HYDRAULIC CONDUCTIVITY OF ASH MIXTURES AND METAL RELEASE UPON LEACHING¹

by

Jeff Skousen, D.K. Bhumbla, Jim Gorman, and John Sencindiver²

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 projects to neutralize acidity and reduce hydraulic conductivity of disturbed overburden materials. 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. This study measured the hydraulic conductivity and leachate quality of various mixtures of three fly ashes: 1) a fly ash with low NP (LNP ash) and two FBC ashes (FBC1 and FBC2). Results indicate that water will flow through these materials at a moderate rate (about 10⁻⁴ cm/sec), but compaction with machinery and with pressure from overlying fill materials may decrease these hydraulic conductivity rates by an order of magnitude. Several trace elements were found at high levels in the leachates of some ash mixtures after sulfuric acid leaching. LNP fly ash leachates had high arsenic and selenium concentrations. Amending LNP conventional ash with FBC ashes reduced arsenic concentrations but not selenium contents. Lead, cadmium, and barium concentrations in fly ash leachates were not high enough to cause water pollution problems. Manganese was released from LNP ash at a constant level, FBC1 ash did not release manganese, while FBC2 ash released manganese only after the NP had been exhausted by 60 pore volumes of sulfuric acid leaching.

Additional Key Words: acid mine drainage, alkaline materials, alkaline amendments, fly ash, reclamation, water flow.

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. Presently, only about 20% is being used with the remainder being deposited in landfills or surface impoundments. Some of this 20% of fly ash and FBC ash are being used in reclaiming surface coal mines by applying the material to the coal pavement 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

¹Paper presented at the 1997 National Meeting of the American Society for Surface Mining and Reclamation, Austin, Texas, May 10-15, 1997.

²Jeff Skousen is Associate Professor and Extension Reclamation Specialist; D.K. Bhumbla is Assistant Professor and Extension Soil/Water Specialist; Jim Gorman is Research Associate; and John Sencindiver is Professor, West Virginia University, Morgantown, WV 26506-6108. 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, particularly metals. During combustion, metals contained in coal and other carbonaceous rocks may be encased within palaerospheres (the melted, glass-like material) or they may be deposited on the surfaces of these palaerospheres and cenospheres. The metals on the surface may be leached and become quite 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 on surface mines is isolating and segregating acidproducing 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

Proceedings America Society of Mining and Reclamation, 1997 pp 480-495

barrier materials. A value of 1.0×10^{-7} cm/sec is usually recognized as the hydraulic conductivity value of a material that can be considered as a barrier. For example, 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 x 10⁻⁶. This mixture reduced hydraulic conductivity to limit water movement substantially, but did not meet the 1.0×10^{-7} cm/sec barrier requirement.

The high NP of FBC ash has also been used to neutralize acidity. Butler (unpublished research at WVU) also found that his mixture produced a average pH of 12.1 and an average alkalinity concentration of 800 mg/L (calcium carbonate equivalent acidity) 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 or fly 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 objectives of this research project were to: 1) determine hydraulic conductivities of various mixtures of fly ash and FBC ash; and 2) determine the release of metals over time from these mixtures by leaching with a .01M sulfuric acid solution.

Materials and Methods

Various mixtures of a LNP conventional power plant fly ash and two FBC ashes were tested to determine their leaching characteristics and hydraulic conductivity. Paste pH and NP 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/1000 tons of material. FBC1 ash had a pH of 11.8 and a NP of 350 tons/1000 tons, while FBC2 pH was 11.5 and NP was 250 tons/1000 tons. Various materials-mixtures were tested and shown in Table 1.

