Fluid Extraction of Metals from Coal Fly Ash: Geochemical Simulation of Natural Leaching

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FLUID EXTRACTION OF METALS FROM FLY ASH:
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Abstract

The objective of this study was to develop data that are broadly applicable to the release of trace metals from fly ash, and to quantify the rate of release as a function of the composition of the ash. Thirty-two samples of Class F fly ash from pulverized coal combustion boilers were leached with seven leaching solutions simulating natural fluids. The leachate was analyzed for 21 cations that were major, minor, or trace constituents of the ash. The rate at which metal ions are released from fly ash is a complex function of the alkalinity of the ash, the distribution of elements in various chemical compounds or minerals, and characteristics of the leachant solution, particularly its pH. In this experiment, the release of cations is defined as a solubility function with respect to the volume of leachant solution. During the first leaching interval, the ashes alkalinity is neutralized, and the release of metal ions, except for Ca, is relatively low. At some point, the release of metal ions increases by one or more orders of magnitude, and remains at that level, until the readily soluble ions are released. Then the elemental release decreases, again by one or more orders of magnitude.

The solubility of an element is defined by the three volumetric functions and the median volumes for those functions. The N LF (neutralization leaching function) is describes the release of cations until the sample is neutralized (dM_N/dV_N, meq/L). The RLF (rapid leaching function) rate is the average slope of cumulative curve between inflection points (dM_L/dV_L, meq/L). The

TLF (terminal leaching function) is the average slope of cumulative curve after 2nd inflection point (dM_T/dV_T, meq/L). In a natural setting, if the infiltration rate is known (L/d), the time dependent release of the elements can be estimated. The results of this study show that most cations in fly ash are only slightly soluble, that elements, other than arsenic, tend to be most soluble in acid solutions, and that non-silicates tend to be more soluble than silicates.

PREFACE

The project on which this dissertation is based was begun at the Pittsburgh Research Center of the US Bureau of Mines. It was originally intended to address environmental issues from the use of fly ash to remediate acid mine drainage. In 1995, when the Environmental Technology Division of the Bureau was transferred to the National Energy Technology Laboratory (NETL) of the U.S. Department of Energy, the project was broadened to include environmental exposure of coal combustion by-products (CCB) to natural fluids in a variety of applications. During the execution of the project, 48 samples were subjected to leaching in seven leaching fluids for as long as six months. As Research Supervisor/Team leader, the general execution of the project was my responsibility; I designed the project and analyzed the leaching data.

However, a project of this magnitude is not the work of one person. I wish to acknowledge the contributions of personnel at the Bureau of Mines and at the Department of Energy to its completion: Robert Kleinmann, Director of the Environmental Technology Division; Frederick Sharp (retired), George Kazonich, Andrew Kociban, Joseph Slivon (retired), Ethyl Burse and Michael Dahlberg who have been responsible at various times for the daily operation of the Column Leaching Laboratory; Willisha Davidson, summer research associate, and Robert Thompson of Parsons Analytical Laboratory for the microwave digestion and analysis of the fly ash samples; Peter Hesbach and Steven Lamey (retired) who collected the information on leaching methods; Bernard Kenny of the NETL library who located copies of all the methods and articles that I asked for, Maurice Deul (retired)and Robert Chaiken (retired), supervisors and supporters, for the opportunities to do good research.

I also wish to express my gratitude to my family and friends for their unfailing support and encouragement. My daughters, Katherine Beiber, Jody Kim and Kerry Kim, by their achievements, reinforced my commitment to continued education; and my husband, Paul Kim, took up the slack in our daily lives so that I could concentrate on writing this dissertation.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

In 1999, over 1 billion metric tons of coal were mined in the US, and 90% (854 million mt) was used to generate electricity (EIA, 2001). Over 50% of the electricity generated in the U.S. is produced by coal burning power plants (Figure 1). In spite of increasing interest in using natural gas as the fuel for new power generation, coal continues to be the dominant source of electricity in the U.S. (Figure 2).

Coal and Coal Combustion By-Products in Energy Production

Coal is classified as a fossil fuel, preserved organic matter that can be burned to produce energy. In addition to combustible organics, coal and other fossil fuels, contain a variable proportion of non-combustible material. In an average year, 10 to 15% of coal burned is recovered by some post combustion collection system. These materials are collectively referred to as fossil fuel combustion wastes (FFCW)[1] by the Environmental Protection Agency (EPA) and as coal combustion products (CCP) by the utility industry and ash marketers. The Department of Energy (DOE) and other federal agencies identify them as coal combustion by-products (CCB) or coal utilization by-products (CUB) which become products when utilized and wastes when disposed.

The CCB are primarily the inorganic residue from coal; they contain iron (Fe), aluminum (Al), magnesium (Mg), manganese (Mn), calcium (Ca), potassium (K), sodium (Na), and silica (Si), and any carbon that was not consumed during combustion. CCB also contain less than 1% of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), selenium (Se) and zinc (Zn). These

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[1] Appendix A contains a list of abbreviations and acronyms.

elements, generally referred to as heavy metals or trace elements are variously considered essential nutrients, toxic elements, or priority pollutants. Most of these elements are believed to have some environmental or public health consequences. The extent to which they can be released from the residues of coal combustion by naturally occurring fluids affects the suitability of CCB for various beneficial uses, like bulk fill and mine remediation.

Due to the large quantity of CCB generated annually and the escalating cost of landfills, there is increased interest in finding new and profitable uses for this material. To reduce costs and to limit the need for off-site disposal, many power producers are actively marketing CCB for a variety of applications, including cement/concrete, structural fill, road base, waste stabilization and agriculture. However, a continuing concern is the potential release of trace elements when the CCB are exposed to environmental fluids such as acid rain, groundwater or acid mine drainage. The U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) has had a research program to promote increased utilization of CCB, particularly large volume uses like mine backfill; the study reported here is a significant part of that program.

Problem Definition

The inorganic portion of coal is composed of various elements in a variety of mineral forms. During combustion, these elements may volatilize, oxidize, react with other elements, undergo heat dependent rearrangement of the mineral lattice or change in physical form. Post combustion cooling will also have an effect on the final form and composition of an ash particle. Many of the elements contained in ash are considered health or environmental risks; however, the magnitude of the risk from release of elements from CCB is not well quantified. In many applications, CCB are exposed to natural fluids, such as acid rain, groundwater, and acid mine drainage. Although there have been numerous studies on the release of trace elements from coal ash, many of these have been restricted to a particular ash under particular conditions. The rate of release of various elements from CCB and the conditions that control solubility have not been quantified in generally applicable terms.

Objective of this Study

The objective of this study was to develop data that are broadly applicable to the problem of the release of trace metals from fly ash and to quantify the release as a function of the composition of the ash.

To that end certain experimental conditions were imposed on the study. First, the sample population must be relatively large and random in order to encompass the inherent variability of the material. The study must involve a long term column leaching experiment to simulate natural conditions, to determine variations in rate with changes in chemical composition and to allow for the development of secondary reactions. The sample size must be sufficiently large to eliminate any problems due to the non-homogeneous material. The study was originally applied to reaction of ash with AMD, but it was broadened to include other leaching fluids. The leachant solutions are synthetic surrogates for naturally occurring fluids, such as acid rain and landfill leachate, and cover a broad pH range.

The objective of this study is to determine solubility of trace elements in coal fly ash as a function of the natural alkalinity of the ash, as a function of leachant pH, and as a function of the concentration of an element in the non-silicate portion of the ash concentration as opposed to the total concentration in the solid. This data are used to develop a quantitative function that relates the release of trace elements to the alkalinity of the ash, the soluble concentration, as well as to fluid volume.

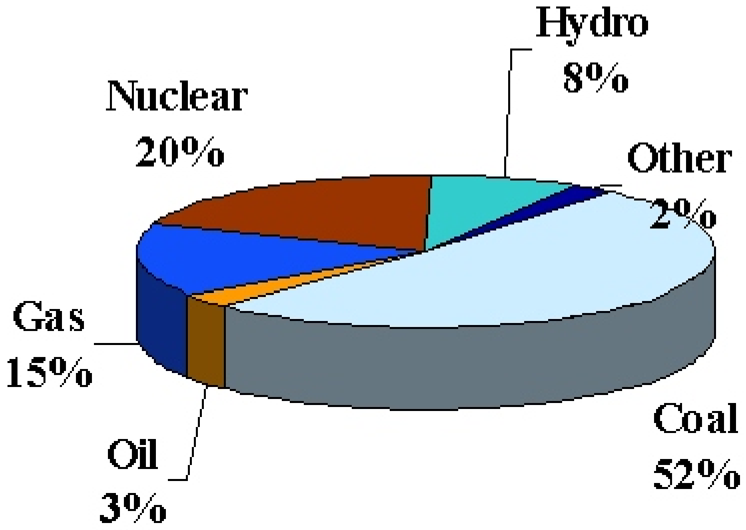
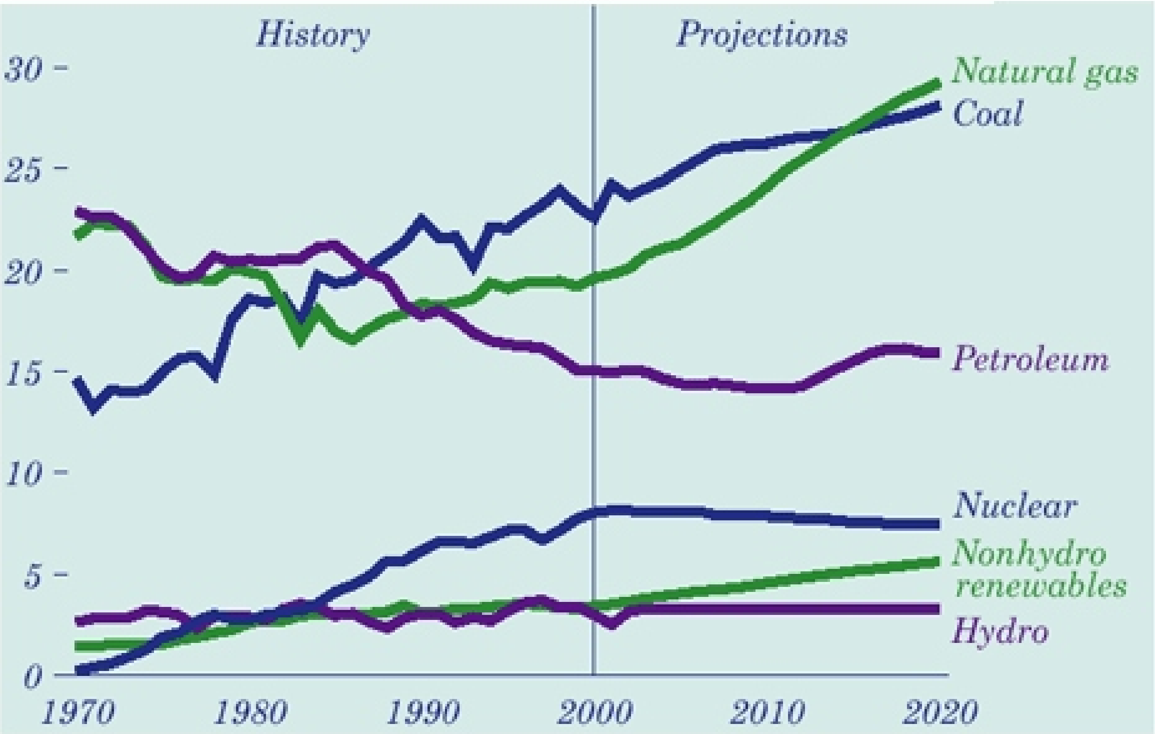


Figure 1. Distribution of electric power generation by fuel. Source: U.S. Department of Energy, Energy Information Agency: Electric Power Annual, V.1, Fig.5, 2001.



History: Energy Information Administration, *Annual Energy Review 2000*, DOE/EIA-0384(2000) (Washington, DC, August 2001). **Projections:** Tables A1 and A18.

Figure 2. Coal use for the generation of electricity is projected to grow until 2020. Source: Energy Information Agency, U.S. department of Energy, Fig. 6., Annual Energy Review, 2000.

Chapter 2

Background

Ash is the inorganic particulate residue of combustion; it may be produced from coal or from other fuels, such as pet coke or biomass. Coal combustion by-products (CCB) are the residues from coal combustion and include materials that are not considered ash.

Types of CCB

In an average year, 10 to 15% of the coal burned to generate electricity in pulverized coal (PC) boilers is recovered as CCB, in the form of fly ash, bottom ash, boiler slag and flue gas desulfurization (FGD) material. These materials are produced in different parts of a coal fired boiler (Figure3). Bottom ash is the heavier material that falls to the bottom of the furnace and is removed as non-molten particles. Boiler slag is molten material that drains to the bottom of wet-bottom furnaces and is discharged to a water filled pit where it cools to form glassy particles, resembling sand. Fly ash is the finely divided residue from the combustion of coal collected by a particulate collection devise, usually an electronic precipitator (ESP) or fabric filter (baghouse). The FGD material is produced by processes to control sulfur emissions, such as wet scrubbers, spray dryers, sorbent injection. It is primarily calcium sulfite or calcium sulfate.

Fly ash is also classified by the source of the coal. According to ASTM C618 (ASTM, 1992), class C ash is the residue from subbituminous coals and lignites. Class F ash is produced from bituminous coals. The sum of silicon, aluminum, and iron oxides must exceed 70.0 % in class F ashes and 50.0 % in class C ashes. Typical composition of class F and class C ashes is given in Table 1. A major difference is the much higher concentration of Ca in class C ashes.

The combustion system also influences the ash characteristics. Pulverized coal firing is the dominant combustion technology for generation of electricity. Since the rate of combustion is controlled by the particle surface area, pulverized coal, ground to a nominal 50 μm diameter burns completely within one to 2 seconds. Temperatures in a PC boiler average 1200 °C, with maximum temperature in the range of 1500 to 2000 °C. Due to the small fuel particle size, most of the ash in PC boilers is fly ash (CIBO, 1997).

In fluidized bed combustion (FBC), fuel is burned in a bed of hot incombustible solid particles suspended in upward flowing air. The temperature is usually maintained between 800 and 900 °C. Limestone, injected into the bed for sulfur capture, eliminates the need for a downstream FGD unit. In FBC fly ash, typically collected by an ESP or baghouse, the concentration of CaO may exceed 40 %, due to the injection of limestone sorbent (CIBO, 1997). Although FBC combustion systems are becoming more common, PC combustion is presently the dominant system used for coal-fired electric power generation.

Annual CCB Production

In 1966, the first year for which data are available, fly ash and bottom ash totaled 25.2 million st (Figure 4) and 3.1 million st were utilized (12%). By 1973, the amount produced had almost doubled, but only 16% was utilized. In the next 15 years, CCB production was between 50 and 60 million st of which 27 % was utilized. Between 1988, when FGD material was included, and 1994, annual CCB production averaged 86 million st (ACAA, 1996). In 1999, the last year for which data are currently available, 107 million st of CCB were produced, including 62.7 million st of fly ash, 16.9 million st of bottom ash, 2.8 million st of boiler slag and 24.6 million st of FGD material (ACAA, 2000).

CCB Utilization

With increased production of CCB, there has been increased interest in utilization. Revenue generated from the sale of CCB is almost all profit, and if the avoided disposal cost is included, CCB sales are financially attractive. Utilization of CCB also preserves other resources, and as a replacement for cement clinker, it reduces the generation of CO_2. A primary driver for the increased utilization of CCB is decreasing landfill capacity. Often space for new landfills is not available near power plants, and the time, effort and money required to permit a new landfill is often considered cost prohibitive.

In spite of the interest in increased utilization, the amount of CCB used has remained constant at approximately 30 %. Half of the fly ash utilized is used in cement and concrete (Table 2). In other countries, a much higher proportion of CCB, from 50 % in Australia to more than 60 % in Finland, and 100 % in parts of Europe (Sloss, 1999).

In a report to Congress (US DOE, 1994), prepared for the U.S. Department of Energy, it was noted that increased use of CCB would produce economic and environmental benefits. These would include reduced solid waste disposal, reduced use of natural resources, and reduced energy consumption and reduced CO_2 emissions in cement production. Although major barriers to increased utilization in the US include inadequate data and inefficient information transfer, inadequate specifications and lack of promotional programs, the most serious barrier is an attitudinal one. CCB are frequently perceived as a waste, and one that poses an environmental danger. The CCB contain the inorganic elements originally present in the coal, and the most frequently cited hazard is the potential release of heavy metals when they are exposed to surface or ground water. Although cases of environmental damage have been reported near CCB disposal sites, there has been a lack of scientifically compelling evidence to settle the question (Kim et al, 2001). There have been a number of leaching studies of CCB, but most dealt with a single ash or particular conditions. This study addressed the need for a broad, multi-sample study conducted by independent third party researchers.

Table 1. Typical major element composition of Class F and Class C fly ashes, wt%.

Component	**Class F**	**Class C**
SiO_2	52	31
Al_2O_3	24	17
FeO	14	5
CaO	3	30
MgO	2	7
SO_3	<1	3
TiO_2	1	1
K_2O	3	<1

Table 2. CCB Utilization, % of amount generated, in 1999 based on data from the American Coal Ash Association (ACAA, 2000)

Use	**Fly Ash**	**Bottom Ash**	**Slag**	**FGD**[1]
Cement/Concrete/Grout	15.9	4.1	<1	1.1
Cement clinker	2.0	1.0	0.0	0.0
Flowable Fill	1.2	<1	0.0	0.0
Structural Fills	5.1	8.3	1.7	2.4
Road Base	1.9	6.5	<1	<1
Soil Modification	<1	<1	<1	<1
Mineral Filler	<1	<1	<1	0.0
Anti-Skid	<1	6.5	1.7	0.0
Blasting Grit/Roofing Granules	0.0	<1	73.4	0.0
Mining Applications	2.3	<1	<1	1.0
Wallboard	0.0	0.0	0.0	12.4
Waste Stabilization	3.0	<1	0.0	<1
Agriculture	<1	<1	0.0	<1
Other	<1	2.7	2.8	<1
TOTAL	33.2	32.1	81.8	18.1
Production, million st	62.7	16.9	2.9	24.6

[1] FGD: Flue Gas Desulfurization Product

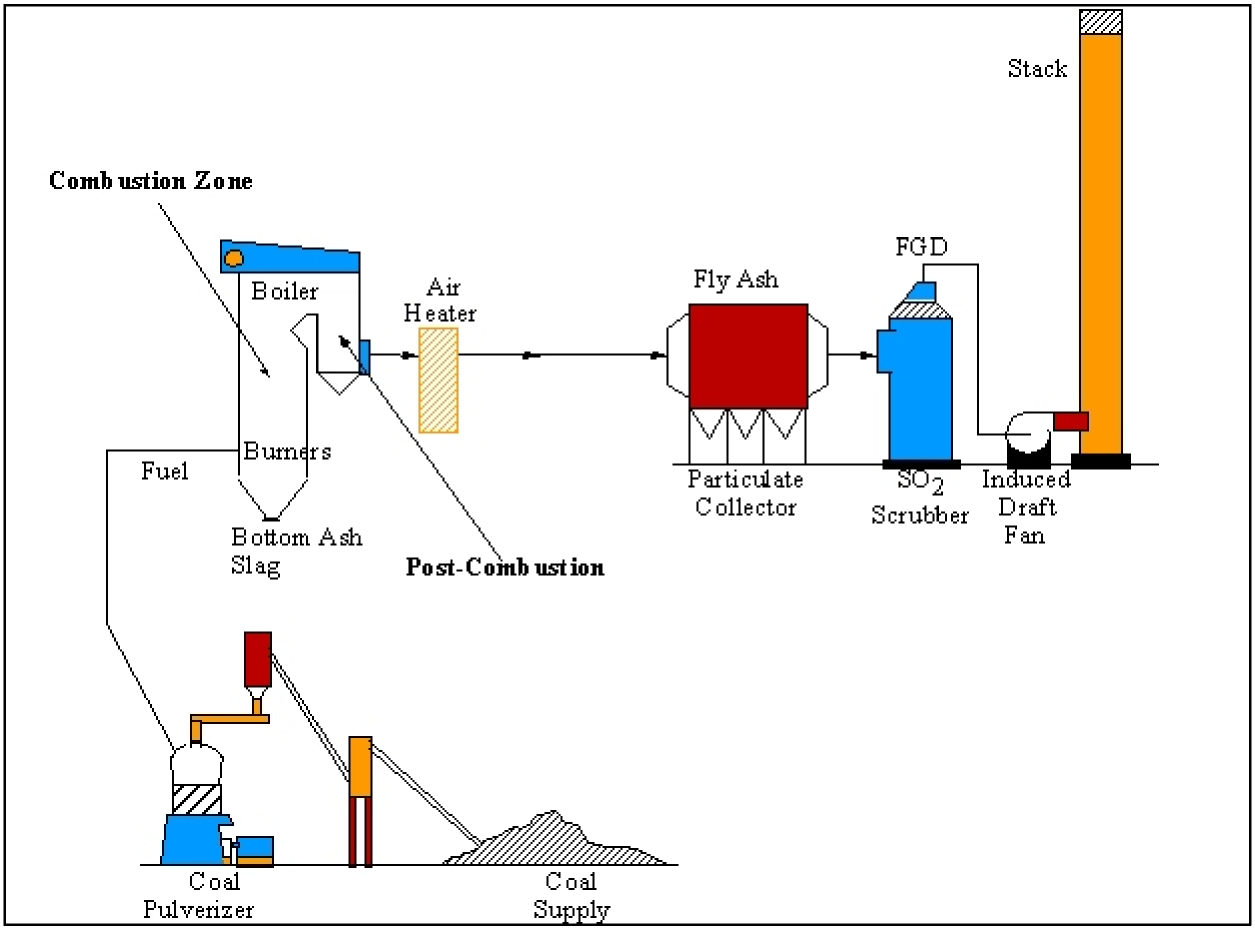


Figure 3. Schematic of pulverized (PC) electric utility boiler, indicating sources of coal combustion by-products (CCB). (After Senior, 2001)

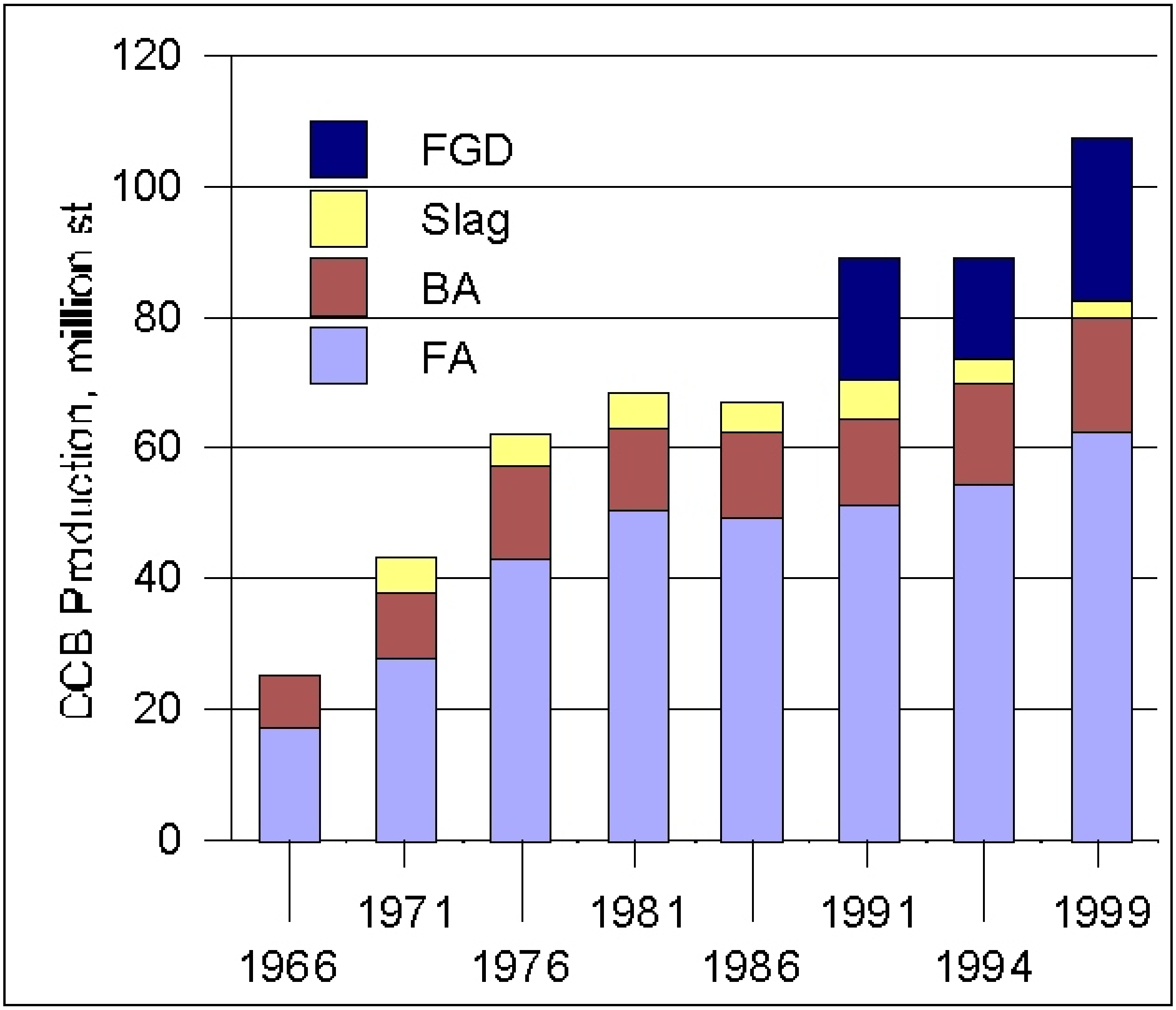


Figure 4. Coal combustion by-product (CCB) production has increased by over 400 % since 1966. Data provided by American Coal Ash Association (ACAA).

Chapter 3

Origin and Composition of Coal Ash

Coal Combustion By-Products (CCB) are formed from the non-combustible mineral portion of coal that has been subjected to temperatures above 500 °C. The origin of this heat treated residue, fly ash or bottoms ash, is related to the formation of coal.

Coal Formation

Coal formation has been described as "an inefficiency in the carbon cycle," (Barghoorn, 1952) when carbon from plants remains in terrestrial sediments and is not recycled to the atmosphere (Figure 5). It can be considered a geologic mechanisms of carbon sequestration. Coal is, by definition, a readily combustible rock containing more than fifty per cent by weight and seventy per cent by volume of carbonaceous material (Schopf, 1966). Another definition describes coal as a combustible solid, usually stratified, which originated from the accumulation, burial and compaction of partially decomposed vegetation in previous geologic ages (Hendricks, T.A. 1945).

The formation of coal deposits required abundant plant material, a suitable climate, areas for accumulating peat and means of preserving the carbonaceous sediment. These conditions were prevalent over large areas during the Pennsylvanian (Carboniferous) period, 240 million years bp. During this period, large areas of what is now the Eastern U.S., Europe, Asia and Australia were located near the equator and apparently had a climate that was tropical to subtropical with mild temperatures, high humidity and heavy rainfall, without cold winters or extended dry periods (White, 1925). Terrestrial plants had been developing for 100 million years, and by the Pennsylvanian, plants adapted to semi-aquatic or marshy areas were abundant.

The majority of coal forming plants were fern-like pteridophytes and club mosses. Both grew to over 30 m and had diameters in excess of 1.2m. Smaller plants, 4.5 to 12 m high, formed dense jungles, similar to canebrakes. (Kummel, 1961; Janssen, 1939).

A site in which carbonaceous sediments could accumulate was created by erosion and the retreat of shallow seas. Broad level areas at or very near sea level, such as coastal plains, deltas or a partially filled basins, could readily develop the marshy conditions needed for the growth of a carbonaceous swamp. The consistent gradual rise in sea level or continuous slow land subsidence was required for between 1,000 and 100,000 years in order to form a 10 m peat deposit which would be converted to a 1.5 m coal seam (Ashley, 1928).

Marshy conditions fostered the formation of peat and the preservation of the organic sediment. Under aerobic conditions, plants are rapidly decomposed to cell carbon, CO_2 and water. In a marshy area, the movement of fresh water is inhibited, and an anaerobic environment develops, slowing the rate of microbial decay and allowing carbonaceous sediments to accumulate. Toxic products also accumulate in the slow moving water, decreasing microbial activity and preserving the sediments from further alteration (Alexander, 1961). A rapid rise in sea level or increase in the rate of subsidence would flood the swamp, halting growth and burying the peat under an inorganic sediment.

In contrast to the slow deposition of peat, the deposition of inorganic sediments was relatively rapid, turbulent and variable. The rocks associated with coal seams are usually fine grained clastics, particularly shales, mudstones and siltstones. Black shales overlying many coal seams represent a gradational change as more sediments were carried into the peat swamp. Sandstones immediately above a coal seam may be related to erosion and subsequent deposition within an existing seam. Channel sands can be seen as stream erosion of an existing coal or peat deposit and deposition of sediments within the stream channel. (McCulloch et al, 1975). The rate of sediment deposition within or immediately above the peat would affect the concentration of syngenetic minerals, while sandstones deposited above a coal seam could increase the concentration of epigenetic minerals.

Peat formation is the biochemical stage of coal formation, during which plant residues are partially decomposed. The geochemical stage of coal formation is a continuous and irreversible process that produces a rock from the organic sediment. Coalification progresses through lignite, subbituminous, high volatile bituminous, medium volatile bituminous, low volatile bituminous to anthracite (Figure 6). Heat and pressure are the primary agents of coal metamorphism, rather than age. Temperature and pressure increase as a function of depth, and high temperature is also related to folding and faulting and the presence of igneous intrusions.

On a proximate basis, coal is composed of moisture, mineral matter, volatile matter and fixed carbon (Hessley et al, 1986). The mineral matter in coal is emplaced during or after coal formation. Minerals that are an integral part of the organic matrix are considered included minerals, while those in the cleats and fractures are termed excluded minerals.

The mineral or inorganic portion of coal was considered a diluent, that reduced the heating value of the coal, and an engineering problem when it caused slagging and fouling in the boiler. In the last 30 years, the non-carbonaceous portion of the coal has been targeted as the source of contaminants in power plant emissions and residues. The potential release of heavy metals from coal combustion by-products is related to the distribution of elements in coal ash.

Minerals in Coal and Ash

The obvious origin of coal ash is the inorganic portion of the coal. However, combustion and post combustion cooling have a significant effect on the mineral phases in CCB.

