

# The Use of FBC Ash for Alkaline Addition at Surface Coal Mines

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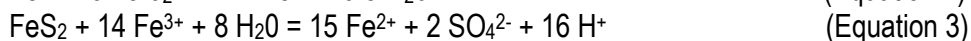
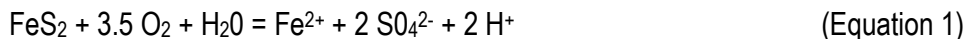
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## ABSTRACT

Surface coal mines with an abundance of naturally-occurring carbonate-bearing (alkaline) strata typically produce alkaline water. Sites that contain little or no alkaline strata tend to produce acidic drainage. One approach used in Pennsylvania on some alkaline-deficient sites is to import alkaline material and amend the spoil in order to obtain alkaline drainage. The amount of alkaline material needed is determined by an overburden analysis. Highly alkaline fluidized bed combustor (FBC) coal ash was used to amend the spoils at two surface coal mine sites during mining and reclamation activities. At the first site, which was a reclamation effort, addition of the FBC ash was sufficient to convert acidic groundwater discharges to alkaline discharges. At the second site, a remaining operation, groundwater in monitoring wells went from neutral to acidic, despite the addition of the alkaline ash. This paper examines the similarities and differences between the two sites and compares them to an alkaline addition site where baghouse lime was used in an effort to suggest reasons why one site was a success and the other a failure.

## INTRODUCTION

Acid mine drainage (AMD) results from the interaction of certain sulfide minerals with oxygen, water, and bacteria. The iron disulfide minerals, pyrite (FeS<sub>2</sub>), and less commonly marcasite (FeS<sub>2</sub>), are the principal sulfur bearing minerals in bituminous coal (Davis, 1981; Hawkins, 1984). The following reactions characterize various stages in the complete AMD reaction (Stumm and Morgan, 1981, pp. 470):



Equation 1 represents the oxidation of the disulfide minerals by oxygen and water. Iron-oxidizing bacteria, notably those of the genus *Thiobacillus*, oxidize Fe<sup>2+</sup> to Fe<sup>3+</sup> as described in Equation 2 and become increasingly active as pH is depressed (Kleinmann et al., 1981; Nordstrom, 1982). In Equation 3, dissolved ferric iron (Fe<sup>3+</sup>) then becomes the oxidizing agent for pyrite, thus increasing AMD production.

It is common to see elevated concentrations of metals, such as manganese and aluminum, associated with AMD. This is not a direct result of pyrite oxidation, but is caused by AMD leaching these cations from other minerals within the spoil, such as clays and siderite, as a secondary reaction.

Surface coal mines with an abundance of naturally-occurring carbonate-bearing (alkaline) strata typically produce alkaline drainage. The carbonate minerals calcite (CaCO<sub>3</sub>) and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) are the main minerals providing

alkalinity (Rose and Cravotta, 1998). The carbonate minerals may occur as layers of limestone or dolostone in the overburden above the coal, as cement in sandstone or shale, or as veins cutting the rock. Minerals that produce alkalinity can affect the generation of AMD in two ways. First, if alkaline conditions can be maintained in the pyritic material, the AMD-generating reactions may be inhibited. This is because the bacterial oxidation of  $\text{Fe}^{2+}$  is minimal in an alkaline environment. Second, once AMD has formed, its interaction with alkaline materials will result in neutralization of the acidity. Using calcite as an example, the initial reaction with an acid solution is:



Third,  $\text{Fe}^{3+}$  is not soluble under alkaline conditions, thus the reactions in Equation 3 will not occur, rather,  $\text{Fe}(\text{OH})_3$  will form.

The overburden analysis (OBA) for proposed surface coal mining operations is an important management tool in Pennsylvania. The strata to be removed during the mining operation are characterized as to thickness, distribution, and acid- or alkalinity-generating capabilities. Acid-base accounting is the most common OBA method, whereby total percent sulfur and neutralization potential (ppt  $\text{CaCO}_3$ ) are determined (Perry, 1998). In some cases, where the OBA shows a deficiency of native alkaline material in the overburden, alkaline materials may be brought to the site and incorporated into the backfill in a manner to ensure that final discharges from the site will be net alkaline (Smith and Brady, 1998).

The OBA also provides a mechanism for determining the amount of alkaline material necessary to be incorporated in order to render the site net alkaline. This determination is in the form of *tons of  $\text{CaCO}_3$  equivalent per 1000 tons of material* to be mined. Various risk factors regarding the site and its setting are evaluated to determine the needed alkaline addition rate, which typically is at least one ton of  $\text{CaCO}_3$  equivalent per one ton of maximum potential acidity. If material proposed for alkaline addition exhibits less than 100%  $\text{CaCO}_3$  equivalency, application rates are adjusted to represent 100%  $\text{CaCO}_3$  (Smith and Brady, 1998).

In order to make an operation economical, it is to the operator's advantage to use low cost (or no cost) alkaline industrial byproducts. For instance, hydrated lime (135%  $\text{CaCO}_3$  equivalency) is significantly more expensive than its associated byproduct baghouse lime (85%  $\text{CaCO}_3$  equivalency). Although more baghouse lime would be required than hydrated lime, the difference in cost of the materials makes it advantageous for the operator to import the baghouse lime. In addition to the economic advantages, the re-use of waste alkaline materials that qualify for beneficial use has the added advantage of removing them from the waste stream.

The effects of alkaline addition can be manifested as AMD suppression or AMD neutralization and is dependent upon the placement of the alkaline material in relationship to the acid forming material and the groundwater regime.

Since alkaline addition does not inhibit the transport of water and oxygen into the spoil, oxidation of pyrite will likely occur. On sites where the recharge contacts the alkaline material first, i.e., the water reacts with the alkaline-producing material placed near the surface, the alkaline recharge could then neutralize any AMD as soon as it is formed and/or inhibit or suppress the production of AMD. A slight increase in the concentrations of the sulfates and iron is likely to occur. Secondary leaching of metals such as manganese and aluminum should be minimal simply because there would no longer be AMD available to leach.

Where the recharge first reacts with acid-forming material, sulfate and iron concentrations may increase over time because reactions in equations 2 and 3 can proceed before neutralization occurs. In this case, increases in metals, such as manganese and aluminum, may also occur.

Ideally, the alkaline material would be applied to the site in a manner that alkalinity would be generated at only a slightly greater rate than acidity over a very long period of time following reclamation. This would result in any acidity being neutralized and a net alkaline discharge. If the rate of alkalinity generation is significantly greater than the rate of acid production, then there is a risk that the alkaline material will be depleted long before the acid production has ceased and the discharges would eventually become acid. The rate of alkalinity generation is dependent upon many factors, including the nature of the alkaline material, surface area available for reaction (particle size), placement within the backfill, carbon dioxide ( $\text{CO}_2$ ) concentration, permeability and porosity of the backfill, water table location and fluctuation range, preferred

groundwater flow paths, and distribution of the pyritic materials. Presently, the consideration of a material's rate of depletion due to solubility is not a factor in determining application rates.

The theory of alkaline addition also assumes that all of the alkaline material, present or added, will eventually dissolve and generate alkalinity. This is a fair assumption because alkaline addition does not necessarily prevent the water within the backfill from contacting the alkaline material. There is also the basic assumption that the neutralization potential will be the same when it is applied in the field as it was when tested in the laboratory. However, these two assumptions may not be valid when considering the use of FBC ash for alkaline addition. Unlike limestone screenings or baghouse lime, when water contacts FBC ash it becomes self-cementing, or pozzolanic. Usually water is added to the ash for conditioning and dust control at the generating station. As discussed in a later section, the result is a reduction in the effective neutralization potential (NP) of the ash as well as a decrease in the availability of the material for dissolution. In fact, the data suggest that the FBC ash may not have the ability to prevent AMD to the degree suggested by its neutralization potential. However, the pozzolanic nature of the ash can benefit the site by restricting groundwater movement through and perhaps isolating the acid forming materials from water and oxygen.

### Field Experience

#### Alkaline Addition Using Baghouse Lime, the Kauffman Site

Baghouse lime, a lime manufacturing byproduct, has been used on several surface coal mine sites for alkaline addition where there is a deficiency of naturally occurring carbonate minerals. The following example illustrates the geochemical responses that may occur at a typical alkaline addition site. At the Kauffman site in Clearfield County baghouse lime was imported as an alkaline material. On one portion of the site, it was applied at a rate of 1212 tons per acre. The rates were set to achieve a net NP of zero, or a one to one ratio of tons of  $\text{CaCO}_3$  to tons deficiency.

