Determine the neutralization potential (NP).

- a. Weigh 2.000 gram of sample and transfer to an appropriate size beaker or flask.
- b. Add the quantity of dilute HCl to the sample that is indicated in the following Table according to the fizz rating that was determined in the preceding step.

FIZZ RATING		VOLUME OF HCl	NORMALITY OF HCl
0	NONE	40 ml	0.1N
1	SLIGHT	40 ml	0.1N
2	MODERATE	80 ml	0.5N
3	STRONG	80 ml	0.5N

- c. Add water to make the volume approximately 100 ml.
- d. Cover with a watchglass and boil gently for 5 minutes.
- e. Cool and then filter using a Whatman 41 filter paper or equivalent, if a clear filtrate is not obtained refilter using a finer grade filter.
- f. Rinse using 20 ml water.

g. Add 5 ml H₂O₂ to the filtrate, cover with a watchglass-and-boil gently for 5 minutes.

h. Cool and then titrate to pH 7 end point for a minimum of 30 seconds with the corresponding normality of NaOH. If a dark green or black precipitate forms during the titration add an additional 3 ml H₂O₂ and continue titrating.

i. Determine reagent blank filtration values by following the NP procedure, 7.2 (b. thru e.), for each fizz rating. Boileasers may be necessary to avoid the loss of acid during the boiling stage of the procedure.

8. CALCULATIONS

$$8.1 A = (b - C * (D / E)) * 25 * N$$

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

N = normality of the acid

9. QUALITY CONTROL

9.1 Precision shall be checked by the running of duplicates. A minimum of 1 in 20 is required but 1 in 10 is considered optimum. Acceptable precision, categorized by fizz rating, is-as follows:

PRECISION		ACCEPTABLE (tons / 1000 tons of material)
Neutralization Potential	0 to 30	<u>+ 5.0</u>
Neutralization Potential	30 to 100	<u>+ 10.0</u>
Neutralization Potential	100 to 500	<u>+ 25.0</u>
Neutralization Potential	500+	<u>+ 50.0</u>

9.2 Accuracy shall be based on the analysis of reagent grade calcium carbonate which has been dried for 4 hours at 250 C.

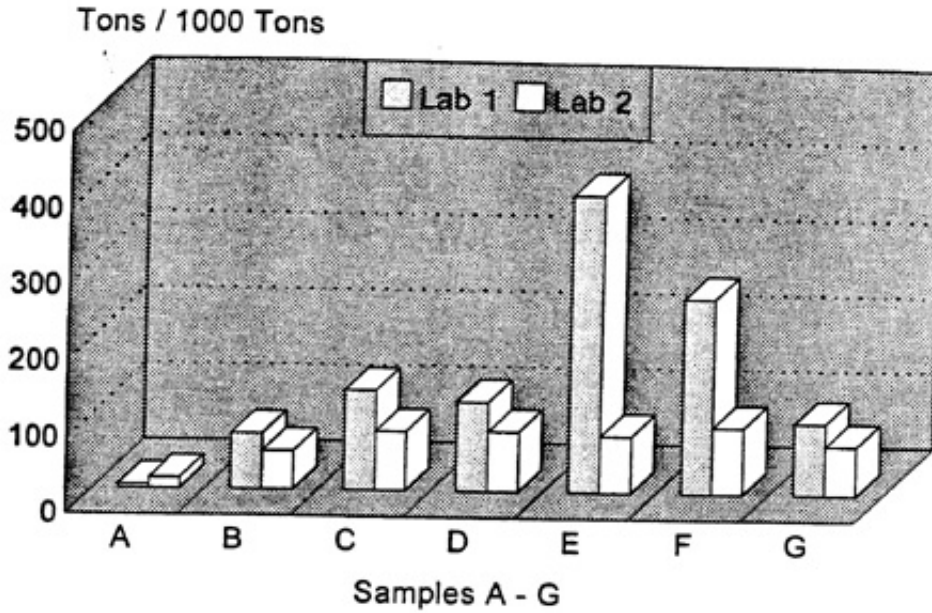
The CaCO₃ standards-shall be run at least once per month and whenever new 0.1 and 0.5 N NaOH or HC1 solutions are prepared.-:-Standards-shall be run as follows:

