

ALKALINE FOUNDATION DRAINS AND ALKALINE AMENDMENTS FOR AMD CONTROL IN COAL REFUSE PILES¹

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Abstract: Coal refuse, a by-product of coal cleaning is normally disposed of in fills. Refuse consists of pyrite and shale. 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 alkalinity. Three studies evaluated the use of alkaline amendments and alkaline subdrains to neutralize the AMD produced by coal refuse. The lab study was designed to measure the effects of placing a layer of limestone directly under the refuse in a series of cells, compared to mixing the limestone in the refuse in the second series. The third series of cells acted as the control and contained only refuse. Each series was studied in triplicate with weekly sampling for the duration of the study. The field study plies contained refuse mixed with the alkaline amendments or were constructed over alkaline subdrains. Samples were collected monthly. The laboratory study acted as a wet cover and prevented acid generation. Both field studies generated a reduced acidity or net alkalinity in the treated refuse pile discharge.

Key Words: Limestone Foundation Drains, Coal Refuse, Acid Mine Drainage, Alkaline Amendments



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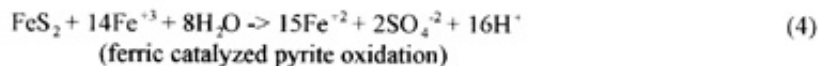
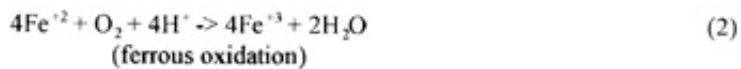
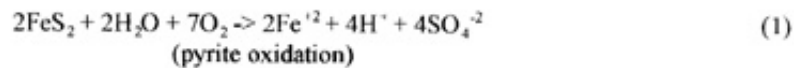
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Introduction

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 11 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.



Pyrite oxidation can occur at varying levels of oxygen, and microorganisms (*Melallogenium*, *Thiobacillus thiooxidans*, and *Thiobacillus ferrooxidans*) can oxidize pyrite in concentrations as low as 1% 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).

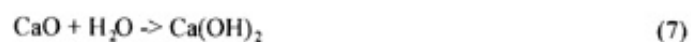
Anoxic Limestone Drains (ALD) are a relatively new method of using limestone to generate alkalinity and treat AMD. The first one was discovered by the Tennessee Valley Authority (TVA) when they constructed a coal refuse dam over an old haul road (made of crushed limestone). They found that the quality 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 a 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 acid 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 to increase the alkalinity. Atmospheric conditions will degass the carbon dioxide from the water (Brodie et al., Hedin and Nairn, and Skousen and Faulkner).

The non limestone alkaline amendments used in this study were a waste product of other industries and were relatively inexpensive. The non limestone alkaline portion of these byproducts is calcium oxide (CaO) or quicklime. As the calcium oxide hydrates it forms lime (Ca(OH)₂). The lime provides the hydroxide to neutralize the acidity produced in the refuse piles (Benefield and Morgan).



Experimental Design

Laboratory Study

Our laboratory is studying the use of anoxic limestone drains as a foundation (ALFD) for the coal refuse to treat any AMD produced. The refuse (150 pounds containing 2% S (6.25% Acid Potential, AP)) was placed over a layer of limestone (20 pounds Neutralization Potential of 80%, (NP)) in the reaction cells. The resulting NP/AP ratio was 1.7:1 to produce a net alkaline discharge in the ALFD cells.

Materials

1. Fresh refuse with a pyrite content of about 2% will be used to produce the AMD.
2. High quality limestone (calcium carbonate content of 80-90%).
3. 9 - 35 gal. HDPE barrels with spigots.
4. Fabric to separate refuse from limestone (figure 1).

Methods

Precipitation that percolates through refuse piles will dissolve and transport a variety of materials in the leachate. The dissolved materials can have a detrimental effect off-site, either to the groundwater or to the surface water runoff from the area (AMD) (Halverson and Gentry). In this study, a series of barrels were used to contain the refuse / limestone mixture to be leached with deionized water. The limestone filled the bottom of the barrel and was

separated from the coal refuse by a geofabric membrane.

All of the cell groups were exposed to atmospheric conditions. The first cell group contained the limestone foundation drains (figure 1). The second cell group contained a mixture of the refuse and limestone (figure 2). The last cell group contained only the refuse (control). Each cell group was analyzed in triplicate yielding a total of 9 cells.

