Overburden Analysis

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EVALUATION OF ACID BASE ACCOUNTING DATA USING COMPUTER SPREADSHEETS[1]

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Abstract. Overburden analysis data in the form of acid-base accounting (ABA) can be efficiently and effectively evaluated using spreadsheet programs for personal computers. The Pennsylvania Department of Environmental Resources (PaDER), Bureau of Mining and Reclamation has developed a spreadsheet which calculates several parameters from ABA data including mass-weighted maximum potential acidity (MPA), neutralization potential (NP) and net neutralization potential (NNP). The spreadsheet also summarizes the overburden analysis in terms of the ratio of NP to MPA and the percent sandstone. With the spreadsheet, aggregate overburden characteristics can be summarized for an entire mine site.

Computer spreadsheet software is ideal for performing the numerous repetitive calculations necessary in integrating large quantities of ABA data. The ABA spreadsheet integrates sulfur content and neutralization potential data, as well as sample interval thicknesses, the percentage of each unit spoiled, and overburden unit weights. The area of influence of each drill hole is determined and the actual mass of strata are calculated by taking into account the geometry of the mine site and overburden unit weights. The ABA summary data can be compared using a variety of significance thresholds for NP and percent sulfur, and other factors can readily be changed to review their impact. The spreadsheet approach permits more complex and detailed analysis of overburden data and facilitates comparison between calculation methods.

Additional Key Words: overburden analysis, acid base accounting, computer spreadsheet.

Introduction

Acid base accounting (Sobek et al. 1978) is the most commonly used overburden analysis technique for predicting the water quality likely to result from a coal mining operation. In Pennsylvania, acid base accounting (ABA) has been used since about 1979 and now accompanies approximately fifty percent of current surface mining permit applications. ABA evaluates the maximum potential acidity (MPA) and the neutralization potential (NP) from individual strata and expresses them as tons per thousand tons of calcium carbonate equivalent. As such, it has been used to identify potentially acid-forming or alkaline-forming strata. Although not originally intended for the purpose, ABA is also used to predict postmining water quality. This is done by individually sampling all of the strata within a proposed mine site. The weighted aggregate of all samples are considered together to evaluate the potential of the site to produce acidic or alkaline water following mining.

Using ABA data for prediction of postmining water quality requires the integration of the chemical characteristics of each individual stratum in order to characterize the entire mine site. The large volume of ABA data which accompanies a typical permit application makes it all but impossible to accomplish this intuitively. However, the widespread availability of personal computers and spreadsheet software greatly enhance one's ability to quantitatively and objectively evaluate ABA data and to evaluate it using a variety of procedures. This paper discusses a method developed by the Pennsylvania Department of Environmental Resources (PaDER) that offers a reliable and convenient means of summarizing large volumes of overburden data.

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History of Quantitative ABA Evaluation

Early users of ABA data as a predictor of postmining water quality tended to balance the MPA against the NP for an overburden column giving equal weight to the strata at the top and bottom. It was presumed that the postmining water quality would be determined by whichever factor predominated. For example, where NP exceeded MPA, alkaline drainage would result. Issuance of surface mining permits based on this assumption frequently resulted in severe acid mine drainage pollution (Brady and Hornberger 1989) leading to the realization that modifications to ABA review procedures were required for reliable predictions of postmining water quality.

The need for a simple method of computing and summarizing ABA data became essential in the early 1980's when coal companies began to propose the addition of supplemental alkaline material as a means of offsetting an NP deficiency (MPA > NP) and the potential for acid production at a mine site. Because of the large number of arithmetic operations required, the concept of using computer spreadsheets for calculating the deficiencies soon followed. Originally, calculations were weighted only according to thickness. However, in most cases the topography is hilly with flat-lying strata so that the uppermost strata are not as aerially extensive as lower strata, making volume or mass-weighted calculations essential. Later developments in the utility of computer spreadsheet software enabled the PaDER to design more sophisticated spreadsheets which considered mass or volumetric weighting of each overburden sampling interval.

As the use of ABA for postmining water quality prediction became more widespread, the spreadsheet was also used to summarize the data numerically for comparison with postmining water quality. Again, this required a quantitative summary of the data which took into account the actual volume or mass of each overburden sampling interval. Two recent studies by diPretoro and Rauch (1988) and Erickson and Hedin (1988) have compared numerical summations of ABA data with postmining water quality. Because of the large number of mine sites required for studies of this type and the effort required to measure the areal extent of each stratigraphic interval, precise volumetric calculations were not performed. diPretoro and Rauch calculated volume-weighted summary values by assuming an idealized right-triangle shaped area to be mined. Erickson and Hedin used essentially the same method. This assumption was easily applied to single core log data where the coal was not steeply dipping. However, it can only be considered as an approximate technique for volumetric adjustment of ABA data. In these studies, aggregate MPA and aggregate NP were calculated. These volumes were then used to determine the net neutralization potential (NNP = NP - MPA) of the aggregate overburden volume and the NP/MPA ratio. Since the strata are represented more realistically, they found that volume-weighted calculations yielded better results than a columnar (equal unit-volume for all strata) approach.

Methodology

The current spreadsheet program used by the PaDER includes several important parameters useful in summarizing aggregate overburden characteristics. These include mass weighting using selected unit weights according to rock type, the percentage of a unit that is spoiled, and threshold significance levels for NP and sulfur content. The current spreadsheet represents a culmination of efforts over the last several years. The concepts presented here could be adopted with almost any commercial spreadsheet software.

Figure 1 is a printout of the overburden calculation spreadsheet used by PaDER, showing the layout of the input data and calculated results. Data input is designed to mimic ABA reports currently in use. Manual data input from the keyboard is kept to a minimum. The only required input columns are bottom depth, rock type, % sulfur, NP, and fizz. All other values are either calculated or can use predetermined defaults.

Area of Influence

The spreadsheet is designed to analyze ABA data for individual drill holes. Where only one drill hole is available to characterize the overburden at a given mine site, quantitative analysis is simplified, although a single hole may not be representative of the entire mine site. In most cases, the information available from surface mining permit applications in Pennsylvania is complete enough such that a more rigorous approach to quantitative evaluation of overburden analysis data can be undertaken. Virtually every site in the state has two (and usually more) overburden holes. Using the outcrop boundary and the limits of mining as delineated in the permit application, the area of influence of each drill hole can be approximated using the Thiessen polygon method (Davis 1973 and Brassington 1988).

An example Thiessen polygon construction at a hypothetical mine site is shown in Figure 2. The areas within each polygon are closer to the data point (drill hole) in the center of the polygon than they are to any other data point. In brief, the polygons are constructed by drawing lines between each drill hole. Each line is then bisected with a perpendicular and the perpendiculars are extended to form polygons. The area of each polygon can be calculated using a planimeter and this value can be used as a factor in determining actual volume or mass or for applying relative weights to each drill hole. Although there are other more elaborate methods which could be employed, they usually require many data points and lengthy, complex calculations. The Thiessen method is more representative than simple arithmetic

OVERBURDEN ANALYSIS SPREADSHEET PAGE-1

OPERATOR: MINE SITE 1
PERMIT NO: DR HOLE: DH EXAMPLE
COUNTY: LYCOMING TOWNSHIP: PINE

THRESHOLD SULFUR NP FIZZ
VALUES: 0 0.00 0
NUMBER OF INTERVALS 21 (Alt A; Alt B to execute)

CLAY	CL	3450
SHALE	SH	3700
SILTSTONE	ST	3750
SANDSTONE	SS	3670
LIMESTONE	LS	3670
COAL	CO	1800
CARBONOLITH	CB	2580
OTHER	OT	2000

ALK ADD(t/a CaCO3):
COAL SEAMS:
STATE PLANE ZONE:
FEET (NORTH/SOUTH):
FEET (EAST/WEST):
SURFACE ELEV. (FT):

BOTTOM DEPTH (FT)	THICKNESS FEET	ROCK TYPE	FIZZ RATING	SULFUR %	NP	DEFICIENCY /EXCESS	ACREAGE	UNIT WT TONS/AC-FT	FRACTION SPOILED	TONS MPA	TONS NP	NET NP (TONS)	TONS OF OVERBURDEN
7.00	7.00	OT	0	0.05	1.90	0.34	10.50	2000	1.00	229.69	279.30	49.61	147000
14.00	7.00	SS	0	0.04	1.65	0.40	13.98	3670	1.00	448.89	592.54	143.65	359115
21.00	7.00	SS	0	0.05	1.90	0.34	15.72	3670	1.00	630.94	767.22	136.28	403800
28.00	7.00	SH	0	0.07	28.99	26.80	17.46	3700	1.00	989.08	13107.86	12118.78	452151
33.00	5.00	CO	0	0.50	2.41	-13.22	18.70	1800	0.10	262.97	40.56	-222.41	16830
37.00	4.00	CL	0	0.08	3.42	0.92	19.69	3450	1.00	679.44	929.48	250.03	271776
46.00	9.00	SS	0	0.07	2.41	0.22	21.93	3670	1.00	1584.53	1745.70	161.17	724358
60.00	14.00	SS	0	0.09	5.19	2.38	25.41	3670	1.00	3671.77	6775.64	3103.87	1305519
71.00	11.00	SS	0	0.12	15.82	12.07	28.14	3670	1.00	4260.41	17973.25	13712.84	1136110
81.00	10.00	SH	0	0.28	30.25	21.50	30.63	3700	1.00	9915.58	34279.58	24364.00	1133209
82.00	1.00	SH	0	1.29	2.41	-37.90	30.88	3700	1.00	4605.31	275.32	-4329.99	114240
86.00	4.00	CL	0	0.49	9.75	-5.56	31.87	3450	1.00	6734.47	4288.07	-2446.40	439802
90.00	4.00	CL	0	0.59	7.09	-11.35	32.86	3450	1.00	8361.74	3215.44	-5146.30	453518
92.50	2.50	CO	0	0.95	2.66	-27.03	33.48	1800	0.10	447.34	40.08	-407.26	15068
98.00	5.50	CL	0	0.54	3.57	-13.31	34.85	3450	1.00	11159.56	2360.87	-8798.70	661308
100.00	2.00	CO	0	0.74	1.65	-21.48	35.35	1800	0.10	294.28	21.00	-273.28	12725
104.00	4.00	CL	0	0.19	5.45	-0.49	36.34	3450	1.00	2977.81	2733.31	-244.49	501525
121.00	17.00	SH	0	0.12	33.04	29.29	40.57	3700	1.00	9568.66	84306.30	74737.63	2551643
127.00	6.00	SH	0	0.10	3.93	0.81	42.06	3700	1.00	2917.74	3669.36	751.61	933678
131.00	4.00	CO	0	0.68	3.17	-18.08	43.05	1800	0.10	658.69	98.26	-560.43	30997
132.00	1.00	CL	0	0.10	2.91	-0.22	43.30	3450	1.00	466.83	434.71	-32.12	149385
										70865.73	177933.85	107068.12	11813759

TOTAL OVERBURDEN VOL.(ACRE-FT):	3305	TOTAL (TONS):	70865.73	177933.85	107068.12
PERCENT SANDSTONE:	32%	TOTAL (TONS/THOUSAND):	6.00	15.06	9.06
DER RATIO:	2.51	diPRETORO METHOD (T/TT):	6.71	15.77	9.06
diPRETORO RATIO:	2.35				
TONS/ACRE REQUIRED (1:1):	2472.70 EXCESS				

ABA SUMMARY VALUES USING % SULFUR * 62.5 = MPA:

DER RATIO:	1.26	TOTAL (TONS):	141731.46	177933.85	36202.38
diPRETORO RATIO:	1.17	TOTAL (TONS/THOUSAND):	12.00	15.06	3.06
TONS/ACRE REQUIRED (1:1):	836.08 EXCESS	diPRETORO METHOD (T/TT):	13.42	15.77	2.34

Figure 1. Example of acid base accounting spreadsheet printout.

averaging of drill hole data since each drill hole represents a volume of overburden proportional to its actual location within the mine site.

Volumetric Calculations

In contrast to thickness weighting and volume weighting using the triangle approximation of diPretoro, the overburden analysis spreadsheet uses actual measured acreages of the area to be mined. For most uses it is impractical to measure the area for each sample (stratigraphic) interval, which would be necessary for precise volumetric calculations. As an alternate and much simpler method, the acreage for the uppermost unit and lowermost unit can be determined, with the spreadsheet interpolating the areas for each intervening sample interval. In most instances, this method will provide acceptable volumetric calculations under a wide range of topographic conditions. The area covered by each sample interval is estimated by determining its depth in the drill hole at the middle of the interval. This technique is illustrated in Figure 3. The spreadsheet calculates this value using the equation:

$$A_I = A_T + [((D_{TOP}+D_{BOT})/2)/D_{TOT}] \times (A_B - A_T) \quad (1)$$

Where: A_I = Acreage at sample (stratigraphic) interval

A_T = Acreage represented by the middle of the uppermost sample interval

A_B = Acreage represented by the middle of the lowermost sample interval

D_{TOT} = Drill hole total depth

D_{TOP} = Depth at top of sample interval

D_{BOT} = Depth at bottom of sample interval

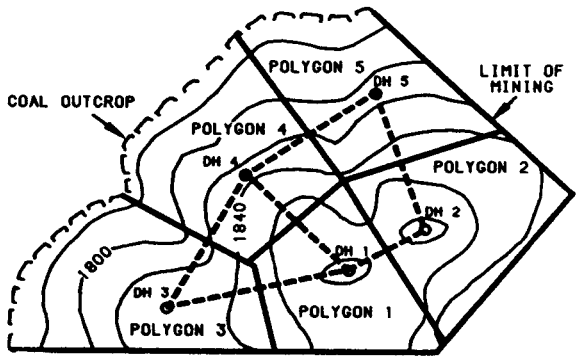

Figure 2. Typical mine plan map showing Theissen polygon method of defining area of influence for each drill hole. Dashed lines are construction lines drawn between drill holes. Polygons are constructed by bisecting the construction lines with perpendiculars. Outer limits of polygons are defined by mining limits and coal outcrop boundary. Interior polygons (1 and 2) are calculated as columns (top acreage = bottom acreage). Remaining polygons calculated using different top and bottom acreages.

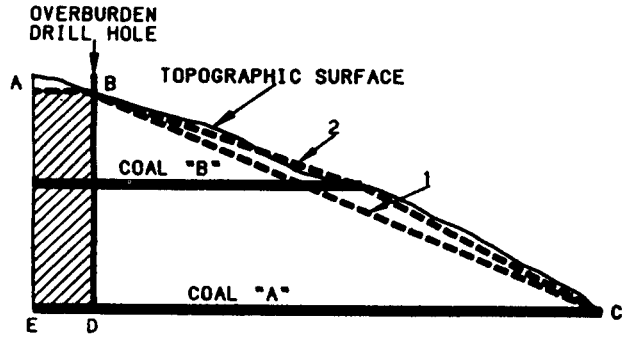

Figure 3. Schematic cross-sectional view of area to be mined with overburden drill hole slightly below point of maximum overburden thickness. diPretoro volume-weighting approximation shown by line 1 includes the area of triangle BCD. Spreadsheet method calculates area of triangle BCD plus the cross-hatched rectangle ABDE. Where necessary due to irregular topography, spreadsheet-calculated volumes can be improved by dividing drill hole into two or more intervals as shown by line 2.

This equation provides a reasonable approximation of acreages covered by each sample interval provided that the strata are not steeply dipping and that the topography, if viewed in cross section, is not markedly convex, concave or irregular. It can be appropriately applied to area mines, contour mines, and mountaintop removal mines and works equally well in steep or gentle topography. The data input requirements are minimal. The acre-acreage represented by the lowermost unit (usually measured as the coal outcrop limit) and the uppermost unit must be provided. Where no acreages are provided, the default value of 1.0 is used for all intervals and the spreadsheet performs column (thickness-weighted) calculations. If the drill hole is located to represent maximum cover, then the top acreage is very small and the default value of 1.0 acre is probably appropriate.

If the drill hole is located where overburden thickness is at a maximum, then the modeled geometry resembles a cone and the calculated results should approximate those using diPretoro's method. However, for most applications where the uppermost unit covers a significant acreage but less than the lowermost unit, the site geometry is modeled as a truncated cone. Area mines are represented with nearly equal top and bottom acreages. For multiple drill hole sites, a combination of geometries may be most appropriate. For example, where interior polygon sections which are bounded by other polygons rather than the coal outcrop limits exist, they are best represented as area mine sections with the bottom acreage equal to the top acreage.

Where unusual topography occurs which renders the linear interpolation method inaccurate, the overburden analysis can be divided into two or more sections. Measured acreages are used for the upper and lowermost units of each section and the values are interpolated between measured units.

Actual volumes are calculated by multiplying the unit thickness by its area. But ABA data are expressed as tons per thousand tons of overburden. Therefore, it is more appropriate to evaluate the data in the same units. The importance of using weight rather than volume units is intensified where the unit weights of the rock types varies significantly. ABA values are expressed in terms of absolute quantities by multiplying their volumes by unit weights. The spreadsheet includes default unit weight values for each rock type. Unit weights typical of Allegheny group rocks in western Pennsylvania were obtained from Geyer and Wilshusen (1982). Coal and carbonolith (carbonaceous sedimentary rock) unit weights were determined from PaDER file data. Through a series of nested "IF" operators, the appropriate unit weight is selected according to the rock type specified. The unit weight for any particular rock type can be changed by entering the desired value in the unit weight table.

Most ABA reports include the "pavement" or underlying strata, which can vary in thickness. Although this material will not be mined, it is presumed that at least the uppermost portion of it will be disturbed by mining and that it will have some impact on mine drainage chemistry. For most applications, it is appropriate to include the upper foot of pavement material as the lowermost sample interval in the spreadsheet.

Fraction Spoiled

Previous quantitative evaluations of ABA data invariably discounted the coal, presuming that its recovery in the mining operation was 100% complete. Typically this is not the case, and pit losses in the order of 5 to 20% can be expected. The spreadsheet includes a column to indicate the fraction of

material to be returned to the backfill. For overburden, this will be 1.0 (i.e., 100%) since all of the overburden will be returned. Thus, the default value is set at 1.0. For coals which will be removed, a fraction representing pit losses can be entered (such as 0.10). This permits the calculations to reflect the retention of potentially acid forming pit cleanings and coal rejects. It may also be possible that various alternate mining schemes are proposed, such as removal of some overburden strata either for commercial purposes or to minimize acid formation. The fraction spoiled column can be used to reflect this.

NP and MPA

For each stratigraphic (or sample) interval the maximum potential acidity (MPA_I) and neutralization potential (NP_I) are calculated and expressed as total tons $CaCO_3$ equivalent using the following equations:

$$MPA_I = \%Sulfur \times 31.25 \times T_I \times A_I \times Unit\ Wt. \times Fraction\ Spoiled \quad (2)$$

$$NP_I = NP \times T_I \times A_I \times Unit\ Wt. \times Fraction\ Spoiled \quad (3)$$

Where: T_I = Thickness of sample (stratigraphic) interval (feet)

A_I = Acreage covered by sample interval

These two values represent the total amount of potential acidity and neutralization potential for a single interval. In this sense, the spreadsheet goes one step beyond volumetric adjustment of the acid base accounting data by using actual densities to calculate total tonnages. Then, for each interval, the net NP (NNP_I) is determined by subtracting MPA_I from NP_I. The total tons of overburden for a sample interval is calculated by multiplying thickness times unit weight times area. This number will be used for subsequent summary parameters.

Alkaline Addition Rate

For mine sites where off-site alkaline materials will be imported, the impact of the additional alkaline material, in terms of ABA summary parameters, can be examined by including it in the ABA calculations. A spreadsheet entry (labelled ALK ADD (tons/ac CaCO3) in Figure 1) is used. The "alkaline addition" rate is entered in units of tons $CaCO_3$/acre. If a different material or impure limestone will be used, it must be converted to $CaCO_3$ equivalent. Since the acreage of the bottom sample interval equals the total surface acreage represented by this drill hole, the alkaline addition rate per acre is multiplied by this number to obtain the total quantity of imported alkaline material as $CaCO_3$. This value is added to the column of NP values and is reflected in the total NP. It is also added to the total overburden weight for calculation of NP and MPA in tons/1000 tons.

Summary Parameters

The principal purpose of the overburden spreadsheet is to provide useful parameters which summarize the aggregate overburden characteristics. The summary parameters calculated by the spreadsheet, along with their formulas, are listed in Table 1. The most obvious parameters are calculated total tonnages of MPA, NP, NNP, and total tons of overburden. They represent absolute amounts expressed in tons and are calculated by summing the value for each individual stratigraphic interval. Total tons MPA, NP and NNP are also expressed as tons per thousand tons of overburden representing the entire overburden volume as if it were a single homogeneous sample.

Table 1. ABA spreadsheet summary parameters

Parameter	Description	Formula
tons overburden	total weight of overburden	Σ tons overburden for each sample interval
MPA (tons)	total maximum potential acidity	Σ MPA for each sample interval
MPA[1] (tons/thousand)	"	(MPA (tons)/tons overburden)x 1000
NP (tons)	total neutralization potential	Σ NP for each sample interval[2]
NP[1] (tons/thousand)	"	(NP (tons) / tons overburden) x 1000
NNP (tons)	total net neutralization potential	NP (tons) - MPA (tons)
NNP[1] (tons/thousand)	"	(NNP (tons)/tons overburden) x 1000
overburden volume (acre-ft.)	total volume of overburden	Σ (thickness x acreage x fraction spoiled) for each interval
percent sandstone	total volume - weighted percent sandstone	(Σ (thickness x acreage x fraction spoiled) for each sandstone interval/overburden volume) x 100
DER ratio	NP to MPA ratio	NP (tons)/ MPA (tons)
diPretoro ratio	"	NP[1] (tons)/MPA[1] (tons)
tons/acre required	C_aCO_3 equivalent required for DER Ratio = 1.0	NNP (tons) / acreage at bottom sample interval (> 0 = excess; < 0 = deficiency)

[1] for diPretoro method, calculated as described by diPretoro 1988.
[2] includes NP from alkaline addition

For comparison, the same parameters are calculated using diPretoro's (1988) triangle-volume weighting method. As part of a study on the effectiveness of alkaline addition in ameliorating acid mine drainage (Brady et al. 1990), the spreadsheet was used to characterize overburden conditions for ten different mine sites. The results using the acreage interpolation method and diPretoro's method are expressed as aggregate NNP and as the NP/MPA ratio and are compared in Table 2. Although they always differ slightly, the results from both methods are usually fairly close, especially the NP/MPA ratio. In most of these cases, the diPretoro method calculated a somewhat lower NNP. This apparently results from the diPretoro triangle-approximation method which tends to underestimate upper, generally higher NP strata where the mine site configuration resembles a truncated cone or where overburden holes were not drilled at maximum cover.

Tons per acre NP required

Especially where alkaline addition requirements are to be determined, it is useful to know the limestone application rate which would be required to fulfill any net neutralization potential deficiency. In practical terms, this amount is expressed as the required tons per acre. It is the total tons NNP divided by the total acreage represented by the drill hole (i.e., the acreage of the bottom sample interval). Positive NNPs are indicated as an excess. Negative NNPs are indicated as deficiencies. Of course, this does not presume that merely bringing the NNP to zero indicates a suitable alkaline addition rate. It is presented only as a summary parameter to be used in

Table 2. Comparison[1] of Net NP Values and NP/MPA Ratios as determined by Pa DER spreadsheet and diPretoro methods[2]

SITE NO.	Net NP (tons/thousand)			NP/MPA Ratio		
	Spreadsheet	diPretoro	difference	Spreadsheet	diPretoro	difference
1	6.10	6.94	+0.84	2.33	2.35	+0.02
2	-3.92	-5.93	-2.01	0	0	0
3	2.85	2.54	-0.31	1.36	1.31	-0.05
4	2.77	1.60	-1.17	1.20	1.11	-0.09
5	15.69	15.29	-0.40	2.33	2.26	-0.07
6	4.10	3.05	-1.05	1.52	1.34	-0.18
7	-3.38	-4.52	-1.14	0.59	0.55	-0.04
8	5.55	4.37	-1.18	2.52	2.12	-0.40
9A	-3.40	-4.89	-1.49	0.25	0.20	-0.05
9B	-6.16	-5.21	+0.95	0.06	0.09	+0.03
9C	-9.68	-11.98	-2.30	0.06	0.05	-0.01
10	170.47	144.14	-26.33	6.74	4.64	-2.10

[1]Mine site data from Brady et al. 1990. [2] Method used in diPretoro 1988.

the review of ABA data. Also, where this parameter is used in combination with the significance threshold values discussed below, the limestone requirement may be very different than for a straightforward balance of total NP versus total MPA.

If an alkaline addition rate has already been specified in the spreadsheet input data, it will be reflected in all of the applicable summary parameters. Therefore, the amount required is in addition to the specified value. By comparing the same spreadsheet with and without alkaline addition or at various alkaline addition rates, the impact of the alkaline addition on the ABA summary parameters can easily be observed. In most cases, only very large (500 tons/acre or more) alkaline addition rates have a noticeable impact on these values.

NP/MPA Ratio

diPretoro (1988) used the ratio of aggregate neutralization potential to maximum potential acidity as an ABA summary parameter. When this ratio equals 1, the NP and MPA are theoretically equal. This parameter is calculated by dividing total tons NP by total tons MPA. diPretoro found that mine sites with a ratio less than 2.4 generally resulted in acid mine drainage, whereas mine sites with ratios above 2.4 usually produced alkaline drainage. For comparison, both the numbers derived from the acreage interpolations (labelled as the DER ratio on Figure 1) and the diPretoro triangle method (labelled diPretoro ratio) are shown.

Percent Sandstone

Several studies have found (diPretoro and Rauch 1987, Williams et al. 1982, Brady et al. 1988, Kanai et al. 1989) that where overburden is mostly composed of sandstone, acid drainage predominates. Consequently, a summary value showing the percentage of sandstone overburden was incorporated into the spreadsheet. This is a volume percentage calculated by summing the volume of each sample interval identified as sandstone and dividing this by the total overburden volume.

Significance Thresholds

Brady and Hornberger (1989) suggested threshold values of NP = 30 tons/1000 tons $CaCO_3$ with "fizz" and percent sulfur = 0.5 as reasonable guidelines to define potentially alkaline or acid-producing strata, respectively. Overburden calculations for alkaline addition were made using this scheme, such that $CaCO_3$ requirements were based only on strata with sulfur contents and NPs exceeding these thresholds. The spreadsheet was designed to perform these or similar calculations. Threshold values for sulfur content, NP, and fizz rating are defined near the top of the spreadsheet. Through a series of "IF" operators, MPA and NP values are only calculated for sample intervals which equal or exceed the threshold value. Using threshold values of 0.5% sulfur, NP = 30, and fizz = 1, for example, MPA will be determined only if the sulfur content equals or exceeds 0.5%. Where sulfur < 0.5%, MPA = 0. NP will only be calculated where the sample NP equals or exceeds 30 <u>and</u> fizz is greater than or equal to 1. Therefore, where NP < 30 or fizz = 0, NP = 0.

Presumably, this method can be used to eliminate the NP or MPA contribution from strata which are insignificant in terms of the production of acidity or alkalinity. Of course, if no threshold calculation is desired, then zero is entered for the threshold values. Any combination of thresholds can be used. In this manner, the summary parameters can be readily calculated for a variety of threshold values.

