

# METAL RELEASE FROM FLY ASH UPON LEACHING WITH SULFURIC ACID OR ACID MINE DRAINAGE<sup>1</sup>

by

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**Abstract.** Generation of electricity by coal-fired power plants produces large quantities of bottom ash and fly ash. New power plants commonly use fluidized bed combustion (FBC) boilers, which create ashes with high neutralization potential (NP). These ashes, due to their alkaline nature, are often used in surface mine reclamation to neutralize acidity and reduce hydraulic conductivity of disturbed overburdens. Conventional fly ashes from older power plants exhibit a range of pH and NP, with some ashes having neutral or acidic pH and low NP values, and may not be good candidates for supplying alkalinity in reclamation projects. In this study, we used two acidic solutions to leach a low NP fly ash (LNP ash) and two FBC ashes (FBC1 and FBC2). After passing 78 pore volumes of sulfuric acid and 129 pore volumes of acid mine drainage (AMD) through these ash materials, several trace elements were found at high levels in the leachates. LNP fly ash leachates had high arsenic and selenium concentrations with sulfuric acid leaching, but showed low arsenic and selenium concentrations after leaching with AMD. Leaching with AMD caused the iron and aluminum inherent in AMD to complex these elements and make them unavailable for leaching. Lead, cadmium, and barium concentrations in fly ash leachates were not high enough to cause water pollution problems with either leaching solution. For both leaching solutions, manganese was released from LNP ash at a constant level, FBC1 ash did not release manganese, and FBC2 ash released manganese only after the NP had been exhausted by >60 pore volumes of leaching.

Additional Key Words: alkaline amendments, beneficial use, reclamation, waste materials.

## Introduction

By the year 2000, the U.S. EPA predicts that about 120 million tons of fly and bottom ash and 50 million tons of fluidized bed combustion (FBC) ash will be produced annually. Presently, only about 20% of the fly ash is being used with the remainder being deposited in landfills or surface impoundments. Some of the fly ash and FBC ash are being used to reclaim surface coal mines by applying the material to the coal pit floor and by mixing the ash with overburden materials (Hamric 1993, Schueck et al. 1996, Ziemkiewicz and Skousen 1992). In this setting, the NP of the ash is being used to offset or neutralize the acidity generated by pyrite oxidation in the overburden and coal pavement. However, all ashes are not alkaline, and some ashes may

have low neutralization potential (LNP) and near neutral or acidic pH values. Fly and FBC ash are enriched with many trace elements.

During combustion, metals contained in coal and other carbonaceous rocks may be encased within palaeospheres (the melted, glass-like material) or they may be deposited on the surfaces of these palaeospheres and cenospheres. The trace elements attached to surfaces may be leached and become mobile, running off into nearby water sources (Hamric 1993). Metal leaching is a concern with low NP ashes, especially when these ashes are placed in acid mine environments.

Some FBC ashes, due to their calcium oxide content, harden upon wetting. This hardening can cause the ash to set up like concrete (Schueck et al. 1996). A strategy for controlling acid mine drainage (AMD) on surface mines is to isolate and segregate acid-producing materials with a barrier to limit its exposure to air and water. FBC ash has been used as a barrier material but several studies have shown that the hydraulic conductivities of fly ash and FBC ash mixtures have not been sufficiently slow to act as true barrier materials. A value of  $1.0 \times 10^{-7}$  cm/sec is usually recognized as the hydraulic conductivity (Ksat) value of a material that can

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be considered as a barrier. We conducted hydraulic conductivity tests with two FBC ashes and one conventional fly ash (the same ashes studied herein) and found the  $K_{sat}$  to be in the  $1 \times 10^{-4}$  cm/sec range (Skousen et al. 1997). Compaction and aging with wet and dry cycles caused the  $K_{sat}$  to decrease about two orders of magnitude, but  $K_{sat}$  of these ashes alone or in various mixtures never achieved the  $1 \times 10^{-7}$  cm/sec required for a barrier material. Similarly, Butler (unpublished research at West Virginia University) showed that a mixture of 65% fly ash, 5% quicklime, 15% bentonite, and 15% FBC ash produced a hydraulic conductivity of  $2.7 \times 10^{-6}$  cm/sec.