Minerals in Coal

A variety of minerals have been identified in coal. Although some of the inorganic compounds originate in the plant material, most are deposited during (syngenetic) or after (epigenetic) coalification. Syngenetic minerals can be formed by precipitation in an anoxic, aqueous medium during the biochemical stage of coalification, or they may be detrital clastics transported into the peat swamp by wind or water. Epigenetic minerals are deposited within the coal seam, in cracks, fractures and bedding planes, by migrating fluids. They may also be produced from syngenetic minerals by increased temperature and pressure. Mackowsky (1968) indicated that most of the silicates, quartz and phosphates had been transported into the peat swamp. Carbonates, sulfides, and chalcedony from the weathering of feldspar and mica were formed within the swamp. These minerals tended to be intimately intergrown with the organic matrix, and are sometimes described as included minerals. Some carbonates, sulfides, and oxides were deposited in cleats and fractures. Since these epigenetic minerals are independent of the organic portion, they are designated as excluded minerals.

Coal mineral matter includes a variety of minor or trace elements. The concentration of these elements in coal may be greater than their average concentration in the earth's crust (Table 3). The distribution of trace elements varies too widely to be described by a general statement. Coals from different areas may show distinctive trace element characteristics, and, within a single coal seam, the trace element distribution may not be consistent. This suggests that no single process has been responsible for the accumulation of trace elements in coal. When compared to the overlying carbonaceous shale, the concentration of trace elements is lower in coal, reflecting the influx of detrital inorganic sediments that eventually terminated the formation of the peat swamp (Table 3).

In a study of 35 coal samples from eight countries, Vassilev and Vassileva (1996) identified approximately 100 minerals. The minerals were characterized as major (> 1% by wt), minor (.1><1% by wt), and trace (<0.1 % by wt). On a semi-quantitative basis, the mineral groups in decreasing order of importance are: silicates > carbonates > oxyhydroxides > sulfides > sulfates > phosphates > others. The coals were divided according to rank, based on dry ash free carbon concentration (C_{daf}). The lower rank coals are enriched in mineral matter, including calcium and magnesium oxides. The highest rank coals have increased contents of silica, aluminum, iron, potassium, sodium, and titanium.

The quartz in 40 samples of a Powder River Basin (PRB) coal was primarily detrital, but trace amounts of β-form quartz, with apatite and zircon, was attributed to air-fall and reworked volcanic ash deposited in the peat swamp (Brownfield et al, 1999). In a study of Gulf Coast lignites, enrichment of some elements was attributed to proximity to igneous rocks or to deposition of volcanic ash(Warwick et al, 1997). The mineral composition of the coal seam can also be modified by post-coalification circulation of geothermal fluids (Kolker, 1999; Daniels et al, 1990).

The minerals phases identified in various coals are summarized in Table 4, and the modes of occurrence and maximum concentration of selected elements is given in Table5.

Combustion System

In addition to their concentration in coal, the distribution and compounds of cations in coal combustion by-products depend on the operating conditions in the combustion zone and post-combustion conditions. In pulverized coal (PC) fired power stations, the furnace operating temperature is typically above 1400 ° C (~2500° F). The finely divided coal particles are injected into the furnace and ignited while suspended in air. The volatile matter and organic matrix react with air to produce heat, CO_2, H_2O, SO_2 and NO_x. At these temperatures, minerals may oxidize, decompose, fuse, disintegrate or agglomerate (Clarke and Sloss, 1992). For instance, most SO_2 is produced from the oxidation of pyrite. Another product of pyrite oxidation is iron oxide, which is found in ash particles either as hematite or magnetite. Excluded mineral particles may undergo fusion and partial melting in the boiler. If the temperature in the post combustion zone decreases slowly, fluid mineral particles may cool slowly and develop the characteristic crystalline structure (Figure 7). If cooling is rapid, the minerals may condense to a spherical, glassy particle. As the coal matrix is removed by combustion, the included mineral grains become fluid, and volatile elements enter the vapor phase. As they cool, gaseous compounds may condense to very small spherical particles or coalesce to slightly larger particles. They may also condense on the surface of other particles, leading to surface enrichment of volatile species. Non-volatile compounds will agglomerate to form fly ash particles. Expansion of trapped volatile matter may cause the particle to expand, forming a hollow, low density cenosphere. Residence time within the boiler is relatively short and some minerals, especially those with high melting points, are transported through the combustion zone unchanged.

Based on their boiling points and the phase change temperature of their oxides, several authors have described the partitioning of trace elements in CCB (Germani and Zoller, 1988, Meij, 1989; Yokoyama et al, 1991). The first group of elements, which are concentrated in bottom ash or equally distributed between bottom ash and fly ash, includes typically lithophile elements: Ba, Mg, Mn. In a second group, trace elements, enriched in the fine particulate fraction are usually chalcophile elements such as As, Cd, Pb, Se, and Zn. Group 3 includes volatile elements which remain in the vapor state, Hg, Br. Several elements partition between groups (Figure 8).

According to Davison et al (1974) the concentration of the elements, Pb, Sb, Cd, Se, As, Ni, Cr, and Zn increased with decreasing particle size. The concentration of the elements Fe, Mn, V, Si, Mg, C, Be, and Al was found to increase with decreased particle size only for particles with a diameter less the 11 µm. These elements showed no size dependence for larger particles. The concentrations of Bi, Sn, Cu, Ti, Ca and K showed no dependence on particle size.

Vaporization and condensation form an ultrafine aerosol during pulverized coal (PC) combustion (Senior et al, 2000a). Factors such as residence time, temperature history and level of turbulence control the size and morphology of the aerosol particles. Fly ash particles with aerodynamic diameters less than 0.4 µm were attributed to condensation. Non-volatile elements, such as Fe, were found to concentrate in larger ash particles. Between 10 and 30 pct of the volatile elements, As, Sb, Se, and Zn, are in the condensed fly ash particles. Arsenic and Sb are soluble in silicate glass and may be retained by glassy particles that form by coalescence of minerals. Correlations between the concentrations of arsenic and calcium in fly ash are assumed to indicate the formation of calcium arsenate.

Radioactive elements, radon, thorium and uranium, are present in coal at concentrations between 1 and 4 ppm (USGS, 1997), which is greater than basaltic rocks but less than common shales and granites. During combustion, radon is transferred to the gas phase. Although uranium may be enriched in finer sized fly ash particles, the concentration of radioactive elements in fly ash is not significantly greater than in common soils or rocks.

Minerals in Ash

Volatilization, melting, decomposition and the formation of new minerals, as well as oxidation are the mechanisms that transform the minerals during coal combustion. The transition of minerals in coal to those found in combustion by-products is related to the high temperature oxidation and to the rate of cooling of the inorganic melt. There is a significant difference between the minerals in coal and those in the ash produced from the same coals. The inclusion of heavy metals or hazardous air pollutants (HAPs) in the ash and their solubility are the primary determinants of toxicity. Concentration is not the only factor; volatility, toxicity and solubility determine the potential for health and environmental effects, and these factors are functions of speciation within the ash. A summary of the minerals identified in coal ash is given in Table 6. Because different authors use different methods of mineral identification and different concentration units, some degree of interpretation was necessary to assemble the comparative table. The mineral association of trace elements is summarized in Table 7.

Chemical Composition of Coal Ash

EPRI (1987a) conducted a study of the composition of 39 fly ash samples and 40 bottom ash samples from power plants in the U.S. The trace element composition indicated that more volatile elements (As, B, Cl, F, S and Se) were preferentially partitioned to the fly ash, and it tended to be higher in fly ash derived from bituminous coal. The mean and range of concentrations for major elements is shown in Table 8; maximum trace element concentrations are given in Table 9. EPRI also conducted an extensive literature search on the inorganic and organic constituents of fossil fuel combustion residues(EPRI, 1987b,c). They concluded that the inorganic composition was highly variable. Some non-volatile elements were evenly distributed between fly ash and bottom ash, while volatile elements tended to be concentrated in fly ash.

The Council of Industrial Boiler Owners (CIBO) conducted a survey of operators of FBC units, requesting information on the physical and chemical characteristics of FBC fly ash. Trace elements were found to be concentrated in the smaller ash particles. The composition of the FBC fly ash, as provided by respondents to the CIBO (1997) survey, is given in Table 8; trace element data are given in Table 9.

The Pennsylvania Department of Environmental Protection (PADEP) allowed DOE personnel to copy applications and reports relative to placement of CCB at surface mine sites (Kim and Cardone, 1997). The information included analyses of 99 fly ash samples. A summary of the major element and trace element data are given in Tables 8 and 9. The mean concentration of major and trace elements in ash from Bulgarian power plants, as reported by Vassilev and Vassileva (1997), is in the same range as the data reported in Tables 6 and 7

In evaluating the chemical composition of fly ash in Tables 6 and 7, it must be recognized that the data provided by several entities have limitations. First, ash is a non-homogeneous material, and it must be assumed that a given sample is representative. In the data submitted, blanks are not always identified as values below detection limits or as elements not included in the analysis. Also, detection limits may vary, which makes comparing analyses difficult. It is also possible to dissolve solid samples by several methods (metaborate fusion, aqua regia, hydrofluoric acid, for example), and the method used may have some effect on the analytical results. Therefore, compilations of fly ash analyses give good indications of the range of compositions, but are not reliable indicators of concentration of elements in an "average" fly ash.

Additional information on the chemical and mineral composition of coal ash is given in Appendix B.

Physical Properties

The physical characteristics of combustion residues include particle size, particle shape or morphology, hardness, density and color. These properties are a function of the particle size of the feed coal, the type of combustion, and the particulate control device. PC boilers typically use fuel that is ground to a diameter of less than 0.075 mm (CIBO, 1997). The fly ash has a particle diameter less than 0.010 mm. Due to the high temperature of P.C. combustion, fly ash particles tend to melt and condense as spheres. Fly ash particles from FBC boilers, although having similar diameters and density, tend to have a less regular shape. Armesto and Merino (1999) also found that residues from PC systems are smaller than those generated in FBC systems.

Sized fractions of fly ashes were found to have similar mineral compositions (Erdogdu and Turker, 1998). However, when used as a cement replacement in concrete, higher strengths were correlated with smaller particle size. The effect was attributed to the decreased porosity due to small particles filling a higher percentage of concrete pores.

Comparing the size distribution of minerals in fly ash with that in the original coal, showed that both types of particles are larger than 1μm, but fly ash particles are larger with a median diameter of 20μm and a maximum diameter in the range of 150 to 200 μm (Wigley and Williamson, 1998). The larger size of fly ash particles is attributed to coalescence of mineral grains during cooling.

In a study of 27 samples of pulverized fuel ash from Australian and Japanese coals, Nagataki et al (1995) determined that specific gravity of the samples varied from 2.01 to 2.31. The maximum bulk density was between 0.7 and 1.4 g/cm^3, while the surface area varied between 0.7 and 37 m^2/g.

The morphology of fly ash grains is determined by the heating and cooling regimes in the PC boiler. Microspheres, typically between 30 and 100 µm in diameter, can be hollow cenospheres or noncrystalline glass beads (Shao et al, 1997). Unburned carbon particles, irregular partially melted minerals, particle fragments and agglomerated particles tend to be slightly larger.

Summary: Minerals in Coal and Ash

Inorganic compounds in coal may originate in plant material, but most are deposited during (syngenetic) or after (epigenetic) coalification. Syngenetic minerals are either chemical precipitates or detrital clastics. Epigenetic minerals are deposited within the coal seam after coalification is complete. Minerals identified in coal include silicates, carbonates, oxides, oxyhydroxides, sulfides, sulfates, and phosphates. In coal, the more volatile elements (As, Hg, Mo, PB, Sb, and Se) tend to be associated with pyrite. The elements, Cd and Cu are associated with sulfides, possibly with Pb and Zn sulfide. The carbonates are apparently limited to Ca, Mg and Mn. Several elements are associated with the organic matrix or with silicates.

During combustion, minerals in coal become fluid, are subject to high temperature oxidation and then are cooled. The maximum temperature and the rate of cooling influence the morphology and composition of the ash. Generally, over 50 % of fly ash is composed of spherical amorphous particles. Inorganic compounds may also be present in fly ash as crystals or as surface coatings on other particles. In fly ash, the major cations are Si, Al, Fe and Ca with lesser amounts of Na, Mg, K, Sr and Ti. Trace elements include As, B, Ba, Cd, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, V, and Zn. The primary minerals are quartz, mullite, hematite, clays and feldspars. Volatilization and condensation are believed to be primary determinants of trace element partitioning in fly ash, but there are limited data on trace element association.

Table 3. Distribution of trace elements in coal ash compared to the average concentration in the earth's crust and shales, ppm. (After Nicholls, 1968)

Element	Crust	Shale	Coal ash, minimum	Coal ash, maximum
Ag	0.7	.07	1	10
As	1.8	13	100	900
B	10	100	86	5800
Ba	425	580	300	3500
Be	2.8	3	1	30
Co	25	19	30	300
Cr	100	90	50	400
Cu	55	45	20	500
Mn	950	830	200	1000
Mo	1.5	2.6	10	200
Ni	75	68	50	800
Pb	12.5	20	5	700
Sr	375	300	80	3500
V	135		100	1000
Zn	70	95	100	1000

Table 4. Minerals Identified in Coal.

Sample	Bituminous[1]	PRB[1]	PRB[2]	Various[3]	Lignite[4]	UK[5]	Bituminous[6]
Units	wt% mm	wt% mm	Ma/ Mi/ T	vol%mm	NA	NA	# of samples
# of Samples	3	1	40	34	48		75
Quartz	12	27	α Ma β T	33	✔ cristobolite ✔	✔	63
Kaolinite	13	19	Ma	10		✔	73
Illite	13	8		4		✔	9
Montmorillonite	<1	2		1			
Feldspar	<1	2		4	✔		
Silicates	27	29		2	✔		15
Pyrite	16	1	T	4	✔	✔	18
Sulfides	<1	1					2
Siderite	<1	<1					15
Calcite	3		Mi	6	✔		62
Carbonates	2	<1		6	✔		56
Rutile/Anatase	<1	3	T				0
Phosphates	<1	6	T	3		✔	47
Micas			Mi	3			
Zeolites					✔		
Barite			T	1			
Zircon			T				
Plagioclase			T				12
Sulfates				10	✔	✔	17
Oxides & Hydroxides				11			1

[1] Senior et al, 2000b
[2] Brownfield et al, 1999
[3] Vassilev et al, 1997
[4] Karayigit et al, 2001
[5] Spears et al, 1999
[6] Kimura, 1998

Ma/Mi/T = Major, Minor, Trace
wt% mm = weight % of mineral matter
PRB = Powder River Basin

UK = United Kingdom

Table 5. Modes of Occurrence and Maximum Concentration (ppm) of Elements in Coal.

Reference	Senior et al		Shao et al		Palmer et al	
Element	Mode	Max	Mode	Max	Mode	Max
As	Py	250	S	25	Py, Sl	45
B	Cly, O	500				
Ba			O, SO_4	500		
Be	Cly,O	30			Sl, O	2
Cd	ZnS	10			S	2.5
Co			S	25	Sl, O	12
Cr	Cly, Fe, OOH	100	O	80	Sl, O	97
Cu	S, O	200				
Fe			S	2000	Py, Sl	2.6 %
Hg	S, E	10			Py, O	0.50
K			O	14000		
Mn	O, CO_3	1000			Sl, CO_3	230
Mo	Py, O	50				
Na			O, SO_4	4500		
Ni	S, O	100	S		Sl, O	48
Pb	Py, S	100			O, S, Py	25
Sb	S, Py	40			Sl, O	2.1
Se					Py	6.1
Sn	Ox, S	20				
Sr			O, SO_4	300		
Zn	S, O	300	O, SO_4	50	Sl, S, Py	190

Py = Pyrite S = Sulfide Cly = Clay CO_3 = Carbonate Sl = Silicate
O = Organic OOH = Oxyhydroxide Ox = Oxide E = Elemental SO_4 = Sulfate

Table 6. Minerals Identified in Fly Ash

Reference	Vassilev & Vassileva (1996)	Mukhopadhyay et al (1996)	Yamashita et al, 1998	Hower et al, 1999	McCartyy et al, 1999	
					Class F	Class C
Units	M-m-T	Vol %	wt%	wt %	wt%	wt %
Quartz	M	5	5 - 40	<0.5	7.1	
Cristobalite	T-M					
Kaolinite						
Illite	M					
Plagioclase	m-M		1 - 20			
K-feldspar	m-M		1 - 10			
Micas	m-M					
Mullite	a-M			<1	13.3	
Hematite	m-M	25	1 - 10		4.1	
Magnetite	T	65			7.0	2.5
Goethite	T-M					
Spinel	T-m					
Gypsum			1 - 20			
Calcite					0.5	5.7
Ettringite					3.5	7.8
Alumino-Silicates			20 - 70			
Corundum	T-M					
Gibbsite	T-M					
Rutile	T-m					
Lime	T-M					
Portlandite	T-M					
Anhydrite	M					
Amorphous	50 - 90 vol %			75-86	64.5	74.8

M-m-T = Major, minor, Trace

Table 7. Trace Element Association in Fly Ash (FA)

Reference	
Huggins et al, 1997	As in FA is As (V); 25% of As in BA is As(III), < 5% of Cr is toxic Cr(VI); Ni is +2 valence and Se may be selinide or selenate.
Finkelman et al, 1997	As = 170 ppm in FA from high S coal and 54 ppm in FA from low S, primarily condensed on ash surfaces. Cr enriched in the Fe-oxide phases, such as spinel. 70 pct of Cr in the glassy silicate. Similar results for Ni and Co. Sb and Zn present in more than one ash phase.
Senior et al, 2000	Elements vaporized during combustion: 40 to 80 % of As & Sb, residual may dissolve in silicates or form Ca compounds; > 80 % Se and Zn volatilized; < 40 % Cr in vapor state.
Furminsky, 2000	Most As, Pb, and Cd in FA; Se and Hg vaporized. Air/coal ratio affects partitioning of elements in vapor and solid phases, shifts condensation to lower temperature.
Hulett et al, 1980	Ba, Sr, Ti, As, Se concentrated in amorphous phase. V, Cr, Mn, Ni, Zn and Cu concentrated in Fe oxide/spinel

Table 8 Major element concentrations in fly ash samples, g/kg.

Element	**EPRI[1] Data**			**CIBO[2] Data**			**PADEP[3] Data**		
	n	Mean	Range	n	Mean	Range	n	Mean	Range
Al	39	113	46-152	14	29.9[4]	.02 - 176	89	30	.012 - 140
Ca	39	62	7.4-223	2	56	37 - 74	19	50	.003 - 265
Fe	39	76	25-177	18	31[4]	.02 - 81	89	35	.009 - 675
K	39	14.3	3-25.3	13	1.5[4]	.001 - 15			
Mg	39	11.8	1.6-41.8	1	10		22	139	.005 - 4
Na	39	9.1	1.3-62.5	1	5				
P	24	3	1.1-10.3	1	0.5[4]				
S	39	12.6	1.3-64.4	2	15	8 - 21			
Si	39	209	90-275	2	115	90 - 115			
Sr	39	1.3	.2 - 7	1	0.3				
Ti	39	7	1.3 - 10	1	2				

[1] EPRI: Electric Power Research Institute

[2] CIBO: Council of Industrial Boiler Owners

[3] PA DEP: Pennsylvania Department of Environmental Protection

[4] Median

Table 9. Trace element concentration in fly ash, mg/kg

Element	**EPRI[1] Data**			**CIBO[2] Data**			**PADEP[3] Data**		
	n	Mean	Maximum	n	Median	Maximum	n	Median	Maximum
Ag				19	1	39	78	0.4	22
As	39	156	385	23	12	46	92	20	21030
Ba	39	1880	10850	20	320	7700	93	212	2960
Be				13	2	12			
B				11	90	652	80	50	3995.4
Cd	2	12	17	23	.6	13	81	1	30
Co				16	14	179	30	28	83
Cr	29	247	651	23	29	141	92	40	360
Cu	39	185	1452	20	43	99	91	41	474
Hg				22.	0.3	7	84	0.4	5.44
Mn	39	357	1332	15	126	57700	86	79	27614
Mo	36	44	236	21	6	61	79	12	108
Ni	39	141	353	22	35	1020	91	39	752
Pb	39	171	2120	24	15	73	93	33	225
Sb	7	43	131	17	5	1370	64	27	140
Se	30	14	49	22	5	46	77	3	201
Sn	18	44	56						
Th				12	3	25			
V	35	272	652	13	61	1120			
Zn	39	449	2880	22	36	105	93	41	1196

[1] EPRI: Electric Power Research Institute

[2] CIBO: Council of Industrial Boiler Owners

[3] PA DEP: Pennsylvania Department of Environmental Protection

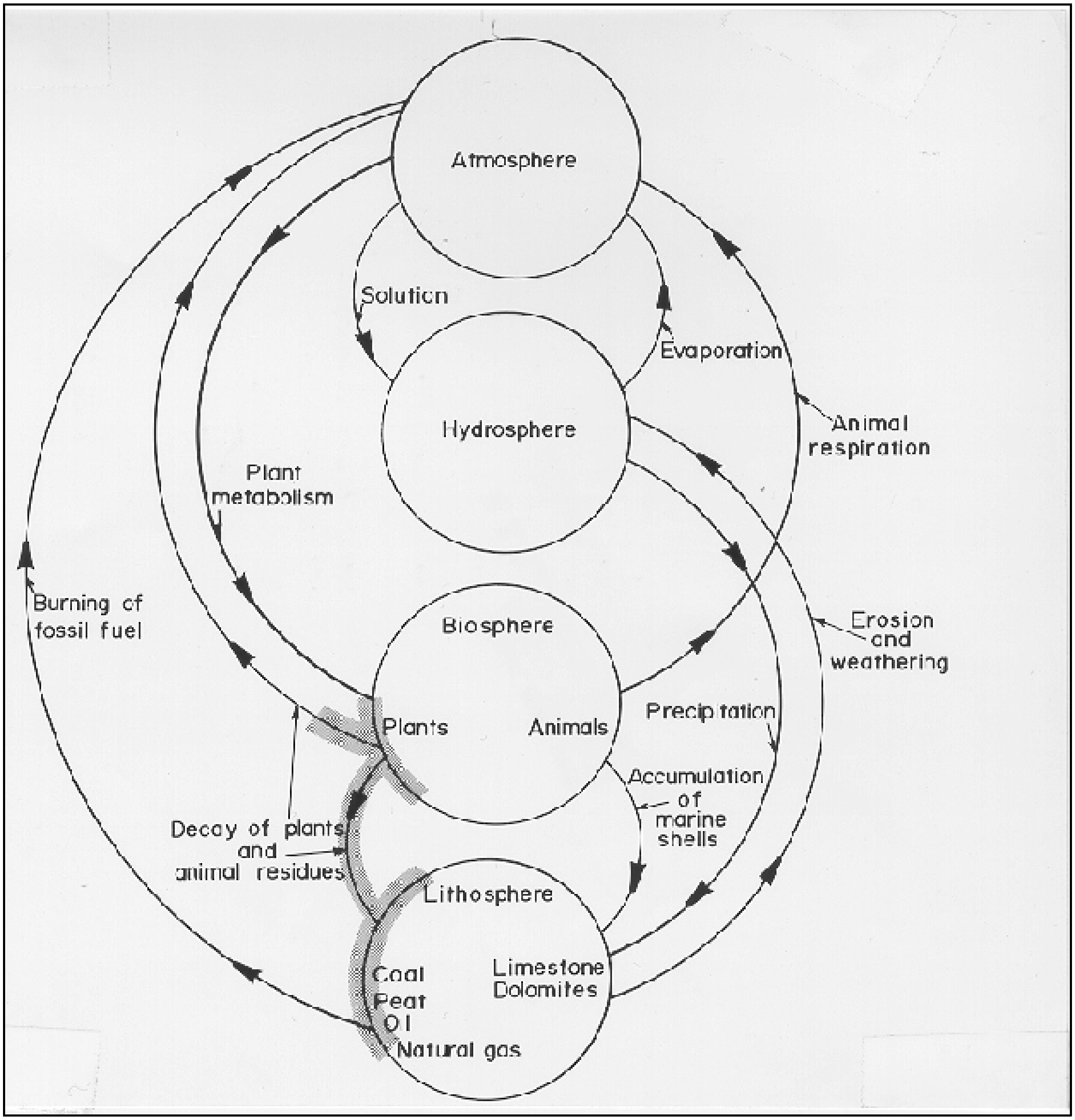


Figure 5. Carbon cycle, highlighting transition from plants to fossil fuel resources. From: Deul and Kim. 1988.

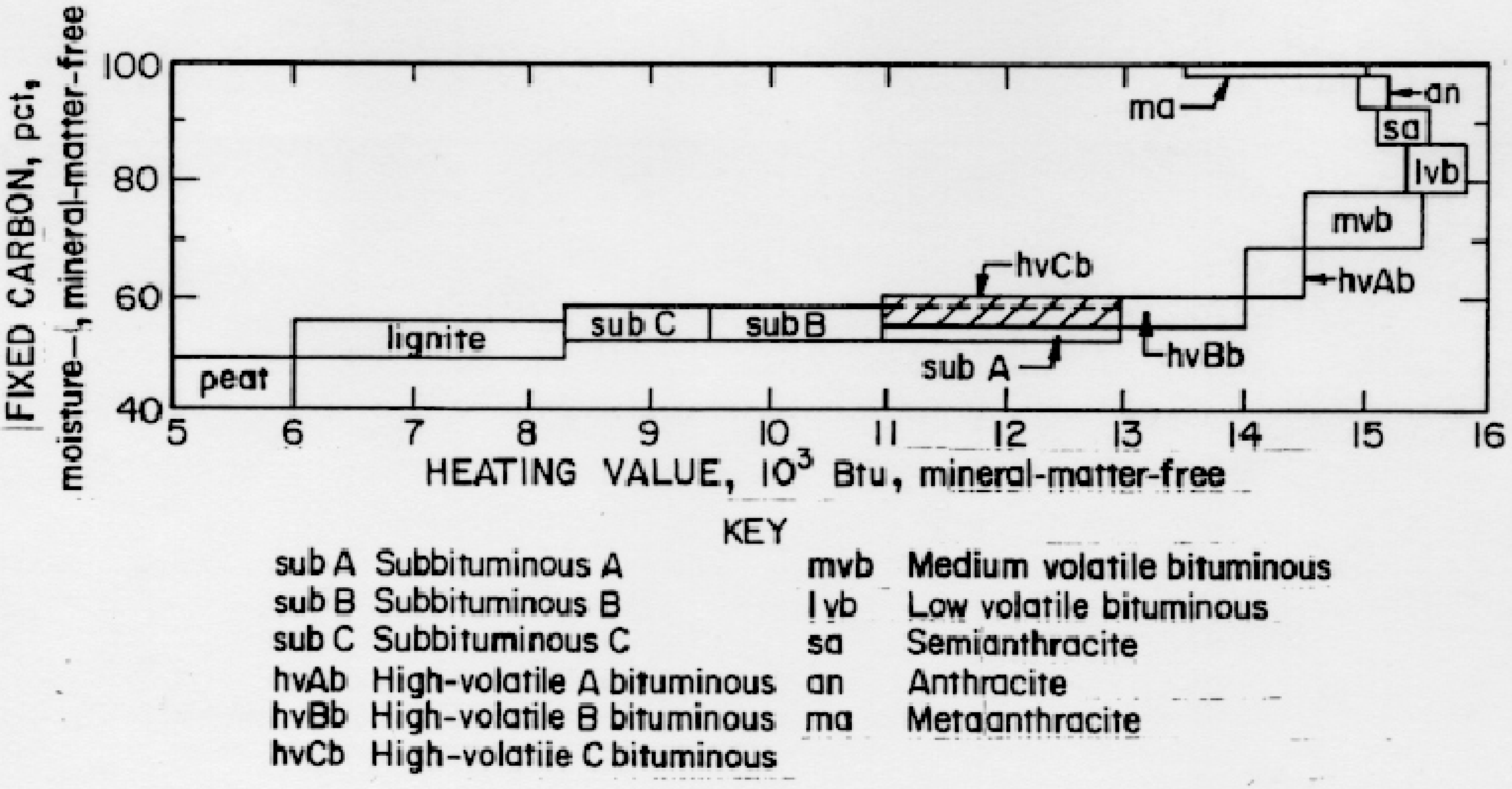


Figure 6. Coal rank - variation of heating value with increase in fixed carbon content. (From Kim and Kissell, 1988)

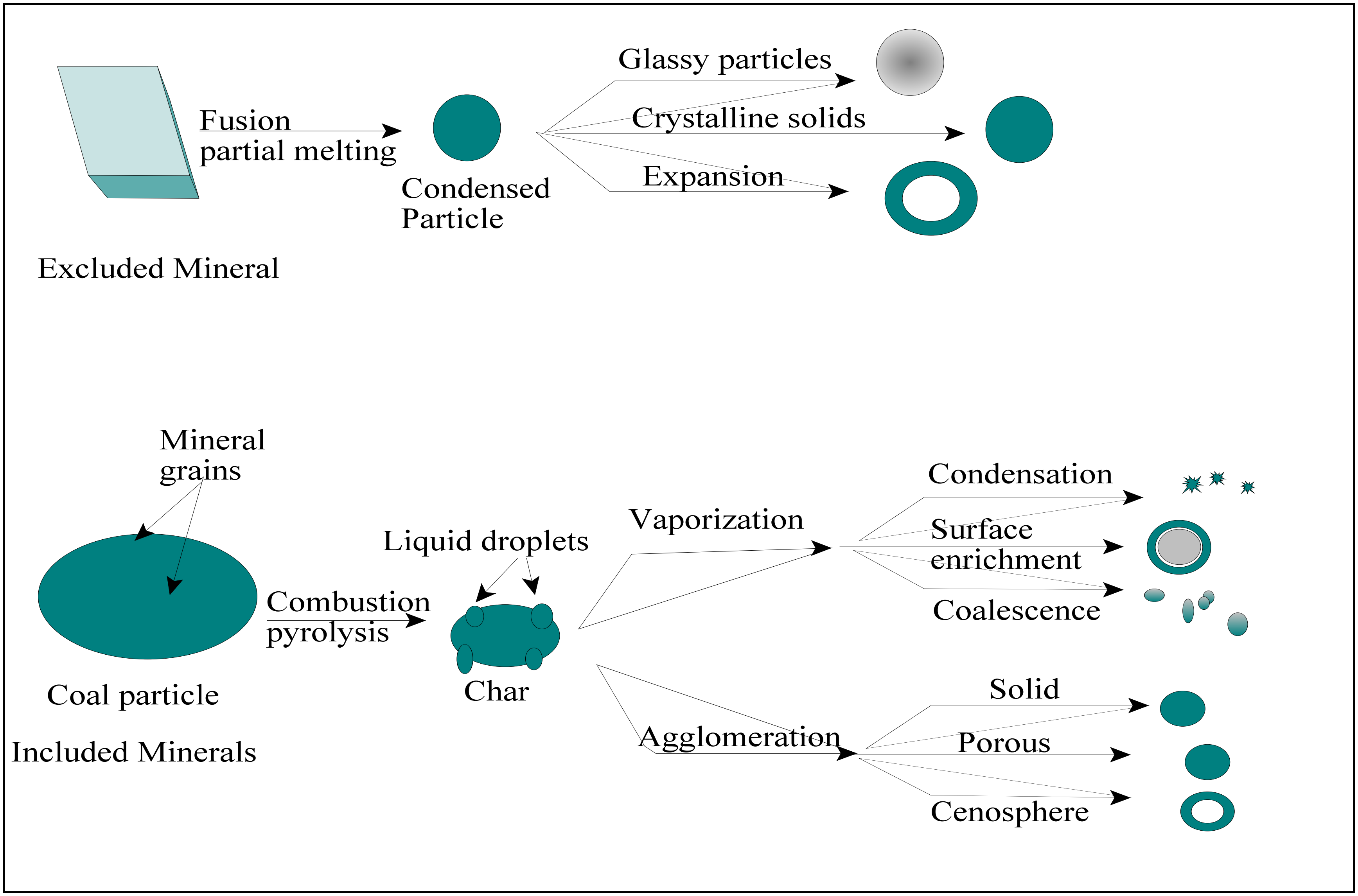


Figure 7. Formation of fly ash particles from excluded and included minerals. After Clarke, and Sloss. 1992.

