

LABORATORY EVALUATION OF ASH MATERIALS AS ACID-DISTURBED LAND AMENDMENTS

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ABSTRACT

Fly ash (FA) and fluidized bed ash (FBA) solutions were evaluated as amendments for acid-disturbed lands, more specifically for treating acidic and metal contaminated soil. While titrating the ash materials with different volumes of acid, pH changes were monitored as a function of time and the acid volume added. The release of metals from the ash materials as a function of pH was also monitored. An acid mine drainage (AMD) solution was equilibrated with ash materials and clay and the metal removal from the solutions evaluated. Both FA and FBA produced solutions of high initial pH. However, FBA indicated a higher buffering capacity resulting in a steeper titration curve. The system pH strongly impacted metal release from the ash materials. The leaching experiment indicated a pattern whereby the basic metals (Ca and Na) were released at higher pH and the acidic metals (Fe and Cr) at lower pH. Limestone had almost double the buffer intensity but a lower initial pH than ash materials. Comparison of ash materials with two types of clay revealed that ash materials were better alternatives for treating acidic and high metal content wastes. Albeit both ash materials were able to treat AMD, their overdose could lead to trace metal accumulation with negative consequences to the environment.

KEY WORDS: fly ash, fluidized bed ash, acid mine drainage

INTRODUCTION

Fly ash (FA) is a residue left after coal has been burned; it is collected from gas stacks using specialized devices. Fly ash properties are diverse and depend on the nature of the coal and the combustion process. Alkalinity is an important FA characteristic. Some FA materials have pH values as low as 4 (EPA, 1986; de Groot *et al.*, 1987), while others have pH as high as 12.0 (Reed

et al., 1976) and 12.7 (de Groot *et al.*, 1987; van der Sloot, 2001). The subbituminous and lignite coal ashes produce alkaline solutions upon contact with water. Minerals such as calcite, amorphous silicates, hematite, quartz, mullite, metal oxides, and free carbon tend to exist along with alkaline FA (EPA, 1986). According to the Electric Power Research Institute (EPRI, 1988), the alkalinity depends on the calcium content

since this element is in the form of highly reactive CaO.

Fly ash is comprised largely of soluble calcium, which is associated with the lime fraction (Theis and Wirth, 1977). The pH measured for several 1:1 (H₂O:FA) suspensions generally shifts with time (EPRI, 1993). Initially, condensation of H₂SO₄ on the surface of the ash particles may lower the system pH. Later, a rapid rise in pH is observed which is caused by the neutralization of the H₂SO₄ via dissolution of alkali and alkaline earth oxides (e.g., CaO, MgO, K₂O, and Na₂O). These oxides are present in the samples in excess of the H₂SO₄ condensate. In such cases, the pH measurements should be conducted after a minimum of 24 hours. Other studies (EPRI, 1993; Daniels *et al.*, 1993) have reported changes in pH of FA suspensions even up to 21 days. The quantity of FA added to an aqueous solution significantly impacts the pH. For instance, decreasing the FA percentage from 1.0% to 0.03% only decreased the pH by 1 unit (Reed *et al.*, 1976). It seems that addition of a small quantity of FA can result in a significant increase of solution pH.

Fluidized bed ash (FBA) is produced during fluidized bed combustion. This process has been used recently to burn low quality coal and to remove sulfur dioxide from exhaust gases. The coal is mixed with limestone or dolomite dust during combustion. Fly ash removed via the air control equipment is mixed with the bottom ash; this blend of ash is called FBA (Canty, 1993). The amount of calcium in FBA is higher than in FA. Limited research has been conducted on FBA related to its alkalinity. FBA has been applied to agricultural and brine contaminated lands as a source of micronutrients and as a neutralizer for low pH soils (Stout *et al.*, 1988; Stout *et al.*, 1997; Pyle, 1996; Meo *et al.*, 1999).