The high NP of FBC ash has also been used to neutralize acidity. Butler (unpublished research at WVU) found that his mixture produced an average pH of 12.1 and an average alkalinity concentration of 800 mg/L as  $CaCO_3$  in water leached through the material. Due to its pozzolan nature, FBC ash hardens releasing only that alkalinity that can be dissolved from the outside. Therefore to maximize alkalinity release from FBC ash, the material should be mixed with a porous material (like conventional bottom ash) which should minimize hardening into a mass and allow continual release of alkalinity for longer time periods. Another approach may be to allow the FBC ash to harden and then to crush it into small pieces allowing for alkalinity release from the small bead-sized particles. These mixtures of conventional fly ash and FBC ash could also allow the development of other beneficial uses of these ashes. The objective of this research was to determine the release of metals over time from three fly ashes by leaching with a 0.01M sulfuric acid solution and a field AMD.

### Materials and Methods

A low NP conventional power plant fly ash (LNP ash) and two FBC ashes were tested alone and also in various mixtures to determine their leaching characteristics. Paste pH and NP for each ash were determined by methods in Sobek et al. (1978). The LNP fly ash had a paste pH (1:1 ash to water) of 6.3 and a NP of 20 tons of calcium carbonate equivalent material per 1000 tons of material (tons CCE/1000 tons). FBC1 ash had a pH of 11.8 and a NP of 350 tons CCE/1000 tons, while FBC2 pH was 11.5 and NP was 250 tons CCE/1000 tons. These three ashes (treatments 1-3) and various mixtures of these ashes were tested (Table 1).

Leaching of the ash material and mixtures was conducted in 2.5-cm diameter by 10-cm long plastic syringes (60 ml). One of two acid solutions was pulled

through the material by a model 24 Centurion Auto Extractor. Forty grams of each material were placed in 60-ml plastic syringes. Based on 50% pore space in the material, a total of 20 ml of fluid was considered a pore volume of fluid. The acid solutions passed through the ash materials were a 0.01 M sulfuric acid solution and a nearby AMD source collected from an underground mine portal. The sulfuric acid solution had a pH of 1.7, total acidity of 1,000 mg/L as  $CaCO_3$ , a sulfate concentration of 960 mg/L, and no measurable concentrations of arsenic, barium, cadmium, manganese, lead, or selenium. The AMD had a pH of 3.7, total acidity of 2,600 mg/L as  $CaCO_3$ , total iron of 440 mg/L, aluminum of 180 mg/L, manganese of 3 mg/L, calcium of 330 mg/L, and sulfate of 2,900 mg/L. Analysis of the AMD showed no measurable amounts of arsenic, cadmium, lead or selenium (<0.5 ug/L), but 15 ug/L of barium. Leachate solutions were leached through the columns at a rate of 2.5 ml/hr. For the sulfuric acid experiments, 78 pore volumes of solution were passed through the materials. For AMD experiments, 129 pore volumes of solution were passed through the materials.

Leachate quality was measured on a composite water sample of three pore volumes (60 ml) in the sulfuric acid experiments and nine pore volumes (180 ml) in the AMD experiments. Effluent samples and acid leaching solutions were analyzed for pH, arsenic, barium, calcium, cadmium, manganese, lead, and selenium. Water pH was measured by a Accumen Scientific pH meter. Elemental analysis of the leachates was performed with a model 400 Perkin Elmer Inductively Coupled Plasmaspectrometer - Atomic Emission Spectrophotometer (ICP-AES). Each ash was replicated two times.

### Results and Discussion

Results of leaching these three ashes alone and in mixtures with sulfuric acid were reported by Skousen et al. (1997). In general, the LNP ash leachates had high arsenic and selenium concentrations, and amending the LNP ash with FBC ashes reduced arsenic, but not selenium concentrations. Manganese was also released from the LNP ash at a constant level throughout the leaching experiment, and manganese was also released from the FBC2 ash only after the NP had been exhausted by extensive leaching.

Results of leaching ash materials with AMD are compared to the leaching results conducted with sulfuric acid. Only the results of leaching each ash type (LNP ash = treatment 1, FBC1 ash = treatment 2, and FBC2 ash = treatment 3) with sulfuric acid and AMD will be

**Table 1. Materials and % of materials in mixtures for leaching studies.**

Treatment Mixture	Material and Percentages		
	LNP	FBC1	Crushed
	Fly Ash	Ash	FBC2 Ash
	-----%		
1	100	0	0
2	0	100	0
3	0	0	100
4	50	50	0
5	50	0	50
6	25	75	0
7	33	67	0
8	10	90	0
9	90	0	10
10	75	0	25
11	0	25	75
12	0	75	25

shown in this paper. Ash mixtures (treatments 4-12) as shown in Table 1 were also leached by AMD in a similar fashion as that done for sulfuric acid, but those results are not given in this paper.

