

# The Release of Base Metals During Acidic Leaching of Fly Ash

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## **ABSTRACT**

Since 1996, over 100 million tons of combustion by-products have been generated by U.S. coal burning power plants each year.<sup>1</sup> Typically, about 1/4 of that total is used for purposes such as cement/concrete, structural fill, wall board and other products and applications. The remaining coal combustion by-products (CCB's) must be temporarily or permanently stored. CCB's are sometimes placed in inactive surface or underground mines, where they may react with naturally occurring fluids such as rain, organic-contaminated runoff, and acid mine drainage. The Federal Energy Technology Center of the United States Department of Energy is investigating the reactions of CCB's with various lixivants in a series of column leaching tests. Seven 1-kg samples of each fly ash are placed in individual 5-cm diameter by 1-meter long acrylic columns. The columns are leached at an average rate of 200 mL/day for 30 to 90 days with seven different lixivants. Lixivants include deionized water, artificial ground water, synthetic precipitation, and dilute solutions of acetic acid, ferric chloride, sulfuric acid and a common base. The leachate is analyzed for pH, acidity or alkalinity, aluminum, calcium, iron, magnesium, manganese, potassium, sodium and 12 trace metals. Column leaching tests have been completed on 32 different samples and are beginning on another set of four samples. The results of some completed leaching tests are presented and analyzed.

## **INTRODUCTION**

In 1997, about one billion tons of coal was consumed for generation of electrical power in the United States. Between 6 and 9% of the coal burned by utilities is recovered as fly ash. Thirty million short tons of fly ash were produced in 1970, approximately 50 million in 1980, and 60 million tons in 1996.<sup>1</sup> Fly ash is currently being considered as a means of control for acid mine drainage from abandoned surface and underground mines. Placing alkaline fly ash in abandoned mines can improve water quality by neutralizing drainage acidity and decreasing dissolved contaminants. However, the fly ash could be exposed to a variety of inorganic and organic acids, possibly releasing high levels of contained metals. It is important that potential problems such as the dissolution of toxic metals in the fly ash be evaluated.

In order to predict the reactions of fly ash with ambient liquids, the United States Department of Energy has initiated a long term column leaching study of the effects of various environmental

lixivants on fly ash. Of particular interest is the relationship between changes in pH of the leachate and the release of RCRA metals from the fly ash. The leaching procedure utilizes seven lixivants ranging from strongly acidic (pH 1) to strongly basic (pH 11). The procedure attempts to simulate naturally occurring liquids such as ground water, acid rain, landfill leachate, etc. Deionized water is used as a baseline lixiviant for the study. The discussion section compares the reactions of two alkaline fly ash samples with 3 acidic lixivants and reports the leachate analyses obtained. Until now, this study has concentrated on fly ash because it was the largest component of CCB's and consequently the biggest disposal problem. Tightening of EPA air quality regulations in recent years has increased the amount of FGD sludge produced and magnified the problems associated with this CCB component (because of the difficulties in handling sludge). In the future, mixtures of FGD sludge and fly ash (and/or other waste products) will be tested to assess this growing disposal problem and possibly utilize the high alkalinity of FGD sludge.

## **EQUIPMENT AND PROCEDURES**

The fly ash leaching system formerly utilized gravity feed of liquid to the columns. Reservoirs of lixiviant were positioned 7 meters above the fly ash columns with lines, delivery manifolds, and flow regulators connecting four columns containing different fly ash samples. A recent move into new facilities required transition to peristaltic pumps at lower flowrates. Nominal flow rates went from 250 mL per day per column with the gravity system to about 130 mL/day/column with the pumps. Actual flow rates varied between plus or minus 100 percent for the gravity system<sup>3</sup> to about plus or minus 5 percent for the pumps. Simultaneous tests with gravity and pumps before the move showed no differences in their chemistries, but pump tests had to be extended to accommodate the lower flowrate. Each fly ash sample is leached from 30 to 90 days. Leachate samples are collected each day for the first week and at 2 to 3 day intervals thereafter. Samples are analyzed for pH, acidity and/or alkalinity, aluminum, calcium, iron, magnesium, manganese, potassium, sodium, sulfate and the heavy metals: antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel and zinc. The pump system maintains the ability to simultaneously test four different samples by seven lixivants using 28 individual columns, seven reservoirs and appropriate distribution equipment.