Several wells were installed within the backfill to monitor the effect the alkaline addition was having on the groundwater. The data from monitoring well BF2 is used in this example. (Different application rates were used on various mining phases with a variety of results. Changes observed in BF2 were not uniform across the site.) Mining up gradient of this well began in 1993 before its installation and initial sampling. The up gradient mining apparently influenced the water quality in this area before sampling as evidenced by the initial  $\text{SO}_4$  level of 422 mg/L. Figure 1 is a graph from BF2 and includes the concentrations for sulfate, net alkalinity, and calcium. Sulfate is included in the graph as a conservative

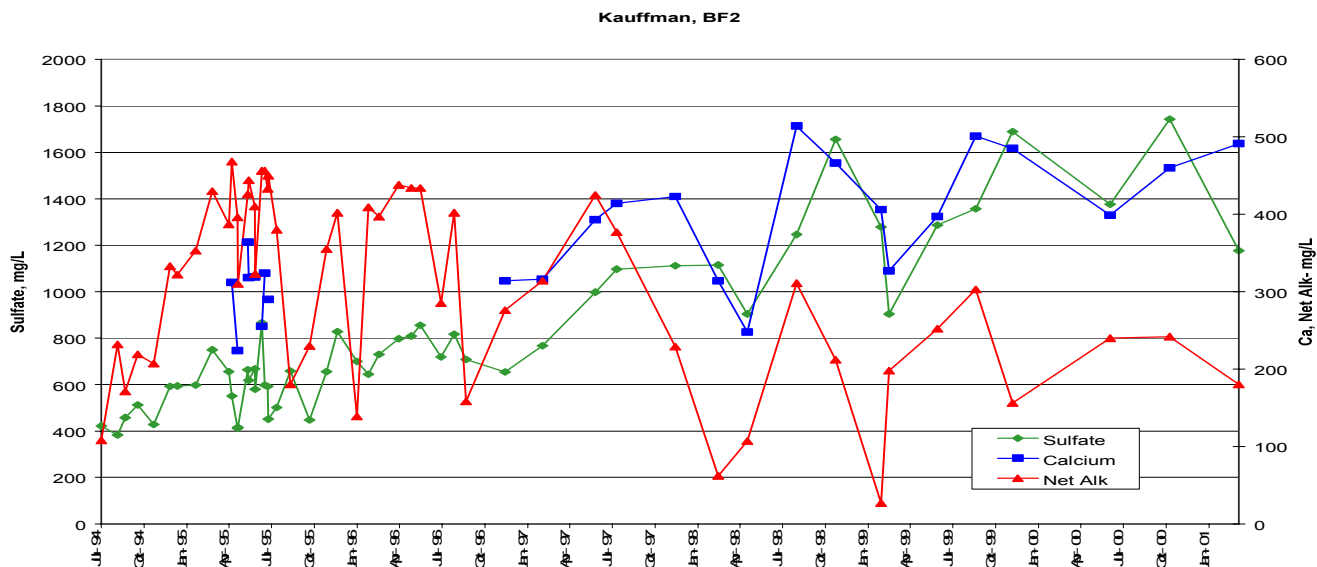
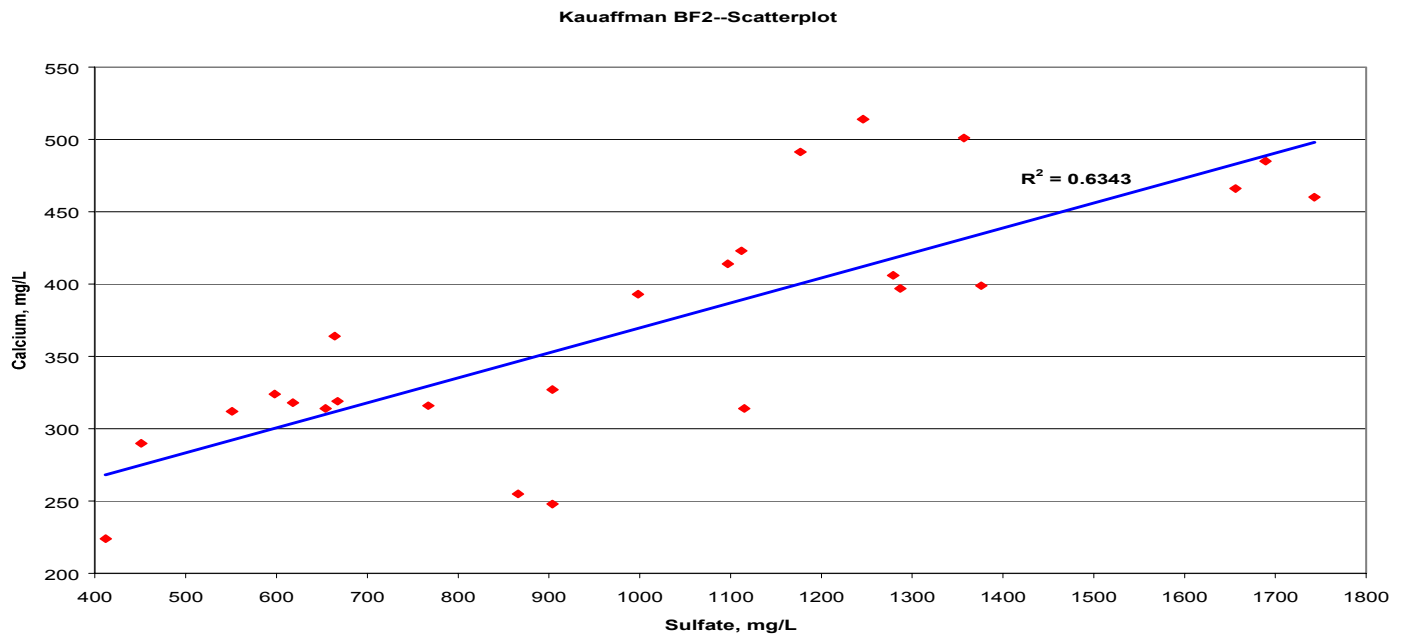


Figure 1. Response of a monitoring well to the use of baghouse lime for alkaline addition.

indicator of AMD formation. The increases in Ca concentrations provide an indication of the neutralization of the AMD by the baghouse lime. Note that, although on different scales, the changes in concentration of Ca mirror those of SO<sub>4</sub> after October 1996

indicating that sufficient lime is available to neutralize the AMD as the need arises. Figure 2, a scatter plot of Ca and SO<sub>4</sub>, indicates a reasonably good correlation between the two ( $R^2=0.6343$ ). Note also that the net alkalinity is gradually decreasing over time while the SO<sub>4</sub> increases from 400 mg/L to 1600 mg/L. Although not shown on Figure 1, Fe and Mn concentrations have also increased over time. This indicates that AMD generation is increasing over time and leaching other minerals before neutralization takes place. According to Hawkins (personal communication, 2001) the acid producing materials were placed at the worst possible level on this site, which is within the zone of the fluctuating water table.



**Figure 2.** Scatter plot of Ca and SO<sub>4</sub> in monitoring well BF2.

In the case of the Kauffman mine site, the use of baghouse lime as an alkaline addition material near monitoring well BF2 appears to be effectively neutralizing the AMD that is produced. The pH of the groundwater has consistently been above 6.0 and the net alkalinity, although lower than initial levels, averages about 200 mg/L. However, the neutralization potential is being converted into alkalinity at a rate in excess of the acidity being generated. Considering the application rate at a ratio of one to one tons CaCO<sub>3</sub> to deficiency, it remains to be seen whether the proper balance between neutralization potential and maximum potential acidity has been reached.

### The Use of FBC Ash for Alkaline Addition

FBC ash was used as an alkaline amendment on the Abel-Dreshman site in Butler County and on the McDermott site in Cambria County, PA. The chemical responses to the ash placement were significantly different at the monitoring points than the response to the baghouse lime placement on the Kauffman site. The data suggest that the FBC ash may not neutralize AMD production as effectively as baghouse lime, despite adjustments to application rates made to account for the lower NP of the ash. However, the data also suggest that improvements in water chemistry can occur. The pozzolanic nature of the ash is one factor that may affect the ability of the ash to prevent AMD in both a positive and negative way. The pozzolanic character of the ash may help encapsulate the pyritic materials and may reduce permeability of the backfill. However, this same property may also limit the availability of the alkalinity generating components of the ash.

## Site 1-Reclamation on the Abel-Dreshman Site

### Site description and history

A permit to mine 55.5 acres of coal on an 81-acre tract in Venango Twp., Butler County was issued in June 1980. The first mining cut was being taken in July 1980 and mining continued intermittently until June 1982. The mining occurred on two contiguous parcels, one parcel owned by an individual named Abel, the other owned by an individual named Dreshman.

The first indication of AMD production occurred during routine sampling in July 1982 when the sediment pond and a toe of spoil discharge on the Dreshman parcel were found to be characteristic of AMD. Additional samples were collected in August and December 1982. Observations of depressed pH, elevated acidity, iron, manganese, aluminum and sulfates were consistent with the production of AMD. The mining operation also contaminated two private water supplies with AMD. This contamination was also first noticed in 1982.

In March 1983, bond forfeiture was recommended. Approximately 65 of the 74.5 bonded acres had been affected. A water impounded pit having approximate dimensions of 150 ft. L x 60 ft. W x 40 ft. highwall height existed on the Abel parcel and a pit of 75 ft. L x 50 ft. W x 40 ft. highwall height remained on the Dreshman parcel.