Alkalinity in a water sample is often measured by titrating the sample with an acid solution. However, the leachates generated from fly ash were highly alkaline because of the dissolution of CaO contained in the ash. Calcium oxide originally present in the ash reacted with water and changed to Ca(OH)<sub>2</sub>, which leached out of the ash. These leachates had a very high pH (around 11 to 12 pH) and a high affinity for CO<sub>2</sub>. In our experiments, the leachates during titration were exposed to laboratory atmosphere. CO<sub>2</sub> in the air reacted with the alkalinity in the leachates, and thereby interfered with the measurement of solution alkalinity. So, calcium concentrations in the leachate were used as a measure of the amount of alkalinity released from the ash due to the reaction of ash with sulfuric acid and AMD.

Calcium concentrations were the lowest in leachates generated from LNP ash (treatment 1) and the calcium contained in the LNP ash was entirely exhausted in the ash after three pore volumes (Fig. 1). This was expected because coal combustion residues from conventional boilers do not have calcium added during the burning process, whereas FBC boilers have limestone added during coal burning. FBC2 (treatment 3) generated significant amounts of alkalinity as evidenced by the calcium concentrations in the leachates. FBC2 ash had undergone a pozzolanic reaction (the ash was

hydrated and hardened to set like cement) and the size of aggregates for this ash was between 6.25 mm and 2 mm. These results show that the amount of alkalinity released by FBC2 ash was significant even when this material was allowed to aggregate and then crushed into particles. FBC2 ash continued to release more calcium than either the conventional LNP fly ash (treatment 1) or FBC1 ash (treatment 2).

The calcium released from these three ashes during leaching with AMD (Fig. 2) was substantially higher than that for sulfuric acid (note change in scale on y-axis in Fig. 2 compared to Fig. 1). The AMD used in this study contained about 300 mg/L calcium, and calcium concentrations in AMD experiments were corrected for calcium contained in the original AMD. On average, calcium concentrations in FBC2 ash leachates were about 250 mg/L higher in AMD than sulfuric acid, and 200 to 400 mg/L higher than solutions from FBC1 ash. The calcium concentrations from LNP ash were also dramatically increased to around 300 mg/L due to AMD leaching versus very low amounts from sulfuric acid leaching. The higher acidity concentration of the AMD in contrast to sulfuric acid caused degradation and dissolution of the ash's spherical particles, causing calcium to continually be released throughout the entire 129 pore volumes. Results of calcium concentrations in leachates from the ash mixtures showed similar trends as those shown in Figure 2.

**Arsenic** is a regulated trace element. Coal combustion residues are known to be major sources of arsenic to the environment (Bhumbla and Keefer, 1994). Among the three ash types, LNP conventional fly ash (treatment 1) had a spike of arsenic that exceeded 12,000 ug/L after 60 pore volumes (Fig. 3). Maximum allowable contaminant levels for arsenic in drinking water is 50 ug/L. Thus arsenic released by LNP fly ash was 2400 times the regulatory standard. These high concentrations of arsenic in the leachates were observed only after a large volume of sulfuric acid passed through the ash. Arsenic in the ash is held by calcium, iron, and aluminum compounds. At the start of the leaching process, these compounds protected arsenic against leaching. However, leaching of ash by sulfuric acid attacked and dissolved these arsenic-retaining compounds and permitted the release of arsenic to the leaching solution. Leachates from FBC2 ash (treatment 3) routinely exceeded drinking water standards for arsenic. Thus there are concerns about the release of arsenic to surface and subsurface waters when these ashes are allowed to react with sulfuric acid.

When leached with AMD, the LNP ash released no measurable arsenic (Fig. 4). Arsenic concentrations were also much lower for FBC ashes, with only two spikes exceeding 50 ug/L. FBC1 ash continued to release arsenic throughout the experiment, while FBC2 ash essentially ceased arsenic release after 70 pore volumes. The reason for much lower arsenic concentrations during AMD leaching is because the high concentrations of iron and aluminum in the AMD caused precipitation and complexation of arsenic during leaching. Therefore, less arsenic was free to be leached.

**Selenium** is another regulated element. This element is an essential nutrient for ruminant animals and human beings. However, this element is toxic at high concentrations and is suspected to cause genetic mutations. Selenium concentrations in leachates during sulfuric acid leaching routinely exceeded the drinking water standard of 10 ug/L (Fig. 5). The highest selenium concentrations in leachates were found in LNP fly ash (treatment 1), which exceeded 400 ug/L on one occasion. Thus release of selenium from this LNP ash can cause water pollution.

