PREVENTION OF ACID MINE DRAINAGE BY ALKALINE ADDITION

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ABSTRACT

Coal companies mining in acid producing areas of the eastern United States control acid mine drainage primarily by water treatment. However, they face the prospect of long-term to indefinite water treatment and its attendant liabilities. It is obvious that cost-effective methods which prevent the formation of acid mine drainage would be preferable.

Recent studies with Appalachian coal refuse types have indicated that certain types of alkaline amendments have the potential to prevent acid mine drainage from pyritic coal refuse. This paper discusses a research project in which kiln dust, Fluidized Bed Combustion (FBC) ash and rock phosphate were mixed with various pyritic coal wastes and subjected to intensive oxidation and leaching in the laboratory.

The results indicate that, at least under laboratory conditions, a ratio of neutralization potential to maximum potential acidity (NP/MPA) of 0.35 or greater resulted in neutral to alkaline leachate. Trials are now underway to evaluate the performance of these materials under large-scale, controlled field conditions.

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. However, it has been subject to criticism since it does not account for the different rates of acid and alkali-generating reactions in rock. Modifications to ABA have been recommended (Smith and Brady, 1990; and diPretoro, 1986). Other methods have developed which accelerate or otherwise control the oxidation and leaching process in rock samples. One such procedure, that of Renton et al. (1988), was employed in this study to simulate the rate of weathering of acid-producing rock samples alone and in combination with alkaline amendments. The results are compared with traditional ABA parameters.

**Recent Studies.**

diPretoro and Rauch (1988) found poor correlations (reported R squared = 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 poor correlation between maximum potential acidity (MPA), NP, net NP from ABA and net alkalinity from drainage water. Both papers related that factors other than overburden characteristics were involved in predicting, post-mining water quality.

diPretoro and Rauch (1988) found that sites which had 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.

Hedin and Erickson (1988) compared water quality from rocks weathered in humidity cells to ABA values. Cumulative sulfate from humidity cells was strongly correlated with total sulfur (R squared = 0.69), while cumulative acidity/alkalinity was correlated with net NP (R squared = 0.37). They also showed sulfate from humidity cells was significantly correlated to sulfate from drainage water (R squared = 0.17), but the correlation was not strong enough to predict post-mining drainage quality.

Bradham and Caruccio (1991) conducted several overburden analytical tests on pyritic wastes from Canada. They found water quality resulting from column leachings, ABA projections, and soxhlets correctly predicted eight out of ten sites where drainage was monitored from refuse piles, with weathering cells predicting ten out of ten results.

There have been several modifications in using ABA in predicting drainage quality. The Pennsylvania Department of Environmental Resources (PaDER) (Smith and Brady, 1990) developed a spreadsheet which calculates mass-weighted maximum potential acidity (MPA), NP, and net NP. The spreadsheet also summarizes the overburden analysis in terms of the ratio of NP/MPA and the percent sandstone. The spreadsheet of ABA data can be compared to significant thresholds or numerical limits for NP and %S and other factors can be changed to estimate the impact on drainage quality. For example, Brady and Hornberger (1989) suggested threshold values of NP equal to or greater than 3% and %S less than 0.5 as
guidelines for delineating alkaline-producing strata.

In the development of its spreadsheet, PaDER (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 (+ or -) 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 additional studies are needed to determine the rates, application and placement of alkaline material during mining.

Brady and Hornberger (1990), after summarizing the work on AMD prediction by ABA made the following conclusions in a recent PaDER mining and Reclamation manual. First, NP from ABA shows the strongest relationship with actual post-mining water quality. This relationship is only qualitative (e.g. acid vs. non-acid), and NP must significantly exceed MPA in order to produce alkaline water. If NP and MPA are similar, AMD will most likely result. Sites with less than 0.5% S will not be significant AMD producers, except where little or no NP exists. High sandstone composition in the overburden (greater than 65%) will almost always result in acid drainage.

Factors Which Induce Error in Acid Base Accounting.

The foregoing discussion makes it clear that interpretations of ABA are diverse. Given the policy and economic implications of ABA it is considered useful to better understand the basis for ABA predictions and, where acid problems are identified, to generate cost-effective solutions.

