LONG TERM BEHAVIOR OF ACID FORMING ROCK: RESULTS OF 11-YEAR FIELD STUDIES [1]

PAUL F. ZIEMKIEWICZ [2] and F. ALLEN MEEK JR. [3]

Abstract: The ability to predict long term acid mine drainage (AMD) under field conditions is limited by the near absence of long-term, well controlled and well documented field sites. Much of the literature on AMD derives from either uncontrolled, operational mine sites or from laboratory studies using a variety of simulated weathering methods.

In February 1982, Island Creek Corporation constructed eleven 400 ton rock piles on plastic lined pads at its Upshur County, WV coal mine. The piles ranged from 100% sandstone to 100% shale with several mixtures of the two rock types. Leachate waters were collected biweekly during the first year and subjected to chemical analysis. Because water volumes were also measured it was possible to estimates mass balances and flux rates for key constituents such as sulfur, calcium and acidity.

Eleven years after construction the piles were again sampled. Data are presented indicating the rates of sulfur flux from each of the piles and changes in water quality over the 11 years of the study. Of particular interest was the tendency of the sulfur flux rate to approximate that reported for pure pyrite under laboratory conditions.

Additional Key Words: Acid mine drainage, coal spoil, alkaline amendment.

Background

Acid Base Accounting.

Acid Base Accounting (ABA) was developed in the early 1970's by researchers at West Virginia University to identify and classify geologic strata encountered during mining (West Virginia University, 1971). A history of Acid Base Account is provided by Skousen et al. (1990).

Since its development, ABA has been used extensively in the United States and several other countries for premining coal overburden analysis. Its popularity largely stems from its simplicity. It uses two key parameters: maximum potential acidity (MPA) and neutralization potential (NP). MPA is estimated by multiplying the percent pyrite sulfur by 3.125 yielding the total acid produced. NP is the acid consumed by the rock in a titration. Both MPA and NP are given in calcium carbonate equivalents. ABA does not address the different rates of acid and alkali-generating reactions in rock.

Introduction

The long term behavior of acid producing rock under field conditions has been the subject of much speculation and modelling but relatively little systematic study.

DiPretoro and Rauch (1988) found poor correlations (reported $R^2=0.16$) between a volume-weighted acid base net neutralization potential (NP) and net drainage alkalinity near thirty mine sites in West Virginia. Erickson and Hedin (1988) showed similar low correlation among MPA, NP, net NP from ABA and net alkalinity from drainage

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water. Both reports related that factors other than overburden characteristics were involved in predicting post mining water quality.

DiPretoro and Rauch (1988) found that sites with greater than 3% calcium carbonate equivalent (NP) in overburden produced alkaline drainages while at 1% or less acidic drainage resulted. Erickson and Hedin's results indicate that 2% calcium carbonate or less produced acidic drainage while 8% or more produced alkaline drainage. (In this later study there were no sampling points between 2% and 8%).

O'Hagan and Caruccio (1986) found that the addition of calcium carbonate at 5% by weight to a coal refuse containing 1% S produced alkaline drainage. In Minnesota, Lapakko (1988) found that 3% calcium carbonate neutralized an overburden material with 1.17% S.

Cravotta et al. (1990) reviewed the calculation of NP in ABA. In current ABA usage, 3.125 g calcium carbonate equivalent is required to neutralize acidity resulting from oxidation of 1 g S. Cravotta et al. (1990) argue that this ratio should double to 6.25:1. Volume-weighted maximum acidities are subtracted from NP giving a positive or negative net NP for the mined area. A negative, or deficient, net NP is interpreted to indicate the amount of calcite that must be added to equalize the deficiency and prevent AMD formation.

Other alkaline materials have higher NP's than calcite. Quicklime, kiln dust and hydrated lime all have higher activities than calcite, though it is not clear that the kinetics of pyrite oxidation favor readily soluble sources of alkalinity.

Brady et al. (1990) conducted a study of 12 sites where ABA data were available. They computed net NP based on both 3.125% and 6.25% to 1% S. Alkaline addition on the sites was conducted to abate potential AMD problems. When using 6.25%, the sign of the net NP (plus or minus) matched the sign of the overall net alkalinity of water at 11 of 12 sites.