Leaching with AMD caused much lower selenium concentrations to be present in ash leachates compared to sulfuric acid leachings (Fig. 6). The highest selenium concentration was about 95 ug/L for the FBC1 ash (treatment 2) at the start of the experiment. The LNP ash showed no measurable selenium from AMD

leaching at any time. Selenium in these ashes was made less available by iron and aluminum contained in the AMD leaching solution; therefore, less selenium was free for release from the ash.

**Lead** concentrations in leachates from LNP fly ash (treatment 1) were routinely lower than leachates collected from either FBC ashes (treatments 2 and 3) (Fig. 7), except at the 54 pore volume leaching stage. Apparently, total amounts of lead in the ash were in limited quantity because lead concentrations in the pore volumes collected near the end of the experiment were close to the detection limit of the instrument.

With AMD leaching, lead concentrations in leachates were decreased by about half from lead concentrations leached by sulfuric acid (Fig. 8). The regulatory standard for lead in drinking water is 15 ug/L and the leachates from FBC ashes commonly had >15 ug/L lead. The LNP ash leachates showed no measurable lead concentrations throughout the AMD experiment.

**Cadmium** concentrations from leaching these three ashes with sulfuric acid did not exceed 50 ug/L (Fig. 9). The drinking water standard for cadmium is 10 ug/L and FBC1 ash was the only ash that was found consistently below this level after 18 pore volumes. No consistent differences among ash sources were apparent for their tendencies to release cadmium with sulfuric acid leaching. Data consistently showed spikes in cadmium concentrations at various times during leaching. These spikes show that cadmium in ashes was not present as a discrete phase and also cadmium-containing compounds of ash were showing incongruent weathering. Thus high concentrations of cadmium were observed when an ash particle containing cadmium disintegrated to release cadmium. These data show that release of cadmium with time by an acid leaching solution will be difficult to predict.

The LNP ash showed a consistent release of cadmium (at between 40 to 50 ug/L) with AMD leaching. FBC1 ash (treatment 2) did not release cadmium until about 115 pore volumes of AMD solution was passed through it, while the FBC2 ash (treatment 3) released cadmium after 80 pore volumes.

**Barium** is a regulated element, with the maximum contaminant level for this element in drinking water being 1,000 ug/L. With sulfuric acid, only three sampling points showed barium concentrations >1,000 ug/L, and these data points were for the FBC1 ash (Fig. 11). Leachates collected from LNP fly ash (treatment 1)

or FBC2 ash (treatment 3) never exceeded drinking water standards. Barium concentrations in AMD leachates never exceeded drinking water standards (Fig. 12), and all leachates showed <300 ug/L barium. Thus utilization of ash will not be limited by the presence of barium in the ash.

Manganese is a regulated element and the drinking water standard is 50 ug/L. This element is an essential nutrient for plants and animals, but manganese concentrations in water are regulated because of aesthetic reasons. Manganese in the leachates from LNP fly ash (treatment 1) was >1000 ug/L initially (Fig. 13). This high concentration of manganese in the first pore volume of leachate indicates that a part of the manganese in this ash was present in the Mn(II) form. The highest manganese concentrations in the leachates with sulfuric acid came from FBC2 ash (treatment 3), which exceeded 2,000 ug/L after 70 pore volumes. However, these high levels of manganese were noted only after the NP in the ash was exhausted and, once the NP was exhausted, the manganese became more mobile. No significant amounts of manganese were released by the other two ashes after the initial sulfuric acid leaching commenced.

Leaching the LNP ash with AMD gave a consistent manganese concentration of about 5 mg/L in the leachate. The average manganese concentration of the AMD was about 3 mg/L, so little attenuation and only a slight release of manganese from this ash probably occurred. FBC1 ash (treatment 2) completely removed the manganese in the leaching solution due to neutralization and precipitation, and also did not cause a release of manganese from the ash particles. FBC2 ash (treatment 3) leachates began showing manganese concentrations after 52 pore volumes, but it never reached the manganese levels released from LNP ash. Therefore, some of the manganese in the water was precipitated as a result of the NP in this ash.

### Summary and Conclusions

Several trace elements were observed in leachates after passing sulfuric acid and AMD through three fly ashes. Some of the elements leached from the ashes exceeded drinking water standards. Arsenic was found in exceedingly high concentrations (>10,000 ug/L) in leachates from the LNP ash with sulfuric acid leaching. Arsenic concentrations in AMD leachates were much lower due to the complexation and precipitation of arsenic with iron and aluminum inherent in the AMD solution. Selenium often exceeded drinking water standards. Unlike arsenic and other trace elements,

selenium in ash is not controlled by a precipitation reaction, but by redox reactions. Like arsenic though, selenium concentrations in leachates from AMD leaching were much lower than those from sulfuric acid leachings due to metals in AMD causing selenium complexation and co-precipitation. With sulfuric acid leaching, manganese was released from LNP fly ash at a constant level, FBC1 ash did not release manganese, while FBC2 ash released manganese only after the NP of the ash had been exhausted. Leaching with AMD gave similar results.