Methods for Determining Hydraulic Conductivity

Saturated hydraulic conductivity (Ksat) was determined on these mixtures of ashes as listed in Table 1. All mixes were made when the materials were airdry. Materials were poured into aluminum cylinders without compaction for the Ksat determination. Cylinders measured 7.5 cm long by 7.5 cm in diameter. After saturation, the cylinders were placed on a dualflow (double-ring) permeameter in the laboratory for Ksat determination following the constant head procedures of Klute and Dirksen (1986) and Hill and King (1982). The procedure was as follows. The top of the cylinder was open and the bottom was covered with cheesecloth and a wire mesh screen. The top of the permeameter, made of plexiglass, had an influent port and a vent port, and was sealed to the top of the cylinder. A 7.5-cm diameter plexiglass tube, 15 cm in height, was fitted on top of the permeameter to allow a head of water varying from 2.5 to 15 cm. The bottom of the cylinder was sealed to a double-ring apparatus. Since the area of the outer ring and the inner ring were the same, the outflow from both areas should be the same. By collecting the outflows separately from each cylinder area, the difference between inner ring and outer ring flow was determined. If outflow differences between inner and outer ring areas are large, some leakage or other problems may be occurring in the cylinder. This permeameter procedure allows Ksat to be determined for the center portion of the core and for the total core. The center flow Ksat is considered to be more accurate than the total flow Ksat.

The tests were performed by placing a 4 cm head of water on top of the cylinder by the use of reservoirs filled with distilled, deionized water. The head pressure forced the water through the rigid-wall cylinders and a hydraulic gradient was imposed along the vertical axis of the ash mixture. Effluent from both inner and outer areas at the bottom of the cylinder were collected separately and measured at regular intervals to determine hydraulic conductivity in cm/sec. Hydraulic conductivity measurements were replicated three times for each ash mixture (12 ash mixtures x 3 reps) for 36 tests.

Bulk density (BD) was determined by drying the material in each of the cylinders in an oven for 24 hrs at 105°C. The volume of each cylinder was calculated and bulk density was calculated as oven-dry weight divided by the volume. Particle density (PD) was determined by the pycnometer method (Blake and Hartge, 1986). Total porosity was calculated by the following equation:

% Porosity =
$$(1 - BD/PD)100$$
 (1)

Methods for Measuring Leachate Quality

Leaching of the ash mixtures was conducted in 2.5-cm diameter by 10-cm long plastic syringes (60 ml),

Treatment Mixture	Material and Percentages			
	LNP <u>Fly Ash</u>	FBC1 %	Crushed <u>FBC2 Ash</u>	
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*	0	50	50	
11	0	25	75	
12	0	75	25	

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

*The treatment 10 mixture as listed here was used for the hydraulic conductivity study. The treatment 10 mixture used in the leaching study was 75% LNP fly ash and 25% FBC2 ash.

and the acid solution was pulled through the material by a model 24 Centurion Auto Extractor. Forty grams of each of the 12 materials/mixtures 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 fluid passed through the ash materials was a 0.01 M sulfuric acid solution (pH=2.0). Effluent quality was measured on a composite fluid sample from 12 pore volumes. As the NP in the ash began to decline, effluent samples were taken from every three pore volumes for analysis. Effluent samples were analyzed for pH, total alkalinity, total acidity, Al, As, Ba, Ca, Cd, Cr, Fe, Hg, Mg, Mn, Ni, Pb, Se, and Zn. Water pH was measured by a Accumen Scientific pH meter. Total alkalinity and acidity were determined by a Titralab VIT-90 automatic titrator (Radiometer-America, Westlake, OH). Elemental analysis were performed by a model 400 Perkin Elmer Inductively Coupled Plasmaspectrometer - Atomic Emission Spectrophotometer (ICP-AES). Each mixture was replicated two times.

The NP in some of the ash mixtures was completely neutralized by acidic solutions by 50 pore volumes, while the NP of other mixtures was not completely neutralized by the end of 120 pore volumes. In these cases, a determination was made as to the necessity of continued leaching past 120 pore volumes. A sample of FBC ash (80 g) has been leached by this process with a dilute sulfuric acid solution for the past several months and there has been no diminuation of alkalinity in the effluent for the first 80 pore volumes.

Results and Discussion

Hydraulic Conductivity

All bulk density values were very low (Table 2). Results of particle density determinations indicate FBC1 ash had the heaviest particles. Total porosity of all materials was greater than 50%, with FBC2 having the highest porosity at 77.5%. The data indicate these ashes to have high water holding capacities.