Another operator proposed taking over the mine. As part of the re-permitting application an OBA was conducted at the site. The results of the testing of the two overburden holes along with the presence of AMD at the site supported the Department's claim that continued mining at the site would likely produce AMD. Since the permittee was unable to demonstrate that AMD pollution would not occur from the continued mining operations, the re-permitting application was denied.

### Alkalinity requirements from the OBA

The mass weighted acid base accounting results showed that the site was alkaline deficient with a strong likelihood of AMD production (see Perry, 1998; Smith and Brady, 1998, for in depth discussion on acid base accounting):

| Overburden Hole # | Highwall Cover Height | Net Neutralization Potential |           |         | Tons CaCO <sub>3</sub> /acre needed to provide |                        | %     |
|-------------------|-----------------------|------------------------------|-----------|---------|--|------------------------|-------|
|                   |                       | tons/1000 tons               | tons/acre |         | 6 ton/1000 ton excess                          | 12 ton/1000 ton excess |       |
|                   |                       | Thresholds                   |           |         | Thresholds                                     |                        |       |
|                   |                       | without                      | with      | without | with   | without                |       |
| OB-1              | 56                    | -2.33                        | -227      | -215    | 780  | 1320                   | 56.5% |
| OB-2              | 46                    | -9.27                        | -612      | -740    | 1090   | 1696                   | 91.1% |

The use of thresholds when evaluating acid base accounting OBA data was discussed in Brady and Hornberger, 1990. The thresholds used were 0.5 % Sulfur and a NP of 30 tons/1000 tons CaCO<sub>3</sub> equivalent with the zone having a fizz with a 20% HCl solution.

As part of a reclamation agreement, Amerikohl Mining Inc. reclaimed the site. The proposal included importing fly ash as an alkaline material to blend with the spoil. The application rates were to be determined from the OBA. From September 1997 until September 1998, fly ash was admixed with the spoil and the entire site reclaimed to approximate original contour. The Dreshman parcel was reclaimed first and was completed in May 1998, and then the Abel parcel was reclaimed. Although the original proposal was to add 200,000 tons of Scrubgrass Generating Project FBC ash, or approximately 4,000 tons/acre, to the site, only 83,600 tons were actually applied/mixed at the site. The ash had a reported 600 tons per 1000 tons of CaCO<sub>3</sub> equivalency. Therefore, approximately 1003 tons of 100% CaCO<sub>3</sub> equivalent per acre were added at the site. This amount

would provide a little more than an average 6 ton/1000 ton excess using thresholds across the site. In order to evaluate the success of the alkaline addition, springs designated as MP-29A (Dreshman parcel), and MP-29B (Abel parcel) were monitored by the Department.

### **Fly ash placement**

The Abel-Dreshman site consists of two parcels. Placement of the ash was slightly different on the two areas. Water was added at the plant to condition the ash for dust control. Sufficient water was added to bring the ash up to a moisture content of about 21%. The ash was brought to the site in bottom dump tanker trucks. The ash was dumped adjacent to the pits. Spoil was then pushed with a dozer, mixing spoil with the ash as it was pushed into the pit. The ratio of ash to spoil was commonly 1:1. Mixing and spreading of the ash often occurred within minutes of the arrival of the ash on the site. On both parcels, the floor of the existing pits was covered with a layer of the ash, approximately 2 to 3 feet thick. The primary difference in backfilling the two parcels was that much of the ash was spread in layers on the Abel site (due to non-availability of equipment and breakdowns) whereas it was thoroughly mixed with the spoil on the Dreshman site. A layer of ash, 1 to 2 feet thick, was placed and compacted on both parcels before placement of the final topsoil material.

### **Monitoring point response to the ash placement**

Ash placement occurred on the Dreshman parcel from September 1997 until May 1998 and on the Abel parcel from May 1998 until September 1998. Tables 1 and 2 display summaries of changes to some of the water quality parameters for monitoring points MP-29A (Dreshman parcel) and MP-29B (Abel parcel) respectively.

| MP-29A<br># of samples (n)     | PreFlyash<br>Application<br>18 | During Flyash<br>Application<br>9 | Post Flyash<br>Application<br>14 | % Improvement |
|--------------------------------|--------------------------------|-----------------------------------|----------------------------------|---------------|
| Median pH                      | 3.35                           | 3.87                              | 6.2                              | 99.8%         |
| Average Net Alkalinity mg/L    | -190.3                         | -200.0                            | -8.6                             | 95.5%         |
| Average Iron (total) mg/L      | 2.9                            | 14.9                              | 0.4                              | 87.7%         |
| Average Manganese (total) mg/L | 59.4                           | 75.2                              | 22.7                             | 61.8%         |
| Average Aluminum (total) mg/L  | 3.3                            | 3.1                               | 0.8                              | 75.1%         |
| Average Sulfates (total) mg/L  | 990.8                          | 926.6                             | 752.0                            | 24.1%         |
| Average Flow (gpm)             | 31.2                           | 27.8                              | 6                                | 81%           |

**Table 1.** Summary of water quality changes resulting from FBC ash addition for MP-29A from the Dreshman parcel.

As can be seen from Table 1, MP-29A shows significant improvement in quality when comparing the pre- and during- fly ash placement chemistry to the post-placement chemistry. The decrease in sulfate concentrations indicates a decrease in or suppression of AMD production from the site. Compare this to the Kauffman site where sulfate concentrations near BF2 continue to increase over time, indicating a continual increase in AMD production. In addition, there has been sufficient alkalinity generation to neutralize any AMD that is formed, resulting in a slightly net alkaline discharge. Also of significance is the reduction in flow from an average of 31.2 gpm before ash placement to an average flow of 6 gpm following completion of the project. The improvement in water chemistry combined with the reduction in flow results in a significant reduction in polluttional loading from the site.

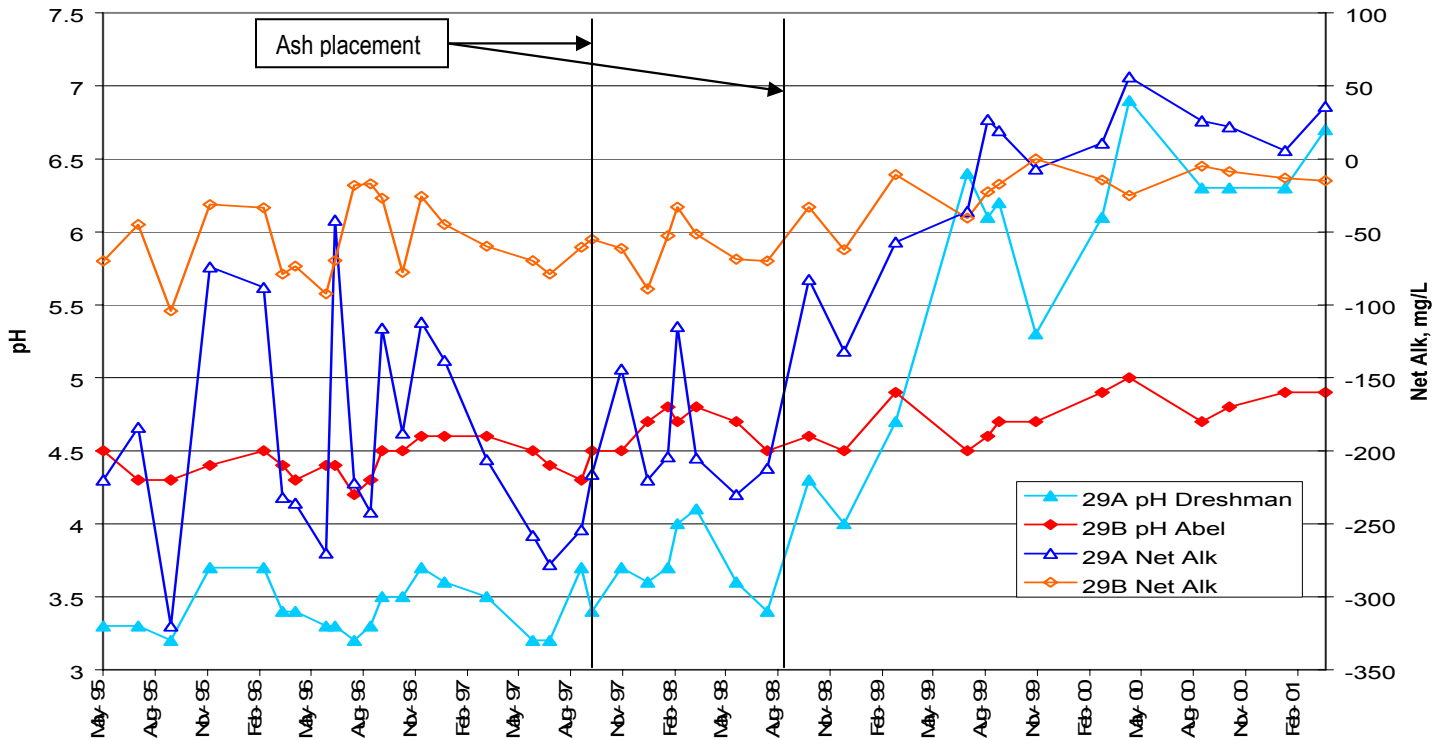
Table 2 provides a summary of the results from sampling MP 29-B. The quality of the MP-29B discharge was much better than that of the MP-29A discharge before the application of the fly ash. However, the quality of MP-29B did not improve near as much as MP-29A as a result of the ash placement, but there are similarities. In both cases, there was an improvement in net alkalinity. The net alkalinity at MP-29B is now near zero mg/L whereas it was -41 mg/L before the ash placement. The average flow of the discharge at MP-29B also decreased significantly, from 27.8 to 9.8 gpm, similar to that of MP-29A. The primary difference in application of the FBC ash is that mixing of the ash with the spoil on the Abel parcel was less thorough than it was on the Dreshman property.

