

NEUTRALIZATION AND RELEASE OF METALS PROPERTIES OF FLY ASH¹

by

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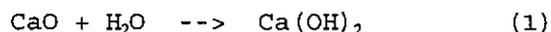
Abstract. The neutralization property and the release of metals for three types of coal combustion ash were evaluated. Fly ash (FA), fluidized bed ash (FBA), and hydrated fly ash (HFA) were assessed for their variation in physical, chemical and mineralogical properties. Acidic solutions of different pH were used to equilibrate the ash in conservative and nonconservative systems. Release studies were conducted for the following metals: iron, manganese, zinc, magnesium, aluminum, calcium, cadmium, sodium, chromium, copper, and nickel. Data indicated that pH was a very significant factor for the release of metals from the fly ash surface. At high pH iron was the least released cation from fly ash, whereas calcium was the most desorbed cation. Comparison of the three ashes indicated that FA and FBA were excellent buffering materials. However in the case of FBA, there seemed to be a critical pH at which a drop in the proton titration curve was apparent, and large amounts of metals were released into solution. On the other hand, HFA showed lower buffering intensity compared to the other two fly ashes. Changes in pH with time were also studied since time had an impact on the titration curve at the equivalence point. Although pH was increasing with time, it had no impact on the titration curve after neutralization had occurred. Comparison of fly ash with limestone for neutralization properties revealed that fly ash had less buffer intensity than limestone, but it gave solutions a higher initial pH.

Additional Key Words: Neutralization, Desorption, Metals, Fly ash.

Introduction

Fly ash is a residue left after coal has been burned; it is collected from gas stacks using specialized devices. The properties of fly ash are diverse depending on the nature of the coal and the combustion process. One of several characteristics of most fly ashes is their alkalinity. Some fly ashes have pH as low as 4.5 while others have pH as high as 12.0. The subbituminous and lignite coal ashes produce alkaline solutions upon contact with water. Alkaline fly ash is associated with the existence of minerals such as calcite, amorphous

silicates, hematite, quartz, mullite, metal oxides, and free carbon (EPA, 1986). According to EPRI (1988) the alkalinity depends on the calcium content since this element is in the form of highly reactive CaO. The contribution of calcium to alkalinity can be described by the following equation:



Theis and Wirth (1977) have mentioned that soluble calcium, which is associated with the lime fraction, represents the basic component of fly ash. The pH measured for several 1:1 H₂O:fly ash suspensions generally

¹Paper presented at the 1996 Annual Meeting of the American Society for Surface Mining and Reclamation, Knoxville, Tennessee, May, 1996.

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shifted with time (EPRI, 1993). Initially, the pH may be lowered by a condensate of sulfuric acid on the surface of the ash particles. Later a rapid rise in pH is observed which is caused by the neutralization of the sulfuric acid 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 sulfuric acid condensate. In such cases, the pH measurements should be done after a minimum of 24 hours. Other studies (EPRI, 1993) have reported changes in pH of fly ash suspensions up to 21 days. There seems to be a correlation between ash pH and the amount of sulfate in the saturated paste extract (Daniels et al., 1993); the lower the amount of sulfate present, the higher is the pH of the fly ash slurry. The quantity of fly ash added to an aqueous solution has significant impact on pH. For instance, Reed et al., (1976) reported that decreasing the percentage of fly ash from 1.00 % to 0.03 % only decreased the pH by one unit. That means the addition of a small quantity of fly ash can result to a significant increase in the solution pH.

The desorption of trace metals from fly ash surfaces in aqueous solutions follows a predictable pattern of decreasing release with increasing pH (Theis and Wirth, 1977). Most trace metals show minimum release at pH values around 9. The degree of desorption of trace metals from the fly ash surface is determined by the extent of solubilization of the oxides they are attached to. On the other hand, zinc is quite soluble in the resulting solutions, but it is very poorly desorbed in the neutral pH range. Lead is relatively insoluble and yet it is released from fly ash to a greater extent than other more soluble species. Large amounts of chloride and sulfate are typically released from fly ash, and it is probable that soluble inorganic complexes are formed (Theis and Wirth, 1977). Trace metals bonded with the surface silica will be released only through the action of long-term weathering processes. Iron oxide was found to control sorbed trace metals more than aluminum oxide. Manganese oxide was found to have a greater sorptive capacity than iron oxide, but

