THE REACTION OF ACID MINE DRAINAGE WITH FLY ASH FROM COAL COMBUSTION[1]

by

Ann G. Kim[2]

Abstract: The placement of alkaline fly ash in abandoned, reclaimed or active surface coal mines is intended to reduce the amount of acid mine drainage (AMD) produced at such sites by neutralization, inhibition of acid forming bacteria, encapsulation of the pyrite or water diversion. A continuing concern with this application is the potential release of trace elements from the fly ash when it is placed in contact with AMD. To investigate the possible release of antimony, arsenic, barium, boron, cadmium, chromium, cobalt, copper, lead, nickel, selenium, and zinc from fly ash, a series of column leaching tests were conducted. A one kg fly ash sample, placed in a 5-cm by 1 m acrylic columns, was leached at a nominal rate of 250 mL/d for between 30 and 60 days. The leachant solutions were deionized water, and dilute solutions of sulfuric acid and ferric chloride. Leaching tests have been completed on 28 fly ash samples. Leachate data, analyzed as the mass extracted with respect to the concentration in the solid, indicate that the release of trace elements is variable, with only barium and zinc extracted at greater than 50 pct of the amount present in the original sample. As a comparison, water quality changes have been monitored at three sites where fly ash grout was injected after reclamation to control AMD. When compared before and after grouting, small increases in pH and decreases in acidity at discharge points were observed. Concentrations of trace metals were found to be comparable in treated and untreated areas. When grouted and ungrouted areas were compared, the effect of the fly ash was shown to be localized in the areas of injection. These studies indicated that when fly ash is used as a reagent to control of AMD, the release of trace elements is relatively small.

Additional key words: Coal Combustion By-Products, AMD Treatment, Coal Mine Reclamation

Introduction

Approximately 80 pct of the coal produced in the U.S., is used for electric power generation. Ten to 15% of this amount is recovered as coal combustion by-products (CCB). In 1997, over 100 million st of CCB were produced, and over 70 % was placed in landfills and ponds (ACAA, 1998) Approximately 1.5 million st of CCB are currently being used in mine remediation.

CCB are fly ash, bottom ash, boiler slag and flue gas desulfurization sludge. Fly ash, 60 pct of CCB, is the finely divided residue from the combustion of coal collected by electronic precipitator (ESP) or filter (baghouse). Both Class F ash from bituminous coal and Class C ash from sub-bituminous coal and lignite are non-hazardous materials that are usually alkaline.

In mine reclamation, CCB may impact the discharge of AMD through four possible mechanisms: neutralization, bacterial inhibition, pyrite encapsulation and water diversion (Kim and Cardone, 1997). If the CCB is alkaline, it can neutralize acidic groundwater; and, at a higher pH, bacterial activity is inhibited. A pozzolanic CCB can encapsulate pyrite, isolating it from air and water and preventing the formation of AMD. The deposition of CCB or a CCB grout can also reduce the permeability of mine strata, diverting water away from acid-forming materials.

Fly ash has been tested as a means of at source control for acid mine drainage (AMD) from abandoned or inactive surface and underground coal mines. When deposited in a mine environment, the fly ash could be exposed to a variety of fluids, acidic, neutral and basic, possibly containing high levels of ferric iron. The potential release of trace elements is one of the primary considerations in placement of fly ash underground. In order to characterize the potential effects, the US Department of Energy is conducting a long term column leaching study of the effects of various leachants on fly ashes. The results of this study are compared to water quality results from field experiments.

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[1]Paper presented at the 16th annual Conference of the American society for Surface Mining and Reclamation in Scotsdae, AZ, August 13-19, 1999.

[2]Ann G. Kim is a Physical Scientist Federal Energy Technology Center, Division of Environmental Science and Technology, U. S. Department of Energy, Pittsburgh, PA 15236.

Proceedings America Society of Mining and Reclamation, 1999 pp 111-117
DOI: 10.21000/JASMR99010111

https://doi.org/10.21000/JASMR99010111

Leaching Study

In order to evaluate the potential release of trace elements from CCB in the coal mine environment, samples were leached with solutions approximating the pH and ionic strength of AMD. For comparison, fly ash samples are also leached with deionized water.