The columns are constructed of 1 meter sections of clear acrylic 2 inch pipe with an approximate volume of 2 liters. Threaded PVC pipe caps close each end and have 1/4 inch fittings tapped into them for lixiviant inflow and leachate outflow. Columns are loaded by putting ten grams of glass wool into an empty column and pushing it against the bottom cap. The fly ash is then poured into the column, and another 10 grams of glass wool is inserted on top. The top cap is affixed and tightened, and the sealed column is hung vertically from a rack. The column is then connected to the lixiviant delivery system.

The lixivants for the column leaching test are: sulfuric acid ( $\text{H}_2\text{SO}_4$ ), pH = 1.2; ferric chloride ( $\text{FeCl}_3$  with 3 ml of concentrated HCl added per 20 liter batch to prevent iron precipitation), pH = 2.0; acetic acid ( $\text{CH}_3\text{COOH}$ ), pH = 2.9; synthetic precipitation (deionized water adjusted to pH 4.2 with 60/40  $\text{H}_2\text{SO}_4/\text{HNO}_3$ )<sup>2</sup>; synthetic ground water<sup>3</sup>, pH = 6.7; sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), pH = 11.1; and deionized water ( $\text{H}_2\text{O}$ ), pH = 6. Two fly ash samples were compared for this report. The first (A) was a very alkaline material typical of fly ash from high efficiency electric power generation plants. The second fly ash sample (B) was a less alkaline material, also from a

commercial power plant. Both of these high density ash materials filled about ½ of the column (approximately 1 liter sample volume) with a 1.0 kg sample.

## DISCUSSION

A large amount of data has been generated by this continuing investigation (more than 12 Mb of leachate analyses) but this paper will only compare samples A and B from local electric utility plants. The major difference in the two fly ash samples was the initial alkalinity. The A sample produced a strongly alkaline solution (pH 12) when mixed with water, while the B sample produced a weaker solution (pH 9). Plots of pH vs time for A are shown in figure 1 and comparable plots for B are shown in figure 2. For clarity, only 3 acid lixivants are plotted on each graph: sulfuric acid (pH 1), acetic acid (pH 3), and synthetic precipitation (“acid rain” pH 4).

Figures 1 and 2 show a rapid drop in pH for the sulfuric and acetic acid leaches after an initial high pH period. This indicates that all of the alkaline materials have been neutralized. This probably also means that lime was added to the coal or flue gases for air pollution control purposes. If basic compounds were an integral part of the fly ash, a shrinking core reaction mechanism would have produced a shallower pH decay curve. The rapid pH change observed in figure 1 and 2 probably indicates neutralization of entrained particles or surface coatings of alkaline materials. In both figures 1 and 2, the acid rain was unable to lower the pH during the course of the test. The acid rain may neutralize the samples over time, but as this lixiviant is only about 1/1000th the strength of the other two acids, the time frame would be extremely long.

The sulfuric and acetic acid leaching results presented here might be considered a worst case scenario. In large deposits, fly ash often forms a thick interface of gelatinous or hard material which acts like an impermeable barrier. The result is that physical limitations to the movement of liquids may stop the reaction before the release of toxic metals occurs.

The increase in copper concentrations in the leachates shown in figures 3 and 4 roughly coincides with the rapid fall of pH discussed above. Copper was chosen as an indicator for the graphs because it can be analyzed down to very low levels and there is usually some copper (50 to 150 ppm) in most fly ash samples. As copper is soluble in an acid solution, it usually shows up in the acidic leachates if present. Fly ash A had low copper levels (less than the solid detection limit of 25ppm). Although this resulted in low concentrations of copper in the leachates of A, the rise in copper still coincided with the fall of pH (shown in figures 5 and 7). Figures 6 and 8 show the same relationship for copper and pH for fly ash B except at higher copper leachate concentrations.

Also, all of the other metals observed had the same inverse pH/concentration relationship as copper except for arsenic, which had decreasing concentrations with decreasing pH. The inverse relationship of pH to concentration for most metals can not be used to predict the extraction of metals from the fly ash. Most fly ash samples release only few percent of the contained metals into the leachates. In fact, only a few metals (such as zinc) will sometimes dissolve more than 50% into the leachate. Variations occur because the reactions of any fly ash with lixiviant is determined by the particular solution chemistry of the mixture. For example, one fly ash tested readily released barium when acidified with acetic acid but did not release barium into sulfuric acid leachates (probably because of reprecipitation of insoluble  $\text{BaSO}_4$ ).