Sulfur Content - Carbonate Equivalence

Cravotta and others (1990) have suggested that by using a stoichiometric equivalence factor of 31.25 to compare percent sulfur (MPA) to NP, the actual neutralization requirements may be understated by a factor of two. The alternate equivalence factor to convert percent sulfur to MPA is 62.5. Accordingly, the spreadsheet also reflects this alternate method. All of the summary values are calculated using both the 31.25 and 62.5 equivalence factors.

Summary and Discussion

Computer spreadsheets are an effective means of summarizing and evaluating ABA overburden analysis data. Volumetric and mass-weighted calculations based on actual mine site geometry and overburden unit weights can easily be performed. Underlying assumptions can be readily changed and the spreadsheet automatically performs any recalculations. Through the use of summary parameters, ABA data from an entire mine site can be integrated to form a conceptual picture of the site's aggregate overburden conditions. Moreover, the spreadsheet can be used to perform various quantitative calculations such as alkaline addition requirements.

A study by Brady et al. (1990) used the spreadsheet method of overburden analysis computation to evaluate the effectiveness of alkaline additives to surface mines in preventing pollution from acid mine drainage. Because it considers rock mass, the fraction spoiled, and a closer approximation of actual site geometry, the spreadsheet offers a better representation of actual field conditions than previous summary methods.

The recent availability of extensive database capabilities and geographic information systems (GIS) provides new uses for summarized ABA data. In many cases, overburden analysis data is functionally irretrievable and can be used only by initiating a very laborious file search and data compilation effort. Computer storage of summarized ABA data through such a database and retrieval system could greatly facilitate its use for cumulative hydrologic impact analysis (CHIA) and comparison of overburden quality with postmining water quality. The computer spreadsheet discussed herein or its modifications could readily support such a system.

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EFFECTIVENESS OF THE ADDITION OF ALKALINE MATERIALS AT SURFACE COAL MINES IN PREVENTING OR ABATING ACID MINE DRAINAGE: PART 1. GEOCHEMICAL CONSIDERATIONS[1]

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Abstract. The addition of alkaline materials to supplement deficient "neutralization potential" (NP) of mine spoil, and thus to prevent or abate acid mine drainage, has not been successful at most surface coal mines in Pennsylvania. A basic problem may have been improper accounting for acid-production potential and thus inadequate addition rates of calcium carbonate ($CaCO_3$), calcium oxide (CaO), or calcium hydroxide [$Ca(OH)_2$] at many mines. The commonly used acid-base accounting method is based on the following overall reaction:

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

where the acidity from 1 mole of pyrite (FeS_2) is neutralized by 2 moles of $CaCO_3$. This method presumes that gaseous carbon dioxide (CO_2) will exsolve, and therefore may underestimate by up to a factor of 2 the quantity of $CaCO_3$ required to neutralize the "maximum potential acidity" (MPA) in the mine spoil. This paper reviews some geochemical reactions involving FeS_2 and various alkaline additives that support the argument that the acid-base accounting method for computing MPA from overburden analyses should be revised. Considering the stoichiometry of the following overall reaction:

$$FeS_2 + 4\ CaCO_3 + 3.75\ O_2 + 3.5\ H_2O \Longrightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 4\ Ca^{+2} + 4\ HCO_3^{-},$$

4 moles of $CaCO_3$ are required to neutralize the <u>maximum</u> potential acidity produced by the oxidation of 1 mole of FeS_2. Therefore, the multiplication factor for computing MPA from the overburden sulfur concentration, in weight percent, should be increased from 31.25 to 62.5.

Introduction

Acid mine drainage (AMD), in which total mineral acidity exceeds alkalinity, is a persistent problem associated with many surface coal mines. AMD typically contains large concentrations of sulfate, iron, and other metals, and results mainly from the exposure and accelerated oxidation of pyrite (FeS_2) and additional iron-sulfide or -sulfate minerals in the coal and overburden. However, where substantial calcium- or magnesium-carbonate materials, such as limestone strata, overlie the coal, mine drainage is commonly alkaline. By corollary, where mined strata contain pyrite but lack naturally occurring calcareous material, the importation and addition of alkaline material to the mine spoil should offset the deficiency and prevent or abate AMD. However, where alkaline additives have been incorporated with mine spoil at surface coal mines in Pennsylvania, few sites have shown improvement in water quality or abatement of AMD (Brady et al. 1990).

This paper describes the chemical reactions that are the basis for computing the <u>maximum</u> potential acidity and net neutralization potential of mine spoil. Emphasis is placed on evaluating reactions with calcite (calcium carbonate, $CaCO_3$), "quick lime" (calcium oxide, CaO), and "hydrated lime" [calcium hydroxide, $Ca(OH)_2$], which are used as alkaline additives intended to produce near-neutral ($6 < pH < 8$) discharge water from surface coal mines.

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Acid-Base Accounting

Acid-base accounting (ABA), which simplifies the complex hydrogeochemical system through use of a limited number of variables, has been used extensively in the past to estimate the quantity of alkaline material required to neutralize the potential acidity of mine spoil (diPretoro 1986; diPretoro and Rauch 1988; Skousen et al. 1987; Erickson and Hedin 1988; Ferguson and Erickson 1988; Brady and Hornberger 1989; Smith and Brady 1990; Brady et al. 1990). ABA was developed on the assumption that the stoichiometry of the following overall reaction of FeS_2 and $CaCO_3$ applies (Sobek et al. 1978; Williams et al. 1982):

$$FeS_2 + 2\ CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \Longrightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 2\ Ca^{+2} + 2\ CO_2(g). \quad (1)$$

The implication of reaction 1 is that acidity produced from 1 mole (mol) of FeS_2 [64 grams (g) of sulfur (S)] is neutralized by 2 mol of $CaCO_3$ (200 g), or 1 g S to 3.125 g $CaCO_3$. On this basis, 31.25 tons of calcium carbonate ($CaCO_3$) will neutralize the acidity from 1,000 tons of rock that contains 1.0 weight percent (%) pyritic sulfur. In accordance with accepted ABA methods (Sobek et al. 1978), the total sulfur concentration in weight percent is multiplied by 31.25 to obtain a "maximum potential acidity" (MPA), which has units of tons of $CaCO_3$ per 1,000 tons of overburden (tons $CaCO_3$/1,000 tons) and which assumes that the sulfur is pyritic and acid producing. The 31.25 multiplication factor was intended to provide equivalent units for direct comparison with "neutralization potential" (NP), which has units of tons $CaCO_3$/1,000 tons. Subsequent workers computed the "net neutralization potential" (NNP) for coal-bearing strata by subtracting volume- or weight-weighted MPA from NP (NNP = NP - MPA) (Erickson and Hedlin 1988; diPretoro and Rauch 1988; Brady et al. 1990). A negative, or deficient, NNP has been interpreted as the quantity of $CaCO_3$ that must be added to abate or prevent AMD. For example, if weight-weighted NP is 30 tons $CaCO_3$/1,000 tons and total sulfur concentration is 1.0%, then MPA = 31.25 tons $CaCO_3$/1,000 tons and NNP = -1.25 tons $CaCO_3$/1,000 tons. To create a net neutral mine spoil, 1.25 tons of $CaCO_3$ would need to be added to every 1,000 tons of overburden. However, the ABA method based on the stoichiometry of reaction 1 may underestimate MPA because of the presumption that CO_2 will exsolve, and thus may underestimate the $CaCO_3$ required to supplement deficient NNP.

Previous Work

Although not originally intended for the purpose, ABA following the method of Sobek et al. (1978) has been used in attempts to predict post-mining water quality. However, several researchers have arrived independently at the conclusion that equal quantities of NP and MPA (computed by multiplying the total sulfur in percent by a factor of 31.25) do not prevent AMD. Brady and Hornberger (1989) identified a given stratum as potentially acid or alkaline producing by using threshold concentrations for total sulfur or NP, respectively, of 0.5 % or 30 tons $CaCO_3$/1,000 tons (and which reacted with dilute hydrochloric acid). These threshold concentrations were corrorabated by laboratory experiments by Williams et al. (1982) and Morrison (1988) and also by Pennsylvania Department of Environmental Resources data on overburden and water quality at numerous surface coal mines. Note that 0.5 percent total sulfur, when multiplied by 31.25 to compute MPA, equals 15.6 tons $CaCO_3$/1,000 tons, roughly half the guideline number of 30 tons $CaCO_3$/1,000 tons for NP. Skousen et al. (1987, p.4) suggested that a stratum which contains values greater than 5 tons $CaCO_3$/1,000 tons as "Max Needed" (negative NNP) produced acid; conversely, values greater than 20 tons $CaCO_3$/1,000 tons as "Excess" (positive NNP) produced alkaline drainage.

diPretoro (1986) and diPretoro and Rauch (1988) showed that NP and MPA were not equivalent in using the ratio derived by dividing the cumulative volume-weighted NP by MPA for composite strata. diPretoro and Rauch (1988) found that sites having a NP/MPA ratio of less than about 2.4 produced acidic drainage, whereas most sites having a ratio greater than 2.4 produced alkaline drainage. Ferguson and Erickson (1988) showed that mine sites with a multiple-strata average NNP of 30 tons $CaCO_3$/1,000 tons or greater always produced alkaline drainage. They also found that 59 percent of mine sites with NNP of 7 to 30 tons $CaCO_3$/1,000 tons produced alkaline drainage, and only 11 percent of the sites with NNP less than 7 tons $CaCO_3$/1,000 tons produced alkaline drainage. Weighted NP in "equivalent" amounts as MPA was not sufficient to prevent AMD.

Geochemistry of Acid Mine Drainage and Alkaline Additives

The following discussion reviews some overall acid-forming and neutralizing reactions that are relevant to AMD, ABA, and the addition of alkaline materials at surface coal mines. No effort is made to account for hydrogeochemical variables such as surface- and ground-water flow paths, proximity and distribution of reacting minerals, solubilities and reaction rates of minerals, or the wide range of hydrochemical conditions in mine spoil.

Production of Acidity

AMD results from the interactions of oxygen, water, bacteria, and sulfide minerals (Singer and Stumm 1970a, 1970b; Nordstrom et al. 1979; Kleinmann et al. 1980; Cathles 1982). Pyrite (FeS_2), and less commonly, marcasite (FeS_2) are the principal sulfur-bearing minerals in bituminous coal (Davis 1981; Hawkins 1984), and because of its wide distribution, pyrite is recognized as the major source of AMD in the eastern United States (Stumm and Morgan 1981, p. 469-471). The following overall stoichiometric reactions may characterize the oxidation of pyrite and other FeS_2 minerals:

$$FeS_2 + 3.5\ O_2 + H_2O \Longrightarrow Fe^{+2} + 2\ SO_4^{-2} + 2\ H^+, \quad (2)$$

$$Fe^{+2} + 0.25\ O_2 + H^+ \Longrightarrow Fe^{+3} + 0.5\ H_2O, \quad (3)$$

$$Fe^{+3} + 3\ H_2O \Longrightarrow Fe(OH)_3 + 3\ H^+. \quad (4)$$

The oxidation of sulfide in pyrite to sulfate (reaction 2) releases dissolved ferrous iron (Fe^{+2}) and "acidity" (H^+) into the water. Subsequently, ferrous iron is oxidized to ferric iron (Fe^{+3}) (reaction 3), which if separated from the pyrite surface, hydrolyzes and forms insoluble ferrihydrite [$Fe(OH)_3$)] (reaction 4), and releases more acidity. The overall combination of reactions 2 through 4 may be written as follows:

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O \Longrightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 4\ H^+. \quad (5)$$

In reaction 5, 3.75 mol of oxygen are consumed to oxidize 1 mol of pyrite, and 2 mol of sulfate, 4 mol of acidity, and 1 mol of ferrihydrite are produced.

Neutralization of Acidity

Acidity produced by the aqueous oxidation of pyrite may react with carbonate, silicate, and hydroxide minerals composing the sedimentary rocks in the coal-bearing sequence. Dissolution of these acid-soluble minerals neutralizes acidity and produces the other major ions in AMD in addition to sulfate and iron, such as manganese, aluminum, calcium, magnesium, sodium, potassium, and silica.

The most acid-reactive minerals are the carbonates: calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], and siderite ($FeCO_3$). Carbonates are present in variable quantities as individual mineral grains and as cementing agents in limestone, dolostone, sandstone, and shale. Limestone and dolostone are composed predominantly of calcite and dolomite, respectively; shale and sandstone are composed predominantly of silicate minerals, but may contain some carbonate as cement or matrix. Dissolution of calcite, dolomite, and other calcium- or magnesium-bearing carbonate minerals tends to reduce acidity, increase alkalinity, and raise pH; however, dissolution of siderite and the subsequent hydrolysis of iron may increase acidity, and reduce pH. The dissolution of calcite by the following sequence of reactions serves as an example:

$$CaCO_3 + 2\ H^+ \Longrightarrow Ca^{2+} + H_2CO_3^*, \quad (6)$$

$$CaCO_3 + H_2CO_3^* \Longrightarrow Ca^{2+} + 2\ HCO3^-. \quad (7)$$

Reaction 6 represents acidic conditions (pH < 6.4) where calcite is not abundant and is totally dissolved by reacting 1 mol of calcite and 2 mol of free acidity and producing 1 mol of dissolved calcium and 1 mol of dissolved carbon dioxide {[$H_2CO_3^*$] = [CO_2(aq) + [$H_2CO_3^o$]}, which is a weak acid (Krauskopf 1979, p. 40-42; Stumm and Morgan 1981, p. 171-214; Hem 1985, p. 92, 105-111). Note that gaseous CO_2 is not indicated as the product in reaction 6. In practice, during laboratory determination of overburden NP, CO_2 may be exsolved when calcite and other carbonate minerals are reacted with dilute acid. However, CO_2 may concentrate in both the gaseous and aqueous phases in mine spoil. Elevated partial pressure of CO_2 in the unsaturated zone of mine spoil is common (Lusardi and Erickson 1985), especially during the growing season, and will cause a concomitant increase in the concentration of $H_2CO_3^*$ and other aqueous carbon-dioxide species (Langmuir 1971; Shuster and White 1972; Harmon et al. 1975).

If calcite is abundant, the dissolved carbon dioxide will continue to react with calcite (reaction 7) producing bicarbonate ions and raising pH. The overall combination of reactions 6 and 7 represents the condition where dissolution of calcite produces "alkalinity" in excess of "acidity" and raises the pH above 6.4 where bicarbonate (HCO_3^-) is the dominant dissolved carbon-dioxide species:

$$CaCO_3 + H^+ \Longrightarrow Ca^{2+} + HCO3^-. \quad (8)$$

Reaction 8 shows that 1 mol of calcite will neutralize 1 mol of free acidity and produce 1 mol each of dissolved calcium and bicarbonate. Reactions 5 and 8 may be combined to indicate a "maximum" neutralization potential of calcite, where no CO_2 is exsolved:

$$FeS_2 + 4\ CaCO_3 + 3.75\ O_2 + 3.5\ H_2O \Longrightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 4\ Ca^{+2} + 4\ HCO3^-. \quad (9)$$

Reaction 9 shows that the acidity produced from the oxidation of 1 mol of FeS_2 (64 g S) may be neutralized by 4 mol of $CaCO_3$ (400 g), which is a mass ratio of 6.25 g of calcite to 1 g of pyritic sulfur. The calcite-to-sulfur mass ratio of 6.25 is twice the ratio of 3.12 which would be derived considering the unlimited exsolution of CO_2 (Williams et al. 1982).

On the basis of the calcite-to-sulfur mass ratio of 6.25, a multiplication factor of 62.5 to compute MPA from total sulfur is appropriate for ABA if all sulfur is from pyrite. Therefore, considering the earlier example for overburden, where NP = 30 tons $CaCO_3$/1,000 tons and total sulfur = 1 % (only now using the 62.5 factor), then MPA = 62.5 tons $CaCO_3$/1,000 tons and NNP = -32.5 tons $CaCO_3$/1,000 tons. Instead of the previously computed 1.25 tons, now 32.5 tons of $CaCO_3$ per 1,000 tons overburden would be required to supplement the deficient NNP.

"Quick lime" (calcium oxide, CaO) and "hydrated lime" [calcium hydroxide, $Ca(OH)_2$] (Rochow 1977, p. 129), which compose lime-kiln flue dust, have twice the neutralization potential as calcite. Because the lime compounds have lower unit mass than $CaCO_3$, they are required in equivalent ratios less than 3.12 according to the following reactions:

$$Ca(OH)_2 + 2\ H^+ \Longrightarrow Ca^{+2} + 2\ H_2O, \quad (10)$$

$$CaO + 2\ H^+ \Longrightarrow Ca^{+2} + H_2O. \quad (11)$$

Reactions 10 and 11 show that 1 mol of hydrated lime (74 g) or 1 mol of quick lime (56 g) may neutralize 2 mol of free acidity. Combining reactions 10 and 5:

$$FeS_2 + 2\ Ca(OH)_2 + 3.75\ O_2 \Longrightarrow Fe(OH)_3 + 2\ SO_4^{-2} + 2\ Ca^{+2} + 0.5\ H_2O. \quad (12)$$

Reaction 12 shows that the acidity produced from the oxidation of 1 mol of pyrite (64 g S) may be neutralized by 2 mol of calcium hydroxide (148 g), which is a mass ratio of 2.31 g of calcium hydroxide to 1 g of pyritic sulfur. Analogously, from combining reactions 5 and 11, a mass ratio of 1.75 g of calcium oxide to 1 g of pyritic sulfur is required to attain neutralization. Thus on a weight basis, 1 ton of $Ca(OH)_2$ has the neutralization equivalent of 2.7 tons of $CaCO_3$.

Siderite ($FeCO_3$) is common in coal-bearing strata and is frequently cited as having no net effect on acid-production or neutralization where CO_2 gas is exsolved (Stumm and Morgan, 1981; Williams et al. 1982). However, considering the argument for conditions with elevated partial pressure of CO_2, oxidation of siderite may produce net acidity in the form of dissolved carbon dioxide:

$$FeCO_3 + 0.25\ O_2 + 2.5\ H_2O \Longrightarrow Fe(OH)_3 + H_2CO_3^*. \quad (13)$$

The $H_2CO_3^*$ generated in reaction 13 may react with additional carbonate, silicate, or hydroxide minerals. The effect of siderite as a potential acid-forming mineral is apparent by combining reactions 7 and 13 as follows:

$$FeCO_3 + CaCO_3 + 0.25\ O_2 + 2.5\ H_2O \Longrightarrow Fe(OH)_3 + Ca^{+2} + 2\ HCO3^- . \quad (14)$$

In reaction 14, the acidity produced from 1 mol of siderite is neutralized by 1 mol of calcite. Thus, if siderite is present, additional alkaline material beyond that required to neutralize the acidity from pyrite may be necessary. Impurities such as Mn, Mg, and to a lesser extent Ca, may substitute for Fe in siderite (Morrison et al. 1990). The Fe and Mn may hydrolyze and produce acid; however, the Mg and Ca may have neutralizing ability similar to dolomite and calcite.

Discussion

The presentation of acid-forming and acid-neutralizing reactions was simplified by writing and then combining independent equations as "neutral overall" reactions that eliminated H^+ as a reactant or product. Thus, the overall stoichiometries in reactions 1 and 9 equate quantities of acid-producing and -neutralizing materials and are useful for acid-base accounting application. However, reactions 1 and 9 are "end-member" reactions; the hydrogeochemical relations in mine-spoil ground water or discharge probably lie soemwhere between the two end members because some CO_2 will exsolve and some will dissolve.

No attempt has been made in the above review to discuss the combined effects of variable purities, degrees of crystallinity, and particle sizes of minerals; microbiological catalysis of reactions; or relative reaction rates. For example, the presumption that 4 mol of $CaCO_3$ are required to neutralize the acidity from 1 mol of FeS_2 (reaction 9) implies that the production of acidity is rate limiting, or slow relative to neutralization, and that neutralization is instantaneous. Furthermore, the computation of maximum potential acidity (MPA) as 62.5 times the total sulfur concentration, in weight percent, should yield a conservative estimate, because not all CO_2 will dissolve nor will all sulfur be pyritic and acid producing. To determine quantities of alkaline additives required at surface coal mines, site-specific characteristics such as mining method, pre- and post-mining overburden composition, post-mining reclamation and hydrogeology, and alkaline additives used and placement technique also must be evaluated. The companion paper by Brady et al. (1990) reviews some of the site-specific factors and compares post-mining water quality and ABA computations of MPA using the conventional and newly proposed multiplication factors of 31.25 and 62.5, respectively, for selected surface coal mines in Pennsylvania.

Summary and Conclusions

In summary, the ABA method currently in use, which presumes 2 mol of H^+ may be neutralized by 1 mol of $CaCO_3$, may underestimate by up to a factor of 2 the $CaCO_3$ required to neutralize the maximum potential acidity from the oxidation of pyrite and the hydrolysis and precipitation of iron, because of the presumption that all CO_2 will exsolve. However, some CO_2 will dissolve forming a weak acid that reacts with carbonate minerals. Assuming no exsolution of CO_2, 1 mol of FeS_2 will produce 4 mol of H^+, which may be neutralized by 4 mol of $CaCO_3$ (reaction 9), 2 mol of $Ca(OH)_2$ (reaction 12), or 2 mol of CaO. On a weight basis then, 1 g of pyritic sulfur may be neutralized by 6.25 g of $CaCO_3$, 2.31 g of $Ca(OH)_2$, or 1.75 g of CaO. Considering these equivalent weights, MPA as tons of $CaCO_3$ deficiency per 1,000 tons of overburden should be computed by multiplying total sulfur, in weight percent, by 62.5. The above discussion is based only on the stoichiometry of the overall reactions (9 and 12) and assumes that the rate of acid production will not exceed the rate of acid neutralization. The actual acidity may be less than the computed MPA because not all CO_2 dissolves and not all sulfur generates acidity. Finally, dissolution of siderite will produce net acidity when the partial pressure of CO_2 becomes elevated and the iron is hydrolyzed and precipitated.

In conclusion, for conservative estimates of overburden net neutralization potential (NNP), a revised multiplication factor of 62.5 should be used to compute maximum potential acidity (MPA) from the total sulfur concentration, in weight percent.

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EFFECTIVENESS OF THE ADDITION OF ALKALINE MATERIALS AT SURFACE COAL MINES IN PREVENTING OR ABATING ACID MINE DRAINAGE: PART 2. MINE SITE CASE STUDIES[1]

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Abstract. The effectiveness of preventing or ameliorating acid mine drainage (AMD) through the application of alkaline additives is evaluated for eight surface coal mines in Pennsylvania. Many of the mine sites had overburden characteristics that made prediction of post-mining water quality uncertain. Alkaline materials were applied at rates ranging from 42 to greater than 1,000 tons as calcium carbonate per acre. In addition, two sites that were mined and reclaimed without alkaline additives are included for comparative purposes.

Overburden sulfur concentration and "neutralization potential" (NP) data for multiple strata at each mine site were used to compute the cumulative, mass-weighted "maximum potential acidity" (MPA) and "net neutralization potential" (NNP = NP - MPA) by using three different calculation methods. Post-reclamation water-quality data were used to compute the net alkalinity (= alkalinity - acidity). The most conservative determination of NNP, whereby MPA is calculated by multiplying the total sulfur concentration, in weight percent, by 62.5 instead of 31.25, yielded the best agreement with net alkalinity (matching signs on NNP and net alkalinity). The error in prediction using each method was that the reclaimed overburden was computed to be alkaline overall (NNP > 0), but the post-reclamation water was acid (net alkalinity < 0).

In general, alkaline addition rates were probably insufficient to neutralize, or too late to prevent, acid production in the mine spoil. At six of the seven mine sites that had overburden with insufficient NP relative to MPA (NNP < 0), the addition of alkaline materials failed to create alkaline mine drainage; AMD was formed or persisted. A control site which also had insufficient alkaline material, but did not incorporate alkaline additives, generated severe AMD. Two sites that had substantial, natural alkaline overburden produced alkaline drainage. Although the addition rates appear to be inadequate, other factors, such as unequal distribution and exposure of the acid-forming or neutralizing materials and hydrogeological variability, complicate the evaluation of relative effectiveness of using different alkaline materials and placement of the acid- or alkaline-producing materials.

Introduction

Acid mine drainage (AMD) from surface coal mines is a severe problem in Pennsylvania as well as other Appalachian coal mining states. Discharges of water from reclaimed mine sites must meet acceptable effluent limits; treatment of the discharges can be a major financial burden to a coal mine operator.

In Pennsylvania, the strata at some mine sites cannot be mined without causing AMD pollution because insufficient quantities of naturally alkaline material are present to neutralize the AMD. At coal mines with abundant naturally alkaline strata, mine drainage is commonly alkaline. Therefore, the importation and addition of alkaline

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material to alkaline-deficient mine spoil may produce sufficient neutralization potential to prevent or abate AMD. However, the majority of mine sites that have been reclaimed using imported alkaline materials produce AMD. One problem is knowing the quantity of alkaline material that must be added to produce the desired effect. Another problem is knowing the best place to add alkaline material within a mine site.

This paper summarizes the history of alkaline addition as a reclamation technique, and presents the results of a study of overburden and water-quality data at 10 reclaimed surface coal mines in the bituminous coal fields of Pennsylvania (fig. 1). Emphasis is placed on evaluating the recommended alkaline-addition rates as compared to the calcium-carbonate deficiency calculated by acid-base accounting (Sobek et al. 1978; Smith and Brady 1990; Cravotta et al. 1990). Factors such as the mine hydrogeology, operational history, mining method, placement and type of imported alkaline material, and selective handling of strata are evaluated. The study sites include mines where alkaline addition was used in an attempt to abate existing AMD problems, as well as mines where alkaline addition was used in an attempt to prevent AMD in areas not previously mined.

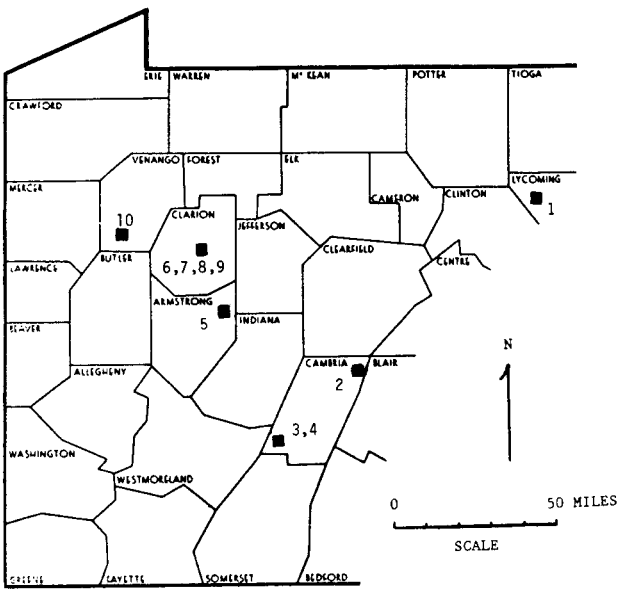


Figure 1. Map showing the locations of mine sites 1 through 10 in western Pennsylvania.

Historical Background on Alkaline Addition in Pennsylvania

The Pennsylvania Department of Environmental Resources (PaDER) is responsible for the review and approval of permits for surface coal mines in Pennsylvania. The PaDER developed procedures for review of plans for alkaline addition on the basis of two reports. The first report is, "Suggested Guidelines for Method of Operation in Surface Mining of Areas with Potentially Acid-Producing Materials," by the West Virginia Surface Mine Drainage Task Force (1979). In "Appendix C" entitled "Immediate Lime Requirement" was the suggestion that, "A realistic lime requirement figure is probably a third of the maximum potential acidity from total sulfur." The second report is, "The Application of Limestone and Lime Dust in the Abatement of Acidic Drainage in Centre County, Pennsylvania" by Waddell et al. (1980). Rock, stratigraphically lower than the coal-bearing units, was excavated and redeposited during construction of Interstate 80. Acidic discharges flowed from the toe of this spoil. A mixture of limestone and lime-kiln flue dust was added to part of the spoil at the rate of 267 tons per acre (tons/acre). Although improvements in water quality were observed within the treated and untreated areas, the improvements in the treated areas were thought to be the most significant.