The results of their study concluded that NP and traditional estimates of MPA (e.g. 3.125% to 1% S) were not equivalent and that overburden NP must be twice the MPA to produce alkaline mine drainage. They also concluded that mining practices (such as alkaline addition, selective handling, and concurrent reclamation) enhanced the effect of alkaline addition on reducing acidity. Lastly, they concluded that additional studies are needed to determine the rates, application and placement of alkaline material during mining.

Methods

Island Creek Corporation constructed a series of 11 test piles at its Upshur County, WV mining complex between January and March 1982. Rocks used in the trials were taken from the company's active mining operations on the site and were sized to exclude roughly +8 in. and -1 in. rocks. Treatments consisted of various combinations of sandstone and shale. Another series of treatments consisted of various amendments for controlling AMD.

About 400 tons of rock were placed in each test pile. Each rock mass was placed on a plastic liner with an 8 inch perforated pipe for collection of drainage to an automatic sampling station. The piles were flat-topped and were roughly 16m X 16m X 2m. The rock units were sampled on placement in each pile and ABA were developed for each. Table 1 describes the treatments and properties of each pile. Treatments can be summarized thus:

Table 1.   Identification, summary of treatments and NP/MPA of the 11 test piles, Upshur County, WV.

PILE #	DESCRIPTION	CODE	NP/MPA
CONTROL, NO AMENDMENT			
PILE 1	100% sandstone	SS	3.94
2	100% shale	SH	0.08
3	sandstone/shale in layers	LAY	0.18
10	sandstone/shale blended	BLD	0.29
LIMESTONE AMENDMENT			
PILE 5	0.5% by mass	LS1	0.46
4	1.65% by mass	LS2	1.07
8	2.4% by mass	LS3	1.26
PHOSPHATE AMENDMENT			
PILE 7	0.15% by mass	RP1	0.15
6	0.3% by mass	RP2	0.31
CALCIUM OXIDE AMENDMENT			
PILE 9	0.62% by mass	CaO	0.15
BACTERICIDE AMENDMENT			
PILE 11	30 lbs. sodium lauryl sulfate +31 lbs Microwet #2 + impregnated pellets	SLS	0.41

Amendments were spread over one foot spoil layers during construction. A rain gauge was maintained on the site during the period of the study. Annual precipitation averaged 45 inches. The pH of the local rainfall averaged about 4.5.

Immediately following pile construction, water samples were collected and analyzed weekly, then later bi-weekly for roughly the first year. Sampling then halted for the next 11 years until January 1993. The following parameters were measured: flow, acidity, alkalinity, pH, sulfate, calcium, magnesium, iron and manganese. Since flow was measured it was possible to develop mass balances for various ions, particularly sulfate.

With the exception of pile 1 all of the piles were undisturbed when sampled in January 1993. About one half of pile 1 had been excavated and could not be sampled. The automatic samplers had been removed from each pile and it was not possible to estimate flows. Therefore, only chemical concentrations are reported for the January 1993 sample. Flow data were based on flow meters attached to the outlet of each pile. They did not always work and some of the flow data is inferential (e.g. calibrated against precipitation). Nonetheless, it was clear that flows varied little among piles at a given time interval.

A key parameter in developing the sulfur dynamics was sulfur flux (Sf). Sulfur flux was expressed as the percent of the original pyrite sulfur mass which had exited the pile as sulfate ion. Sulfur flux integrates both pyrite oxidation and sulfate leaching rates into a single, empirical parameter.

Results

The results are based on 400 ton test piles constructed in mid-winter 1982. Only one sample was taken of each rock unit during placement so that on a given pile NP and MPA are based on a one shale sample and/or one

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sandstone. It is likely that the distribution of pyrite and alkalinity were neither homogeneous nor random and that reported NP/MPA ratios may be subject to error. It is also possible that the placement of alkaline amendments was not uniform. Results of the sampling program are presented in figures 1-6. Treatments are summarized in table 1.

Control, No Amendment. In piles SS and SH pH fell rapidly to about 4.2 over the first 7 months while sulfate rose from near zero to the range 2000 to 2500 ppm. Leachate sulfate concentrations from LAY and BLD rose to about 2700 ppm while pH fell less dramatically to 4.9 and 6.2 respectively. By January 1993, pH had changed little while sulfate concentrations dropped to less than 100 ppm. At least over the first year, blending seemed to improve the pH of the piles while there appeared to be little effect on sulfate generation. See figures 1 and 2.