Samples were collected from each cell at weekly intervals for the duration of the project. Each sample was analyzed for the following parameters using the procedures found in Standard Methods for the Examination of Water and Wastewater: pH, conductivity, alkalinity, acidity, iron, manganese, aluminum, calcium, magnesium, and sulfate. At the end of the project, the cells were dismantled and studied for limestone armoring.

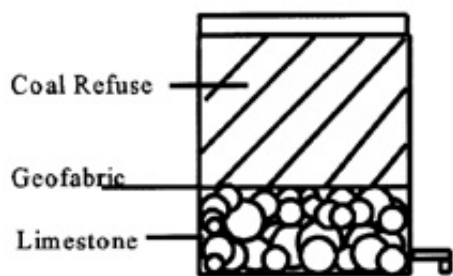


Figure 1 - Anoxic Limestone Drain

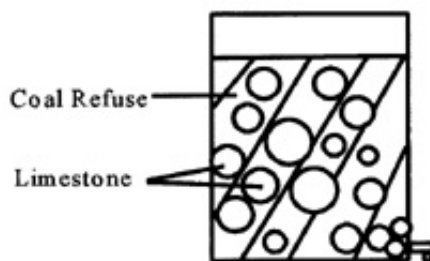


Figure 2 - Limestone / refuse

Field Design

Site 1

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.

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 Examination of Water and Wastewater: pH, conductivity, alkalinity, acidity, iron, manganese, aluminum, calcium, magnesium, and sulfate.

Figure 3 - Test Pile Locations

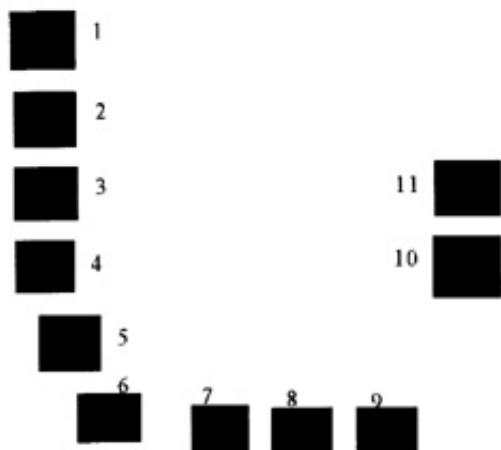


Table 1 - Test Pile Treatments

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

Site 2

The second field study consisted of nine 100 ton refuse piles constructed similar to the lab study. All the piles were also underlain with plastic liners to collect the AMD produced. The first series of refuse piles was constructed over an anoxic limestone drain (ALFD) (figure 4). The second group contains a mixture of the refuse and limestone (figure 5). The last group will contain only the refuse (control). All refuse piles drain into 1,000 gal. tanks for sample collection and treatment (if required). Each cell group was analyzed in triplicate yielding a total of 9 cells. The construction of test piles was finished in April 1996, with the first monthly sample collection starting in May 1996. Each sample was analyzed for the following using the procedures found in Standard Methods for the Examination of Water and Wastewater: pH, conductivity, alkalinity, acidity, iron, manganese, aluminum, calcium, magnesium, and sulfate.

