LEACHING BEHAVIOR OF FLY-ASH PILES:
THE PHENOMENON OF DELAYED RISE
IN TOXIC CONCENTRATIONS

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ABSTRACT

Large fly-ash piles from coal-burning power plant utilities are generally viewed as innocuous solid wastes, because leachate generated by contact of rain water with fresh fly-ash particles is often very low in dissolved toxic concentrations. This view may be erroneous. With increased percolation of rain water, the concentrations of Cu, Zn, As, Cr, and other toxics in the run-off leachate may increase significantly, often over an order of magnitude. Fly-ash management practices must take this effect into consideration to avoid long-term groundwater contamination. The study reported here also shows that concentrations of dissolved non-toxic species–namely calcium, sodium, or potassium may be used as surrogate indicators to forewarn the impending rise in concentrations of various toxic species. Mass balance analysis on zinc shows that heavy metals distributed in various matrices of the fly-ash particles (glass, magnetic spinel and quartz) are quite accessible for complete dissolution in rain water.

INTRODUCTION

Fly ash, the combustion by-product of coal-fired power stations is, volume wise, the single largest solid waste produced by any industry. Every year, the electric utilities in the United States alone dispose of over sixty million tons of fly ash in landfills or ponds [1]. The quality of run-off leachate produced by percolation of rain water through fly-ash piles is a cause for concern, because, first, the presence of various dissolved toxic inorganics, such as arsenate, chromate, copper (II), lead

(II), etc., in the leachates from huge fly-ash piles poses a significant long-term threat to contaminate groundwaters and aquifiers; and, second, a drop in rain-water pH (acid rain) to as low as less than 4.0 in many places around the world is likely to worsen the leaching problem by reducing the buffer capacity of the fly ash sooner. Surprisingly, no long-term data (for 10 years or so) on the quality of leachates from existing fly-ash piles are yet available. Results from the laboratory-run leaching tests in accordance with the procedure of U.S. Environmental Protection Agency for solid wastes are misleading because they provide only the total amount of leachable toxics and do not account for the dynamic nature of the leaching process where the rain water is continuously percolating through the stationary fly-ash piles [2]. On the other hand, representative pilot scale studies have been slow to produce definitive results: the fly-ash test cell in the Montour Plant site of Pennsylvania Power and Light Co. has not produced any significant understanding about the long-term leaching behavior of fly-ash piles even after five years of operation [3].

To help address this gap in current understanding, we carried out an accelerated leaching test. Five grams of fly ash from a power plant of Pennsylvania Power and Light Co. were progressively leached by stirring in beakers for thirty minutes with 200 ml batches of fresh deionized water at pH = 4.0, which functions as an acid-rain simulant, in accordance with reference methods of the National Bureau of Standard [4]. Conceptually, we moved the fixed amount of fly ash through a pool of water in stages where fly ash and water where in equilibrium with each other at every stage. Various dissolved species were analyzed at every stage. Dilute nitric acid (0.02N) was used for pH adjustment. The average composition of the fly ash used in the study is shown in Table 1. This simple accelerated leaching test has two key advantages: 1) unlike the U.S. Environmental Protection Agency's EP (Extraction Procedure) Toxicity Test [2] and Recirculation Column Test [5], our procedure mimics the interactions between water and fly ash in a fly-ash pile; and 2) since the ratio of the volume of rain water to the mass (or volume) of fly ash can be kept very high, the concentration profiles as well as the sequence of leaching of various contaminants of interest can be obtained quite readily. Under actual site conditions, it may take well over a decade depending on the amount of rainfall and fly-ash composition to observe the leaching pattern. Hjelmar [6] and Wasay [7] conducted both column and batch experiments using fly ash from coal-based thermal power plants. However, comparison of our results with theirs is difficult due to very different experimental conditions.

METAL ANALYSIS

The collected leachates were stored in Nalgene polyethylene bottles for analyses of various metal concentrations. Chemical analyses were performed on an atomic absorption spectrophotometer (Perkin Elmer Model 2380) with flame