## SUMMARY

Plots of concentration versus time and pH versus time show a strong inverse relationship between leachate pH and concentration of most metals in the leachate.

In the very alkaline fly ash A, most soluble metals were not released into the sulfuric acid leachates until neutralization occurred nearly two months after starting the test. The acetic acid leach of A neutralized the fly ash earlier than the sulfuric acid but this was probably the result of precipitation of sulfates in the sulfuric acid leach which restricted acid additions (precipitates were observed in the transparent columns).

Weakly alkaline fly ash B reacted typically with acids, releasing almost no metals while the leachate solutions were still basic. Fly ash B reacted similarly to A when acidified, releasing metals just after the leachates turned acidic. Sulfuric acid neutralized fly ash B slightly earlier than acetic acid because of a slightly higher concentration and a slightly higher flowrate. Calculations of the milliequivalents of acid added before neutralization occurred are nearly identical for sulfuric and acetic leaches of fly ash B.

## REFERENCES

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2. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. Methods for Evaluating Solid Waste: Vol I, Section C, Laboratory Manual, Physical/Chemical Methods, Method 1312, 1990, 31 pp.
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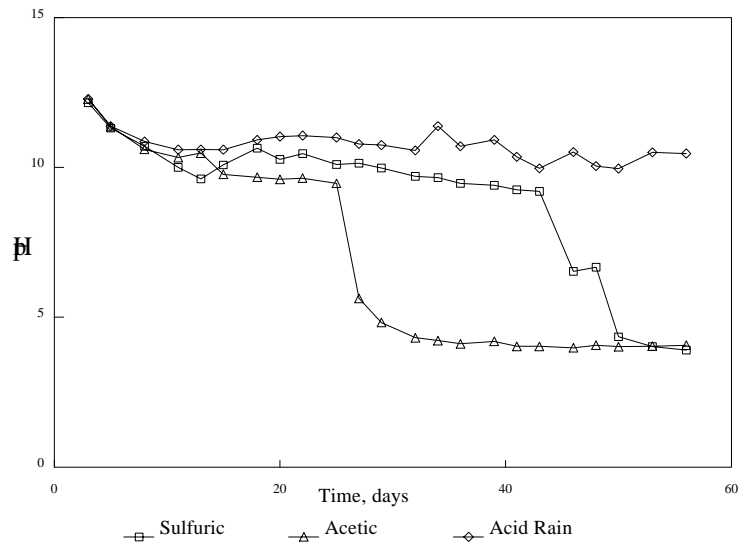