Laboratory Parameters

One kg samples of fly ash are placed in 5 cm by 1 m acrylic columns. The 1 eachant solution flows through the column at a nominal rate of 250 mL/day; actual flow rates varied between 158 and 275 mL/d. Leachate samples, collected at 2 to 3 day intervals, are analyzed for pH, acidity and/or alkalinity, ferrous iron, total iron, aluminum, manganese, magnesium, calcium, sodium, potassium, sulfate and the heavy metals arsenic, barium, beryllium, cadmium, cobalt, chromium, copper, nickel, lead, antimony and zinc. (Kim and Sharp; 1995, Kazonich and Kim, 1997). Leaching tests have been completed on 28 samples; results have currently been analyzed for 20 of the samples of which 17 are fly ash samples from PC power plants. Average results in this paper are based on these 17 samples and include only information on the trace elements.

Although seven leachants are used in the study, this paper focuses on the AMD surrogates sulfuric acid (H_2SO_4), pH = 1.2; and ferric chloride ($FeCl_3$ with HCl), pH = 1.95. The results with deionized water (H_2O), pH = 7 are included as the baseline standard. The length of the leaching test varies between 30 and 120 days.

Results

When the results of the leaching tests are averaged, the amount of trace element released from the samples is comparable for all leachants for several trace elements, but varies with the leaching solution for other elements (Table 1). The amount of arsenic, beryllium, cadmium, lead and antimony is approximately equal for the three leachants. Barium is most soluble in the ferric chloride solution, and cobalt, chromium, copper, lead, nickel and zinc are apparently more soluble in sulfuric acid.

Comparing the amount leached from the fly ash for individual samples, the variation appears to be related to the individual element. For example, the amount of barium leached by water and sulfuric acid is low for almost all samples, independent of the concentration of barium in the solid (Figure 1). In ferric chloride, the amount leached does vary with the concentration in the solid. The amount of zinc leached in sulfuric acid, water, and ferric chloride appears to be unrelated to the concentration in the solid ash (Figure 2).

Table 1. Total Trace Elements: Average for All PC Fly Ash Samples, mg/kg

Element	H_2O	$FeCl_3$	H_2SO_4
Arsenic	3.93	4.67	3.34
Barium	20.39	64.30	4.35
Beryllium	0.00	0.45	0.87
Cadmium	0.03		0.20
Cobalt	0.02	0.86	1.85
Chromium	0.71	BDL	4.30
Copper	BDL	1.01	8.20
Nickel	BDL	0.39	4.82
Lead	0.03	BDL	0.37
Antimony	0.06	0.16	0.05
Selenium	0.39	1.43	1.01
Zinc	BDL	7.85	26.97

BDL = Below Detection Limit

When the amount of trace element released is related to the concentration in the solid, less than 10 % by weight of most elements are released during leaching. More than 10 pct by weight is released by sulfuric acid only for beryllium, selenium and zinc (Table 2). Selenium is the only element released at greater than 10 pct in ferric chloride. Tables 1 and 2 are not directly comparable because of the use of different averaging routines.

Table 2. Relative Trace Element: Average for All PC Fly Ash Samples, % by weight

Element	H_2O	$FeCl_3$	H_2SO_4
Arsenic	2.97	2.81	2.82
Barium	1.32	6.43	0.51
Beryllium	0.03	6.47	11.80
Cadmium	0.09	1.97	1.65
Cobalt	0.05	3.63	6.71
Chromium	0.26		2.88
Copper			8.13
Nickel		1.73	4.82
Lead	0.01		0.69
Antimony			
Selenium	5.21	16.43	12.68
Zinc		0.71	31.61