| MP-29B<br># of samples (n)     | Pre Flyash<br>Application<br>18 | During Flyash<br>Application<br>9 | Post Flyash<br>Application<br>14 | % Improvement |
|--------------------------------|---------------------------------|-----------------------------------|----------------------------------|---------------|
| Median pH                      | 4.4                             | 4.7                               | 4.7                              | 48.3%         |
| Average Net Alkalinity mg/L    | -41.2                           | -16.2                             | -2.2                             | 94.7%         |
| Average Iron (total) mg/L      | 0.6                             | 0.1                               | 0.2                              | 69.3%         |
| Average Manganese (total) mg/L | 18.9                            | 6.8                               | 4.8                              | 74.4%         |
| Average Aluminum (total) mg/L  | 3.1                             | 1.8                               | 1.1                              | 66.6%         |
| Average Sulfates (total) mg/L  | 292.8                           | 194.3                             | 202.8                            | 30.7%         |
| Average Flow (gpm)             | 28.7                            | 18.5                              | 9.8                              | 66%           |

**Table 2.** Summary of water quality changes resulting from FBC ash addition for MP-29B from the Abel parcel.

The graph shown in Figure 3 depicts the change in pH and net alkalinity of both monitoring points in response to the placement of the ash. Sulfate concentrations also dropped, indicating a decrease in or suppression of AMD production, not just neutralization. Both sites reported significant decreases in manganese and aluminum concentrations at the discharge locations, further signifying AMD abatement. In addition, some of the reduction may be attributed to encapsulation of the pyritic minerals within the self-cementing ash. Schueck, et. al, 1996 noted similar reduction in concentrations of typical AMD-related metals when a FBC grout was injected into pyrite-rich piles of buried pit cleanings.

**Abel-Dreshman- MP29A & MP29B**



**Figure 3.** Changes in pH and net alkalinity for MP-29A and MP-29B in response to reclamation of the Abel-Dreshman site with FBC ash.

## Site 2-Alkaline Addition on the McDermott Operation

### Site description and history

In July 1995, Laurel Land Development submitted an application to mine on the McDermott property located in Jackson Twp., Cambria County. The original application was to mine 25.5 acres of Lower Kittanning coal, 28.8 acres of Middle Kittanning coal, and 8.6 acres of Lower Freeport (more likely Upper Kittanning) coal. After the permit had been issued and activated it was amended to increase the acres of Lower Kittanning mining to 26.5 and the acres of Middle Kittanning mining to 32.1, as well as to add 10.8 acres of Worthington Sandstone removal. A small portion of the site had been previously surface mined on the Lower Kittanning seam. In addition, two small room-and-pillar mines were also present on the Lower Kittanning. Because of pre-existing discharges, the McDermott operation was permitted as a Subchapter F site (Rahall type mining).

As part of the permitting requirements, an OBA was completed. The overburden data were evaluated using thresholds of 30 NP with a positive fizz rating and using 0.5% total sulfur. Numerous overburden holes were drilled on the site. Table 3 summarizes the site overburden data in terms of site NP both before and after ash addition. Based on the OBA, the Department determined that 320 tons of  $\text{CaCO}_3$ /acre were required for mining of both the Middle and Lower Kittanning seams. That amount of  $\text{CaCO}_3$  was needed to reach a site net NP of 0, the minimum the Department will typically accept on remining sites. The ash to be used exhibited a NP that ranged from 150 to 250, and the applicant proposed an application rate of 2060 tons of fly ash per acre. Assuming a typical NP for the ash of about 200 tons/thousand tons, this alkaline addition rate would raise the overall site net NP to 0.88 tons/1000 tons. Originally, the ash came from the Colver Generating Station. However, the bulk of the ash placed at the site is from the Cambria Cogeneration Plant.

| Net Neutralization Potential |           | Net Neutralization Potential After Alkaline Addition |           |
|------------------------------|-----------|--|-----------|
| -3.07                        | -320      | 4.2  | 440       |
| tons/1000 tons               | tons/acre | tons/1000 tons                                       | tons/acre |

**Table 3.** Net neutralization potential for the McDermott operation before and after ash placement.

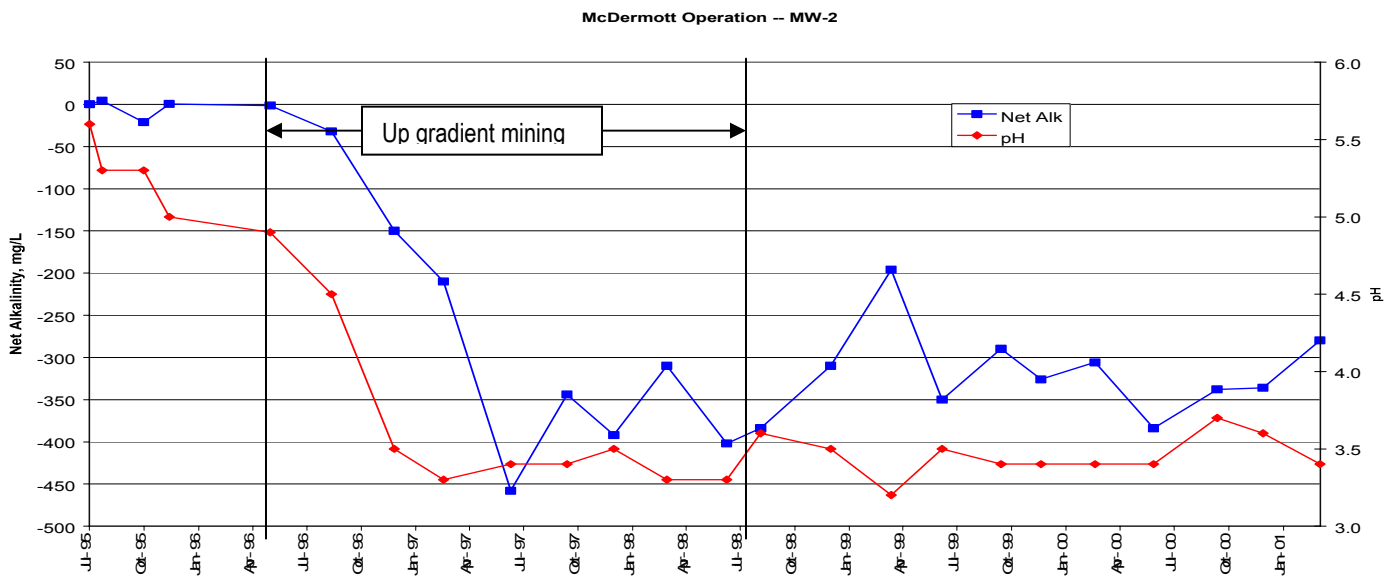
The permit was issued on January 18, 1996 and mining commenced in the eastern portion of the mine site. Shortly after mining began, water quality problems began to manifest themselves. In response to concerns raised by the Department, the permittee agreed to increase the ash addition rate to 3200 tons per acre. In late 1999, the operator proposed adding ash to the site at a rate of 4500 tons per acre in conjunction with a request to also mine sandstone. The ash addition rate at the site has varied with time, as has the NP of the ash, which has generally decreased with time. Records kept by the ash suppliers show that the average ash placement rate over the course of the operation has been approximately 3800 tons per acre. Again, assuming an average NP of 200, the ash added to the site has been sufficient to bring the overall site net NP to 4.2.

Similar to the ash from the Scrubgrass plant, moisture is added at the silo before loading to bring the natural moisture up to about 21%. Also similar to the Abel-Dreshman site, a layer of ash, two to three feet thick, was placed on the pit floor before backfilling. However, it was observed that blending of the ash with the spoil was not nearly as complete at the McDermott operation. Also, in terms of the overall site net NP, the amount of ash added to the McDermott site, especially early on, was significantly less than that added to the Abel-Dreshman site. Delivery of the ash to the site was based upon availability at the plant. Because the ash did not arrive on a consistent basis, there were periods of time where the ash was stockpiled for several months before being used and other periods of time where no ash was available to mix with the spoil. Similar to the Abel-Dreshman site, a layer of ash was applied to some areas of the surface before final backfilling.