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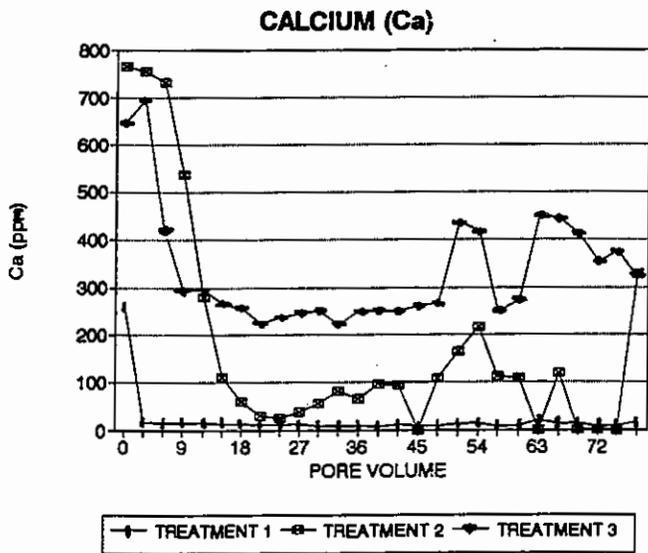


Fig. 1. Calcium concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

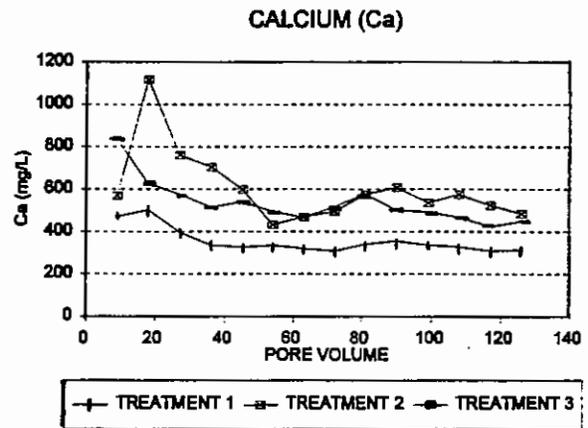


Fig. 2. Calcium concentrations in leachates generated by leaching fly ashes with acid mine drainage. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