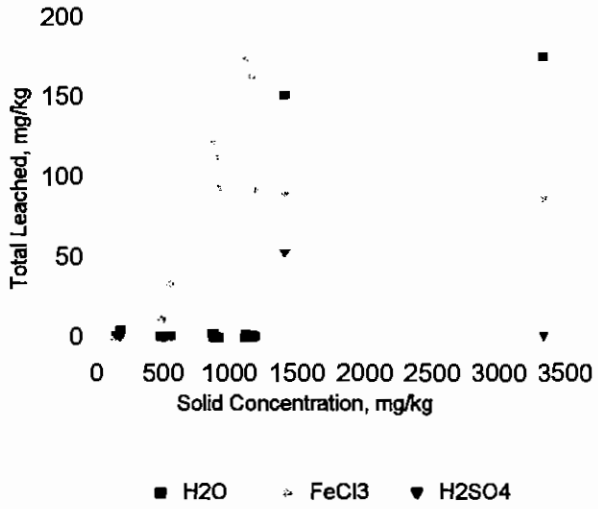

Figure 1. Total amount of barium leached (mg.kg) versus concentration in the solid (mg/kg).

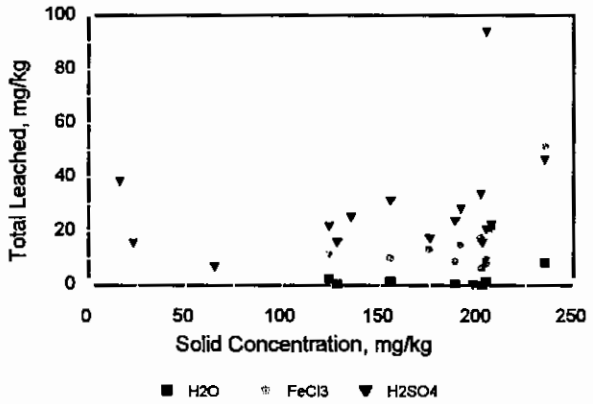

Figure 2. Total amount(mg/kg) of zinc leached from fly ash versus concentration in the solid (mg/kg).

On a volumetric basis, the average concentration of arsenic, beryllium, cadmium, lead and antimony is equivalent in all three leachant solutions (Table 3). Barium appears to be more soluble in ferric chloride, and the average concentration cobalt, chromium, nickel and zinc is apparently greater in sulfuric acid.

The data from the leaching study indicate that the trace element and leachant combination may determine the amount of an element released from the fly ash. The trace elements in fly ash are believed to occur as substitutions within a mineral matrix, i.e., silicate, clay, etc. In a sequential leaching study of coal, the USGS relates leachant/element specificity to mineralogical association (Palmer et al, 1999). Variations observed in this study may also be related to the mineral associations

Table 3. Average Concentration of Trace Element in Leachate, mg/L.

Element	H_2O	$FeCl_3$	H_2SO_4
Arsenic	0.454	0.692	0.354
Barium	2.358	9.537	0.461
Beryllium	0.000	0.067	0.092
Cadmium	0.003	BDL	0.021
Cobalt	0.003	0.128	0.196
Chromium	0.082	BDL	0.456
Copper	BDL	0.150	0.868
Nickel	BDL	0.058	0.511
Lead	0.003	BDL	0.039
Antimony	0.007	0.024	0.005
Selenium	0.045	0.212	0.107
Zinc	BDL	1.165	2.857

BDL = Below Detection Limit

Based on the average behavior of the 17 fly ashes from PC boilers in this leaching study, the amount of a trace element released by AMD surrogates is relatively low. Although the relative amount of a particular element released may vary for an individual fly ash, it is unlikely to constitute a significant hazard.

Field Studies

To evaluate the effect of fly ash injection on AMD, water quality was monitored at three reclaimed surface mines (Bognanni, Fran and Pierce), where a grout prepared from fly ash, water, and lime was injected into subsurface areas believed to be zones of acid production (Ackman et al., 1996).

Water samples were collected at outflows, from boreholes within injection areas, and from boreholes in ungrouted control areas. These were analyzed for pH, acidity/alkalinity; the concentrations of the trace elements, arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), copper (Cu), cobalt (Co), chromium (Cr), lead (Pb), nickel (Ni), and zinc (Zn) were also determined. Water samples were collected for a year or more before the injection of the fly ash and for a year or more after grout injection. In addition to the before and

after comparison, inflow and discharge samples were also compared, as were samples from the grout injection areas and from ungrouted control areas.

Site Descriptions

The three sites described below were all surface coal mines that had been reclaimed with conventional methods; all had developed acid seeps after reclamation.