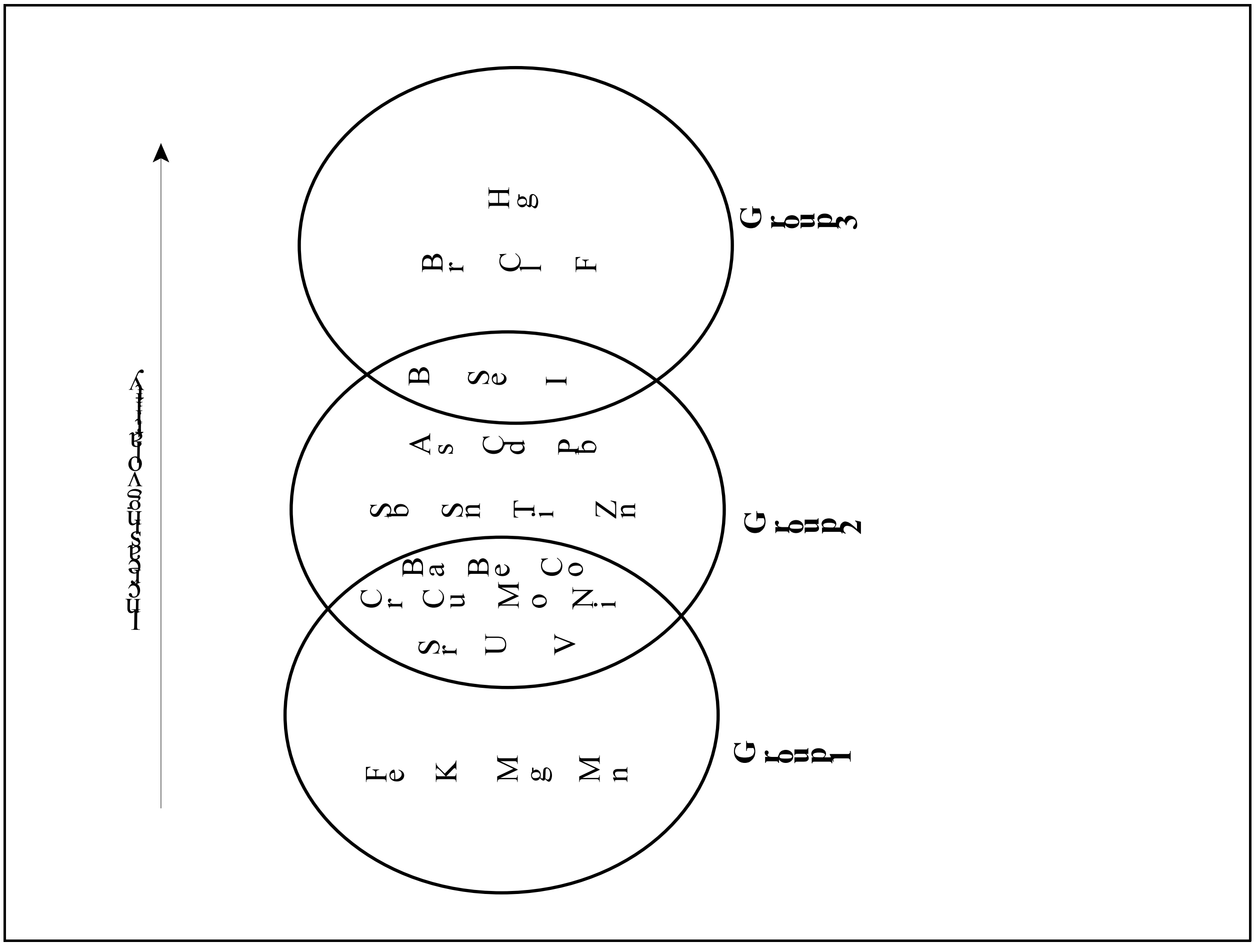


Figure 8. Partitioning of trace elements during combustion: Group 1 - Elements concentrated in coarse residues; Group 2 - Elements concentrated in fine grained particles; Group 3- Vapor phase elements. After Clarke, L.B. and L.L. Sloss. 1992.

Chapter 4

Leaching Studies of Coal Ash

Overview of Leaching Chemistry and Methods

Introduction

The release of metals from CCB has been studied using a variety of methods, samples and leachant solutions. The leaching behavior of all types of materials is related to several critical factors, including specific element solubility or release potential. Solubility can be influenced by pH, complexation by inorganic species or dissolved organic matter, and reducing properties. A recent survey of the literature identified over 100 leaching methods to remove soluble components from a solid matrix (Hesbach and Lamey, 2001). Many leaching methods are intended to mimic natural conditions, and others are used obtain information about the nature of the extractable material within a particular solid. The methods vary in the amount and particle size of leached sample, the type and volume of leachant solution(s), the leachant delivery method, and time. Most procedures are performed at ambient temperature, although a few decrease the time required to solubilize components by increasing the temperature. Although some methods have been developed for a specific type of material, most leaching methods have been applied to a variety of materials.

Leaching can be described as the fluid extraction of a compound or element from a solid. It is an interactive process in which both leachant and solid variables can control the results. The pH of the leachate, which is determined by the pH of the leachant and the alkalinity/acidity of the solid is generally recognized as a controlling factor. The effects of oxidation reduction potential, dissolution/precipitation equilibrium, complexation, temperature, the concentration of dissolved CO_2 and O_2, is not addressed in most leaching methods. Many natural materials (ores) and those produced by industrial processes (slags and ashes) are not simple chemical compounds. They may be discrete particles fused into a larger mass or small particles trapped in a different matrix. For these materials, porosity and diffusion rate will affect the solubility rate determined by a leaching procedure.

Summaries of many of the more commonly used leaching methods are given by Sorini (1997) and Wilson (1995) . The International Ash Working Group (IAWG) based in Europe has done extensive work on the integration of a variety of tests into a comprehensive leaching system (Eighmy and van der Sloot, 1994; van der Sloot, 1998).

Leaching Chemistry

As it applies to this study, leaching involves the dissolution of a solid by an aqueous chemical solution. This process can be complicated by secondary reactions such as precipitation, adsorption or the formation of complexes. Leaching reactions are characterized as hydrolysis, caustic (alkaline), acidic, or oxidative reductive (Demoupolous, 1999; Stumm and Morgan, 1995; van der Sloot, 1998). Although biochemical leaching, either direct or indirect, is frequently important in natural processes and hydro metallurgy, it is not usually considered in regulatory or laboratory leaching tests. In addition to water, acids and bases are commonly used as leaching agents. Basic leachants, hydroxides, soluble carbonates and cyanides, are more selective than acid solutions.

The dissolution of mineral components and the behavior of dissolved components is controlled by the system variables, pH, Eh and the activities of the dissolved species. The pH is a function of the acid base character of the system, and the Eh determines the relative stability of multivalent species. Activities are the product of the activity coefficient and the concentration; in dilute solutions, activity and concentration are comparable.

For a general chemical reaction written as:

The Gibbs free energy change is:

$$\Delta G = \Delta G^0 + RTln\frac{[C]^c}{[A]^a[B]^b} \tag{2}$$

At equilibrium, $\Delta G = 0$, and the last term in Eq. 2, the reaction quotient, is equal to K, the equilibrium constant. If $\Delta G < 0$, the reaction is thermodynamically favorable. However, a thermodynamically favored rate does not occur unless the reaction proceeds at a rate such that measurable changes in the concentration of reactant and products occur.

The rate of a reaction can be written as:

where A and B are reactants, a and b define the reaction order, and k, the rate constant for the reaction is negative. In terms of the product, the reaction rate is:

$$r = k[C]^c \tag{4}$$

where [C] is the concentration of the product and k, which has the units of 1/t, is positive. The above reactions are relatively simple and apply to homogeneous reactions in one phase. Leaching involves heterogeneous reactions with at least two phases, liquid and solid. Because reactants must diffuse across the liquid solid interface, the surface area of the solid is a variable, and the rate equation is more complicated. A non-homogeneous material, in which an element is distributed in more than one chemical compound or crystalline phase, also complicates the formulation of rate equations for leaching systems. In most leaching systems, it is assumed that the leachant remains a dilute solution with respect to the soluble species and that there is sufficient time for the reaction to reach equilibrium or go to completion. It is also assumed that the diffusion rates of a reactant across the liquid-solid interface and the diffusion of products into the leaching solution are much less than the time frame of the leaching test. Competing reactions, secondary reactions and precipitation may also complicate the interpretation of leaching results.

The shrinking core model has been applied to a variety of solids leaching processes (Batarseh et al, 1989). The model describes a reaction front starting at the surface of the particle of radius r and moving inward with a velocity

$$v=\frac{d\lambda}{dt} \tag{5}$$

in which λ is the distance the reaction front has moved from the surface at time t. When applied to homogeneous isotropic spherical particles, the rate of reaction, R, is given by the equation:

$$R(t)=4\pi\rho_r[r-\lambda(t)]^2 v \tag{6}$$

where r is considered constant, and ρ_r is the density of the solid reactant. According to this model the reaction rate is greatest when the leaching solution is at the surface of the particle. Calculation of the reaction rate is more complex if the particle is not homogeneous, if more than one chemical reaction occurs, and if transport rates for reactants and products must be considered.

An adsorption/desorption model of intra-particle diffusion was developed by Chaiken (1992) to account for spatial heterogeneity of particle porosity and temporal changes in porosity due to leaching reactions. This model defines λ as the shortest path to a reactive site, and values of λ within a particle or assemblage of particles are assumed to have a log-normal distribution.

$$f(\lambda) = \frac{h}{\lambda\sqrt{\pi}} e^{-h^2(\ln\lambda/\ln\lambda_0)^2} \tag{7}$$

where h is the spread factor of the distribution and λ_0 is the median “shortest path.” The rate of reaction is

$$R(t) = \frac{2he^{[-h\ln(\frac{t+t_a}{t_0})]^2}}{(t+t_a)\sqrt{\pi}(1-erf[h\ln(\frac{t_a}{t_0}])} \tag{8}$$

where t_0 is the time for the diffusion front to travel the median shortest distance, and t_a is a pre-aging factor to account for reaction that occurred prior to leaching. In standard leaching methods, it is assumed that all particles are equally in contact with the leachant solution.

Leaching Methods

In this dissertation, leaching methods are categorized as: (1) regulatory - those promulgated and approved by a regulatory agency to generate specific information for submission in a legal context; (2) standard methods are those adopted by a standards organization (ASTM, ISO) for a specific set of conditions and, sometimes, for specific materials; and (3) research methods developed for a particular objective. Most of this discussion deals with regulatory and standard methods, although examples of some commonly used research methods are included. Regulatory and standard methods are frequently used for research projects. However, only if the method is appropriate to the problem studied and if the procedure is followed exactly can results from different projects be considered comparable. Leaching methods are categorized as static or dynamic methods. Within these categories, static methods are divided into batch and monolithic; and dynamic methods are column, serial batch, or sequential batch, although some methods are not uniquely defined within these categories. Due to the number of leaching methods, this discussion cannot be comprehensive. The intent is, rather, to identify commonly used leaching methods and use examples to identify method characteristics.

Static Leaching Methods

Static or batch leaching methods can be described as those in which a sample is placed in a given volume of leachant solution for a set period of time. Most of the methods require some type of agitation to insure constant contact between the sample and the leachant. At the end of the leaching period, the liquid is removed and analyzed. Commonly used batch leaching methods are listed in Table 10 and described in Appendix C.

In serial batch methods, a sample of waste is leached successively with fresh aliquots of the same leaching fluid. This method is intended to eliminate the effect of concentration on solubility and to simulate long-term exposure to the leachant solution. The EPA's Multiple Extraction Procedure (MEP), the Standard Test Method for Sequential Batch Extraction of

Waste with Acidic Extraction Fluid (ASTM D 5284), and the Standard Test Method for Sequential Batch Extraction of Waste with Water (ASTM D 4793) are described in Appendix C.

Dynamic leaching Methods

Dynamic leaching methods are those incorporating a change in leaching fluid, either as a function of time or of composition. Column leaching tests are considered as simulating the flow of percolating groundwater through a porous bed of granular material. The flow of the leaching solution may be in either down-flow or up-flow direction and continuous or intermittent. The flow rate is generally accelerated when compared to natural flow conditions. However, it should be slow enough to allow leaching reactions to occur. A basis assumption in column leaching is that the distribution of the leaching solution is uniform and that all particles are exposed equally to the leachant solution. Precipitation or sorption within the column may affect the results.

The Standard Test Method for Leaching Solid Material in a Column Apparatus (ASTM D-4874) and the Dutch Standard Column Test (NEN 7343) are up-flow column procedures. Column experiments more closely approximate the flow conditions, particle size distribution and pore structure, leachant flow and solute transport found in the field (Zachara and Streile, 1990). They can be conducted in both saturated and unsaturated conditions. Unsaturated conditions are usually intended to mimic vadose zone placement. Intermittent addition of a given volume of leachant solution at the top of the column can provide uniform distribution of the fluid and approximate a constant fluid front moving through the unsaturated column. Saturated columns are obtained by a constant fluid flux, and allowing the fluid to pond at the top of the column. Variables, such as leachate collection, sampling frequency, leachant flow rate, and duration of the experiment, are determined by the experimental objectives.

Sequential leaching tests use a single sample that is leached by a series of different leaching fluids. The constituents extracted with a particular leachant are associated with a particular mineral phase or chemical species. Speciation is considered one of the controlling factors in the potential release of cations to the environment. The USGS Sequential Leaching Method was developed as a rapid indirect method of determining the modes of occurrence of trace elements in coal (Palmer et al, 1999).

Leachant Solutions

Selection of a leachant solution is critical to the success of a leaching study, and it depends on the objective of the study. Water, either DI or RO, is frequently used as the leaching solution. It is readily available, and it is an acceptable leachant to mimic natural weathering processes.

When methods to evaluate toxicity were developed, disposal in a municipal solid waste landfill was the scenario being modeled, and acetic acid was the appropriate solution to use. It is not particularly applicable to disposal in other situations, but it is often used because it is commonly accepted and because it is a weak acid, more aggressive than water, but less aggressive than mineral acids. Stronger mineral acids are used to leach metals and non-silicate minerals. Oxyanions are normally leached with bases. Leachant solutions and the types of compounds they normally dissolve are listed in Table 11.

Comparison of Leaching Methods

Several studies have attempted to compare different leaching methods, frequently in an attempt to correlate data from disparate techniques. Most comparisons were based on comparative release of particular elements by two or more specific procedures. Differences in such factors as test objective, leachant volume, sample size, and test duration were not considered.

In 1981, researchers at the Department of Energy/Los Alamos Scientific Laboratory (DOE/LASL) compared EPTOX with a procedure used at the laboratory (Heaton, et al, 1981). The samples were coal preparation wastes. The LASL static leach procedure was similar to EPTOX and the release of RCRA elements was found to be comparable with both procedures. The differences between one day and longer term tests were not large.

The Electric Power Research Institute (EPRI) sponsored a round robin evaluation of TCLP and EPTOX (Mason and Carlile, 1986)that was intended to evaluate the reproducibility of the TCLP and compare the results to those obtained with EPTOX. Seven CCB samples were sent to each of three laboratories which performed duplicate determinations with both TCLP and EPTOX. For the individual procedures, most of the variability was related to consistent differences in the results from one of the three laboratories. When comparing the methods, the TCLP and EPTOX concentrations of 14 elements were comparable for approximately 60 % of the determinations. Eighty-three per cent of the concentrations determined with TCLP were equal to or greater then those determined with EPTOX.

The Netherlands Energy Research Foundation (ECN) compared regulatory test procedures used in the US, Canada, Germany, France, Switzerland and the Netherlands (van der Sloot et al, 1991). Although the effect of pH on release is established, the effects of changes in redox potential and the concentration of complexing agents, as well as the effect of temperature differences, are not known.

Leaching methods include those to determine regulatory compliance, those approved by standards organizations, and methods developed for a particular objective. With exact duplication of regulatory or standard methods, tests conducted by different laboratories with the same protocol will probably produce comparable results. However, compliance tests and standard methods are not necessarily appropriate for leaching tests to simulate natural processes, obtain data on reaction mechanisms or unravel complex solubility relationships. For these, it is necessary to select or develop a procedure that addresses the experimental objective, meets the procedural constraints, and produces data that is directly or functionally related to the problem being studied. Data obtained by different laboratories using standard or regulatory tests are probably comparable. Studies performed with different leaching methods do not necessarily produce comparable data, although researchers using different methods may arrive at similar conclusions.

Previous Studies of CCB Leaching

The potential release of cations, particularly heavy metals, from CCB has been the subject of a number of research studies conducted with a variety of protocols.

Laboratory Studies

A number of researchers have addressed the release of cations, particularly heavy metals from CCB. Most of these address the question of the potential effects on groundwater if the CCB are placed as bulk fills or used in mine remediation. Studies conducted during the last 25 years are summarized below. The differences in leaching conditions, the duration of leaching and the different samples, make direct comparisons of results very difficult. However, the results of the individual studies can be correlated sufficiently to discern general trends. The leaching studies are summarized in Table 12; additional information is include in Appendix D.

Field Tests

Leaching tests are intended to predict the results of exposing CCB to environmental fluids. Although field tests are not directly comparable to laboratory tests, several were reviewed to determine if the general results showed the similar trends.

Power plant fly ashes were placed in mined out areas of the Wujek mine in Silesia (Cempiel et al, 2000). The concentration of trace elements is higher in the unamended mine water, although the concentration of major cations and anions increased in the leachate.

In Illinois, Colorado and Ohio, test cells were constructed to hold 700 to 1000 st of by-products from Clean Coal Technology processes (Solc et al, 1995). Relatively high precipitation and the porosity of the CCB compared to the low permeability of surrounding soil facilitated leaching within the cells. Anhydrite was apparently converted to gypsum; thaumasite ($Ca_3Si(CO_3)(SO_4)(OH)_6{\bullet}6H_2O$) and ettringite ($Ca_6Al_{12}(SO_4)_3(OH)_{12}{\bullet}26H_2O$) were also produced. The concentration of Na, K, Cl, SO_4 decreased with time in the cell pore water.

The pore water from borehole samples of fly ash in the unsaturated zone of a disposal mound was analyzed to investigate the long term natural weathering (Lee and Spears, 1997). The concentration of Al, Na, Ca, SO_4, B, Co, Cr, Li, Mo, Ni, Pb ans Sr increased with depth, while the pH of the pore water, between 7.8 and 8.9, showed no consistent variation with depth.

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 fly ash grout was injected into subsurface areas believed to be zones of acid production (Ackman et al. 1996). At the Bognanni site, the difference in the concentration of trace elements in grouted and ungrouted areas was less than 0.5 mg/L. At the Fran site, average concentrations of As, Co, Cu, Ni and Zn were higher in the injection area than in background areas. However, the concentrations in downdip and discharge samples were closer to those in the ungrouted spoil . Trace element concentrations, at the Pierce site were higher in the injection, downdip and discharge samples than in inflow or ungrouted spoil samples. Only the concentrations of Co, Ni and Zn exceeded 0.2 mg/L; all values were less than freshwater aquatic life criteria (Kim, 2000).

Mixtures of FBC by-products and Class F fly ash were placed in test cells, constructed to mimic a utility landfill, in Illinois (Weinburg et al, 1997). TCLP characterization indicated high pH and low soluble metals concentration. Leachate migration to groundwater resulted in transient increases in several metals, but no MCL exceedences.

Results of Leaching Studies

The research studies summarized here used a variety of methods and experimental conditions. Studies that quantify the amount leached versus the amount in the CCB mention that almost all of the cations in CCB, including the trace elements, are sparingly soluble at circumneutral pH. In several studies, most cations are found to be more soluble in acid solutions, except for those cations that form oxyanions, which are more soluble at high pH.

In evaluating the results of leaching studies of CCB, it is apparent that the wide variety of experimental conditions reflect the broad spectrum of conditions in natural environments to which CCB may be exposed. However, it should be noted that all of these studies were performed with different samples and were often an attempt to simulate a particular situation. Since the results were not correlated to an inherent characteristic of the CCB, there was always a question of whether a different samples would produce the same results under the same conditions.

Table 10. Batch leaching Methods

Method	**Leachant**	**Sample size, g**	**pH**	**L/S**	**Time, hr**
ASTM D-3987	Water	70		20	18
EPTOX	Water	100	5.0	20	24
SPLP	Water acidified with nitric and sulfuric acids	100	4.2	20	18
TCLP	Acetic Acid or Acetate Buffer	100	2.88	20	18
CA WET	0.2 M sodium citrate	50	5.0	10	48
NEN7341			4,7	100	4
LEP	Water acidified with 0.5 N acetic acid	50	5.0	16	24
SGLP	Synthetic Groundwater - site specific	10		20	1440

L/S: Liquid to Solid ratio, L/kg

Table 11. Common leachant solutions

Leachant Solution	**Soluble Compound**
Ammonium Acetate	Exchangeable cations
HCl	Carbonates, monosulfides
HF	Silicates
HNO_3	Metals, Disulfides
$MgCl_2$	Extractable metals
Hydroxylamine hydrochloride	Fe and Mn oxides
H_2O_2, Hydroxylamine hydrochloride, HNO_3	Organically bound metals

Table12. Summary of Experimental Parameters and Results for Laboratory Leaching Experiments

Reference	**Leach Type**	**Sample Size**	**Leachant**	**Volume/ Flow Rate**	**pH**	**Time**	**Summary of Results**
Dreher et al 1990	Column		H_2O	1 pore volume /wk	>8	15 wk	B, Ni, Mo, Se and Sr reported in alkaline leachate generated by FBC ash
	Batch		H_2O	L/S = 4:1	>8	3<>180 d	
Dreesen et al 1977	Batch		0.1 M citric acid 1.0 M HCl 0.001 to 1.0 M HNO_3 H_2O 0.1 M NH_4OH	L/S = 4:1		3 h	Maximum extraction = 30 % in strongly acid solution
Dudas 1981	Column	250 g	H_2O	124 L 245 L 421 L	> 12 to 8	2 yr max	Initial release of cations from simple salts, followed by dissolution of glassy ash matrix.
Fishman et al 1997	Batch		DI H_2O	L/S = 20:1	>8 <4	18 hr	Ash spheres coated with soluble, poorly crystalline aluminum potassium sulfate
Fleming et al 1996	Column		Acetic Acid		3.0 4.1 6.8		Acid leachable Cd, Cr, Al, Pb, Hg and Ag assumed to be present as oxides
Griffin et al 1980	Batch		H_2O + NaOH	10% weight to volume	8.8	3 - 6 months	Concentration of Al, B, Be, Ca, Cd, Cu, Co, Mg, Mn, Ni, Si, Sr, and Zn increased at low pH; K, Mo and Na more soluble at high pH.
			H_2O + NaOH		8.0		
			H_2O		4.0		

			H_2O +HNO_3		2.7		
Hequet et al 1999	Batch	5 g	H_2O Acetic Acid or Acetate buffer	L/S = 10:1	>6.5	24 hr	Cu and Zn adsorbed from solution on FA, <1 % Cu and < 15 % Zn released by subsequent leaching with H_2O, higher % released in acid , acetate buffer.
					2		
					4.6		
Hjelmar 1990	Lysimeter	10-18 t	Rain/snow			7 yr	Na and K leached initially; Ca dominates long term leachate. Concentration decreases with increased L/S
	Column	8-16 kg	SP	17-145 mm/d	>11		
	Serial Batch		H_2O	L/S = 2.5, 5.8		5 d	
Karapanagiota & Atalay 1996	Batch	10 g	H_2SO_4	20 - 1900 mL	1		AMD metals adsorbed by alkaline CCB when pH=4. Metals released at pH=1.Buffer capacity related to Ca in ash.
					4		
Kim & Kazonich 2001	Column	1 kg	H_2SO_4	~130 mL/d to 230 mL/d	1.2	from 15 d to > 6 mo	Solubility not a function of concentration in solid; solubility influenced by pH, <50 % of metal extracted.
			H_2O		6		
			Acetic Acid		2.88		
			SGW		6.7		
			SP		4.2		
			$FeCl_3$		1.95		
			$NaCO_3$		12.1		
Nathan et al 1997	Batch	1 kg	H_2O	2, 10, 20	>10	18, 24 hr	Release of heavy metals related to source of coal more than to pH of leachate
			Acetic Acid	20	>4	18 hr	

Nugteren et al 1999	NEN7343		H_2O	L/S = 10:1	4	3 wk	Washing FA with buffers reduced Cr, Mo, Sb, Se, and V leached from residues
Paul et al 1994	Batch		HAc H_2O	L/S = 20		18 hr	Some elements adsorbed from groundwater by CCB. ASTM was considered superior to TCLP.
	Column		Ground water	<100 mL/d	6±.2	~1 yr	
Pritts et al 1999	TCLP						Concentration of RCRA metals in the leachate of 50/50 mixtures of hazardous waste and CCB was below the detection limit
Querol et al 2001	Column	2 g	H_2O	50 mL/hr			Water soluble major and trace elements more soluble in open system due to loss of alkalinity. Dissolution of small particles or coatings on particle surfaces.
	Batch		DI H_2O	50 mL/g		24 hr	
Rice et al 1999	Batch	10 g	H_2O	200 mL		18 hr	
	Batch		H_2O	L/S = 20/1		< 1 hr	pH of leachate is controlling factor, soluble aluminum potassium sulfate (APS) coating adsorbed on glassy particles; Cd, Co, Cu, Mn, Ni, Pb, and Zn are acid leachable, As, Mo, and V soluble in alkaline leachates
	Column		H_2O	0.75:1 - 15:1		64 d	
Roy & Griffin 1984	Batch	1700 g	DI H_2O	17 L	Varied	140 d	Anhydrite controlled release of Ca; Al in equilibrium with mullite and insoluble hydroxide
Seidel et al 1999	Batch	Varies	H_2SO_4	300 mL		24 hr	Calcium sulfate precipitation on particles inhibit the solubility of Al
Seidel & Zimmels 1998	Batch		H_2SO_4	300 mL		12 d	30 % of the Al and Fe in the ash leached, formation of porous layer of calcium sulfate inhibits solubility. 90 % of the Ca, As, Cd, Cr, Cu, Hg, Pb and Zn were extracted at a pH < 1
Shabtai & Mukmenev	Batch	70 kg	H_2O & H_2SO_4	230 L	0.9	2 hr	<25% of al, ti, Fe and Si was leached from the ash .>70% of As, Cd, Cr, Cu, Hg, Pb and Zn leached at very low pH

Steenari et al 1997	Batch		H_2O H_2SO_4	L/S = 16		10 x 24	80 % of Ca soluble in acid, less than 20 % of K was leached from the fly ash samples
Stewart et al 1996 1997	Column		SP	2.5 cm /4 d	4.6	4 yr	Coal ash buffered acid formation from coal refuse. Alkalinity from CCB limits oxidation of pyrite in the coal refuse; metal release at low pH
	Column	Varies	SP	2.54 cm/wk		3 yr	
Talbot et al 1978	Batch	1 g	H_2O	L/S = 1000		~ 6 months	Fe, Al, Si - acid soluble; Ca, Mg, Na solubility not pH dependent below 10
	Batch		H_2O		1<>12	1 wk	
Teixeira et al 1992	EPTOX		H_2O, HAc	16/1	5	24 hr	Ca & Mg acid and alkaline soluble; Na & K more soluble in alkaline solution. Mn, Ni, Co, and Cu soluble in acid; Mo, Cr, and V alkaline soluble. Trace element solubility < 20 %
	INSA	100 g	H_2O	3 x 1 L	>9	3 x 24 hr	
	Column	100 g	H_2O	20 L	>9	546 hr	
Theis & Wirth 1977	Sequential		NH_4Oxalate Hydroxylamine Hydrochloride H_2O	200 g/L	Varied	24 hr	Mullite, hematite and magnetite on the surface of amorphous particles controlled the release of trace elements. Except As, elements acid soluble.
Wang et al	Column	20 g	HNO_3	120 mL	2.0 4.0 6.5	60 h	Sr, Zn, Pb, Ni, and As - leaching intensity increases with decreased pH.
Yaman & Kucubayrak 1977	Batch @ 200°C		H_2O	200 mL		1 hr	Alkaline fly ash extract neutralized the sulfuric acid produced in the oxydesulfurization of Turkish lignite

Chapter 5

Materials and Methods

The objective of this study was to determine the factors that control the release of heavy metals from fly ash. The samples were to be a random population from several states. A column method using 1 kg samples and several leachant solutions was designed to simulate exposure to natural fluids.

Sample Acquisition

The samples were obtained through contacts with local (western Pennsylvania, West Virginia) utilities and by requesting samples from ash managers and ash marketeers at CCB conferences or through referrals. The request was simply to ship two 20 L (5-gal) buckets of fly ash or other CCB to the researcher at the U.S Bureau of Mines (later to the U.S. Department of Energy). In order to obtain a sample representative of what would be utilized or disposed, there were no pre-selection criteria.

In addition to fly ash from PC boilers, there were several fly ash samples from FBC units, a bottom ash sample, a weathered ash from a disposal pond, and steel slag fines. CCB are inherently variable, based on the composition of the coal and the combustion conditions. To limit the number of extraneous parameters, the samples included here are class F fly ashes from PC boilers.