Trace metal desorption from FA decreases with increasing pH (Theis and Wirth, 1977). Most trace metals show minimum release at pH values around 9. The desorption degree of trace metals from FA is determined by the solubilization extent of their oxide forms. In contrast, Zn is quite soluble in the resulting solutions, but it is poorly desorbed at neutral pH. Lead is relatively insoluble and yet it is released from FA to a greater extent than other more soluble species. Large amounts of Cl and SO₄²⁻ are typically released from FA, which could potentially pro-

duce soluble inorganic complexes (Theis and Wirth, 1977). Trace metals bonded with the silica present on the ash surface can only be released through the action of long-term weathering. Iron oxide controls sorbed trace metals more than aluminum oxide. Manganese oxide has a greater sorptive capacity than iron oxide, but it is present in comparatively small amounts. Each trace metal is associated with a certain oxide. In order to prevent the release of trace metals, the dissolution of iron and manganese should be controlled (Theis and Wirth, 1977).

Leaching alone generally desorbs trace metal amounts from FA. To increase the effectiveness of leaching, the use of higher solvent volumes, higher temperatures, longer contact times and lower solid-to-liquid ratios are required. However, it is not probable that the above conditions will occur in natural systems (Burnet, 1987). Baba (2000) observed lower leaching when using water alone compared to acid addition. Sulfur and Ca are the major soluble elements in pore waters and leachate. Most of the solubility-controlling solids are SO₄²⁻ and OH⁻ bearing compounds (Fruchter *et al.*, 1990). Zevenbergen *et al.* (1999) have observed that FA after years of application to fields is converted to fertile soil.

Preliminary investigation has shown that FA is capable of neutralizing acid mine drainage (AMD) of pH 5 and adsorbing the metals present (Atalay *et al.*, 1992). Twenty grams FA per liter of AMD resulted in lower turbidity solutions compared to other FA:AMD ratios. Fly ash has also been used in several sorption studies involving cations; many of them reported removal of cations. The only cation that FA proved unable to adsorb efficiently was Hg (Gangoli *et al.*, 1975). Moreover, sorption of metal ions on the FA surface is substantially reduced when the pH of the final solution is in the acid range (Gangoli *et al.*, 1975). For lead, the percentage sorption on FA increases in the pH range of 3 to 5 (Mathur and Rupainwar, 1988). The removal of Cd by sorption on FA increases with increased pH values from 2 to 8, and is maximum between 7 and 8 (Viraraghavan and Rao, 1991). For Zn, the maximum removal is noted at pH 7.5 (Singh *et al.*, 1991). Several authors (Mathur and Rupainwar, 1988; Sen and De, 1987; Panday *et al.*, 1985) have reported pH values where maximum sorption on FA occurred and the oxides that were responsible

for the sorption of certain ions. Sorption is observed to decrease for FA at very high pH values where the cations are involved in the formation of soluble OH^- complexes (Yadava *et al.*, 1987). Ricou *et al.* (1999) have used FA and lime for Cu, Zn, and Pb sorption, whereas Konstantinou and Albanis (2000) have observed herbicide bonding in FA-soil mixtures.

The objectives of this study are to: (a) evaluate the neutralization capacity of the ash materials, (b) study the metal release from these ash materials with pH shift, (c) document the metal removal from AMD samples with the addition of ash materials, and (d) compare the ash material properties with those of limestone and 2 clay materials.

Previous studies on ash properties have not utilized equilibrium conditions. In this study, efficiency of the ash material was examined in systems that had reached equilibrium. This is significant since ash materials that are used for treatment or disposal are generally accompanied by a lengthy contact time (equilibration).