Values of Ksat determined by the normal saturation procedure are presented in Table 3. Except for samples 3 and 12, the Ksat values are very similar. It is not clear why sample 12 (75% FBC1 and 25% crushed FBC2 ash) was too fast to measure. Since samples 10 and 11 had reasonable Ksat values compared to the other samples, one would assume that sample 12 should also have had a Ksat value in the 10^{-4} cm/sec range. Because only one core was used, this sample could have been an anomaly. All values for samples with a determined Ksat are considered to be moderately high.

Saturation of the FBC ash cores for seven days beyond the normal procedure reduced the Ksat of the center flow region for 100% FBC1 ash (sample 2) and 90% FBC1 ash (sample 8) (Table 4). Ksat of the other two mixtures of LNP fly ash and FBC1 ash was not changed. Longer periods of saturation tended to cause swelling of the FBC1 ash in the cylinders, which could have caused reduction in Ksat since swelling should have reduced the pore space.

Sample	N	Bulk Density	Particle Density	Total Porosity
		Mg/m ³	Mg/m ³	%
1-100LNP	4	0.96	2.31	58.5
2-100FBC1	3	0.86	2.77	69.1
3-100FBC2	3	0.56	2.47	77.5
4-50LNP:50FBC1	3	1.02	2.51	59.2
5-50LNP:50FBC2	4	0.78	2.38	67.2
6-25LNP:75FBC1	3	0.94	2.63	64.3
7-33LNP:67FBC1	3	0.93	2.57	63.7
8-10LNP:90FBC1	3	0.94	2.72	65.6
9-90LNP:10FBC2	3	0.94	2.32	59.6
10-50FBC1:50FBC2	3	0.83	2.62	68.2
11-25FBC1:75FBC2	3	0.83	2.54	67.5
12-75FBC1:25FBC2	1	0.65	2.71	76.1

Table 2. Bulk density, particle density, and total porosity of ash mixtures.

When various saturation procedures were used on the 25% LNP fly ash and 75% FBC1 ash samples, some differences in Ksat were found (Table 5). The two types of saturation without vacuum (treatments 2 and 3) reduced the Ksat of the samples. Saturation without vacuum likely caused air pockets to be trapped in the cores, which reduced the Ksat.

Leaching Study

Alkalinity in an extract 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 calcium oxide contained in the ash. Calcium oxides that were originally present in the ash reacted with water and changed to calcium hydroxide, which leached out of the ash. These leachates had a very high pH and a high affinity for carbon dioxide. In our experiments, the leachates during titration were exposed to laboratory atmosphere. Carbon dioxide in the air reacted with the alkalinity in the leachates. This reaction of carbon dioxide with alkalinity in leachates interfered with the measurement of solution alkalinity. So in this study, calcium concentrations in the leachate were used as a measure of the amount of NP in the ash that was released due to the reaction of ash with sulfuric acid.

Calcium concentrations were the lowest in leachates generated from treatment 1 (100% LNP fly ash) (Fig. 1). This was expected because coal combustion residues from conventional boilers do not contain or add calcium during the burning process, whereas fluidized bed burners add limestone during coal burning. Therefore, ashes from fluidized bed plants are higher in NP than ashes from conventional pulverized fuel coal burners. FBC2 generated significant amounts of alkalinity as evidenced by the calcium concentrations in the leachates from the treatment 3 (100% FBC2 ash) (Fig. 1). 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. FBC2 ash (treatment 3) continued to release more calcium than either the conventional LNP fly ash (treatment 1) or FBC1 ash (treatment 2).