The samples are identified in Table 13. In subsequent sections the samples are identified by sample number, which was determined by the order in which the samples were obtained and used in the leaching experiment. Missing numbers in the sequence were other types of CCB samples that are not included in this discussion. The station or power plant is listed in the second column. The generator or operating company is in the third column and the state in which the station is located is in the fourth column. The last column gives any additional information on the source of the sample. A generating company may operate more than one power plant, and a power plant may include more than one boiler, usually designated as a unit. As an example, Samples 4 and 5 came from different power plants owned by the same company; samples 6 and 7 came from different boilers at the same power plant. How the fly ash is handled also varies. In some cases, all the fly ash generated may go to a storage facility (silo) until it is full, then a second silo will be used. In other cases, all the fly ash from a unit will go to a particular silo. A few samples were identified as coming from a particular control device, a mechanical precipitator, ESP or baghouse.

All of the samples were obtained directly from a collection device or storage facility. None of the samples included in this discussion were taken from surface impoundments or landfills. Most utilities take fly ash samples directly from the stack with an in-line sampler (10 g) and handle it in truck load (ton) quantities. Obtaining a sample of approximately 50 kg is outside their normal operation, and we appreciated their cooperation.

Leaching System

A column leaching system was chosen for this test because, at low flow rates, the release of metals from a solid matrix can be determined as a function of volume, pH changes, and time. The system is designed to simulate the reaction of materials during exposure to natural fluids, such as acid rain or acid mine drainage, and is appropriate for unconsolidated materials with a particle diameter of less than 0.5 cm. Because CCB are not a homogeneous material, each column was made large enough to hold a representative 1 kg sample.

The columns are constructed of 1 meter sections of 5 cm ID acrylic pipe with an approximate volume of 2 L. Threaded PVC pipe caps close each end; 0.635 cm fittings are tapped into the ends for leachant inflow and leachate outflow. Ten g of glass wool is placed in the bottom of the column, then the sample, usually 1 kg, is poured into the column. Another 10 g of glass wool is placed on top of the sample; a cap seals the column and it is hung on a distillation rack (Figure 9). In all, seven groups of four samples are assembled, simultaneously leaching 4 samples with 7 leaching solutions (Figure 10).

The leaching solutions, listed in Table 14, were selected as standards or as surrogates for naturally occurring liquids and to cover a broad pH range. Deionized (DI) water is the primary standard; acetic acid is a weak acid and an indicator of leaching during co-disposal in a MSW landfill. It also allows comparison to TCLP leaching results. Sodium carbonate is a high pH solution for elements that are caustic soluble, and synthetic groundwater (Hassett,1992) is used to determine if other naturally occurring ions affect solubility. Synthetic precipitation is the leachant used in EPA's SPLP protocol; it mimics the effect of acid rain on bulk fills. The ferric chloride solution is an oxidizing solution and ferric ions are the primary cations in AMD. Sulfuric acid is a strong acid and is also a component of AMD.

Each solution is placed in a 20 L reservoir. A peristaltic pump delivers the leachant solution to individual delivery lines for each of the four columns. The flow rate is approximately 130 mL/d. The leaching system originally used a gravity feed system to distribute leachants to the leaching columns. Each reservoir of solution was situated 7 meters above the columns with a distribution system and flow regulators connecting it to 4 columns containing different CCB samples. Normal flow rates went from 250 milliliters per day per column with the gravity system. When this system was replaced with peristaltic pumps, the flow rate averaged 200 mL/day/column. Actual flow rates varied between plus or minus 100% for the gravity system to plus or minus 15% for the pumps. Simultaneous tests utilizing both gravity and pumps showed no differences in leaching results except that the pump tests took longer to achieve acidification because of the lower acid feed rate.

Leachate is collected in 1 L volumetric cylinders; samples are generally collected at 2 to 3 day intervals; the pH and the volume are determined when the samples are taken. The leachate is then split, and half is used for the determination of acidity and/or alkalinity. The other portion of the sample is acidified with 2 N HCl and sent to a contract analytical laboratory for analysis by ICP-AES. All samples were analyzed for 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. Each fly ash sample was leached until acidified with the pH 2.9 acetic acid solution (typically from 30 to 90 days for Class F fly ash samples).

Table 13. CCB sample ID and sources.

Sample #	Station	Generator	State	Other
4	HF	AGH1	PA	Unit # 3
5	FM	AGH1	WV	
6	CNM	GPA1	PA	Unit 1
7	CNM	GPA1	PA	Unit 2
8	FM	AGH1	WV	
11	CNM	GPA1	PA	Silo 1A
12	CNM	GPA1	PA	Silo 1B
13	CNM	GPA1	PA	Silo 2B
14	BI		PA	
15	MNTR	PPA2	PA	Unit # 1
16	MNTR	PPA2	PA	Unit # 2
17	ELR	DO1	PA	Unit #2
18	ELR	DO1	PA	Unit #1
19	NEM	AGH1	PA	Truck Silo
20	MNTR	PPA2	PA	Unit #1
21	CSWK	DO1	PA	Silo
24	JAM	AWV1		Silo#2
25	NEM	AGH1	PA	ESP
26	ELR	DO1	PA	Unit #4
27	MNR	APA2	WV	
28	KWA	APA2	WV	Truck Silo
30	PTM	PMD1	MD	
31	BR	TTN1	TN	
33	FM	AGH1	WV	
36	LLD	MML2	FL	
38	HF	AGH1	WV	
39	CRV	APA2	WV	
40	M	APA2	WV	
41	RPT	APA2	WV	
44	GLN	APA1	VA	
46	ELR	DO1	PA	Baghouse
49	ELR	DO1	PA	ESP

Table 14. Leachant solutions used in column leaching test

Leachant Solution	**ID**	**pH**
Sulfuric Acid	H_2SO_4	1.2
Ferric Chloride	$FeCL_3$	2.0
Acetic Acid	HAc	2.9
Synthetic Precipitation	SP	4.2
Synthetic Ground Water	SGW	6.7
Deionized Water	H_2O	6
Sodium Carbonate	Na_2CO_3	11.1

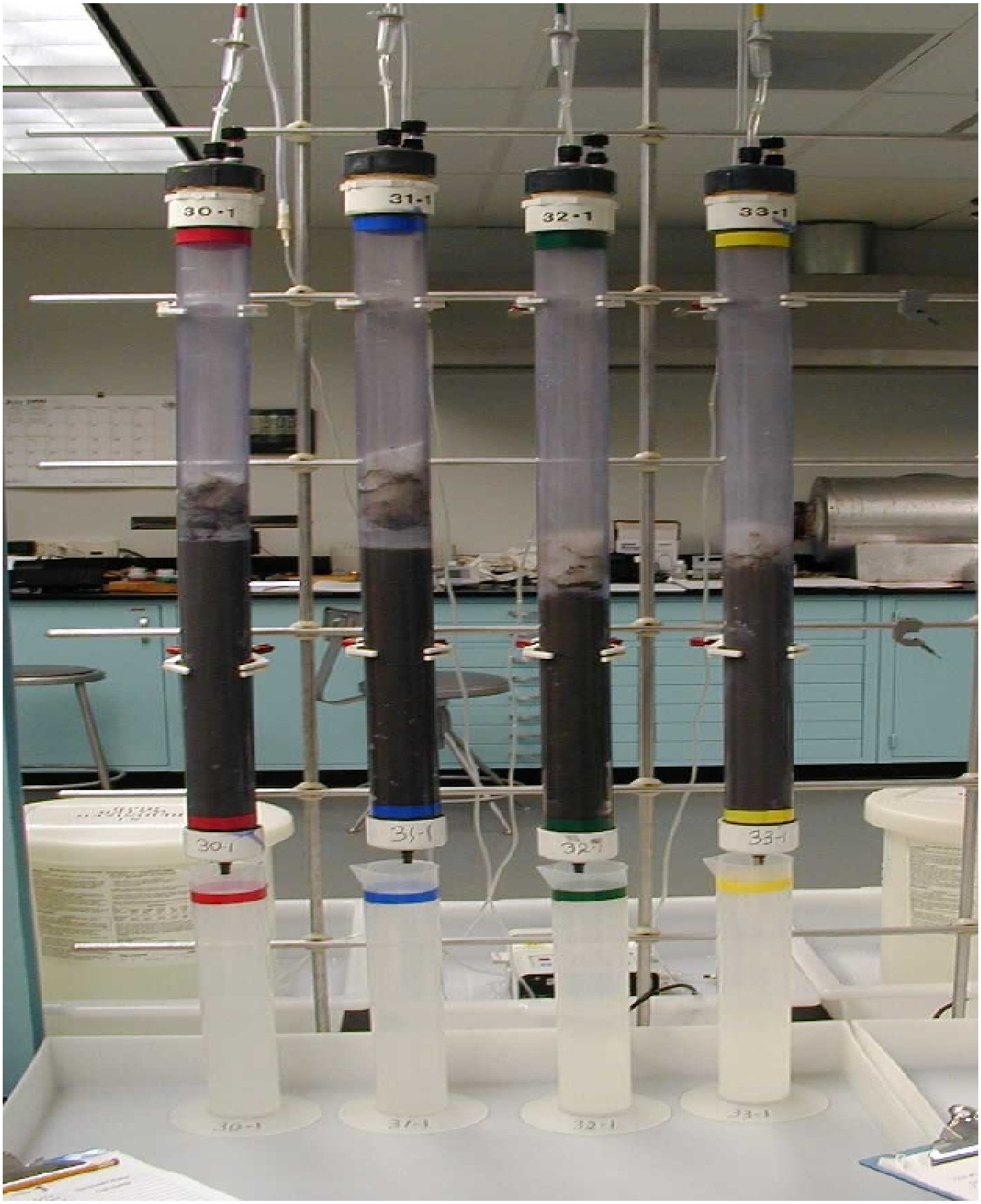


Figure 9. Group of four 1 m by 5 cm acrylic columns holding 1 kg fly ash samples

Figure 10. Seven groups of four columns constitute one leaching test.

Chapter 6

Results and Discussion

Sample Composition

The samples used in this project were Class F fly ashes obtained from PC electric power plants; the majority were located in Pennsylvania and West Virginia, but samples were also obtained from plants in Florida, Maryland and Tennessee. Because of the significant differences in chemical and mineral composition, other types of samples, used in the project, were not included in this dissertation.

The major chemical constituents are shown in Figure 11. The concentrations of major and minor elements as oxides are given in Table 15, and Table 16 lists the concentration of trace elements in ppm.. The non-silicate concentrations of the major and minor elements, in ppm, are in Table 17 and the trace elements in Table 18, and the ratio of non-silicate to silicate concentrations are listed in Table19 and Table 20.

Table 15. Major and minor element concentration of PC-FA samples, wt % as oxide.

FA#	FeO	CaO	MgO	Al_20_3	Na_2O	MnO	K_2O	SiO_2	PO_5
4	14.39	5.52	1.02	23.65	0.75	0.04	1.73	50.11	0.35
5	13.44	4.95	0.90	24.46	0.49	0.03	1.92	51.44	0.47
6	13.86	1.82	0.68	25.35	0.31	0.03	2.05	46.81	0.74
7	14.95	1.67	0.69	25.12	0.30	0.03	2.09	45.89	0.68
8	13.19	5.17	0.92	25.02	0.51	0.03	1.89	51.80	0.56
11	15.05	2.02	0.68	25.55	0.29	0.03	1.87	45.43	0.62
12	13.76	2.02	0.68	25.98	0.30	0.03	1.91	45.63	0.64
13	13.77	1.93	0.68	25.54	0.30	0.03	1.88	45.12	0.60
14	13.22	2.72	0.71	23.32	0.47	0.03	1.62	46.55	0.58
15	12.45	1.23	0.76	27.06	0.17	0.03	2.30	48.48	0.32
16	13.07	1.69	0.78	26.20	0.14	0.03	2.41	50.09	0.30
17	9.13	1.78	0.74	20.08	0.59	0.03	2.06	48.92	0.22
18	13.08	2.14	0.87	21.61	0.59	0.04	2.09	52.08	0.16
19	13.23	3.80	0.88	22.63	0.52	0.04	2.00	49.96	0.30
20	13.28	3.58	0.77	25.03	0.17	0.03	2.16	46.86	0.33
21	11.52	2.83	0.79	24.58	0.53	0.04	1.80	48.14	0.24
24	2.90	0.61	0.80	29.17	0.24	0.02	2.64	57.41	0.11
25	13.69	4.41	0.95	23.49	0.69	0.03	2.02	50.88	0.38
26	31.35	2.52	0.62	18.52	0.35	0.06	1.18	41.13	0.10
27	3.38	0.95	0.84	31.12	0.28	0.02	2.61	59.05	0.10
28	3.54	0.65	0.72	29.14	0.20	0.02	2.37	55.92	0.12
30	15.65	1.44	0.57	26.34	0.45	0.02	1.70	45.82	0.42
31	11.74	1.57	0.94	28.13	0.60	0.03	2.39	49.62	0.24
33	12.94	4.86	0.87	24.26	0.74	0.03	1.75	49.69	0.45
36	10.24	2.12	0.91	23.88	0.63	0.06	2.34	46.93	0.36
38	14.23	4.85	0.95	23.64	0.84	0.04	1.52	48.00	0.39
39	8.26	5.53	1.75	25.07	0.42	0.06	2.37	50.73	0.26
40	5.03	0.64	0.70	28.92	0.19	0.03	2.11	55.98	0.06
41	5.48	15.71	3.88	22.95	1.09	0.03	1.14	44.45	0.73
44	6.93	0.86	0.90	25.96	0.40	0.04	2.56	57.07	0.23
46	27.36	3.01	0.76	21.77	0.39	0.05	1.59	44.16	0.22
49	39.18	3.51	0.68	17.98	0.34	0.05	1.23	37.03	0.17

Table 16. Trace element concentration of PC-FA samples, ppm.

Sample #	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Se	Zn
4	<100	121	<5	<25	<50	<50	<25	<50	<50	5	16
5	<100	155	<5	<25	<50	<50	<25	<50	<50	4	23
6	171	1140	11	<10	41	175	114	107	90	5	201
7	166	1090	10	<10	39	170	105	107	64	5	191
8	67	855	8	<10	31	171	74	1040	59	3	135
11	<200	859	<10	10	<100	173	115	<100	113	11	202
12	<200	893	<10	<10	<100	165	119	<100	112	10	207
13	<200	866	<10	<10	<100	164	112	<100	109	12	188
14	<100	456	12	15	40	184	93	124	71	8	175
15	229	844	14	15	42	185	158	106	124	9	235
16	301	1160	13	15	42	170	139	109	121	8	204
17	<100	471	<5	<15	<25	132	72	71	81	18	204
18	77	529	2	<1	11	97	76	85	<1	1	124
19	125	511	6	<1	16	111	76	92	<1	2	155
20	277	1380	10	<1	44	110	155	135	<1	2	197
21	148	849	12	<1	31	92	122	125	<1	2	128
24	53	789	14	<1	59	176	152	120	134	2	113
25	143	699	4	<1	23	136	74	84	116	4	136
26	44	469	6	1	33	114	53	124	12	1	34
27	28	765	18	<5	86	176	156	137	65	9	112
28	69	703	19	<5	79	211	176	131	99	8	121
30	90	781	11	<.1	50	205	117	119	24	13	139
31	175	951	27	<.1	73	193	255	171	109	20	252
33	91	892	9	<.1	42	181	79	101	77	9	140
36	144	1070	19	2	21	174	1610	482	173	19	609
38	60	888	8	<.2	24	150	90	84	45	6	122
39	128	1540	11	0	45	167	178	91	83	26	168
40	8	693	13	0	47	155	79	102	16	0	45
41	25	4170	9	1	36	105	184	87	48	27	111
44	113	1400	18	2	55	157	140	103	53	22	80
46	70	620	7	<10	30	144	62	71	66	4	37
49	60	496	5	<10	38	122	65	82	45	5	26

Table 17. Concentration of major and minor elements in non-silicate portion of fly ash, mg/kg,

Sample #	Fe	Ca	Mg	Al	Na	Mn	K	Si	P
4	54800	27833	3207	28400	1748	115	2345	196	1237
6	48350	8564	1543	20900	1342	72	2990	161	1597
7	44300	7822	1463	16833	1153	65	2598	141	1398
8	46333	24500	2177	21333	760	90	1760	218	1448
11	53517	9513	1457	19667	870	68	2387	186	1493
12	NO	SAMPLE							
13	NO	SAMPLE							
14	44600	12583	1377	16633	847	67	1727	396	889
15	33233	3443	895	16500	284	41	2218	225	604
16	33700	6743	865	14633	267	44	2123	148	514
17	31033	8320	1205	15200	865	92	1970	279	636
18	44067	8783	1095	10580	559	114	1353	530	456
19	46733	16867	1650	19267	781	115	2153	485	816
20	35433	22000	1042	12400	225	41	1640	317	648
21	39683	12067	1552	18900	768	110	1773	435	617
24	19617	217	978	42833	1450	51	14033	229000	638
25	102033	21800	3110	71267	4773	166	13667	187000	1800
26	56207	11133	962	7765	386	103	510	382	167
27	6497	2757	725	13333	290	36	1768	170	185
28	9413	2087	869	19367	303	42	2488	165	209
30	50867	5140	615	11833	242	50	1057	251	919
31	26367	5160	1117	18167	508	38	2615	175	532
32	44633	28167	1440	18500	1380	197	2455	510	417
33	34000	23233	1977	18667	620	79	1493	1015	1482
36	23100	8638	1033	9975	985	205	1708	241	832
38	35567	22200	2312	18783	1197	84	1367	1024	1080
39	NO	SAMPLE							
40	NO	SAMPLE							
41	23167	82467	15767	60467	3875	105	3027	22	1607
44	12467	1648	619	8410	313	53	1473	94	337
46	69167	12700	1138	7460	365	122	706	301	323
49	31367	38789	7102	20431	1624	63	682	108	1786

Table 18. Non-silicate concentration of trace elements, mg/kg,

Sample #	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	Zn
4	94	279	3	3	16	67	36	40	17	<IDL	6	111
5	NO	SAMPLE										
6	135	441	3	3	20	46	81	93	27	5	15	228
7	133	403	3	2	18	32	90	81	24	4	13	182
8	47	331	3	2	18	68	65	86	14	3	6	146
11	140	395	3	3	21	51	45	49	27	4	14	134
12	NO	SAMPLE										
13	NO	SAMPLE										
14	74	161	4	2	18	55	29	47	15	5	6	66
15	177	321	4	2	17	44	53	37	29	7	7	110
16	254	500	3	2	16	41	46	37	26	8	7	85
17	63	106	1	1	10	43	19	26	9	4	15	88
18	29	84	1	2	10	29	14	23	5	4	9	39
19	81	123	1	2	12	60	19	27	11	2	11	60
20	219	636	1	1	14	35	40	34	18	4	10	66
21	87	255	3	2	15	53	36	37	17	<IDL	10	57
24	41	68	12	14	63	149	138	109	53	8	8	74
25	96	470	5	13	39	119	56	75	44	5	16	125
26	18	77	1	2	11	18	7	29	2	<IDL	10	14
27	21	142	3	1	17	45	36	26	23	<IDL	16	39
28	39	176	4	1	23	57	49	33	26	<IDL	13	44
30	51	272	2	2	20	34	30	37	10	3	10	58
31	123	247	6	2	20	51	76	43	32	6	13	85
32	48	267	3	6	11	102	25	37	32	9	13	295
33	47	296	2	2	14	61	21	28	11	<IDL	8	55
36	123	232	4	2	13	28	157	97	54	13	12	200
38	57	243	2	2	9	52	24	22	12	<IDL	7	52
39	NO	SAMPLE										
40	NO	SAMPLE										
41	22	2855	6	3	25	63	114	47	20	<IDL	15	72
44	73	378	3	1	12	29	28	18	12	2	14	25
46	18	126	1	2	11	26	11	24	3	<IDL	11	26
49	9	1549	1	2	9	22	28	20	5	<IDL	7	43

Table 19. Mass fraction of elements in non-silicate phases to total amount in fly ash: Major and minor elements.

	Al	Ca	Fe	K	Mg	Mn	Na	P	Si
FA4-1	0.31	0.93	0.85	0.21	0.75	0.55	0.34	0.86	0.00
FA6-1	0.24	0.97	0.85	0.22	0.70	0.44	0.42	0.54	0.00
FA7-1	0.20	0.89	0.77	0.20	0.66	0.38	0.37	0.59	0.00
FA8-1	0.24	0.84	0.93	0.14	0.68	0.48	0.20	0.68	0.00
FA11-1	0.14	0.64	0.74	0.14	0.32	0.35	0.26	0.60	0.00
FA18-1	0.13	0.76	0.85	0.09	0.30	0.55	0.14	0.78	0.00
FA19-1	0.21	0.76	0.84	0.15	0.40	0.50	0.22	0.82	0.00
FA20-1	0.14	0.94	0.66	0.11	0.38	0.28	0.17	0.52	0.00
FA21-1	0.20	0.78	0.85	0.14	0.47	0.52	0.21	0.53	0.00
FA24-1	0.32	7.08	0.28	0.16	0.75	0.56	0.20	0.30	0.00
FA25-1	0.22	0.93	0.42	0.14	0.65	0.52	0.19	0.55	0.00
FA 26-1	0.11	0.79	0.69	0.07	0.39	0.62	0.15	0.39	0.00
FA27-1	0.15	1.20	0.40	0.10	0.27	0.39	0.16	0.32	0.00
FA 28-1	0.23	1.77	0.54	0.15	0.38	0.44	0.21	0.62	0.00
FA31-1	0.19	0.71	0.56	0.19	0.29	0.33	0.28	0.82	0.00
FA 33-1	0.18	0.82	0.55	0.11	0.44	0.47	0.18	0.81	0.01
FA 36-1	0.12	0.81	0.49	0.12	0.30	0.64	0.24	0.72	0.00
FA 38-1	0.27	0.76	0.58	0.15	0.71	0.45	0.20	0.81	0.00
FA 39-1	0.31	0.87	0.48	0.18	0.53	0.53	0.26	0.70	0.00
FA 44-1	0.12	0.54	0.49	0.12	0.22	0.43	0.19	0.80	0.00
FA46-1	0.10	4.13	2.72	0.06	0.41	0.98	0.22	0.77	0.00
FA49-1	0.10	0.33	3.98	0.03	0.22	1.02	0.16	1.53	0.00

Table 20. Mass fraction of elements in non-silicate phases to total amount in fly ash: Trace elements

	As	Ba	Be	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	Zn
FA4-1	0.94	0.44	0.56	0.22	0.40	0.56	0.44	0.46	0.35	0.00	1.43	0.95
FA6-1	0.89	0.56	0.40	0.20	0.37	0.29	0.90	0.93	0.45	1.22	1.15	1.47
FA7-1	0.94	0.53	0.36	0.18	0.36	0.22	1.13	0.84	0.44	1.68	1.20	1.29
FA8-1	0.86	0.46	0.42	0.19	0.35	0.48	1.11	0.92	0.36	0.00	1.74	1.16
FA11-1	0.97	0.43	0.39	0.21	0.38	0.28	0.46	0.49	0.43	0.74	1.81	0.69
FA18-1	0.83	0.21	0.33	0.15	0.33	0.34	0.32	0.37	0.23	0.50	1.05	0.42
FA19-1	0.95	0.30	0.22	0.18	0.32	0.48	0.42	0.38	0.28	0.35	1.28	0.55
FA20-1	0.98	0.65	0.12	0.12	0.37	0.26	0.33	0.29	0.29	0.48	1.02	0.44
FA21-1	0.92	0.40	0.27	0.16	0.32	0.40	0.43	0.37	0.36	0.00	1.07	0.57
FA24-1	0.67	2.37	0.24	0.07	0.23	0.27	0.27	0.23	0.30	0.40	0.94	0.51
FA25-1	0.82	0.37	0.39	0.19	0.29	0.28	0.41	0.34	0.21	0.00	0.78	0.41
FA 26-1	0.78	0.23	0.29	0.17	0.42	0.24	0.49	0.49	0.30	0.00	0.56	0.57
FA27-1	0.65	0.45	0.24	0.07	0.22	0.28	0.29	0.23	0.38	0.00	0.67	0.46
FA 28-1	0.73	0.80	0.30	0.08	0.28	0.30	0.33	0.29	0.36	0.00	0.61	0.47
FA31-1	1.18	0.41	0.41	0.20	0.38	0.46	0.51	0.41	0.50	0.29	0.99	0.52
FA 33-1	0.97	0.41	0.44	0.16	0.32	0.44	0.42	0.35	0.31	0.00	0.73	0.45
FA 36-1	1.05	0.31	0.31	0.15	0.27	0.56	0.52	0.31	0.36	0.74	0.75	0.58
FA 38-1	0.93	0.44	0.42	0.15	0.27	0.49	0.43	0.32	0.33	0.00	0.57	0.52
FA 39-1	0.93	0.57	0.57	0.16	0.34	0.53	0.49	0.38	0.40	0.00	0.78	0.66
FA 44-1	0.91	0.46	0.28	0.08	0.26	0.26	0.35	0.28	0.36	0.24	0.81	0.46
FA46-1	0.22	0.15	0.11	0.25	0.24	0.24	0.14	0.37	0.10	0.00	0.65	0.47
FA49-1	0.23	0.21	0.37	0.37	0.67	0.19	0.25	1.05	0.10	0.00	0.77	0.62

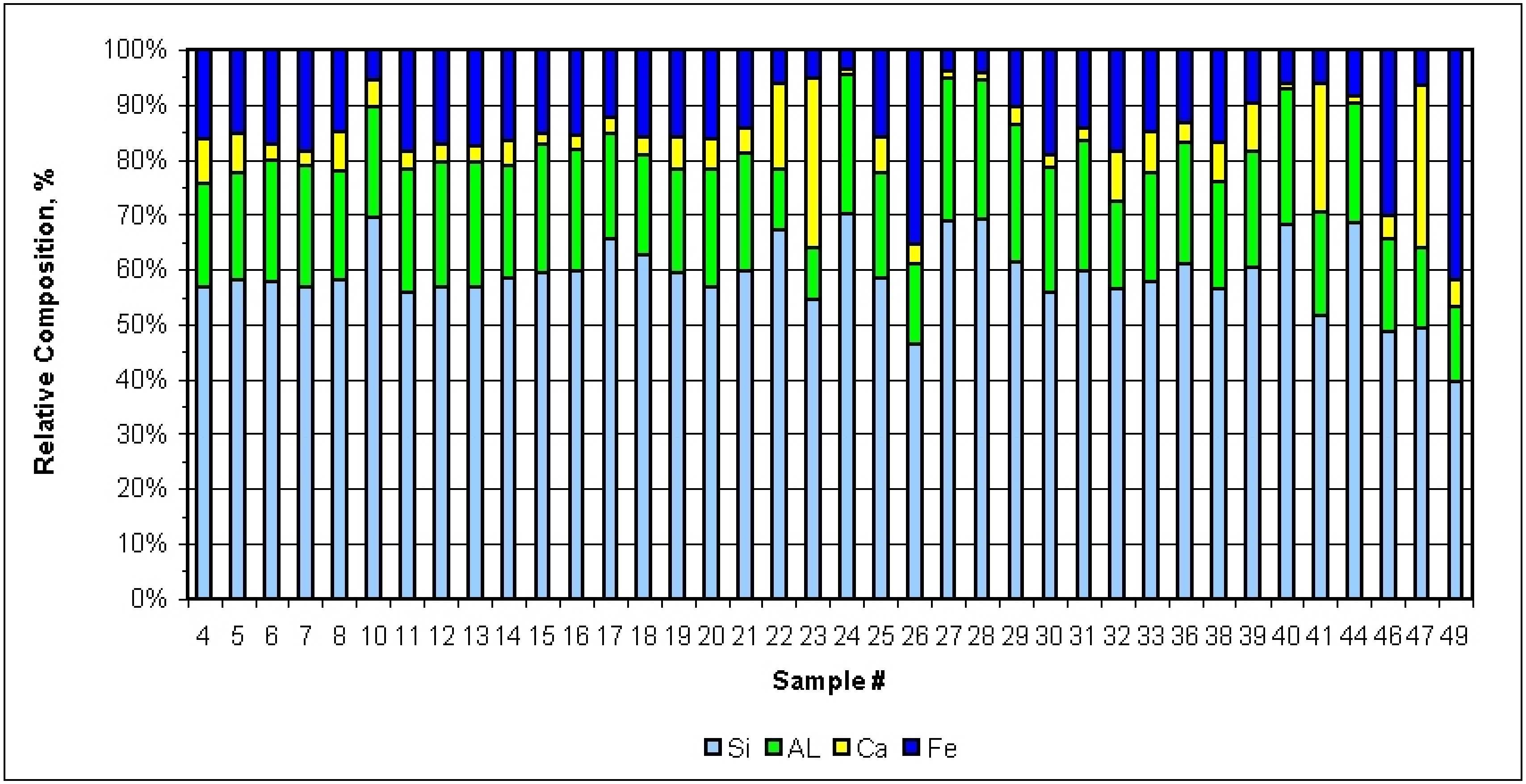


Figure 11. Relative concentration of major elements in fly ash samples.

Cation Solubility

Because CCB are a mixed material, containing a variety of cations in different matrices, the solubility of the metals is not a simple function of the concentration in the solid. Some elements may be more or less soluble than others and the solubility of a given element is not the same in all leachant solutions. The solubility of each cation was determined, assuming that each leach test had reached completion, by calculating the total amount of each element leached for each fly ash sample. The cumulative amount leached M_L is equal to the sum of the concentrations measured in each leachate sample times the volume of leachate divided by the weight of the sample.

where $M_{L =}$ cumulative amount leached , mg/kg

C = the concentration in the leachate, mg/L

V = volume of individual leachate samples, L

S = sample weight, kg.

The mass ratio of a cation leached during the experiment was calculated by dividing the cumulative amount leached by the total concentration of that element in the solid.

$$M_{\frac{L}{T}} = M_L / M_T * 100 \tag{10}$$

where $M_{L/T}$ = mass leached relative to the total concentration in the solid

M_L = Cumulative amount leached , mg/kg

M_T = Total concentration of an element in the solid sample, mg/kg.

The calculation was performed for all major, minor and trace elements in four leachant solutions: water (H_2O), sodium carbonate ($Na_2CO_{3)}$, acetic acid (HAc) and sulfuric acid (H_2SO_4). A frequency distribution of the $M_{L/T}$ values for the set of 31 Class F fly ash samples was determined for each element in the four selected leachant solutions. Four solubility ranges were defined as < .02, 0.02<> 0.20 , 0.20<>0.65 and >.65. As an example, a frequency distribution for the relative amount of Mn leached is shown in Table 21. In column labeled # under H_2O, the mass ratio of Mn leached was less than .02 for 11 of the 31 samples. The value of $M_{L/T}$ was greater than .65 for 27 of the 31 samples in sulfuric acid.