These early suggestions of success in correcting AMD encouraged the PaDER to permit alkaline addition at surface coal mines where the strata, according to acid-base accounting (ABA), showed only a slight deficiency of calcareous material. ABA considers two variables--neutralization potential (NP), in tons of calcium carbonate per 1,000 tons of overburden (tons $CaCO_3$/1,000 tons), and total sulfur, in weight percent (%), which is converted to "maximum potential acidity" (MPA) reported as tons $CaCO_3$/1,000 tons. A detailed discussion of the chemical stoichiometric relations that are assumed in ABA is given in Cravotta et al. (1990). The net neutralization potential (NNP) of mine spoil is computed by subtracting mass-weighted MPA from NP. A negative, or deficient, NNP has been interpreted as the quantity of $CaCO_3$ that must be added to prevent or abate AMD. Alkaline addition rates were generally calculated at one-third the NNP as suggested by the West Virginia Surface Mine Drainage Task Force (1979), although sometimes the addition rate was increased slightly as a "safety factor." As this study clearly shows, most reclamation using alkaline addition at surface coal mines in Pennsylvania has failed to prevent or abate AMD.

Previous studies focused on alkaline addition as a means of abating existing AMD problems (Geidel 1982; Lusardi and Erickson 1985; Caruccio and Geidel 1984, 1986; Waddell et al. 1980) and not as part of the ongoing mining operation. In general, two alkaline-treatment schemes were advanced: (1) Waddell et al. (1980) hypothesized that it was unnecessary to neutralize all the potential acidity in pyritic spoil because the addition of alkaline materials to create pH greater than 4.5 would inhibit the bacterial catalysis of pyrite oxidation. (2) Lusardi and Erickson (1985) assumed that most acid is produced near the surface and that it was only necessary to add sufficient limestone to balance the net deficiency in the upper spoil zone. However, these attempts to abate AMD by adding alkaline material to pyritic spoil resulted in limited, if any, success because effluent limits were seldom met or maintained.

The advent of alkaline addition and selective handling, as well as the poor success of literal interpretation of ABA, necessitated the development of guidelines for understanding which strata were potentially alkaline or acid producing. On the basis of PaDER's experience it was concluded that a NP of 30 tons $CaCO_3$/1,000 tons (and "fizz", effervescence during reaction with dilute hydrochloric acid) and a total sulfur content of 0.5% were

reasonable guidelines to be used in defining strata that were potentially alkaline or acid producing (Brady and Hornberger 1989). Addition rates were generally calculated on the basis of total sulfur values greater than 0.5%; the permittee was given "credit" for strata with NP's greater than 30 tons $CaCO_3$/1,000 tons.

Methods

The method of selection of mine sites for this study was one of gathering data and then eliminating sites for which necessary information was lacking. The data required for site selection included ABA overburden data and post-mining discharge or ground-water-quality data (pH and concentrations of alkalinity, acidity, iron, manganese, and sulfate). Overburden samples must have been collected from drill holes no farther than a few hundred feet from the area mined. Furthermore, the mining methods and plans must have been documented and the alkaline addition must have been performed as specified in the permit. All sites that met the selection criteria were included.

Overburden analysis data for total sulfur and NP at sites 1 through 8 and 10 (fig. 1) were obtained from PaDER permit files. Data for mine site 9 were obtained from U.S. Geological Survey (USGS) project files. Cumulative mass-weighted NNP was calculated by using a computer-spreadsheet program (Smith and Brady 1990) that included multiplication factors of 31.25 and 62.5 to compute MPA from the total sulfur data (Cravotta et al. 1990).

Water-quality data were obtained from coal-company files and PaDER permit or USGS project files; PaDER and USGS samples were analyzed by the PaDER laboratory. Water samples were collected from toe-of-spoil seeps, monitor wells, and (or) deep mine discharges that were downflow from the mine site. Net alkalinity [in milligrams per liter as calcium carbonate (mg/L $CaCO_3$)] was calculated by subtracting acidity (base-neutralizing capacity) from alkalinity (acid-neutralizing capacity) (Stumm and Morgan 1981, p. 163-166). Net alkalinity was used in previous AMD studies (diPretoro 1986; diPretoro and Rauch 1988; Erickson and Hedin 1988) because it reflects the regulatory requirement that alkalinity exceed acidity, and it allows comparison of a single water-quality parameter with overburden NNP.

Water-quality data were evaluated using "notched" boxplots (Velleman and Hoaglin 1981; Helsel 1987) (fig. 2). The box is defined by the interquartile range (IQR = 25th to 75th percentiles). The median (50th percentile) is shown as a "+" within the box. Notches "()" identify the 95-percent confidence interval around the median (Hettmansperger and Sheather 1986) and are useful in testing the difference between median values for data subsets. For example, a pair of boxplots in figure 2 shows that the medians for two subsets of data are significantly different at the 95-percent confidence level. The notches enclosing the median do not overlap--the right-side notch of the upper box is not greater than the left-side notch of the lower box. However, if the notches for a pair of boxplots overlap, then the medians for the two subsets are not significantly different at the 95-percent confidence level.

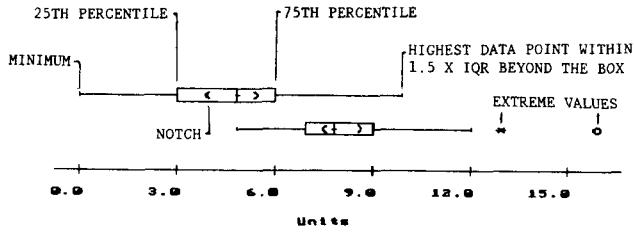


Figure 2. Explanation of boxplots showing median "+" (50th percentile), interquartile range (IQR = 25th to 75th percentile), notches "( )", and extreme values "*" and "o". Horizontal lines are drawn to the data points farthest from the box, yet within a distance 1.5 times the IQR beyond the box. Extreme values beyond this distance are plotted individually.

The mining history for individual case studies was determined from permit-file inspection reports, discussions with coal-company personnel and PaDER mine inspectors, and field investigations by the authors. The historical information gathered includes the area mined, mining method and equipment used, compliance record, hydrologic conditions during mining, speed of the operation, and size of the active mine.

Case Studies

Eight surface-coal mines where alkaline addition was permitted by the PaDER met the selection criteria for inclusion in this study. Two additional mines, where alkaline materials were not added, are also included: Mine site 3 is a control for comparison with site 4, and site 10 is an example with abundant naturally alkaline strata. For comparison of similarities and differences of the ten mine sites selected for study, table 1 lists site characteristics, and table 2 lists the NNP of the overburden and net alkalinity of post-mining water samples. Each mine site is unique in terms of mining methods, size of the mine, hydrogeology, stratigraphic interval, overburden quality, pre- and post-mining water quality, monitoring programs, and so forth. With the exception of mine sites 3 and 9, the mines were developed after 1980, and modern mining and reclamation practices were used. Overburden NP and total sulfur data were available for all sites except site 2, for which only total sulfur data were available. Pre- and post-mining water-quality information was available for all sites except mine site 10. References to MPA and NNP are based on the revised chemical stoichiometry of Cravotta et al. (1990). The following discussions are provided to address the mine and overburden characteristics, methods and materials used for alkaline additives, and related water-quality data.

Mine Site 1: Lycoming County. Mine site 1 is situated on a relatively flat, isolated hilltop. Approximately 210 acres of the lower Kittanning (Bloss) coal were mined, along with lesser acreages of the overlying middle Kittanning, upper Kittanning, and lower Freeport coals. Maximum highwall height was about 135 ft. The mining area includes an abandoned deep-mine complex of approximately 70 acres in the lower Kittanning coal. It also

Table 1: Mine Site Characteristics

MINE SITE	COUNTY	AREA (ACRES)	NO. OF OVERBURDEN HOLES	-------Tons as CaCO3 per acre------- ALKALINE ADDITION TOTAL	PIT FLOOR	SPOIL	SPOIL SURFACE	QUALITATIVE OVERBURDEN COMPOSITION**	SELECTIVE OVERBURDEN HANDLING
1	Lycoming	45	3	500	50	350	100	Low NP/Low S	NO
2	Cambria	26	1	42	22	10	10	Low NP/Low S	YES
3	Cambria	47	2	0	0	0	0	Low NP/Med S	NO
*4	Cambria	75	2	648	54	0	594	Low NP/Med S	YES
5	Armstrong	19	1	140	0	0	140	Med NP/Med S	NO
6A	Clarion	54	2	100	20	0	80	Low NP/Low S	NO
7	Clarion	60	2	300	20	0	280	Low NP/Low S	NO
*8	Clarion	29	2	54	0	0	54	Low S/Low NP	YES
*9A	Clarion	2.5	2	1.120	0	0	1,120	Low NP/High S	NO
*9B	Clarion	2.5	2	724	0	0	724	Low NP/High S	NO
*9C	Clarion	2.5	2	6	0	0	6	Low NP/High S	NO
10	Venango	41.5	2	0	0	0	0	High NP/Med S	YES

*Alkaline material includes hydrated lime, $Ca(OH)_2$, which is reported as equivalent tons $CaCO_3$ (see Cravotta et al., 1990).

**NP = neutralization potential, in tons $CaCO_3$ /1000 tons; S = total sulfur concentration, in weight percent.

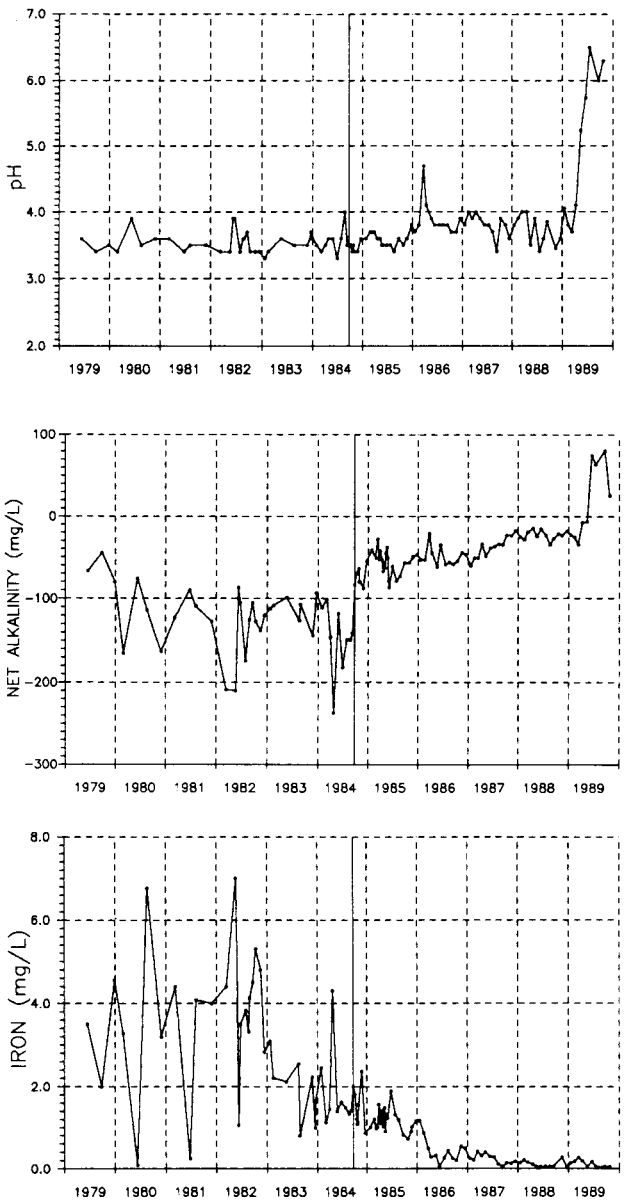
Table 2: Comparison of net neutralization potential of overburden [1], [2] and post-treatment net alkalinity[3] of coal-mine drainage

Mine Site[5]	NNP Before Alkaline Addition (no thresholds)		NNP After Alkaline Addition MPA = 31.25 x % S		NNP After Alkaline Addition MPA = 62.5 x % S		Post-treatment Median Net Alkalinity of Coal-Mine Drainage
	MPA = 31.25 x %S	MPA = 62.5 x %S	(no threshold)	(thresholds)[4]	(no threshold)	(thresholds)[4]	
1	+6.03	+1.51	+6.90	-0.31	+2.31	-1.43	+67
2	-3.92	-7.84	-3.06	-1.73	-6.98	-4.32	-62
3	+2.85	-4.97	+2.85	-3.76	-4.97	-7.71	-468
4	+2.77	-10.81	+4.91	-6.07	-7.97	-13.03	-74
5	+15.69	+3.91	+16.68	+14.65	+4.91	+7.06	+11
6 A	+4.10	-3.82	+4.36	+2.88	-3.56	-1.71	-55
7	-3.88	-11.67	-1.14	-1.03	-9.43	-4.30	-685
8	+5.55	+1.90	+5.76	+3.17	+2.32	+1.88	-184
9 A	-3.40	-7.92	-0.81	+0.61	-2.91	+1.04	-2190
B	-6.16	-13.23	-3.65	-2.20	-9.99	-6.19	-860
C	-9.68	-20.74	-9.66	-6.83	-20.70	-13.65	-3332
10	+170.47	+156.81	+170.47	+168.77	+156.81	+156.6	+118

1 "Net neutralization potential" (NNP = NP-MPA) reported in tons $CaCO_3$/1,000 tons (Smith and Brady 1990); "maximum potential acidity" (MPA) computed by multiplying total sulfur (S), in weight percent by 31.25 and 62.5, respectively (Cravotta et al. 1990).
2 An appendix with the actual overburden analysis data is available from the authors.
3 Net alkalinity (= alkalinity - acidity) in mg/L as $CaCO_3$.
4 Threshold where total S<0.5%, calculated MPA=O; where NP<30 or no effervesence reaction with dilute HCl, calculated NP=0.
5 Mine sites 3 and 10 did not have alkaline additives incorporated with the mine spoil. These sites are included for comparative purposes.

includes approximately 34 acres where the lower Freeport coal was previously surface mined; drainage was diverted from the surface mined lower Freeport to the deep mine via an underdrain system. Mining has taken place continuously since the early 1970s and continues to date. Underground mine workings were first encountered in late 1984. Approximately 45 acres have been daylighted using a dragline.

Most ground water from the site discharges from the abandoned underground mine via an air shaft. Water quality was monitored at this discharge point since 1979, and flow rates were monitored continuously since 1982. Prior to the 1985 water year (October 1, 1984 through September 30, 1985), pH and net alkalinity were relatively constant, while iron and manganese concentrations varied by a factor of 10 (fig. 3).



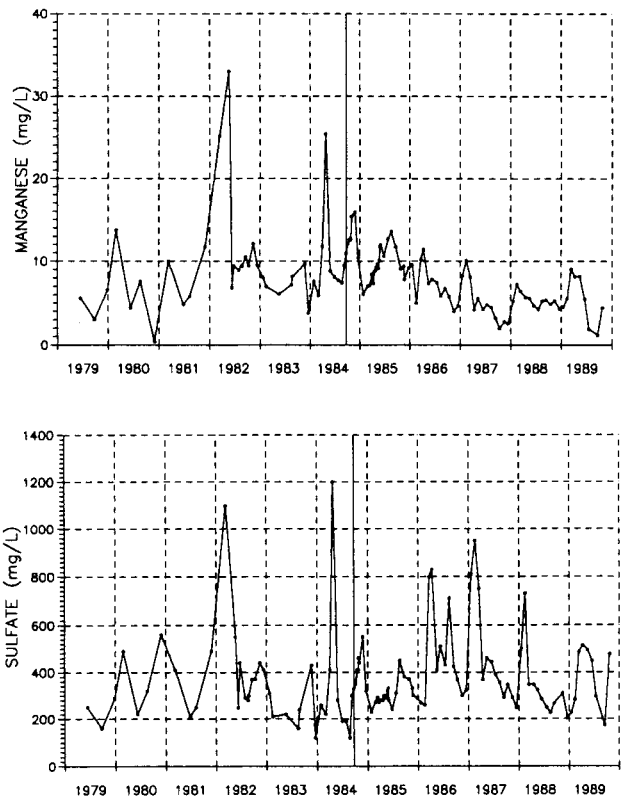


Figure 3. Changes in selected water-quality characteristics over time at mine site 1 in Lycoming County. The vertical line in 1984 indicates the time when deep mine daylighting and increased alkaline addition began.

Overburden from the three drill holes sampled is characterized by low total sulfur and low NP contents. However, many samples are composites of strata from large intervals (up to 28 ft thick). The highest total sulfur content measured was 1.29%. Only one sample, other than the coals, contained sulfur exceeding 0.5%. The highest NP was 33 tons $CaCO_3$/1,000 tons.

Pit cleanings were segregated from the overburden using a loader and were placed high in the backfill. The operator initially applied nearly-pure $CaCO_3$ (a limestone crusher screening waste product) to the pit floor and upper part of the backfill at a total rate of about 50 tons/acre. In late 1984, roughly at the same time the deep mine complex was encountered, this rate was increased to approximately 500 tons/acre, a rate that exceeded permit requirements. Approximately 50 tons/acre were spread on the pit floor and 100 tons/acre were applied to the upper surface of the rough backfill. The remaining 350 tons/acre were distributed through the backfill using limestone crusher screenings as blast hole stemming. From January 1985 through September 1989, a total of 19,000 tons of calcareous material were applied over 48 acres. Table 2 indicates that the overburden NNP increases, and is positive, after the addition of limestone on the basis of MPA computed by multiplying total sulfur by 31.25 or 62.5; however, NNP is negative if thresholds are used. For site 1 the NNP computed using the thresholds is unreliable because large intervals of strata were sampled and composited causing the possible dilution of high-sulfur or high-NP concentrations.

Figure 3 shows that a dramatic increase in net alkalinity, accompanied by a decrease in iron concentrations, occurred during the 1985 water year and continued through the 1989 water year. Sulfate and manganese concentrations, however, show little change (fig. 3). Manganese has a tendency to remain dissolved in acidic to neutral solutions (pH < 8) whereas iron will readily precipitate at pH > 4.5 (Hem, 1985). This increase in alkalinity is concurrent with the deep-mine daylighting and the application of alkaline material at a rate of 500 tons/acre. The increasing alkalinity of the water in combination with the persistently elevated sulfate concentrations indicates that acid production continues in the spoil but is neutralized.

Since 1988, water quality at the deep-mine discharge has attained "conventional mine-drainage effluent standards" (alkalinity > acidity; 6 < pH < 8; Fe < 6 mg/L; Mn < 4 mg/L).

The apparent neutralization of acidity indicates that the addition of alkaline materials played the dominant role in effecting the water-quality improvement. The removal of unmined, pyritic coal pillars by daylighting may have reduced that contribution of sulfate; however, surface mining may have produced additional sulfate which offsets the daylighting reduction. Furthermore, if neutralizers were liberated from the overburden, net alkalinity would have increased prior to the alkaline addition.

Mine Site 2: Cambria County. Site 2 encompassed 26 acres of Mercer coal removal by surface mining. No part of the permit area had been previously mined, although the adjacent property had been extensively mined, with AMD resulting. A period of 43 months elapsed from initiation of mining on mine site 2 to final backfilling (0.6 acres/month). Maximum highwall height was 45 ft.

Site 2 occupies the crest of a gently sloping hill and recharge to the site is predominantly from precipitation. Because AMD occurred at an adjacent mine, the permit approval for mining at site 2 required overburden analysis and alkaline addition. The strata were assumed to lack substantial carbonate minerals, so only total sulfur was determined in the overburden samples.

The sulfur concentrations and lithologic descriptions of samples from one overburden hole drilled within the area mined were used in ABA calculations (table 2); however, additional lithologic data from other drill holes were used to define the stratigraphy. The overburden composition and thickness differed across the site, because of removal of strata by erosion and replacement by channel sandstones, and because of bifurcation (splitting) of the coal seam. The number of splits in, and thickness of the coal (2 to 5 ft), differed from hole to hole. The majority of the strata consists of sandstone, with "coal spars" at the base. In most drill holes a 0.5- to 3-ft-thick, black, carbonaceous shale was encountered immediately above the coal. The overburden hole encountered 1.5 ft of this black shale, which contains 1.12% total sulfur, and 2 ft of coal, which contains 2.64% total sulfur. Because of the numerous binders in the coal, approximately 30 percent of the coal horizon was spoiled as "pit cleanings." The pit cleanings were segregated and placed in pods a minimum of 10 ft above the pit floor to keep them above the water table after the mine was reclaimed. Because of the large amount of pit cleanings and the thin cover, some of this material was placed within a few ft of the final graded surface.

The alkaline material consisted of baghouse limestone (captured air-borne particulate material), which was applied at a rate of 42 tons/acre. About 22 tons/acre were added to the pit floor; about 10 tons/acre were added to the tops of the pit-cleaning pods and to the backfilled surface prior to replacement of topsoil.

About 200 ft downslope and downdip from mine site 2, water discharges from a seep on the adjacent, previously mined area. Samples collected over 3.5 years define conditions prior to mining at site 2 (fig. 4). Since mining at site 2, the pH of the seep has decreased, and acidity, sulfate, iron, and manganese concentrations have increased. Following backfilling, the seep water quality has maintained significantly lower pH and net alkalinity and greater iron, manganese, and sulfate concentrations than are present in the premining samples (fig. 4). Water from a monitor well screened through the backfill was similar in quality to that from the seep. Alkaline addition has not prevented acid formation at this mine site. AMD may have been predicted on the basis of the negative NNP (table 2).

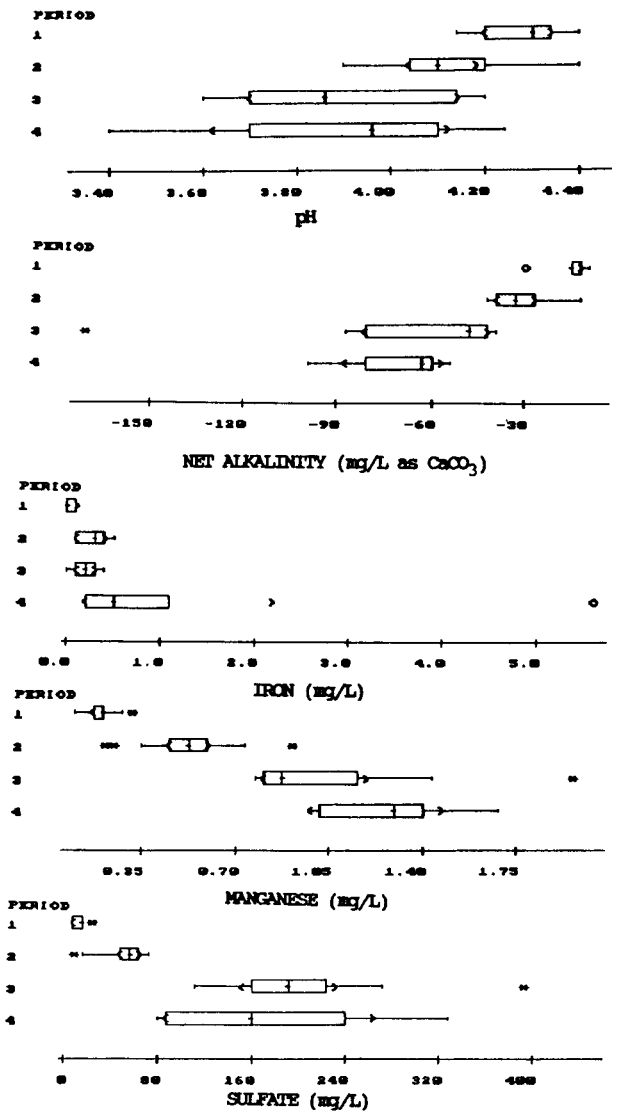


Figure 4. Boxplots showing changes in water quality at mine site 2 in Cambria County. Period 1 represents data collected over a 3-year period prior to activation of mining (N=14). Period 2 is the first 20 months of mining (N=14), and period 3 is the second 20 months of mining (N=11). Period 4 represents post-mining water quality (N=6).

Mine Sites 3 and 4. Cambria County. Site 3 is an unreclaimed mine similar in size and configuration to the adjacent mine site 4. No alkaline addition or special handling was conducted at mine site 3, and the backfilling and reclamation are incomplete. In contrast, mine site 4 is a recently reclaimed mine where alkaline materials have been added to a 75-acre area where the lower Kittanning, lower Kittanning rider, and upper Kittanning coals were mined. The site was active for 60 months (1.25 acres/month). Site 4 can be categorized as a contour block-cut operation with a maximum highwall height of 125 ft. Mining and backfilling were on a continuous basis; the open pit area did not exceeded 100 ft by 300 ft.

Surface and ground waters affected by nearby deep mining or surface mining of the lower Kittanning are severely degraded, whereas waters from unmined areas have near-neutral pH, low buffering capacity, and low concentrations of metals. Although mine site 4 is adjacent to previously affected areas (including mine site 3), it is neither upflow nor downflow from preexisting AMD.

Overburden-analysis data for mine sites 3 and 4 indicate the presence of some potentially acid-producing strata associated with and overlying the lower Kittanning and lower Kittanning rider seams and the absence of strata having NP greater than 30 tons $CaCO_3$/1,000 tons. Overburden quality is summarized in tables 1 and 2. Selective handling of pyritic materials, removal of pit cleanings, and alkaline addition were performed at mine site 4 to avoid post-mining water-quality problems associated with mine site 3. Hydrated lime was added at a total rate of 240 tons/acre [648 tons $CaCO_3$/acre, assuming $Ca(OH)_2$ has 2.7 times the neutralization capacity of $CaCO_3$ (Cravotta et al. 1990)]--a rate that exceeded permit requirements. The alkaline material was distributed on the pit floor at a rate of 54 tons $CaCO_3$/acre; the remaining 594 tons $CaCO_3$/acre were spread over the surface of the rough backfill prior to topsoil replacement (table 1). In accordance with the $CaCO_3$ deficiency, the above alkaline addition rate represented 44% of the total calculated deficiency. The plans for special handling and alkaline addition were diligently implemented, and most of the pyritic materials associated with the lower Kittanning coal were exported from the mine site.

Figure 5 compares the post-mining water quality for two toe-of-spoil discharges at the downdip boundaries of mines 3 and 4. Both sites have AMD; except for iron, the water quality at the alkaline addition site 4 is significantly better than that at site 3. The traditional method of computing the overburden MPA yields positive NNP (table 2); however, use of thresholds or a multiplication factor of 62.5 in ABA computations yields negative NNP values (table 2), which are consistent with the negative value for post-treatment net alkalinity at both sites. The water-quality difference between sites 3 and 4 is attributable to the addition of alkaline materials and the different mining and reclamation methods employed at the two sites.

Mine Site 5: Armstrong County. Mine site 5 encompasses 19 acres. The lower and middle Kittanning coal were removed by surface mining of cover that was 30 to 80 ft thick. The area had been mined previously to a depth of 30 to 40 ft. Eight months elapsed from initiation of mining to completion of backfilling (2.4 acres/month). Reclamation was concurrent with mining.