MATERIALS AND METHODS

FA samples were shipped in plastic containers from the Oklahoma Gas and Electric Plant in Muskogee, OK. FBA samples were generated at the Shady Point Power Plant in Latimer, OK and were shipped in plastic containers by Brazil Creek Minerals, Inc., Fort Smith, AR. The acid mine drainage sample was collected from the abandoned mine "Red Oak" near Latimer, OK. The limestone used for comparison with fly ash was purchased from Fisher Scientific Company, Pittsburgh, PA. The bentonite clay was purchased from Central Bag Company, Kansas City, MO. The kaolinite clay was purchased from The Feldspar Corporation, Edgar, FL.

Two H_2SO_4 solutions were used as titrants, one at $\text{pH}=1$ and the other at $\text{pH}=4$. A series of 10 g samples of ash and limestone (CaCO_3) were weighed and placed separately in high-density polyethylene flasks. For the first batch of samples, different amounts of prepared acid solution, ranging from 20 to 1900 ml, were added in each flask. The flasks were tightly capped, placed on a shaker and shaken at constant speed. The pH was measured using an Orion pH-meter, model 470A. For the first 3 days, pH was measured every day; later, the measurements were taken once every 3

days until 30 days. When the pH had stabilized, samples were considered equilibrated. For the second batch, 100 ml of AMD sample was added to flasks containing 2 g of ash or clay materials. The AMD samples were either used at their natural pH strength or acidified to $\text{pH}=1$. The flasks were shaken for 2 days and pH measurements were recorded.

In both batches, the samples were filtered with Whatman No. 2 filter paper. The solutions were digested with nitric acid using a Tecator Digestion Apparatus. Each digested sample was diluted to 100 ml with double deionized water containing 2 g l^{-1} lanthanum oxide. The diluted samples were either stored in high-density polyethylene bottles or analyzed immediately. Digested samples were analyzed for metals (Fe, Mn, Zn, Mg, Al, Ca, Cd, Na, Cr, Cu and Ni) using a Buck Scientific Atomic Absorption Spectrophotometer VGP System Model 210. Calibration metal standards (1000 mg l^{-1}) were purchased from Fisher Scientific. Nitrous oxide/acetylene flame was used to measure Al concentrations; all other metals were analyzed with air/acetylene flame (Welz, 1985). The raw ash materials and AMD samples were digested and analyzed in a similar fashion.

RESULTS AND DISCUSSION

Table 1 presents the metal concentrations in ash materials and AMD samples. It is apparent that both ashes contain high levels of Ca, which came from the coal combustion process. In particular, the Ca content of FBA is higher than FA because the fluidized bed combustion process operates at a lower temperature and utilizes more lime than the conventional process to strip out the sulfur from the coal. The concentration of Al, Fe, and Mg are so high in the ashes that their use could prove environmentally prohibitive. These results are consistent with data provided by Muskogee generation station for FA and previous analyses (Canty, 1993) for FBA. These elements can produce acidity upon oxidation and accumulate to toxic levels.

Neutralization Capacity of Ash Materials

The ash materials used in this study were considered alkaline, and titration curves were generated for their acid neutralization. Three parameters were monitored: (a) pH, (b) amount of acid added, and (c) time. Ash buffer intensity charac-

Table 1. pH and metal concentrations in ash materials and AMD sample

Sample	FA	FBA	AMD
pH	11.9	12.4	4.5
Metals	mg kg ⁻¹		mg l ⁻¹
Mn	170	510	6.8
Fe	35,000	55,000	190
Zn	180	250	3.8
Al	52,000	13,000	8
Mg	40,000	18,000	56
Ca	210,000	300,000	75
Na	7,500	1,000	N/A
K	2,900	3,300	4.1
Cu	2,200	35	N/A
Cr	65	50	N/A
Ni	110	70	N/A
Pb	68	85	N/A
Cd	<2	<2	N/A
Ag	<30	<30	N/A

FA: Fly ash; FBA: Fluidized bed ash; AMD: Acid mine drainage; N/A: not analyzed

terizes the neutralization capacity of the ash. In this case, buffer intensity is defined as the number of moles of strong acid required to change the pH of the solution by 1 pH unit (Benefield *et al.*, 1982), and expressed by the following equation:

$$\text{Buffer Intensity} = dC \, dpH^{-1}$$

where, dC = differential quantity of strong acid added to the solution.

dpH = differential change in pH due to the addition of a strong acid.