Leachates from treatment 4 (50% LNP fly ash and 50% FBC1 ash) and treatment 5 (50% LNP fly ash and 50% FBC2 ash) also contained significant amounts of alkalinity as shown by the calcium concentrations

Sample	N	Ksat-center	Ksat-total
		(cm/sec)	(cm/sec)
1-100LNP	3	1.4 x 10 ⁻⁴	1.6 x 10 ⁻⁴
2-100FBC1	3	1.6 x 10 ⁻⁴	1.8 x 10 ⁻⁴
3-100FBC2	3	*	*
4-50LNP:50FBC1	2	1.3 x 10 ⁻⁴	1.4 x 10 ⁻⁴
5-50LNP:50FBC2	4	5.4 x 10 ⁻⁴	8.1 x 10 ⁻⁴
6-25LNP:75FBC1	3	1.9 x 10 ⁻⁴	2.1 x 10 ⁻⁴
7-33LNP:67FBC1	3	1.6 x 10 ⁻⁴	2.3 x 10 ⁻⁴
8-10LNP:90FBC1	3	1.2 x 10 ^{-₄}	1.2 x 10 ⁻⁴
9-90LNP:10FBC2	3	1.7 x 10 ⁻⁴	2.3 x 10 ⁻⁴
10-50FBC1:50FBC2	3	2.1 x 10⁴	4.1 x 10 ⁻⁴
11-25FBC1:75FBC2	3	8.6 x 10 ⁻⁴	7.2 x 10 ⁻⁴
12-75FBC1:25FBC2	1	*	*

Table 3. Saturated hydraulic conductivity of ash mixtures in cores saturated under vacuum for 24 hours.

* Flow too fast to measure.

in these materials (Fig. 2). No significant differences were observed in the amounts of calcium released by addition of two sources of FBC ash to the LNP conventional fly ash.

Fortification of LNP fly ash with more FBC2 ash resulted in significant increase in the amount of alkalinity released (Fig. 3). These results show that alkalinity and calcium in the LNP fly ash leachates can be increased by amending it with FBC2 ash.

Fortification of the LNP fly ash with FBC1 ash at levels exceeding 50% of the mix had an insignificant effect on the amount of alkalinity that was released to the leaching solutions (Fig. 4). The lowest amount of alkalinity was generated in treatment 8 (Fig. 4). FBC1 ash contains more alkalinity than the LNP conventional fly ash, thus the lower amount of alkalinity generated by increasing FBC1 ash to 90% appears to be due to the pozzolonic reaction between fly ash and FBC1 ash. Silica and aluminum oxides in LNP fly ash were activated by the calcium oxide content of FBC1 ash to form a cementitious material. The presence of such cementitious material was observed in this experiment because the contents of treatment 8 were very slowly permeable. These results show that addition of FBC1 ash to more than 50% of the mix will not add any significant neutralization capacity (alkalinity) to the LNP fly ash/FBC1 mix.

Arsenic is a regulated trace element. Coal combustion residues are known to be major sources of arsenic to the environment. Among the three types of ashes, LNP conventional fly ash (treatment 1) had spikes of arsenic that exceeded 12,000 ug/L (Fig. 5). Maximum allowable contaminant level 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 had been 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 100% FBC2 ash (treatment 3) routinely exceeded drinking water standards for arsenic. Thus there are concerns about the release of arsenic to surface and

Table 4.	Saturated hydraulic	conductivity of ash	mixtures in cores	saturated by tw	o different methods.
,	Total Flow			-	

Sample	N	Method A ¹	Method B ²
		(cm/sec)	(cm/sec)
2-100FBC1	3	1.8 x 10 ⁻⁴	6.2 x 10 ⁻⁵
6-25LNP:75FBC1	3	2.1 x 10 ⁻⁴	1.3 x 10 ⁻⁴
7-33LNP:67FBC1	3	2.3 x 10 ⁻⁴	1.1 x 10 ⁻⁴
8-10LNP:90FBC1	3	1.2 x 10 ⁻⁴	1.3 x 10 ⁻⁴
Center Flow			
Sample	N	Method A ¹	Method B ²
		(cm/sec)	(cm/sec)
2-100FBC1	3	1.6 x 10 ⁻⁴	6.6 x 10 ⁻⁵
6-25LNP:75FBC1	3	1.9 x 10 ⁻⁴	1.4 x 10 ⁻⁴

1.6 x 10⁻⁴

1.2 x 10⁻⁴

1.1 x 10⁻⁴

8.6 x 10⁻⁵

¹ Method A = Saturation of the sample for 24 hours, then determining Ksat.