it is present in comparatively very small amounts. On the average, Theis and Wirth (1977) have associated each trace metal with a certain oxide. From their observations, it is apparent that in order to prevent the release of trace metals, the dissolution of iron and manganese should be controlled. Desorption of trace metals from fly ash by leaching alone is generally low. To increase the effectiveness of leaching, the use of higher solvent volume, higher temperature, longer contact time and lower solid-to-liquid ratios are required. However, it is not probable that the above conditions will occur in natural systems (Burnet, 1987). Fruchter et al. (1990) studied the effect of solubility on metal release from fly ash samples. Calcium and sulfur were found to be the major soluble elements in pore waters and leachate. Most of the solubility controlling solids were found to be (in the referred article) sulfate and hydroxide compounds.

Materials and Methods

Materials

Both fly ash (FA) and hydrated fly ash (HFA) samples were shipped in plastic containers from Oklahoma Gas and Electric Plant, Muskogee, OK. Fluidized bed ash (FBA) samples were generated at the Shady Point Power Plant, Latimer County, OK and shipped to us in plastic containers by Brazil Creek Minerals, Inc., Fort Smith, AR. The limestone that was used for a comparison study with fly ash was purchased from Fisher Scientific Company, Pittsburgh, PA.

Sample Preparation

Two sulfuric acid solutions were prepared, one at pH=1 and another at pH=4. These solutions were used as titrants along with double deionized water (DDI water), which had been purified with a triple-bed filter consisting of cation, anion, and organic exchangers. A series of 10 g samples of fly ash and limestone (CaCO₃) were weighed and placed separately in high density polyethylene flasks. For the first batch of samples, different amounts of prepared acid solutions, ranging from

20 to 1900 ml, were added in each flask. The flasks were placed on a shaker and shaken at constant speed for variable time periods. Each flask was tightly capped. In the end, the pH was measured using an Orion pH meter, model 470A. For the first three days sample pH was measured every day; later, the measurements were taken once in three days. When the pH had stabilized, samples were assumed to have reached equilibrium. This method simulates conservative conditions which can be found in systems where the water enters the system and stays for a long period of time (Corbitt, 1990).

For the second batch of samples, a continuous leaching method was employed. In this case, 200 ml of prepared acid solutions or double deionized water were added in the flasks containing 10 g fly ash samples. The flasks were shaken for two days and pH measurements were taken as described above. This method simulates nonconservative conditions which can be found in systems where the water enters but stays only for a short period of time (Corbitt, 1990). The samples were then filtered and fresh acid solutions added to the remaining fly ash samples. This procedure was repeated until the pH of the fly ash solution was below 2 or 5 depending on the initial pH of the sulfuric acid solution. 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 DDI water containing 0.2 % lanthanum oxide. The diluted samples were stored in high-density polyethylene bottles until they were analyzed for metals.

Sample Analysis

Digested samples were analyzed for metals using Buck Scientific Atomic Absorption Spectrophotometer VGP System Model 210. High concentration standard metals (1000 mg/l) were purchased from Fisher Scientific and used to prepare diluted standards for calibration. Nitrous oxide/acetylene flame was used to measure aluminum concentration. All other metals were analyzed with

air/acetylene flame as suggested by Welz (1985).

Results and Discussion

Neutralization Capacity of Fly Ash

The fly ash used in this study was considered alkaline, and titration curves were generated for its neutralization with mineral acids. Three parameters were monitored that evaluated the neutralization capacity of fly ash: pH, amount of acid added, and time. The results were separated into two groups based on conservative or nonconservative control conditions as described in the materials and method section.