Errors in conventional application of ABA result from variance in total S content (Rymer et al. 1991), and perhaps more significantly, non-homogeneous placement of spoils. For example Schueck (1990) reported AMD generation from a surface mine site in Pennsylvania resulted largely from buried refuse and pit cleanings within an otherwise neutral to alkaline spoil matrix as identified by ABA.

Acid neutralization in spoil dumps-a paradigm. Obviously, some spoils will be composed
entirely of acid forming rocks. Others such as refuse tend to have little NP at all. But in cases where AMD forms despite significant alkalinity in the overburden, it appears to originate from localized sites within the backfill. While finding the path of least resistance to the downstream side of the dump, the acidity is influenced only the alkalinity directly in its path. Once this is overcome, AMD flows freely to the nearest stream while the remaining alkalinity persists as a spectator to the process. This is to be expected since dissolution of calcite is controlled by pH and the partial pressure of carbon dioxide. Where pore water gas is confined, and exposed to mineral acidity, its pH will remain around 6.2 the-buffering point of bicarbonate and carbonic acid. In the absence of mineral acidity, its pH will reflect bicarbonate saturation - 8.3. In either case, additional calcite will dissolve only upon addition of acidity and outgassing of carbon dioxide. So, unless contacted directly by acidity, most of the spoil calcite will simply remain in solid form. So, the presence of alkalinity in the dump does not ensure that it will be a factor in neutralizing acidity. To be an efficient process, the acid-forming and alkaline rock must be thoroughly mixed.

This largely becomes a materials handling issue. Where there is insufficient alkalinity available it would be necessary to add it to the rock. Otherwise, if one relies on random spoil dumping the system would need an overwhelming supply of alkaline rock. This probably accounts for the above reported field observations that twice or more NP is required for each unit of MPA.

This paper presents results of accelerated weathering trials on various acid-producing rock units and identifies levels of amendment which appear to neutralize generated acidity. The amendments were kiln dust, rock phosphate and Fluidized Bed Combustion (FBC) ash. This project was not initially intended to evaluate ABA parameters. It was only during data analysis that relationships with ABA logic began to appear. They are presented here in the hope that the results can shed some light on the broader issue of ABA interpretation and its application to reclamation policy.

**MATERIALS AND METHODS**

Nine cores were drilled on a prospective mining site in West Virginia and samples of these cores were subject to hot oxidation (105 deg. C) and leaching in soxhlet apparatus after the methods of Renton et al. (1988). The stratigraphic sequence was of the Allegheny Formation, specifically from the base of Lower Freeport seam to the base of the Lower Clarion seam. Lithic units which generated acidity were identified. All of the simulated refuse materials (via 160 float-sink tests) were acid generators as were several of the spoil units.

Following identification of the acid-producing rock types a complete core was obtained which encompassed the full mining sequence. The purpose of the study was to:

1. establish the acid producing potential of the various lithic units,
2. evaluate the relative ameliorative effectiveness of 2wt% and 4wt% of rock phosphate, kiln dust, and circulating fluid bed combustor ash on selected samples from the core,
3. evaluate the relative effectiveness of two application schedules (2wt% and 4wt%) for each treatment material, and

**SAMPLING**
Twenty seven samples were selected from the core for analysis. The samples included both overburden and the rocks immediately associated with the coals. Initial screening indicated that most of the overburden samples had no sulfur and were strongly to mildly alkaline. Those which contained measurable sulfur were processed for further evaluation.

**SAMPLE PREPARATION**

Each sample was crushed to a top size of 1/4” and the -200 mesh fraction was removed by dry sieving to fulfill the procedural requirements of the acid evaluation procedure. Each sample was thoroughly blended and statistically sampled using a Jones Splitter to provide 100 gram samples for the acid evaluation procedure and for total sulfur analysis. The sample removed for sulfur analysis was ground to -200 mesh in a Spex Shatterbox. All samples were sealed in plastic until analyzed.

**ACID EVALUATION**

The acid producing potential of the untreated and treated samples was determined by the procedure reported by Renton et al. (1988). One hundred gram portions of each sample were weighed into 123mm cellulose Soxhlet extractor thimbles. The amended samples were prepared by adding FBC ash, lime kiln dust (from APG Lime), rock phosphate (Texasgulf code 31). Distilled, deionized water was added to make a slurry and each sample was thoroughly mixed. The treated samples were then transferred quantitatively into 123mm. cellulose thimbles. All samples were prepared and run in triplicate.