Limestone Amendment. Addition of limestone had no effect on the rate of sulfate generation and, by inference, the rate of pyrite oxidation. Over the first year, the pH of LS1 AND LS2 remained above neutral while LS3 became acid. Nonetheless, 11 years later the final pH of LS1, LS2 AND LS3 were 5.2, 6.4 and 6.6 respectively. It is not clear why LS3, with the highest NP/MPA initially became acid. Sulfate generation was the same as the other piles so the difference must lie in the efficiency with which the available alkalinity was utilized. This could be a result of initial placing and mixing but records indicate no compelling cause for this result. It is also not clear how long LS3 remained acid. By year 11, at any rate, it had the highest pH.

Sulfate generation was the same as the control piles (SS, SH, LAY, BLD) and by year 11 sulfate concentrations had dropped to below 350 ppm. See figures 3 and 4.

Phosphate Amendment. Sulfate profiles of the two phosphate treatments over the 11 years of the study indicate that pyrite oxidation is not affected by phosphate addition. Effluent pH remained above or near neutral for the first year. The pH of RP1 AND RP2 then dropped to 4.7 and 3.8 respectively. It is not clear why the heavier phosphate application reached a lower pH or whether the difference is even significant. It is clear that phosphate does not control pyrite oxidation, but simply acts as a lime by neutralizing produced acidity. Mindful that it is usually much more expensive than limestone, it should if used, be applied at rates similar to those at which limestone is effective. See figures 5 and 6.

Calcium Oxide Amendment. Sulfate concentrations, like all of the other plots rose rapidly over the first 7 months of the study, reached a peak of about 2500. By year 11 sulfate concentration on this pile was less than 100 ppm. Over this period pH declined rapidly, and by year 11 was about 4.2, the pH of the local rainwater. See figures 5 and 6.

Bactericide Amendment. Sodium lauryl sulfate is a bactericide, meant to control the rate of pyrite oxidation by killing the Thiobacillus ferroxidans bacteria. The sulfate concentration profile for this treatment suggests that pyrite oxidation was little affected by the treatment and that the primary effect of the treatment was to increase the pH over the first year. By year 11 pH was about 4.2. The pH and sulfate profiles are consistent with an alkaline amendment applied at less than adequate rates. See figures 5 and 6.

Sulfur Flux. Sulfur flux through each pile ranged from 0.064% per day to slightly less than 0.01% per day. With only two exceptions all values fell between 0.01% and 0.03% per day (figure 7). For comparison, the literature value of Taylor et al. (1984) of 0.02% per day is presented. This is a surprising level of agreement given the inherent errors expected in estimating original pyrite sulfur contents of the rock masses.

When the results were ranked according to sandstone content (figure 8) it was apparent that sulfur flux is strongly influenced by the proportion of sandstone. Sulfur flux took about nine months to reach its maximum observed rate. Figures 9 and 10 indicate the acceleration of sulfur flux in selected piles.
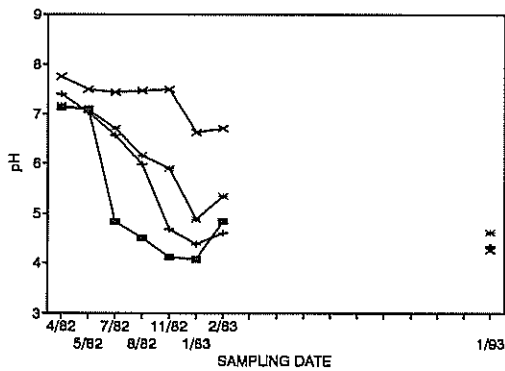
Figure 1. LEACHATE pH-UNTREATED PILES

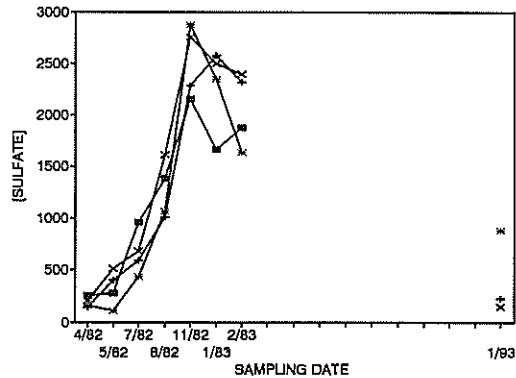Figure 2. LEACHATE SULFATE (PPM) UNTREATED PILES