Buffer intensity is one characteristic of fly ash which defines its neutralization capacity. In this case, buffer intensity is defined as the number of moles of strong acid required to change the pH of the solution by one pH unit (Benfield et al., 1982). Buffer intensity is best represented by a differential such that:

$$\text{Buffer Intensity} = dC / dpH \quad (2)$$

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

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

High buffer intensity means strong resistance to pH change. The pH value where the solution presents high intensity is where the titration curve is flat, and tends to remain in that range even after continued addition of the titrant. The end point is another characteristic that can be determined from titration curves. The end point may be defined as the point where the amount of alkali material, for instance has been neutralized by the added acid and the solution starts to become acidic. The amount of acid needed to neutralize a given amount of fly ash provides useful information for the utilization of fly ash 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

Table 1: Buffer characteristics of three fly ashes under a conservative (contained) and nonconservative (free flow) conditions. (CCE: calcium carbonate equivalence).

Titrator	Type of fly ash or CaCO ₃	Conservative system		Nonconservative system	
		pH with higher buffer intensity	ml acid to reach end point (%CCE)	pH with higher buffer intensity	ml acid to reach end point (%CCE)
0.1 M H ₂ SO ₄	FA	10.5, 8.5	450 (45)	4	250 (25)
	FBA	12.5, 9.8	500 (50)	12.5, 12	550 (55)
	HFA	10.5	500 (50)	4	550 (55)
	CaCO ₃	6.5	1000 (100)	-	-
10 ⁻⁴ M H ₂ SO ₄	FA	10.5	1300 (0.13)	5.5	800 (0.08)
	FBA	11.5	850 (0.08)	12.2	1100 (0.11)
	HFA	10.5	550 (0.05)	6.5	550 (0.05)
double deionized water	FA	-	-	12, 10	-
	FBA	-	-	12, 10	-
	HFA	-	-	12, 10	-

Benefield et al. (1982) was employed. This method involves calculation of the second derivative of the pH versus the volume added, as well as conversion of the volume of acid added to equivalence of calcium carbonate.

Table 1 presents the titration characteristics of fly ash under conservative and nonconservative conditions. For the conservative conditions the systems were allowed an average of seven days in order to reach equilibrium, whereas for the nonconservative conditions the solutions were repeatedly renewed every two days.

When the titrator was 0.1 M sulfuric acid, and the pH was raised to > 8.5, FBA showed higher buffer intensity than either FA or HFA. At low pH (i.e. pH = 4) and nonconservative conditions, FA and HFA maintained higher pH values than FBA. Use of CaCO₃ under conservative conditions provided twice the buffering

intensity of any of the fly ashes. As the concentration of H₂SO₄ was diluted to 10⁻⁴ M, FA was a better buffer at pH > 10.5 in the conservative systems. Under nonconservative condition the 10⁻⁴ M sulfuric acid reduced the pH of FA to

5.5 and HFA to 6.5 where as the pH of FBA remained 12.2.

The high volume of 10⁻⁴ M sulfuric acid (1100 ml) needed to reach the equivalence point with FBA further indicates that FBA is a better buffer than either FA or HFA.

Figure 1 presents a comparison of the buffering potentials of FA, FBA, HFA, and calcium carbonate when titrated against sulfuric acid of pH=1.

The stepwise titration curves observed for each component is indicative of its buffering behavior. For instance, FA demonstrates several

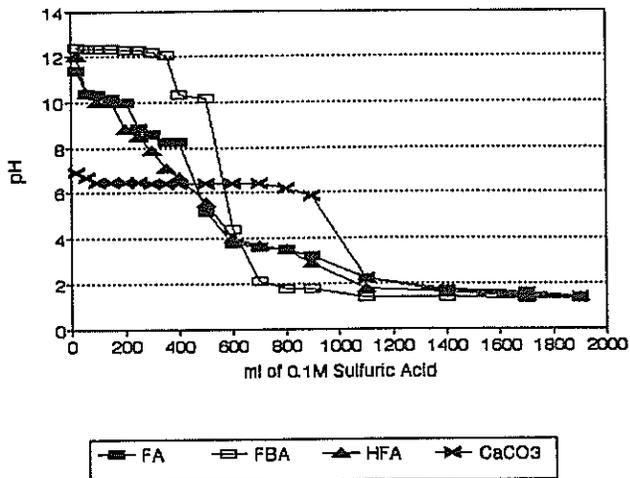
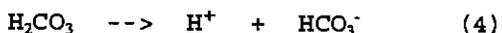