The Bognanni site is a 14.6 ha reclaimed strip mine in Greene County, PA. The depth of buried spoil ranges between 5 and 15 m, averaging about 10 m, under 2 m or less of vegetated cover. If it is assumed that the porosity of the material is 20 %, the pore volume in the 10 m of spoil above the pit floor is estimated as 7,500 m^3. Terrain conductivity indicted that groundwater flow at the site was from east (the area of a buried highwall) to west through the reclaimed area to a seep approximately 70 m south of the site boundary. Thirty-four wells were used for injection, with the majority of these located in a 1.2-ha central section of the reclaimed area. Nine monitoring wells are located in the grouted area and four wells are in spoil areas that were unaffected by grout injection. Three additional monitoring points are located outside the injection area: Well A, located at the edge of the site, is considered representative of ground water, Well C, near the buried highwall, is in the area where water enters the mined area. The primary discharge point is Seep A. The seep is outside the target area and drains portions of the reclaimed mine that were unaffected by grout injection. In this paper, monitoring points are identified as: incoming water (Well A); water as it enters the reclaimed portion of the site (Well C); water in the ungrouted control area (Spoil (0); and water in the grouted area before (Spoil (B) and after (Spoil (A) grouting. Values for Well A, Well C, and Spoil (0) are averages of all samples from the beginning of the project. For Spoil (B) and Spoil (A), the values are averages for the appropriate time period.

The Fran site is a 15 ha reclaimed strip mine in Clinton County, northern Pennsylvania. Discrete piles of tipple refuse or pit cleanings are believed to be buried beneath spoil of pyritic shale and sandstone (Schueck et al., 1996). Geophysical techniques were used to estimate the location of the buried refuse and the direction of water flow. Infiltrating precipitation is believed to flow through the area and then leave the site either through a seep or through fractures. Forty-two monitoring wells were drilled on and adjacent to the site. Water samples were also collected at the surface discharge 66 m south of the site. For this site, values are averages of all samples for the ungrouted area (Spoil), for the area where grout was placed (Injection), for the area that would have been affected by water from the injection area (Downdip), and for the seep (Discharge 1) and fractured area (Discharge 2).

The Pierce site is a 6 ha section of a 32 ha reclaimed surface mine in Upshur County, West Virginia (Hawkins et al., 1991). The spoil contained part of the Lower Kittanning coal seam, gray carbonaceous shale and a gray sandstone. Samples of water entering the site were obtained from a well (B-1) located in the undisturbed high wall to the northwest of the injection area. Within the injection area, 15 monitoring wells were drilled and cased with PVC pipe. Water samples were also obtained at a discharge point at the edge of the reclaimed area. At this site, monitoring wells are grouped as Inflow, Injection for the grouting area, Downdip for the area receiving water from the grouted area, Spoil for the ungrouted area, and Seep for the discharge. The values for each set are averaged for: 1989, pre-grouting; 1990, immediate post-grouting; and 1995, later post grouting.

Materials

At the Bognanni site, the fly ash grout was prepared with water from the AMD treatment system and AMD treatment sludge or lime waste, consisting of about 30 pct unused lime. Three fly ashes were used, two from conventional power plants and one fluidized bed combustion (FBC) ash. The amount of fly ash injected into a single hole varied between 0.4 and 41 m^3 with an average of 5.5 m^3. On a volume basis, fly ash constituted less than 6 pct of the injected grout; 192 m^3 of fly ash is equivalent to less than 5 pct of the estimated pore volume in the 1.2 ha section.

At the Fran site, a grout of FBC ash and water (1 m^3/800 L) was injected into pods of refuse in order to divert water away from the acid-producing materials. The same grout mixture, which formed a low-strength cement, was used to cover piles of coal refuse and to seal fractures in the pit floor. Grout was pumped to refusal in 650 holes, averaging 3 to 9 m in depth. The 3440 m^3 of injected grout is the equivalent to 4 % of the total volume of voids at the site.

The grout used at the Pierce site was a mixture of 375 g of cement and 750 g of fly ash per L of water. A total of 380 m^3 of grout was injected through 62 cased wells, primarily in two areas near the buried highwall. The volume of injected grout is comparable to less than 1% of the estimated void volume at the site.