High buffer intensity means strong resistance to pH change, which results in flat titration curves. The end point is another characteristic that can be determined from the titration curve. The end point is where the alkali material has been neutralized and the solution starts to become acidic.

The amount of acid needed to neutralize a given amount of ash material provides useful information for the utilization of this material in remediation of acid impacted environments. In order to calculate the end point of the titrations and the Calcium Carbonate Equivalence (CCE), the method proposed by Benefield *et al.* (1982) was employed. This method involves calculation of the second derivative of the pH versus volume added curve, as well as conversion of the volume of acid added to equivalent calcium carbonate.

Figure 1 presents the titration curves of FA, FBA, and CaCO_3 with H_2SO_4 solution of pH=1. The stepwise titration curves observed for each component is indicative of its buffering behavior. For instance, FA exhibits several steps before it reaches the end point whereas, FBA demonstrates 2 flat titration steps, and the curve is very steep at the point of neutralization. For FA and FBA, the

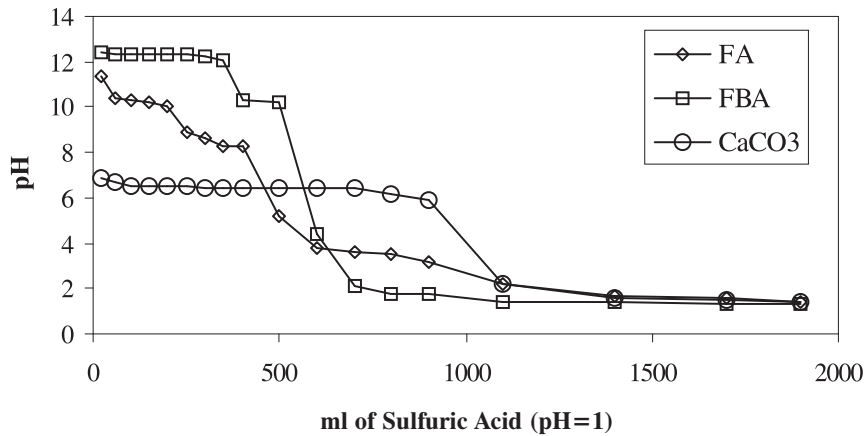


Figure 1. Titration curves for 10 g of ash materials and limestone against H_2SO_4 , pH=1 (FA: Fly ash; FBA: Fluidized bed ash).

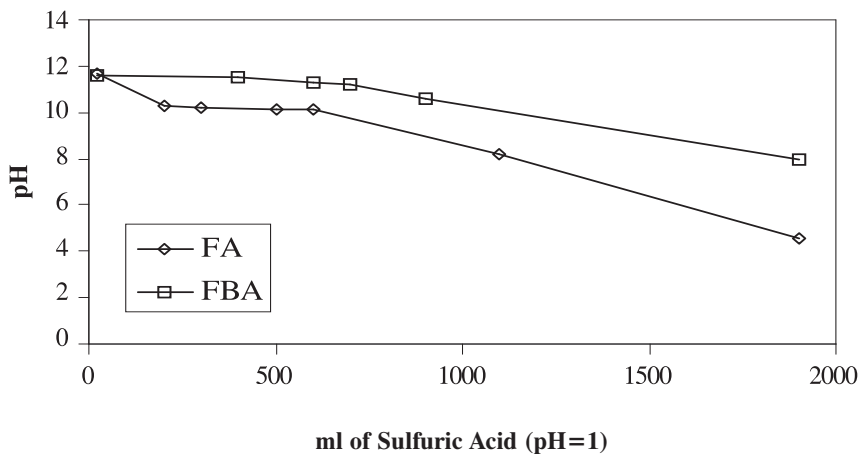


Figure 2. Titration curves for 10 g of ash materials and limestone against H_2SO_4 , pH=4 (FA: Fly ash; FBA: Fluidized bed ash).

two pH values with high buffer intensity were 10.5 and 8.5 and 12.5 and 9.8, respectively. The CCE values calculated for FA and FBA were 45% and 50%, respectively. The greatest buffering capacity was obtained when pure $CaCO_3$ was used as a source of alkalinity (CCE=100%). The higher buffer intensity was observed at pH 6.5.