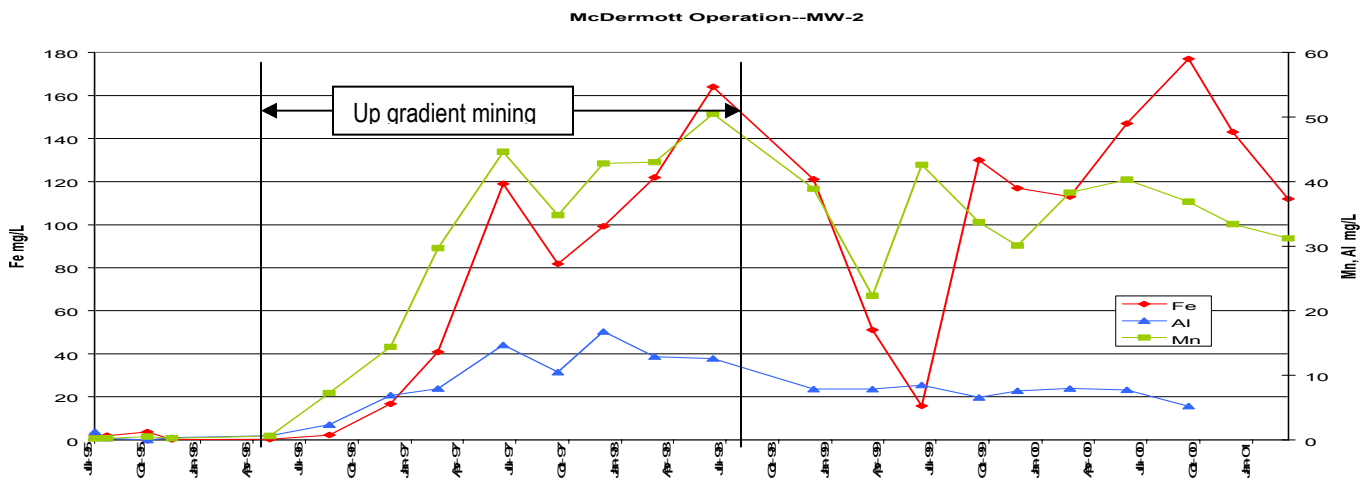


### Monitoring point response to the ash placement

The response of the various monitoring wells on the site show that groundwater degradation occurred shortly after mining began, despite the addition of the alkaline ash. Monitoring well MW-2 is located in the Kittanning Sandstone, below the Lower Kittanning crop line. The response in MW-2 is characteristic of the other monitoring points on the site. As can be seen in Figure 4, the pH dropped from 5.6 before mining to the low 3's after mining began. Net alkalinity dropped from near zero to about -350 mg/L in a corresponding time frame. Thus, the FBC ash is not providing the needed alkalinity to neutralize or prevent the AMD being generated. MW-2 also exhibits high concentrations of iron, manganese and aluminum that were not present before mining, Figure 5. This is an indication that AMD is being generated at the site and is leaching other metals. It is also noteworthy that the water quality was poorest when the active mining was closest to this monitoring well (1996-1998). Water quality improved somewhat after the recharge area was backfilled and reclaimed. This may be attributable in part to reduced permeability of the near surface backfill material resulting from the placement of a layer of ash on the spoil before applying topsoil.



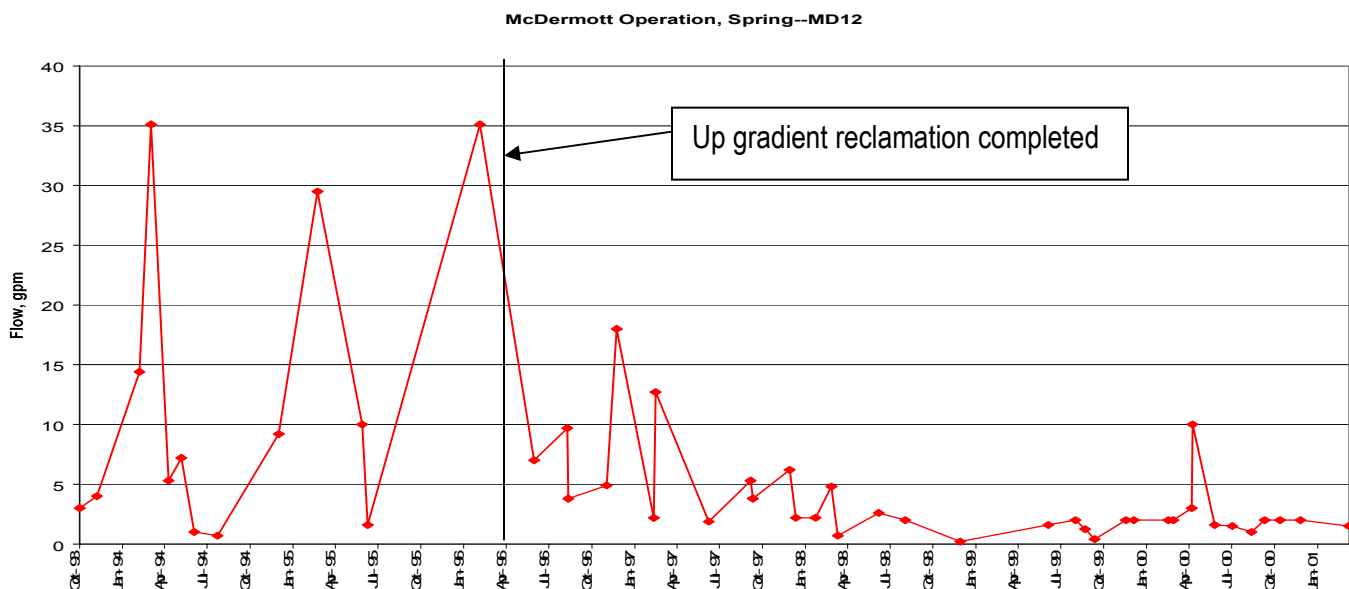
**Figure 4** Decrease in pH and net alkalinity on the McDermott operation despite the addition of FBC ash as alkaline addition material



**Figure 5** Iron, manganese and aluminum concentrations increased on the McDermott operation, but showed minor improvement following the completion of reclamation.

### Flow reduction in response to ash placement

Hellier, 1998 documented the ability of a layer of FBC ash placed beneath the topsoil to greatly inhibit infiltration on the Upper Three Runs site in Clearfield County. On this site, 55-gallon drums were cut in half and buried in the spoil to monitor infiltration of precipitation. On the areas not treated with ash, the drums filled with water on a regular basis in response to precipitation. In contrast, the drums buried beneath the areas where the ash blanket was applied remained dry. It was noted earlier that the flow rates at MP-29A and MP-29B on the Abel-Dreshman site were diminished by 66 to 81% following reclamation in this fashion. For monitoring point MP-29A, the average acid load before reclamation was 72.4 lbs/day. Considering the improvement in chemistry alone, the average post reclamation acid loading was 11.2 lbs/day. However, when the reduction in flow is considered, the loading is a mere 2.2 lbs/day. Diminished flows following reclamation are also noted on the McDermott operation. MD-12 is a spring whose recharge area is the part of the McDermott operation. The measured flows from MD-12 are indicated in the graph, Figure 6. Reclamation using the FBC ash up gradient of the spring was completed in 1997. Note the apparent reduction in flows measured at the spring following reclamation activities. Flow reduction is a significant factor when calculating pollutional loadings.



**Figure 6.** Flow rates measured at a down gradient spring on the McDermott operation. Note the apparent reduction in flows following up gradient reclamation.

### FBC Ash for Alkaline Addition

The primary requirement for a material to be used as an approved material for alkaline addition is whether the material has significant neutralization potential. The amount of material that must be imported to the site is based upon its  $\text{CaCO}_3$  equivalency. FBC ash typically has a  $\text{CaCO}_3$  equivalency of between 15 and 30%. Thus for every ton of  $\text{CaCO}_3$  per acre that would be needed, 5 tons of 20%  $\text{CaCO}_3$  equivalent ash would need to be imported to ensure sufficient alkalinity is present to neutralize AMD. The data from the Kauffman site clearly demonstrates that baghouse lime can and does neutralize AMD in the vicinity of well BF2; however, the Department has observed alkaline addition sites using lime at rates similar to the Kauffman site where AMD did occur. On the Abel-Dreshman site, the monitoring data indicate a reduction or abatement of AMD generation. The increase in net alkalinity also suggests that neutralization is occurring as well. The FBC ash used on the McDermott operation had significantly less NP than that used on the Abel-Dreshman site. The overall site net NP achieved on the McDermott was significantly less than that achieved on the Abel-Dreshman site. Other significant differences observed include the length of time before mixing occurred and a much less thorough blending with the spoil. On the McDermott operation the net alkalinity dropped substantially, indicating little if any neutralization of AMD is

taking place. Further, the only observation where the AMD parameters decreased in concentration was after final reclamation where a layer of compacted ash was placed beneath the topsoil. The McDermott site remains active as of this writing, so the final water quality may differ from that presented here; however, at this point in the operation it seems unlikely that it would turn net alkaline.