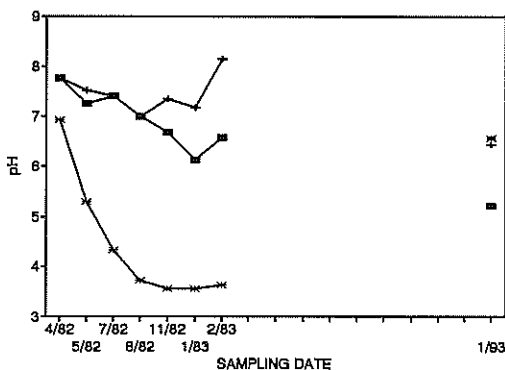Figure 3. LEACHATE pH-LIMESTONE TREATED PILES

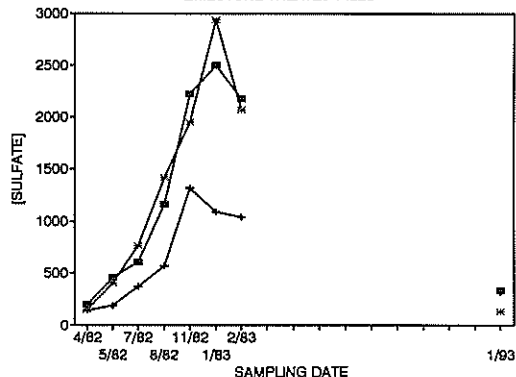
Figure 4. LEACHATE SULFATE (PPM) -LIMESTONE TREATED PILES

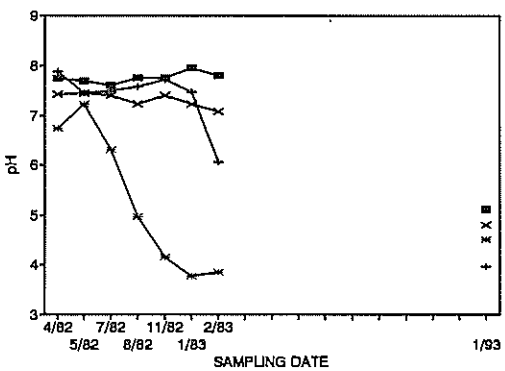

Figure 5. LEACHATE pH-PHOSPHATE, CaO, SLS TREATED PILES

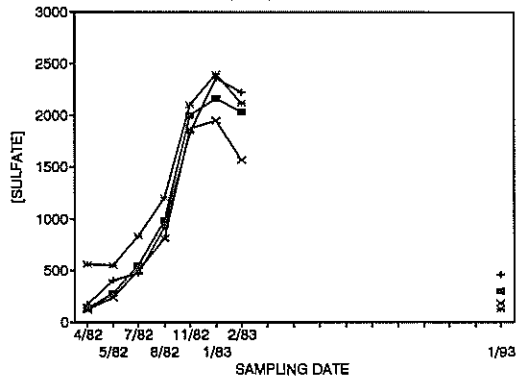Figure 6. LEACHATE SULFATE (PPM) -PHOSPHATE, CaO, SLS TREATED PILES

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Figure 7. SULFUR LOSS RATES FROM THE 11 TEST PILES AND A LITERATURE VALUE (LIT)
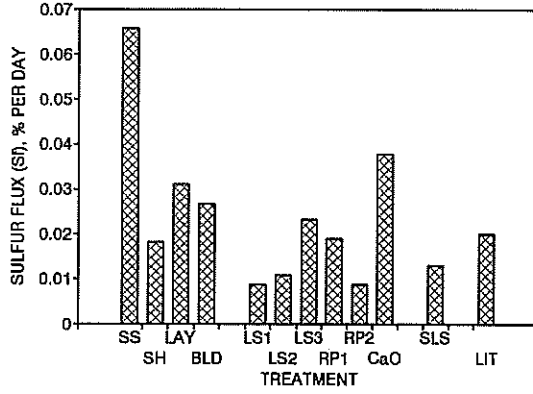