Water Quality

The water entering the Bognanni site (Well A) had an average pH of 7 and contained 2 ppm total iron, 1 ppm aluminum, 35 ppm sulfate, less than 1 ppm barium, and approximately.0 1 ppm each cobalt, chromium, nickel, antimony and zinc. The pH of the water decreased to 5 where it entered the reclaimed area (Well C), then decreased to almost 3 within the spoil. Prior to grouting, the water at the seep had a pH of 3.2.

After grouting, the average pH at wells in the grouted area increased by 0.5 pH units, and pH of water at the seep increased to 3.3. Trace element analysis indicated that barium (Ba), present in the incoming water, was not detected at the seep (Figure 3). Only the concentrations of cobalt (Co), nickel (Ni), and zinc (Zn) were greater than 1 mg/L. In the grouted area, there was little difference in the concentrations of these before and after grouting. At the seep, the concentrations of these metals were comparable to the concentrations in the ungrouted control area.

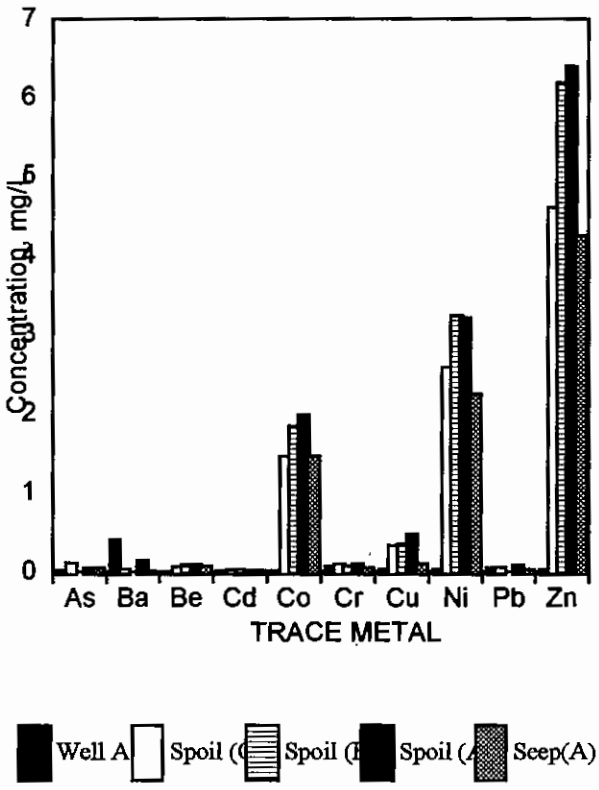

Figure 3. Average concentration of trace elements in water samples from Bognanni site, mg/L.

At the Pierce site, water samples were obtained monthly prior to grouting (1989) and immediately after grouting (1990). During 1995, water samples were collected at 3 month intervals. The average pH of the water in the injection area decreased in the year after injection, but had increased when the water was sampled five years later. Similar changes in average pH were observed in the samples from areas downdip of the injection area and at the discharge point. However, the water entering the site (inflow) and in the ungrouted spoil area also had a higher average pH in 1995. Acidity, measured as ppm of $CaCO_3$, decreased in the injection area, as well as in the inflow and discharge samples. In the untreated spoil area, acidity increased. Although water quality improved at the discharge point, a pH less than 4 and an acidity of approximately 100 ppm indicate continued release of AMD. Trace element concentrations, determined in 1995, were higher in the injection, downdip and discharge samples than in inflow or ungrouted spoil samples (Figure 4). However, only the concentrations of cobalt, nickel and zinc exceeded 0.2 mg/L; all values were acceptable with respect to freshwater aquatic life criteria.

Table 4. Average Post-injection Concentration of Trace Elements, Pierce Site, mg/L.

