

# Characterization of Acid Leaching Reactions in Coal Refuse/Coal Fly Ash Bulk Blends

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## ABSTRACT

The exclusion of coal fly ash from regulation as a hazardous waste has led to increased interest in returning ash to the coalfields for co-disposal with coal refuse. A column study used coal refuse with high potential acidity (4% total-S), and two ashes with varying levels of alkalinity. The ashes were bulk blended at varying ratios (0, 5, 10, 20 and 33%) with the coal refuse and packed into replicated (n=3) leaching columns. The columns were run unsaturated, and received 2.5 cm of simulated rainfall per week for 165 weeks. The unamended refuse acidified rapidly, producing acidic (pH 1.7) leachates, high in dissolved metals. Columns treated with a low alkalinity ash acidified sequentially over time, releasing significant levels of Fe, Mn, Zn, and Cu to the eluted leachates. Treatments blended with 20 and 33% of the more alkaline ash produced alkaline (pH >8.4) leachates with low metal levels. Examination of solid phase materials in the columns indicated that pyrite oxidation was occurring in all treatments, and a highly significant linear regression was developed to predict acid breakthrough over time based on total alkaline loading to the system. Our data clearly indicated that ash alkalinity and refuse potential acidity must be balanced to insure long term water quality protection from ash/refuse co-disposal practices and that the breakthrough of acidic leachates may take greater than five years under certain co-disposal scenarios as modeled in our study.

## INTRODUCTION

The U.S. EPA excluded coal fly ash from regulation as a hazardous waste in 1993 and this has led to increased interest in returning ash to the coalfields for co-disposal or beneficial reutilization. Current mining regulations allow for the release of acidic mine drainage (AMD) from refuse piles to holding ponds, where the drainage is impounded and treated with caustics to neutralize the acidity before the water is released to local waters. The AMD and the associated impoundments present a threat to the quality of both ground and surface waters near the refuse pile. One may also question the effects of releasing high pH water into surface waters. An alternate solution would be to bulk blend a liming agent, such as limestone, with the refuse at a rate that would neutralize all the acidity potentially produced by pyrite oxidation within the refuse pile. A problem with this treatment is the cost, however.

Alkaline fly ash could offer a cheaper alternative to limestone. Fly ash is produced at coal fired power plants, which burn coal that was cleaned at a prep plant with an associated with a refuse pile. The fly ash is usually land filled at a suitable site near the power plant. Back hauling fly ash could offer a cost effective liming agent for use on refuse piles and surface mined lands. Returning the ash to where the coal was mined and cleaned also makes some sense from a material balance point of view. Bulk-blending alkaline fly ash with acid forming coal refuse may present a disposal option that aids in the control of acid mine drainage. A preliminary column leaching study<sup>1</sup> examined the leachate quality from acid-forming coal refuse:fly ash blends. The coal refuse columns acidified quickly, producing peak leachate levels of acidity (pH 1.7), Fe (10,000 mg l<sup>-1</sup>), SO<sub>4</sub><sup>-2</sup> (30,000 mg l<sup>-1</sup>), and Mn (300 mg l<sup>-1</sup>). Both ash blended treatments (at 20 and 33% w:w) produced alkaline leachates with low metal levels.

This paper reports some results from a subsequent column study, with more treatments and larger columns, using refuse with higher potential acidity (4% total-S), and two alkaline ash sources; one blended at two rates (20% and 33%) and one at four rates (5%, 10%, 20%, and 33%). Bulk-blended ground agricultural limestone, rock phosphate ore, and topsoil treatments were also studied but only the ash and limestone treatments will be discussed in this paper.