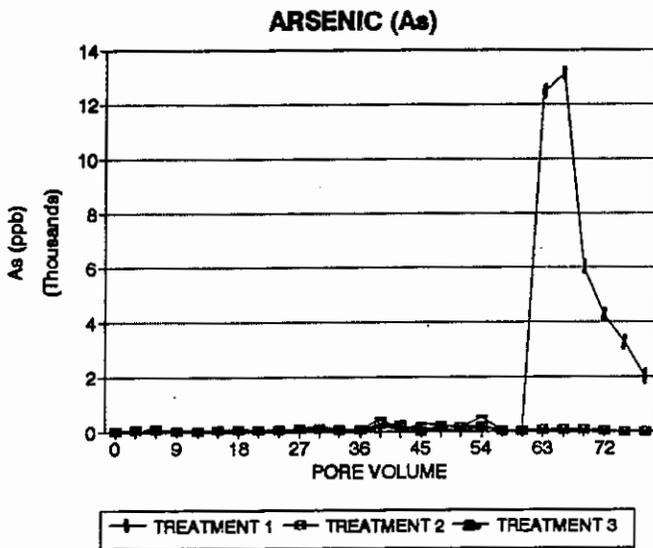


Fig. 3. Arsenic concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

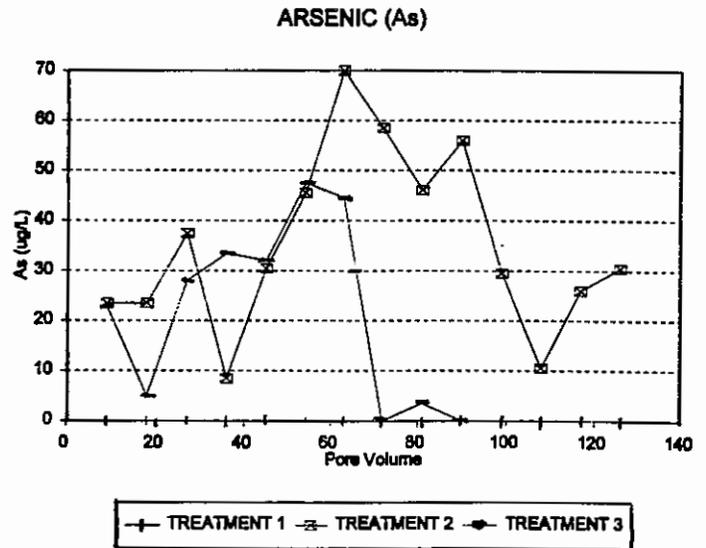


Fig. 4. Arsenic concentrations in leachates generated by leaching fly ashes with acid mine drainage. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

### SELENIUM (Se)

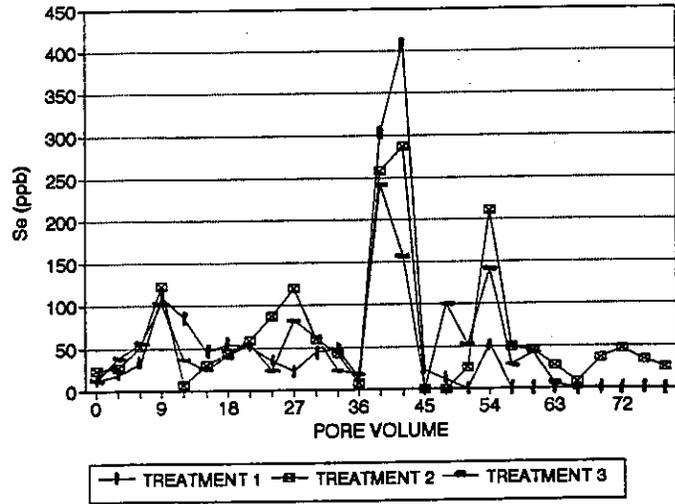


Fig. 5. Selenium concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

### SELENIUM (Se)

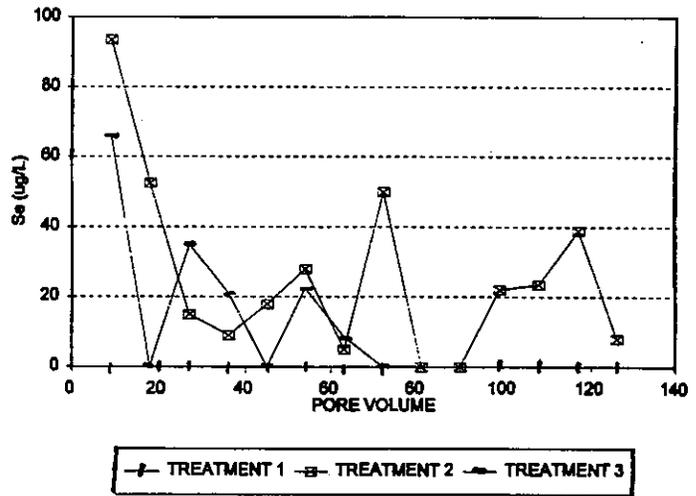


Fig. 6. Selenium concentrations in leachates generated by leaching fly ashes with acid mine drainage. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

### LEAD (Pb)

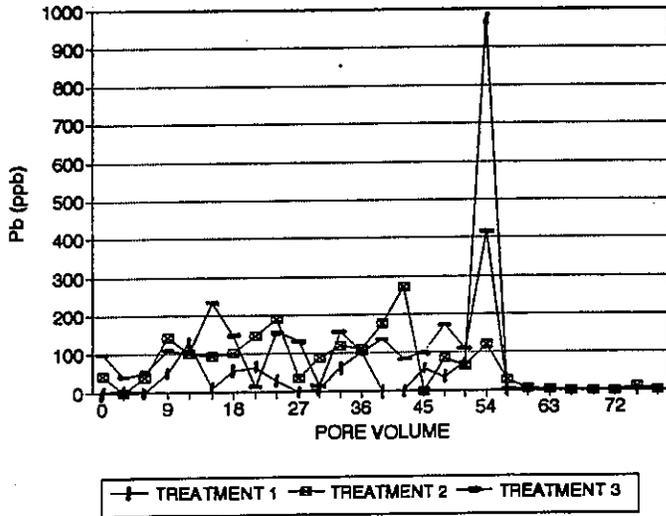


Fig. 7. Lead concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP fly ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