Figure 1 Titration curves for 10 g of FA, FBA, and CaCO₃ against 0.1M H₂SO₄ at pH=1 in a conservative system with an average equilibration time of 7 days.

steps before it reaches the end point whereas FBA demonstrates two flat titration steps, and the curve is very steep at the point of neutralization. HFA demonstrates a smooth and continuous neutralization curve with very short titration steps, almost linearly decreasing in each buffering potential. The greatest buffering was obtained when pure CaCO₃ was used as a source of alkalinity. In this particular study, the buffering power of CaCO₃ is directly related to its equilibrium reaction with added sulfuric acid:



In reaction (3) gypsum is formed, which traps all of the SO₄²⁻ as CaSO₄ and all the hydrogen ions react with the CO₃²⁻ species to form H₂CO₃ in this manner all of the acid is neutralized effectively. Carbonic acid is a weak acid with pK_{a1}=4.2x10⁻⁷ for reaction (4) and pK_{a2}=4.8x10⁻¹¹ for reaction (5). The resulting carbonate-bicarbonate system was able to buffer the acidity much longer (until 1000 ml of the acid was added) than any of the fly ashes. However, once the buffer was exhausted with continuous

additions of the acid, the pH quickly dropped from approximately 6.5 to 2.0. Limestone has a Calcium Carbonate Equivalence (CCE) of 100%, whereas fly ash has a CCE of about 50%.

Figure 2 presents the titration curves for FA, FBA, and HFA titrated with sulfuric acid of pH=4. Dramatic changes in the titration curve patterns are apparent. All three ashes showed similar buffering potential when the acid load was low. In terms of utilizing these ashes for treating acid mine drainage any of

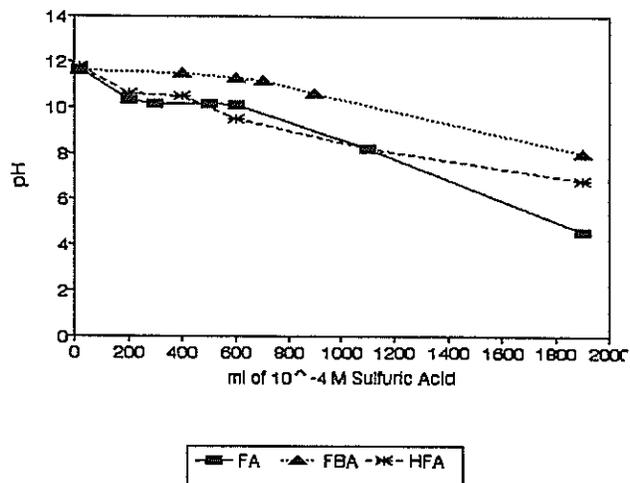


Figure 2 Titration curve for 10 g of FA, FBA, and HFA against 10⁻⁴M H₂SO₄ at pH=4 in a conservative system with an average of equilibration time of 7 days.

them could be used. However, FBA shows greater buffering with increased addition of the diprotic acid. After the addition of almost 2 liters of 10⁻⁴ M sulfuric acid, the pH in the initial 10 g FBA was only reduced from 12 to 9. Comparing the two sulfuric acid solutions of pH 1 and 4 (Figures 1 and 2), it is apparent that the solution with pH 1 causes more release of neutralizing material from the fly ash than the solution with pH 4. It appears that FA and HFA have a limited amount of buffering material, which they release constantly under low acidity conditions. FBA, having a large amount of buffering material, shows similar behavior when exposed to mineral plus acid solutions of pH 1 and 4. In the nonconservative system.

the titration curves were very similar to those simulating the conservative system (Titration curves not shown).

