# ALKALINE FOUNDATION DRAINS AND ALKALINE AMENDMENTS FOR AMD CONTROL IN COAL REFUSE PILES <sup>1</sup>

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<u>Abstract:</u> Coal refuse, a by-product of cleaning coal is normally disposed of in fills. The composition of this refuse is pyrite and other minerals that are rejected during the coal cleaning process. Pyrite is the main environmental concern because it will oxidize to form Acid Mine Drainage (AMD). AMD produced at a mining operation is ideally neutralized by alkaline material in the overburden, but refuse usually lacks alkaline material. Recent studies with Appalachian coal refuse types have indicated that certain types of alkaline amendments have the potential to prevent AMD formation from pyritic coal refuse. This study evaluated the use of alkaline amendments (FBC ash, kiln dust, limestone sand, limestone sand mixed with quick lime, alkaline sandstone, and alkaline shale) to neutralize the AMD produced by coal refuse. The study consisted of constructing refuse piles mixed with the alkaline amendments or containing the alkaline sandstone or shale in subdrains to treat the AMD produced by the refuse. Samples were collected monthly and analyzed for pH specific conductance, alkalinity, acidity, iron, manganese, aluminum, calcium, magnesium, and sulfates.

Key Words: Coal Refuse, Acid Mine Drainage, Alkaline Amendments

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#### Introduction

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The large deposits of coal in the eastern United States have been the foundation for the industrialization of the area. They extend from northeastern Pennsylvania south to Alabama and as far west as the Great Plains. The deposits were originally developed by deep mining but since the end of World War II have been developed largely by surface mining. Unfortunately, most of the coal found in this region has a high sulfur content and must be cleaned prior to being used as a fuel. The sulfur occurs as organic sulfur (sulfur bound to the coal) and as inorganic sulfur (found as pyrite).

Physical coal cleaning removes ash-forming impurities along with pyrite. This process includes

crushing the coal to a size where mineral and coal particles can be separated by using the differences in density or surface properties. One of the resulting by-products of cleaning coal is coal refuse. The refuse is usually disposed of in fills. It normally contains the pyrite and other minerals that are rejected in the cleaning process. The pyrite is the main environmental concern, because it oxidizes to form ferrous iron and sulfuric acid, the main components of Acid Mine Drainage (AMD) (equation 1). The ferrous iron is further oxidized to ferric iron (equation 2). The ferric iron works as a catalyst to increase the oxidation of the rest of the pyrite by an order of magnitude (equations 3 & 4). The following equations summarize pyrite oxidation.

$2FeS_2 + 2H_2O + 7O_2 -> 2Fe^{+2} + 4H^+ + 4SO_4^{-2}$ (pyrite oxidation)	(1)
$4Fe^{+2} + O_2 + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O$ (ferrous oxidation)	(2)
Fe <sup>+3</sup> + 3H <sub>2</sub> O -> Fe(OH) <sub>3</sub> + 3H <sup>+</sup> (ferric hydrolysis)	(3)
$FeS_2 + 14Fe^{+3} + 8H_2O \rightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+$ (ferric catalyzed pyrite oxidation)	(4)

Pyrite oxidation can occur at varying levels of oxygen, and microorganisms (*Metallogenium*, *Thiobacillus thiooxidans*, and *Thiobacillus ferrooxidans*) can oxidize pyrite in concentrations as low as I% oxygen. The problems occur when there is an insufficient amount of alkaline material in the refuse to neutralize the acid produced and the resulting AMD seepage is formed (Watzlaf and Hammack). The iron and sulfur rich AMD contaminates both ground and surface waters, killing aquatic life and renders the water supply unfit for recreation or consumption.

Numerous methods of treatment have been tried to eliminate AMD, however, most of these are expensive. Limestone is one exception, it is the most inexpensive of the common acid neutralizing reagents, the only problem with using limestone is that it will coat (armor) with iron hydroxide precipitates in the presence of oxygen (Nairn et al). This armoring of the limestone slows the dissolution rate of the carbonate and reduces the buffering effects of the stone (Brant and Ziemkiewicz and Ziemkiewicz et al).