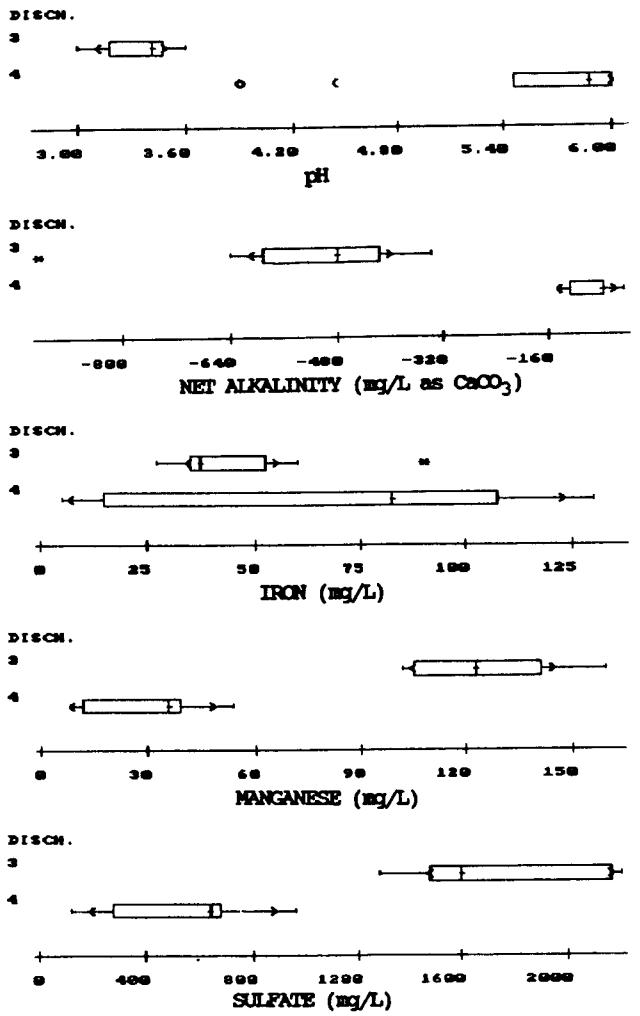


Figure 5. Boxplots showing comparison of water quality data for mine sites 3 (N=8) and 4 (N=5) in Cambria County. Mine site 4 had alkaline addition; mine site 3 did not and served as a control.

Several toe-of-spoil discharges emanated from the previously mined area. The water quality was generally alkaline, and the pH was 5 to 6. Site 5 is located on a hillside with a substantial area upslope from the mine. Ground-water recharge to the site is from direct precipitation and from the drainage of upslope areas.

The overburden hole closest to the area mined was drilled above the highwall through strata that were not mined. The unmined, upper cover was not included in the ABA calculation, and the top part of the hole, to the weathered depth of 20 ft, was assumed to be inert (NP and sulfur are 0). Nine ft of shale above the lower Kittanning coal had total sulfur content ranging from 0.69 to 1.36%, and 28 ft of overlying strata had NP ranging from 30 to 72 tons $CaCO_3$/1,000 tons. The composite strata from this hole contained an equivalent NP as 3,875 tons $CaCO_3$/acre extrapolated over the area mined. Although the overburden analysis for the area mined shows an overall excess of neutralizers (table 2),

overburden holes outside the area mined lacked alkaline strata, and AMD discharges from nearby mines. Therefore, alkaline addition was performed at mine site 5 because of the uncertain effect of mining on water quality and the variable overburden composition. The alkaline material consisted of imported limestone dust that was added at a rate of 140 tons/acre to the backfill surface prior to topsoil replacement.

Boxplots in figure 6 show the quality water from a toe-of-spoil seep below mine site 5. The initial water quality is representative of the effects of the preexisting shallow-cover mining on water quality. The subsequent samples illustrate water quality during and after the thick-cover mining. There is no significant difference between the pre- and post-mining water quality (pH, net alkalinity, iron, manganese, and sulfate) at the 95-percent confidence level. Even the lowest pH and highest concentrations of sulfate and metals measured during the post-mining period meet conventional effluent limits. The positive net

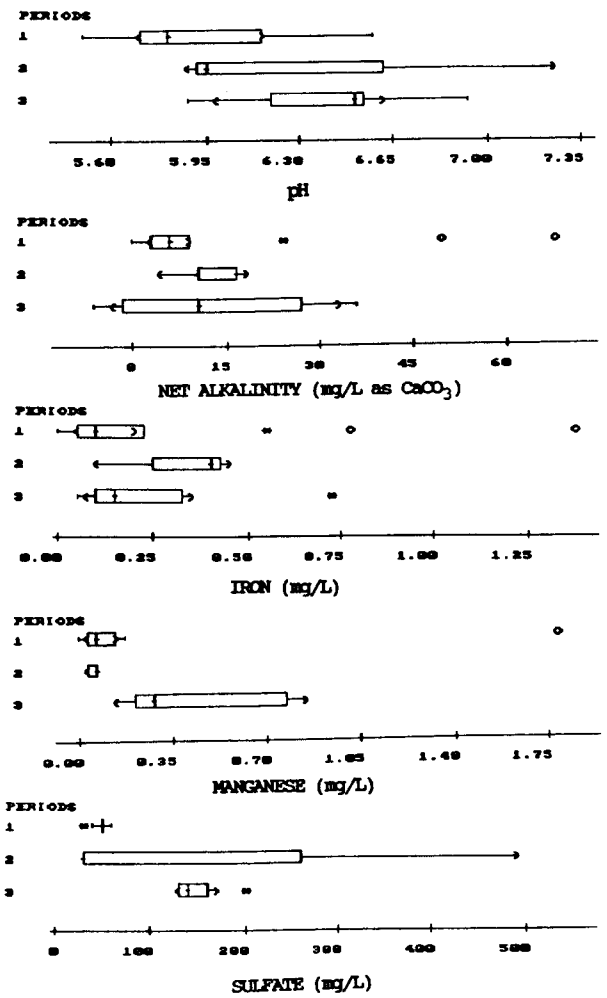


Figure 6. Boxplots showing changes in water quality through time for mine site 5 in Armstrong County. Time 1 represents "premining" data (N=13) over a 2-year period. Time 2 is data collected during mining (N=3), and time 3 is 1 year of post-mining water quality (N=7).

alkalinity of the post-treatment drainage is consistent with positive NNP computed by any method (table 2).

The mining and reclamation at site 5 did not cause degradation of the seep; however, the remedial effects of alkaline addition cannot be isolated from those of naturally occurring calcareous strata. The quantity of naturally alkaline material in the mine spoil was much greater than that of imported alkaline material. Additionally, ground water seepage to the open pit was probably alkaline, and the mining operation proceeded very quickly, thus limiting the aeration of the spoil.

Mine Site 6: Clarion County. Mine site 6 consists of two adjacent, similarly-sized mines, 6A and 6B. Approximately 54 acres of upper and lower Clarion coal were mined at site 6A where alkaline materials were applied during mining and reclamation. The same seams of coal were removed at mine site 6B, but alkaline addition was not implemented; mine site 6B serves as a control. Both mines are located on the side of a hill, and both mines receive some recharge from areas above the area mined. Prior to mining at site 6A, water did not discharge from the coal outcrop, but during mining, seepage(?) water was observed in the open pit.

Rock samples from the two overburden holes indicate considerable differences in the stratigraphic positions of the high-sulfur and alkaline strata. The strata with the highest sulfur content were encountered between the lower and upper Clarion coal seams. Other than the coal samples, no strata contain sulfur greater than 1.0%. Drill hole 1 encountered a 12-ft-thick shale between the Clarion coals that had NP of 36 to 43 tons $CaCO_3$/1,000 tons. Drill hole 2 encountered strata between the coals that had a maximum NP of 21 tons $CaCO_3$/1,000 tons and strata immediately above the upper Clarion coal that had a NP of 32 tons $CaCO_3$/1,000 tons. The amount of naturally alkaline material (composite NP for all strata) was equivalent to 1,925 tons $CaCO_3$/acre for the mined area. A summation of the overburden quality is given in table 2.

Approximately 21 months elapsed from initiation of mining to completion of backfilling at mine site 6A (2.6 acres/ month). Maximum highwall height was about 85 ft. Pit cleanings were selectively handled, and placed at least 10 ft above the pit floor. Alkaline materials were applied as a "safety factor." Baghouse limestone with a $CaCO_3$ equivalent of nearly 100 percent was applied to the pit floor at a rate of 20 tons $CaCO_3$/acre and near the top of the backfilled spoil, but beneath the topsoil, at a rate of 80 tons $CaCO_3$/acre. Application rates on the pit floor on at least one occasion were greater than 20 tons $CaCO_3$/acre. Nevertheless, the quantity of alkaline material added to the spoil may not have been adequate to offset the pre-treatment, negative NNP (table 2). If MPA is computed by multiplying total sulfur by 31.25, then NNP is positive after alkaline addition; however, if MPA is computed by multiplying total sulfur by 62.5, then NNP is negative. Addition of limestone increased the overburden NNP from -3.82 to only -3.56 tons $CaCO_3$/1,000 tons on the basis of the 62.5 factor (table 2).

Discharges from mine sites 6A and 6B were both alkaline and acidic. Special handling of overburden or addition of alkaline material was not performed at mine site 6B, which serves as a control. Post-treatment water-quality data for several discharges are grouped by mine site and are shown as boxplots in figure 7. There is no significant difference between the post-treatment water quality of sites 6A and 6B at the 95-percent confidence level. The negative values of NNP after alkaline addition, on the basis of MPA computed using the factor of 62.5 (table 2), suggest that acidic discharge from mine site 6A may have been predicted. Thus, the alkaline-addition rate at site 6A may not have been adequate to cause substantial improvement in the water quality.

Mine Site 7: Clarion County. Minesite 7 encompassed a mined area of approximately 60 acres of lower Clarion coal and 31 acres of upper Clarion coal. A period of 20 months elapsed from initiation of mining to completion of backfilling (3 acres/month). The maximum highwall height was 60 ft. Although mine site 7 is situated on a hilltop, in a groundwater recharge area, considerable water was encountered during mining. The downflow monitor well consistently had a static water level of 0.5 to 1 ft above the bottom of the coal.

A 2- or 3-acre portion of site 7 was previously mined and abandoned. It had developed a mildly acidic discharge, which could possibly be eliminated by additional mining and reclamation. Because the overburden analysis characterized this site as low sulfur and low NP (tables 1 and 2), mining of the additional 60 acres was planned with an alkaline addition rate of 300 tons $CaCO_3$/acre (about 19 percent of the calculated NNP, where MPA is computed using a factor of 62.5). A 2-ft-thick sandstone stratum contained total sulfur of 0.78% and NP of 28 tons $CaCO_3$/1,000 tons, the highest measured in the overburden, respectively. A 5-ft-thick shale stratum had 0.53% total sulfur. Other than the coal, these are the only strata that contained greater than 0.5% total sulfur.

There was no selective handling plan, however the rock between the Clarion coal seams was routinely placed high in the backfilled mine spoil above the mine floor. Baghouse limestone with a $CaCO_3$ equivalent of nearly 100 percent was applied at a total rate of 300 tons $CaCO_3$/acre. Approximately 280 tons $CaCO_3$/acre were placed on the backfilled surface, below the topsoil, and an additional 20 tons $CaCO_3$/acre were spread on the pit floor.

Figure 8 shows temporal variations in concentrations of acidity and iron in water sampled from a downflow monitor well from 1982 through 1986. Water quality of seepage prior to mining in 1982 can be characterized as mildly acidic with moderate metals and sulfate concentrations, which indicate some effects from previous mining. Figure 8 shows that the concentrations of acidity and iron increased through the period of mining, and then decreased following backfilling. The addition of

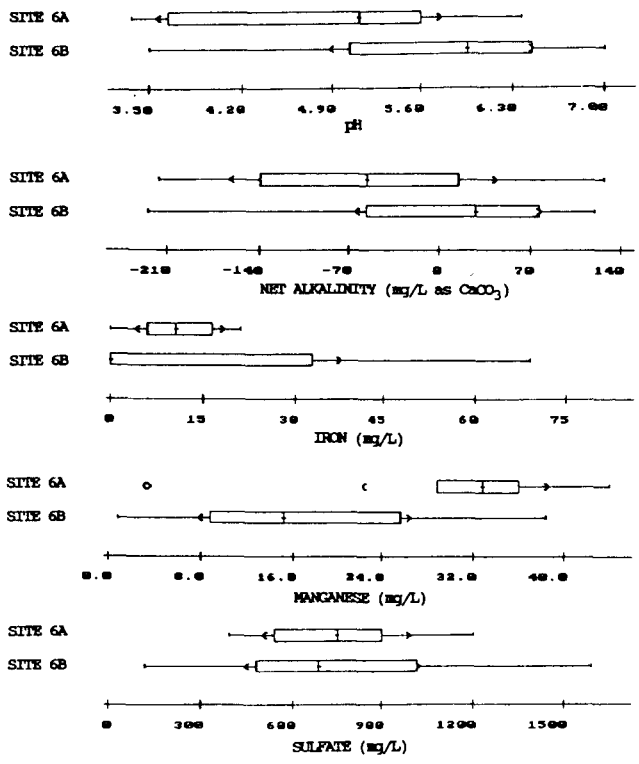


Figure 7. Boxplots comparing water quality of multiple discharges from mine site 6A (N=6) with those from mine site 6B (N=11) in Clarion County. Mine site 6A had alkaline addition; mine site 6B did not and served as a control.

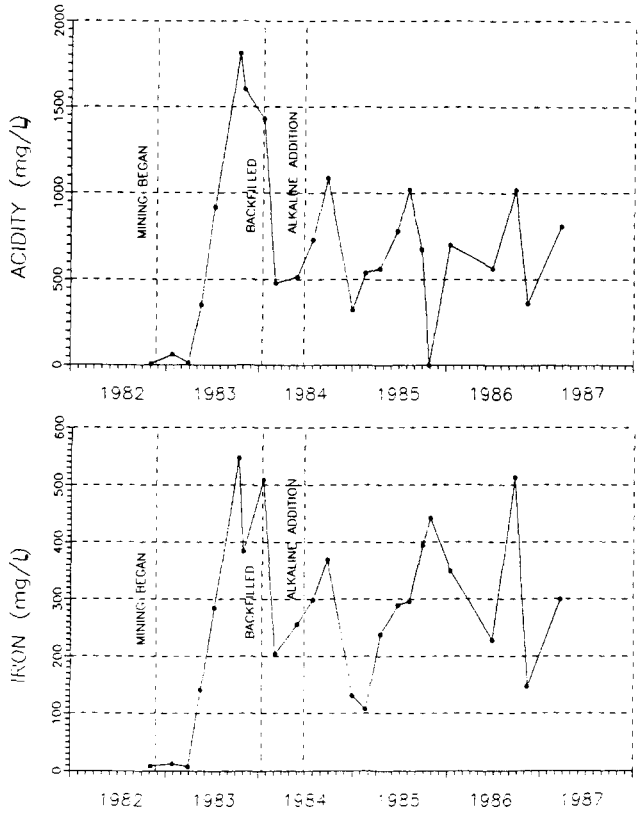


Figure 8. Acidity and iron concentrations over time for a downflow monitor well at mine site 7 in Clarion County.

alkaline materials had no apparent effect on the water quality, which remained considerably worse than that of the pre-mining period. Although the preexisting discharge disappeared, alkaline addition failed to prevent or abate acid ground water. The negative NNP after alkaline addition (table 2) suggests that insufficient quantities of alkaline materials were added and that acidic, post-mining water quality may have been predicted.

Mine Site 8. Clarion County. Mine site8 encompassed a 29-acre area mined for the middle Kittanning coal, 2 acres of which were mined for the upper Kittanning coal. The mine site can be characterized as a hilltop removal/block-cut operation. The maximum overburden thickness was 85 ft. Mining occurred on a continuous basis over a 22 month period (1.3 acres/month), and the open pit area did not exceed 300 by 500 ft. The premining water quality at site 8 can be characterized by near-neutral pH, positive net alkalinity, and low concentrations of iron, manganese, and sulfate (fig. 9).

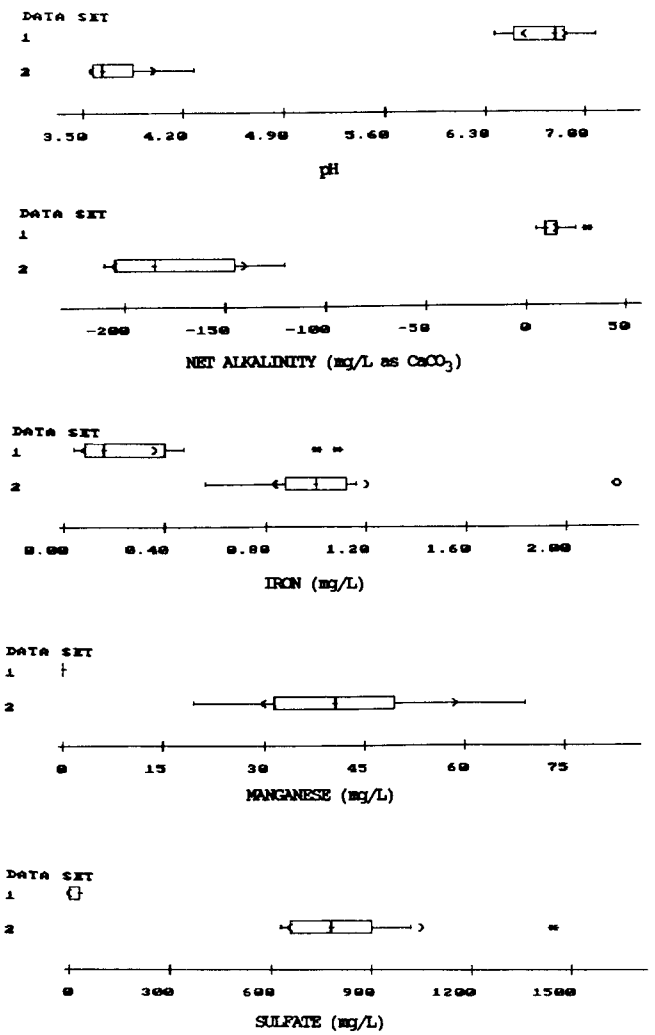


Figure 9. Comparison of pre- (data set 1) and post-mining (data set 2) water quality at mine site 8 in Clarion County. Data set 1 is for a monitor well (subsequently mined through) (N=12). Data set 2 is for a toe of spoil discharge (N=6).

Two holes were drilled in overburden at or near the maximum anticipated final highwall. One of the holes penetrated some strata with NP exceeding 30 tons $CaCO_3$/1,000 tons, but overall the strata had only a slight positive NNP; however, the overburden penetrated by the other hole exhibited a negative NNP (alkaline deficiency). Table 2 summarizes the ABA results of the overburden analysis. The overburden is predominantly sandstone, which contains carbonaceous inclusions and which extends down to the middle Kittanning coal. The sandstone interval from the top of the coal to 2.5 ft above the coal had total sulfur contents ranging from 0.56 to 2.63%.

Most mining took place in the alkaline-deficient area; only a small part of the mine uncovered alkaline strata. Table 2 shows a positive NNP, which is probably higher than was actually encountered by mining. The alkaline-deficient strata encountered by one overburden hole are probably representative of the majority of the strata mined. However, overburden data for samples from both holes were used in ABA calculations.

The 2-ft thick sandstone stratum overlying the middle Kittanning coal seam was selectively handled and segregated. For the alkaline-deficient part of the permit area, alkaline materials were applied a rate of 52 tons $CaCO_3$/acre over the surface of the backfill prior to topsoil replacement.

Following backfilling and reclamation, acidic water began to discharge from an adjacent area downflow from site 8. Figure 9 compares the pre-mining quality of water from a well within the area mined with that from the post-mining discharge. The pH is lower, and concentrations of net alkalinity, iron, manganese, and sulfate are higher in the post-mining discharge than in pre-mining water at the 95-percent confidence level. No mitigative effects are apparent following the alkaline addition. Furthermore, alkaline, not acidic, discharge would be predicted on the basis of the positive NNP data in table 2; however, the calculated NNP may not be accurate because few alkaline strata were mined.

Mine Site 9. Clarion County. Approximately 48 acres of upper and (or) lower Clarion coals were mined intermittently from 1961 through 1975 at mine site 9. About half the area was mined for the lower Clarion coal leaving a 70-ft highwall separating an upper and lower bench. At the completion of mining, the mine was backfilled with overburden and coal waste, including tipple refuse from other mines, and was regraded to the original hillside configuration. A toe-of-spoil seep produced severe AMD that required treatment. In 1984, calcareous waste materials were applied to the surface in quantities that were not sufficient to neutralize MPA but sufficient to produce alkaline water in the unsaturated zone (pH > 4.5) that would presumably inhibit bacteria thought to catalyze pyrite oxidation (Waddell et al. 1980).

The mine receives recharge from the reclaimed hillside and undisturbed hilltop. The reclaimed mine spoil has a total thickness ranging from about 10 to 70 ft, in which ground-water saturation varies from less than 5 to nearly 20 ft. The lower Clarion coal crops out along an intermittent stream at the southern boundary of the mine. The coal was not mined near the stream channel in an attempt to restrict the discharge of ground water from the

mine; this ground water is acidic (pH < 3) and contains substantial concentrations of dissolved sulfate, iron, and manganese (Williams et al. in press).

The overburden and coal are characterized as having high sulfur and negligible calcareous contents (tables 1 and 2). Eleven samples collected during drilling of a 90-ft-deep drill hole through the highwall represent a relatively complete stratigraphic column; typical concentrations of total sulfur range from 0.05 to 4.77%. The highest sulfur concentrations were from the lower Clarion coal and from strata about 1 ft above and below the coal. None of the sampled strata had a NP greater than 3.5 tons $CaCO_3$/1,000 tons. Samples of the tipple refuse had a sulfur content of 1.5 to 2.18%.

In the spring of 1984, limestone fragments (nearly pure $CaCO_3$) and lime-kiln flue dust [$Ca(OH)_2$] were applied on the land surface within two 2.5-acre treatment plots and a control plot. ABA computations were performed using overburden analyses of samples from two or more drill holes in each 2.5-acre plot. Treatment plot 9A had a net deficiency of -1,769 tons/acre and received 40 tons/acre limestone plus 400 tons/acre hydrated lime. Treatment plot 9B had a net deficiency of -2,955 tons/acre and received 400 tons/acre limestone plus 120 tons/acre hydrated lime. However, the control plot 9C had a net deficiency of -3,990 tons/acre and received only 2.4 tons/acre hydrated lime (to allow grass planting). Thus, after alkaline addition, assuming hydrated lime has 2.7 times the neutralization capacity as $CaCO_3$, the net neutralization potentials for plots 9A, 9B, and 9C, respectively, were about -649, -2,231, and -3,984 tons $CaCO_3$/acre.

Ground-water-quality data were collected from two or three monitor wells in each of plots 9A, 9B, and 9C that were screened through the spoil to the mine floor (bedrock). Data for plots 9A and 9B were collected monthly during 1 year before and 3 years after surficial treatment with calcareous materials; however, monthly data for plot 9C were collected only 1 month before but 3 years after treatment. Figure 10 shows that the ground water in the mine spoil, before and after treatment, contained high concentrations of acidity (pH < 4.5; net alkalinity < 0) and of dissolved sulfate, iron, and manganese and that the water-quality generally differed between 9A, 9B, and 9C, reflecting variations in overburden composition and possibly other factors. A comparison of data before and after alkaline addition at plot 9B, shows that none of the parameters (pH, net alkalinity, Fe, Mn, or SO_4) is significantly different at the 95-percent confidence level. Data collected at plots 9A and 9C before and after treatment indicate that pH increased, and Mn concentrations decreased significantly after treatment. However, because the water quality at the control plot 9C may have improved, the improvement in water quality at treatment plot 9A cannot be attributed solely to the addition of alkaline material. Because pyrite and leachable minerals will be depleted as the spoil weathers, a gradual improvement in water quality is expected in both untreated and treated spoil. Nevertheless, if alkaline additives were to prevent or slow the oxidation of pyrite, a difference in the rate of improvement would be expected for the treatment plots 9A and 9B compared with the control plot 9C.

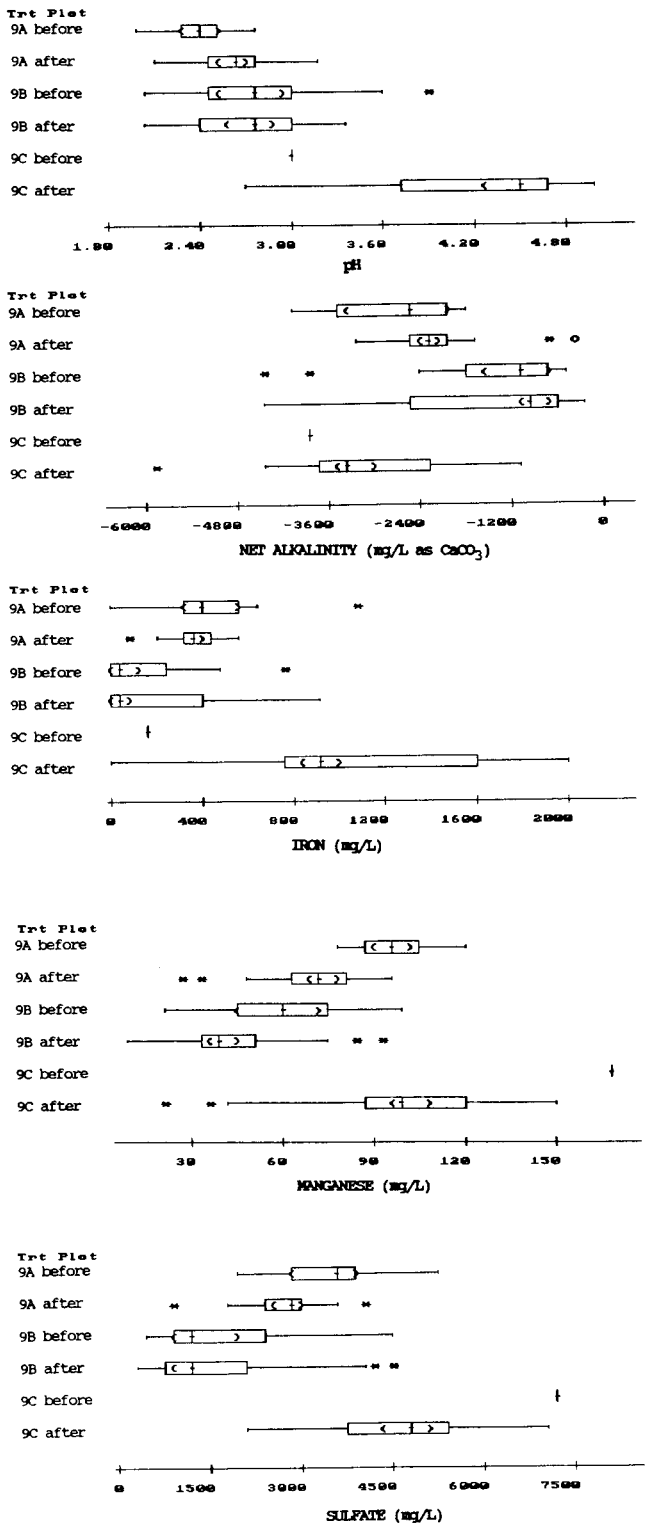


Figure 10. Boxplots of water quality from monitor wells for three 2.5-acre plots at mine site 9 in Clarion County. Plots 9A and 9B had alkaline addition, plot 9C served as a control. The boxplots compare water quality before and after treatment with alkaline additives. Number of samples for each boxplot are as follows: 9A before (N=12), after (N=39); 9B before (N=23), after (N=70); 9C before (N=1), after (N=61).