3

3

² Method B = After Method A was completed, the cores were saturated without vacuum for 7

days. Then vacuum was applied for 24 hours after which Ksat was determined again.

Table 5. Saturated hydraulic conductivity of sample	6 (25% LNP fly ash and 75% FBC1 FBC ash) after
various treatments.	

Treatment*	N	Ksat-center	Ksat-total
		(cm/sec)	(cm/sec)
1	3	1.3 x 10 ⁻⁴	1.5 x 10 ⁻⁴
2	3	1.8 x 10 ⁻⁵	8.1 x 10 ⁻⁶
3	2	3.2 x 10 ⁻⁶	5.7 x 10 ⁻⁶
4	3	1.9 x 10 ⁻⁴	2.1 x 10 ⁻⁴
5	3	1.4 x 10 ⁻⁴	1.3 x 10 ⁻⁴

*Treatments:

7-33LNP:67FBC1

8-10LNP:90FBC1

1. Cores saturated 24 hours without vacuum;

- 2. Cores in treatment #1 allowed to dry for 7 days after Ksat determination, then saturated without vacuum for 24 hours and Ksat determined again.
- 3. Cores saturated for 3 weeks without vacuum.
- 4. Cores saturated 24 hours under vacuum.
- 5. Cores in treatment #4 allowed to dry for 7 days after Ksat determination, then saturated under vacuum for 24 hours and Ksat determined again.

subsurface waters when these ashes are allowed to react with acid materials such as sulfuric acid.

When LNP conventional fly ash was amended with FBC ashes, arsenic concentrations were lower than those observed for LNP ash alone (Fig. 6). When LNP fly ash was amended with 50% FBC1 ash (treatment 4), arsenic concentrations in the leachates never exceeded 500 ug/L. When LNP fly ash was amended with 50% FBC2 ash, arsenic concentrations in the leachates increased to 3600 ug/L. These data show that mixing LNP ash with either of the fluidized bed materials tended to reduce and delay the release of arsenic to surface and subsurface waters. Application of FBC2 ash at only 10% suppressed arsenic mobility (Fig. 7). However, the net effect of amending LNP ash with FBC2 ash was only a delay in the release of arsenic. Arsenic concentrations over 20,000 ug/L were observed in the LNP ash treated with 10% FBC2 ash (treatment 9). Amending LNP fly ash with more than 50% FBC1 ash resulted in maintaining arsenic concentrations below 500 ug/L (Fig. 8). There were a few spikes of high arsenic in the leachates, but arsenic concentrations in the leachate solutions were generally within drinking water standards.

Selenium is another regulated element. This element is an essential nutrient for ruminant animals and human beings. However, at high concentrations this element is toxic and is suspected to cause genetic mutations. Selenium concentrations in leaching solutions routinely exceeded drinking water standards (Fig. 9). The highest selenium concentrations in leachates were found in 100% LNP fly ash (treatment 1), which exceeded 400 ug/L. Thus release of selenium from this LNP ash can cause water pollution.

Fortification of LNP fly ash with 50% FBC1 ash (treatment 4) and 50% FBC2 ash (treatment 5) had very insignificant effects on the selenium content of leachates (Fig. 10). Selenium is a relatively mobile element. Data show that most selenium from the ash mixtures was lost in a few spikes between 36 and 55 pore volumes. For LNP ash treated with FBC2 ash, selenium concentrations declined to below detection levels in leachates collected near the end of the experiment. Increasing the amounts of FBC2 ash had no effect on the concentrations of selenium in the leachates (Fig. 11). No consistent relationship between the amount of FBC1 ash and concentrations of selenium in leachates was observed (Fig. 12).