**CHEMICAL ANALYSIS**

Sulfur analyses were performed using a LECO IR432 Automatic sulfur analyzer. Each determination was an average of three analyses. Each leachate from the soxhlet procedure was clarified by using a 0.45 micron filter and analyzed for:

1. pH
2. Specific Conductivity
3. sulfate ion concentration
4. acidity to pH 8.3
5. alkalinity to pH 4.5

**RESULTS AND DISCUSSION**

Six rock units were identified as the chief acid producers and were selected for further testing. The rock units were identified as Upper or Middle Kittanning (UK, MK), Upper and Lower Clarion (UC,LC) refuse or spoil. Sulfur contents in the samples ranged from 0.22 to 2.27%. Samples of each rock unit were treated with amendment and, with an unamended control sample, were subjected to the 10 week hot oxidation and soxhlet leaching process of Renton et al. (1988).

Table 1 summarizes the analyses of leachates and ABA from each of the six rock units. NP and MPA are the sum of values measured in the raw rock samples and the amounts added via the
All ABA units are in percent by weight (tons/1000 tons multiplied by 0.1). The data showed a wide range of sulfur contents, resulting acidities and required amendments. Clear patterns were evident, however. While each amendment controlled AMD, kiln dust did so more consistently and at lower application rates than either FBC ash or phosphate. This was expected in the case of FBC ash since it only contains about 20% CaO on an otherwise inert alumino-silicate coal ash matrix. Phosphate was inefficient, generally requiring twice as much as kiln dust for control.
Since delivered phosphate would cost about four times more than kiln dust, it is unlikely that it will find a role as an AMD controlling amendment, at least in the eastern U.S. coal fields.

The measured NP expressed in percent calcium carbonate equivalent for each of the amendments were:

- Kiln dust: 99
- FBC ash: 26
- Phosphate: 14

Pyrite oxidation did not appear to be strongly affected by any of the treatments. Cumulative sulfate data suggest that oxidation was similar to slightly lower in the kiln dust samples relative to the control while sulfate was similar to slightly higher on the phosphate samples. FBC ash, however, probably due to its inherent gypsum content consistently produced more sulfate than the control samples. Figures 1, 2 and 3 indicate cumulative sulfate and final pH levels for three rock units. Thus, it appears that while pyrite oxidation proceeds unhindered, its products are precipitated in situ as either hydroxides in the case of kiln dust and FBC ash or as a combination of iron phosphates and hydroxides in the case of phosphate addition.

Supporting the latter contention is the NP/MPA ratio at which AMD is controlled in the laboratory tests. For kiln dust and FBC ash the ratio was 0.35 or greater. Phosphate was lower in two cases, generating neutral drainage (e.g. greater than pH 6.0) with ratios of 0.18 (samples 8078 and 8096). The NP of the rock phosphate used in this study was only 0.14% suggesting that at least some of its effect on acidity reduction may stem from precipitation of iron phosphate. Except for these two phosphate treatments, every sample which had an NP/MPA ratio of 0.35 or greater generated neutral drainage.

Figure 4 draws a weakly correlated linear regression line through control, FBC ash and kiln dust observations for net alkalinity and NP/MPA ratio. Among other things, the data points suggest that the function is probably not linear. Nonetheless, while an R squared of 0.14 is nothing to get excited about, the prediction line crosses the zero net alkalinity line intriguingly just below an NP/MPA ratio of 1. This compares with a prediction
FIGURE 1. 8077 UK/MK SPOIL S=1.35%
FIGURE 2. 8078 UK REFUSE S=0.49%
FIGURE 3. 8096 LC REFUSE S=0.96%
model presented by diPretoro (1986) taken from seeps within two kilometers of uncontrolled field sites of various ages. That prediction line crossed zero net alkalinity at an NP/MPA ratio of about 3.2 though diPretoro indicated that neutral drainage would probably result at a ratio of 2.4 or above (figure 5).

The data, excluding the phosphate data, were used to develop a simple curvilinear regression model to predict pH on the basis of NP and MPA. A model with an R squared of 0.73 was produced (figure 6). Other parameters such as NP/MPA ratio were evaluated but none with an R squared above 0.5 was found. The field data reported in diPretoro (1986) were subjected to the same analysis and produced a model of similar form with an R squared of 0.40 (figure 7).