## METHODS

The columns used in this study were constructed from smooth bore ABS plastic pipe, which were 24 cm diam. and varying lengths. Each column was packed with the same amount of refuse (36 kg) and the prescribed amount of amendment(s) for each treatment. Each treatment was replicated three times. The treatments discussed in this paper are summarized in Table 1. Additional detail on the construction of these columns may be found in Jackson<sup>2</sup> and Stewart<sup>3</sup>. These columns were run under unsaturated conditions and leached with 2.5 cm of a simulated rain<sup>4</sup> each week. Refuse used in this experiment was about 4% total sulfur. The Clinch River Fly Ash (CRF) is an alkaline ash with a pH of 11 and a Calcium Carbonate Equivalence (CCE) of about 10%. The Westvaco fly ash (WVF) was collected an ash landfill at the Westvaco paper mill in Covington, VA and had a pH of 8.5 and a CCE of 3%. Leachates were collected weekly and were analyzed for pH, EC, Fe, Mn, SO<sub>4</sub>, and B regularly. Other elements (Ca, Mg, K, Na, Cu, Zn, Al, Ni, As, and Se) were monitored on a less frequent basis. Leaching of these columns began in March of 1992.

Beginning in July of 1995 the columns were removed from their racks, laid horizontally on a greenhouse table, and cut open using a circular saw. The weekly dosing schedule was maintained until the columns were disassembled, and most were cut open three to five days after dosing. Two columns from each of the ash-blended treatments, unamended control, and 13% Lime treatments were dissected. The materials in the columns were examined for evidence of oxidation and weathering features. The material toward the center of the columns was sampled incrementally with depth, and 1:1 (v/v) soil:water pH was determined using a portable pH meter equipped with a combination electrode. The increments were 0, 7.5, 15, 22.5, 30, 45, 60, 75, 90, and 105 cm with depth. In addition, one sample was taken at the bottom of each column. The samples taken were stored in a refrigerator. Samples from five treatments (Refuse, 10% WVF, 33% WVF, 33% CRF, Lime) were taken under more strident conditions than the others. These

samples were cooled over ice as they were taken and stored in a refrigerator and then shipped on ice to the US Bureau of Mines Research Centers at Albany, OR and Salt Lake City, UT for analysis of biological activity and chemical characterization. The results of the chemical characterization were presented in a US Bureau of Mines file report<sup>5</sup>.

**Table 1. Descriptions of treatments and abbreviations used in the column studies.**

<u>Treatment</u>	<u>Code</u>	<u>Description</u>
Refuse Control	Refuse	36 kg refuse
33% Westvaco ash	33% WVF	16.1 kg Westvaco ash bulk blended with 36 kg refuse
20% Westvaco ash	20% WVF	7 kg Westvaco ash bulk blended with 36 kg refuse
10% Westvaco ash	10% WVF	3.2 kg Westvaco ash blended with 36 kg refuse
5% Westvaco ash	5% WVF	1.3 kg Westvaco ash blended with 36 kg refuse
33% Clinch River ash	33% CRF	18 kg Clinch River ash blended with 36 kg refuse
20% Clinch River ash	20% CRF	9 kg Clinch River ash blended with 36 kg refuse
13% ground limestone	Lime	5 kg of ground limestone blended with 36 kg refuse

## RESULTS AND DISCUSSION

The unamended refuse treatment acidified rapidly and produced acidic (pH 1.7) leachates with high peak dissolved metal levels ( $>15,000 \text{ mg l}^{-1} \text{ Fe}$ ;  $200 \text{ mg l}^{-1} \text{ Mn}$ ). Treatments blended with 33% ash produced alkaline (pH  $>8.4$ ) leachates with low metal levels ( $\text{Al} < 1.0 \text{ mg l}^{-1}$ ;  $\text{Cu} < 0.10 \text{ mg l}^{-1}$ ;  $\text{Fe} < 2.0 \text{ mg l}^{-1}$ ;  $\text{Mn} < 3.0 \text{ mg l}^{-1}$ ). Treatments containing less ash eventually acidified and ash bound metals (Mn and Cu) were stripped from the ash and eluted in quantities proportionate to the amount of ash in the blend as described by Stewart<sup>3</sup>. Overall, the inhibition of pyrite oxidation by high ash blends was attributed to alkalinity effects, chemisorption, decreased hydraulic conductivity, and decreased oxygen diffusion to pyritic surfaces. Ash alkalinity and refuse potential acidity must be balanced for environmental safety in this co-disposal environment.