Figure 2 presents the titration curves for FA and FBA against H_2SO_4 solution of pH=4. Dramatic changes in the titration curve patterns are apparent. Both ashes showed similar buffering potential when the acid-load was low. In this case either ash material can be used to treat the AMD. However, FBA shows greater buffering with

increased addition of the diprotic acid. After the addition of almost 2 liters of H_2SO_4 of pH=4, the pH in the FBA solution had only dropped from 12 to 9 indicating the strong buffering capacity of the ash. For FA and FBA, the pH values with higher buffer intensity were 10.5 and 11.5, respectively. Comparing the two sulfuric acid solutions (Figures 1 and 2), it is apparent that the solution with pH=1 causes more release of neutralizing material from the ash than the solution with pH=4. It appears that both ashes have a certain amount of buffering capacity, which was effective in neutralizing low acidity conditions. Similar magnitude results were observed for a milder acid

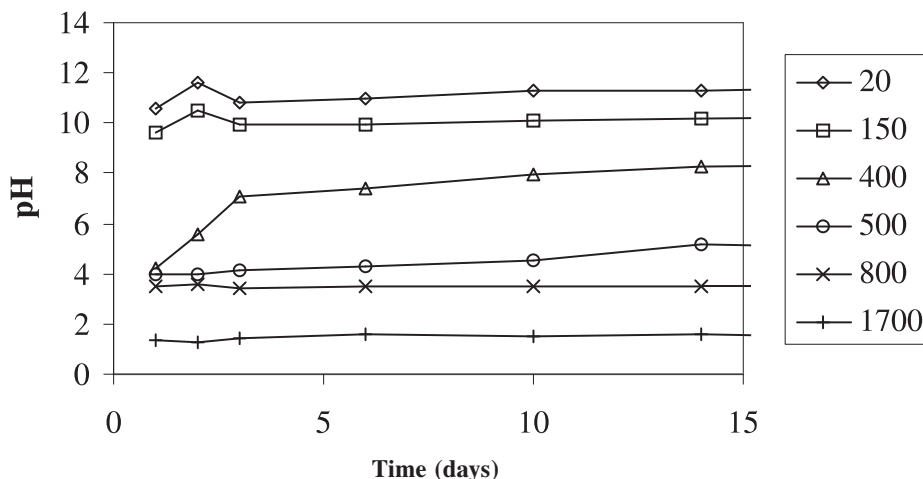


Figure 3. pH with time for 10 g of fly ash titrated with different volumes of H_2SO_4 ($\text{pH}=1$). Numbers in legend represent ml of acid added.

titration ($0.02 \text{ N H}_2\text{SO}_4$) under anoxic conditions for these materials (Canty, 2001). For FA and FBA, pH values of 4.3 occurred at 175 and 450 ml of acid g^{-1} of ash, respectively. Similar titrations with nitric acid (of $\text{pH}=2$) required 800 ml per 10 g of FA and 1100 ml per 10 g of FBA to reach $\text{pH}=7$ (Karapanagioti, 1995). In a field study 0.7 g of FBA l^{-1} of acid mine drainage of $\text{pH}=4.4$ were used to bring the $\text{pH}=6.3$ (Meo *et al.*, 1999). It is important to note that the volume of acid per mass of ash depends both on calcium present in the ash material (van der Sloot, 2001) and the strength of the titrating acid.