Fig.1 pH of A with 3 lixiviants

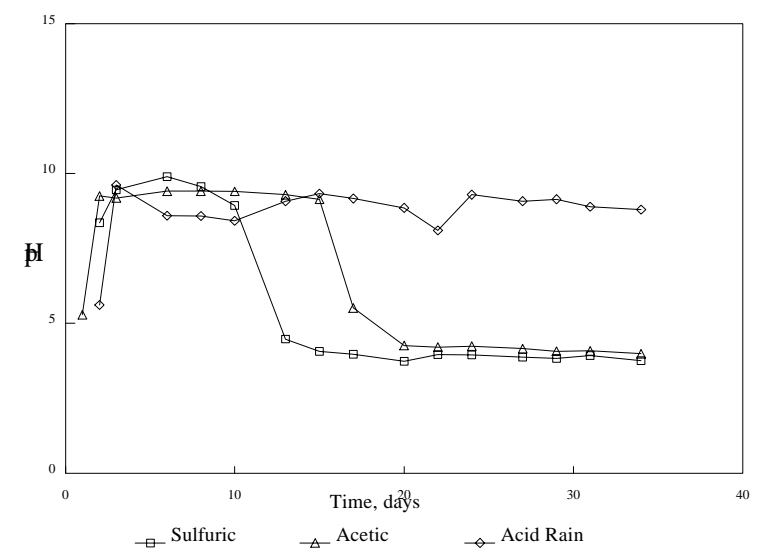


Fig.2 pH of B with 3 lixiviants

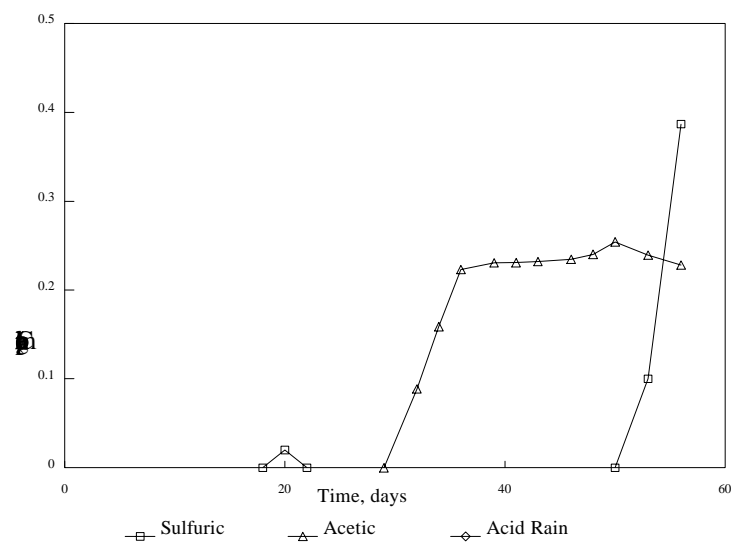


Fig.3 Copper in 3 leaches of A

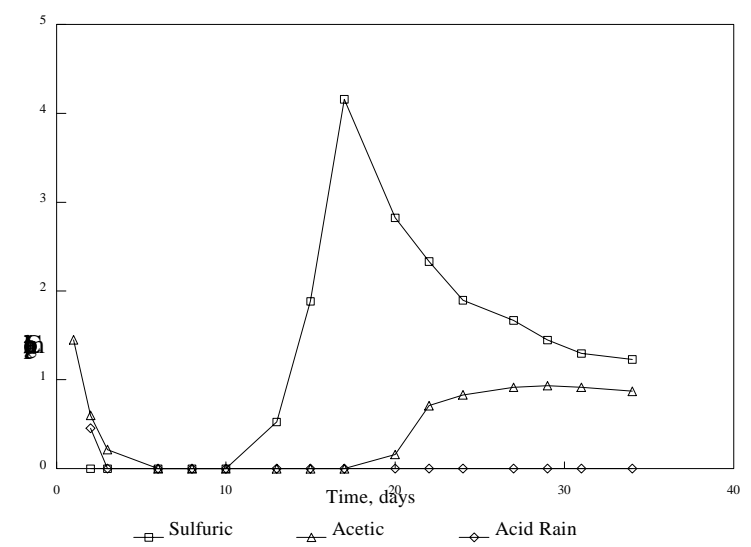


Fig.4 Copper in 3 leaches of B

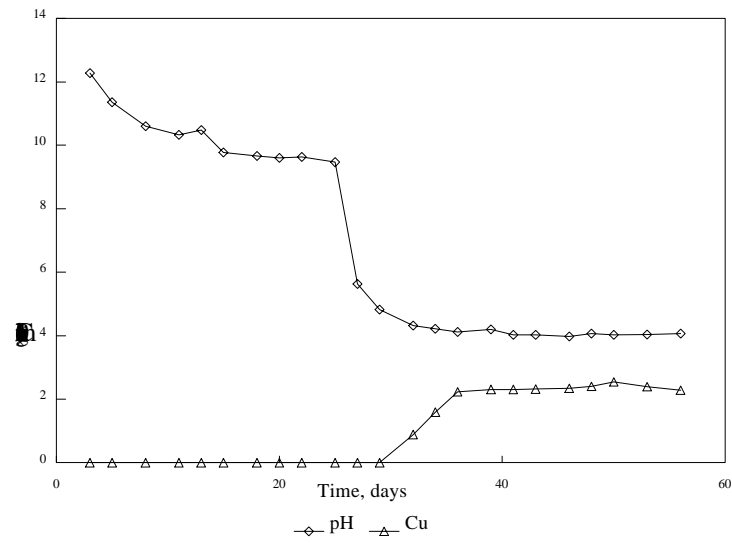