Why the divergence between laboratory and field requirements? Intimate mixing of the materials is undoubtedly one of the reasons. Also, the reactivity of alkaline amendments in the laboratory study were greater than that of calcite. Kiln dust has about 20% CaO with the remainder unreacted calcite. FBC ash has about 20% CaO with no calcite. Both of these amendments would provide higher levels of readily soluble alkalinity than would be encountered within naturally occurring spoils.

Why did neutral drainage occur at NP/MPA ratios below 1? The obvious response is that within the 10 week term of the laboratory trials the pyrite was not completely oxidized. This may be true and only rigorous comparison to field trials with identical rock types can resolve this question. Another explanation is that up to one half of the total sulfur in coal-related rocks
can be in the organic form, particularly in the more carboniferous units. This sulfur will only oxidize very slowly and would not contribute significantly to acidity. Also, Renton, et al., 1988 indicated that roughly 35% of the total pyrite in coal refuse is only very slowly oxidized owing to its position within the rock matrix.

In a similar experiment, a West Virginia refuse was subjected to the same hot oxidation/leaching procedure and amended with 0.22% CaO, 0.4 and 0.8% kiln dust. The results were compared to the company’s operation in which 2% kiln dust is added to its refuse. Table 2 indicates observed pH and predicted pH (^pH) based on a prediction model developed in this study. The results indicate that while the model predicts a pH of 4.6 under controlled conditions, 4.0 was observed, while after amendment with 2% kiln dust a pH of 7.42 was predicted and 7.2 to 7.6 is observed. These results are from a three year-old refuse dump which was completed in 1991.

It is too early to suggest the NP/MPA ratio which will prevent AMD under operational conditions. However, a good deal of excellent research, much of it cited in this paper, has brought us to a point where we may begin to narrow the range of uncertainty. It seems that between amended systems and randomly spoiled rock an
FIGURE 6. pH VS. NP AND MPA R2=0.73

\[ \hat{\text{pH}} = 5.88 + (1.49 \text{ NP}) - (0.58 \text{ MPA}) \]
NP/MPA ratio somewhere between 0.35 to 2.4 will prevent AMD.

This is actually a remarkable level of consensus and one where properly controlled field studies will be of great benefit. Of particular interest is the prospect of identifying rock units with acid potential and treating them in a predictable manner with alkaline amendments.
The National Mine Land Reclamation Center at West Virginia University will continue to explore this technique and generate the required information for both regulatory agencies and the industry.

CONCLUSIONS

CFBC ASH. At an application rate of two percent CFBC ash was only able to stop acid production in the mild acid producing rocks. At four percent it stopped acid generation in all but the two strongest acid producers: Middle Kittanning spoil and Upper Clarion refuse.

KILN DUST. Kiln dust performed better than the CFBC ash. The two percent application of kiln dust prevented AMD production in all rock units except the Upper Clarion refuse. At a rate of four percent kiln dust prevented AMD production in all of the rock samples.

PHOSPHATE. Like CFBC ash phosphate was able to control AMD in mild acid producing rock units at two percent application rates but required four percent to achieve significant reductions with the strong acid producing rocks.

Kiln dust outperformed CFBC ash and phosphate. It is relatively inexpensive and has the added advantage (with FBC ash) of improving trafficability for mobile equipment operating on refuse dumps. Particularly those with high moisture content filter cake, the free CaO stabilizes the moisture in the fines fraction to the extent that heavy trucks can move freely over the freshly dumped surface (Rich and Hutchison, 1990).

Rock phosphate originating in North Carolina would cost about $80/Ton while the cost of the waste product CFBC ash would largely reflect haulage costs. Unfortunately, while production is likely to increase rapidly over the next decade, relatively little CFBC ash is presently generated. This results in potential supply problems leaving kiln dust, applied at rates of 2 to 4%, the most attractive of the three amendments included in this study. At these levels it is expected to control formation of AMD on any of the rocks found on this site.

Fortunately, there is a precedent for this treatment. Rich and Hutchison (1990) indicated that on an operationally scaled application of 2% kiln dust, AMD was controlled at a mine near Drennen, WV. This project is now three years old and the treated sites are producing compliance water.

LITERATURE CITED


West Virginia University. 1971. Mine spoil potentials for water quality and controlled erosion. 14010 EJE 121-71. Contract with West Virginia University by the U.S. Environmental Protection Agency, Washington, D.C.