Anoxic Limestone Drains (ALD) are a relatively new method of using limestone to generate alkalinity and treat AMD. The first one was discovered by the Tennessee Valley Authority (TVA) when they constructed a coal refuse dam over an old haul road (made of crushed limestone). They found that the quality of water seeping through the roadbed was better than the water in the impoundment, further investigations led to the concept of the ALD. In its buried, anoxic state, the crushed limestone dissolved, raised the pH and increased the alkalinity of the water. Researchers at TVA concluded that the anoxic state of the drain prevented the dissolved iron from precipitating and coating or armoring the limestone. Once the effluent was oxidized at the surface, the dissolved minerals precipitated in an settling pond. ALDs are currently being constructed throughout the coal mining regions of Appalachia to compliment wetlands or as stand-alone systems to treat AMD. They are designed to exclude oxygen from the drain, preventing metal precipitation and clogging or armoring of

the stone and allowing the carbonate to dissolve (if the iron present is the reduced species (ferrous)). The following equations describe the dissolution of limestone under attack.

Equation 5 reacts limestone with the acidity in AMD to form free calcium and bicarbonate alkalinity. Equation 6 reacts the bicarbonate with acid to form dissolved carbon dioxide (carbonic acid). In anoxic conditions the carbonic acid reacts with limestone In equation increase alkalinity.

$CaCO_3 + H^+ \rightarrow Ca^{+2} + HCO_3^-$	(5)
$HCO_3 + H^+ \rightarrow H_2CO_3$	(6)

Atmospheric conditions will degass any excess carbon dioxide from the water as the solution is aerated (Brodie et al., Hedin and Nairn, and Skousen and Faulkner).

The non limestone alkaline amendments used in this study were also relatively inexpensive, primarily due to being considered a waste product of other industries. The non limestone alkaline portion of these byproducts is calcium oxide (CaO) or quicklime. As the calcium oxide becomes hydrated it forms lime (Ca(OH)<sub>2</sub>). The lime provides the hydroxide to neutralize the acidity produced in the refuse piles (Benefield and Morgan).

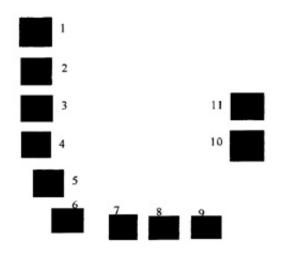
$CaO + H_2O \rightarrow Ca(OH)_2$	(7)
$Ca(OH)_2 + 2H^+ -> 2H_2O + Ca^{+2}$	(8)

# Experimental Design

Representative spoil and refuse samples examined for AMD production in phase 1. This portion of the study determined the amount and types of amendments to be used in the field study. This was accomplished by adding amendments to the samples and subjecting these treated samples to 20 one week soxhlet extraction and oxidation cycles. The chemical analysis of the leachate allowed the sulfate/acid production rates to be calculated to identify successful treatments.

Successful treatments (Table 1) were then applied under field conditions (Fig. 3) to a series of 400 ton test piles of refuse obtained from the preparation plant at the mine site. The piles were underlain by plastic liners to collect the leachate. The leachate is piped into 1000 gallon tanks for collection and chemical analysis.

#### Figure 3 - Test Pile Locations



#### Table 1 - Test Pile Treatments

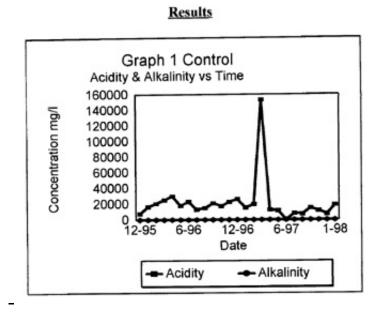
Pile	Treatment
1	None - Control
2	1.31% Limestone Sand
3	3.93% Limestone Sand
4	0.73% Limestone Sand + 0.5% CaO
5	3.19% limestone Sand + 0.5% CaO
6	4.19% FBC Ash
7	12.56% FBC Ash
8	1.08% Kiln Dust
9	3.24% Kiln Dust
10	1.5 Ft. Alkaline Sandstone Subdrain
11	1.5 Ft. Alkaline Shale Spoil Subdrain