### LEAD (Pb)

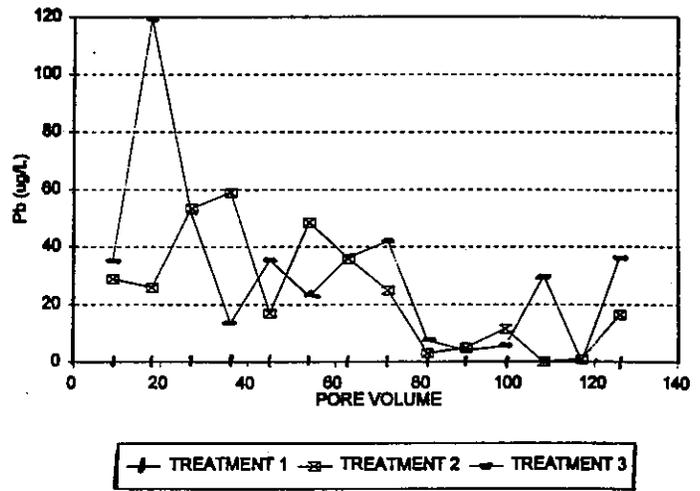


Fig. 8. Lead concentrations in leachates generated by leaching fly ashes with acid mine drainage. Treatment 1 (100% LNP fly ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

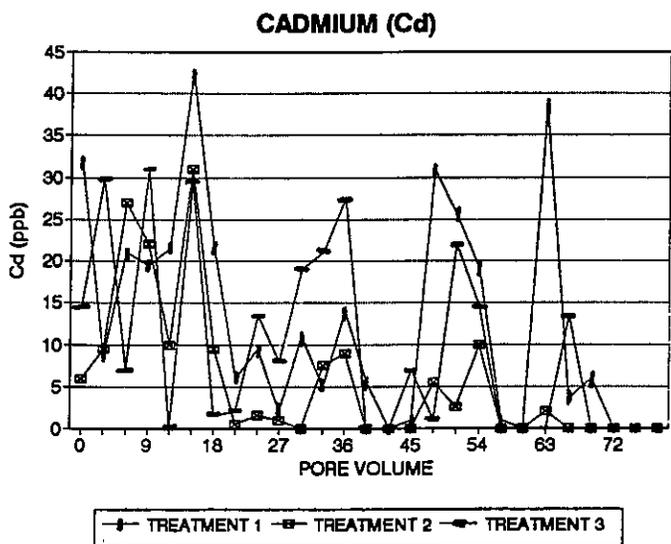


Fig. 9. Cadmium concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

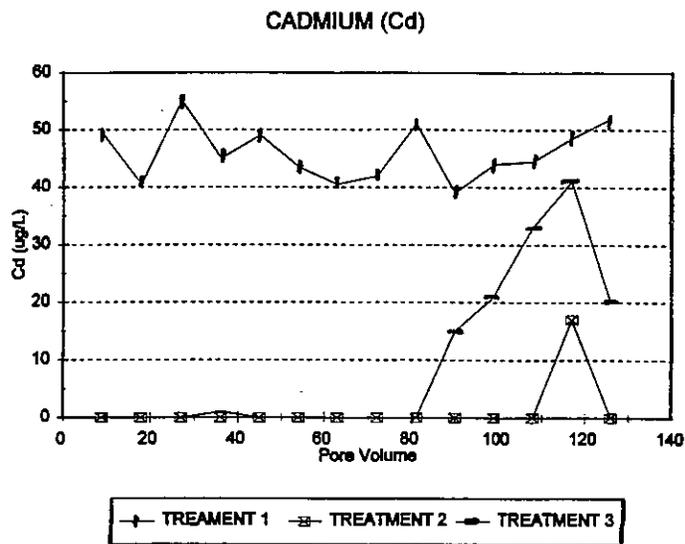


Fig. 10. Cadmium concentrations in leachates generated by leaching fly ashes with acid mine drainage. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