Table 1. Properties of Fly Ash from Montour Plant, Pennsylvania

Average Chemical Composition of Bulk Constituents	Toxic Metal Contents	Physical Properties
Silicon oxide 48.6%	Arsenic 275 mg/kg	Bulk density 1.43 gm/cm^3
Aluminum oxide 25.1%	Chromium 160 mg/kg	Mean particle size 0.03m
Iron oxide 14.5%	Copper 230 mg/kg	Volumetric porosity 40%
Calcium oxide 2.1%	Zinc 115 mg/kg	
Manganese oxide 0.62%	Lead 110 mg/kg	
Sodium oxide 0.27%	Nickel 150 mg/kg	
Potassium oxide 2.3%		
Magnesium oxide 0.05%		

attachment or graphite furnace accessory, depending upon the analyte concentrations. The methods used for each metal analysis were those approved by U.S. EPA [8], including acid digestion methods for total metal determinations. All arsenic analyses were based on the graphite furnace. An electrodeless discharge lamp at operation current 8 mA with analysis wavelength at 193.7 nm was used for arsenic determinations. A spectral bandpass of 0.7 nm was selected and argon gas stopped during atomization step. The pyrolysis and atomization temperatures were 1200°C and 2500°C, respectively. The duration for the latter was four seconds. Instrumental running conditions were changed accordingly for the determinations of the different elements. Routine quality assurance protocols were used [8]. Briefly, they include analysis of matrix-matched standards at the beginning and end of sample series, replicates, and spiked samples. The standard solutions for calibrations were made daily from the stock solution. These were evaluated to assess detection limits, precision, accuracy, and matrix workability. Sulfate concentrations were conveniently determined on a Dionex ion chromatograph (Model 4500i). pH meters were calibrated using two buffer solutions. Depending on the pH of the samples to be measured, the buffers were pH 4 and pH 7, or pH 7 and pH 10. The higher pH-value buffer solution was rechecked after each fifteen measurements. If the measured value was not within 0.1 pH units (1%) of the accepted value, the data for the previously measured samples were rejected. If the measured value was within 0.1 pH units of the accepted value, the data for the previously measured samples were accepted. Following the quality check, the pH meter was restandardized using the two buffered solutions.

RESULTS AND DISCUSSION

Figures 1a through 1g show a composite diagram of concentration profiles of dissolved toxic (As, Cu, Zn) and non-toxic (Ca, K, $SO_4 2-$) species, along with pH, during the leaching test as a function of pore volume of simulated rain water added. The leaching test was repeated for the second time to double-check the elution behaviors of dissolved zinc. The following observations were noteworthy:

- Unlike the toxic species, calcium, potassium, and sulfate leach out rapidly and exhibit a monotonic drop in concentrations;
- Only after calcium, potassium, and sulfate concentrations have dropped significantly, does arsenic appear in the leachate. Copper and zinc appear in the leachate long afterwards;
- There remains a generic similarity in the leaching patterns of arsenic, copper, and zinc in the fact that their concentrations are low in the beginning followed by a steep rise and subsequent drop to almost zero, so resembling a bell-shaped distribution. Leaching of chromate follows the same pattern (not included here) and appears to lie between arsenic and zinc. The period of high concentrations of toxics in fly-ash leachates may span well over several years depending on the amount of rainfall.

Although not intuitively expected, the experimental results suggest that aged fly ash which has been in contact with a significant volume of percolating rain water poses more threat toward groundwater contamination than fresh fly ash. On-site verification in regard to the nature of variation of dissolved toxic concentrations against time or pore volumes of leachate collected will take an inordinate length of time, probably decades. However, the field study with a prototype fly-ash cell at the Montour plant site of Pennsylvania Power and Light Co. [3], shows that although toxic concentrations in the leachate collected from the bottom of the test cell are extremely low even after three years of operation, the pore waters collected from the intermediate depths show higher concentrations for many of the toxic species. This observation is in qualitative agreement with our experimental results, and suggests that at a later date, with further passage of rain water through the test cell, high dissolved concentrations of toxics will appear at the bottom of the pile.