However, nonparametric trend tests of the post-treatment data indicate that the rates of concentration changes are not significantly different between treated and untreated plots (Cravotta, U.S. Geological Survey, written commun., 1989).

Acid-mine drainage was not abated nor ground-water quality noticeably improved by the surficial application of alkaline materials at mine site 9. The NNP data in table 2 suggest that acidic ground water at each plot likely could have been predicted considering the MPA computed using the factor of 62.5 following the method of Cravotta et al. (1990). One possible explanation for the persistent acidic ground water in the reclaimed mine spoil is that prior to treatment, pyrite in the stockpiled overburden or mine spoil had been oxidized to ferric-sulfate minerals, which then provided a source of long-term, leachable acid, sulfate, and iron; the alkaline materials may have been applied too late to inhibit the oxidation of pyrite. Another explanation is that the rate of pyrite oxidation exceeds the rate of dissolution of calcareous materials.

Mine Site 10: Venango County. Mine site 10 was included in the study because limestone and other calcareous rock were present and abundant relative to potentially acid-producing strata. Forty-one acres of Brookville coal were mined, using the box cut method, with trucks and loaders. Maximum highwall height was about 50 ft.

About 8 to 10 ft of marine limestone strata is present about 25 ft above the coal at site 10. The limestone has NP ranging from 536 to 932 tons $CaCO_3$/1,000 tons. Another 7 to 13 ft of strata has NP over 100 tons $CaCO_3$/1,000 tons. However, a 1-to-1.5-ft-thick stratum immediately above the coal contains 1.09 to 5.5% sulfur, and underclay below the coal contains 1.53 to 2.9% sulfur. No alkaline addition was proposed because the natural strata contained the equivalent of about 18,000 tons $CaCO_3$/acre. The sulfur-bearing strata immediately overlying the coal were segregated and placed high above the mine floor in the backfilled mine spoil.

The NNP and net alkalinity data in table 2 indicate that the discharge would be alkaline on average. Post-mining discharge quality, however, has varied from highly alkaline to moderately acid (fig. 11). The most acidic water was collected after heavy rains. The acidity probably result from recharge that dissolves ferric-sulfate minerals that had accumulated in the unsaturated zone during drier periods and from unequal rates of pyrite oxidation and dissolution of limestone. The water samples contain iron and manganese concentrations that exceed conventional effluent limits (6 and 4 mg/L, respectively). These metals and the elevated sulfate indicate that the abundant alkaline material has not prevented the oxidation of pyrite in the backfill, but has neutralized the acidity produced by the oxidation reaction.

Results and Discussion

Every mine site is unique. Overburden composition, mining methods employed, volume of rock disturbed, pre- and post-mining ground-water chemistry, hydrogeology, weathering, and many other factors differ among the sites. Each of these factors affects the associated post-mining water

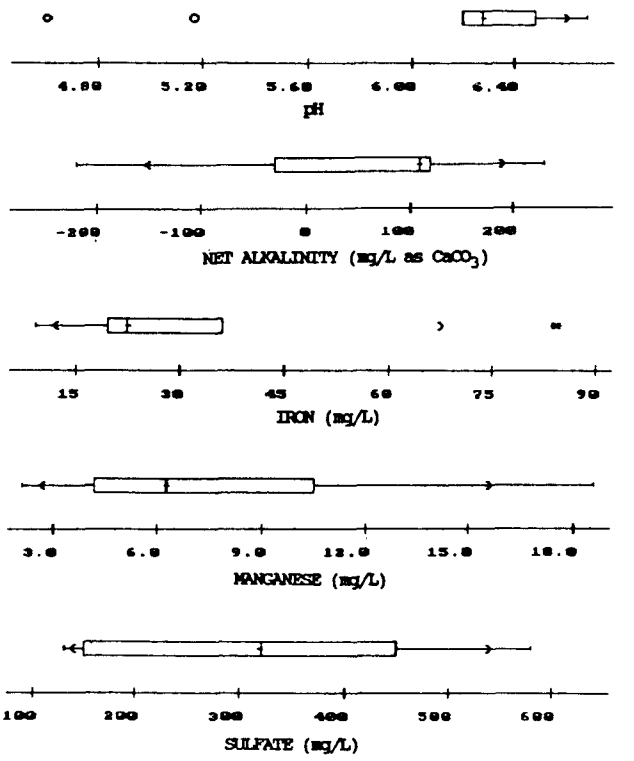


Figure 11. Post-mining water quality of discharge from mine site 10 in Venango County (N=5). This mine had abundant naturally occurring alkaline strata.

quality. Consequently the water quality at each mine site is monitored according to a unique program. Table 1 illustrates some similarities and differences among mine sites in this study. Alkaline-addition rates ranged from zero at sites 3 and 10, which were included for comparative purposes, to greater than 1,000 tons $CaCO_3$/acre for a part of site 9.

The uniqueness of the mines and number of variables to be considered makes a comparison of mine sites difficult; however, some relations between post-treatment, cumulative NNP of overburden and median net alkalinity of mine drainage from the 10 mine sites are apparent (table 2). Six of the eight alkaline-addition plans (mine sites 2, 4, 6, 7, 8, and 9) failed to prevent AMD. Of the two sites where post-treatment discharge water was alkaline (sites 1 and 5), site 5 has a substantial thickness of naturally alkaline strata, which were likely to produce alkaline drainage without the supplemental addition of limestone. After alkaline addition, the overburden NNP at mine site 1 was positive (+6.90 tons $CaCO_3$/1,000 tons) if calculated by the traditional methods of ABA; however, NNP was slightly negative (-0.31 tons $CaCO_3$/1,000 tons) if calculated using thresholds (table 2). The water quality at site 1 improved after the addition of alkaline material (fig. 3). The formerly acidic discharge from the deep mine that underlies much of the site now meets conventional mine-drainage effluent standards. Although discharges from alkaline-addition site 4 do not meet conventional effluent limits, the water quality is substantially better than that of nearby discharges from mine site 3, an untreated control (fig. 5).

Mine sites 1 and 4, the two sites where water quality improved after the addition of imported alkaline materials, had several things in common: (1) They were treated with the largest total quantities and the second and third largest alkaline-addition rates of the sites studied (table 1). (2) The mining and reclamation techniques used at both sites included selective handling of pyritic materials, timely backfilling, and alkaline-addition rates that exceeded permit requirements. (3) Some potentially acid-forming strata were removed from the mine sites. The coal seam on mine site 1 that was causing acid water to emanate from the deep-mine discharge was removed from the mine site by daylighting. Mine site 4 included removal of most of the pit cleanings.

Two adjacent mine sites were also examined in Clarion County. Mine site 6A received alkaline additives, and mine site 6B did not. No observable improvement in water quality is apparent from the alkaline additives, which may not have been applied in adequate amounts.

Mine site 9 is the only site in this study where alkaline material was applied solely as a remedial measure 9 years after completion of mining and reclamation. Three 2.5-acre plots were studied, two with alkaline addition and one without. All three continued to produce severe AMD through 1987 fig. 10). The AMD production results from the limited amount of alkalinity generated from the limestone relative to the amount of acidity produced by pyrite oxidation and by leaching of previously formed ferric-sulfate minerals in the mine spoil.

Alkaline materials were not added at mine site 10, but the site was included in this study to illustrate the potential effect of large amounts of naturally alkaline strata on water quality at a site where there is also some potentially acid-producing strata. The strata at site 10 contained the equivalent of 18,000 tons $CaCO_3$/acre. On average, the post-mining water quality was alkaline, but the concentrations of metals and sulfate were elevated (fig. 11). Apparently, the presence of large amounts of naturally alkaline material do not always preclude pyrite oxidation and the dissolution of metals and sulfate from the mine spoil.

The variable alkaline and acidic water quality of several discharges from site 6 show that alkaline and acid conditions can be created within the same spoil. Mine site 10, which had an abundance of limestone strata, had a single discharge that varied from alkaline to acid following recharge events. Alkaline-addition sites also have produced alkaline and acidic discharges, but with median net alkaline discharge. Clearly, the processes of pyrite oxidation and carbonate neutralization are complicated by the unequal distribution of acid-forming and neutralizing materials. Under some conditions, alkaline waters need to contact the locally pyritic zones of the mine spoil to prevent or neutralize AMD. Hydrogeochemical factors such as the microbial activity; mineral-surface areas; O_2, CO_2, nutrient, and moisture contents; temperature; and pH of mine spoil also must be considered.

Table 1 generally indicates mine sites where imported alkaline materials were placed, and if special overburden handling was implemented. Each of the eight alkaline-addition sites, except site 1, had alkaline materials placed entirely, or mostly, at the spoil surface--the easiest method of application. Alkaline materials were incorporated on the pit floor and within the spoil at five and two of the sites, respectively. Although alkaline-materials were spread on the pit floors at mine sites 1 and 4, where water quality improved after alkaline addition, alkaline materials were also incorporated with the backfill at site 1 and pyritic materials were selectively handled at site 4. Furthermore, sites 2 and 8 also employed selective handling of pyritic material and small amounts of variably placed alkaline additives, but both produced AMD (table 2). Therefore, effects of placement of alkaline materials or selective handling of acidic materials cannot be readily evaluated in this study.

Table 2 shows the overall mass-weighted NNP for each study site before and after alkaline addition. Although total quantities, or rates of application, of alkaline materials appear to be large, they generally are insignificant relative to the NP or NNP of the entire overburden volume before alkaline addition. Table 2 also shows the median post-mining net alkalinity of associated mine drainage or ground water for the 10 mine sites. Mine site 9 was subdivided into three plots 9A, 9B, and 9C, which in combination with mine sites 1-8 and 10, allows comparison of overburden NNP and water-quality net alkalinity for 12 sets of data. By comparing the sign on NNP and net alkalinity values in table 2, it is apparent that the traditional ABA computation of MPA, by multiplying total sulfur, in weight percent, by 31.25, results in mismatched signs--a wrong prediction of water quality--for 4 of the 12 sites. The errors in prediction are that the mine spoil is alkaline (NNP > 0), whereas the associated water is acidic (net alkalinity < 0). Prediction was not improved by using thresholds, where only values of NP greater than 30 tons $CaCO_3$/1,000 tons (with fizz) and of total sulfur greater than 0.5% are used to compute NNP, although substantially different values of NNP resulted. However, if MPA is calculated by multiplying total sulfur, in weight percent, by 62.5 following the method of Cravotta et al. (1990), then the sign of NNP matched the sign of the overall net alkalinity of waters at 11 of 12 sites (table 2). The acidic discharge from mine site 8 was not predicted by any of the acid-base accounting computation methods, possibly because of an inaccurate estimate of NNP.

The method of ABA calculation that used "thresholds" eliminated some of the problems associated with low-NP overburden, which typically produces AMD even though the sulfur content may be low. For example, mine sites 3 and 4 produced AMD which was correctly predicted by the NNP "with thresholds" (table 2). Using only NP values greater than 30 tons $CaCO_3$/1,000 tons, with a "fizz," eliminated much of the presumed influence of siderite on NP determinations (Morrison et al. 1990). Unless the influence of siderite in NP determinations can be eliminated, thresholds remain a useful concept. However, a disadvantage of assuming strata are inert if total sulfur and NP content do not exceed the threshold values is when large intervals of strata are sampled and composited, causing dilution of high-sulfur or high-NP concentrations. For example, the NNP calculated using thresholds are unreliable for mine sites 1 and 9, for which large thicknesses (up to 28 ft) of composite overburden samples were analyzed.

The results of this study are consistent with previous reports that concluded that NP and "traditional" MPA values, despite being reported in the same units (tons $CaCO_3$/1,000 tons), are not equivalent. In previous practice, it appeared that overburden NP must be at least twice MPA to produce alkaline mine drainage (diPretoro 1986; Skousen et al. 1987; Brady and Hornberger 1989; Ferguson and Erickson 1988). The observed inequality in NP and MPA is partly attributable to the incorrect assumption that CO_2 is completely exsolved during neutralization. Cravotta et al. (1990) argue that some CO_2 will dissolve in the ground water and form $H_2CO_3^*$, a weak acid. Therefore, MPA should be computed by multiplying total sulfur, in weight percent, by a factor of 62.5 instead of the traditional factor of 31.25. Use of the 62.5 factor assumes that the total sulfur is pyritic and that 4 moles of $CaCO_3$ are required to neutralize the acidity from 1 mole of pyrite.

Mining practices such as selective handling of coal pit cleanings, removal of acidic material from the mine site, and concurrent reclamation, appear to have enhanced the success of the alkaline addition.

Summary and Conclusions

In summary, empirical as well as theoretical considerations suggest that alkaline-addition rates are typically inadequate to neutralize AMD. Application rates for alkaline additives are best computed by considering a conservative estimate of MPA, which may be computed by multiplying total sulfur, in weight percent, by a factor of 62.5 (Cravotta et al. 1990; Smith and Brady 1990). Furthermore, the alkaline material may be most effective if incorporated concurrent with mining and backfilling, when and where the acid-production reactions occur. The alkalinities that can be generated from alkaline additives may be insufficient to abate the acidity of severe AMD and the localized production of acidity from reactive pyrite and ferric-sulfate minerals. Adequate alkaline-addition rates that create positive NNP at mine sites containing acidic strata may neutralize acidity and produce alkaline effluent water, which still contains unacceptable concentrations of sulfate, iron, and other metals.

On the basis of this study of the addition of alkaline materials to selected surface coal mines in western Pennsylvania, the following conclusions were made:

1) Previous methods for determining alkaline-addition rates, especially the concept that only one-third the calculated deficiency was necessary, have failed to prevent or abate AMD. Most alkaline addition rates are negligible relative to calculated deficiencies (NNP < 0) and insufficient to prevent or neutralize AMD.

2) The addition of alkaline materials to prevent AMD from surface coal mines may be effective providing that the alkaline-addition rates are sufficient (to offset negative NNP) and the overburden has relatively low-sulfur content. Alkaline materials added to high-sulfur mine spoil, even if sufficient to neutralize acid water, may not reduce concentrations of dissolved iron, manganese, and sulfate.

3) Certain mining practices, such as addition of more alkaline material than required by permit conditions, selective handling of pit cleanings, removal of pyritic material from the mine site, and concurrent reclamation appeared to enhance the effect of alkaline addition on reducing acidity.

4) There is good agreement of signs on post-treatment overburden NNP and median net alkalinity of associated mine-drainage water when overburden MPA is computed by multiplying total sulfur, in weight percent, by 62.5.

5) Additional studies are needed to determine the most beneficial rates of application and placement of the alkaline materials. Calculations of deficiencies (NNP) and application rates should be conservative and consider the theoretical arguments given by Cravotta et al. (1990) and the empirical results of this study.

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THE USE OF CO_2 COULOMETRY IN DIFFERENTIATING AND QUANTIFYING THE CARBONATE PHASES IN THE COAL-BEARING STRATA OF WESTERN PENNSYLVANIA: ITS APPLICABILITY IN INTERPRETING AND MODIFYING NEUTRALIZATION POTENTIAL (NP) MEASUREMENTS[1]

by

J.L. Morrison, S.D. Atkinson, Alan Davis, and B.E. Scheetz[2]

Abstract. CO_2 coulometry is a rapid, highly accurate technique which can be used to determine the carbonate carbon contents of coals and associated overburdens. The rate at which the CO_2 is evolved during the acid digestion process is a function of which carbonate phases are present. Calcite and dolomite reaction times are approximately six to eight minutes under the conditions described herein, with the maximum change in reaction rates occurring between two and four minutes. Siderite requires a lengthy 10 to 15 minutes to completely react with the maximum change in reaction rate occurring between six and eight minutes. The determination of neutralization potential (NP) in the coal-bearing overburdens of the eastern United States is inaccurate when siderite is present because of the slow conversion of Fe^{2+} to Fe^{3+}. To alleviate the effects of siderite on NP, a 30 wt.% H_2O_2 solution can be used to accelerate the conversion of Fe^{2+} to Fe^{3+} during the titration process. The addition of H_2O_2 increases both the accuracy and precision of the NP determination. Despite the addition of H_2O_2, many siderite-bearing overburdens still possess NP. This is interpreted as being the result of: 1) the incomplete oxidation of Fe^{2+} to Fe^{3+} and the incomplete precipitation of iron hydroxide, and/or 2) the presence of Ca and/or Mg occurring in solid solution in the siderite.

Additional key words: fizz rating, hydrogen peroxide, ferrous and ferric iron, carbonate carbon, CO_2 coulometry, x-ray diffraction, microprobe analysis.

Introduction

Prediction of acidic mine drainage is based in part on the ability to accurately characterize overburdens with respect to sulfur and carbonate. The acid/base accounting method is the most frequently used type of overburden characterization. The acid/base accounting method is composed of two determinations: 1) total sulfur, and 2) neutralization potential. Total sulfur contents are then multiplied by 31.25 to calculate potential acidity. Total sulfur determinations are relatively rapid and accurate. Neutralization potential is determined by digesting the overburden in HCl, back titrating with NaOH to an endpoint of pH = 7 which is held for 30 seconds (Noll, Bergstresser, and Woodcock 1988). This determination was originally used to find the neutralization equivalence of limestone (Jackson 1964). When applied to determining the neutralization potential of overburdens, this method is less accurate when siderite is present. Siderite, a common constituent in overburdens, is believed not to have the

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same neutralization capabilities as other carbonates (Williams et al. 1982; Palmer 1973). Siderite ($FeCO_3$) is at least partially digested in the HCl digestion step of the NP determination and will ultimately affect the stability of the titration endpoint because of the slow and incomplete conversion of Fe^{2+} to Fe^{3+}. This instability affects both the accuracy and precision of the NP determination.

Because the differentiation of the various carbonate phases is essential in the prediction of acidic mine drainages, several studies have attempted to differentiate and quantify the various carbonate phases present in coal-bearing strata. The most conventional method used to ascertain variations in carbonate mineralogy is quantitative x-ray diffraction (QXRD) (Despard 1988; Morrison 1988). The primary difficulty with this technique is the lower detection limit of one to two percent. Less conventional methods of carbonate characterization include evolved gas analysis (Hammack 1987) and automated pressure cells (Evangelou, Roberts, and Szekeres 1985).

This paper will present an alternative method of carbonate characterization known as CO_2 coulometry (Huffman 1977). CO_2 coulometry is an analytical technique which is routinely used to determine carbon (both total and carbonate). It is a two-step process in which total carbon is determined by measuring the amount of CO_2 evolved when the sample is heated to 1000°C. Carbonate carbon is determined by digesting the sample in hot perchloric acid and measuring the amount of CO_2 evolved during the digestion. Organic carbon is then determined by difference.

Because calcite, dolomite, and siderite exhibit different rates of dissolution in acids (Evangelou, Roberts, and Szekeres 1985) the CO_2 coulometer was used to measure the evolution of CO_2 with respect to time. To augment the CO_2 coulometry data, x-ray diffraction was used for carbonate phase identification.

Materials and Methods

CO_2 coulometry is a relatively rapid analytical technique which can accurately determine the carbonate carbon content of a given sample. The schematic of the CO_2 coulometer apparatus is shown in Figure 1.

The overburden sample was accurately weighed (20 to 25 mg) in a ceramic weighing boat and then placed in the sample tube housing shown in Figure 1. The side of the sample housing was rinsed with one mL of deionized water to ensure that any particles adhering to the side of the sample housing would be rinsed down to the zone in which the acid will be introduced. This rinse was kept constant at one mL to prevent creating subtle variations in the normality of the perchloric acid which might have an impact on the rate of digestion. The sample housing was then closed and the system degassed for approximately two minutes to remove the atmospheric CO_2 introduced into the system when the sample was placed in the sample housing. After degassing, the analysis is commenced by the addition of 2 mL of 2 N perchloric acid. The CO_2 evolved during the hot perchloric acid digestion is carried to the CO_2 coulometer cell where it is electrochemically titrated. Results are expressed as wt% carbonate carbon and reported to the nearest 0.01%.

Calcite, dolomite, and siderite standards were analyzed on the CO_2 coulometer. Calcite and dolomite standards were provided by Bellefonte Lime of Bellefonte, Pennsylvania and are reported as being 97.73% and 98.85% in purity, respectively. Sample (195) is a high quality limestone (Valentine member of the Linden Hall Fm. collected from Bellefonte, PA) and sample (196) is a high quality dolomite (Ledger dolomite member collected in southeast PA near Devault, PA) in which

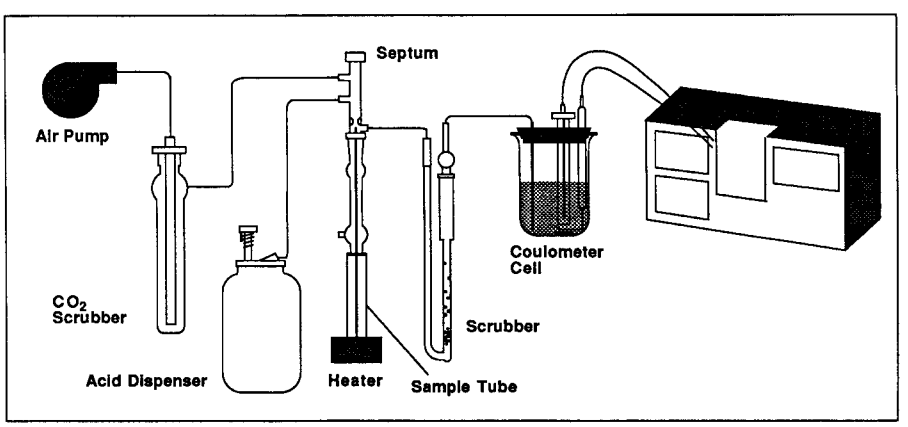


Figure 1: Schematic of CO_2 coulometer.

the atomic ratio of Ca/Mg is nearly one. Siderite standards are more difficult to obtain. The siderite standard (197) is an in-house standard.

Results and Discussions

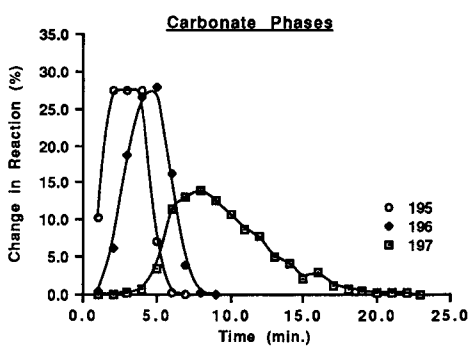
Figure 2 summarizes the CO_2 coulometry profiles and the measured NP values for the various standards described above. When viewing the CO_2 coulometry profiles in Figure 2, the following observations should be noted: 1) the time for 100% reaction, 2) the time at which the maximum change in reaction occurs, and 3) the overall geometry of the profile. The calcite (195) and dolomite (196) profiles are characterized by relatively short reaction times over which the rate of the reaction is relatively rapid. In contrast to this, the siderite (197) profile is characterized by a much longer reaction time and a more sluggish reaction rate as evidenced by a much broader profile. It is important to note that siderite did not generate any CO_2 until the two to three minute reading.

Figure 3 illustrates the CO_2 coulometry profiles for three overburden samples with wide ranging NP's, fizz ratings, carbonate carbon contents, and lithologies.

Figure 3A is a CO_2 coulometry profile for a dark gray shale and appears to be very similar to the siderite standard. This profile is characterized as being relatively broad with the maximum rate of reaction occurring at the six minute mark. In addition, CO_2 is undetectable until the two to three minute mark. X-ray diffraction analysis found siderite to be the only detectable carbonate phase. Multiplying the carbonate carbon content (1.30) by $FeCO_3/C$ ratio determines there is 12.54% siderite present.

In Figure 3B, the CO_2 coulometry profile for a siderite concretion (sample 71) is illustrated. Again, the CO_2 profile is relatively broad and the rate of reaction is slow. Unlike the previous CO_2 profile, however, there is the indication of a slight reaction having occurred at the one to two time interval. X-ray diffraction analysis found siderite to be the only detectable carbonate phase present. Microprobe analysis of this sample determined 3.52 +/- 0.93 wt% Ca present in the siderite (Morrison, Atkinson, and Scheetz 1990). This presence of Ca in the siderite may explain the slight reaction encountered during the one to two minute reaction time. Assuming that all the carbonate present is in the siderite phase, the carbonate content of 7.11 translates into 68.58% siderite.

In Figure 3C, the CO_2 coulometry profile for an Upper Freeport limestone is presented. This profile is very different from the previous two profiles (173 and 71). This profile is characterized by a rapid reaction rate but requires a relatively long time (13 mins.) to react completely. Although the two minute mark



Sample	Description	Carbonate Carbon	Theoretical Carbonate Carbon for Pure Sample	Time (min) for 100% Reaction	Neutralization Potential
195	High Calcium Ls	11.885	12.000	7	971.58
196	Dolomite	12.952	13.026	9	1054.66
197	Siderite	10.573	10.367	23	37.10

Figure 2: CO_2 coulometry profiles for calcite, dolomite, and siderite standards.

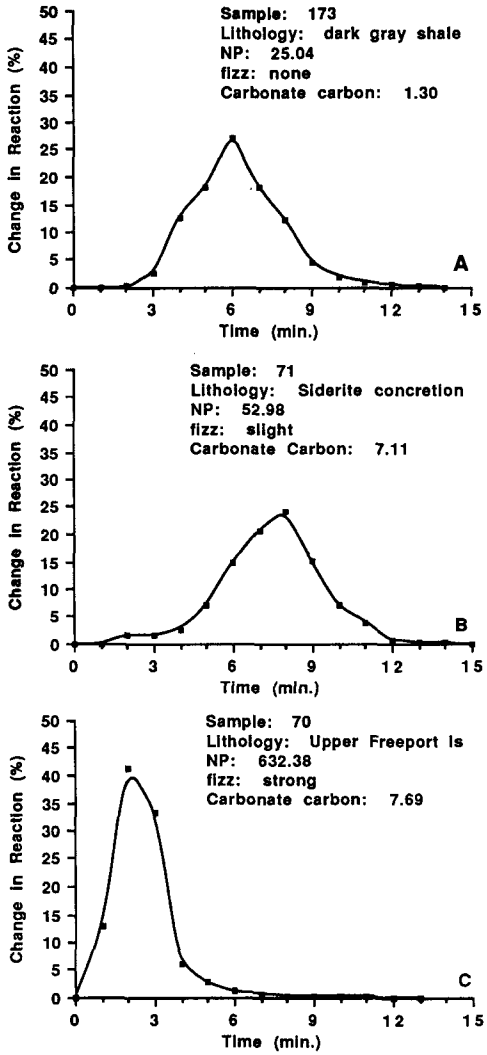


Figure 3: CO_2 coulometry profiles for selected overburden samples.

for reaction time is similar to that of calcite, the lengthy time for 100% reaction indicates that other carbonate phases are present. X-ray diffraction identified abundant calcite and ankerite. The presence of ankerite is interpreted as being responsible for the lengthy reaction time. Despite this, multiplying the carbonate carbon (7.69) by the $CaCO_3/C$ ratio indicates there is 64.08% calcite present which translates to a NP of 640.08 which is in very good agreement with the actual measured NP of 632.38.

The primary difficulty in determining the neutralization potential of overburdens is that the presence of siderite affects both the accuracy and the precision of the method. Because siderite is very common in the coal-bearing strata of the eastern United States, NP values are often questioned. This is particularly true if the NP is accompanied by an assigned fizz rating of zero (none). NP's which have fizz ratings of zero are often discounted because they are interpreted as being attributable to the presence of siderite. If the overburden sample exhibits a fizz of one or more (e.g. 71), there is no criterion by which one can interpret the NP as being valid. In the case of overburden sample (71), the dominant carbonate phase is siderite, yet it produced an NP of 52.98. CO_2 coulometry can very accurately differentiate calcite from siderite. This method also can determine if the carbonate is present as a mixture by a bimodal CO_2 coulometry profile; however, the method cannot yet accurately quantify individual components of a multiple phase system.