Maximum

			Weight CaCO ₃ (grams)	Allowable Range (tons / 1000 tons of material)
FIZZ	=	1	0.100	50.0 +/- 2.5
FIZZ	=	2	1.000	500.0 +/- 25.0
FIZZ	=	3	2.000	1000.0 +/- 50.0

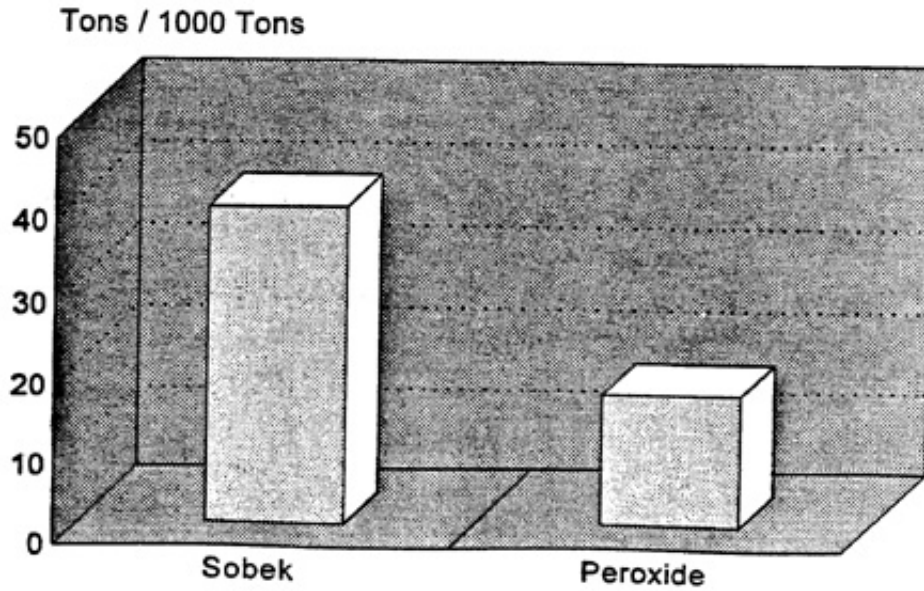
NP

Lab 1 Vs. Lab 2 Sobek



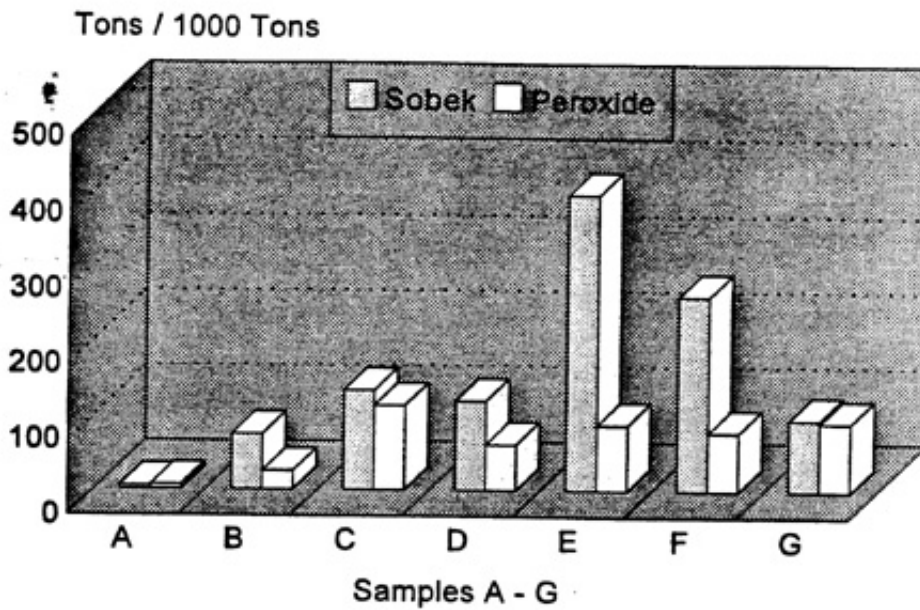
Standard Deviation

lab to lab



NP

Sobek Vs. Peroxide



NP

Lab 1 Vs. Lab 2 Peroxide