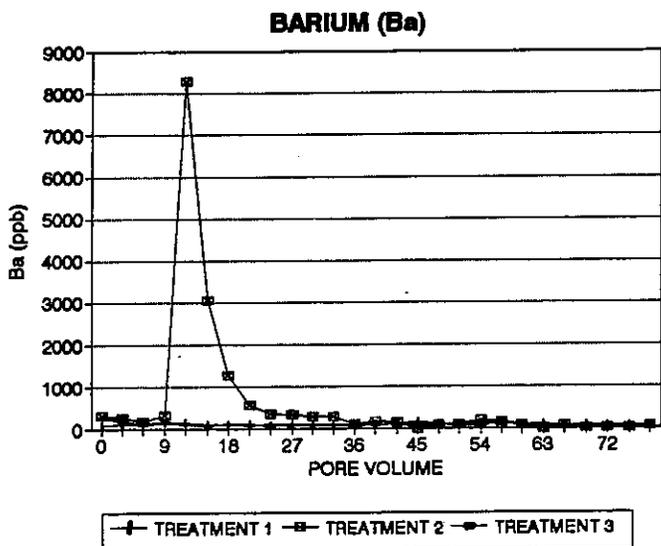


Fig. 11. Barium concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

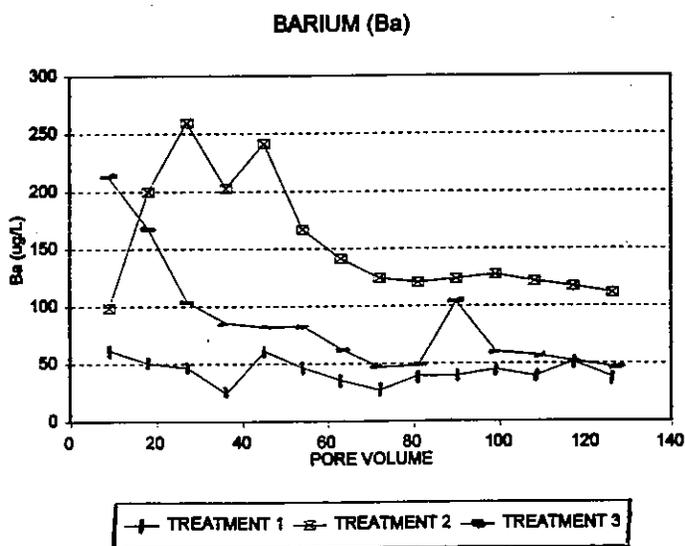


Fig. 12. Barium concentrations in leachates generated by leaching fly ashes with acid mine drainage. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

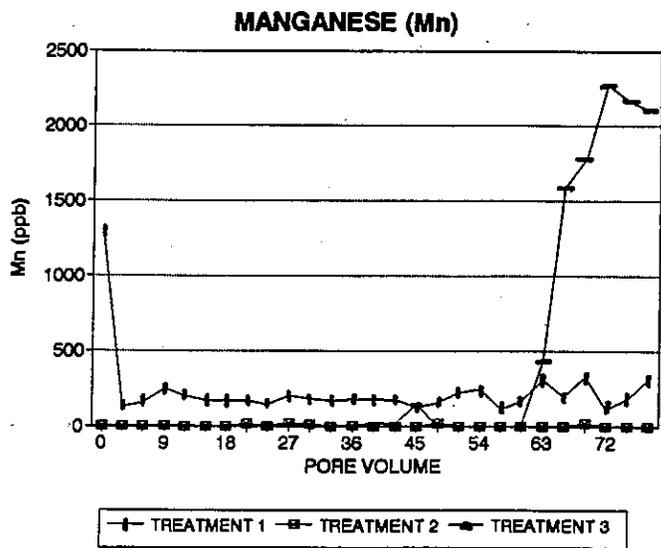


Fig. 13. Manganese concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

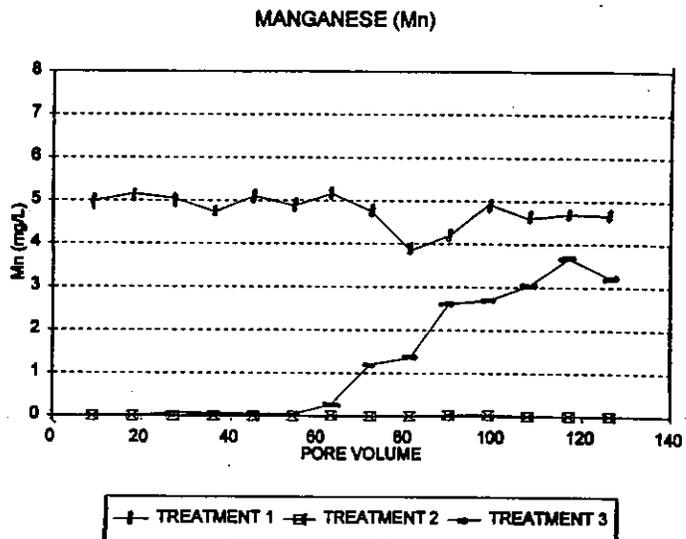


Fig. 14. Manganese concentrations in leachates generated by leaching fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).