From these data, a relative frequency distribution was calculated, as shown in the columns labeled % in Table 21. Based on a population of 31 samples, $M_{L/T}$ was < 0.2 for Mn in water for 35 % of the samples. But $M_{L/T}$was greater than 0.65 for 87% of the samples when sulfuric acid was the leachant solution.

Solubility was defined according to $M_{L/T}$, the relative amount of an element leached. If $M_{L/T}$ was equal to or less than 0.02 more than 50 % of the samples, the element was defined as insoluble (I) in that leaching solution. If $M_{L/T}$ was between 0.02 and 0.20 for more than 50 % of the samples the cation was slightly soluble(SS). If the relative amount leached was between 0.20 and 0.65 for the majority of samples, that element was considered moderately soluble (MS). If $M_{L/T}$ was greater than 0.65 for at least 50 % of the samples, that element was very soluble (VS) in that leachant solution. If less than 50% of $M_{L/T}$ values fell within all categories, the solubility was assigned as that category that had the maximum number of values. Solubility categories for each element in the four leachant solutions are shown in Table 22.

Based on this sample set of Class F PC fly ashes, Fe, Mg, Ba, Pb, and Sb are insoluble in all types of leachant. Several elements that are acid soluble (Ca, Mn, Be, Cr, Cu and Zn) have similar solubilities in both acid solutions, but the Al, Cd, Co and Ni are slightly soluble in sulfuric acid but insoluble in the weaker acetic acid. Only Ca, Mn, K, and Na are soluble in H_2O, and As is the only element that is soluble in the basic Na_2CO_3 leachant. The variation in solubility of an element in different leachants indicates that the elements are present in different chemical compounds or mineral forms.

The solubility classification of an element is assigned based on the range in which the majority of values fall. The distribution of the soluble concentrations are shown in box plots (Figures 12 to 17) for the major, minor and trace elements in H_2O and H_2SO_4. In the figures, the box represents the soluble concentrations between the 10th and 90th percentile; the bars are the 5th and 95 percentiles. Points above and below the boxes are outlier values. The median is represented as a solid line, and the mean is a dashed line.

Table 21. Frequency distribution of the mass ratios of Mn leached from Class F fly ash (#) and relative frequency distribution (%).

$M_{L/T}$	H_2O		Na_2CO_3		HAc		H_2SO_4	
	#	%	#	%	#	%	#	%
<0.2	11	35	12	39	1	3	2	6
0.2<>0.20	9	29	11	35	1	3	1	3
0.20<>0.65	10	32	8	26	6	19	1	3
>0.65	1	3	0	0	23	74	27	87

Table 22. Solubility of various elements in Class F fly ash samples.

Element	H2O	Na2CO3	HAc	H2SO4
Fe	I	I	I	I
Ca	SS	SS	MS	MS
Al	I	I	I	SS
K	SS	SS	SS	SS
Mg	I	I	I	I
Mn	MS	SS	VS	VS
Na	SS	X	SS	SS
As	I	MS	I	I
Ba	I	I	I	I
Be	I	I	SS	SS
Cd	I	I	I	SS
Co	I	I	I	SS
Cr	I	I	SS	SS
Cu	I	I	SS	SS
Ni	I	I	I	SS
Pb	I	I	I	I
Sb	I	I	I	I
Se	I	I/SS	I	I
Zn	I	I	SS	SS

I:	Insoluble
SS:	Slightly Soluble
MS:	Moderately Soluble
VS:	Very Soluble

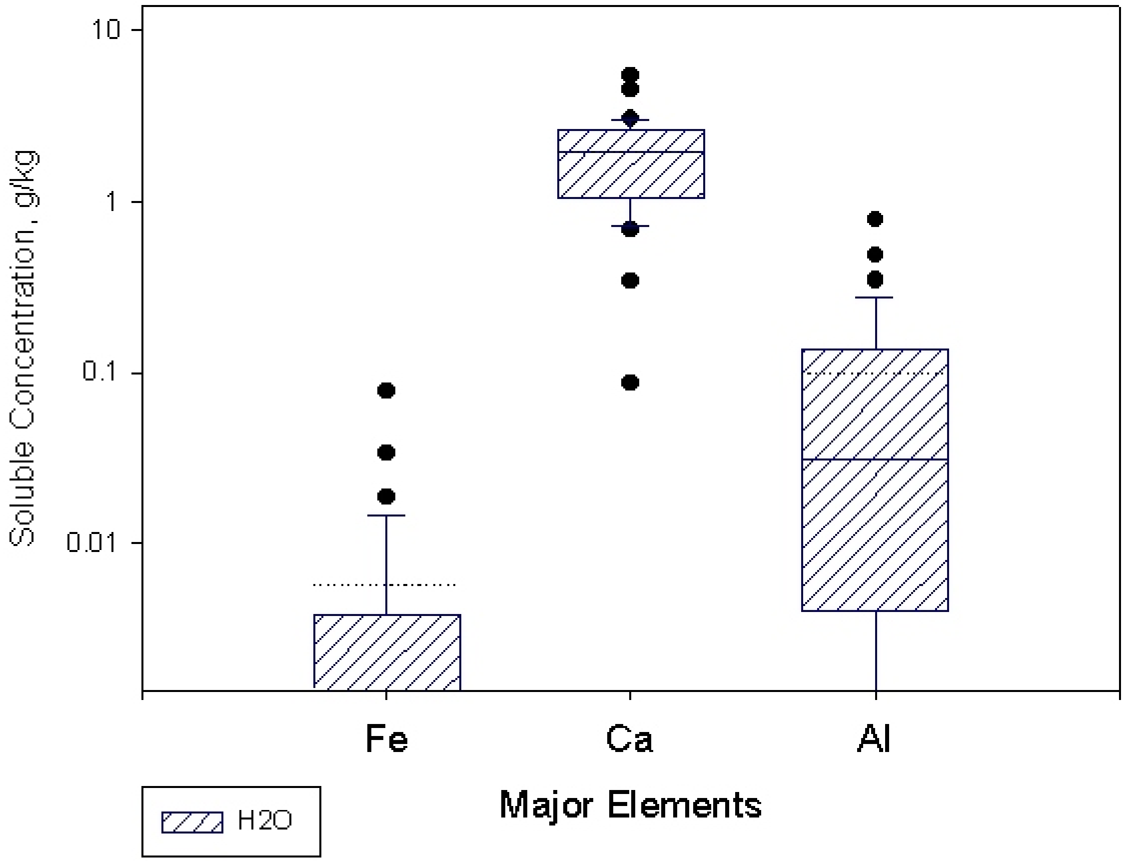


Figure 12. Box plot showing distribution of soluble concentration values for major elements in H_2O. Solid line is median; dotted line is mean soluble concentration (g/kg).

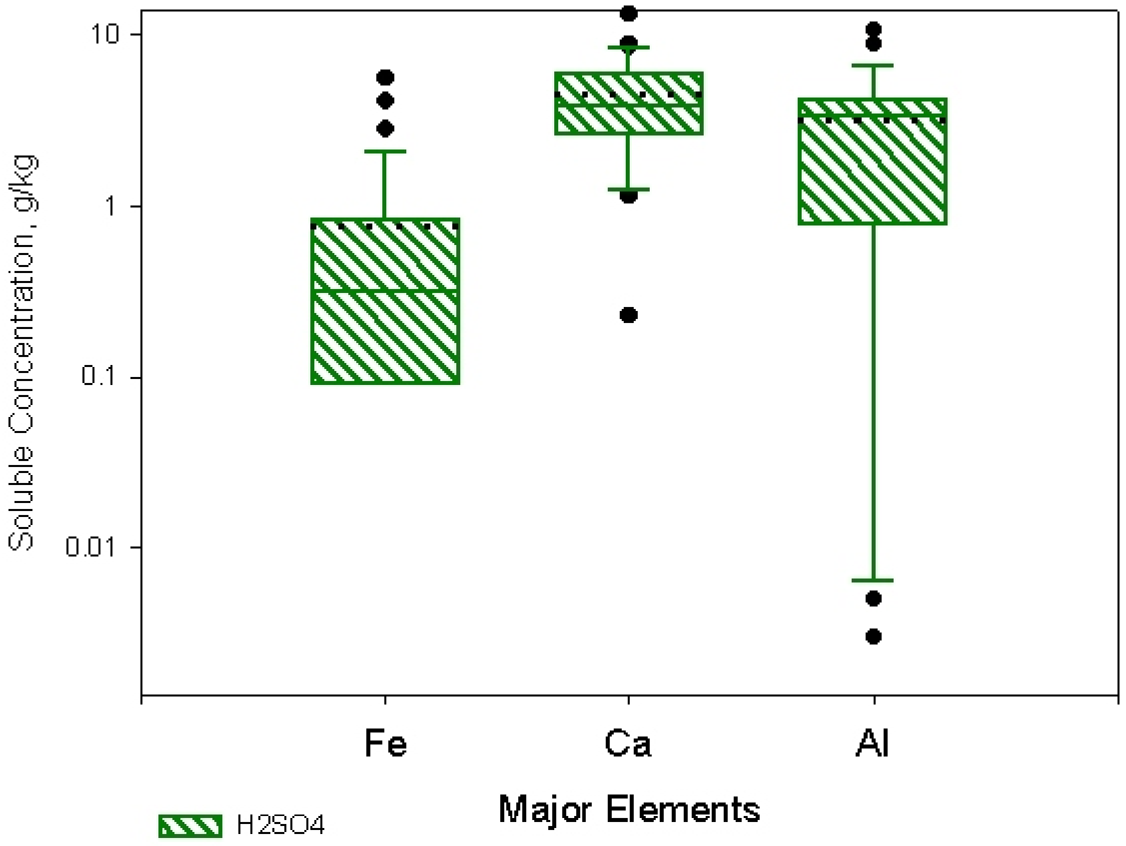


Figure 13. Box plot of distribution of soluble concentrations of major elements in H_2SO_4. Solid line is median value; dotted line is mean soluble concentration (g/kg).

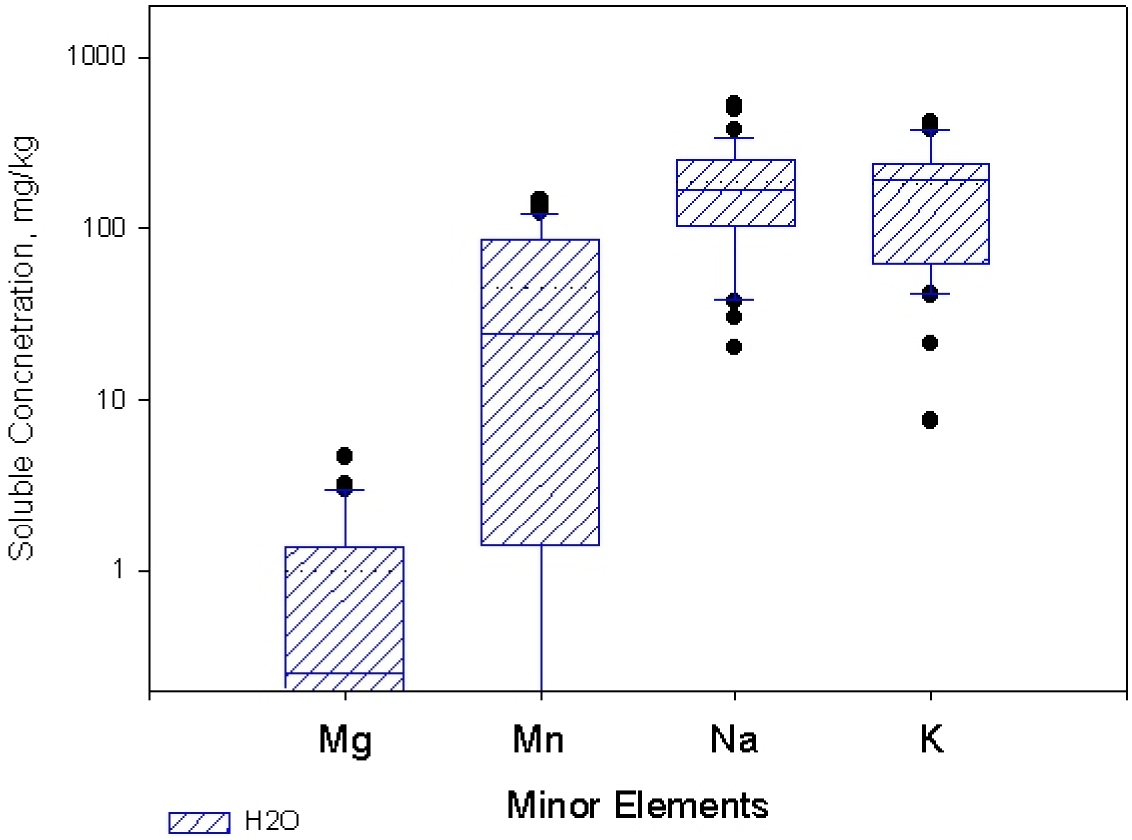


Figure 14. Box plot of distribution of solubilities of minor elements in H_2O. Solid line is the median value; dotted line is the mean (mg/kg).

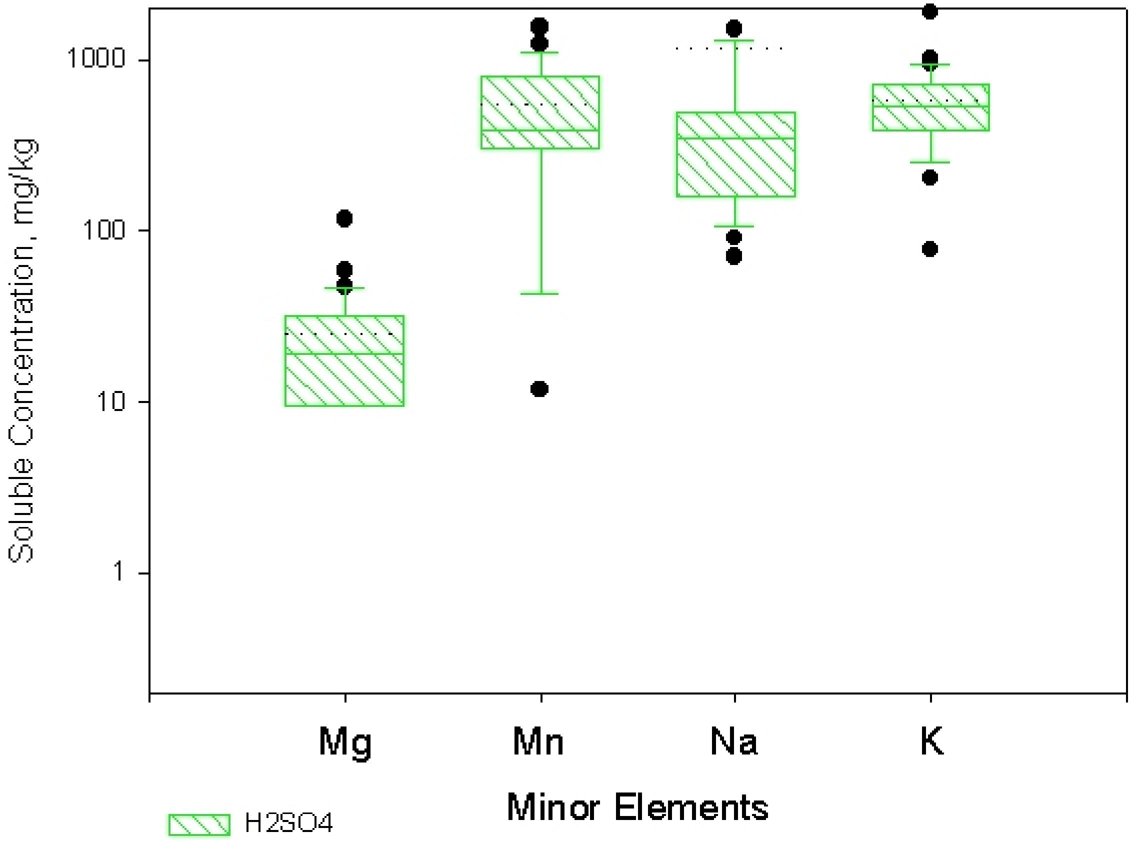


Figure 15. Box plot of distribution of solubilities of minor elements in H_2SO_4. Solid line is the median soluble concentration; dotted line is the mean value (mg/kg).

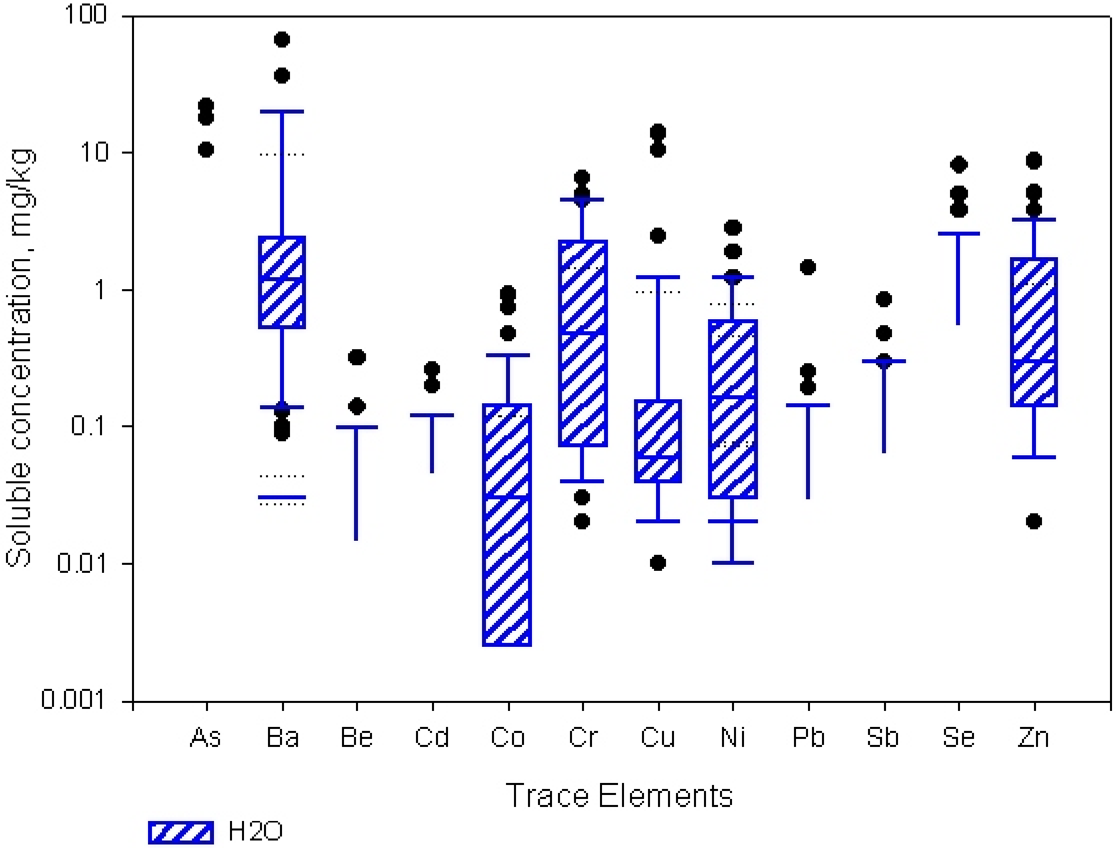


Figure 16. Bos plot of distribution of soluble concentrations for trace elements in H_2O. For elements without boxes, 95 % of the concentration values are below the detection limit.

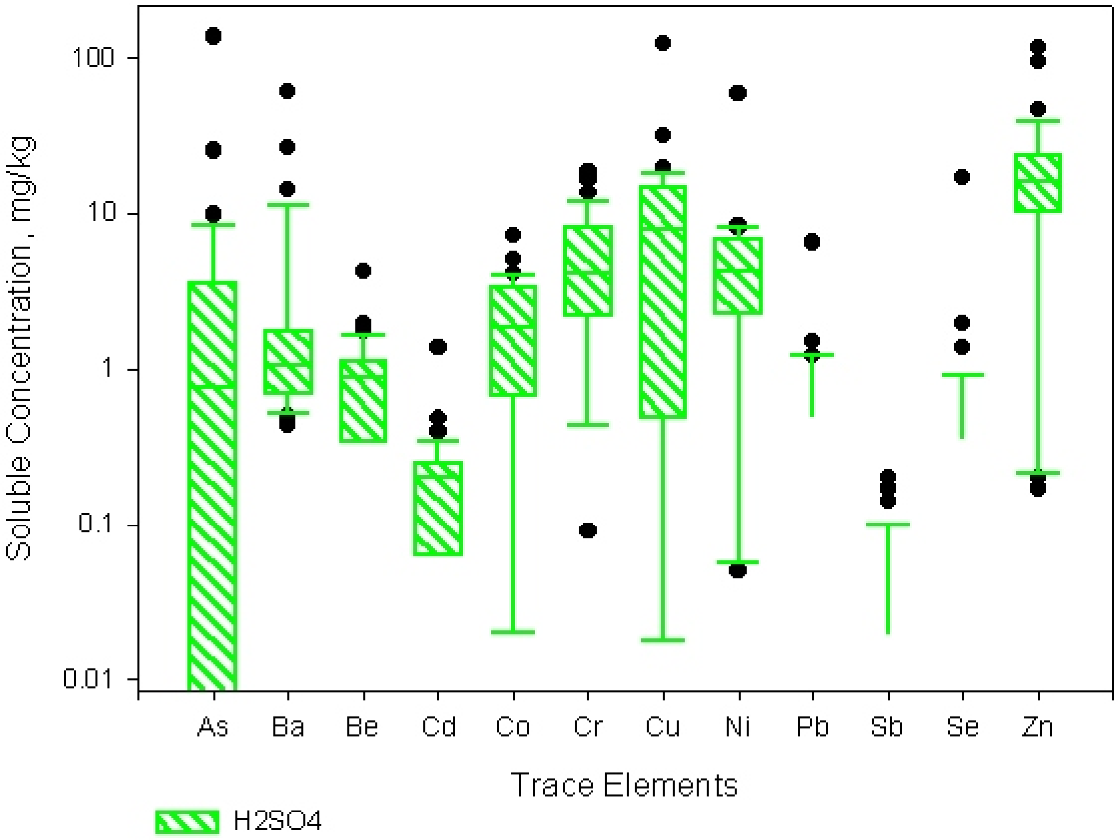


Figure 17. Box plot of distribution of soluble concentrations (mg/kg) of trace elements in H_2SO_4. For elements without a box, 95 % of the soluble concentrations are below the detection limit.

Solubility of Cations in CCB as a Function of the Alkalinity of the Ash

Many CCB are alkaline materials, including Class F fly ashes, FGD materials, and some Class F fly ashes. Alkalinity is assumed to control the release of acid soluble metals from CCB by controlling the pH of the leachate. Most metals are believed to be insoluble until the alkalinity of the CCB is reduced (Kazonich and Kim, 2001). If the alkalinity can be estimated as a simple function of composition, the extent to which the release of most cations will be delayed can be estimated.

For this set of Class F PC fly ash samples, the alkalinity was estimated by a variation of Method # 2310 (APHA, 1996). Each ash sample was digested in a set amount of acid, then titrated with NaOH. The difference between the amount of hydroxide required to raise the pH of the fly ash solution to 8.3 and the initial acid addition was the alkalinity of the sample in meq of NaOH. These alkalinity values are listed in Table 23. The concentrations of Ca and other alkaline elements are also included.

Alkalinity is usually a function of the concentration of ions of strong bases, Ca, Mg, Na and K. Plotting the alkalinity versus the concentration of calcium yields a straight line with a correlation coefficient $R^2 = 0.81$ (Figure 18). A plot of alkalinity versus the sum of alkaline cations also yields a straight line with a correlation coefficient $R^2 = 0.77$. While the concentrations of Na and K vary, the sum of the these minor elements is relatively constant (0.50 to 0.70 eq/kg). This shifts the alkalinity/concentration line to the right without any improvement in correlation. Plotting alkalinity versus non-silicate concentration (as determined by EPA Method 3051) also yields a straight line with a correlation coefficient $R^2 = 0.84$ (Figure 19). Since the non-silicate concentration is usually over 90 % of the total Ca concentration, this result is not unexpected. When the alkalinity is plotted versus the sum of the concentration of alkaline cations, the line shifts to the right and the correlation coefficient is $R^2 = 0.70$. The alkalinity is most closely related to the non-silicate calcium concentration. The sum of the Na^+ and K^+ does not appear to influence the alkalinity, indicating that these elements are not present in the ash as soluble hydroxides.

The alkalinity is positively correlated with the non-silicate Ca concentration. Although the initial pH in H_2O is more variable, it is also positively correlated with the non-silicate Ca concentration (Figure 20). The change in pH of the leachate corresponds to the change in the slope of the cumulative leached Ca concentration (M_L), as seen in Figure 21. When the pH decreases, approximately 50 % of the non-silicate Ca has been leached from the sample.

Comparing the initial pH in H_2O, HAc, and H_2SO_4, indicates that some of the samples have significant buffer capacity (Figure 22). Using the difference between the pH in H_2O and acids, the samples were divided into alkaline and acid fly ashes (Table 24). The fly ash samples that had an initially high pH in the acid leachant solutions generally had a constant pH until a neutralization point was reached. Then the pH dropped rapidly with a small addition of acid, similar to a titration curve (Figure 23.). The volume of acid needed to neutralize the fly ash sample was calculated as the cumulative volume at the last measured pH greater than 6.5 plus the interpolated volume from the measured values greater and less than pH 6.5. For some acidic samples, the first addition of acid lowered the pH below 6.5. The neutralization volumes for the acidic samples were less than one L of 0.1 N acid, and the values for HAc and H_2SO_4 generally agreed. The acid volumes (HAc and H_2SO_4) agreed for the majority of alkaline samples.

There seems to be little correlation between the empirically determined alkalinity and the neutralization volume for either HAc or H_2SO_4, but here is an apparent relationship between the neutralization volume and the non-silicate Ca concentration. The acid samples all have non-silicate Ca concentrations of 10 g/kg or less. The non-silicate Ca concentration is higher than 10 g/kg for 67 % of the alkaline samples. Of the samples with lower concentrations of non-silicate Ca, the majority were neutralized with less than one L of one of the acid leachants.

The ratio of soluble concentration ($M_{L/S}$) in H_2SO_4 to that in HAc was determined for acid soluble elements (Table 25). For alkaline samples, the median of this ratio is between 1.1 and 2.0, except for Cr which is apparently more soluble in HAc. These acid soluble elements are approximately two times as soluble in H_2SO_4 as in HAc. For the acid samples, the ratios are tend to be higher, and fewer samples are more soluble in HAc. The higher solubility of elements in H_2SO_4 may be related to the higher activity of the strong acid. The higher HAc solubility may indicate that the elements exist in multiple species which control relative solubility.