In cases where the titrant was H_2SO_4 of $\text{pH}=1$ and the pH was raised above 8.5, FBA showed higher buffer intensity than FA. Use of CaCO_3 provided twice the buffering intensity of any of the ashes. When H_2SO_4 solution was diluted to $\text{pH}=4$, FA was a better buffer at pH values above 10.5.

The contribution of contact time towards pH stabilization (buffering) was studied in detail using sulfuric acid. Figure 3 presents the variation of pH over time for FA equilibration using different quantities of acid. The data points at the beginning of each titration curve reflect the inherent variability in the source of alkalinity in fly ash. The reason for this variation is not clear, but could be caused by interactions between the various cations and anions, which are released

from fly ash during the initial reaction with the added acid. This is in agreement with results obtained in other studies (Theis and Wirth, 1977). After neutralization (volume of acid added >500 ml), the titration curves reached their equilibrium value on the first day, as indicated by the long plateau region. When the amount of acid added increased from 500 ml to 1700 ml, the FA was overwhelmed and its buffering capacity was exhausted. As a result, the pH of the solution remained below 4.0. This observation agrees with those made by other investigators (EPRI, 1993). The highest shift in pH observed was 4 units for the FA sample titrated against 400 ml of sulfuric acid. Field studies using FBA with acid mine drainage showed that the solution pH was raised to 12.2 in 15 hours after FBA addition and then, decreased to 6.3 after 1 year (Canty and Everett, 1999; Meo *et al.*, 1999). This is not in agreement with the current observations, but the discrepancy can be attributed to field conditions, which could lead to incomplete mixing of ash and AMD.

From the results presented previously it may be inferred that the contact time between the FA and the acid is not critical for systems with high acidity. However, for systems with low acidity, contact time and quantity of buffering material could be important. Given sufficient equilibration

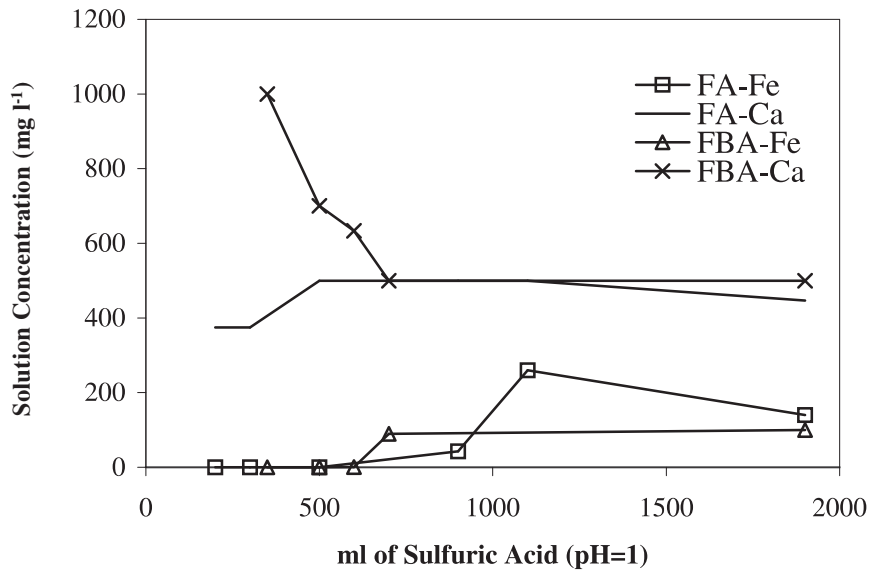


Figure 4. Iron and Ca released from ash materials after the addition of different volumes of H_2SO_4 , pH=1 (FA: Fly ash; FBA: Fluidized bed ash).

time, more alkalinity might be released to neutralize the acidity present in the solution.