FBC ash exhibits a characteristic unlike that of many other alkaline amendments such as baghouse lime. FBC ash is pozzolanic: it reacts with water to form a low-strength cement. This characteristic reduces the availability of the potentially alkalinity generating components and the effect is that the neutralization potential of material is reduced. This pozzolanic action also prevents the free infiltration of ground water through the FBC itself, therefore reducing the alkalinity generation by reduction of the reactive surface area available to ground water. Thus, the FBC ash may not generate alkalinity at the same level as the equivalent amount of NP added in the form of lime. However, the fact that the ash forms low-strength cement has the advantage of being able to encapsulate some of the pyrite, thus rendering it unavailable to oxidize to form AMD.

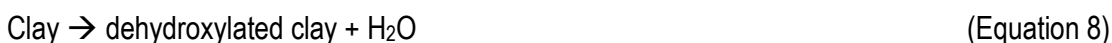
Samples of ash that had been stockpiled on the site for a period of seven months were collected from the McDermott Operation. The ash had agglomerated into clumps that visually ranged in size from that of coarse sand to medium gravel. A sample was dried and crushed to minus 60 sieve and tested for neutralization. The NP reported for this sample was 235 tons/1000 tons. A second sample was tested for NP in the same condition as it existed on the stockpile (without drying and crushing). The NP reported for this sample was 177 tons/1000 tons, or a 25% reduction in NP. The following discussion details why NP of FBC fly ash is reduced once it is exposed to additional moisture.

### ***The combustion process***

In the combustion process of a fluidized bed combustor, limestone is added to the circulating bed of finely ground fuel primarily for the purpose of off gas pollution control. The combustor is operated above the decomposition temperature for limestone thus forming "lime", calcium oxide. In turn, the lime reacts with the SO<sub>x</sub> produced from the oxidization of sulfide minerals to form anhydrite, CaSO<sub>4</sub>. Normally the ratio of limestone to sulfur in the fuel is maintained so that there is excess lime available to handle fluctuations in the sulfur content. The consequences of this approach are that there is always excess free lime in the ash.

### ***Reactions in the ash***

The mineralogy of the ash is typically:



Any quartz in the system will process through the FBC chemically and mineralogically unaffected. If combustion conditions within the reactor are sub-stoichiometric, carbon, in the form of char, could be present. Fines, collected above the unit, may contain dust from the limestone addition.

### ***Mineralogical changes with weathering***

For the purpose of this discussion, two forms of weathering are exposure to the natural elements in an uncompacted form and treatment with moisture for dust control purposes or deliberately to ensure chemical reactions. FBC ash, in an unconsolidated form, exposed to moisture and atmospheric carbon dioxide will result in

the formation of secondary mineralization that will consume alkalinity. Furthermore, the calcium is present in a form that is the most water-soluble form for calcium in the ash mixture and therefore has the ability to be washed from the ash. In the presence of moisture (or water in ash-grout composites), several chemical reactions that consume calcium into the secondary mineral phases will also contribute to the removal of alkalinity from the system and hence contribute to the lowering of NP.

Several chemical reactions spontaneously occur within the FBC ash upon the addition of moisture and exposure to the atmosphere. Initially, the lime will begin to absorb both atmospheric moisture and carbon dioxide:



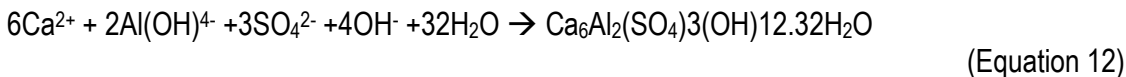
The initial reaction will remove lime from the chemical reaction pathway and begin to reduce NP. The second reaction establishes the controlling pH of the system at 12.4. Slaked lime is singularly the most soluble form of calcium in the ash.

A third reaction with the anhydrite and water contributes to the short term mechanical properties of ash:



This reaction is similar to the “plaster of Paris” reaction that everyone is familiar with.

The fourth reaction is the most well know and contributes the most to the early term mechanical properties:



In a simplistic manner the above reaction can be written:



where the gypsum is derived from the ash and the tri-calcium aluminate is derived from the slaked lime and the aluminosilicate from the dehydroxylated clay. Ettringite forms in the elevated pH range established by the slaked lime. As can be recognized, the ettringite reaction consumes calcium ions from the mix thus further reducing NP.

### ***Discussion on the use of ash for alkaline addition***

AMD was produced when mining occurred but was neutralized by the baghouse lime on the Kauffman site in the vicinity of monitoring well BF2. Figure 2 depicts a strong correlation between concentrations of SO<sub>4</sub> and Ca (R<sup>2</sup>=0.6343). It is reasonable to assume that the baghouse lime was providing the necessary alkalinity for the neutralization reactions to occur. Figures 7 and 8 depict how calcium concentrations vary with changing sulfate concentrations on the Abel-Dreshman site and Figure 9 presents this same information for the McDermott operation. By itself, this information would lend itself to the conclusion that the FBC ash was providing alkalinity for neutralization purposes. However, this conclusion is questionable when the data for Mg is considered.

Before the application of the FBC ash, the Ca and Mg concentrations at MP-29A from the Dreshman parcel averaged 162 mg/L and 133 mg/L, respectively. The Ca and Mg concentrations from the Abel parcel, MP-29B averaged 72 mg/L and 50 mg/L respectively. This indicates the presence of carbonate material on the site, perhaps dolomitic shale. Shale with an NP of 14 was noted in the overburden holes completed on the Dreshman parcel. Ca and Mg concentrations were less than 10 mg/L initially on the McDermott operation; however, the Johnstown Limestone formation is present and was mined. Mg concentrations are also plotted on Figures 7,8, and 9. Note that when Ca concentrations increase or decrease, Mg concentrations follow suit. On the Abel-Dreshman site, the Ca and Mg concentrations are actually lower

following the FBC ash application than before the application. Following the application of the ash, there was only a slight increase in Ca:Mg ratio, from 1.2:1 to 1.5:1 on the Dreshman parcel and from 1.42:1 to 1.46:1 on the Abel parcel. At the McDermott operation, the Ca:Mg ratio decreased from 2.7:1 to 2.2:1 following mining. Scatter plots for the Abel-Dreshman monitoring point MP-29A, Figure 10, and for the McDermott operation, monitoring well MW-2, Figure 11, show little scatter and a strong linear relationship when comparing Ca concentrations to those of Mg.

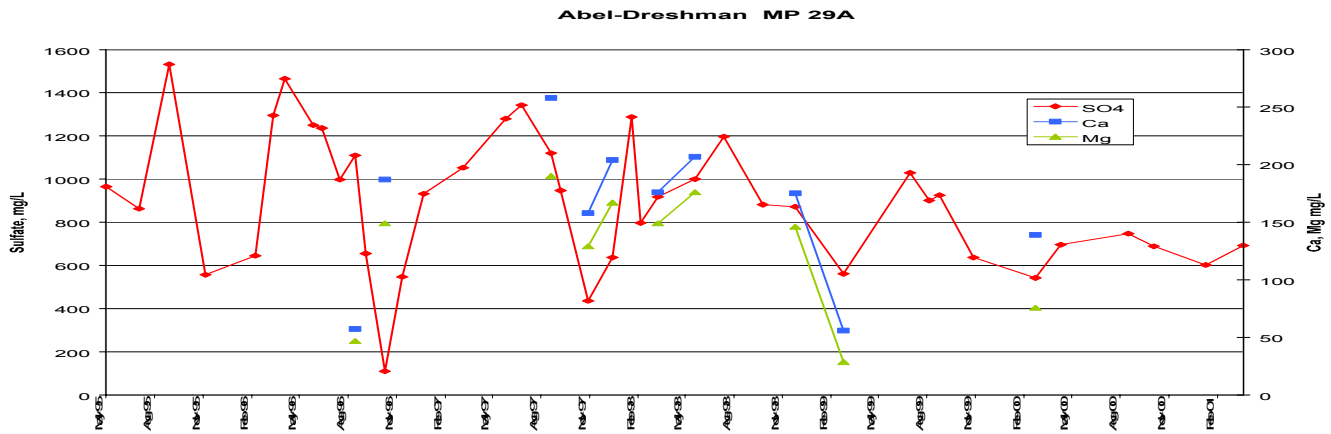


Figure 7. Relationship between SO<sub>4</sub>, Ca and Mg on the Abel Dreshman site, MP 29A

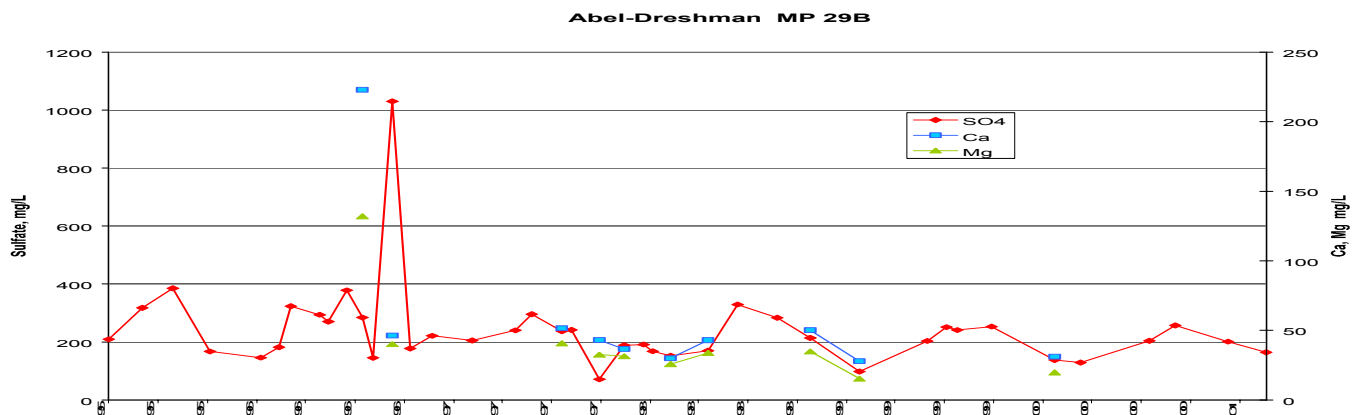


Figure 8. Relationship between SO<sub>4</sub>, Ca and Mg on the Abel Dreshman site, MP 29B