Table 23. Alkalinity of PC fly ash samples, eq/kg as NaOH, and concentration of alkaline elements, eq/kg

FA#	Alkalinity	Na^+	K^+	Ca^{++}	ΣCA,Na,K	ΣNa,K
4	296.2	0.24	0.37	1.97	2.58	.61
5	NS	0.16	0.41	1.77	2.33	.57
6	225.7	0.10	0.44	0.65	1.18	.54
7	214.9	0.10	0.44	0.60	1.14	.54
8	288.7	0.16	0.40	1.84	2.41	.56
11	222	0.09	0.40	0.72	1.21	.49
12	NS	0.10	0.41	0.72	1.22	.51
13	NS	0.10	0.40	0.69	1.18	.50
14	242.5	0.15	0.34	0.97	1.47	.49
15	NS	0.05	0.49	0.44	0.98	.54
16	218.5	0.05	0.51	0.60	1.16	.56
17	224.5	0.19	0.44	0.63	1.26	.63
18	239.6	0.19	0.44	0.76	1.40	.63
19	260.3	0.17	0.42	1.36	1.95	.59
20	NS	0.05	0.46	1.28	1.79	.51
21	296.6	0.17	0.38	1.01	1.56	.55
24	210.7	0.08	0.56	0.22	0.86	.64
25	277.5	0.22	0.43	1.57	2.22	.65
26	246.9	0.11	0.25	0.90	1.26	.36
27	200.5	0.09	0.55	0.34	0.98	.64
28	199.1	0.06	0.50	0.23	0.80	.56
30	218.3	0.15	0.36	0.51	1.02	.51
31	208.3	0.19	0.51	0.56	1.26	.70
33	296.4	0.24	0.37	1.73	2.34	.61
36	234	0.20	0.50	0.76	1.46	.70
38	290.1	0.27	0.32	1.73	2.32	.59
39	315.3	0.14	0.50	1.97	2.61	.64
40	254.4	0.06	0.45	0.23	0.74	.51
41	NA	0.35	0.24	5.60	6.20	.59
44	207.8	0.13	0.54	0.31	0.98	.67
46	256.6	0.13	0.34	1.07	1.54	.47
49	NA	0.11	0.26	1.25	1.62	.37

NA	Not Analyzed
NS	No Sample

Table 24. Alkalinity, volume of acid added to pH = 6.5, Ca_{ns}, non-silicate calcium concentration, g/kg, and Ca_{ns} relative to total Ca, %

FA#	Alkalinity, eq/kg as NaOH	HAc, L	H_2SO_4, L	Ca^{++}_{ns}, g/kg	Ca_{ns}/Ca_T, %
Alkaline samples					
4	296.2	7.08	NA	28	93
5	ND	6.20	6.18	ND	
8	288.7	3.80	8.14	25	84
14	242.5	3.14	3.84	13	96
16	218.5	1.20	0.49	7	97
17	224.5	1.90	2.03	8	99
18	239.6	3.02	2.81	9	76
19	260.3	4.11	4.51	17	76
20	ND	9.72	>3.56	22	94
21	296.6	3.27	3.82	12	78
25	277.5	5.70	7.20	20	93
26	246.9	3.21	2.97	11	79
30	218.3	0.85	4.68	5	74
33	296.4	5.83	10.18	23	82
36	234	3.35	<1.09	9	81
38	290.1	6.72	8.83	22	76
39	315.3	10.25	>7.25	29	87
41	613.4	5.47	>12.8	ND	
46	256.6	4.47	5.05	13	79
49	ND	5.48	5.47	17	87
Acid Samples					
6	225.7	<0.53	<0.68	9	97
7	214.9	<0.55	<0.60	8	89
11	222	<0.86	0.76	10	64
12	ND	0.44	0.89	ND	
13	ND	<0.38	<0.48	ND	
15	ND	<0.46	<0.25	3	98
27	200.5	<0.14	0.46	3	120
28	199.1	<0.06	<0.10	2	100
31	208.3	0.33	0.37	5	71
40	254.4	<0.75	<0.85	0.3	9
44	207.8	<0.64	<0.76	2	54

ND Not determined

Table 25. Ratio of soluble concentration in H_2SO_4 and HAc

	Mn	Na	K	Cr	Be	Zn	Cu
Alkaline Samples							
FA4-1	NA	NA	NA	NA	NA	NA	NA
FA5-1	1.20	1.32	2.35	0.47	2.62	2.22	3.37
FA8-1	1.97	3.40	0.00	0.00	0.00	0.00	0.00
FA14-1	1.61	0.89	1.74	0.99	2.42	2.12	3.66
FA16-1	2.63	1.06	1.85	0.88	2.59	10.51	1.06
FA17-1	1.34	1.01	1.71	0.51	2.76	1.57	1.63
FA18-1	1.73	1.45	2.12	1.30	2.75	0.84	0.00
FA19-1	1.33	0.20	2.17	0.42	1.75	2.92	4.71
FA20-1	0.00	0.70	1.12	0.01	0.00	0.07	0.00
FA21-1	1.37	0.25	1.76	0.33	1.75	1.58	3.42
FA24-1	2.43	12.16	3.25	1.34	3.41	4.42	1.77
FA25-1	1.39	29.97	1.85	0.15	1.32	1.67	0.41
FA 26-1	0.85	2.73	1.31	0.06	0.00	0.44	1.13
FA30-1	1.73	0.86	4.68	2.86	6.39	3.05	2.88
FA 33-1	1.67	1.08	1.52	0.77	2.21	1.93	1.35
36-1	0.24	34.29	1.57	0.59	0.00	0.04	0.05
FA 38-1	3.37	1.68	3.64	10.17	9.26	3.03	7.53
FA 39-1	1.36	0.65	1.86	0.49	1.17	2.15	1.80
FA 41-1	1.87	0.91	2.94	4.67	3.27	1.67	1.34
FA46-1	3.00	1.70	3.84	3.33	3.39	2.65	2.53
FA49-1	1.94	1.22	1.90	3.16	2.16	1.98	20.25
Acid Samples							
FA6-1	6.50	3.90	12.67	5.20	7.40	6.93	3.01
FA7-1	7.62	4.03	13.27	6.43	6.71	5.79	2.35
FA11-1	2.68	2.78	3.50	5.00	4.98	1.87	1.87
FA12-1	1.80	0.79	1.81	3.60	3.85	1.67	1.78
FA13-1	3.22	3.32	5.65	4.86	5.43	2.36	2.28
FA15-1	1.92	0.61	1.40	0.43	2.02	2.85	0.71
FA27-1	1.72	3.11	1.78	0.88	2.10	2.04	1.41
FA 28-1	1.76	3.94	1.51	0.91	2.05	1.55	1.31
FA31-1	1.73	0.86	4.68	2.86	6.39	3.05	2.88
FA 40-1	1.00	1.16	1.80	0.06	0.00	0.05	0.44
FA 44-1	19.32	2.37	3.94	21.28	0.38	1.23	2.22

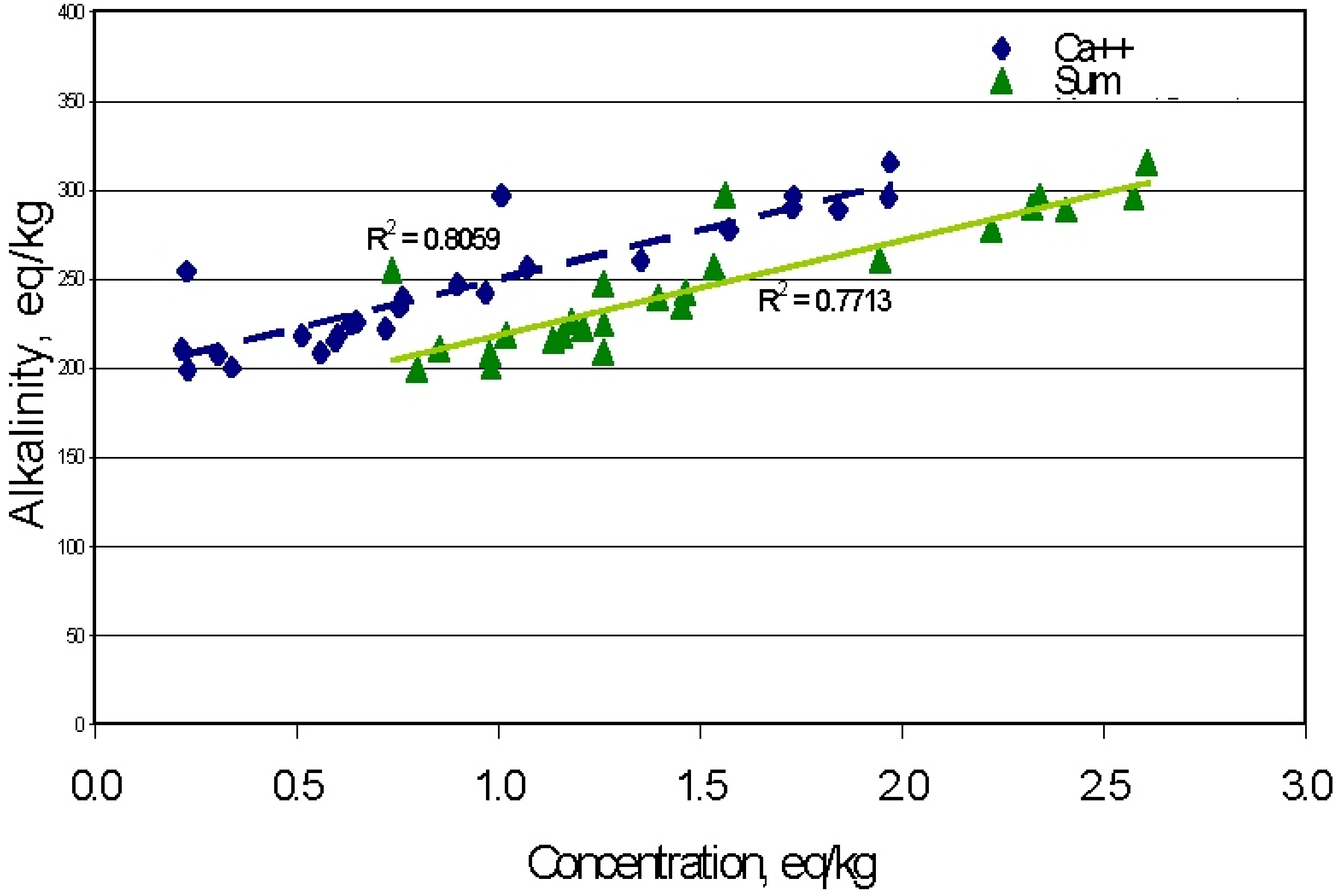


Figure 18. Correlation of alkalinity with Ca concentration and with sum of alkaline cations.

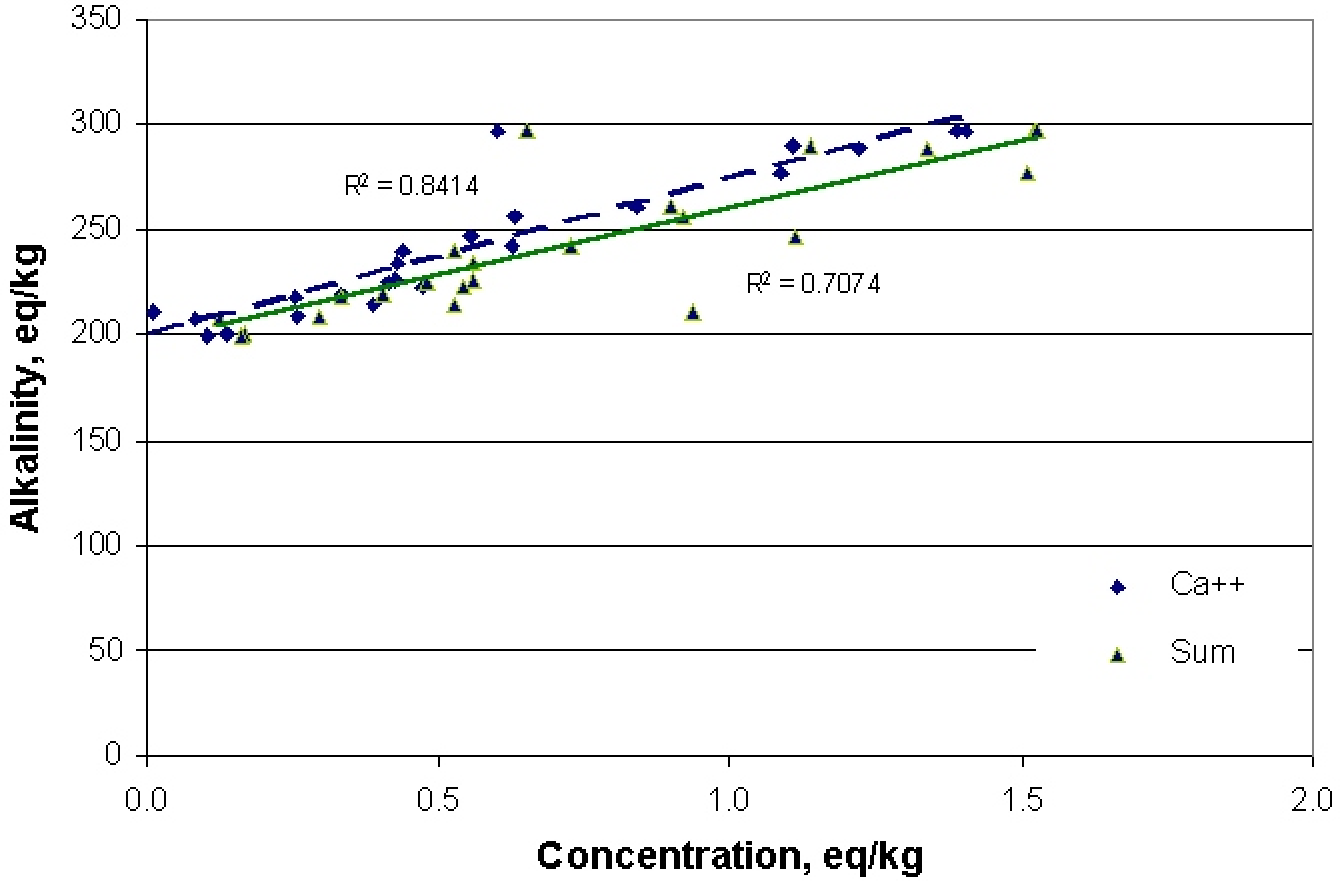


Figure 19. Correlation of alkalinity with non-silicate Ca concentration and non-silicate alkaline cations.

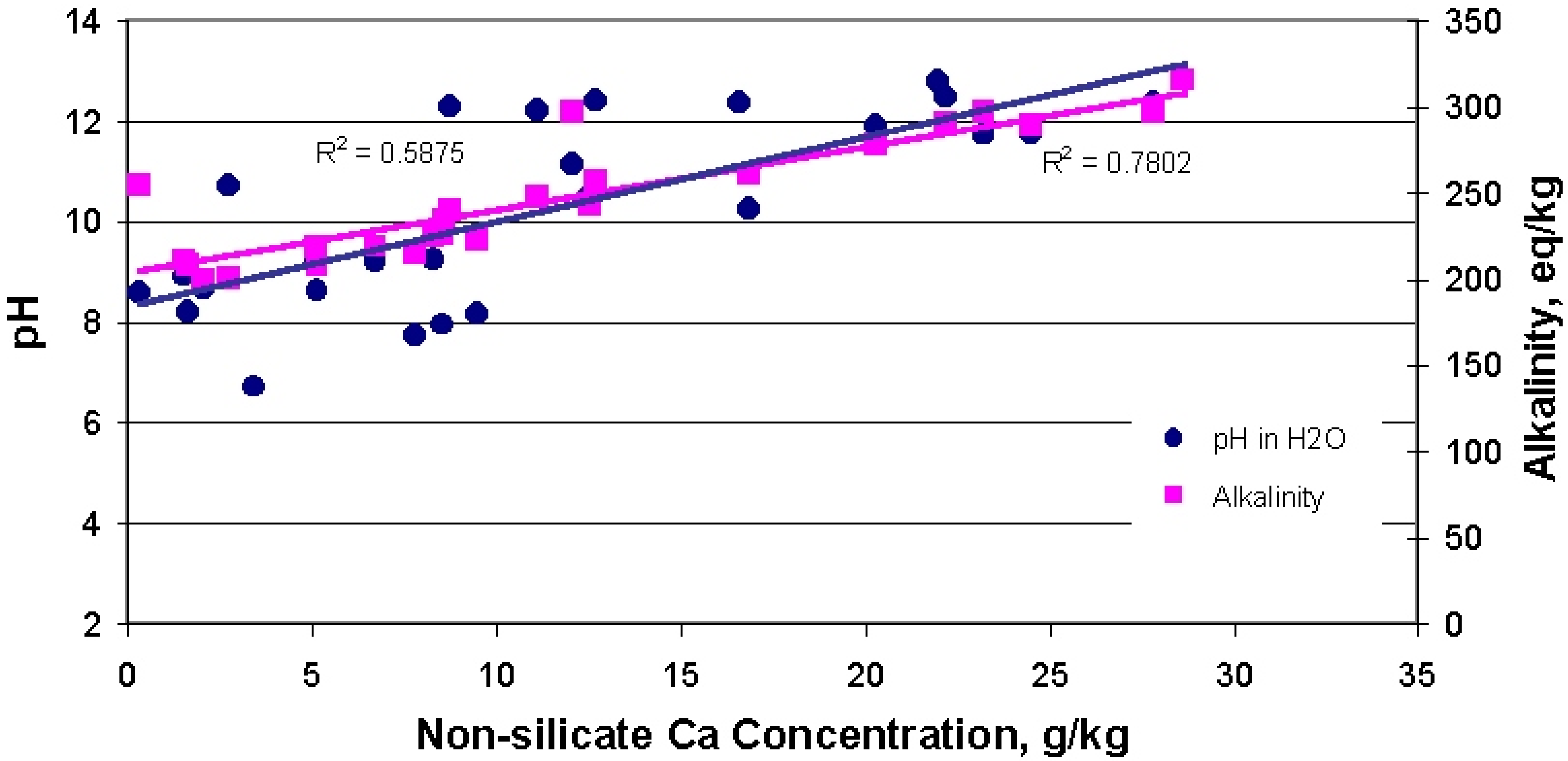


Figure 20. Correlation of initial pH in H_2O and alkalinity with non-silicate Ca concentration.

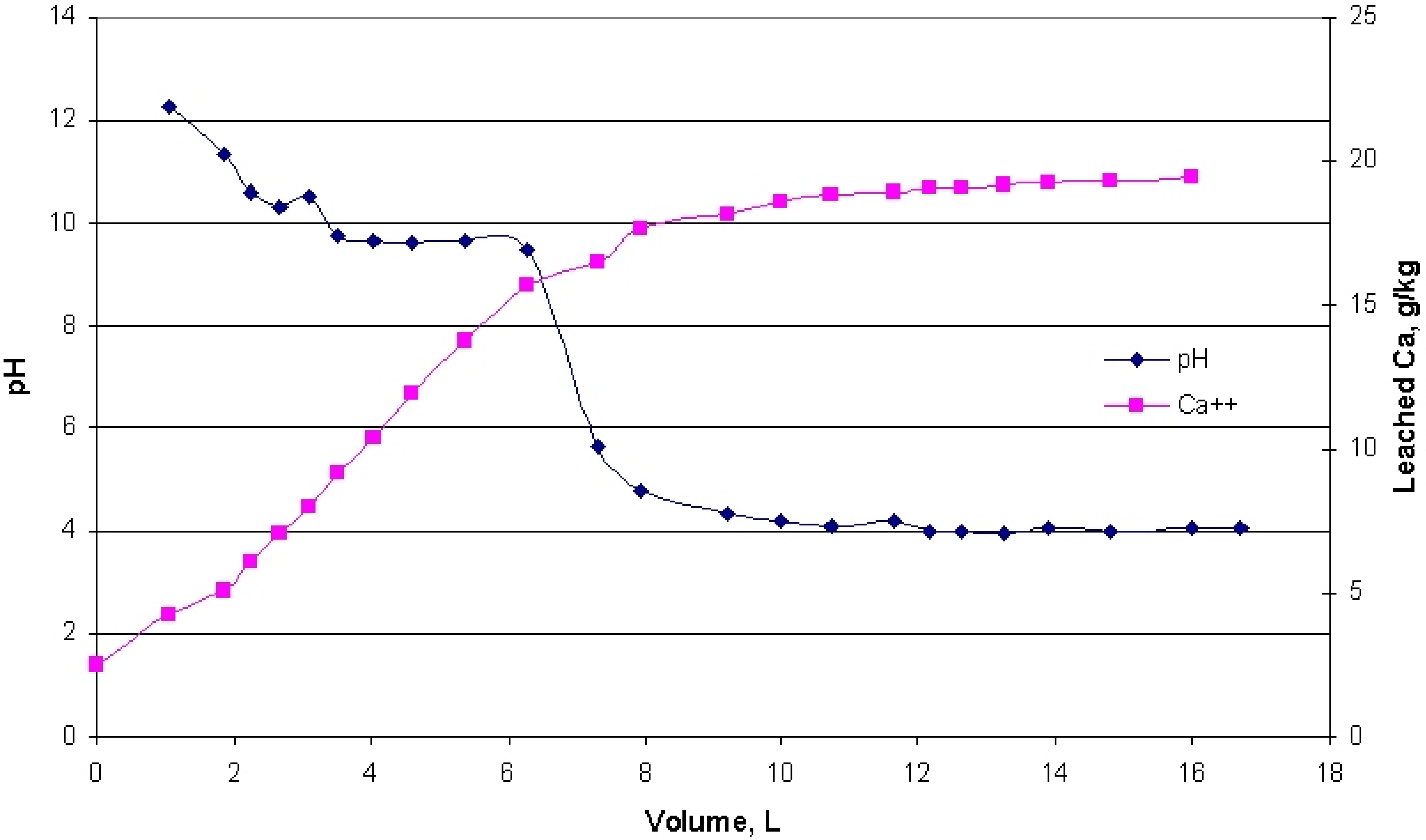


Figure 21. Cumulative Ca leached (M_L, (g/kg) and pH as a function of leachant volume.

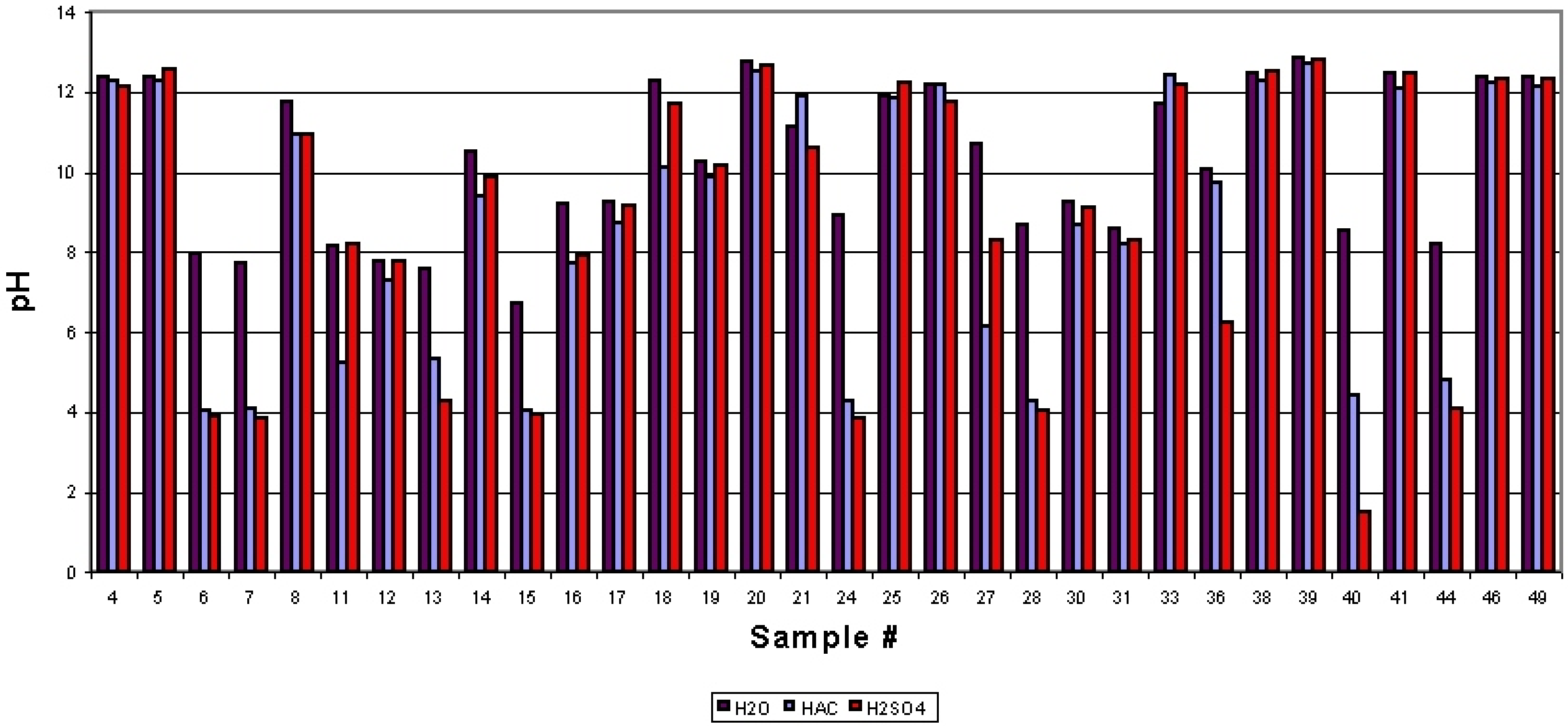


Figure 22. Initial pH of samples in H_2O, HAc H_2SO_4 to distinguish acid and alkaline samples.

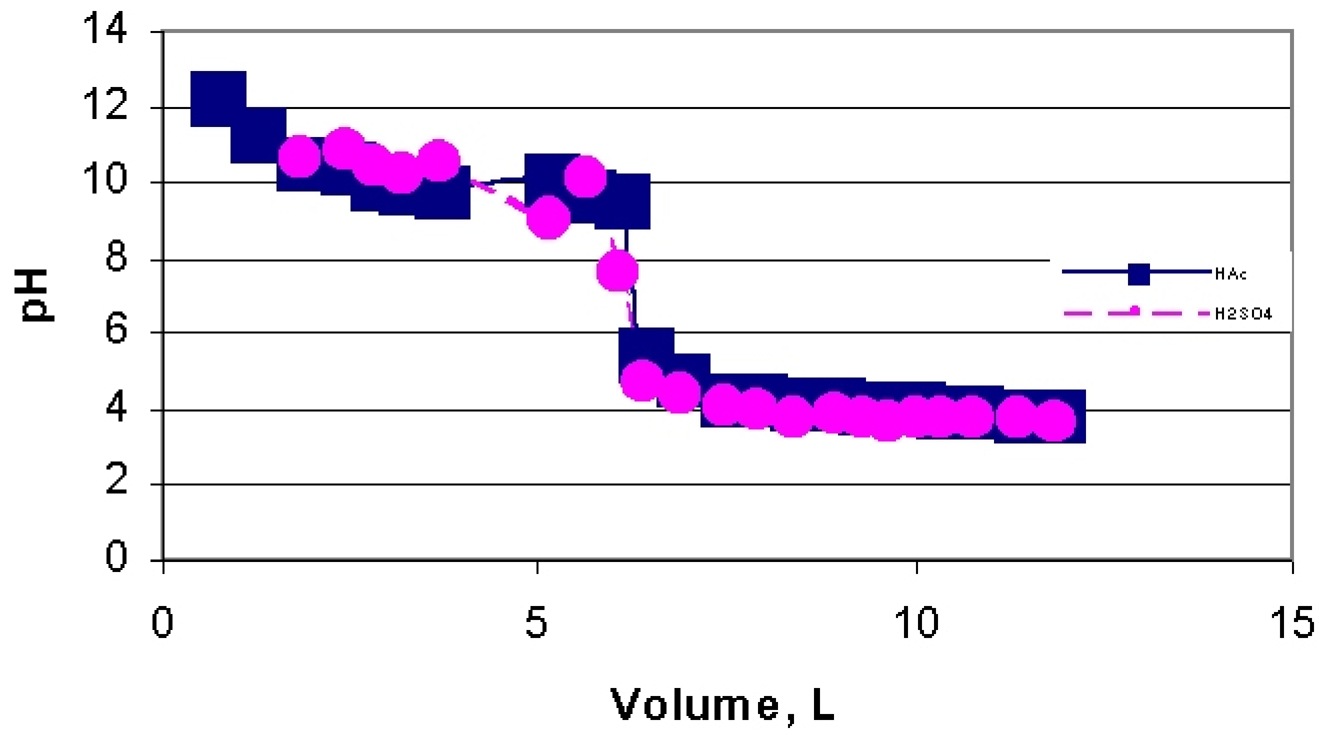


Figure 23. Change in pH as a function of acid addition.

Solubility as a Function of Non-silicate Concentration

During the course of a leaching experiment, a finite amount of each cation is released from the fly ash sample. The soluble mass (M_L) of most elements is a relatively small proportion of the amount present in the ash. As shown in Figures 12 through 17 less than 10 g of the major elements, less than 1 g of the minor elements, and less than .01 g of the trace elements per kg of sample is released during leaching. If the slope (first derivative) of the cumulative concentration curve approaches zero, the leaching of that element from a given sample is considered complete. Considered over all leaching solutions and all samples, the percentage of elements that were completely leached during the experiment varied from 20 to 100 (Kim & Kazonich, 2000) in the different leaching solutions. Even if leaching is not complete, the release of an element occurs at a relatively low rate, and the soluble concentration will not increase significantly in a short period of time.

The total concentration of cations in the sample has been determined by microwave digestion with hydrofluoric acid and ICP analysis. Elements in a non-silicate matrix were determined by microwave digestion in concentrated nitric acid. The difference between the two methods is assumed to be the silicate portion of the fly ash, either as quartz, alumino-silicates or amorphous particles. The non-silicates would be other minerals, such as oxides, or coatings on amorphous particles. The proportion of the elements in non-silicate compounds for each sample is listed in Table 26. The proportion of soluble elements, like Ca, is generally higher in the non-silicate fraction, but insoluble elements, like Fe, also occur as non-silicates.

Plotting the non-silicate concentration of an element versus the total concentration indicates how constant is the distribution between the silicate and non-silicate phases. In Figure 24, the non-silicate concentrations of Al, CA and Fe are plotted versus the total concentrations of those elements. The slope of the line is the mass fraction of the non-silicate to total concentrations. For example, the slope of the Fe line is 0.69, indicating that 69% of the total iron is in the non-silicate portion of the fly ash. The correlation coefficient of 0.81 indicates that his relationship holds for the majority of samples. The relationship for Ca is similar. The slope of the line for Al is 0.20, indicating that 20 % of the Al is in the non-silicate portion of the ash: the correlation coefficient is approximately 0.15. Not only is the concentration of Al much lower in the non-silicate phase, but the distribution of Al between the two phases is much more random. The median ratio of non-silicate concentration to total concentration for each element is shown in Figure 25. The correlation coefficient for this ratio is also shown. For elements with high correlation coefficients (>0.8), the ratio of non-silicate to total concentration is relatively constant for all the fly ash samples.

The total amount of each element leached from a sample, the soluble mass - M_L, has been calculated for all samples in four of the leachant solutions (H_2O, Na_2CO_3, HAc and H_2SO_4). The relative solubility ($M_{L/T}$) was determined by dividing the maximum amount of an element leached, irrespective of the leaching solution, by the total amount of that element in the sample. The same calculation was made with respect to the non-silicate concentration. The medians of the cumulative amount leached (M_L), the relative solubility ($M_{L/S}$) with respect to the total concentration, the non-silicate concentration, and the silicate concentration are given in Table 27. When the proportion of an element in the non-silicate fraction is high, the relative solubility with respect to non-silicate concentration and total concentration is relatively close (Figure 26).

The cumulative leached amount (M_L) was correlated to the silicate, non-silicate, and total concentrations of each cation. The solubility was most strongly correlated to the non-silicate concentration for most elements. Only Se had a positive correlation with the silicate concentration in the fly ash. For Co, Ni, Pb, and Zn, the highest correlation was to the total concentration, indicating that at least some of the element is extracted from the both silicate and non-silicate fractions. The differences in solubility indicate that the speciation, probably in silicate and non-silicate minerals influences the release of metals from fly ash.

Table 26. Mass ratio of cations in non-silicate portion to total solid concentration.