Metal Release from Ash Materials

An experiment was conducted to evaluate the impact of gradually decreasing pH on the type and quantity of metals and their potential release from ash materials. It was observed that each metal had specific pattern of leaching from ash relative to pH. As the pH decreases, the order of metals released observed in the current study was as follows (data not shown):

Ca - Na - Ni - Mg - Pb - Mn - Cu - Zn - Al - Fe - Cr	(most released at high pH)	(most released at low pH)
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Ca and Na are easily released into solution at high pH, whereas Fe and Cr required very acidic conditions for their release. Higher concentrations of Ni, Cu, Cr and Fe were released from FA. The FBA released high concentrations of Mg and Ca due to higher solution pH. Table 2 presents the maximum amount of metals released and those released at pH 7 per kg of ash.

Figure 4 presents Fe release from FA and FBA titrated with H_2SO_4 of pH=1. The highest amount of Fe released occurred after the addition of 1900 ml of acid solution to 10 g of FA whereas the highest concentrations of Fe in solution were

found after the addition of 1100 ml sulfuric acid. Iron began to leach from FA after 500 ml of acid had been added and the pH approached 4.0. Almost no Fe was released from the solution until the point of maximum release (pH=4) was reached.

Figure 4 also shows Ca release from FA and FBA using the same acidic environment as for Fe. Calcium started to be released as soon as titration began which is in agreement with the previous observations relative to the neutralization capacity of the ash material.

The solubility of metals bonded onto ashes and other alkaline materials (Fruchter *et al.*, 1990) is controlled by either sulfate or hydroxide compounds. Qualitatively, for metals such as Ca whose solubility is controlled by sulfate compounds, dissolution should not be an issue for systems where sulfuric acid is added. High concentrations of sulfate anions are introduced in the solution in the form of sulfuric acid and should lead to precipitation of the compounds. The presence of Ca and other metals in solution is explained by other mechanisms, such as desorption or ion exchange. The occurrence of Al is attributed to dissolution since its solubility is dependent on the availability of hydroxide compound. While Fe solubility is also dependent on the hydroxide availability, its concentration was

Table 2. Concentrations of metals released from 10 g of ash materials while titrated against H₂SO₄ (pH=1).

Metals	Maximum Amount* Released in Solutions from the Ash Material		Amount* Released at pH=7	
	FA	FBA	FA	FBA
	(mg kg of ash ⁻¹)			
Ca	85000 ¹	95000 ¹	13000	16000
Na	5700 ²	1000 ²	1500	230
Mg	40000 ²	16000 ²	20000	3700
Pb	33 ¹	57 ¹	4.8	6.5
Mn	150 ¹	480 ¹	90	0
Cu	180 ¹	35 ¹	7.5	0
Zn	180 ¹	25 ¹	14	0
Al	70000 ¹	5000 ¹	0	0
Fe	28000 ¹	20000 ¹	0	18
Cr	19 ¹	19 ¹	0	0

FA: Fly ash; FBA: Fluidized bed ash

¹at pH region 1-2

²at pH region 3-4

* Note these values are amounts released from fly ash and not concentrations in solution. They are directly comparable with values in Table 1.

above that expected when dissolution was the only mechanism of action. From these observations, it appears that desorption is the predominant mechanism for the release of most metals from the ash materials.

Metal Removal from AMD Using Ash Materials and Clay

The treatment of ash with the AMD sample produced predictable results. Table 3 presents the percent removal of metals from AMD. In Case I an AMD sample which was further acidified to meet the worst case scenario (i.e., pH=1) was used whereas the AMD sample used in Case II was used as obtained from the field.

Both ash samples were able to remove effectively metals present in both acidified and natural AMD samples. Iron and Mn were totally removed from both solutions, whereas Zn was partially removed.

