

ELEMENTAL CHARACTERIZATION OF COAL ASH LEACHATES

by

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INTRODUCTION

Over 50 million tons of coal ash are produced annually in North America [Warren and Dudas, 1989]. Technological improvements in air pollution control have decreased stack emissions but have also increased contaminant concentrations in the ash of coal-fired boiler applications. The leaching of heavy metals and other elements during regulatory tests may cause coal ash to be classified as hazardous waste, complicating land disposal. The hazardous nature of coal ash remains unclear because current toxicity tests fail to characterize effectively the elemental distribution and chemical solubility of trace metals in the landfill environment. Leaching characteristics of ash samples can be investigated with various laboratory extraction procedures in association with multi-elemental techniques (e.g. Neutron Activation Analysis and Inductively Coupled Plasma Atomic Emission Spectroscopy). Such methods provide a more thorough analysis of coal ash leaching dynamics than the regulatory assessments can demonstrate. Experimental results may assist operators of coal-fired boiler industries in selecting coal types and operating conditions to minimize the leaching of environmentally key elements.

RESEARCH OBJECTIVES

Recent state environmental agency concern about the classification of coal-fired boiler technology wastes may result in substantial cost increases for waste disposal. The objective of this research study is to investigate the hazardous potential of industrial coal-fired boiler technology wastes. A laboratory leaching procedure known as a water-batch extraction was performed on fly ash samples. Additionally, through the use of multi-elemental analytical techniques, the fly ash and corresponding coal samples were characterized. In this way, the elemental leaching dynamics and relationships of elemental levels between coal, ash, and leachates have been examined.

COAL ASH CHARACTERISTICS

Certain physical and chemical properties undoubtedly play key roles in ash-water interactions. Coal fly ash is the partially combusted solid waste particulates of small enough diameter to be entrained in flue gas. One study determined 63% of the examined fly ash particles were in the range of 2-50 μm in diameter [El-Mogazi et al., 1988]. Forms of potentially toxic metals are selectively deposited on the outer surface of coal ash particles [Hopke, 1983]. Such surface components are not bound to the internal silicate matrix and therefore are readily leachable [Hopke, 1983]. Three major matrices compose fly ash, silicate glass, mullite quartz, and magnetic spinel [El-Mogazi et al., 1988]. Investigations have found the magnetic matrix to be particularly important in the release of toxic elements [El-Mogazi et al., 1988].

SAMPLE DESCRIPTION

The coal, and fly ash samples for this study were provided by the United States Army Construction Engineering Research Lab (USACERL). The samples originated from Abbott Power Plant (Champaign, Illinois), Chanute Air Force Base (Rantoul, Illinois), and the Rock Island Arsenal (Rock Island, Illinois).

REGULATORY CONSIDERATIONS

The current regulatory benchmark test designed to identify wastes likely to leach hazardous concentrations of toxins is the toxicity characteristic leaching procedure (TCLP). If extract concentrations of certain elements or organic compounds exceed regulatory limits the waste is classified as hazardous. The eight regulated elements are As, Ba, Cd, Cr, Hg, Pb, Se, and Ag. The TCLP replaced the existing extraction-procedure (EP) toxicity test standard in 1990, which was inadequate for organic compounds [Bishop, 1990]. With the implementation of the TCLP, the regulatory focus is now on

environmental impact, behavior, and leachability of contaminants instead of on contaminant levels in waste [Bishop, 1990]. The TCLP uses acetic acid as the extractant and is run for 18 hours in a closed vessel. Acetic acid is a common product of the anaerobic degradation processes found in municipal solid waste landfills. The test, however, fails to effectively characterize the elemental distribution and chemical solubility of coal ash in an ash monofill.

Waste stabilization may be used to reduce leaching in conjunction with land disposal. Such processes attempt to immobilize a waste within an inert matrix. Examples include using Portland Cement, specialized polymers, and plastics as binding agents but such processes are often cost prohibitive [Wentz, 1989]. The TCLP may be implemented following stabilization to gauge the success of the such processes [Biedry, 1990].

LEACHING TECHNIQUES

Previous workers have employed a variety of methods to examine coal ash leaching. Techniques have ranged from laboratory scale extractions to monitoring large outdoor test plots of ash. Some researchers used aggressive, 'worst-case' approaches trying to leach as much from the ash as possible. Such methods most likely involve leaching conditions which would never be encountered naturally.

The preferred strategy is to construct a leaching scheme which accelerates the natural behavior of ash buried in a landfill [Buchholz, 1993]. The EP and TCLP regulatory leaching tests were not specifically designed to measure the behavior and toxicity of coal ash in an ash monofill. The use of acetic acid as an extractant in the above tests may not be representative of the leaching conditions found in an ash monofill.

For this study, the long term washing of coal ash in an ash monofill was simulated in the laboratory using a water (deionized) batch extraction technique. The deionized water used was a simulated acid-rain solution with low levels of nitric and sulfuric acid added. The resulting pH was a mildly aggressive 5.2. The liquid-to-solid (LS) ratios were slowly increased, using short intervals initially to better characterize the first stages. Samples for each LS ratio were prepared over consecutive days with orbital agitation periods of approximately 24 hours in between.

ELEMENTAL ANALYSIS

Thorough analysis of trace elements present in coal, ash and leachate samples usually involves the use of atomic emission spectroscopy. Multi-elemental techniques in which many elements can be analyzed simultaneously are desirable. Elemental concentrations in the coal and ash samples were determined using Neutron Activation Analysis (NAA). Furthermore, the leachates produced by the laboratory extraction methods were characterized with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Quality assurance and quality control were maintained through the use of standard reference materials, procedure blanks and appropriate trace metal laboratory procedures such selecting ultra-pure reagents.