Because CO_2 coulometry can accurately differentiate between calcite-bearing and siderite-bearing overburdens, the NP determination methodology has been modified in an attempt to provide siderite-free NP's. The modification is very simple. Because siderite is at least partially digested in the NP digestion step, a large amount of Fe^{2+} can potentially go into solution. During the titration process, the Fe^{2+} is partially oxidized to Fe^{3+}; however, this reaction does not necessarily go to completion over the short time span of the determination. Because the precipitation of ferric hydroxide generates H^+ it is necessary to accelerate the oxidation of Fe^{2+} to Fe^{3+} which will eventually precipitate as a ferric hydroxide (ferrihydrite) during the NaOH titration step. In order to speed up the Fe oxidation, a 30 wt% H_2O_2 solution is added. The overburden sample is digested as in the conventional NP determination; however, after cooling the leachate is filtered, five mL of 30 wt.% H_2O_2 is added and then reboiled for three to five minutes. After cooling, the leachate is titrated using the conventional NP guidelines.

Table 1 summarizes some of the results. The NP's of samples (173) and (171) are slightly different from those reported in Morrison, Atkinson, and Scheetz (1990) because they were redetermined from different splits. In the first set of data (173, 71, and 63) the addition of H_2O_2 had a profound impact on the NP value. In these samples, where siderite is present, the NP's were lowered by 54.07, 38.20, and 13.90%, respectively. In overburden sample (63), the NP value was not as affected as in samples (173) and (71) because calcite was the dominant carbonate phase.

The second set of data in Table 1, sample (171), focuses on the problem of incorrectly assigned fizz ratings. Because determining fizz ratings is very subjective, the addition of H_2O_2 is warranted. Overburden sample (171) is a siderite-bearing black to dark gray shale. Three sets of analyses were run, all in triplicate. In the first sequence, the sample was run according to the correct conventional NP determination. In the second sequence, an incorrect fizz rating was intentionally assigned to determine to

Table 1. Comparison of conventional and modified NP determinations among selected overburden samples.

Sample	Fizz	Carbonate Mineralogy	NP	$NP_{hydrogen\ peroxide}$
173	0	Siderite (12.54%)	25.04	11.50
71	1	Siderite (68.58%) Calcite ?	52.98	32.73
63	1	Calcite, siderite	65.59	56.47
171	0	Siderite (6.63%)	14.41 ± 1.47	-
171	1	Siderite (6.63%)	23.51 ± 1.03	10.25 ± 0.13

what extent a larger volume of HCl would effect the NP value when using the conventional NP methodology. In the third sequence, an incorrect fizz rating was intentionally assigned; however, this time the modified NP determination was used. All of these determinations were performed manually, as opposed to using an automated titration system. Comparing these runs clearly indicates that an incorrectly assigned fizz rating, and therefore digestion procedure, can have a profound impact on the resulting NP. By adding H_2O_2, the error is lessened and the precision of the method increased.

Despite the addition of five mL of 30 wt.% H_2O_2, the NP's of overburdens in which siderite was the only identifiable carbonate phase, did not go to zero. The explanation for this may be two-fold.

The first explanation is that not all of the Fe^{2+} has oxidized to Fe^{3+} and has not precipitated as ferric hydroxide. Because this reaction has not gone to completion, erroneously high NP values could be reported.

The second explanation is more complex and requires further research to substantiate. Siderite is rarely phase pure in nature (Mozley 1989). Microprobe analysis presented in Morrison, Atkinson, and Scheetz (1990) has documented the occurrence of Ca and Mg present in siderites as well as Mn. If Ca and/or Mg is present in significant amounts it may explain why certain siderite-bearing overburdens still possess NP despite the addition of H_2O_2. The relationship between the field neutralization of acidic drainages by Ca-bearing siderites has yet to be documented.

Conclusions

The characterization of the carbonates present in the coal-bearing strata of the eastern United States using the conventional NP determination can be inaccurate. This inaccuracy is due to the presence of siderite which affects the stability of the NaOH titration endpoint. Conclusions of the research completed thus far include: 1) siderite is ubiquitous in the coal-bearing strata examined thus far; 2) the presence of siderite can profoundly effect the NP value; 3) incorrectly assigned fizz ratings, and thus digestion procedures, can affect the accuracy of the NP determinations; 4) CO_2 coulometry can be used to very accurately determine the carbonate carbon contents of overburdens; 5) the CO_2 evolution rate during the carbonate carbon determination is a function of which carbonate phases are present, and these rates can be used to determine if the overburden contains calcite, siderite, or a mixture of carbonate phases; 6) the effect of siderite on the determination of NP can be minimized using H_2O_2; 7) because siderite occurs in overburdens which contain reactive carbonate phases (e.g. calcite and/or dolomite), the addition of H_2O_2 is warranted because there is no criterion to judge the validity of an NP whose assigned fizz rating is greater than zero; 8) the observed siderites were not phase pure, an observation in good agreement with the literature; and, 9) despite the addition of H_2O_2 many siderite bearing overburdens still possess NP. This may be attributable to the pH of the NaOH back titration endpoint (pH = 7.0) and/or the presence of Ca and Mg in the siderite.

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DELINEATION OF POTENTIAL MANGANESE SOURCES IN THE COAL OVERBURDENS OF WESTERN PENNSYLVANIA[1]

by

J.L. Morrison, S.D. Atkinson, and B.E. Scheetz[2]

Abstract. Manganese is a common and regulated metal in acidic mine effluents. Because the precipitation and removal of manganese from mine effluents is complex and expensive, it is advantageous to ascertain the distribution of manganese in the stratigraphic section prior to mining. By identifying certain stratigraphic horizons that have high amounts of manganese, it may be possible to implement special handling plans to minimize or prevent mine drainages from having elevated manganese contents. Because the source of manganese in mine drainages is poorly documented, the overburden from a mine site having drainages characterized by elevated manganese concentrations (70 to 80 ppm Mn) was examined in detail. Bulk manganese analyses determined the majority of the manganese to be present in a 13.5 foot thick sequence of black to dark gray shales which also contained highly variable amounts of sulfur. CO_2 coulometry, and x-ray diffraction determined this stratigraphic interval to be enriched in siderite ($FeCO_3$). Increases in the manganese were accompanied by increases in the siderite content. Manganese substitution in the siderite structure appears to be the source of manganese in this mine site.

Additional key words: Siderite, CO_2 coulometry, solid solution, microprobe analyses and bulk Mn determinations.

Introduction

Because the source of the Mn in coal-bearing strata is poorly understood, predicting the occurrence of Mn in mine drainages is difficult. To gain a better understanding of why certain mine drainages have elevated concentrations of manganese, the overburden from a mine site having an acidic high-Mn drainage was examined using a variety of techniques.

The primary objective of the overburden analysis is to characterize the overburden from this particular mine site using a variety of techniques that will provide more information than the typical acid-base accounting data. Although the source of Mn in coal-bearing strata is poorly documented, the following sources are potential candidates: 1) pyrolusite (MnO_2), and/or 2) Mn in solid solution associated with the various carbonate phases (e.g. siderite and/or calcite).

One particular area of interest is the characterization of the various carbonate phases present. The characterization of carbonates involves: 1) determining both the nonreactive carbonate (e.g. siderite) and the reactive carbonate (e.g. calcite and/or dolomite) phases and 2) determining if the presence of Mn is related to the occurrence of carbonates. The occurrence of Mn in solid solution in carbonates is well documented in the literature (Hurlbut

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and Klein 1977; Pearson 1979; Teodorovich 1961; Mozley 1989; and Pye 1984).

Materials and Methods

The majority of overburden in this surface mine is characterized by low sulfur (S_T < 0.35 wt. %) and low NP (NP < 20) in which fine to medium grained sandstones are the dominant lithology. The conventional acid/base accounting data (total sulfur, NP, and fizz rating) were obtained from Geochemical Testing of Somerset, PA. CO_2 coulometry, bulk Mn determinations, x-ray diffraction, and the simulated weathering experiments were performed at The Pennsylvania State University.

Total Sulfur

Total sulfur analyses were performed using a Leco SC-32 sulfur analyzer. Vanadium pentoxide was used as an accelerator. This high temperature combustion technique is described in Noll, Bergstresser, and Woodcock (1988). Total sulfur can then be converted to maximum potential acidity by multiplying total sulfur by 31.25.

Neutralization Potential

Neutralization potential, as the name implies, is used to determine the neutralization ability of a given sample. This entails determining the amount of calcite, and/or dolomite and expressing these contents as tons of $CaCO_3$ equivalent/1000 tons of overburden. The determination of neutralization potential is described in Noll, Bergstresser, and Woodcock (1988).

In theory, siderite does not report in the NP determination and is believed not to have the neutralization ability of calcite or dolomite. As a consequence, siderite may be very abundant in a given overburden, yet will go undetected in the NP determination. As a result of this, CO_2 coulometry was used to determine the carbonate content.

CO_2 Coulometry

CO_2 coulometry is a highly accurate analytical technique that is routinely used in the determination of both inorganic and carbonate carbon. Because the various carbonate phases react at different rates, the CO_2 coulometer was used to measure the rate of CO_2 evolution when the sample is introduced to an acid. Because siderite reacts much slower than the other carbonate phases (e.g. calcite and/or dolomite), CO_2 coulometry was used to quantify the occurrence of siderite. The methodology employed here is described in detail by Morrison et al. (1990). In theory, this is a very similar approach to Evangelou, Roberts, and Szekeres (1985).

Bulk Manganese Analyses

Bulk manganese analyses were performed on selected samples to determine the distribution of manganese throughout the stratigraphic sequence. Overburden samples were digested in a HF - H_2SO_4 solution, until only a minimal residue remained. The solution was boiled to drive off the volatile silica. The residue from the HF - H_2SO_4 leach was then introduced to a HNO_3 leach, to ensure complete digestion. Manganese, if present in any form, (e.g. pyrolusite and/or Mn in solid-solution) would leach out under these various acid leaches. The combined leachates from these digestions were analyzed for manganese using a Spectrametrics Spectra Span III atomic emission spectrometer. The excitation source was a DC plasma sustained in argon gas. Liquid aliquots were serially diluted to the linear range of 1 to 5 ppm. All unknowns were analyzed by first running a series of reference solutions and then the unknowns. This procedure was then repeated in reverse order to account for instrumental drift. The duplicate values were averaged and these averages reported. When operated in this manner, the experimental detection limits were estimated to be 0.01 ppm (10 ppb).

Simulated Weathering Experiments

Simulated weathering experiments are a useful technique to compare overburden samples under controlled laboratory conditions. Their usefulness in predicting the field occurrence of acidic mine drainage is more problematic. Overburden samples were prepared by stage crushing to -1/4 inch. The samples were placed in one quart HDPE plastic storage containers (Figure 1). Deionized water was added to the plastic leaching vessels and allowed to react in an enclosed chamber in which humidified air was circulated. Leachates were collected on a weekly basis (hourly and weekly leachates combined) and characterized with respect to pH, acidity, sulfate, total iron, manganese, and aluminum.

X-Ray Diffraction

Overburden samples were examined for their crystalline phase composition using conventional x-ray powder diffraction methods. All data were collected with copper K-alpha radiation on a fully automated Scintag PAD V diffractometer equipped with a cryogenic detector. All specimens were ground to -325 mesh and mounted on a zero background substrate cut from a single crystal of quartz which was oriented just off the c-axis. The range of data collection was from 15 to 55 degrees 2-theta at 1 degree/minute and a step size of 0.02 degrees. Phase identifications were made by comparison to the JCPDS-ICDD reference patterns. The lower detection limit is estimated to be approximately 1%.

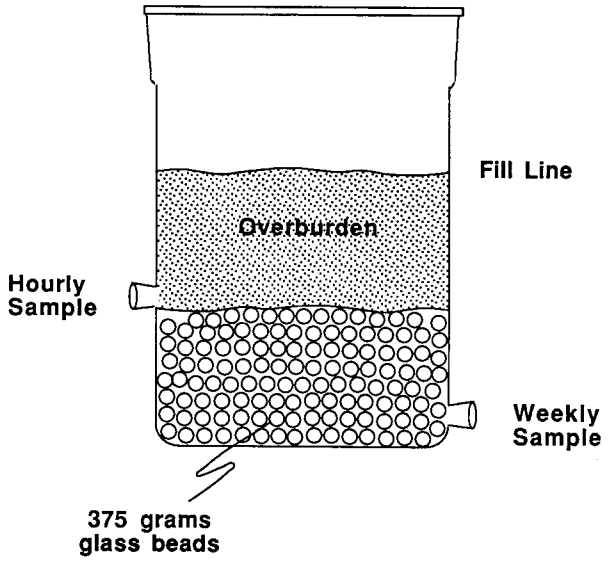

Figure 1: Simulated Weathering Vessles.

ETEC Microprobe

Overburden specimens were processed to -20 mesh and then pelletized. The -20 mesh particles were mixed with a Hexacol epolite resin and hardener, pressed into one inch diameter stainless steel molds at 10,000 psi for two minutes. After the two minute press, the resin was allowed to cure overnight. These pellets were polished with 400 and 600 grit paper for three minutes each. The next phase of polishing involved using 0.3 micron aluminum slurry on a Texmet cloth for two minutes, followed by the final polish using a 0.5 micron aluminum slurry on a silk polishing cloth. The samples were washed in an ultrasonic bath between all polishing steps. The polished pellets were wiped dry and analyzed within 18 to 24 hours.

An ETEC Auto Microprobe was employed to analyze the chemical composition of siderite by a combination of energy dispersive and wavelength dispersive techniques. Siderite grains were selected from the overburden fragments based upon the chemical composition determined by using semi-quantitative EDX. The criterion used to establish a grain of siderite versus clays was the presence of significant amounts of silica (> 1.00 wt %). In this case, these grains were not counted due to clay contamination. Grains which contained only traces of silica (< 1.00 wt %) were analyzed for Mg, Al, Ca, Mn, and Fe. This latter category of grains was analyzed individually by wavelength dispersive techniques using LIF, PET, and TAP crystal monochromators. All analyses were run at 15Kv acceleration potential with a sample current of 0.02 microamps.

Results and Discussion

Figure 2 summarizes the stratigraphic and overburden data from one of the core holes on the mine site. Total sulfur contents were generally less than 0.35% except in samples 170, 171, 185, and 189. NP's were typically less than two except for samples 170 to 175 and 183 to 185. The majority of the total sulfur and NP occurred within a 13.5 foot thick sequence of black to dark gray shale/siltstones. The NP from this horizon would typically be considered negligible as a neutralizer by Pa DER (Brady and Hornberger 1989) because of the assigned fizz rating and the low NP's. These NP's would be interpreted as being the result of siderite and therefore discounted because of siderite's inability to neutralize acidic drainages (Williams et al. 1982).

Because NP determinations do not accurately quantify all of the carbonates present (excludes the majority of siderite) carbonate carbon measurements were performed on selected samples. The majority of the carbonate present was associated with samples 170 - 175. CO_2 coulometry data, as interpreted and discussed by Morrison et al. (1990) indicated that the dominant carbonate phase present in these overburdens was siderite. This interpretation was also verified using x-ray diffraction.

Figure 3 shows a portion of the x-ray diffractograph for sample 173. The portion of the diffractograph presented here represented the 2 theta interval where the main carbonate peaks would occur if present (27 to 33 degrees 2 theta). The stick figures below the x-ray diffractograph are the JCPDS-ICDD reference patterns for siderite, calcite, and ankerite respectively.

Bulk manganese determinations revealed that the majority of manganese present in the overburden also occurred in this 13.5 foot thick shale sequence. Of particular importance to note here was that increasing carbonate carbon (siderite) contents were accompanied by both increasing amounts of NP and Mn. The increase in NP's with increasing siderite contents exemplifies the shortcomings of the conventional NP determination. As the amount of siderite increased, the accuracy of the NP determination became questionable because of the increased Fe in solution Morrison et al. (1990). The parallel increase in both siderite and Mn strongly suggested that the Mn is associated with the siderite probably occuring in solid solution.

Rosenberg (1960, 1963, 1967) described the subsolidus relationships in the system $CaCO_3$-$MgCO_3$-$FeCO_3$-$MnCO_3$. His data and more recent studies reported by Essene (1983) demonstrated that complete solid solution exists in the $MgCO_3$-$FeCO_3MnCO_3$ system. Figure 4 gives an example of the subsolidus relationships in the $MgCO_3$-$FeCO_3MnCO_3$

Log Interval	Thick-ness	Scale	Graphic Log	Lithologic Description	OB Analys No.	% Total Sulfur	NP	Fizz Rating	CC	Mn
0-3	36"			Light gray, medium grain sandstone	153	0.01	0.54	none		95
3-6	36"				154	0.00	0.26	none		15
6-9	36"	10			155	0.00	0.41	none		
9-12	36"				156	0.00	0.51	none		15
12-15	36"				157	0.00	0.28	none	0.01	15
15-18	36"			Light gray, medium to fine grained sandstone	158	0.00	0.33	none		
18-21	36"	20			159	0.00	0.48	none		
21-24	36"				160	0.00	0.66	none		
24-27	36"				161	0.00	1.02	none		
27-30	36"	30		Light gray, medium grained sandstone with increasing amounts of organic debris with depth	162	0.00	0.51	none		20
30-33	36"				163	0.00	0.43	none		
33-36	36"				164	0.00	0.64	none	0.00	15
36-39	36"	40			165	0.02	0.74	none		
39-42	36"				166	0.01	0.56	none		
42-45	36"				167	0.03	0.46	none		
45-47'1	25"				168	0.01	0.54	none		
47'1-49'2	25"	50			169	0.15	0.26	none		
49'2-52'2	36"			Dark-gray shale with increasing siltstone laminate with depth	170	4.42	2.81	none	0.04	220
52'2-55'2	36"				171	0.66	10.20	none	0.69	1650
55'2-58'2	36"	60			172	0.20	16.43	none	1.23	2700
58'2-61'2	36"				173	0.26	18.29	none	1.30	3100
61'2-62'10	17"				174	0.32	10.25	none	0.80	2050
62'10-65'10	36"			Light gray medium-grain sandstone, black shale partings	175	0.25	4.03	none	0.36	550
65'10-68'10	36"				176	0.24	1.91	none		290
68'10-71'10	36"	70		Light to whitish gray, medium-grain sandstone with some pyritic nodules, decreasing organic debris with depth	177	0.09	-1.32	none		
71'10-74'10	36"				178	0.02	0.20	none	0.00	30
74'10-77'10	36"				179	0.02	0.41	none		
77'10-80'10	36"				180	0.00	0.00	none		
80'10-83'10	36"	80			181	0.03	0.38	none	0.00	30
83-86'10	36"				182	0.07	0.64	none		30
86'10-89'10	36"				183	0.01	3.01	none		
89'10-92'5	31"	90			184	0.13	13.47	slight	0.25	270
92'5-94'5	24"			Dark gray laminated siltstones	185	0.51	2.58	none		
94'5-96'5	24"				186	0.27	-2.21	none		240
96'5-99'5	36"			Olive to dark gray poorly indurated shale/underclay with plant fragments	187	0.01	-0.22	none	0.01	130
99'5-101'11	30"	100			188	0.35	0.87	none		105
101'11-104'11	36"			Coal	189	1.50	1.38	none		
104'11-106'5	18"			Dark gray underclay	190	0.06	1.61	none		115
106'5-107'10	17"			Black carbonaceous/boney shale	191	0.23	1.35	none		
107'-110'4	30"	110		Dark gray siltstone with small vitrinite bands	192	0.00	0.48	none	0.00	75
110'4-112'10	30"				193	0.02	0.66	none		65
112'10-115'5	31"				194	0.08	1.05	none	0.01	90

Figure 2: Overburden Characterization Data.

system showing extensive solid solution between siderite and magnesite and a limited solid solution with Fe in calcite. The pure Fe-analog of dolomite, ankerite, was seen from this data not to exist, but exhibited a partial solid solution between dolomite and ankerite. Limited solid solution was reported (Reeder and Dollase, 1989) in the binary compounds in this system with increased amounts increasing with temperatures. A large three phase area was present in this diagram in which calcite solid solution/ankerite solid solution and siderite-magnesite solid solution coexist. The diagram was representative of the phase relationship at 400°C. All of these studies were reported on experimental or natural samples that were formed at elevated temperatures or pressures above 350°C and 400MPa.

In contrast, literature citations of sedimentary carbonates were restricted mainly to calcite and dolomite with only very limited data reported on siderite (Mozely 1989; Pearson 1979). Mozley (1989) reported on the differentiation between marine and fresh water diagenetic

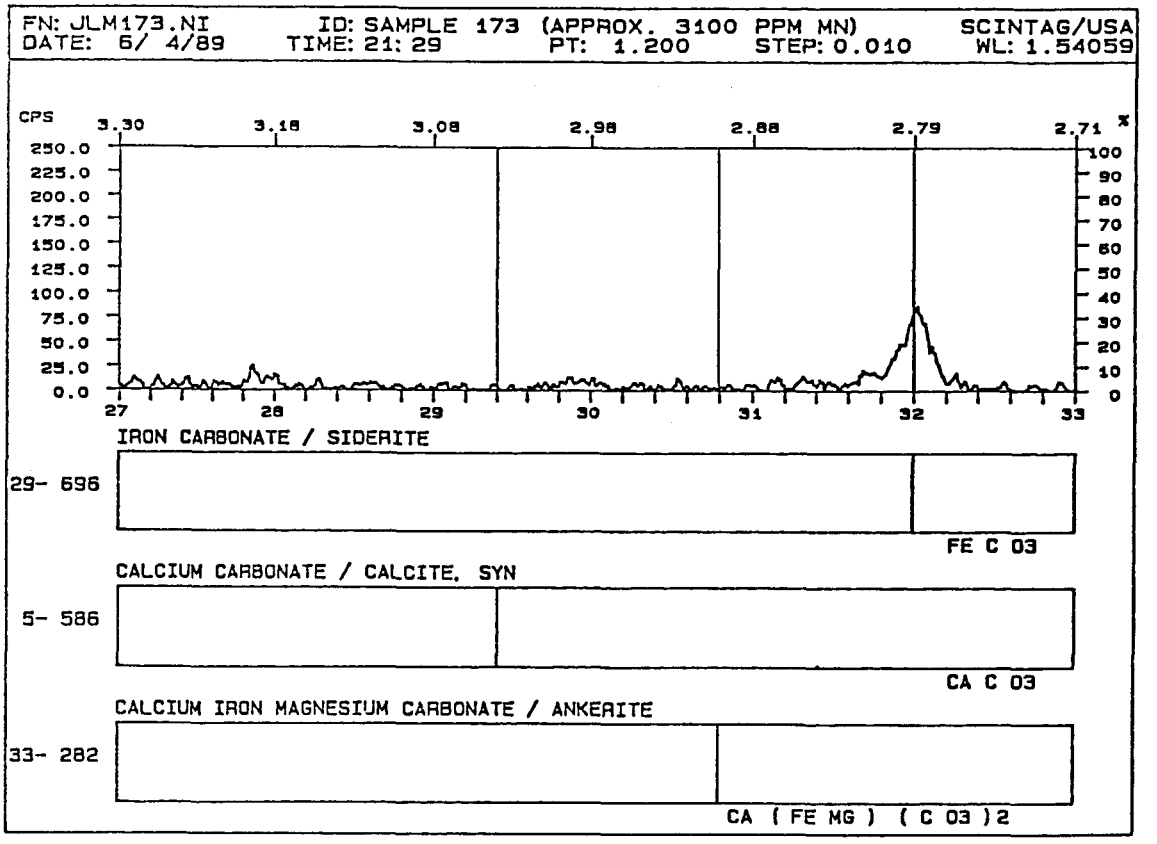

Figure 3: X-ray Diffractograph of Overburden Sample #173.

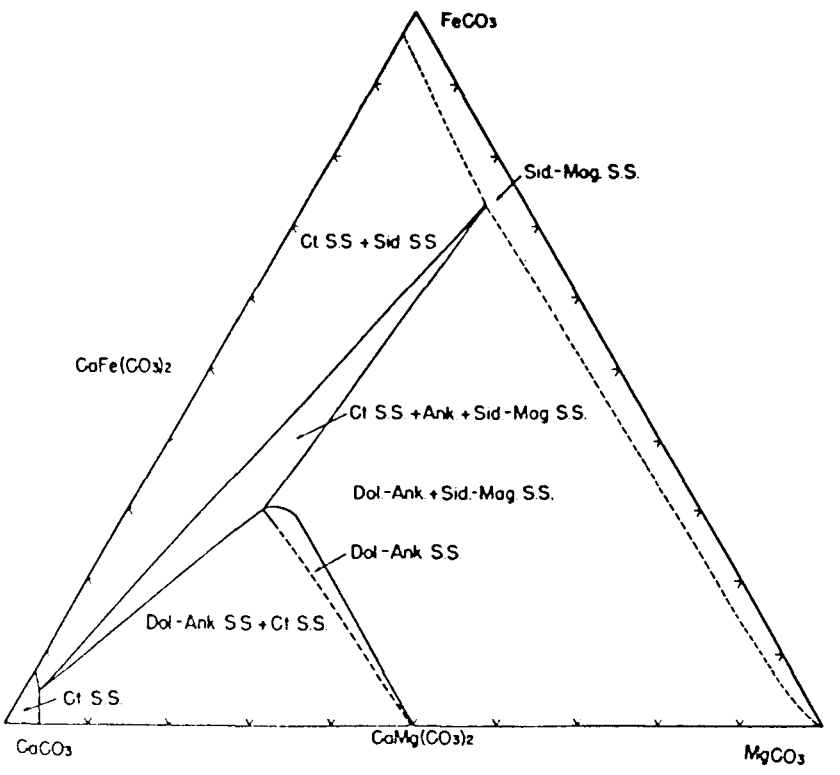

Figure 4: Subsolidus Relationships in the $MgCO_3$-$FeCO_3$-$CaCO_3$ System (after Rosenberg, 1960).

siderites, based upon the crystal chemical substitution of Ca, Mg and Mn for Fe in siderites. The observed degree of substitution in Mozley (1989) was larger at lower temperatures than reported by other authors, perhaps reflecting the differences in depositional environments. This sparcity of information was attributed by Dresel (1989) to the inability to identify fine-grained siderite in the field. As a consequence, very little is known with regards to the degree of solid solutions that form in siderite under these depositional conditions. The subsolidus phase relations of this system at lower temperatures (as in sedimentary siderite) will change from those presented in Figure 4.

Further data to support the observation that Mn is contained in siderite as a crystal chemical substituent was obtained from a siderite concretion (not from this mine site), (Morrison et al. 1990) for which 40 grains of siderite were analyzed for Fe, Mn, Mg and Ca. These data, Table 1, show an average Mn-substitution of 3500 ppm which is equated to a molar substitution of: $(Fe_{.86}Mg_{.02}Ca_{.1}Mn_{.01})CO_3$. Table 2 further supports the presence of a nearly constant, within experimental error, concentration of Mn in this 13.5 foot sequence of black shales. With the exception of the first three foot interval in this section (an interval with high pyrite concentrations) the concentration of Mn in the siderite (carbonate carbon) was relatively constant, showing perhaps a slight trend to higher concentrations with depth.