The release of alkaline earth metals (Ca and Mg) from ash was also measured. Interestingly, Mg was not released from fly ash using the natural AMD sample, but it was released in high amounts when the acidified AMD was used (Table 3). In both situations, FBA showed the same pH and metal removal capacity. However, when the pH of the AMD was in the acid range (pH<4), the Ca released was low. The release of Al in Case II was not consistent with the results obtained in the previous section. Since the pH value for FBA was the same in both cases, a higher release of Al in Case II was thought to be due to human error (such as improper data logging, etc.).

In order to compare the ash sorption characteristics to materials of similar sorptive behavior, two clays (kaolinite and sodium (Na)-bentonite) were evaluated. Kaolinite was selected for having low specific surface area and cation exchange capaci-

Table 3. Percent metals removed for (2g) materials titrated with 100 ml of AMD. Percent values correspond to the initial AMD solution metal concentrations presented at the 2nd line of each Case.

Case I: Acidified AMD, pH = 1; Fe: 190 mg l⁻¹; Mn: 7 mg l⁻¹; Zn: 4.2 mg l⁻¹; Ca: 70 mg l⁻¹; Mg: 57 mg l⁻¹; Al: 8 mg l⁻¹							
Material	Final pH	Fe	Mn	Zn	Ca	Mg	Al
FA	5.7	96%	71%	9.5%	-1600%	-130%	63%
FBA	12.2	100%	99%	55%	-3100%	100%	0%
Kao	1.3	-8.4%	14%	24%	-230%	2.6%	75%
NaB	2.9	37%	-95%	26%	-1000%	-35%	-160%

Case II: Natural AMD, pH = 4.5; Fe: 180 mg l⁻¹; Mn: 6.5 mg l⁻¹; Zn: 2.5 mg l⁻¹; Ca: 80 mg l⁻¹; Mg: 55 mg l⁻¹; Al: 8 mg l⁻¹							
Material	Final pH	Fe	Mn	Zn	Ca	Mg	Al
FA	11.1	100%	100%	52%	-440%	100%	-400%
FBA	12.3	100%	99%	40%	-2000%	100%	-100%
Kao	2.4	82%	5.5%	-40%	-200%	5.5%	0%
NaB	6.4	70%	74%	-220%	-210%	64%	-62%

AMD: Acid mine drainage

FA: Fly ash

FBA: Fluidized bed ash

Kao: Kaolinite

NaB: Sodium-Bentonite

Negative values indicate release of metals compared to initial concentrations.

ty (Brady, 1974). Na-bentonite is considered a high cation exchange capacity material because the sodium ion present on the active sites is easily displaced by other cations of higher valency and its high specific surface area (Lewis, 1993).

When kaolinite was titrated with the acidified AMD (pH=1), Mn, Zn, Mg and Al were adsorbed (see Table 3). However, when it was treated with the natural AMD sample, mostly Fe (82%) and some Mn (5.5%) and Mg (5.5%) were adsorbed. During titration with the acidified AMD sample, some Fe (37%) and Zn (26%) were adsorbed by Na-bentonite (see Table 3). However, when the titration was performed using natural AMD, some Fe (70%), Mn (74%), and

Mg (64%) were adsorbed by Na-bentonite. The Na-bentonite solution resulted in a higher pH (pH=6.4) when used with natural AMD (Case II) than did the FA solution (pH=5.7) using acidified AMD (Case I). However, the percent metal sorption of Fe, Zn and Al for Na-bentonite was lower as compared with FA (for data see Table 3). In general, both clay materials demonstrated lower sorption behavior than the ash materials.

CONCLUSIONS

The ash products used in this study proved to be excellent buffering materials and could have great potential in improving the quality of acidic water. FBA showed a stronger buffering capacity than

FA by releasing large quantities of alkaline material to the acidic medium. Consequently FBA could neutralize larger volume of AMD than FA when equal amounts of the ash materials are added. Calcium and Na were the metals most released at high pH, whereas Al, Fe and Cr were released at lower pH. Ash materials were able to neutralize AMD samples and remove metals from solution. Either FA or FBA could be recommended for AMD treatment.

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