Lead concentrations in leachates from 100% LNP fly ash (treatment 1) were routinely lower than

those collected from 100% FBC1 ash (treatment 2) and 100% FBC2 ash (treatment 3) (Fig. 13). However, the highest lead concentration of more than 960 ug/L was observed in a leachate collected from LNP fly ash. 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 (Fig. 13).

Fortification of LNP fly ash with 50% FBC1 ash (treatment 4) and 50% FBC2 ash (treatment 5) resulted in a slight decline in the concentrations of leachable lead (Fig. 14). The maximum concentration of lead in the leachates never exceeded 250 ug/L. Increasing the amount of FBC2 ash in the mix resulted in lowering lead concentrations in the leachate solutions (Fig. 15). No consistent effect of increasing the amount of FBC1 ash on leachability of lead was observed (Fig. 16).

Cadmium concentrations from leachates of all ten treatments rarely exceeded 50 ug/L (Figs. 17 to 20). No consistent differences among ash sources or ash mixtures were apparent for their tendencies to release cadmium to the leaching solutions. 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 incongruous 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.

Barium is a regulated element. Maximum permissible contaminant level for this element in drinking water is 1,000 ug/L. Data in Figures 21 to 24 show that barium concentrations in the leachates rarely exceeded these standards. Leachates collected from 100% FBC1 ash (treatment 2) exceeded 8,000 ug/L. However, leachates collected from 100% LNP fly ash (treatment 1) or 100% FBC2 ash (treatment 3) never exceeded drinking water standards (Fig. 21). When LNP fly ash was amended with FBC1 ash and FBC2 ash, barium concentrations in the leachates never exceeded drinking water standards (Fig. 22). Thus utilization of ash will not be limited by the presence of barium in the ash.

Manganese is a regulated element. 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 100% LNP fly ash (treatment 1) was more than 1000 ug/L (Fig. 25). This high concentration of manganese in the first pore volume of leachate indicates that a part of manganese in this ash The highest was present in the Mn(II) form. manganese concentrations in the leachates from 100% FBC2 ash (treatment 3) exceeded 2,000 ug/L. 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.

Fortification of the LNP fly ash with 50% FBC1 ash (treatment 4) had a significant effect on the manganese content of the leachates (Fig. 26). When LNP ash was fortified with 50% FBC2 ash (treatment 5), manganese concentrations exceeding 4,500 ug/L (4.5 mg/L) were observed in the leachate solution. These data show that manganese was released from the FBC2 ash after 60 pore volumes of leachate passed through. Increasing levels of FBC2 ash resulted in increasing concentrations of manganese in the leachate solutions (Fig. 27). These data suggest that manganese from FBC2 ash can become mobile with a decline in the leachate pH. Data for treatment 9 indicate that total amounts of manganese released by this ash were very small. Although this ash can release manganese to a leaching acidic solution, the data show that the manganese concentration is declining. Therefore, high concentrations of manganese will not be sustained for an extended period of time. Fortification of LNP fly ash with FBC1 ash reduced manganese concentrations in the leachates to insignificant levels (Fig. 28).

Summary and Conclusions

This study evaluated the Ksat of various ash mixes using a constant head permeameter. Samples were uncompacted and had no overburden pressure. Therefore, the results of this study apply to a layer of ash applied to the ground surface with no additional aboveground pressure or only a relatively thin layer of material applied above the ash layer. Results indicate that water will flow through these materials at a moderate to moderately high rate. If these materials become saturated in the field, it appears that swelling may occur, reducing the total porosity. This swelling may reduce the Ksat from that which was determined in the laboratory. Compaction due to machinery or overburden weight may also reduce the Ksat. However, swelling and/or compaction will probably not reduce the Ksat to much lower than 10⁻⁵ or 10⁶ cm/sec.