The test pile construction was completed in November,

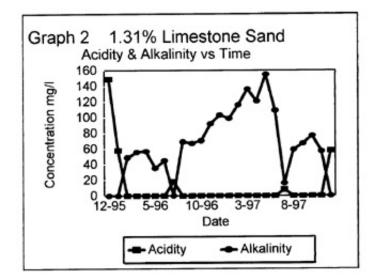
1995, with the first monthly leachate collection and analysis

starting December 5, 1995. Prior to the sample collection, the storage tanks were calibrated with river water and a 55 gallon barrel, This test determined that 1 inch of water in the tanks was equivalent to 16 gallons. The sample frequency has been monthly since the initial sampling in December. Each sample was analyzed for the following using the procedures found in Standard Methods for the Analysis of Water and Wastewater: pH, conductivity, alkalinity, acidity, iron, manganese, aluminum, calcium, magnesium, and sulfate.

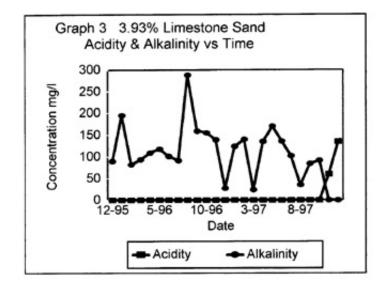
# **Results**



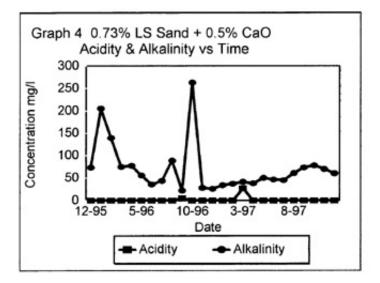
Graph 1 compares the alkalinity to the acidity generated for the length of the experiment. As expected, the control pile generated a high amount of acidity and no alkalinity.



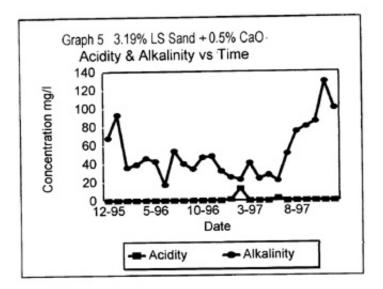
Graph 2 compares the alkalinity to the acidity generated by the addition of 1.31% limestone sand to the refuse. After the first two months the effluent was alkaline except for the July 1996 and January 1998 samples.



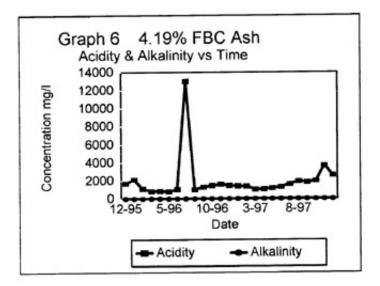
Graph 3 compares the alkalinity to acidity generated by the addition of 3.93% limestone sand to the refuse. the effluent has been alkaline for the start of the project until the December 1997 sample was collected and found to be acidic.



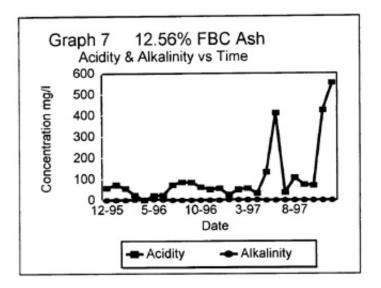
Graph 4 compares the alkalinity to the acidity generated using 0.73% limestone sand and 0.5% calcium oxide as the amendment. the calcium oxide was used to produce a quick boost of alkalinity in the system, until the limestone sand started to react. This system has produced net alkaline water since the start of the project.