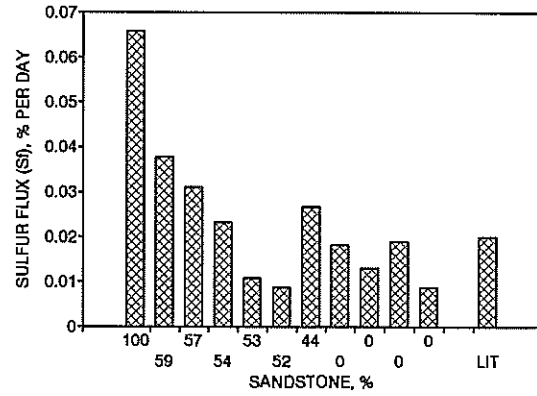Figure 8. SULFUR LOSS RATES FROM THE 11 PILES RANKED BY SANDSTONE CONTENT

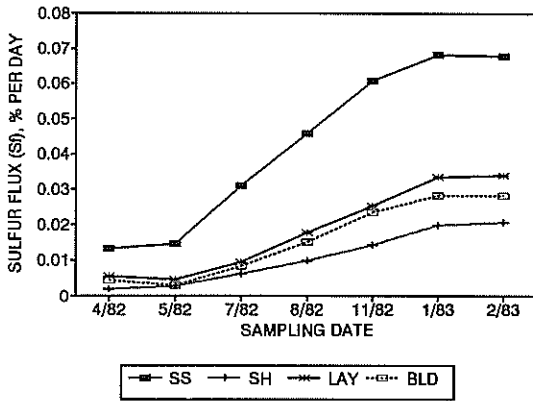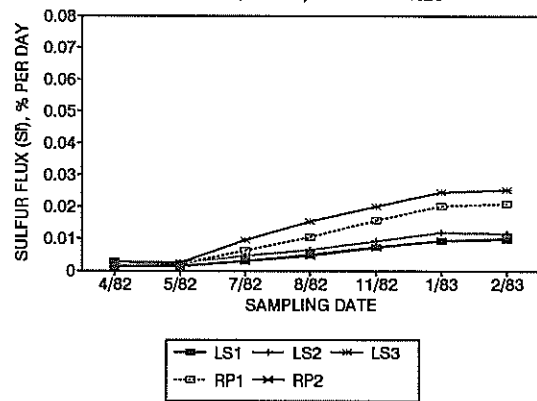Figure 9. CHANGE IN SULFUR FLUX DURING THE FIRST YEAR, UNAMENDED PILES

Figure 10. CHANGE IN SULFUR FLUX RATES DURING FIRST YEAR, AMENDED PILES

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Conclusions

The following conclusions pertain to the results of observed leaching of eleven 400 ton piles of acid producing rock under field conditions in Upshur County, WV. The piles had a large surface area and were only 2 m thick. It is likely that leaching was optimized by this design and that storage was minimized. Sulfur flux rates would be much lower on a large, conventional rock dump. In the following discussion, therefore, sulfur flux is taken to estimate pyrite oxidation.

1. Pyrite oxidation in rock dumps is independent of overall leachate pH. While pH in the immediate vicinity of oxidizing pyrite grains would be low, circumneutral pore water pH will cause most metal ions to precipitate near the point of oxidation and the acidity to be quickly neutralized

2. At the rates tested in this trial pyrite oxidation was little affected by any of the following amendments: limestone, rock phosphate, calcium oxide and sodium lauryl sulfate.

3. There was no clear relationship between NP/MPA and pH performance of the piles. Since sulfate generation appeared to be consistent with estimated rock pyrite sulfur contents it is likely that substantial error occurred in the estimation of effective NP. The error could have had several causes: poor mixing of amendments and spoil types, inherent overestimation in the NP analysis procedure or sampling error.

4. It appears that gross physical phenomena, independent of pyrite forms, surface area, amendment, pH or micro properties of the rock control the rate of pyrite oxidation within relatively narrow limits. Since the rate increased with the proportion of sandstone, oxygen diffusion is the likely candidate.

5. In most, but not all cases, alkaline amendments tended to maintain a circumneutral pH over the first year while untreated piles quickly became acid.

6. In the two cases where limestone addition raised the NP/MPA above 1.65 a circumneutral pH was observed after 11 years. Untreated piles and those treated with rock phosphate, calcium oxide and SLS remained acid.

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