A number of trace elements were observed after leaching these coal ash mixtures with sulfuric acid and some of those elements exceeded drinking water standards. Arsenic was the first such element that was found in exceedingly high concentrations in the leachates from the LNP fly ash. We also observed that concentrations of arsenic in the leachates can be controlled by developing proper mixtures. Selenium, on the other hand, often exceeded drinking water standards. Unlike arsenic and other trace elements, selenium in ash is not controlled by a precipitation reaction. Thus various combinations of ash had very little effect on selenium concentrations in leachate samples. Use of these ashes in an acid environment may be limited due to the high mobility of selenium. 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. Mixing FBC1 and FBC2 ashes with LNP ash reduced the amount of manganese in leachates, however after 60 pore volumes of leachate the FBC2 ash mixtures released manganese.

References

- Blake, G.R., and K. H. Hartge. 1986. Particle density. p. 377-382. In: Klute, A. (ed). Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. Second Edition. Amer. Soc. of Agron. Madison, WI.
- Hamric, R. 1993. Utilization of CFB ash in reclamation to prevent post-mining acid mine drainage. In: Proceedings, Fourteenth West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV.
- Hill, R.L., and L.D. King. 1982. A permeameter which eliminates boundary flow errors in saturated hydraulic conductivity measurements. Soil Sci. Soc. Am. J. 46:877-880. https://doi.org/10.2136/
- SSSail 1982. 0361 59950 6460 040042x 1986. Hydraulic conductivity and diffusivity: laboratory methods. p. 687-734. In: Klute, A. (ed). Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. Second Edition. Amer. Soc. of Agron. Madison, WI.
 - Schueck, J., M. Dimatteo, B. Scheetz, M. Silsbee. 1996. Water quality imiprovements resulting from FBC ash grounting of buried piles of pyritic materials on a surface coal mine. p

308-320. <u>In</u>: Proceedings, Thirteenth American Society for Surface Mining and Reclamation Conference, 18-23 May 1996, Knoxville, TN.

Knoxville, TN. https://doi.org/10.21000/JASMR96010308

- Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M Smith. 1978. Field and laboratory methods appliable to overburdens and minesoils. EPA-600/2-78-054. U.S. Govt. Printing Office. Washington, D.C.
- Ziemkiewicz, P.F., and J.G. Skousen. 1992. Prevention of acid mine drainage by alkaline addition. Green Lands 22(2): 42-51. West Virginia Mining and Reclamation Association, Charleston, WV.



Fig. 1. Calcium concentrations in leachates generated by leaching various types of 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 various mixtures of fly ashes with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 5 (50% LNP ash and 50% FBC2 ash).



Fig. 3. Calcium concentrations in leachates generated by leaching various mixtures of fly ash and FBC2 ash with sulfuric acid. Treatment 5 (50% LNP ash and 50% FBC2 ash); treatment 9 (90% LNP ash and 10% FBC2 ash); and treatment 10 (75% LNP ash and 25% FBC2 ash).



Fig. 4. Calcium concentrations in leachates generated by leaching various mixtures of fly ash and FBC1 ash with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 6 (25% LNP ash and 75% FBC1 ash); treatment 7 (33% LNP ash and 67% FBC1 ash); and treatment 8 (10% LNP ash and 90% FBC1 ash).



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



Fig. 6. Arsenic concentrations in leachates generated by leaching various mixtures of fly ashes with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 5 (50% LNP ash and 50% FBC2 ash).



Fig. 7. Arsenic concentrations in leachates generated by leaching various mixtures of fly ash and FBC2 ash with sulfuric acid. Treatment 5 (50% LNP ash and 50% FBC2 ash); treatment 9 (90% LNP ash and 10% FBC2 ash); and treatment 10 (75% LNP ash and 25% FBC2 ash).



Fig. 8. Arsenic concentrations in leachates generated by leaching various mixtures of fly ash and FBC1 ash with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 6 (25% LNP ash and 75% FBC1 ash); treatment 7 (33% LNP ash and 67% FBC1 ash); and treatment 8 (10% LNP ash and 90% FBC1 ash).



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

Fig. 10. Selenium concentrations in leachates generated by leaching various mixtures of fly ashes with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 5 (50% LNP ash and 50% FBC2 ash).