The contribution of contact time towards pH stabilization (buffering) was studied in detail using sulfuric acid as the titrant for the conservative system. Figure 3 presents variation of pH with time for FA equilibrium with 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 the fly ash surface during the initial reaction with the added acid. This finding is in agreement with a similar observation made by Theis and Wirth (1977). After neutralization, the points of the titration curves reached their equilibrium value (indicated by the long plateau

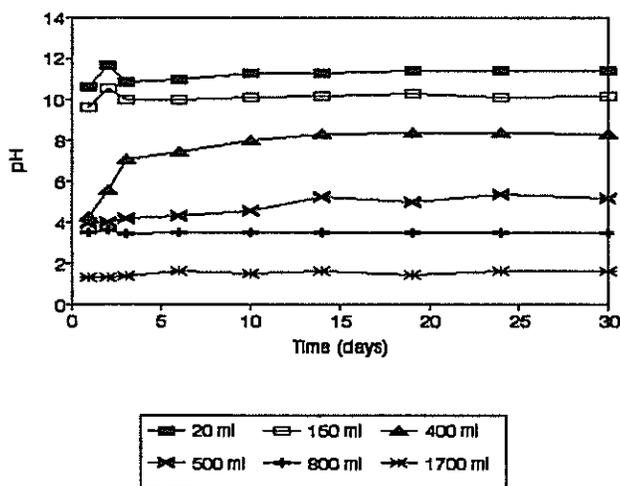


Figure 3 pH vs time for titration of 10 g FA samples against 0.1M H₂SO₄ at pH=1 in a conservative system.

region) the first day. Although fly ash may have released all of its buffering material initially in order to neutralize the added acid, its buffering potential was not significantly reduced with time upon the addition of 400 ml of the acid. When the amount of acid added was increased from 500 ml to 1700 ml, the

fly ash was overwhelmed and its buffering capacity was exhausted. As the 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 FA sample titrated against 400 ml of sulfuric acid.

From the discussion presented, it may be inferred that the controlled conditions that were created to effect sufficient contact time between the fly ash and the acid were not critical factors that change the chemistry of the system with high acidity. For systems with low acidity, contact time and quantity of buffering material present in fly ash could be important. Given sufficient equilibration time, more alkalinity might be released from fly ash to neutralize the acidity present in the solution. Fly ash with high alkalinity content can keep the pH of acidic solutions high by releasing all of its buffering materials until no more alkalinity is left, at which time the pH drops suddenly.

FA, FBA, and HFA were titrated with DDI water of pH 5 simulating a nonconservative system. Under conditions where fly ash comes in contact with non-acidic solutions, the pH of these solutions will be influenced by the added alkaline material. The double deionized water had a pH of 5, as the result, addition of fly ash raised the pH of the solution above 10 almost immediately.

Release of Cations from Fly Ash

Conservative and nonconservative systems served as control conditions to study the release of metals from surfaces of uncontaminated fly ashes. A sulfuric acid solution of pH=1 was used. Such a study was conducted to find out the type and quantity of metals and their potential release from raw fly ash material as the pH of the solution was gradually decreased. It appeared that each metal had a specific pattern of release from fly ash which is related to pH. In the conservative system with sulfuric acid as the titrant, as the pH

Table 2: Higher Concentrations of Metals Released in 0.1M Sulfuric Acid Solutions.

Metals	Conservative Systems			Nonconservative Systems		
	FA	FBA	HFA	FA	FBA	HFA
	Maximum Amount Released in Solutions (mg/kg)					
Calcium	85000	95000	95000	12000	26000	12000
Sodium	5720	1140	7980	660	120	1540
Nickel	-	-	-	28	14	2.2
Magnesium	45000	15500	35000	22000	11600	32000
Lead	33	57	38	4	7	12
Manganese	150	475	225	62	200	100
Copper	176	42	171	64	4	42
Zinc	175	25	375	75	50	90
Aluminum	70000	5000	60000	18000	4000	20000
Iron	27500	20000	20000	9000	4000	9000
Chromium	19	19	38	16	6	8

decreased, the order of release of metals from fly ash was as follows:

Ca-Na-Ni-Mg-Pb-Mn-Cu-Zn-Al-Fe-Cr

(most released at high pH)

(most released at low pH)

calcium and sodium were easily released into solution at high pH, whereas iron and chromium need very acidic conditions for their release. In the nonconservative system, the order of release was similar to that observed in the conservative system. However, for each addition of acid a different metal showed a maximum release. In each system, FA presented the highest concentration released for nickel, copper, chromium, and iron; FBA for manganese and calcium; HFA for magnesium, aluminum, zinc, sodium, and lead (Table 2).