A mass balance study was conducted with respect to zinc, which remains distributed primarily in glass and magnetic spinel matrices of the fly ash [9]. Total zinc content (115 mg/kg) in fly-ash was determined by vigorously agitating 2.0 grams of fly-ash in 500 ml of 2 percent HCl plus 2 percent HNO_3 for fourteen days. The accelerated leaching test with rain water at pH = 4.0 accounted for almost 100 percent of zinc present in the fly ash, suggesting that trace metals in the different matrices are quite accessible for dissolution by rain water. The discrepancy between total copper associated with fly-ash particles (Table 1) and the cumulative amount of copper in the leachate (Figure 1b) may be due to the
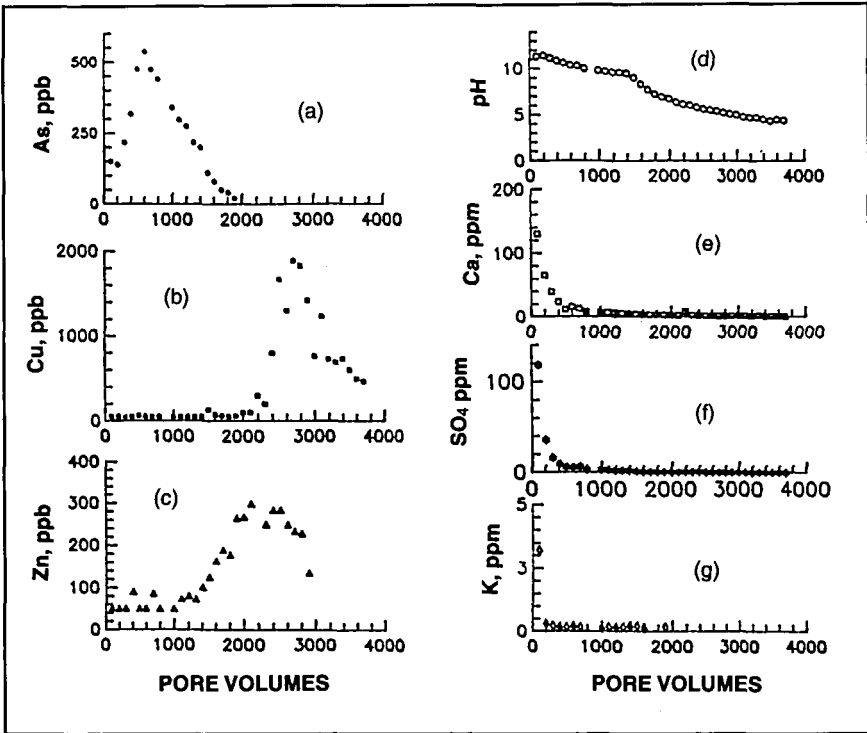
Figure 1. A complete diagram showing leaching behaviors (concentration vs. pore volumes of water) of various dissolved constituents in fly-ash.
(1 gm of fly-ash particle was found to have approximately 0.4 ml of pore volume.)

variability of elemental content in the fly ash. Further work on the subject is in progress. A mechanistic explanation is provided below in support of the results presented in Figures 1a through 1g.

Rapid dissolutions of calcium and potassium indicate that these elements exist primarily on the surface as oxides and sulfates. This is a low calcium (less than 10%) fly-ash with high silica content, and, like the one studied by Hulett et al. [9], the glass matrix is primarily of siliceous type. Since arsenic (V) in the fly-ash is formed by condensation of relatively volatile arsenic oxide, As_2O_5, on the surface of fly-ash particles in the electro-static precipitators, it is readily accessible for dissolution as oxy-anions, namely, $H_2AsO_4.$, $HAsO_42-$, AsO_43-. However, high concentration of calcium (or barium which is chemically very similar to calcium) in the leachate tends to maintain low arsenic concentration during the early period because of extremely low solubility products of calcium or barium arsenates. During this period, both calcium and sulfate concentrations drop rapidly along

with alkali metals (Na and K) with a slight drop in pH at the end of which arsenic concentration in the leachate increases sharply. As more and more arsenic is dissolved, the dissolution rate decreases due to reduced liquid-solid interfacial area causing a drop in concentration till all the arsenic oxides are essentially dissolved from the surface.

For zinc and copper, hydroxide is the controlling solid phase and they are present in all three phases of fly-ash particles [9]. Since the pH remains above neutral for a prolonged time, they appear long after arsenic. It is possible that cation-exchange capacities of hydrous Fe(III) and Al(III) oxides present in fly-ash matrices also retard the mobility of Zn(II) and Cu(II) through sorption.

CONCLUSIONS

This study provides three distinct observations which might aid in formulating guidelines and assessing the groundwater-contamination hazard in conjunction with long-term fly-ash management. First, although fly ashes are viewed as innocuous fine particles with fairly high porosity, the toxic constituents generally appear in the leachate only after a significant volume of rain water has percolated through the ash pile. Second, concentration profiles of alkali- and alkaline-earth metal ions (Ca^{2+}, Na^+, K^+) in the leachate may be used as surrogate indicators for the impending breakthroughs of other toxic species because most of the toxic species (arsenic, chromium, molybdenum, copper, and other heavy metals) will appear only after calcium, sodium, or potassium have been almost completely eluted. Third, although toxic elements in the fly-ash particles are distributed in three different phases, namely glass (rich in silica), mullite-quartz (rich in Al and silica), and magnetic spinel (rich in iron) [9], they appear to be sufficiently accessible for complete dissolution during the leaching process.

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