Fig. 11. Selenium concentrations in leachates generated by leaching various mixtures of fly ash and FBC2 ash with sulfuric acid. Treatment 5 (50% LNP ash and 50% FBC2 ash); treatment 9 (90% LNP ash and 10% FBC2 ash); and treatment 10 (75% LNP ash and 25% FBC2 ash).

Fig. 12. Selenium concentrations in leachates generated by leaching various mixtures of fly ash and FBC1 ash with sulfuric acid. Treatment 4 (50% LNP fly ash and 50% FBC1 ash); treatment 6 (25% LNP ash and 75% FBC1 ash); treatment 7 (33% LNP ash and 67% FBC1 ash); and treatment 8 (10% LNP ash and 90% FBC1 ash).

SELENIUM (Se)

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

Fig. 14. Lead concentrations in leachates generated by leaching various mixtures of fly ashes with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 5 (50% LNP ash and 50% FBC2 ash).

Fig. 15. Lead concentrations in leachates generated by leaching various mixtures of fly ash and FBC2 ash with sulfuric acid. Treatment 5 (50% LNP ash and 50% FBC2 ash); treatment 9 (90% LNP ash and 10% FBC2 ash); and treatment 10 (75% LNP ash and 25% FBC2 ash).

Fig. 16. Lead concentrations in leachates generated by leaching various mixtures of fly ash and FBC1 ash with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 6 (25% LNP ash and 75% FBC1 ash); treatment 7 (33% LNP ash and 67% FBC1 ash); and treatment 8 (10% LNP ash and 90% FBC1 ash).

Fig. 17. Cadmium concentrations in leachates generated by leaching various types of fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

Fig. 18. Cadmium concentrations in leachates generated by leaching various mixtures of fly ashes with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 5 (50% LNP ash and 50% FBC2 ash).

Fig. 19. Cadmium concentrations in leachates generated by leaching various mixtures of fly ash and FBC2 ash with sulfuric acid. Treatment 5 (50% LNP ash and 50% FBC2 ash); treatment 9 (90% LNP ash and 10% FBC2 ash); and treatment 10 (75% LNP ash and 25% FBC2 ash).

Fig. 21. Barium concentrations in leachates generated by leaching various types of fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

Fig. 22. Barium concentrations in leachates generated by leaching various mixtures of fly ashes with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 5 (50% LNP ash and 50% FBC2 ash).

Fig. 23. Barium concentrations in leachates generated by leaching various mixtures of fly ash and FBC2 ash with sulfuric acid. Treatment 5 (50% LNP ash and 50% FBC2 ash); treatment 9 (90% LNP ash and 10% FBC2 ash); and treatment 10 (75% LNP ash and 25% FBC2 ash).

Fig. 24. Barium concentrations in leachates generated by leaching various mixtures of fly ash and FBC1 ash with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 6 (25% LNP ash and 75% FBC1 ash); treatment 7 (33% LNP ash and 67% FBC1 ash); and treatment 8 (10% LNP ash and 90% FBC1 ash).

Fig. 25. Manganese concentrations in leachates generated by leaching various types of fly ashes with sulfuric acid. Treatment 1 (100% LNP ash); treatment 2 (100% FBC1 ash); and treatment 3 (100% FBC2 ash).

Fig. 26. Manganese concentrations in leachates generated by leaching various mixtures of fly ashes with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 5 (50% LNP ash and 50% FBC2 ash).

Fig. 27. Manganese concentrations in leachates generated by leaching various mixtures of fly ash and FBC2 ash with sulfuric acid. Treatment 5 (50% LNP ash and 50% FBC2 ash); treatment 9 (90% LNP ash and 10% FBC2 ash); and treatment 10 (75% LNP ash and 25% FBC2 ash).

Fig. 28. Manganese concentrations in leachates generated by leaching various mixtures of fly ash and FBC1 ash with sulfuric acid. Treatment 4 (50% LNP ash and 50% FBC1 ash); treatment 6 (25% LNP ash and 75% FBC1 ash); treatment 7 (33% LNP ash and 67% FBC1 ash); and treatment 8 (10% LNP ash and 90% FBC1 ash).