In the conservative system, the highest amount of iron released into the solution occurred after the addition of 1900 ml of acid solution to 10 g of FA (Figure 4). The highest concentrations of iron in solution were found after the

addition of 900 and 1100 ml of nitric and sulfuric acid, respectively. By contrast, in the nonconservative system the concentrations of iron released were the highest after the addition of 1200 ml of the acid. Figures 4 and 5 present the quantity of iron released from FA, FBA, and HFA under conservative and nonconservative conditions respectively. In the conservative system, when pH=1 H₂SO₄ solution was used as the titrant, iron started to be released from FA after 500 ml of the acid has been added and the pH approached 4.0. In the nonconservative system, where pH=1 H₂SO₄ solution was used as the titrant, iron was released from FA at pH=2, which is lower than that observed in the conservative system. This was true for all three different ash materials. Almost no iron was released from the solution until the pH of maximum release (pH=4) was reached. Also, in the nonconservative system, where the contact time between the acid and the ash was shorter high volume (1200 ml) of the acid was needed to effect iron release.

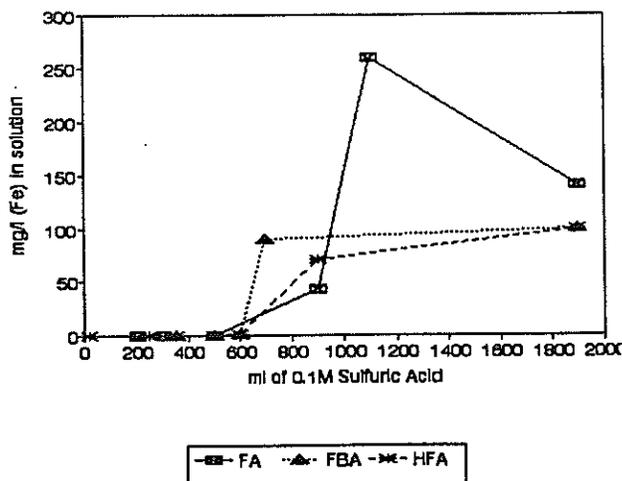


Figure 4 Iron release from 10 g FA, FBA, and HFA under conservative system using 0.1M sulfuric acid.

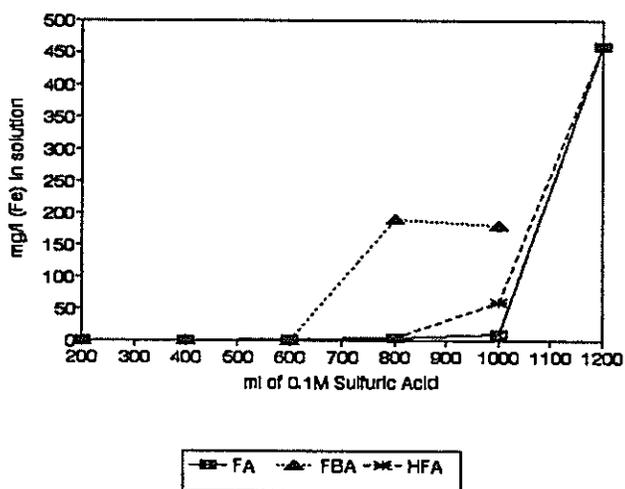


Figure 5 Iron release from 10 g FA, FBA, and HFA under nonconservative system using 0.1M sulfuric acid.

its highest calcium release at pH 11 after the addition of 400 ml of pH=1 H₂SO₄. Comparatively greater amount of calcium was released from fly ash under nonconservative conditions than under conservative conditions.

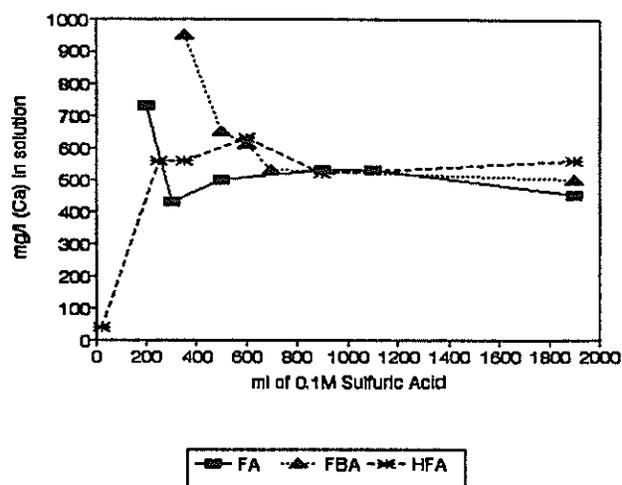


Figure 6 Calcium release from 10 g FA, FBA, and HFA under conservative system using 0.1M sulfuric acid.