	Al	As	Ba	Be	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Zn
4 avg.	0.31	0.94	0.44	0.56	0.93	0.22	0.40	0.56	0.44	0.85	0.21	0.75	0.55	0.34	0.46	0.35		1.43	0.95
6 avg.	0.24	0.89	0.56	0.40	0.97	0.20	0.37	0.29	0.90	0.85	0.22	0.70	0.44	0.42	0.93	0.45	1.22	1.15	1.47
7 avg.	0.20	0.94	0.53	0.36	0.89	0.18	0.36	0.22	1.13	0.77	0.20	0.66	0.38	0.37	0.84	0.44	1.68	1.20	1.29
8 avg.	0.24	0.86	0.46	0.42	0.84	0.19	0.35	0.48	1.11	0.93	0.14	0.68	0.48	0.20	0.92	0.36		1.74	1.16
11 avg.	0.14	0.97	0.43	0.39	0.64	0.21	0.38	0.28	0.46	0.74	0.14	0.32	0.35	0.26	0.49	0.43	0.74	1.81	0.69
18 avg.	0.13	0.83	0.21	0.33	0.76	0.15	0.33	0.34	0.32	0.85	0.09	0.30	0.55	0.14	0.37	0.23	0.50	1.05	0.42
19 avg.	0.21	0.95	0.30	0.22	0.76	0.18	0.32	0.48	0.42	0.84	0.15	0.40	0.50	0.22	0.38	0.28	0.35	1.28	0.55
20 avg.	0.14	0.98	0.65	0.12	0.94	0.12	0.37	0.26	0.33	0.66	0.11	0.38	0.28	0.17	0.29	0.29	0.48	1.02	0.44
21 avg.	0.20	0.92	0.40	0.27	0.78	0.16	0.32	0.40	0.43	0.85	0.14	0.47	0.52	0.21	0.37	0.36	0.00	1.07	0.57
24 avg.	0.32	0.67	2.37	0.24	7.08	0.07	0.23	0.27	0.27	0.28	0.16	0.75	0.56	0.20	0.23	0.30	0.40	0.94	0.51
25 avg.	0.22	0.82	0.37	0.39	0.93	0.19	0.29	0.28	0.41	0.42	0.14	0.65	0.52	0.19	0.34	0.21	0.00	0.78	0.41
26 avg.	0.11	0.78	0.23	0.29	0.79	0.17	0.42	0.24	0.49	0.69	0.07	0.39	0.62	0.15	0.49	0.30	0.00	0.56	0.57
27 avg.	0.15	0.65	0.45	0.24	1.20	0.07	0.22	0.28	0.29	0.40	0.10	0.27	0.39	0.16	0.23	0.38	0.00	0.67	0.46
28 avg.	0.23	0.73	0.80	0.30	1.77	0.08	0.28	0.30	0.33	0.54	0.15	0.38	0.44	0.21	0.29	0.36	0.00	0.61	0.47
30 avg.	0.11	0.85	0.45	0.28	0.74	0.15	0.36	0.22	0.35	0.65	0.07	0.23	0.37	0.14	0.38	0.32	0.15	0.55	0.51
31 avg.	0.19	1.18	0.41	0.41	0.71	0.20	0.38	0.46	0.51	0.56	0.19	0.29	0.33	0.28	0.41	0.50	0.29	0.99	0.52
33 avg.	0.18	0.97	0.41	0.44	0.82	0.16	0.32	0.44	0.42	0.55	0.11	0.44	0.47	0.18	0.35	0.31	0.00	0.73	0.45
36 avg.	0.12	1.05	0.31	0.31	0.81	0.15	0.27	0.56	0.52	0.49	0.12	0.30	0.64	0.24	0.31	0.36	0.74	0.75	0.58
38 avg.	0.27	0.93	0.44	0.42	0.76	0.15	0.27	0.49	0.43	0.58	0.15	0.71	0.45	0.20	0.32	0.33	0.00	0.57	0.52
39 avg.	0.31	0.93	0.57	0.57	0.87	0.16	0.34	0.53	0.49	0.48	0.18	0.53	0.53	0.26	0.38	0.40	0.00	0.78	0.66
40 avg.	0.01	0.19	0.03	0.02	0.09	0.02	0.04	0.04	0.13	0.12	0.01	0.03	0.12	0.07	0.08	0.13	0.00	0.00	0.31
44 avg.	0.12	0.91	0.46	0.28	0.54	0.08	0.26	0.26	0.35	0.49	0.12	0.22	0.43	0.19	0.28	0.36	0.24	0.81	0.46
46 avg.	0.10	0.22	0.15	0.11	4.13	0.25	0.24	0.24	0.14	2.72	0.06	0.41	0.98	0.22	0.37	0.10	0.00	0.65	0.47
49 avg.	0.10	0.23	0.21	0.37	0.33	0.37	0.67	0.19	0.25	3.98	0.03	0.22	1.02	0.16	1.05	0.10	0.00	0.77	0.62

Table 27. Median values of the cumulative leached amount, M_L, the leached amount relative to the total, non-silicate and silicate concentrations in the fly ash, and the ratio of non-silicate to total concentration

Element	M_L, mg/kg	M_L/M_T	M_L/M_{ns}	M_L/M_{Si}	M_{ns}/M_T
Al	3537	0.04	0.22	0.05	0.20
As	27	0.44	0.50	4.80	0.93
Ba	10	0.02	0.04	0.03	0.44
Be	1	0.12	0.33	0.26	0.34
Ca	6135	0.65	0.74	2.98	0.86
Cd	0.21	0.02	0.10	0.02	0.17
Co	2	0.04	0.12	0.06	0.35
Cr	6	0.06	0.16	0.08	0.33
Cu	10	0.10	0.19	0.30	0.43
Fe	367	0.01	0.01	0.03	0.68
K	535	0.05	0.35	0.05	0.14
Mg	416	0.20	0.46	0.27	0.46
Mn	20	0.17	0.35	0.22	0.51
Na	393	0.18	0.84	0.22	0.21
Ni	5	0.05	0.11	0.10	0.38
Pb	0.04	0.01	0.03	0.00	0.36
Sb	0.11	0.07	0.10	0.03	0.38
Se	1	0.18	0.28	4.42	0.78
Zn	16	0.18	0.25	0.45	0.57

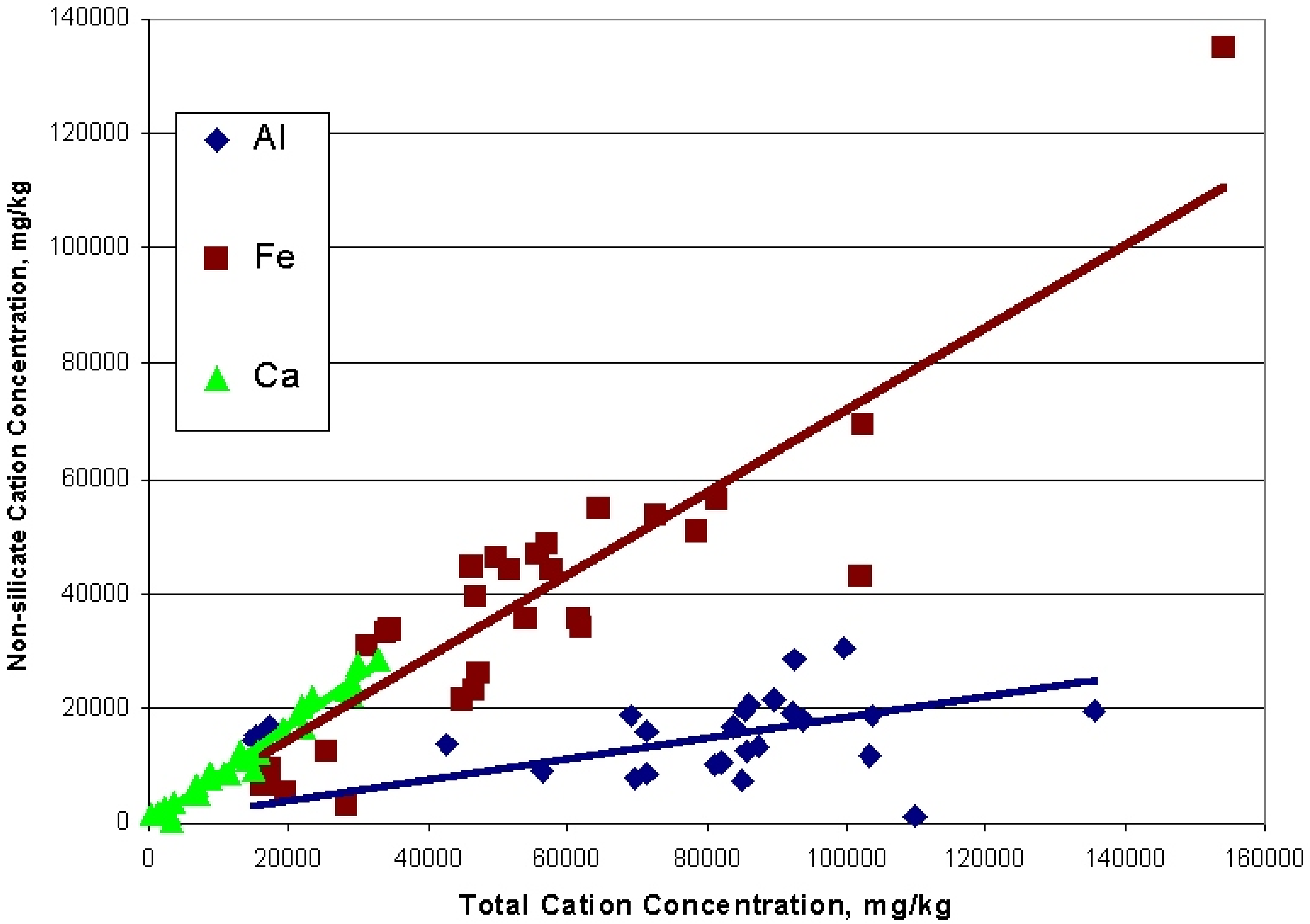


Figure 24. Relationship between non-silicate concentration and total concentration in fly ash samples.

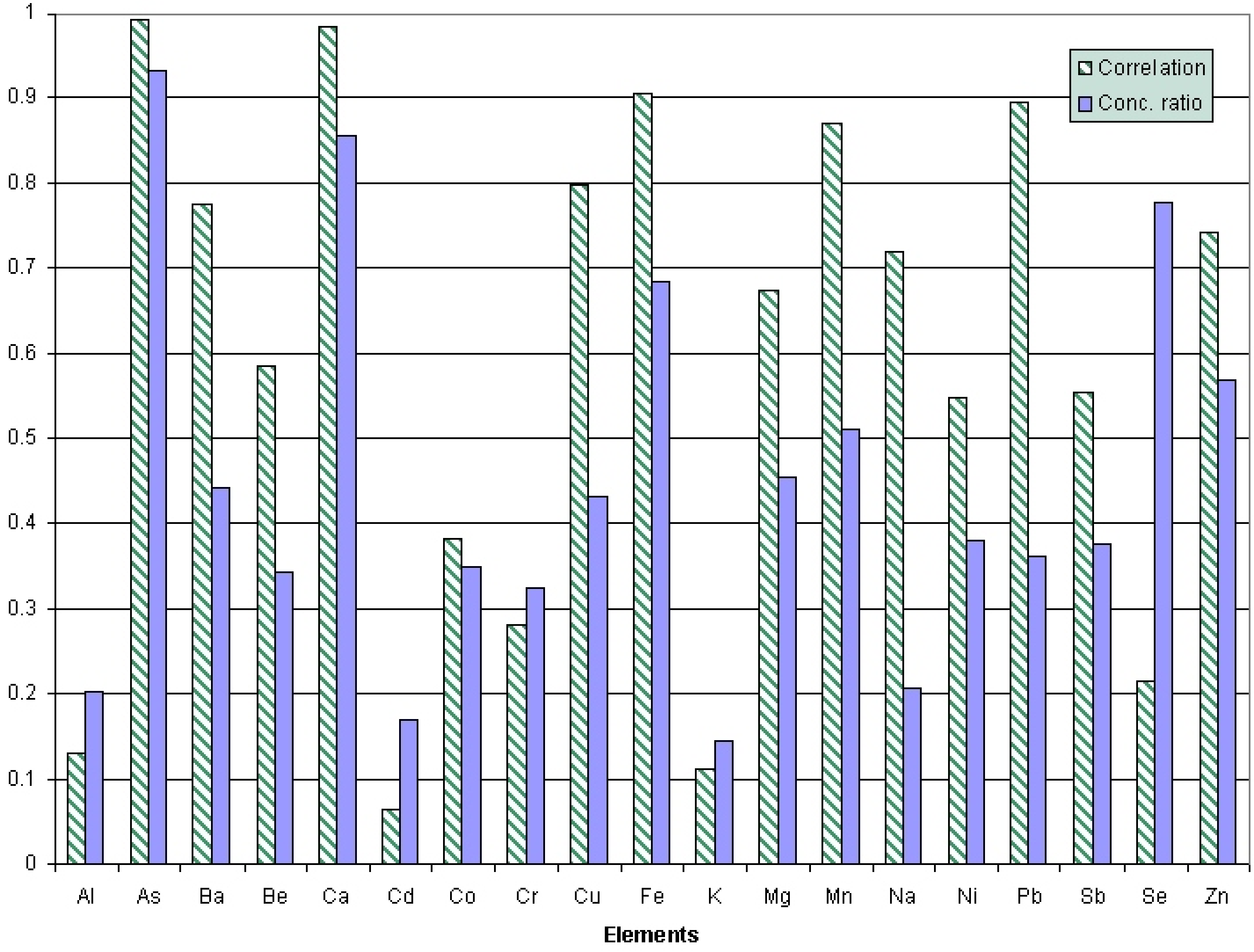


Figure 25. Ratio of non-silicate (non-silicate) concentration to total concentration and correlation coefficient of non-silicate to total concentration.

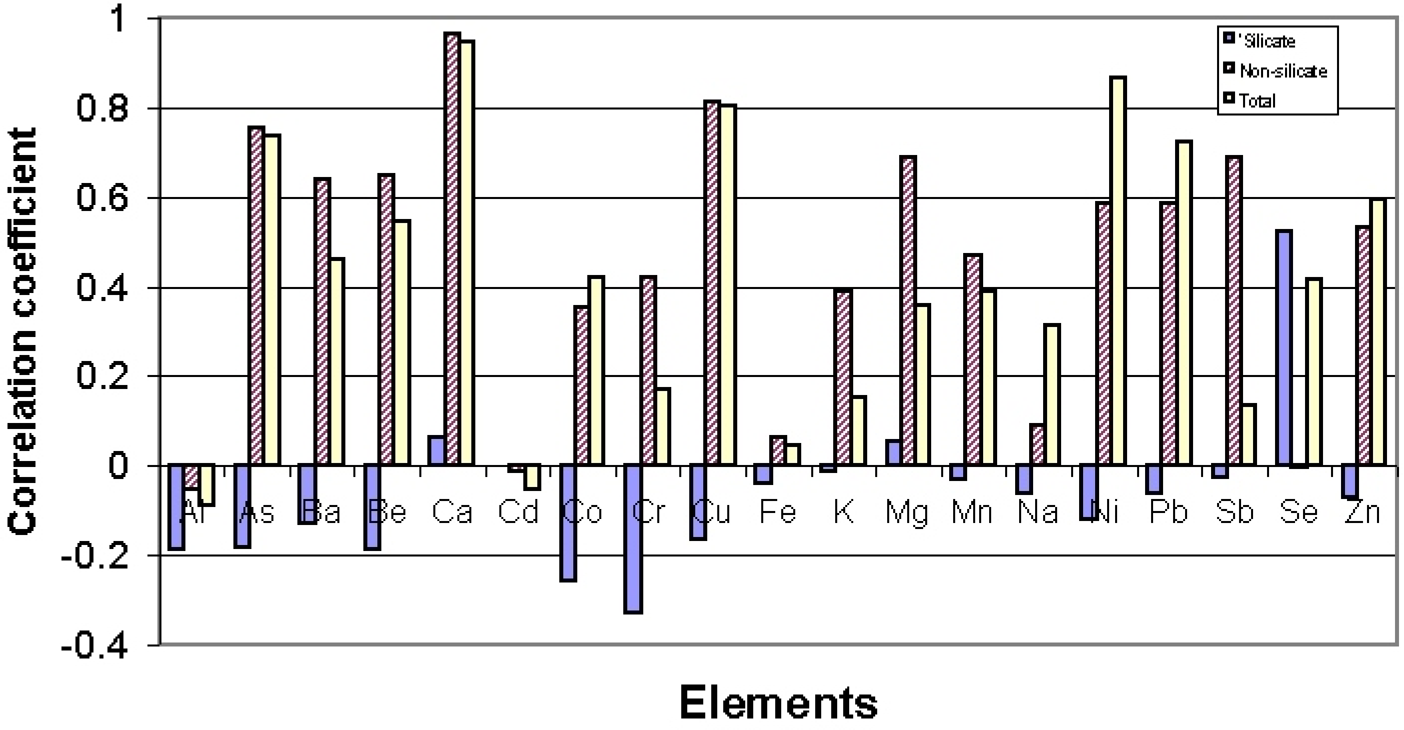


Figure 26. Correlation coefficients for cumulative leached element (M_L) versus non-silicate concentration, silicate concentration, and total concentration in the fly ash sample.

The relationship of solubility to mineral composition

The fly ash samples were sent to a commercial laboratory for mineral determination by XRD. The composition was calculated by summing the peak intensities and dividing the strongest peal for a given mineral by that total. This is not a standard method, and it effectively normalized the concentration to the amount of crystalline material rather than to the whole sample. The data, Table28, are considered qualitative. A few of the samples were analyzed at NETL, and the concentration was calculated versus a standard. These values, Table 29, give the concentration in the whole sample. The second line for each sample gives the normalized concentration, which agrees fairly well with the values from the commercial laboratory.

Quartz is the dominant mineral in this set of fly ash samples (Figure 27). Mullite, a high temperature clay is the second most abundant mineral. Both hematite and magnetite are identified in over 75 % of the samples, and either hematite or magnetite is identified in another 10 %. Hematite or magnetite, an oxide that could have formed at high temperature from the dissociation of pyrite. Gypsum or anhydrite is identified in 1/3 of the samples, which could be the reaction products of calcium from $CaCO_3$ and sulfur from the dissociation of pyrite.

The solubility of a mineral is defined by the solubility product constant (K_{sp}), which is the product of the single ion activities of the cation and anion. In dilute solutions, the molar concentrations, rather than the activities, can be used.

$$K_{sp} = [X^+][Y^-] \tag{11}$$

K_{sp} values are for some of the minerals in the fly ash samples are listed in Table 30. Equilibrium constants and solubilities are also used to denote mineral solubility. The K_{sp} values actually define whether a solution is over- or under-saturated with respect to a given compound, and if in a solution of a given composition a compound will precipitate. They give a general indication of which compounds are more soluble than others. They do not give any information about the rate at which a mineral will dissolve, nor does the K_{sp} value give any information about chemical reactions other than with H_2O.

For the major minerals in the fly ash samples, the solubility constants are used to evaluate the leaching results in terms of possible mineral solubility. This approach is limited, because solubility data are not available for all compounds, particularly alumino-silicates. Also, this approach cannot be applied to minor and trace elements which are not identified as particular minerals.

The iron minerals, hematite and magnetite, have very low K_{sp} values, which is reflected in the low solubility of Fe from fly ash samples in this study. Based on ionic radii (Table 31), Ni, Mg and Zn are the elements most likely to be substituted for Fe in the iron oxide lattice. Assuming that the ion substitution is constant in all Fe oxide particles, the molar ratio of Fe to X should be constant. Then it is also assumed that the substitute ion and Fe would be dissolved by the leachant solution in the same proportion. In other words, if a Ni ion is substituted for 1 out of 1000 Fe ions, the molar ratio of Fe to Ni would be 1000. If the leachant dissolving the mineral is non-selective, the proportion of moles of Fe ions to moles of Ni ions in solution should also be close to 1000. However, their solubility patterns are not similar (Table 32). Also, the ratio of Fe to other ions is not constant in the different leachant solutions. The ratios of solubility in the two acids and in H_2SO_4 to H_2O are significantly different. Based on this type of evaluation, Ni, Mg and Zn in the fly ash samples cannot be identified as substitutes for Fe in hematite or magnetite.

Calcium sulfate, either as anhydrite of gypsum, is the primary form of Ca identified in the fly ash samples. These minerals are slightly soluble (Table 30), and in this test, 10% is the average solubility of Ca in H_2O (Figure 28). As much as 25% of the Ca appears to be soluble in H_2SO_4 and 50% in HAc. The K_{sp} values are constants, a fixed product of the cation and anion concentrations. As the concentration of SO_4 ions in solution increase due to the ionization of a strong acid, the concentration of Ca would decrease. This common ion effect may account for the lower solubility of Ca in H_2SO_4.

Minerals containing the elements Na and K are not identified in the samples by XRD. However, feldspars have been identified in coal, and these would probably contain both K and Na. Other than Ca, these are the only elements that are consistently soluble in H_2O (Table 33). Although K has a higher concentration in the samples, Na is apparently more soluble. Both K and Na can be dissolved from feldspar to convert it to kaolinite. The relative solubility of the two ions is consistent with the K_{sp} values given in Table30.

The mineralogical information obtained from XRD analysis of the fly ash samples is too limited to explain the apparent differences in solubility for the various cations. It provides limited support for the solubility of the major ions. There are insufficient data to speculate about the possible distribution of trace elements in mineral lattices.

Table 28. Qualitative mineral analysis of PC class F fly ash samples, %.

Sample #	**Quartz**	**Mullite**	**Hematite**	**Magnetite**	**Gypsum**	**Anhydrite**	**Portlandite**
	SiO_2	Al_2SiO_5	Fe_2O_3	Fe_3O_4	$CaSO_2 \cdot H_2O$	$CaSO_4$	$Ca(OH)_2$
4	43	19	15	10	0	7	5
6	40	32	12	7	9	0	0
7	44	33	10	8	5	0	0
8	43	21	20	7	0	8	0
11	38	34	13	10	5	0	0
14	44	29	14	6	trace	6	0
15	36	40	12	11	0	0	0
16	43	38	12	7	0	0	0
17	58	24	12	6	0	0	0
18	64	18	11	6	0	0	0
19	56	18	12	9	0	5	0
20	35	35	15	5	trace	trace	5
21	51	30	10	8	0	0	0
24	41	11	0	0	0	0	0
25	55	19	13	7	0	5	0
26	53	25	15	6	0	0	0
27	52	39	9	0	0	0	0
28	48	41	10	trace	0	trace	0
30	35	38	12	15	0	0	0
31	41	39	13	7	0	0	0
33	46	26	11	9	0	7	0
36	57	28	8	6	0	0	0
38	44	26	19	10	0	0	0
39	60	29	trace	10	0	0	0
40	33	53	13	trace	0	0	0
41	67	17	trace	trace	0	15	0
44	66	21	9	4	0	0	0
46	54	19	14	13	0	trace	0
49							

Table 29. Mineral composition of class F fly ash samples determined at NETL, %, NETL values normalized and compared to those from commercial laboratory (ALCA)

Sample	Source	**Quartz**	**Mullite**	**Hematite**	**Magnetite**	**Gypsum**	**Anhydrite**	**Illite**	**Sillmanite**
FA15	NETL	15	10	5	3				5
	normalized	45	30	15	9	0	0	0	15
	ALCA	36	40	12	11	0	0		
FA16	NETL	12	12		5		trace		5
	normalized	41	41	0	17	0		0	17
	ALCA	43	38	12	7	0	0		
FA17	NETL	15	10		2				5
	normalized	56	37	0	7	0	0	0	19
	ALCA	58	24	12	6	0	0		
FA18	NETL	15	5	5	3		3		4
	normalized	48	16	16	10	0	10	0	13
	ALCA	64	18	11	6	0	0		
FA24	NETL	15	15	3	trace				5
	normalized	45	45	9		0	0	0	15
	ALCA	41	11	0	0	0	0		
FA25	NETL	10	10	5	3		3		
	normalized	32	32	16	10	0	10	0	0
	ALCA	55	19	13	7	0	0		

Table 30. Solubility product constant (K_{sp}) of minerals in water.

Mineral	**K_{sp}**	Solubility, mg/L
Quartz	$1.0x10^{-4}$	12
Amorphous Silica	$1.82x10^{-3}$	120
Hematite	$10^{-42.7}$	
Magnetite		
Anhydrite	$1.2x10^{-6}$	2100
Gypsum	$10^{-4.62}$	2410
Portlandite	$10^{-5.19}$	1830
Albite → Kaolinite	$10^{-0.68}$	
K-feldspar → Kaolinite	$10^{-3.54}$	

Sources: Evangelou, V.P. 1998. Environmental Soil and Water Chemistry. John Wiley and Sons, pp. 58-60.

Freeze , R.A. and Cherry, J.A. Groundwater. Prentice Hall, p. 106.

Morel, F.M.M. and Hering, J.G. 1993. Principles and Applications of Aquatic Chemistry. John Wiley & Sons, pp.243-246.

Handbook of Chemistry and Physics. 1972. 52nd Ed., pp. B-77 - B-79.

Table 31. Comparison of elements based on ionic radii.

Element	Atomic Weight	Valence	Ionic radius, Å
Be	9.01	2	0.35
Si	28.09	4	0.42
Se	78.96	4	0.50
Al	26.98	3	0.51
As	74.92	3	0.58
Co	58.94	2	0.63
Cr	52.01	3	0.63
Mg	24.31	2	0.66
Ni	58.71	2	0.69
Fe	55.85	3	0.74
Zn	65.38	2	0.74
Sb	121.76	3	0.76
Mn	54.94	2	0.80
Cu	63.55	1	0.96
Na	22.99	1	0.97
Cd	112.41	2	0.97
Ca	40.08	2	0.99
Pb	207.21	2	1.20
K	39.10	1	1.33
Ba	137.36	2	1.34
O	16.00	2	1.40

Table 32. Comparison of molar solubility of ions of similar in size to Fe.

		H2O	Na2CO3	HAc	H2SO4	H2SO4/HAc	H2SO4/H2O
Fe	mmol/kg	0.11	0.10	2.22	13.87	6.25	129.41
Mg	mmol/kg	0.04	0.02	1.01	0.95	0.94	23.59
Fe/Mg		2.65	4.35	2.19	14.55		
Zn	mmol/kg	0.02	0.01	0.13	0.31	2.34	18.21
Fe/Zn		6.25	8.22	16.64	44.46		
Ni	mmol/kg	0.01	0.01	0.04	0.10	2.72	12.79
Fe/Ni		13.90	8.97	61.17	140.61		

Table 33. Solubility of K and Na in H_2O

Sample #	K	Na	K	Na	K	Na
	Solid concentration		Leached concentration		Relative Solubility	
	mmol/kg	mmol/kg	mmol/kg	mmol/kg	%	%
4	367	242	3.55	5.53	0.97	2.28
5	408	158	1.22	1.60	0.30	1.01
6	435	100	1.05	1.32	0.24	1.32
8	444	97	0.54	1.69	0.12	1.75
11	401	165	1.25	2.15	0.31	1.31
12	397	94	2.65	2.90	0.67	3.10
13	405	97	4.17	5.33	1.03	5.50
1	399	97	1.04	0.85	0.26	0.88
4	344	152	5.41	10.61	1.57	6.99
15	488	55	9.75	4.53	2.00	8.25
16	512	45	7.40	3.62	1.45	8.00
17	437	190	5.21	13.43	1.19	7.05
18	444	190	5.13	12.24	1.16	6.43
19	425	168	5.38	10.44	1.27	6.22
20	459	55	9.56	4.63	2.09	8.44
21	382	171	5.23	13.93	1.37	8.14
24	560	77	6.21	6.48	1.11	8.36
25	429	223	9.02	16.25	2.10	7.30
26	251	113	2.55	8.18	1.02	7.24
27	554	90	3.21	5.77	0.58	6.38
28	503	65	4.86	7.70	0.97	11.93
30	361	145	1.22	6.26	0.34	4.31
31	507	194	9.73	10.16	1.92	5.25
32	372	239	5.43	12.06	1.46	5.05
33	497	203	10.60	21.65	2.13	10.65
36	323	271	4.57	23.25	1.42	8.58
38	503	136	6.52	9.52	1.30	7.03
39	448	61	0.19	5.52	0.04	9.01
40	242	352	1.11	8.88	0.46	2.52
41	543	129	3.86	7.40	0.71	5.73
44	338	126	5.07	10.90	1.50	8.66
49	261	110	0.00	11.41	0.00	10.40

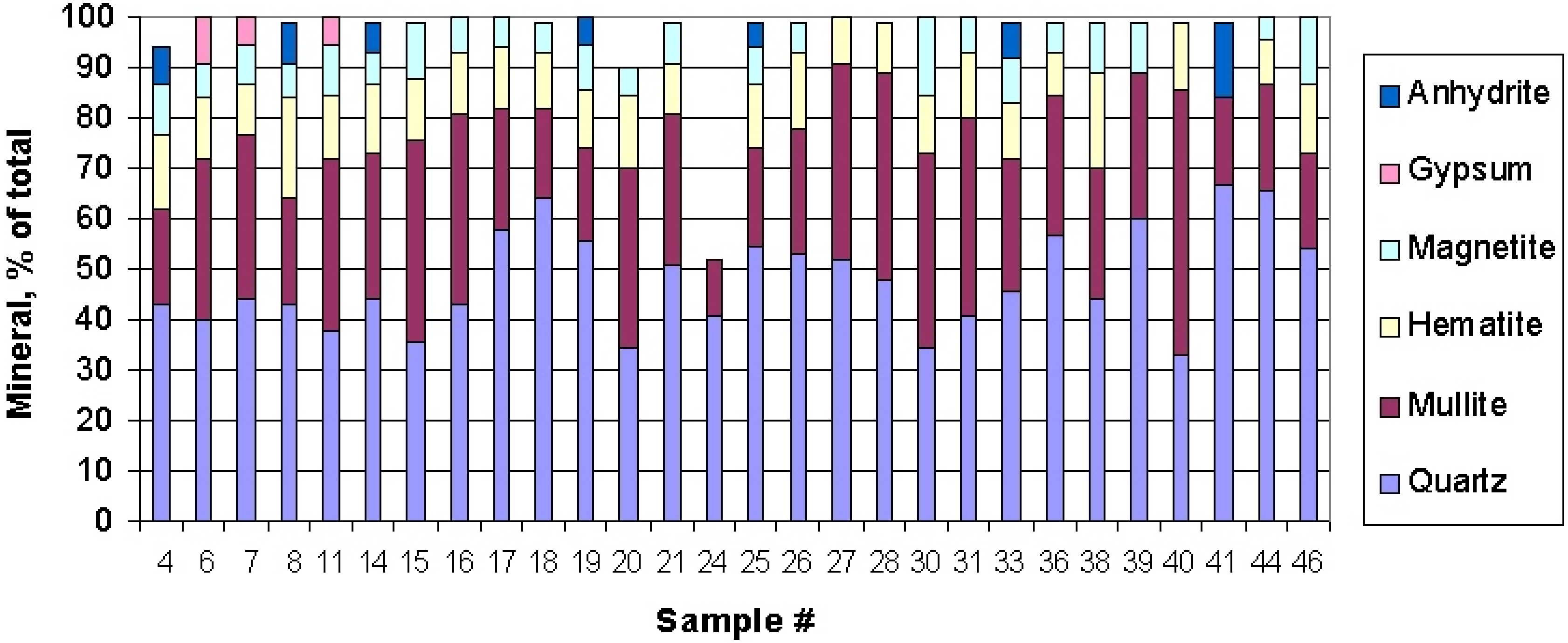


Figure 27. Major minerals in fly ash samples as determined by XRD. Distribution normalized to % of total minerals.