Element	Inflow	Injection	Downdip	Spoil	Outflow
Arsenic	BDL	BDL	BDL	BDL	BDL
Barium	0.029	0.013	0.022	0.034	0.018
Beryllium	BDL	0.012	0.016	BDL	BDL
Cadmium	BDL	BDL	0.016	BDL	BDL
Cobalt	0.021	0.327	0.173	0.064	0.113
Chromium	0.016	BDL	0.020	0.015	BDL
Copper	0.011	BDL	0.101	0.017	BDL
Nickel	0.063	0.455	0.272	0.096	0.163
Lead	BDL	BDL	0.112	BDL	BDL
Antimony	BDL	0.119	BDL	0.117	BDL
Selenium	BDL	BDL	BDL	BDL	BDL
Zinc	0.119	1.210	0.458	0.228	0.321

BDL = Below Detection Level

At the Fran site, water samples were collected on a fairly regular basis before and after grouting. These are grouped as before (1990), immediately after (1992) and recent (1994). The pH increased in samples from the injection area, the downdip areas, and from two discharge areas. The pH of water in the untreated spoil also increased immediately after injection, but then decreased. The acidity decreased in all areas, except the

untreated spoil. The pH of the discharges at less than 3 and acidity exceeding 2000 ppm indicate that the site continues to produce a significant amount of AMD. Average trace element data for 1994 indicates that higher concentrations of arsenic, cobalt, copper, nickel and zinc were detected in the injection area (Figure 10). However, in downdip and discharge samples, the concentration of these elements were closer to background levels determined in the samples from the ungrouted spoil.

Table 5. Average Post-injection Concentration of Trace Elements, Fran Site, mg/L.

Element	Spoil	Injection	Downdip	D1	D2
Arsenic	0.246	1.466	BDL	BDL	0.241
Barium	BDL	0.024	0.027	BDL	BDL
Beryllium	0.043	0.207	0.079	0.039	0.052
Cadmium	0.019	0.161	0.067	BDL	0.050
Cobalt	0.972	2.906	1.203	1.578	1.272
Chromium	0.208	0.805	0.259	0.136	0.202
Copper	1.215	4.582	1.043	0.587	1.195
Nickel	2.012	7.390	2.164	1.961	2.484
Lead	BDL	0.285	BDL	0.104	BDL
Antimony	BDL	BDL	BDL	BDL	BDL
Selenium	BDL	BDL	BDL	BDL	BDL
Zinc	3.135	16.222	3.538	3.263	4.409

Field Study Results

At three sites, differences in water quality between areas injected with fly ash and areas of untreated spoil were indicative of localized effects, particularly a decrease in acidity and an increase in pH. Water samples taken from spoil areas before and after grouting also indicated transient increases in alkalinity. In the area of the monitoring wells, an increase in pH and a decrease in acidity and ferrous iron concentration were observed after fly ash grouting. These changes may be related to decreased production of AMD, either due to encapsulation of the pyrite, to water diversion or to alkaline addition. Although either mechanism could be responsible for this local effect, long term improvement in water quality are more likely to be due to pyrite encapsulation or water diversion. Changes in water quality at the discharges, even though small, indicate the potential effectiveness of the method.

Comparison of the water quality between the spoil and the discharge indicated that the fly ash grout produced a measurable change at the discharge point, even though the amount of fly ash injected and the volume of subsurface area it could have affected are relatively small. The magnitude of the improvement may signify that the relatively small size of the test sections at all three sites was a controlling factor in continued AMD discharge. Also, the subsurface distribution of the grout within an unknown hydrologic network may not have been uniform, and may have allowed the continued production of AMD within the treated areas.

The presence of trace elements, particularly nickel and zinc, appears to be significant in the discharge. However, comparison to the spoil areas indicates that the concentration of these elements is not related to the addition of fly ash. The concentration of copper, nickel and zinc in the untreated spoil and in the spoil before grouting exceed the criteria for the preservation of freshwater aquatic life. The change in the average concentration of these elements after grouting is less than 0.2 ppm.

Summary

The laboratory leaching studies indicate that several trace elements , particularly barium and zinc, may be released from the fly ashes tested upon exposure to AMD, but that the amount is relatively small. The data from the leaching tests also indicate that the mobilization of trace elements from CCB is not a simple function based on pH or the concentration in the solid.

The field studies also indicate that when CCB is used to control AMD from inactive coal mines, there is no evidence that trace element release should be considered a potential problem. However, water quality analysis at the sites monitored show that consistent and long term improvement may require larger volumes of CCB and a more efficient method of application.

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