Treatment effects were clearly observable in the column material. The Refuse (Control) treatment displayed a yellowish cast that coated all particles, particularly on coarse fragments, that was thought to be jarosite. The yellow material was quite sticky and hard to remove from the knife used for sampling. The surface 0 - 15 cm portion of the column was noted as a more oxidized zone with brighter colors of Munsell 2.5Y 8/6, 8/8, 7/6, and 7/8. The matrix color of the material in the column was 5Y 8/3 or an intermingling of 5Y 8/3 and a black surface. The pH of the material was 2.6 in the surface (0-2 cm) of the column and 2.1 at the bottom of the column (Figure 1). These pH values are slightly higher than the leachate pH values observed for this treatment. This difference may be due to the differences between the  $\text{O}_2$  concentration in the



The glass wool at the bottom of the 20% WVF treatment was coated with an iron precipitate. Two distinctly colored iron minerals were observed, one seemed to be an oxidized iron mineral with a Munsell color of 7.5 Y/R 5/8, the other was lighter in color (5Y 8/6) and was thought to be jarosite. The surface 23 cm was oxidized with an abundance of the 7.5 YR mineral, and had a pH < 3 (Figure 1). The bottom of the column was very wet. The material in the 33% WVF treatment was black in color. Only four oxidized bodies 6 mm in diameter were observed in the top 45 cm, and a lone oxidation feature was noticed at 60 cm. The surface pH was 7.1, but pH increased to 7.95 at 15 cm. The pH varied between 7 and 7.5 below 45 cm (Figure 1).

The color of the 33% CRF treatment was grey and similar to the CRF ash. Some oxidized bodies were visible but they were isolated throughout the diameter of the column and no trends were observed. The zone from 60 to 100 cm was noted as being compact, this may have been due to the pozzalonic nature of this ash. The material in that zone resembled concrete with black coarse fragments suspended in a grey matrix. The surface material was pH 8.7, and the material at 7.5 cm had a pH of 5.19 indicating some pyrite oxidation was taking place in material at the surface (Figure 1). The material from 38 to 100 cm had pH values in excess of 9.5. Oxidized spots were observed along the column wall in the 20% CRF treatment. The spots were brighter near the surface and duller toward the bottom of the column, although a few oxidized features were observed below 38 cm. The pH with depth profile of this material exhibited large swings, from 6.2 at the surface, to 3.8 at 7.5 cm, and back to 9.5 at 90 cm (Figure 1). Both CRF treatments were undergoing pyrite oxidation at the surface, and the acidity was apparently being neutralized by the alkalinity in the ash.

The glass beads at the surface of the Lime treatment were heavily iron stained. Many oxidized zones were observed in this material, particularly in areas of high coarse fragment content. Discrete limestone particles were observed near the bottom of the column. The surface pH of this blend was 8.1 and that value declined with depth to 7.24 (Figure 1).

It should be noted that nearly every column showed the most oxidative features near the surface, and 0-15cm was the most oxidized. This was particularly true if a network of coarse fragments was present to allow air penetration and result in areas of oxidation. The ash treatments, particularly the 20% and 33% blends contain large amounts of fines and few of these pockets of coarse fragments occurred. Under saturated conditions these zones would represent areas of preferential rapid flow. Under dry conditions, it is unlikely water would move into these zones. Connected to the atmosphere, these are zones of rapid oxidation and were common features in treatments which acidified. These zones would control the leachate chemistry and may explain the observed differences in leachate pH and solid pH. The leachate pH was controlled by the conditions in these flow zones, while solid material was mixed in from outside the zone for pH measurements.