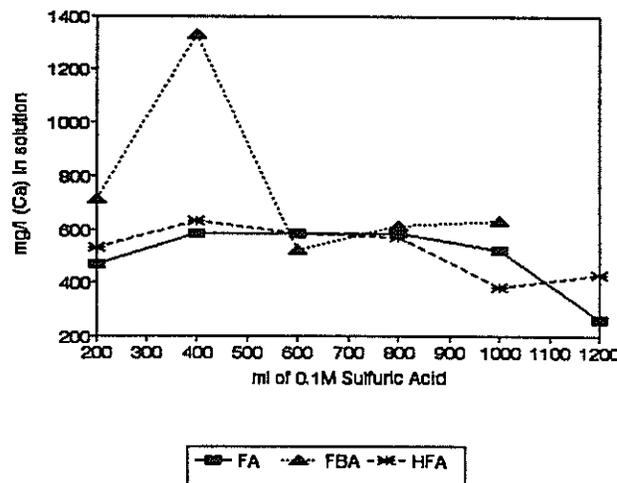


Figure 7 Calcium release from 10 g FA, FBA, and HFA under nonconservative system using 0.1M sulfuric acid.

Figures 6 and 7 present calcium release from FA, FBA, and HFA using a similar acidic environment as in Figure 4 and 5, respectively. In the conservative system, when sulfuric acid was used as the titrant, calcium release depended on the amount of acid present in the solution. Calcium started to be released as soon as titration began regardless of the type of acid used. The release was, however, greatest when nitric acid was used as the titrant. In the nonconservative system, FBA showed

The release of these metals was also monitored during the titration of fly ash with DDI water. The release of other metals, besides calcium, was not significant and did not follow any distinguishable pattern. This could be interpreted

to mean that no true desorption had occurred, but only a random release of cations that were loosely bonded to the surface of fly ash was apparent. FBA released the same amount of calcium in DDI water as it did when it was titrated with nitric or sulfuric acid solution of pH 1. This fact could lead to the conclusion that the calcium release is more dependent on the calcium concentration in solution than the pH of the solution. This observation is in agreement with Fruchter et al. (1990).

The solubility of the metals studied in this paper have been found (Fruchter et al., 1990) to be controlled by either sulfate or hydroxide compounds. Qualitatively, for metals such as calcium which their solubility is basically controlled by the sulfate compound should not be an issue for the 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 the precipitation of the compounds instead of their dissolution. The presence of calcium and other metals in the solution should be explained by other mechanisms, such as desorption or ion exchange. The presence of aluminum could be attributed in dissolution since its solubility is more dependent on the hydroxide compound. Iron solubility is also dependent on the hydroxide compound however the concentrations found in solution in the present study were much above those that would be caused by dissolution mechanism only. Considering these observations the mechanism of desorption is the predominant cause for the release of metals in the fly ash aqueous solutions.

Conclusions

The ash products used in this study were proved to be excellent buffering materials. Fluidized bed ash (FBA) showed a stronger buffering capacity than FA or HFA by releasing large quantities of alkaline material to the acidic titrant. As a result, FBA-treated acid would be expected to have a higher pH when compared with FA-treated acid with equal amount of

ash added. For highly acidic solutions, FBA released all its buffering materials and kept the pH at very high levels until the buffering material was exhausted. HFA was not a good buffering material since a decrease in pH directly corresponded to increased addition of the acidic solution. These conclusions were made based on the ash products that are described in the material and methods section. Calcium and sodium were the metals most released at high pH whereas aluminum, iron, and chromium were released at low pH.

Acknowledgements

This study was financially supported by the Oklahoma Conservation Commission and the United States Environmental Protection Agency.

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<https://doi.org/10.1021/es00078a004>