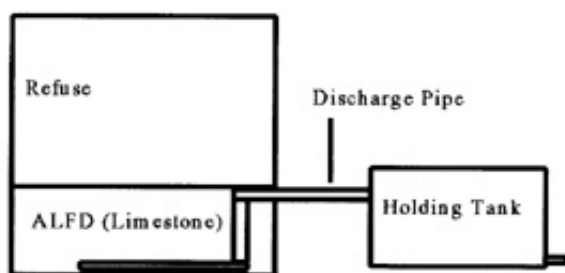


Figure 4 - ALFD

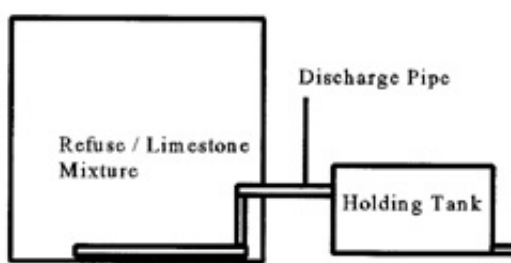
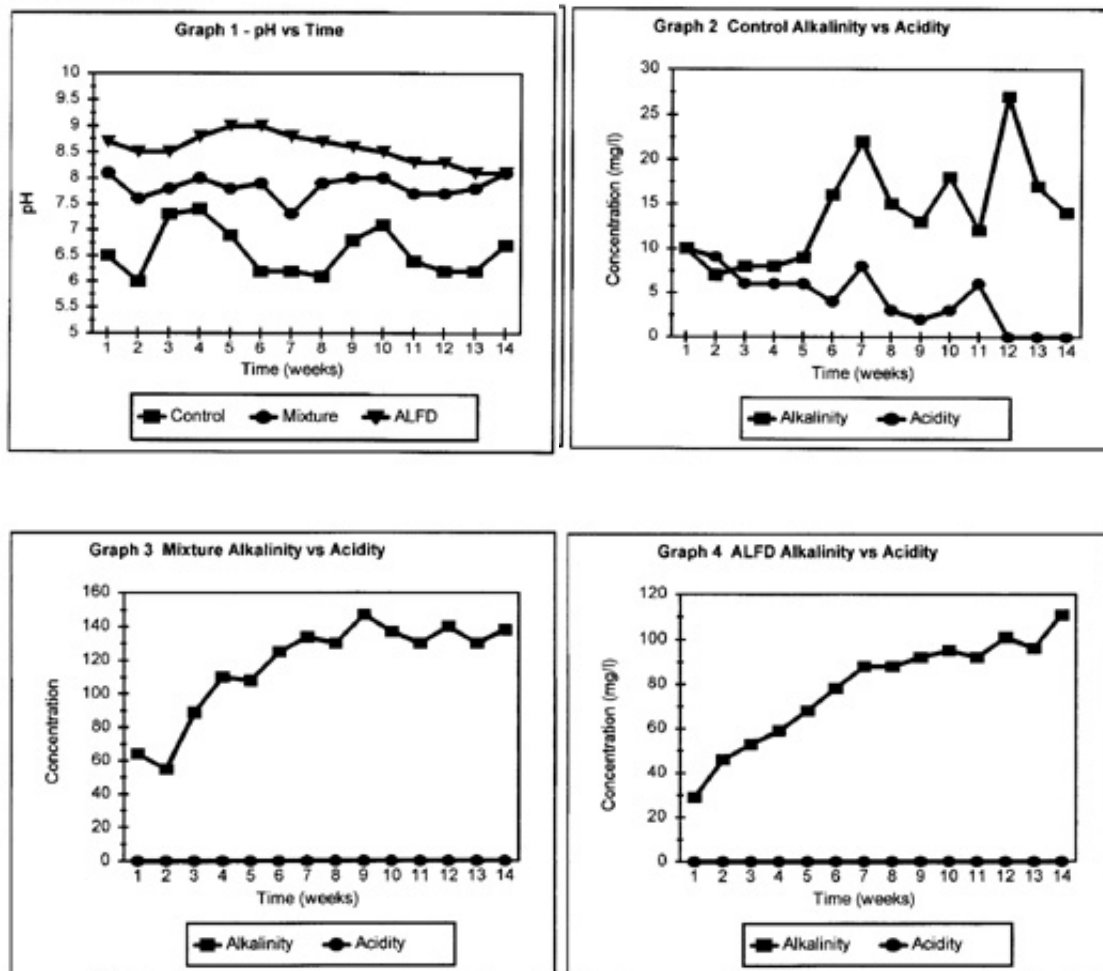