Most columns showed some evidence of oxidation at the bottom of the column, from bright yellow iron minerals over the holes in the endcap, to a bright yellow/orange oxidation rind in the glass bead layer at the bottom of the column. These indicate that some oxygen was penetrating the funnels. The likely place for air leakage would be at the column funnel interface which we

attempted to seal with silicon sealer. We believe the total amount of oxygen flow was limited, however. Also oxygen flow into the material at the bottom of the column would be impeded by the nearly saturated conditions that occurred at the bottom of the columns.

A detailed examination of the column solids macroscopic and microscopic fabric was performed by the U.S. Bureau of Mines<sup>5</sup> and a summary of the some of the findings follows. Optical microscopy and SEM analyses confirmed that pyrite was oxidizing to form Fe-sulfates. The probable oxidation product identified was copiapite ( $\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_2 \cdot 20\text{H}_2\text{O}$ ), a ferrous-ferric sulfate that is a common oxidation product of pyrite<sup>6</sup>. Most of the oxidation taking place was found to be in direct association with pyrite grains. A lack of Fe-oxides proximal to the pyrite was noted. This was significant in that, if the pyrite were oxidizing to an oxide mineral (e. g. limonite or hematite) phase, it would be expected that solid phase would be found close to the pyrite. The lack of oxide coatings on the pyrite also indicated that the retardation of pyrite oxidation observed in the ash-treated columns was not due to the presence of coatings. Evangelou<sup>7</sup> has presented methodology for the microencapsulation of pyrite through the formation of stable Fe-oxide coatings on pyrite. These coatings inhibit  $\text{O}_2$  diffusion to the pyrite surface.

The pH with depth relations did indicate that pyrite oxidation was occurring at least near the surface in all treatments. Oxidation appears to be a process that starts near the surface and creates an acidified zone that then migrates down the column. Pyrite oxidation, probably by  $\text{O}_2$ , has taken place near the surface, producing acidity and  $\text{Fe}^{3+}$ . As more acidity was generated,  $\text{Fe}^{3+}$  was able to remain in solution and act as an oxidizer for more pyrite. Subsequently, as more acidity was produced, the low pH zone was able to extend deeper into the profile allowing  $\text{Fe}^{3+}$  to remain in solution. The acidic/oxidation front moves slowly down the column (Figure 1). The pH with depth profiles indicate that eventually the 33% ash treatment columns will most likely become acidified. Based on the observation of acidification in the 20% WVF columns, it is likely that this will be a slow process, occurring over several weeks or possibly years. Peak metal levels will likely be lower than those observed in the other ash treatments, however they will remain at an elevated level for a longer period of time. Higher total masses of Mn and Cu are expected to be leached from the 33% WVF treatments than from the other blended WVF treatments because the 33% WVF blend contains more of these metals.

A regression equation was plotted to examine the relationship between the amount of alkalinity added and the number of weeks needed for leachate pH to reach 2.5. Using the data from the Refuse (control), 5% WVF., 10% WVF, and 20% WVF treatments a regression equation of:

$$\text{Weeks to pH 2.5} = 0.32 + (0.676 \times (\text{g of alkalinity in mix})) \quad (1)$$

was generated. This equation had good linear fit, with an  $r^2$  of 0.95. The equation predicts that it would take 243 weeks (4.69 years) for the 33% WVF columns to produce leachate with a pH of 2.5. Applying this regression coefficient to the to the CRF treatments, the 33% CRF treatment and the 20% CRF treatment would take 298 weeks (5.74 years) and 598 weeks (11.5) years to produce pH 2.5 leachates respectively. This equation gives some perspective on the long-term stability of the ash treatment.

Through alkaline ash addition we have greatly slowed the oxidation of pyrite in the refuse but we have not stopped the process. These columns were under-loaded with respect to their alkalinity/potential acidity balance. The augmentation of the alkalinity in the ash with the addition of some ground agricultural limestone may be an important (and required) option. The blending of ash with potentially acidic refuse is therefore not recommended unless the alkalinity and potential acidity are at least balanced, if not manipulated slightly to the alkaline side. Refuse with low amounts of S (<1%) would obviously be better candidates for ash blending than the 4% S refuse used in this study.

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