Fig.5 Cu vs pH for Acetic leach of A

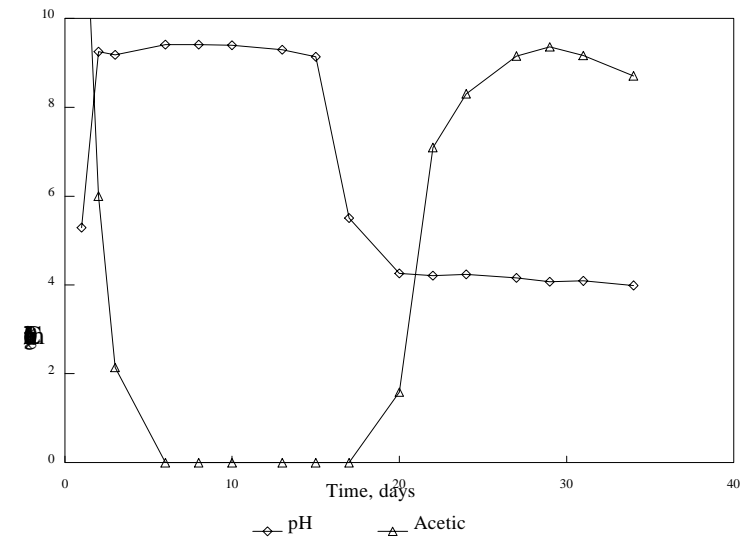


Fig.6 Cu vs pH for Acetic Leach of B

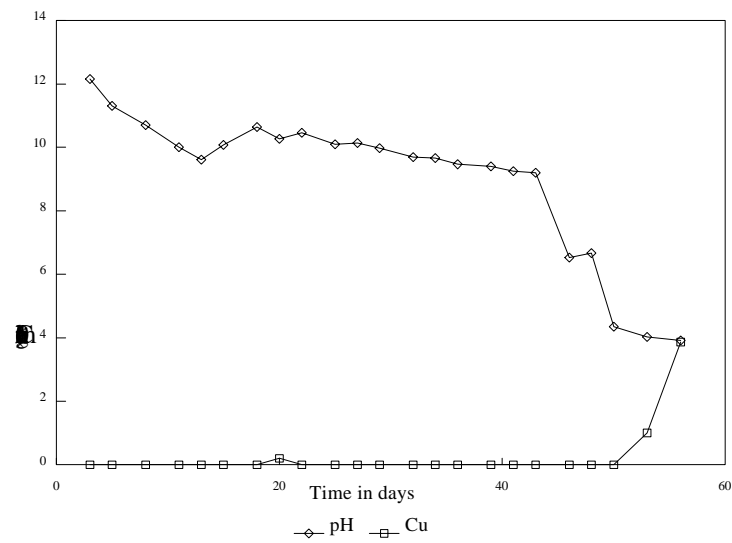


Fig.7 Cu vs pH for Sulfuric Leach of A

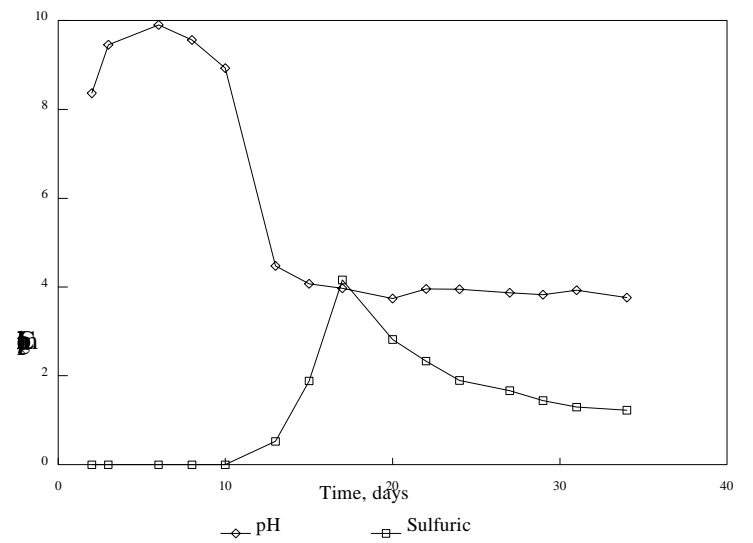


Fig.8 Cu vs pH for Sulfuric Leach of B