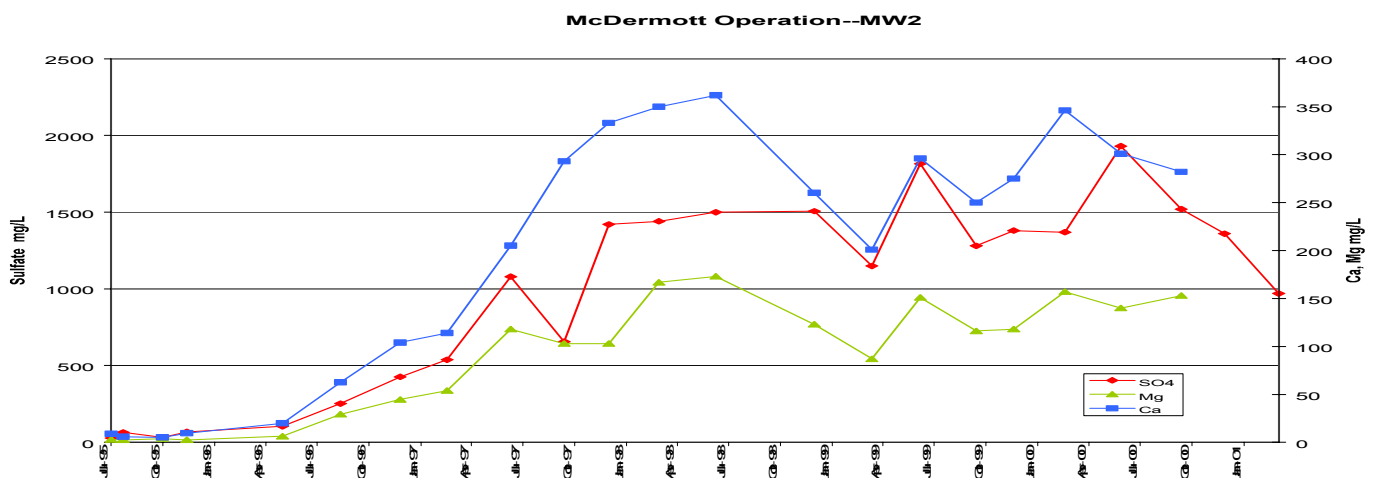


Figure 9. Relationship between SO<sub>4</sub>, Ca and Mg on the McDermott operation

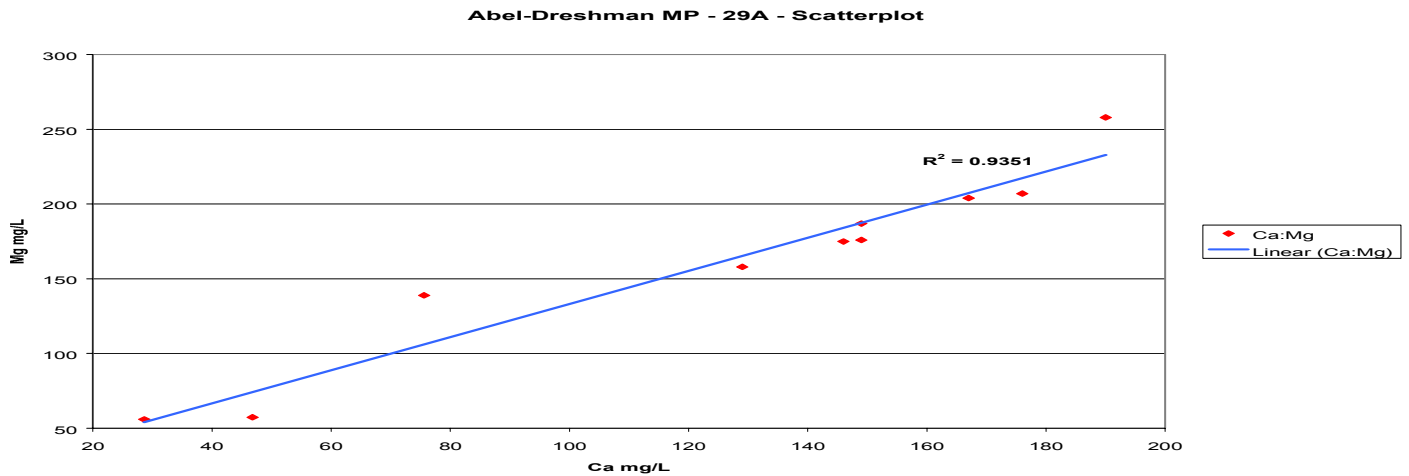


Figure 10. Scatter plot of Ca and Mg from Abel Dreshman MP-29A

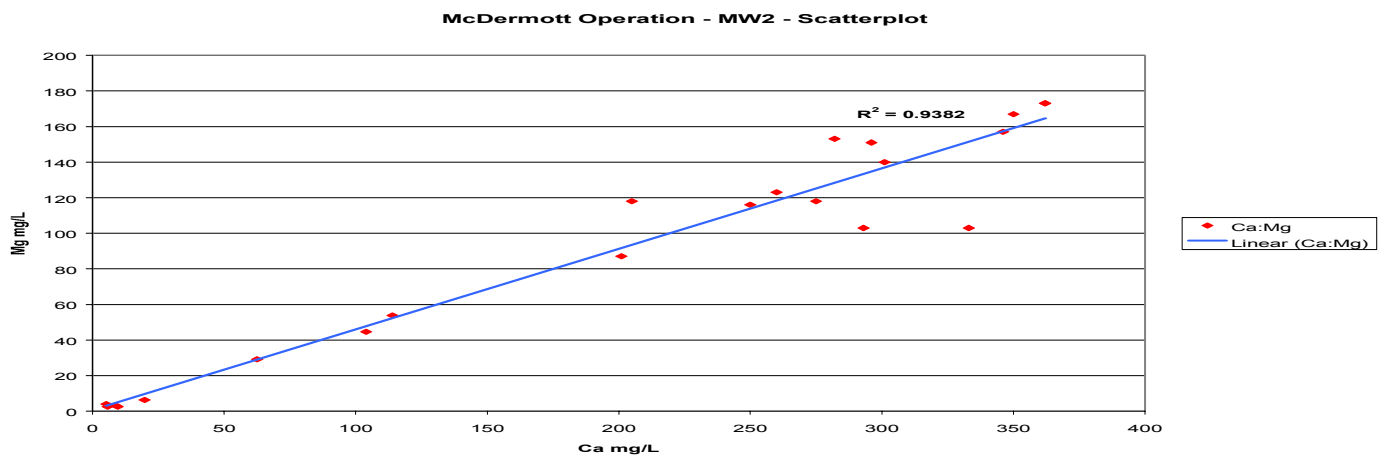


Figure 11. Scatter plot of Ca and Mg from the McDermott operation, MW-2

FBC ash contains approximately 30% CaO and less than 1% MgO, based on the analysis of the ash from several sources. Thus if the ash was the source of the alkalinity for neutralization, the strong linear relationship between the two should not be observed. FBC ash was used as a grout to encapsulate pyritic materials on the Fran Contracting site in Clinton County in 1992 and 1993 (Schueck, et. al, 1996). A large quantity of FBC ash grout was injected near monitoring well L25 in July 1993 and in September 1993 a near surface pod of dry FBC ash was placed near the well. The grout consisted of only FBC ash and water. Figure 12 shows the relationship between Ca and Mg before and after the grout injection in L25. The initial peak in Ca was most likely from the supernatant (washing out of CaO) associated with the grout. Figure 13 is a scatter plot showing the relationship between Ca and Mg for well L25. There is no relationship as the tremendous amount of scatter demonstrates.

There is strong correlation between Ca and Mg on the Abel-Dreshman ( $R^2=0.9351$ ) and the McDermott operations ( $R^2=0.8264$ ) and a lack of correlation ( $R^2 = 0.0238$ ) on the Fran Contracting site (where the measured response was directly attributed to FBC ash placement). Considering this, it appears that the alkalinity for neutralization on these sites is derived primarily from the naturally occurring carbonate minerals present and not from the FBC ash. If the fly ash were providing the alkalinity, then the Mg concentrations should not rise and fall with those of Ca. However, considering the slight increase in the Ca:Mg ratio of the Dreshman parcel and the post-ash application increases in Ca on the Fran Contracting site, it is likely that the FBC ash is providing some degree of neutralization capability to the sites.