Figure 5 - Limestone / Refuse mixture

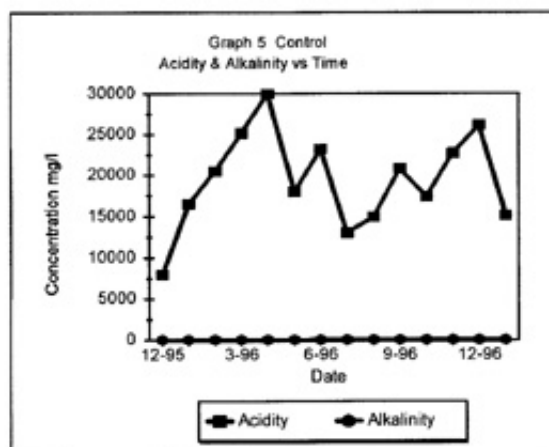
Results

Laboratory Study

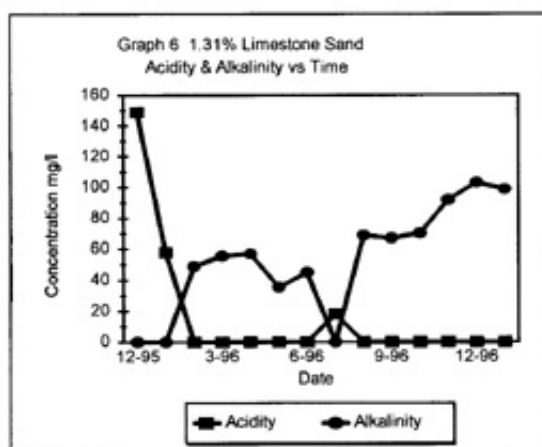


Graph 1 compares the pH of the laboratory study cell effluent as the project progressed. Graph 2 compares the alkalinity and acidity of the effluent from the control samples. Graph 3 relates the alkalinity and acidity of the limestone / refuse mixture cells. Graph 4 plots the alkalinity and acidity of the limestone subdrains. At the end of the study limestone was extracted from the cells and armoring was not present in any of the cells. The results indicate that the systems did not oxidize. This could be due to a low permeability of the refuse in the cells leaving a thin (<0.25 inch) layer of water on top of the refuse, producing a barrier to oxidation (wet cover).

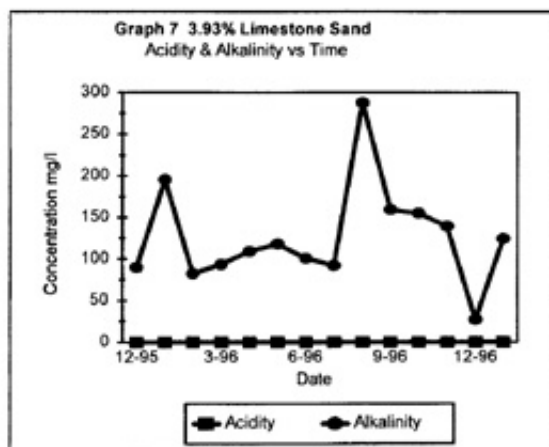
Field Study



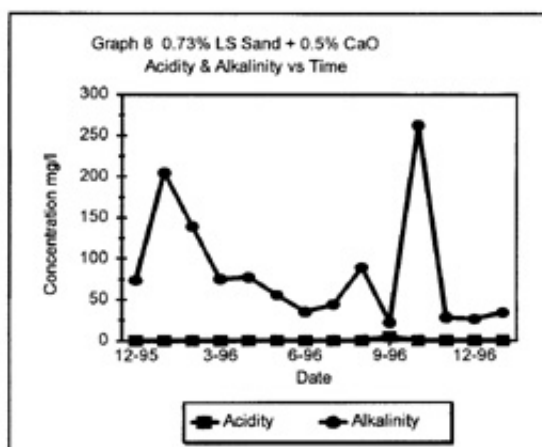
Graph 5 compares the alkalinity to the acidity generated for the length of the experiment. As expected, the control pile generated a high amount of acidity and no alkalinity.



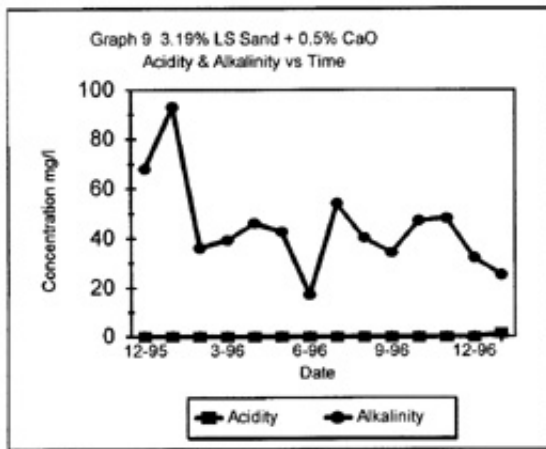
Graph 6 compares the alkalinity to the acidity generated by the addition of 1.31% limestone sand to the refuse. After the first two months the effluent was net alkaline except for the July 1996 sampling when the acidity increased to 20 mg/l CaCO_3 eq. and the alkalinity dropped to zero.