ELEMENTAL COMPOSITION OF COAL AND FLY ASH SAMPLES

Figures 1 and 2 depict the levels of the TCLP elements in the coal and fly ash samples, respectively. Cadmium and levels were not determined for the coal and ash samples but were examined in the leachate analysis. Levels of Hg and Ag are below detection limits for all three varieties of coal and ash. Ba and Cr are the most dominant TCLP elements in the coal and ash samples. Concentrations are elevated in the fly ash compared to the coal as expected, most likely due to the high surface area to volume ratio differences.

ELEMENTAL COMPOSITION OF LEACHATES

Levels of Ag (MDL = 8 ppb), As (MDL = 280 ppb), Cd (MDL = 24 ppb), Cr (MDL = 18 ppb), Hg (MDL = 40 ppb), Pb (MDL = 51 ppb) and Se (MDL = 490 ppb) were below method detection limits (MDL) for all LS ratios. Be, Cu, Fe, Sb, Sn, Ti, and Tl levels were also below detection limits for all samples. The MDL is defined as the minimum concentration of a substance that can be identified, measured, and reported with a 99% confidence of a greater-than-zero concentration. Therefore, of the TCLP elements, only Ba was found at significant levels. Figure 3 depicts the Barium leaching pattern. The detectable elements with the highest levels in the leachates included, in descending order, S, Ca, Na, K, B, Si, Mg, Al, Sr, Mo, Li, Ba, V, Cr, Zn, Mn, Co, Ni, and P. Figure 4, depicts the leaching pattern for boron which is somewhat common for elements susceptible to quick initial leaching with decreasing levels thereafter. In contrast, the Ba pattern for the Abbott ash (Figure 3) shows increasing levels after reaching an apparent minimum. This may be explained by the outer layers of the ash matrices having been washed off thereby exposing more barium to the leaching solution.

DISCUSSION AND CONCLUSIONS

Bowen (1966) reported average boron levels in soil to be approximately 10 ppm. Elevated levels of boron in leachates may be of environmental interest. El Mogazi et al. (1988) described a coal ash which leached boron levels toxic to plants. It should be stressed that slightly elevated levels of naturally occurring elements may not result in readily apparent effects, but such levels may be toxic to soil microbial communities and surface vegetation.

The coal fly ash varieties examined in this study apparently are not likely to leach high concentrations of TCLP elements when disposed of in an ash monofill. High levels of sulfur would be expected to leach quite readily. Space limitations in this preprint prohibit the discussion of other, possibly environmentally significant leaching patterns of elements such as Al, V, Co and Ni.

CONTINUING RESEARCH AND ACKNOWLEDGMENTS

The research presented above is a small part of a larger project involving 40-element characterizations of three coal varieties, 40-element characterizations of corresponding fly and bottom ash samples, and 32-element characterizations of water batch and selective-reagent sequential extractions of the fly and bottom ash. The sequential technique employed was developed by Tessier et al. (1979). Selective reagents were used to partition trace elements into chemical forms likely to be released under various environmental conditions. A rough idea of the chemical speciation of trace metals can be inferred from the analysis. The chemical partitions are readily exchangeable, bound to carbonates or surface oxides, bound to iron and manganese oxides, and bound to organic matter. [Tessier, et al., 1979]. The use of sequential techniques provides the researcher with a significant improvement in characterization over the regulatory extraction tests.

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Figure 1
TCLP ELEMENTS IN COAL SAMPLES

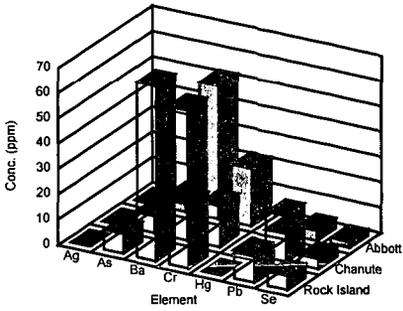


Figure 2
TCLP ELEMENTS IN FLY ASH SAMPLES

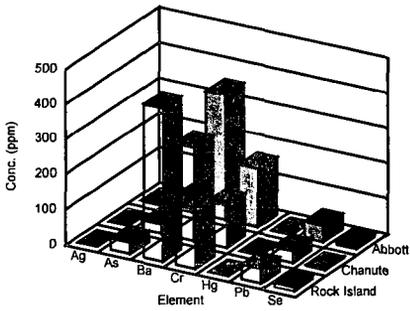


Figure 3 Barium (Ba) MDL = 0.002 ppm
Water Batch Extraction - Fly Ash

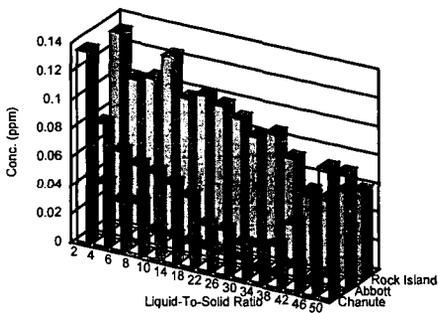


Figure 4 Boron (B) MDL = 0.030 ppm
Water Batch Extraction - Fly Ash

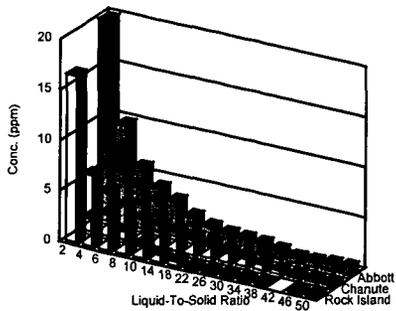


Figure 5 Sulfur (S) MDL = 0.090 ppm
Water Batch Extraction - Fly Ash