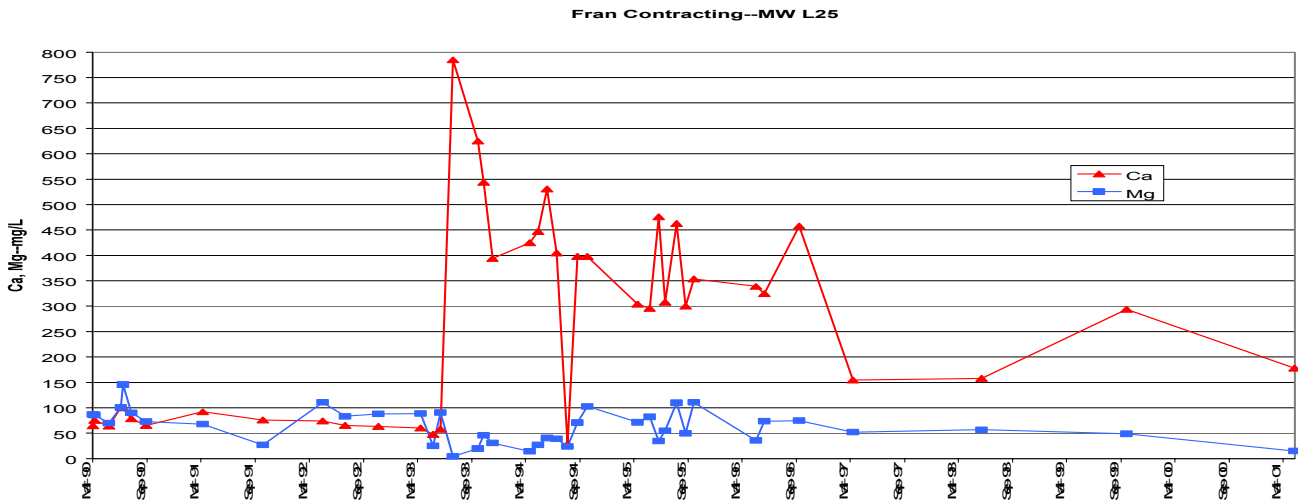


Figure 12. Relationship between Ca and Mg before and after FBC grout injection near the monitoring well

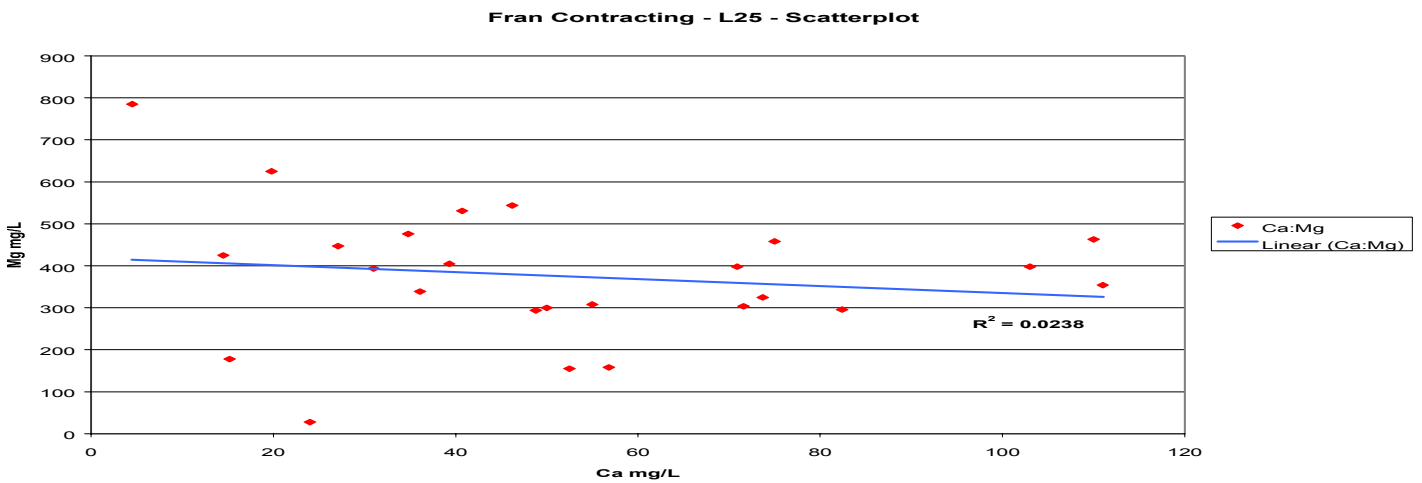


Figure 13. Scatter plot of Ca and Mg for monitoring well L25. Note the lack of relationship present.

### Conclusions

Considering the information provided from the various sites studied in this paper, it appears that the ability of FBC ash to neutralize or prevent AMD may not be as easily correlated to the results of NP test results as is the case with baghouse lime. The pozzolanic nature of the ash is one factor that may account for its apparent lesser ability to prevent or neutralize AMD, as compared to limestone. However, mine sites can benefit in other ways from the FBC ash. Because the ash is pozzolanic, or self-cementing, the ash should be applied as cement. There are three primary applications. First, placing a layer of ash on the pit floor can limit AMD generation where the pavement is pyritic. The second is that the pyrite-rich materials encountered or transported to a site can be encapsulated with the FBC ash. This prevents their contact with oxygen and water, thus limiting AMD generation. The third is providing a shallow subsurface, compacted layer of the ash, limiting infiltration.

Timing of these processes is critical; however, especially where moisture is added to the ash at the generating station for dust control. As soon as moisture is added to the ash, the pozzolanic reactions begin. In order to gain full benefit from the cementitious nature of the ash, immediate placement upon arrival at the site is best. If the generating station could load dry ash onto the trucks, the operators would have greater flexibility in placing the material in order for the application to be effective.

It is also possible that, when ash is used as an alkaline additive, the amount needed to offset the site maximum potential acidity, as defined by an OBA, is greater than that suggested by the NP of the ash. Additional ash placement sites need to be examined to determine if the conclusions drawn here are general or are only specific to the three sites examined in this paper. Also, more work needs to be done to determine just how much the effective NP is reduced with time as a result of the pozzolanic nature of the FBC ash.

Although not a topic of this paper, the data from the Kauffman site suggests that additional alkaline addition sites should be studied to determine the best way to incorporate the alkaline materials into the backfill and to determine if material solubility should be a factor in determining the application rates.

### References Cited

- Brady, K.B.C. and R.J. Hornberger, 1990. The prediction of mine drainage quality in Pennsylvania. *Water Pollution Control Assoc. of PA Magazine*, v. 23, no. 5, pp 8-14.
- Davis, Alan, 1981. Sulfur in coal: *Earth and Mineral Sciences*, Pennsylvania State University, University Park, v. 51, no. 2, pp 13-21.
- Hawkins, J.W., 1984. Iron disulfide characteristics of the Waynesburg, Redstone, and Pittsburgh coals in West Virginia and Pennsylvania. Morgantown, W.V., West Virginia University, M.S. thesis, 195 p.
- Hawkins, J.W., 2001, personal communication.
- Hellier, W.W., 1998. Abatement of acid mine drainage pollution to Upper Three Runs by capping an acid producing reclaimed surface mine with fluidized bed combustion fly ash. In: *Proceeding 1998 West Virginia Surface Mine Drainage Task Force Symposium*, Morgantown, W. VA, 12 p.
- Kleinmann, R.L.P., D.A. Crerar, and R.R. Pacelli, 1981. Biogeochemistry of acid mine drainage and a method to control acid formation. *Mining Engineering*, v. 33, pp. 300-303.
- Nordstrom, D.K., 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals, Kittrick, J.A., Fanning, D.S. and Hossner, L.R. eds. *Acid sulfate weathering*. Soil Science Society of America, pp. 37-63.
- Perry, E.F., 1998. Interpretation of acid-base accounting. In *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*, Brady, K.C.B., Smith M.W., and Schueck J. eds. Harrisburg, Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256, pp. 11.1-11.18.
- Rose, A.W. and Cravotta, C.A. III, 1998. Geochemistry of coal-mine drainage. In *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*, Brady, K.C.B., Smith M.W., and Schueck J. eds. Harrisburg, Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256, pp. 1.1-1.22.
- Schueck, J., M. Dimatteo, B. Scheetz, and M. Silsbee, 1996. Water quality improvements resulting from FBC ash grouting of buried piles of pyritic materials on a surface coal mine. In: *Proceedings Seventeenth Annual West Virginia surface Mine Drainage Task Force symposium*, Morgantown, W WA.
- Smith, M.W. and K.B.C. Brady, 1998. Alkaline addition. In *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*, Brady, K.C.B., Smith M.W., and Schueck J. eds. Harrisburg, Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256, pp. 1.1-1.22.
- Stumm, W. and J.J. Morgan, 1981. *Aquatic chemistry*. Wiley Interscience, 470 p.