Table 1: Microprobe Analysis of Siderite (Wt.%)

	Fe	Mn	Ca	Mg
Avg.	39.05	0.35	3.52	0.38
std. dev.	1.42	0.26	0.93	0.10
number	41	41	41	41

Simulated weathering experiments were conducted on selected overburden samples within this 13.5 foot sequence of shales. Figure 5 summarizes the simulated weathering data for samples 170, 171, and 175. Sample 171 produced the highest weekly average of Mn among these three samples and also possessed both the highest amount of Mn and siderite in these samples. Mn concentrations in the mine backfill were approximately an order of magnitude greater (ranged from 78 to 84 ppm Mn) than the sample 171 simulated weathering Mn levels.

Table 2: Ratio of Mn to Carbonate Carbon

Sample #	Carbonate Carbon (wt %)	Mn (ppm)	Mn/C. Carbon Ratio
170	0.04	220	5.5×10^{-1}
171	0.69	1650	2.2×10^{-1}
172	1.23	2700	2.4×10^{-1}
173	1.30	3100	2.6×10^{-1}
174	0.80	2050	2.6×10^{-1}

Conclusions

It is clear that increasing amounts of manganese in this particular mine site, are accompanied with increasing amounts of both carbonate carbon and NP. CO_2 coulometry and x-ray diffraction data indicates that this carbonate is solely in the form of siderite. Therefore, at this particular site, the source of the manganese appears to be a Mn-bearing siderite. Of particular importance is that the siderite in this stratigraphic horizon occurs in intimate contact with some of the highest sulfur contents encountered. This accelerates the dissolution of siderite and therefore the release of Mn. Simulated weathering experiments produced leachates with Mn levels approximately an order of magnitude less than those values found in the mine backfill.

The occurrence of Mn in carbonates is well documented. Although the Mn in this particular mine site appears to be in the siderite, ongoing research at The Pennsylvania State University is establishing a Mn database in order to gain a better understanding of the distribution of Mn-bearing phases in coal-bearing stata. Such a database will hopefully lead to determining what level of Mn in the overburden has the potential to produce a mine drainage with elevated levels of Mn.

Acknowledgements

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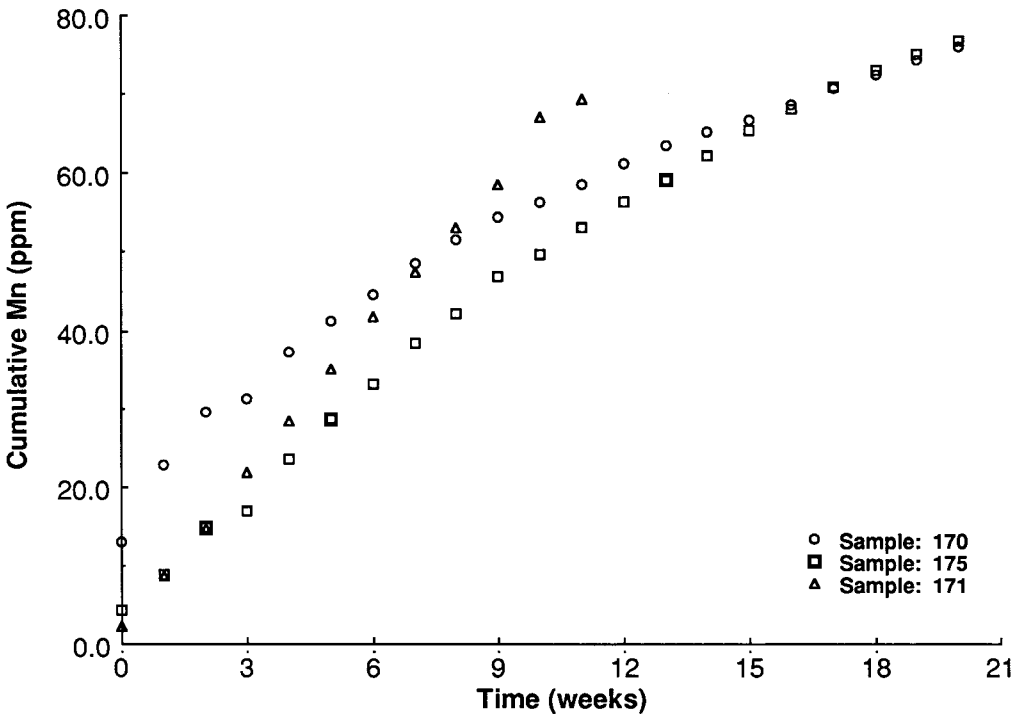

Sample	Acid / Base Account Data			Carbonate Carbon	Bulk Mn (ppm)	Simulated Weathering	
	Total Sulfur (wt %)	Neutralization Potential	Fizz Rating			Range Mn (ppm)	Weekly Avg. Mn (ppm)
170	4.42	2.81	none	0.04	220	1.7-12.9	3.4
171	0.66	10.20	none	0.69	1650	2.2-7.1	5.8
175	0.25	4.03	none	0.36	550	1.8-6.0	3.5

Figure 5: Characterization of Manganese Levels in Simulated Weathering Experiments.

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THE EFFECT OF OXYGEN ON PYRITE OXIDATION[1]

By

Richard W. Hammack and George R. Watzlaf[2]

Abstract. The oxygen dependence of abiotic and biotic pyrite oxidation was examined on three scales: 1) pyrite surfaces to a depth of 20 angstroms, 2) 5 g quantities of pyrite in small columns, and 3) 175 kg quantities of pyritic shale in large columns. Results of these studies indicated that the initial abiotic oxidation of fresh pyrite surfaces was independent of oxygen partial pressures above 10% (0-order reaction) and was proportional to oxygen partial pressures below 10% (first-order reaction). However, the rates of abiotic oxidation measured in small columns were proportional to oxygen partial pressures between atmospheric (21%) and 5%. Small column and large column results indicated that with bacteria present, the rate of pyrite oxidation was independent of oxygen partial pressures down to 1%. Below 1% oxygen, the reaction rate was proportional to oxygen partial pressures (first-order reaction). The oxygen-impermeable and oxygen-consumptive barriers other than water that are economically feasible at present are not capable of maintaining oxygen levels below 1%. Therefore, no reduction in the rate of pyrite oxidation would be would be realized using these techniques unless bacteria were inhibited. The best method for limiting pyrite oxidation was to place pyritic material below a permanent water table. Results of large column experiments indicated that a 96% reduction in pyrite oxidation could be realized by inundating the pyritic material. Results of large column tests corroborated previous work by other researchers that indicated leaching frequency had no effect on pyrite oxidation and total sulfate load.

Additional key words: pyrite oxidation, oxygen dependency.

Introduction

Early laboratory studies (Braley 1960; Clark 1965; Morth and Smith 1966; Rogowski and Pionke 1984; Nicholson, Gillham and Reardon 1988) showed that the rate of pyrite oxidation was dependent on the partial pressure of oxygen. However, there was no general concensus among researchers: reaction orders of 1/2, 2/3, 0.81, and 1 were proposed (Nicholson, Gillham and Reardon 1988; Lowson 1988).

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Although there was no agreement on reaction order, all studies indicated that the rate of pyrite oxidation could be reduced by limiting oxygen partial pressures. In the field, several strategies including clay capping, plastic liners, and even standard reclamation practices have reduced oxygen partial pressure in spoil and refuse to less than 10 or even 5% (Watzlaf and Erickson 1986; Lusardi and Erickson 1985). However, reducing oxygen partial pressure to these levels did not significantly slow the overall pyrite oxidation rate (Watzlaf and Erickson 1986). A laboratory study (Pugh, Hossner and Dixon 1984) partially explained the discrepancies between field and laboratory results. The study was carried out using framboidal pyrite in an aqueous suspension inoculated with a pure culture of Thiobacillus ferrooxidans. Results of this study indicated that the rate of pyrite oxidation was independent of oxygen partial pressures (0-order) above 8% when bacteria were present. Below 8% oxygen, the pyrite oxidation rate dropped sharply. Based on these results, no reduction in the pyrite oxidation rate would be expected in spoil or refuse piles unless the oxygen partial pressure could be sustained at levels less than 8% or unless bacteria could be inhibited.

Previous studies (Lusardi and Erickson 1985) indicated that the bulk of pyrite oxidation occurred in the unsaturated zone above the water table. Because many published laboratory pyrite oxidation rates (Braley 1960; Clark 1965; Morth and Smith 1966; and Pugh, Hossner, and Dixon 1984) were determined using aqueous pyrite suspensions, these results were not directly applicable to the field. This study was intended to be a comprehensive evaluation of abiotic and biotic pyrite oxidation rates under unsaturated conditions with different oxygen partial pressures. Pyrite oxidation was examined on three different scales: (1) pyrite surfaces to a depth of 20 angstroms; (2) 5 g quantities of pyrite in small columns; and, (3) 175 kg quantities of pyritic shale in large columns. The rationale of this approach was to determine the oxygen dependency of pyrite oxidation in the simplest case (ie. the oxidation of a surface) and observe apparent changes in oxygen dependency with increasing system complexity. Use of this approach could enable an interpolation to field scale.

Methods and Materials

Materials

The pyrite used in surface and small column studies was hand picked from a sample of the Pittsburgh coalbed collected in Barbour County, WV. The pyritic material was crushed to -60 mesh and subjected to a density separation using tetrabromoethane (2.96 g/cc). The sink portion was washed in boiling 6N HCl to remove sulfate and iron oxides and to kill bacteria. Evolved gas analysis indicated that the pyrite concentrate contained no sulfate sulfur and less than 1% organic sulfur. The material was determined to contain greater than 96% iron disulfide based on total sulfur measurements by combustion furnace.

The material used for large column experiments was a dark gray pyritic shale, superjacent to the Clarion coalbed in Clearfield County Pennsylvania. The shale was crushed to pass 3.8 cm and loaded into four columns containing approximately 175 kg each (Watzlaf and Hammack 1989). The crushed material was analyzed by the combustion furnace method and found to contain 3.5% sulfur.

Surface Weathering Studies

X-ray photoelectron spectroscopy (XPS), a surface analysis technique, was used to examine weathering pyrite surfaces. Because mass transfer or diffusional effects are minimal during the early stages of pyrite surface oxidation, the measured rates better reflect the kinetics of the electron transfer component of pyrite oxidation.

XPS provided quantitative elemental information with a detection limit of approximately 1% of atoms comprising the outermost monolayers. Different formal oxidation states could be distinguished based on chemical shift information (Brundle 1982). Chemical shifts in the sulfur (2p) electron binding energy (Fig. 1) were used in this study to distinguish between pyritic sulfur (reactant) and sulfate sulfur (product). The XPS analysis depth for pyrite was estimated to be about 2.3 nm based on measured inelastic mean free paths for similar semiconductors (Buckley, Woods, and Wouterlood 1987). This depth corresponded to the thickness of 4.24 pyrite unit cells (0.54175 nm/unit cell).

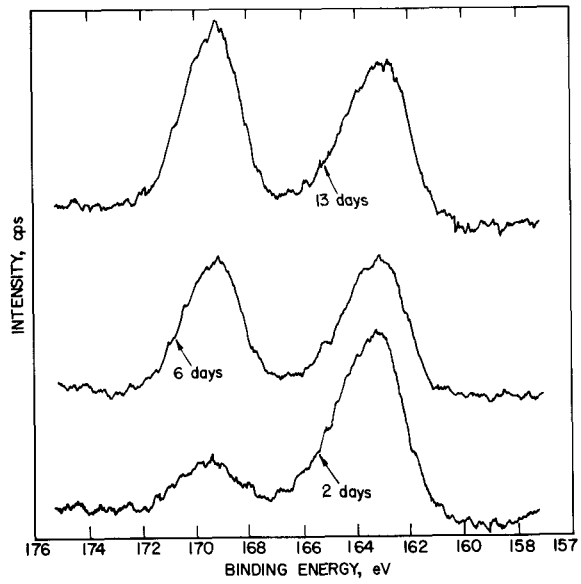

Figure 1. XPS scans of a pyrite surface showing the S (2p) electron region after 2, 6, and 13 days of weathering. Pyritic sulfur and sulfate sulfur peaks occur at 163.5 eV and 169.5 eV, respectively.

The pyrite was weathered at room temperature with a constant humidity of 88% and a oxygen partial pressure of 0.5, 5.0, 10.0, or 21%, balance nitrogen. The conversion of sulfide sulfur to sulfate sulfur was monitored. For each sample, a percent conversion was calculated from the integrated photoelectron intensities for sulfate sulfur (binding energy = 169 eV) and pyritic sulfur (binding energy = 163 eV):

$$\text{Pct. conv.} = \frac{I\ \text{sulfate sulfur}}{(I\ \text{sulfate sulfur} + I\ \text{sulfide sulfur})} \times 100\%$$

where I = integrated photoelectron intensity, arbitrary units.

Because sulfate sulfur and sulfide sulfur were the only observed sulfur species, the equation can be rewritten:

$$\text{Percent conv.} = \frac{\text{I sulfate sulfur}}{\text{I total sulfur}} \times 100 \text{ pct}$$

Immediately prior to weathering, samples for XPS analysis were washed with boiling 4.8 N HCl to remove sulfate, rinsed with methanol, and dried under vacuum. Cylindrical wafers (13 mm diameter by 0.5 mm) were pressed under 700 kg/cm^2 pressure. Weathering chambers (Fig. 2) were constructed so that wafers could be removed without disturbing the atmosphere within the chamber. Prior to each experiment, the chambers were washed with an acidified surfactant (sodium lauryl sulfate) solution and then rinsed with methanol to reduce the likelihood that bacterial catalysis could occur.

Periodically during the test, one wafer from each oxygen atmosphere was removed and placed in a Leybold-Heraeus LHS-10 photoelectron spectrometer operated at a pressure of $2X10^{-8}$ mbar or lower. X-rays from a magnesium anode (Mg K = 1253.6 eV) and an analyzer pass energy of 100 eV were used for the acquisition of S(2p) data. Binding energy calibrations were carried out by adjusting the measured binding energy for the C(1s) spectrum of adventitious carbon to 284.6 eV and shifting all other measured binding energies correspondingly. Peak areas within the S(2p) region attributable to sulfide sulfur and sulfate sulfur were determined with the Leybold-Heraeus DS-5 data system. The percent conversion was calculated for each wafer and plotted versus weathering time.

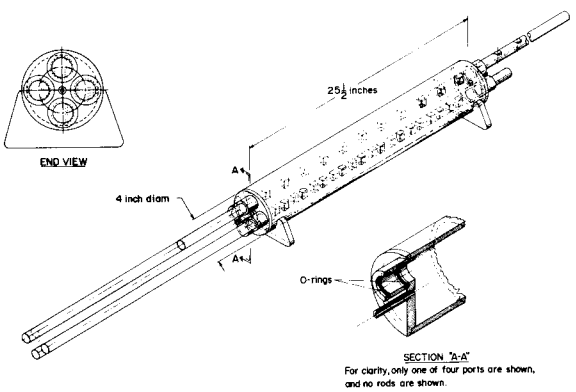

Figure 2. Schematic of chamber used for the XPS-monitored weathering of pyrite wafers. Wafers are placed in rod cut-outs where they can be removed one at a time without disturbing the environment in the chamber.

Small Column Studies

Four 40-cm by 2.54-cm I.D. columns (Fig. 3) were filled with 5 g each of pyrite dispersed in 100 g of 30 - 60 mesh acid-washed silica sand. Glass wool at the base of each column prevented the sample from washing out of the column. The columns were designed to allow pyrite to weather under unsaturated conditions in known oxygen atmospheres. Certified gas mixtures containing 0.005, 0.1, 0.3, 0.5, 1.0, 5.0, 9.6, or 14.5% oxygen, 5.0% carbon dioxide, and balance nitrogen were obtained in compressed gas cylinders. Gas mixtures were

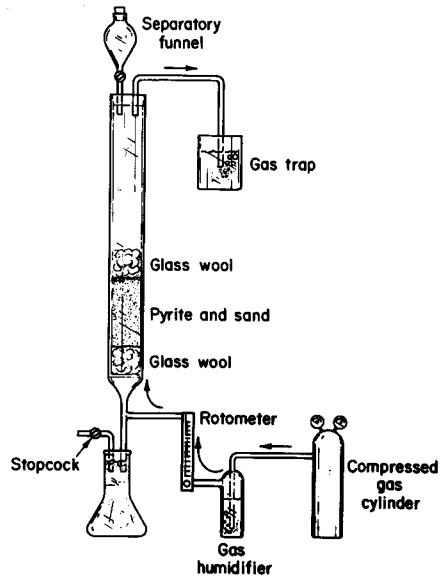

Figure 3. Schematic of set-up used for small column weathering tests.

bubbled through water to humidify the gas stream, passed through a rotometer, and then introduced into the base of each column (Fig. 3). The gases flowed up through the pyritic material and were exhausted to the atmosphere through a gas trap. A flow rate of 20 ml/min was maintained through each column. Analysis of gases exiting the columns showed that this flow rate was sufficient to maintain constant oxygen content throughout the column. The columns were leached weekly with 200 ml of 16 megohm deionized water (controlled oxygen atmospheres were maintained during leaching periods). A most probable number (MPN) type of bacterial enumeration (American Public Health Association 1985; Cobley and Haddock 1975) was performed on each leachate to determine the presence/absence or number of bacteria.

Large Column Studies

The large columns were constructed using 1.92-m lengths of 0.29-m diameter cast acrylic (Fig. 4). Three room temperature experiments were conducted with the large columns: (1) comparison of two applied oxygen partial pressures during unsaturated leaching; (2) comparison of four unsaturated leaching frequencies; and (3) comparison of unsaturated leaching with water-saturated leaching. Deionized water was added through the top of the columns for all leaching and flushing tests. For the first test, the tops of the columns were closed to the atmosphere. Certified gas mixtures containing 1.5% and 10.5% oxygen, balance nitrogen were humidified and flowed through the columns at a rate sufficient to maintain a constant oxygen partial pressure throughout the columns (3.1 L/min). For tests two and three, the top of the columns remained open to the atmosphere. During all unsaturated leaching tests, the valve on the final leachate collection system remained open with the end of the tube kept under water to avoid oxygen inflow. During flushing tests, the columns remained saturated with water with a constant water level maintained at 0.15 m above the surface of the shale. Twenty

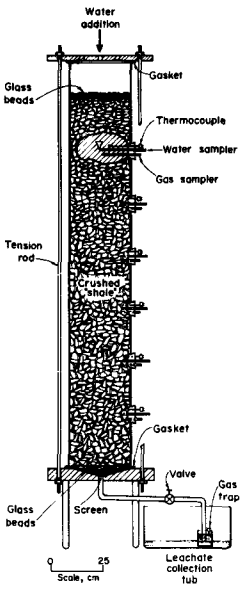

Figure 4. Schematic of set-up used for large column weathering tests.

liters of water were added and withdrawn simultaneously to maintain this water level. MPN bacterial enumerations were performed periodically to insure the presence of viable bacterial populations.

Analytical

The leachates from both the small column and large column tests were analyzed for sulfate using ion chromatography. Gas chromatography was used to determine oxygen in the effluent gases from the columns.

RESULTS AND DISCUSSION

Surface Studies

The room temperature oxidation of pyrite surfaces was carried out under abiotic conditions at 0.5, 5.0, 10.0, and 21% oxygen and 88% relative humidity. The surface oxidation of pyrite at 21% oxygen is shown in Figure 5. Initial oxidation rates are rapid. The apparent passivation that occurs after 300 hrs of weathering is an artifact of the XPS technique resulting from the mobilization and recrystallization of oxidation products. However, the slope of the least-squares fit line through the initial points is indicative of the oxidation rate. Abiotic surface oxidation rates at 0.5, 5.0, 10.0, and 21% oxygen are shown in Figure 6. Oxidation rates measured by XPS in this study are based on the amount of pyrite at the surface and "available" for reaction and, are significantly faster (20 to 40 times) than rates typically reported. Published oxidation rates are based on bulk pyrite content (amount of sulfate produced or oxygen consumed per gram bulk pyrite per hour) although only a small fraction of the bulk pyrite is at the surface and available for reaction.

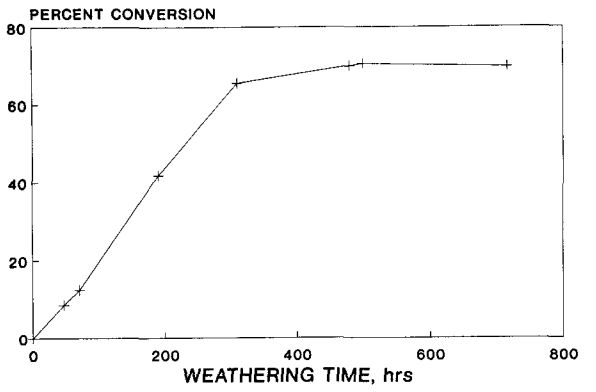

Figure 5. XPS-monitored abiotic weathering of a pyrite surface at 21% oxygen and 88% relative humidity.

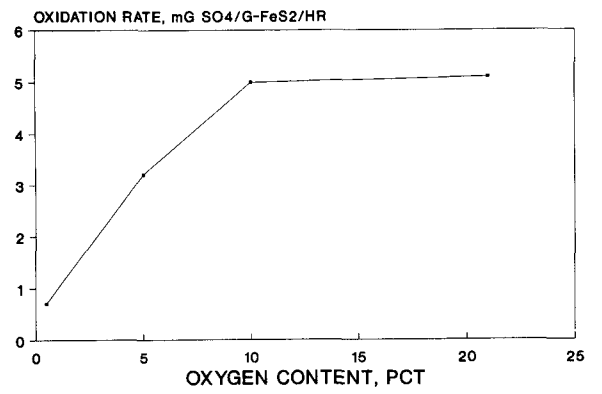

Figure 6. Abiotic surface oxidation rate at different oxygen partial pressures.

In this study, the abiotic surface oxidation rate (Table 1) is found to be independent of oxygen content above 10% (0-th order reaction). Below 10% oxygen, the rates are proportional to the oxygen content (first order reaction).

Table 1. Abiotic Oxidation of Pyrite Surfaces

Oxygen	Reaction order	Rate equation
Below 10 pct	1st	$dSO_4/dt = (0.45 \text{ mg } SO_4/\text{g-}FeS_2/\text{hr/pct } O_2)(\text{pct } O_2) + 0.64$
Above 10 pct	0	$dSO_4/dt = 5.0 \text{ mg } SO_4/\text{g-}FeS_2/\text{hr}$

Small Columns

Oxidation without Bacteria. Abiotic oxidation experiments were carried out on HCl-washed pyrite under unsaturated conditions at oxygen contents of 0.5, 5.0, 9.6, and 14.5%. MPN bacterial counts performed on the leachates indicated that the columns were sterile throughout the experiment. Plots of cumulative sulfate in the leachates versus weathering time (Fig. 7) are linear and show that abiotic pyrite oxidation is highly dependent on the oxygen content of the column atmosphere. Oxidation rates were calculated from the slope of the least-squares line fit to cumulative sulfate plots. Abiotic oxidation rates at different oxygen contents are shown in Figure 8 (without bacteria) and Table 2. The abiotic oxidation of pyrite at small-column scale is 1st order above 5% oxygen. Below 5% oxygen, the reaction order appears to fall below 1 which agrees with published results (Nicholson, Gillham, and Reardon 1988). In surface studies, pyrite oxidation was independent of oxygen partial pressures above 10%. However, at small column scale, the reaction is first order in this range. It can be speculated that at surface scale, the diffusional component of pyrite oxidation (the most sensitive to oxygen partial pressure) is minimal.

Oxidation with Bacteria. The room temperature biotic oxidation of pyrite was carried out under unsaturated conditions at oxygen contents of 0.005, 0.1, 0.3, 0.5, 1.0, and 10% (5% oxygen column broke during test). Each column was inoculated with 30 ml of acid drainage from a coal mine in Westmoreland County, PA. MPN's were performed during the experiment to make certain that each column contained viable bacteria.

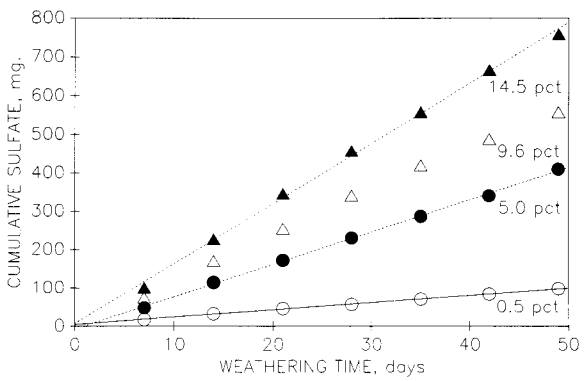

Figure 7. Plots of cumulative sulfate load versus weathering time for the abiotic weathering of pyrite in small columns under different oxygen partial pressures.

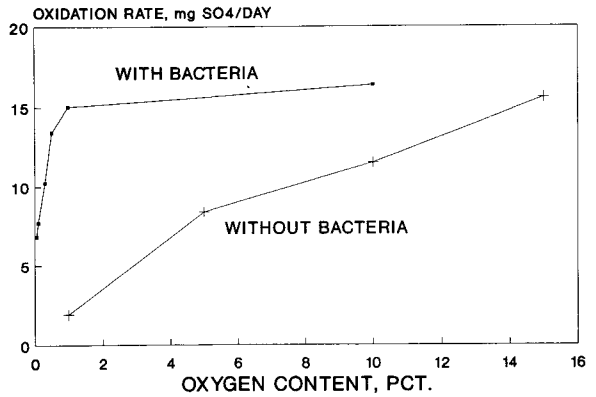

Figure 8. Abiotic rates of pyrite oxidation in small columns maintained at different oxygen partial pressures.

Cumulative sulfate versus weathering time plots for biotic oxidation are shown in Figure 9. Oxidation rates were determined from the slope of the least-squares fit line through the stationary phase. At this time, the effect of sulfate or ferric iron added with the inoculum would be insignificant. The inoculum could, at most, contribute only about 60 mg of sulfate including sulfate from the oxidation of pyrite by ferric iron in the inoculum. Unlike abiotic oxidation, biotic

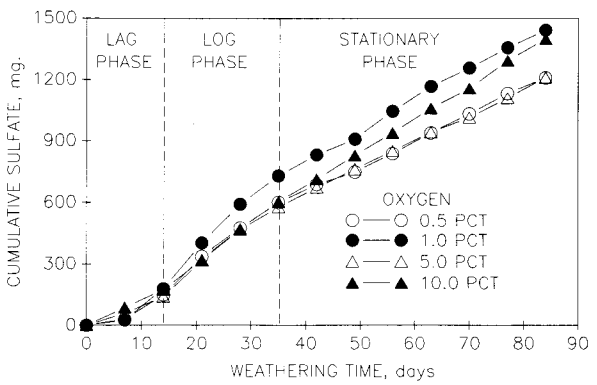

Figure 9. Plots of cumulative sulfate load versus weathering time for the biotic weathering of pyrite in small columns under different oxygen partial pressures.

Table 2. Abiotic Oxidation in Small Columns

Oxygen	Reaction order	Rate equation
Below 5 pct	Fractional	Insufficient data
Above 5 pct	1st	dSO_4/dt = (0.006 mg SO_4/g-FeS_2/hr/pct O_2)(pct O_2) + 4.63

Table 3. Biotic Oxidation in Small Columns

Oxygen	Reaction order	Rate equation
0.1 - 1 pct	1st	$dSO_4/dt = (0.073 \text{ mg } SO_4/g\text{-}FeS_2/hr/pct\ O_2)(pct\ O_2) + 7.22$
Above 1 pct	0	$dSO_4/dt = 0.13 \text{ mg } SO_4/g\text{-}FeS_2/hr$

oxidation is not significantly inhibited by reduced oxygen contents (Fig. 8, with bacteria) and Table 3. In fact, the reaction rate is independent of oxygen partial pressures (0-order reaction) above 1%. Below 1% oxygen, the reaction appears to be first order until some point below 0.1%.