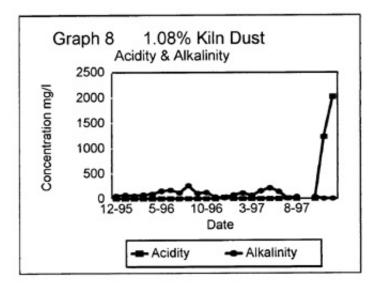
Graph 5 compares the alkalinity to the acidity generated by the addition of 3.19% limestone sand and 0.5% calcium oxide. the alkalinity of this mixture produced alkalinities that ranged from 20 to 130 mg/l CaCO<sub>3</sub> eq. The acidities produced were zero except during March and July 1997 samples, even then the discharge was net alkaline.



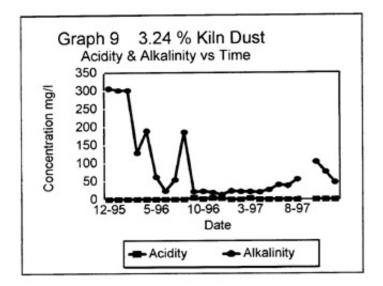
Graph 6 compares the alkalinity to the acidity produced for the 4.19% FBC ash amendment. This pile is consistently discharging acidic effluent. The alkalinity is zero and the acidity production is slowly increasing between 2,00 and 4,00 mg/l CaCO<sub>3</sub> eq. However, this pile is treating some acidity because the discharge is less acidic than the control (Graph 1)



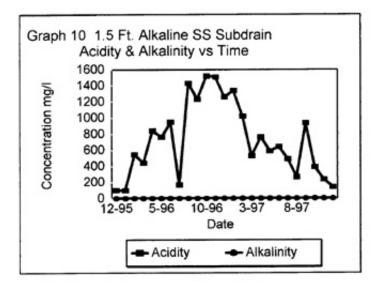
Graph 7 plots the alkalinity vs the acidity generated for the pile containing the 12.56% FBC ash. This pile also discharges a net acidic effluent and zero alkalinity. However, the acidities are at least an order of magnitude less than the control pile discharge.



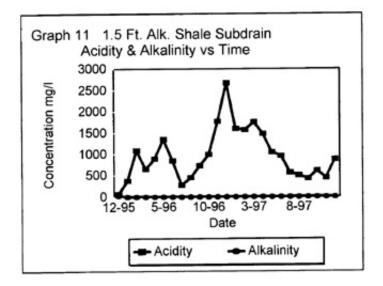
Graph 8 plots the alkalinity vs the acidity for the pile with 1.08% kiln dust added to the refuse. This system has been net alkaline since the start of the project except during the December 1996 sampling and since August 1997.



Graph 9 compares the alkalinity and acidity generated from the pile containing 3.24% kiln dust in the refuse. This system started out producing over 300 mg/l CaCO<sub>3</sub> eq. alkalinity, but has been less than 100 mg/l CaCO<sub>3</sub> eq. since September 1996. This system has not produced any acidity since it was installed.



Graph 10 is a plot of acidity production vs alkalinity for the pile constructed over a 1.5 feet thick layer of alkaline sandstone used as a subdrain. This system had an acidic discharge since the start of the project. However, the discharge contains an order of magnitude less acidity than the control pile.



Graph 11 represents the results obtained from the pile constructed over a 1. 5 feet thick layer of alkaline shale used as a subdrain. This pile also discharges an acidic effluent, but it is normally 115 less acidic than the control.

# **Conclusions**

The data from this study produced results that indicate effective treatment strategies for acidic refuse disposal. Although the alkalinities in some of the treated piles is decreasing, the acidities being produced are not as high as the control piles, suggesting that the effluent will be easier and less costly to treat than the effluent from the untreated piles. The most consistent combination is the limestone sand and calcium oxide refuse mixtures, followed by the 3.24% kiln dust addition. These were the only piles that have not produced net acidic effluents. The rest of the piles are producing net acidic effluents, but the acidity levels are

not as high as the controls, indicating that there is still some treatment occurring. The monitoring is also continuing, to evaluate the longevity of each of these amendments.

#### <u>Acknowledgments</u>

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