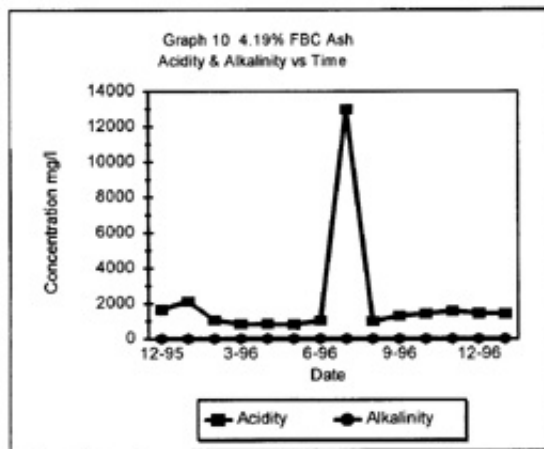
Graph 7 compares the alkalinity to acidity generated by the addition of 3.93% to the refuse. The effluent has always been net alkaline since the start of the project. The lowest alkalinity occurred during the Dec. 1996 sampling, when it fell to 25 mg/l CaCO_3 eq.



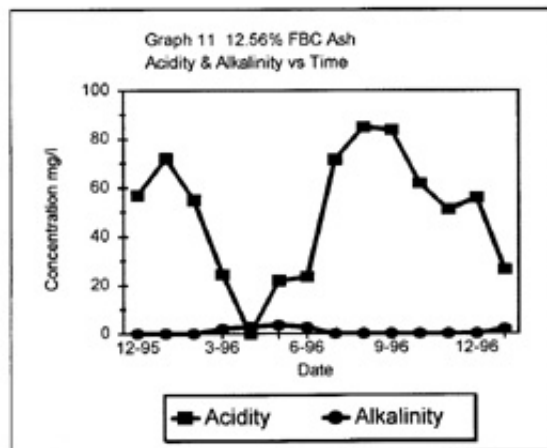
Graph 8 compares the alkalinity to the acidity generated using 0.73% limestone sand and 0.5% calcium oxide as the amendment. The calcium oxide was used to give the system a quick boost of alkalinity until the limestone sand started to react. This system has also produced net alkaline water since the start of the project. However the alkalinity is starting to level off around 25 mg/l CaCO_3 eq. Since the Nov. 1996 sampling.



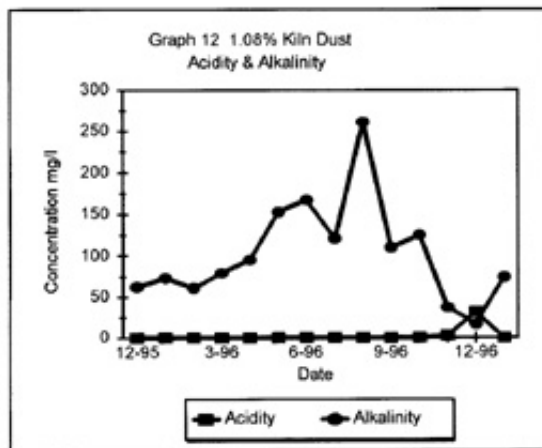
Graph 9 compares the alkalinity to the acidity generated using 3.19% limestone sand and 0.5% calcium oxide as the amendment. This mixture has an average alkalinity production of about 45 mg/l CaCO_3 eq. ranging from 25 to 95 mg/l CaCO_3 eq. And an acidity production of zero.



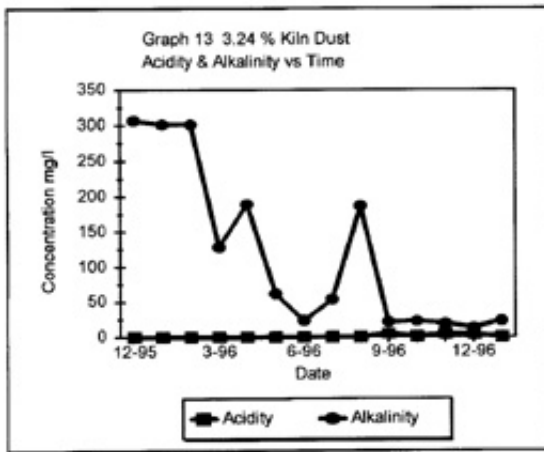
Graph 10 compares the alkalinity to the acidity generated for the 4.19% FBC ash amendment. This pile is consistently discharging acidic effluent. The alkalinity is zero and the acidity has leveled off around 1000 mg/l CaCO_3 eq. However, this pile is still treating some of the discharge because the effluent is normally less acidic than the control pile (Graph 5).