The oxidation rate at oxygen partial pressures above 1% (0.13 mg $SO_4/g\text{-}FeS_2/hr$) is in good agreement with published rates (Table 4). It is also apparent that the rates of abiotic and biotic pyrite oxidation are not significantly different at oxygen partial pressures above 15% (Fig. 8). The role of bacteria is to sustain high oxidation rates at low oxygen partial pressures.

Large Columns

Small column tests indicated that the rate of biotic pyrite oxidation was independent of oxygen partial pressures (0-th order reaction) above 1%. This indicates that measures taken to reduce oxygen partial pressures would be ineffective at reducing pyrite oxidation unless oxygen could be maintained at levels below 1%. This is not economically possible at present using barriers other than water. In large column tests, no difference in biotic pyrite oxidation rate was found between columns with applied atmospheres of 1.5% and 10.5% oxygen (Fig 10). These results corroborate the results of small column tests and indicate that current oxygen-impermeable or -consumptive barriers (except water) will not be effective at limiting pyrite oxidation without bacterial inhibition.

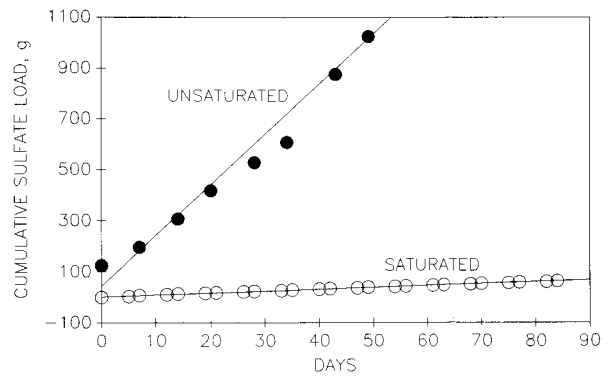

Figure 10. Plots of cumulative sulfate load versus weathering time for saturated and unsaturated pyritic shale in large columns.

Table 4. Pyrite oxidation rates, oxygen dependence, and water dependence reported by other authors.

Investigator	Observed rate	O_2-dependence	H_2O-dependence	Pyrite type	Particle size	Temperature	Species Monitored	Remarks
Braley (1960)	0.13 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Linear (first-order)	NA	Sulfur ball	-8 + 40 mesh		Sulfate	
Clark (1965)	0.11 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Linear (first-order) for dissolved oxygen	NA	Sulfur ball	-40 + 50 mesh	20° C	Sulfate	
Morth and Smith (1966)	0.06 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Non-linear (fractional order)	Non-linear (order exceeds 1 as 100% relative humidity is approached)	Sulfur ball	-70 + 100 mesh	25° C	Oxygen	
Rogowski and Pionke (1984)	0.16 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	ND	ND	Not spec.	2-8 mm	25° C	Sulfate	Spoil sample
Nicholson and others (1988)	0.13 mg $SO_4^{-2}g^{-1}FeS_2$ hr^{-1}	Adsorption (Langmuir-type)	NA	Massive, from various locations	76 um	23° C	Sulfate	Carbonate buffered

NA - Not applicable.
ND - Not determined.

The effect of leaching frequency is shown in Figure 11. Columns 1-4 were leached as follows: column #1, 1L every day; column #2, 7L every 7 days; column #3, 14L every 14 days; and column #4, 21L every 21 days. The results of this experiment indicated that the build up of weathered products did not retard pyrite oxidation by surface passivation. An alternative explanation is that the solubilization of sulfate minerals under these conditions may be slower than pyrite oxidation. Therefore, leaching frequency tests may only be indicative of the rate of oxidation product solubilization rather than pyrite oxidation.

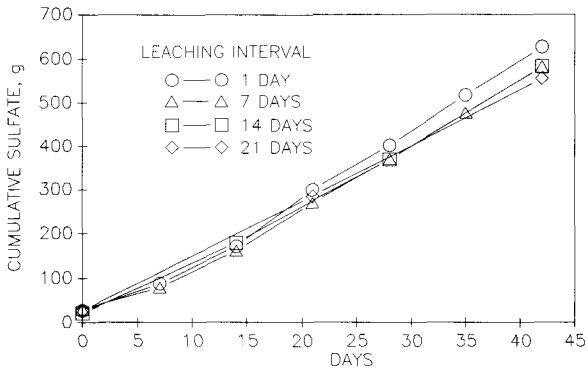

Figure 11. Plots of cumulative sulfate load versus weathering time at different leaching frequencies.

Results of this study indicate that attempts to limit pyrite oxidation under unsaturated conditions would be difficult and undoubtedly expensive. However, water is an effective oxygen barrier. Figure 12 compares the rates of release of sulfate under unsaturated and water-saturated conditions. For unsaturated leaching, sulfate was released at a rate of 18.2 g/day compared to 0.7 g/day when the shale remained inundated and flushed biweekly with 20 L of oxygen-saturated water (D.O. = 8 mg/L). Stoichiometrically, the amount of oxygen added through flushes with oxygen-saturated water can account for 0.2 g/day of sulfate from the oxidation of pyrite. The remaining 0.5 g/day of sulfate released could be due to additional pyrite oxidation from ferric iron resident in the columns or dissolved oxygen transferred from the atmosphere. It is also possible that some of the sulfate is from the continued solubilization of previously formed sulfate compounds. Additional tests using oxygen-depleted water for the 20-L flushes resulted in a sulfate release rate of 0.5 g/day.

The importance of maintaining complete water inundation was illustrated during these tests. A leak developed between tests that dropped the level of the water to 0.5 m below the suface of the shale. It is not known how long this upper 0.5 m of shale was exposed, but it was for no more than 32 days. During and for a short period after resaturation, the sulfate release rate into solution was a minimum of 6.9 g/day, ten times the rate during saturation. After resaturation, the sulfate release rate dropped to pre-leak levels.

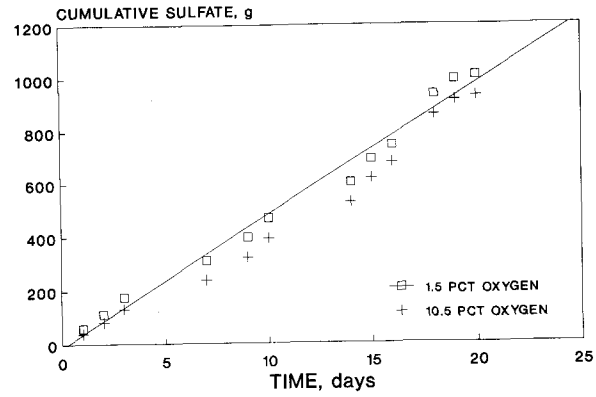

Figure 12. Plots of the cumulative sulfate load versus weathering time for large columns maintained at oxygen partial pressures of 1.5% and 10.5%.

Implications for Spoil Handling

When material is first exposed by mining, fresh pyrite surfaces occur along fractures in the newly broken rock. The pH of the material is near-neutral, which limits ferric ion solubility and the catalytic effect of bacteria on pyrite oxidation. In this scenario, the abiotic surface oxidation rates determined by XPS are applicable. These rates are rapid because the reaction is not diffusion-limited at this point. The oxygen partial pressure would have to be maintained below 10% to affect pyrite oxidation rates in fresh material. Although these conditions may only exist for a few days, the initial abiotic oxidation is important because it establishes the low-pH, ferrous iron-rich environment necessary for the growth of iron-oxidizing bacteria.

Once bacterially-mediated pyrite oxidation is established, the oxygen partial pressure would have to be maintained below 1% to realize any reduction in oxidation rate. Reducing oxygen partial pressures to this level with solid covers is not practical. However, if bacteria are inhibited, any reduction in oxygen partial pressure from atmospheric (21%) will result in a proportional decrease in pyrite oxidation rate.

The most effective strategy for limiting pyrite oxidation is to place pyritic material below a permanent water table. Results of this study indicate that pyrite oxidation rates can be reduced by at least 96% with inundation. However, it is important that pyritic spoil be immediately flooded. Any storage above the water table will result in rapid pyrite oxidation even at low lovels of oxygen unless bacteria are inhibited. The oxidation products that form during storage will be solubilized when the material is flooded, resulting in an slug of degraded water. However, once the stored oxidation products are removed, water quality will improve. Any field trial of inundation must allow for differentiation between sulfate derived from product solubilization and sulfate from on-going pyrite oxidation. It is also desirable that groundwater flow through the impoundment be slow and from an oxygen-depleted source, if possible. Oxidation rates determined for oxygen-saturated aqueous pyrite suspensions

(Nicholson, Gillham, and Reardon 1988) are equivalent to the rates determined in this study for unsaturated conditions. This indicates that flooding will not reduce pyrite oxidation if the pyrite is contacted by a high flow of oxygen-saturated water. However, these conditions are unlikely to exist in an inundated backfill.

Results of this study indicate that under unsaturated conditions, pyrite oxidation rates can only be reduced by bacterial inhibition in conjunction with an oxygen-consumptive or oxygen-impermeable barrier. Inundating pyritic material will reduce oxidation rates by at least 96% and is the the most effective means of controlling pyrite oxidation.

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AN APPLICATION OF ACID-BASE ACCOUNTING FOR HIGHWAY CONSTRUCTION IN EAST TENNESSEE[1]

by

J.T. Ammons, C.B. Coburn, Jr., and P.A. Shelton[2]

Abstract. Concern over the environmental impact of highway construction on the foothills Scenic Parkway in east Tennessee prompted the use of acid-base accounting to evaluate overburden rocks. Samples were acquired during active construction to evaluate the acid producing potential of the overburden. A core was provided representing the middle portion of the overburden for acid-base accounting and mineralogical analyses. Substantial quantities of pyrite were noted in a few zones in the overburden. Most of the overburden contained sufficient neutralizers to neutralize the potential acidity if the overburden was blended in the fill during construction. Higher neutralization potential values in the overburden were directly related to the relative proportion of dolomite detected in the samples.

Additional key words: acid-base accounting, highway construction, east Tennessee.

Introduction

The Tennessee Department of Transportation (TDOT) had expressed concern that acidity problems might be encountered during the construction of the Foothills Scenic Parkway in East Tennessee (Fig. 1). These concerns were based on sporadic vegetation failures observed on the previously completed section of the parkway.

Certain sections of the precambrian rocks of east Tennessee contain pyrite (FeS_2), (Byerly and Middleton, 1981) and the oxidation of pyrite will result in the formation of acidity. Drastic land disturbances, such as highway construction, expose iron disulfide to the air and water necessary to promote the following reaction presented in a simplified form:

$$4FeS_2 + 15O_2 + 14H_2 \text{ ----> } 4Fe(OH)_3 + 8H_2SO_4$$

The production of sulfuric acid affects water and soil quality. Minerals are dissolved in the acid environment developed during the oxidization process, and elements are mobilized in the soil which could impact water quality in the immediate watershed.

Jago and Byerly (1988) conducted a leaching study on pyritic precambrian rocks containing pyrite in east Tennessee. Using acid-base accounting, they established that the acid-producing potential for the material under evaluation was 23.7 tons per 1000 tons material ($CaCO_3$ equivalent). They concluded that additions of interlayer lime to fill material improved the leachate quality.

The objectives of this study were to identify the acid producing strata in the overburden core and to access the environmental impact for revegetation and water quality.

Materials and Methods

Several samples were analyzed from the active construction site to assess whether the overburden had acid-producing potential. An overburden core was provided by TDOT from the geologic section affected during construction. Water quality sampling stations were in place to monitor

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chemical parameters for pre-construction, active-construction, and post-construction phases of the project.

The first sampling was completed on-site during active construction. Six samples were removed at random from disposal piles. Different rock types were selected to determine if materials placed in the fill were potentially toxic. The Tennessee Department of Transportation provided a thirty-two foot section of the overburden for laboratory analyses. The upper twenty-five feet of the core was not sampled. The overburden core and the pile sample sites were located near Caylor Gap on the Wear Cove, Tennessee Geologic Quadrangle (Fig. 1).

Both overburden core and pile samples were ground to less than 60 mesh and were analyzed using acid-base accounting (Smith et al. 1974; Sobek et al. 1978). Total sulfur values were used to calculate the acid-base account. The neutralization potential followed the guidelines presented by Shelton et al. (1984).

Mineralogical analyses were conducted on the overburden core samples. Ground samples (less than 60 mesh) were placed in metal powder sample holders and scanned from 2 degrees to 60 degrees 2 theta using copper (k) alpha radiation (McMurdie et al. 1986).

Water quality has been monitored since the inception of the construction on the parkway. Station I (Fig.1) is a water monitoring sampling station in the watershed draining Caylor Gap where the overburden core and the pile samples were collected. Data reported are an average of twelve months for each year.

Results and Discussion

Preliminary sampling

Results from the pile samples obtained during active construction are reported in Table 1. The rocks were identified as part of the Anakeesta formation, Precambrian age, from the Great Smokey Mountain Group. The Anakeesta formation consists of "dark gray, bluish-gray, black slates with interbeds of fine-grain sandstone" (Hardeman 1966). Three of the pile samples were potentially toxic (Table 1). Samples showing a deficiency of 5 tons/1000 tons material ($CaCO_3$ equivalent) are considered potentially toxic (Smith et al. 1974; Sobek et al. 1978).

Overburden Analysis

All of the samples contained a significant concentration of total sulfur (>0.4%) (Table 2). In most samples, sufficient neutralizers were present to counteract potential acidity.

Potentially toxic zones were found at depths of 30 to 37 feet and 47 to 52 feet (Table 2 and Fig. 2). The potentially toxic

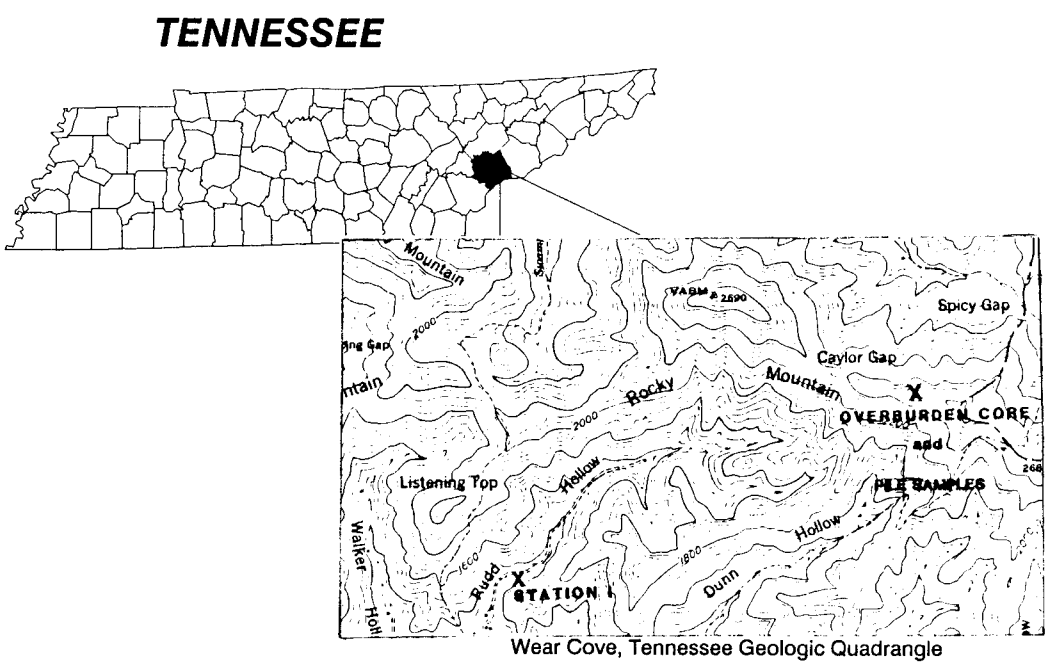

Figure 1. Location of Overburden Core, Pile Samples, and Water Monitoring Station on the Foothills Scenic Parkway.

Table 1. Acid-Base Account of Grab Samples. Foothills Scenic Parkway.

Sample Number	Paste pH	Munsell Color	Fizz	Percent Sulfur	$CaCO_3$ equivalents (tons/1000 tons material) Max From Sulfur	N.P.	Deficiency	Excess
1	5.8	2.5Y6/0	None	.063	1.98	1.03	.95	
2	5.4	5Y8/1	None	.019	.58	.11	.47	
3	7.4	5Y6/1	Slight	.031	.96	1.03		.07
4	6.2	2.5Y6/0	Slight	2.149	67.16	2.86	64.30	
5	7.3	2.5Y7/0	Slight	.684	21.38	.92	20.46	
6	7.0	2.5Y6/0	Slight	2.358	73.69	2.86	70.83	

rocks were sandstone conglomerates with a dark shale-slate intercalate. Pyrite was visually confirmed between the bands of shaly slate and the sandstone conglomerate with the aid of a 10X hand lens. Revegetation and water quality problems can be anticipated if the potentially toxic materials are deposited on the surface.

The physical stability of the pyrite containing rocks were not evaluated in this study, but the rapidity of rock disintegration in the fill indicates that water quality and revegetation may be impacted. Future studies on the Precambrian rocks in east Tennessee should include physical stability and\or weatherability evaluations. If these rocks are resistant to physical and chemical breakdown in the construction fill, products from the oxidation of pyrite will be minimized. This will enhance success of revegetation and reduce affect on water quality in the watershed. A rapid, chemical and physical breakdown may affect the stability of the fill plus increase surface area which will increase oxidation reactions in rocks containing pyrite.

Mineralogy

Primary minerals present in the overburden samples were chlorite, muscovite, orthoclase, quartz, and dolomite (Table 3). Pyrite was not detected in the x-ray analysis. Samples containing less than 10% dolomite were potentially toxic (Table 2). The presence of dolomite contributed heavily to the high NP values. In the absence of dolomite, the NP's are low. The dolomite is probably responsible for the majority of the bases in these overburden rocks.

Water Quality

Sulfate and magnesium concentrations in the water varied over the five-year period (Fig. 3), but showed a slight increase. The variation in sulfate was probably due to differences in rainfall over the five-year period. The increase in magnesium concentrations were probably related to weathering of dolomite in the fill.

Conclusions

Substantial quantities of pyritic

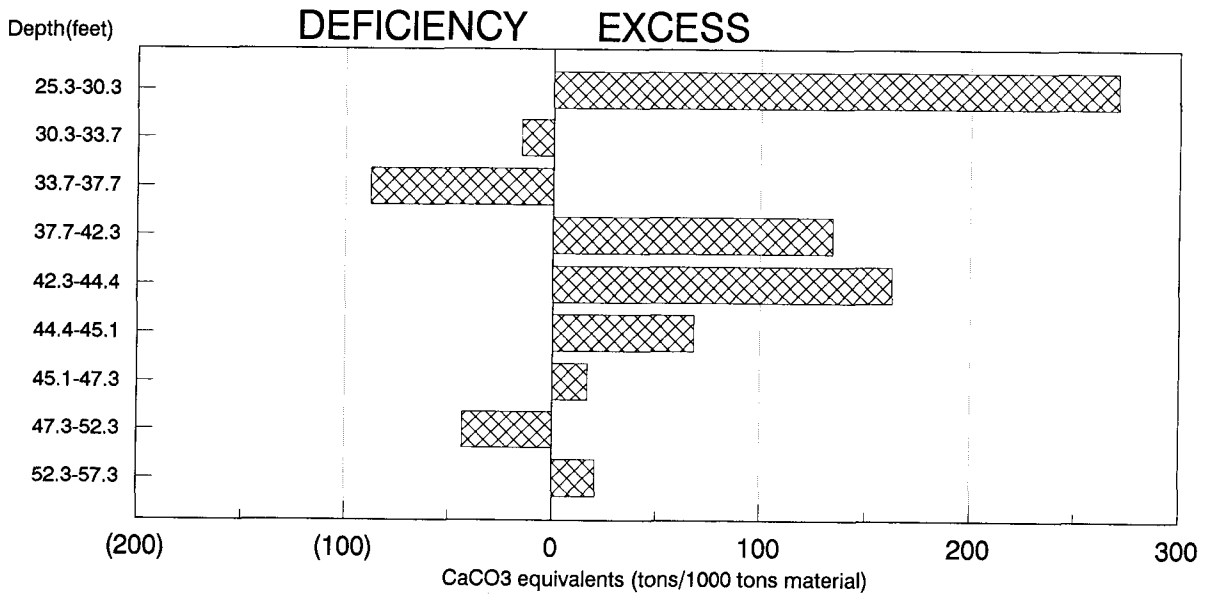

Figure 2. Acid-Base Account of Foothills Parkway Overburden Core.

Table 2. Acid-Base Account of Overburden Core. Foothills Scenic Parkway.

Sample Number	Depth	Munsell Color	Fizz	Percent Sulfur	$CaCO_3$ equivalents (tons/1000 tons material) Max From Sulfur	N.P.	Deficiency	Excess
	ft							
1	25.3-30.3	N 6/0	Strong	.843	26.35	297.43		271.08
2	30.3-33.7	N 6/0	Slight	.717	22.40	7.00	15.40	
3	33.7-37.3	N 5/0	Slight	2.840	88.88	1.00	87.88	
4	37.3-42.3	N 6/0	Strong	.674	21.07	155.38		134.31
5	42.3-44.4	N 5/0	Strong	1.160	36.25	199.09		162.84
6	44.4-45.1	N 5/0	Moderate	.810	25.31	93.47		68.16
7	45.1-47.3	N 5/0	Moderate	1.443	45.09	61.90		16.81
8	47.3-52.3	N 5/0	Moderate	2.853	89.16	46.12	43.04	
9	52.3-57.3	N 5/0	Moderate	.925	28.91	49.76		20.85

Table 3. Summary of Mineralogical Analyses for Overburden Core. Foothills Scenic Parkway.

Sample	Depth	Minerals Present: Chlorite[1]	Muscovite[2]	Orthoclase[3]	Dolomite[4]	Quartz[5]
	ft	Approx. Percentage				
1	25.3-30.3	20-30	10-20	ND	10-30	>30
2	30.3-33.7	ND	10-20	20-30	ND	>30
3	33.7-37.3	ND	20-30	20-30	ND	>30
4	37.3-42.3	ND	10-20	20-30	10-20	>30
5	42.3-44.4	ND	20-30	20-30	20-30	>30
6	44.4-45.1	ND	20-30	10-20	10-20	>30
7	45.1-47.3	ND	20-30	10-20	10-20	>30
8	47.3-52.3	ND	20-30	10-20	10-20	>30
9	52.3-57.3	ND	20-30	10-20	<10	>30

[1] - Chlorite - $(Fe,Al,Mg)_6(Si,Al)_4O_{10}(OH)_8$

[2] - Muscovite - $KAl_2(Si_3,Al),O_{10}(OH,F)_2$

[3] - Orthoclase - $KAlSi_3O_8$

[4] - Dolomite - $Ca,Mg(Co_3)_2$

[5] - Quartz - SiO_2

materials are present in the Precambrian rocks studied on the Foothills Scenic Parkway. Byerly and Middleton (1981) reported acid-base account values for potentially deleterious rocks southwest of the Great Smoky Mountains in Monroe County, Tennessee. Values in this study ranged from a deficiency of 7.69 to 42.88 calcium carbonate equivalent (tons/1,000 tons material). This is compared to samples from the Foothills Parkway where the pile samples ranged from an excess of .07 to a deficiency 70.83 and the overburden samples ranged from an excess of 271.08 to a deficiency of 87.88 calcium carbonate equivalent (tons/1,000 tons material). Most zones in the overburden tested on the Foothills Parkway contain sufficient quantities of basic materials to neutralize potential acidity in the fill if the materials are blended. This is supported, in part, by results reported by Jago and Byerly (1988). In a pyritic material encapsulation study involving Precambrian rocks, they found the best leachate quality was achieved by interlayering limestone with the fill material.

Higher NP values in the Foothill's study are directly related to the relative proportion of dolomite detected in the samples. This is probably responsible for elevated levels of magnesium in the water quality samples.

The following are suggested guidelines to accomplish the best post-construction environmental quality:

1. Complete an overburden analysis (acid-base accounting) on the geologic section to be removed during construction.

2. During construction, monitor overburden for changes in depth or sequence of acid-toxic rocks.

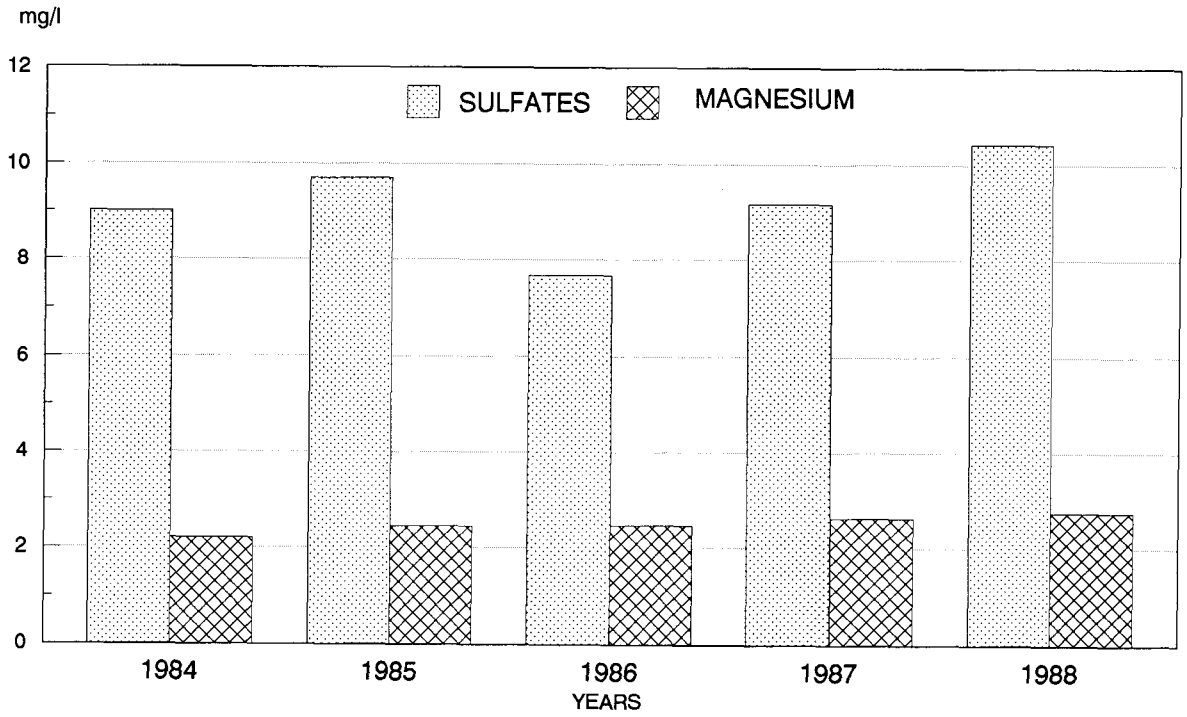

Figure 3. Five-Year Average of Sulfate and Magnesium Water Quality Data.

Station I, Foothills Scenic Parkway.

3. Examine older fills constructed from the same geologic materials for presence of acid-toxic rocks and vegetation success.

4. Study the physical stability of overburden rocks under controlled experimental conditions.

5. Monitor water quality in watersheds affected by construction activities.

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