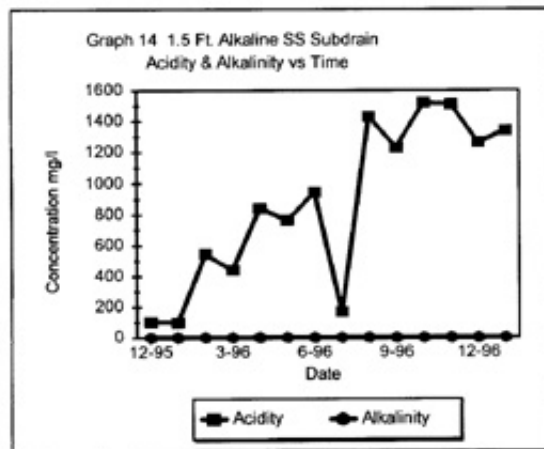
Graph 11 plots the alkalinity vs the acidity generated for the pile amended with 12.56% FBC ash. This pile also generates some acid (<90 mg/l CaCO_3 eq.) and zero alkalinity. However, it ranges from 100 to 300 times less acidic than the control pile.



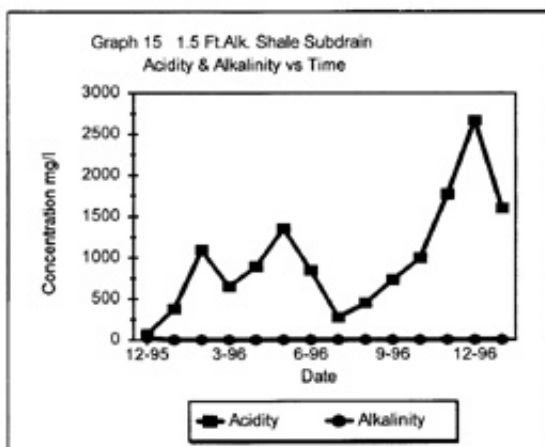
Graph 12 compares the alkalinity to the acidity generated in the 1.08% kiln dust amended pile. This system has been net alkaline since the start of the project except during the Dec. 1996 sampling when the acidity was about 5 mg/l CaCO_3 eq. greater than the alkalinity.



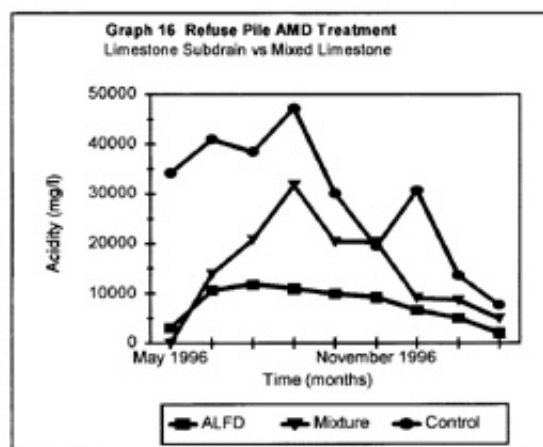
Graph 13 compares the alkalinity to acidity generated from the 3.24% kiln dust amended pile. This system started out producing over 300 mg/l CaCO_3 eq. alkalinity but has since leveled off around 15 - 20 mg/l CaCO_3 eq. without any acidity in the effluent.



Graph 14 is a plot of acidity production vs alkalinity for the pile with the 1.5 foot alkaline sandstone subdrain pile. This system has had an acidic discharge since the project started but is consistently discharging effluent 10 - 100 times less acidic than the control pile.



Graph 15 represents the results obtained from the 1.5 foot alkaline shale subdrain pile. This pile also contains acidity in the discharge, but it is producing 1/5 to 1/100 the amount of acid as the control pile.



Graph 16 compares the acidities generated in the second field study. Although none of the piles produced any alkalinity, the limestone subdrain piles and limestone mixed with the refuse piles are generally producing less acidity than the control pile.

Conclusions

The data from the laboratory study indicates that wet covers can be an effective way to dispose of acidic materials that are not oxidized. Graphs 5 - 15 compare alkalinity and acidity produced in the field study number 1. Graph 16 compares the acidities produced in the second field study. Both field studies indicate that there is some treatment occurring in all the amended piles. The alkaline subdrain piles and the mixed piles in the second study are all producing acidities in the effluent, but they are only producing 1/2 to 1/10 as much acid as the controls. The piles amended with FBC ash are also producing an acidic effluent, but the acid levels are less than the control pile is producing. The rest of the piles are discharging net alkaline water. The most consistent piles were the ones containing the limestone sand in the

mixture. 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.

Acknowledgements

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