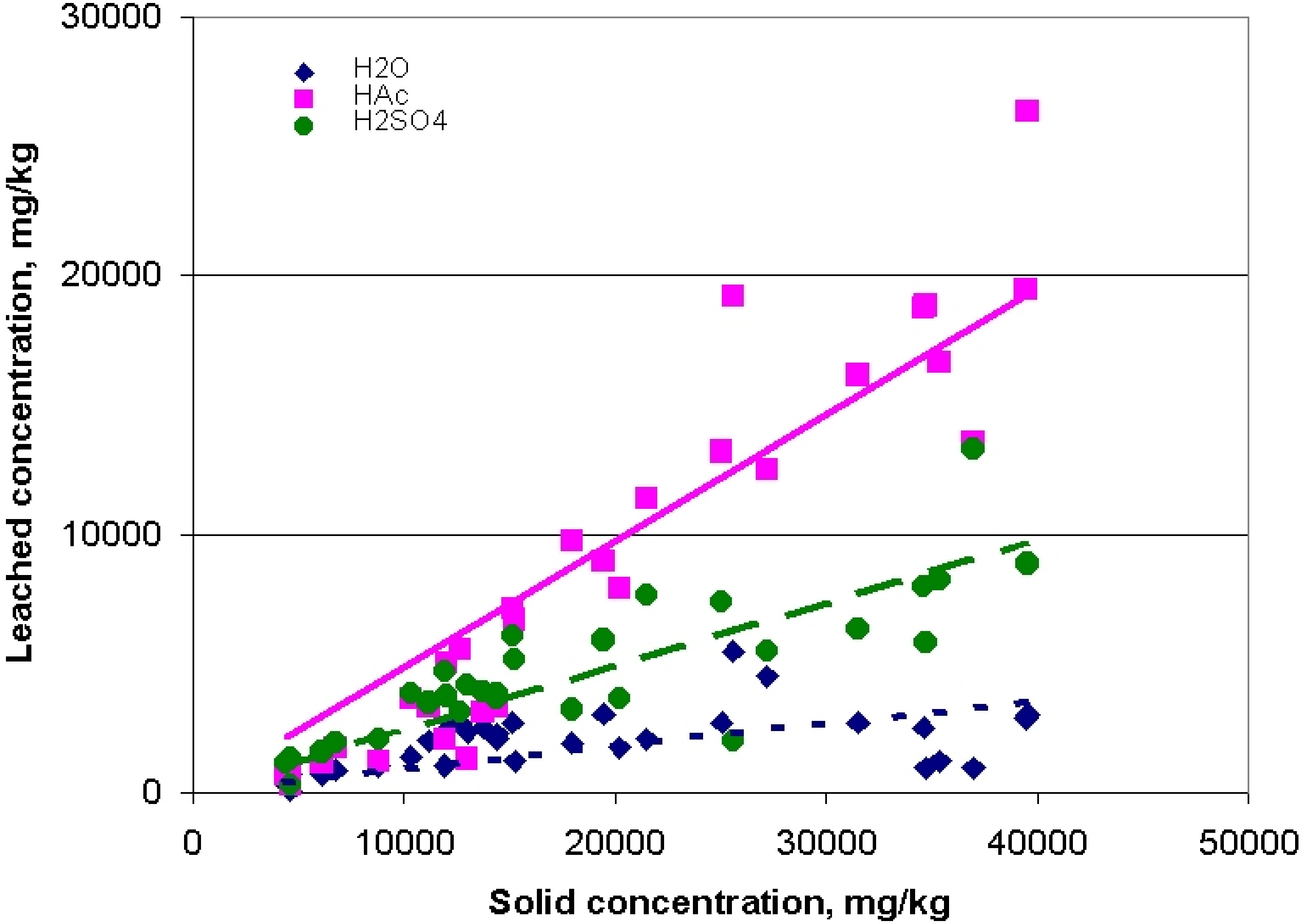


Figure 28. Comparison of solubility of Ca for all samples in H_2O, HAc, and H_2SO_4.

Volumetric Leaching Function

In this column study, the release of cations from the fly ash particles was not primarily a function of time. It is a function of the volumetric flow rate, and the volume of leachant is the independent variable against which the cumulative mass leached from the sample is measured. The volumetric leaching function is a complex function of the alkalinity of the ash, the distribution of elements in various chemical compounds or minerals, and characteristics of the leachant solution, particularly its pH. Discrete leaching processes have different volumetric leaching functions. During the first leaching interval, the alkalinity of the ash is neutralized, and the release of metal ions, except for Ca, is relatively low. At some point, the release metal ion increases by one or more orders of magnitude, and remains constant until the readily soluble ions are released. Then the release of an element decreases, again by one or more orders of magnitude. Theoretically, the release of metal ions from the fly ash can continue until all of the soluble element is dissolved.

An example of the change in cumulative mass leached as a function of leachant volume is plotted in Figure 29. The cumulative mass of an element leached is calculated as:

$$M_L = \sum_{V=0}^{V_t} C_t * V_t / S \qquad \textbf{(12)}$$

where M_L = cumulative leached mass, mg/kg

C_t = measured concentration in a leachate sample at time t, mg/L

V_t = the volume of leachant solution for one leachant collection cycle, L

S = sample mass, kg

The first derivative of the cumulative concentration curve is the mass leached as a function of the change in volume. This is the slope of the cumulative curve and is defined as the volumetric leaching function for each leaching phase.

$$\frac{dM_L}{dV} = \frac{M_{v2} - M_{v1}}{V_2 - V_1} \qquad \textbf{(13)}$$

As shown in Figure 29, there are three distinct leaching functions, comparable to neutralization, rapid leaching and the terminal phase when leaching occurs for a prolonged period.

Neutralization Leaching Function	$NLF = M_{L_N} / V_N$
Rapid Leaching Function	$RLF = M_{L_R} / V_R$
Terminal Leaching Function	$TLF = M_{L_T} / V_T$

Calculating the second derivative of the cumulative leached mass curve shows the inflection points where the volumetric leaching functions change.

$$\frac{dM^2}{d^2V} = \frac{\frac{dM_2}{dV_2} - \frac{dM_1}{dV_1}}{V_2 - V_1} \qquad \textbf{(15)}$$

If the rapid leaching function rate is greater than the neutralization function, the first inflection point is a maximum, and if the terminal leaching function is less than the rapid leaching function, the second point is a minimum. Using the "match" and "index" functions in an excel spreadsheet, the cumulative mass and the cumulative volume at each inflection point are determined. These values are used to calculate the volumetric leaching function for each phase.

If there is no neutralization phase, the cumulative leaching curve has 2 rates, and different inflection points (Figure 30). Although the occurrence of the maximum first and the minimum later is considered "normal," the spreadsheet can be adjusted to determine the appropriate leaching functions for other configurations.

Three leaching function values were determined for each element in each sample. To compare the leaching functions for different elements, they were converted from mg/kg/L to units of meq/kg/L. The median leaching functions for the alkaline samples are listed in Table 34 (H_2O), Table 35 (HAc), and Table 36 (H_2SO_4). Leaching functions for acid samples are given in Table 37 (H_2O), Table38 (HAc), and Table 39 (H_2SO_4).

The mean volumetric leaching function is:

$$VLF = \frac{NLF * V_N + RLF * V_R + TLF * V_T}{V_N + V_R + V_T} \tag{16}$$

The mean volumetric leaching function can also be calculated as the maximum cumulative concentration divided by the final leachant volume; it is not the average of the three functions.

The median volume for the neutralization and leaching phases are determined from the experimental values. The terminal volume is calculated as:

$$V_T = (C_{NS} - (NLF * V_N + RLF * V_R)) / TLF \qquad \textbf{(17)}$$

where V_T = volume of leachant to dissolve the mass of an element remaining in the non-silicate portion of the fly ash after neutralization and rapid leaching

C_{NS} = non-silicate concentration, meq/kg

The solubility of an element is defined by the three rates and the median volumes. The NLF is the initial leaching until samples is neutralized (dM_N/dV_N, meq/L). The RLF is the average slope of cumulative curve between inflection points (dM_L/dV_L, meq/L), and the T LF is the average slope of cumulative curve after 2nd inflection point (dM_T/dV_T, meq/L). In a natural setting, if the infiltration rate is known (L/d), the time dependent release of the elements can be estimated. Since one kg samples were used in this study, the volumes are equal to the liquid to solid ratio (L/S). A L/S of1 has been assumed to be equivalent to leaching for approximately 10 yr, L/S over 10 are considered equivalent to leaching for 100 years (van der Sloot, 1998). From the V_T values in the tables, complete leaching of some elements from fly ash could take more than 1000 yr.

Table 34. Median elemental volumetric leaching functions (meq/kg/L) and leachate volumes for alkaline samples in water.

Element	NLF	V_N, L	RLF	V_R, L	TLF	Mean VFL	$V_{T, L}$
IRON	0.0028	2	0.0000	3	0.0024	0.0043	1000075
CALCIUM	26.3014	1	24.2614	2	6.4759	11.7019	72
MAGNESIUM	0.0058	2	0.0012	3	0.0074	0.0134	12098
ALUMINUM	0.3535	4	0.3570	6	0.4016	0.5078	4199
SODIUM	1.4991	2	0.2332	1	0.2173	0.9943	138
MANGANESE	0.0000	3	0.0000	4	0.0001	0.0007	40786
POTASSIUM	0.9128	1	0.1846	1	0.1613	0.5696	271
ARSENIC	0.0000	0	0.0000	0	0.0000	0.0000	0
BARIUM	0.0030	1	0.0028	3	0.0020	0.0027	1313
BERYLLIUM	0.0000	0	0.0000	0	0.0000	0.0000	0
CADMIUM	0.0000	0	0.0000	0	0.0000	0.0000	13658
COBALT	0.0000	0	0.0000	0	0.0000	0.0001	0
CHROMIUM	0.0043	4	0.0000	4	0.0042	0.0070	559
COPPER	0.0003	1	0.0000	2	0.0002	0.0003	5376
NICKEL	0.0000	1	0.0000	2	0.0001	0.0004	10057
LEAD	0.0000	0	0.0000	0	0.0000	0.0000	0
ANTIMONY	0.0000	0	0.0000	0	0.0000	0.0000	0
SELENIUM	0.0000	0	0.0000	0	0.0000	0.0000	0
ZINC	0.0006	3	0.0002	3	0.0006	0.0006	3514

Table 35. Median elemental volumetric leaching functions (meq/kg/L) and leachate volumes for alkaline samples in acetic acid.

Element	NLF	V_N, L	RLF	V_R, L	TLF	Mean VFL	V_T, L
Iron	0.0032	3	0.0040	3	0.0038	0.0048	628819
Calcium	4.8993	1	0.5723	1	1.0465	2.5848	525
Magnesium	0.0111	4	0.0179	5	0.0288	0.0394	3123
Aluminum	0.1573	2	6.2514	4	4.1247	4.5805	404
Sodium	91.2018	4	95.3162	6	92.7179	92.7655	0
Manganese	0.0000	1	0.0000	1	0.0001	0.0006	39450
Potassium	0.2386	1	0.0723	1	0.1757	0.8641	255
Arsenic	0.0000	1	0.1324	2	0.1262	0.1251	14
Barium	0.0006	1	0.0002	3	0.0002	0.0004	14974
Beryllium	0.0000	0	0.0000	1	0.0001	0.0002	4687
Cadmium	0.0000	0	0.0000	0	0.0000	0.0000	0
Cobalt	0.0000	0	0.0000	0	0.0000	0.0001	0
Chromium	0.0093	1	0.0073	2	0.0046	0.0114	508
Copper	0.0001	3	0.0000	3	0.0002	0.0003	5752
Nickel	0.0001	3	0.0000	3	0.0002	0.0003	5746
Lead	0.0000	0	0.0000	0	0.0000	0.0000	0
Antimony	0.0000	0	0.0000	1	0.0000	0.0001	23618
Selenium	0.0000	0	0.0000	0	0.0000	0.0000	0
Zinc	0.0006	3	0.0003	4	0.0004	0.0006	4536

Table 36. Median elemental volumetric leaching functions (meq/kg/L) and leachate volumes for alkaline samples in sulfuric acid.

Element	NLF	V_N, L	RLF	V_L, L	TFLF	Mean VFL	$V_{T,\,L}$
Iron	0.0155	4	1.7669	5	2.8107	1.2880	839
Calcium	31.7717	2	34.5494	7	26.6964	30.6963	9
Magnesium	0.8780	3	13.7657	5	5.2223	6.8613	3
Aluminum	0.5651	5	55.1203	8	69.8950	26.6895	18
Sodium	1.8602	5	0.6971	5	1.3193	1.8984	16
Manganese	0.0087	3	0.2720	5	0.1424	0.1058	14
Potassium	1.9547	3	1.4033	6	1.1977	1.4383	26
Arsenic	0.0000	1	0.0000	1	0.0014	0.0004	1440
Barium	0.0021	1	0.0021	4	0.0014	0.0019	1921
Beryllium	0.0000	4	0.0237	5	0.0217	0.0126	15
Cadmium	0.0000	2	0.0004	4	0.0003	0.0002	103
Cobalt	0.0002	5	0.0157	6	0.0088	0.0051	78
Chromium	0.0069	4	0.0461	6	0.0408	0.0227	51
Copper	0.0005	4	0.0165	5	0.0271	0.0051	31
Nickel	0.0003	4	0.0283	6	0.0268	0.0128	41
Lead	0.0000	0	0.0000	0	0.0000	0.0000	0
Antimony	0.0000	0	0.0000	0	0.0000	0.0000	0
Selenium	0.0000	0	0.0000	0	0.0000	0.0000	0
Zinc	0.0017	4	0.0546	5	0.0686	0.0408	25

Table 37. Median elemental volumetric leaching functions (meq/kg/L) and leachate volumes for acid samples in water.

Element	NLF	V_N, L	RLF	V_R, L	TLF	Mean R	$V_{T, L}$
Iron	0.0000	3	0.0000	4	0.0000	0.0000	503196
Calcium	9.0000	2	0.0000	3	3.0000	8.0000	53
Magnesium	0.0000	2	0.0000	1	0.0000	1.0000	1322
Aluminum	0.0000	3	0.0000	4	0.0000	0.0000	43878
Sodium	1.0000	4	0.0000	4	0.0000	1.0000	91
Manganese	0.0000	2	0.0000	2	0.0000	0.0000	2101
Potassium	1.0000	3	0.0000	1	0.0000	1.0000	1178
Arsenic	0.0000	3	0.0000	4	0.0000	0.0000	57
Barium	0.0000	2	0.0000	5	0.0000	0.0000	9351
Beryllium	0.0000	0	0.0000	1	0.0000	0.0000	0
Cadmium	0.0000	1	0.0000	2	0.0000	0.0000	5896
Cobalt	0.0000	1	0.0000	1	0.0000	0.0000	8608
Chromium	0.0000	4	0.0000	4	0.0000	0.0000	3434
Copper	0.0000	4	0.0000	5	0.0000	0.0000	2847
Nickel	0.0000	4	0.0000	5	0.0000	0.0000	2337
Lead	0.0000	0	0.0000	1	0.0000	0.0000	0
Antimony	0.0000	0	0.0000	1	0.0000	0.0000	0
Selenium	0.0000	1	0.0000	1	0.0000	0.0000	249
Zinc	0.0000	2	0.0000	4	0.0000	0.0000	1812

Table 38. Median elemental volumetric leaching functions (meq/kg/L) and leachate volumes for acid samples in acetic acid.

Element	NLF	V_N, L	RLF	V_R, L	TLF	Mean VLF	$V_{T, L}$
Iron	0.0507	6	0.0518	6	0.1456	0.0000	0
Calcium	0.0000	2	-2.4075	2	4.4561	9.0000	39
Magnesium	0.3347	3	0.0788	3	0.6656	2.0000	109
Aluminum	0.0000	1	0.0000	1	0.0000	0.0000	0
Sodium	0.1701	1	0.0975	1	0.1397	1.0000	92
Manganese	0.0165	1	0.0051	1	0.0178	0.0000	82
Potassium	0.0660	1	0.0297	1	0.1688	1.0000	336
Arsenic	0.0175	4	0.0068	4	0.0043	0.0000	345
Barium	0.0027	6	0.0458	6	0.0413	0.0000	55
Beryllium	0.0038	4	0.0085	4	0.0060	0.0000	92
Cadmium	0.0006	3	0.0000	3	0.0001	0.0000	0
Cobalt	0.0092	2	0.0017	2	0.0024	0.0000	349
Chromium	0.0082	4	0.0063	4	0.0083	0.0000	215
Copper	0.0176	4	0.0219	0	0	0.0000	0
Nickel	0.0170	2	0.0040	2	0.0046	0.0000	236
Lead	0.0000	1	0.0000	1	0.0000	0.0000	0
Antimony	0.0000	1	0.0000	1	0.0000	0.0000	0
Selenium	0.0000	1	0.0000	1	0.0000	0.0000	0
Zinc	0.0708	2	0.0129	2	0.0170	0.0000	70

Table 39. Median elemental volumetric leaching functions (meq/kg/L) and leachate volumes elemental leaching rates for acid samples in sulfuric acid.

Element	NLF	V_N, L	RLF	V_L, L	TLF	Mean VLF	$V_{T, L}$
Iron	3	4	3.4922	7	4.3969	3.5600	315
Calcium	24	3	21.1096	6	13.7386	14.6741	0
Magnesium	4	4	2.8772	6	2.6767	3.9334	15
Aluminum	59	4	69.7981	7	68.5028	65.1349	17
Sodium	1	4	0.6081	6	0.5883	0.7241	10
Manganese	0	3	0.0534	4	0.0548	0.0837	18
Potassium	2	4	1.4631	7	1.7231	1.7006	24
Arsenic	0	3	0.0000	5	0.0138	0.0174	114
Barium	0	4	0.0013	7	0.0014	0.0017	1805
Beryllium	0	4	0.0303	7	0.0248	0.0294	12
Cadmium	0	3	0.0002	6	0.0005	0.0006	48
Cobalt	0	4	0.0126	7	0.0163	0.0141	44
Chromium	0	4	0.0364	7	0.0268	0.0301	56
Copper	0	4	0.0411	7	0.0408	0.0629	22
Nickel	0	3	0.0170	4	0.0225	0.0244	44
Lead	0	1	0.0002	3	0.0006	0.0004	352
Antimony	0	0	0.0000	0	0.0000	0.0000	0
Selenium	0	0	0.0000	1	0.0000	0.0005	0
Zinc	0	3	0.0621	4	0.0741	0.0793	11

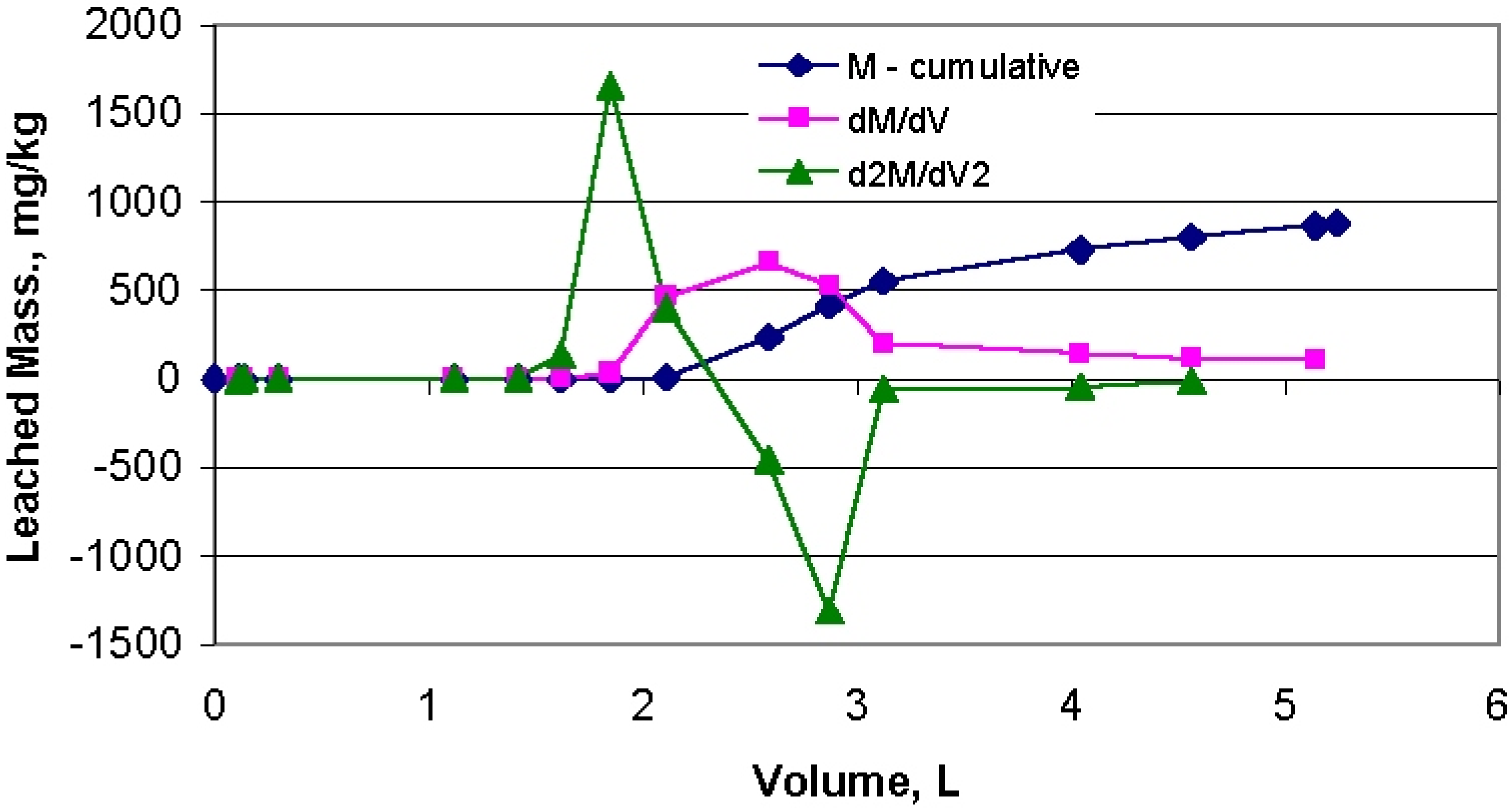


Figure 29. Cumulative leached mass curve with first and second derivatives, showing 3 leaching functions.

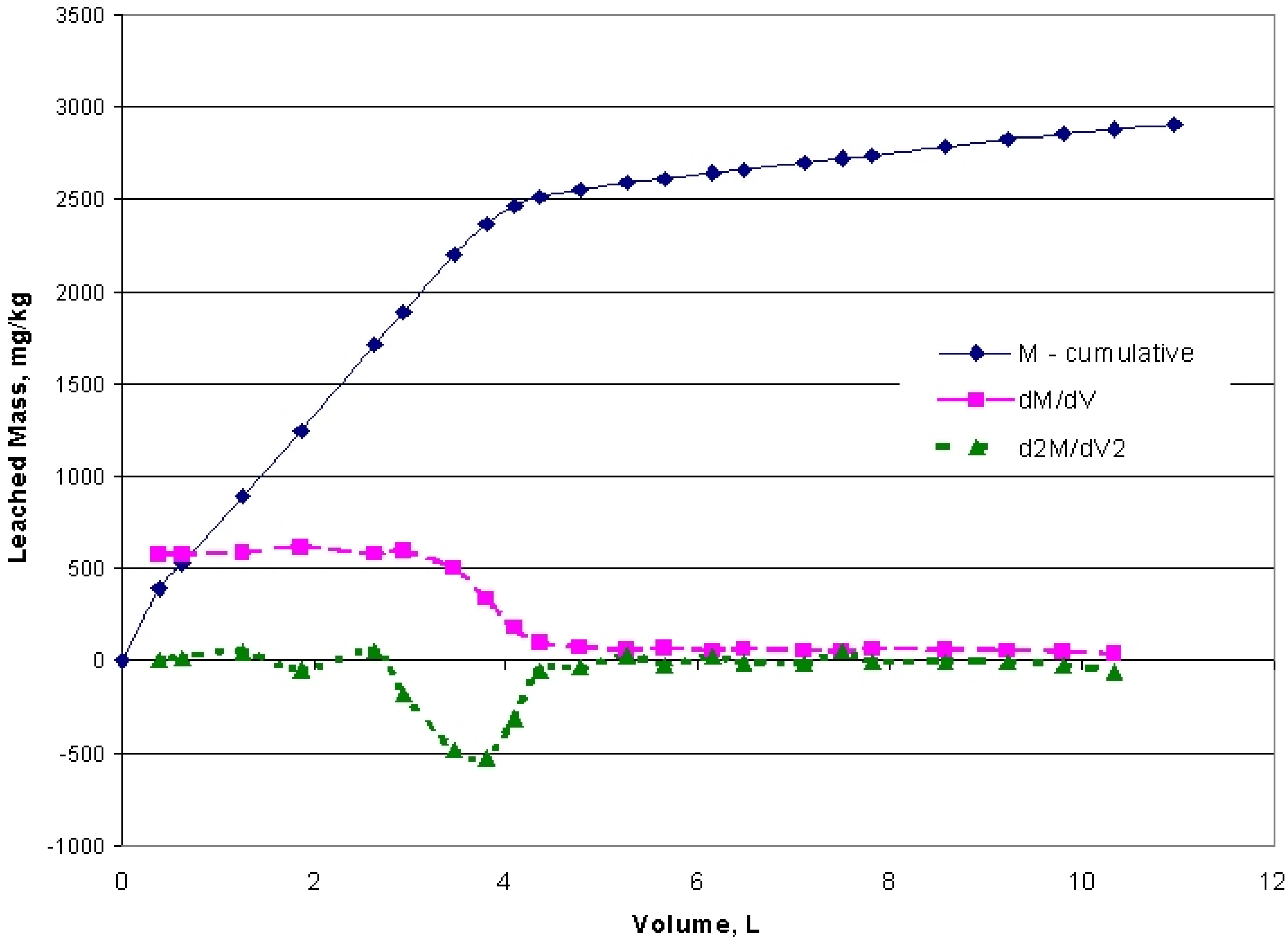


Figure 30. Cumulative amount of an element leached from fly ash with first and second derivatives of leaching curve, indicating two leaching functions.

Chapter 7

Summary and Conclusions

Summary

Leaching System

The objective of this study was to develop data that are broadly applicable to the problem of the release of metals from fly ash and to quantify the rate of release as a function of the composition of the ash. It was also intended to determine solubility of trace elements in coal fly ash as a function of the natural alkalinity of the ash and as a function of the non-silicate concentration. Based on these leaching data, quantitative rate function that describes the release of trace elements from ash in three phases (neutralization, primary leaching, secondary leaching) has been developed. It can be used to estimate potential release of metals from fly ash as a function of time and fluid infiltration rate.

In this study, the sample population of Class F PC fly ashes was relatively large and random in order to encompass the inherent variability of the material. It represented a broad range of chemical composition and included minerals commonly found in fly ash. Both alkaline and acidic samples were included in the sample set. The number and variability of the samples produced a large data set, but ensured that the conclusions were representative of Class F PC fly ashes.

The long term column leaching experiment simulated natural conditions. The leachant solutions were synthetic surrogates for naturally occurring fluids and covered a broad pH range. The use of multiple leachants allowed for the correlation of leaching data to differences in leaching conditions. The relatively large sample (1 kg) eliminated bias due to the non-homogeneous material. The large sample size combined with the low leachant flow rate provided measurable concentrations of released ions at low L/S (volume to sample mass) ratios and also allowed for the determination of long term rates at discrete intervals. The determination of sequential leaching rates was possible because of the design of the leaching system.

Metal Solubility

Coal combustion by-products (CCB) are a mixed material, containing a variety of cations in different matrices, and the solubility of the metals is not a simple function of the concentration in the solid. Some elements may be more or less soluble than others and the solubility of a given element is not the same in all leachant solutions. A frequency distribution of the $M_{L/T}$ values for the set of 31 Class F fly ash samples was determined for each element. Solubility ranges were defined as < 2 % = insoluble, < 20 % = slightly soluble, moderately soluble< 65% and >65% = very soluble, in which the percentage is the maximum amount of that element that was released from the fly ash sample during the experiment. Based on this sample set of Class F PC fly ashes, Fe, Mg, Ba, Pb, and Sb are insoluble in all types of leachant. Several elements that are acid soluble (Ca, Mn, Be, Cr, Cu and Zn) have similar solubilities in both acid solutions, but the Al, Cd, Co and Ni are slightly soluble in sulfuric acid but insoluble in the weaker acetic acid. Only Ca, Mn, K, and Na are soluble in H_2O, and As is the only element that is caustic soluble.

Ash Alkalinity

Alkalinity is usually a function of the concentration of cations of strong bases, Ca, Mg, Na and K. In this set of samples, the alkalinity was found to correlate most strongly with the concentration of non-silicate Ca ($R^2 = 0.84$). The concentrations of Na^+ and K^+ did not appear to influence the alkalinity, indicating that these elements are not present in the ash as soluble oxides or hydroxides.

Comparing the maximum pH in H_2O, HAc, and H_2SO_4 indicates that some of the samples have significant buffer capacity. On this basis, the samples were divided into groups of alkaline and acid fly ashes . The initial phase of leaching the alkaline samples is similar to an acid base titration. The volume of 0.1 N acid added to produce a leachate with a pH of 6.5 is a measure of the buffer capacity of the fly ash.

Non-silicate Solubility

During the course of a leaching experiment, a finite amount of each cation is released from the fly ash sample. The soluble concentration of most elements is a relatively small proportion of the amount present in the ash. Less than 10 g of the major elements, less than 1 g of the minor elements, and less than .01 g of the trace elements is released from a kg sample of fly ash during the leaching experiment.

The total concentration of metallic elements in the fly ash samples was determined by microwave digestion with hydrofluoric acid (EPA Method 3052) and ICP analysis. Elements in a non-silicate matrix were determined by microwave digestion in concentrated nitric acid (EPA Method 3051A). The difference between the two methods is assumed to be the silicate portion of the fly ash, either as quartz, alumino-silicates or amorphous particles. The non-silicates would be other minerals, such as oxides, or coatings on amorphous particles. For several elements, (Ba, Be, Cr, K, Mg, Mn, and Sb) the amounts leached can be correlated with the non-silicate concentration. The higher correlation of the soluble concentration with the total concentration for other elements (Co, Na, Pb, Se and Zn) indicates that at least some of the element is extracted from the silicates in the ash. The differences in solubility indicate that the speciation, probably in silicate and non-silicate minerals influences the release of metals from fly ash particles.

Mineral Solubility

The mineralogical information obtained from XRD analysis of the fly ash samples is too limited to explain the apparent differences in solubility for the various cations. It does not identify minor minerals, it and gives no information on trace element distribution. However, the data can be used to support the solubility determinations for the major ions, Fe and Ca, and inferences about a limited number of other ions. The major mineral constituent in fly ash is quartz. Iron is present as hematite or magnetite, oxides that could have formed at high temperature from the dissociation of pyrite. Calcium is present as a sulfate, either anhydrite or gypsum, which could be the reaction products of calcium from $CaCO_3$ and sulfur from the dissociation of pyrite. Based on their ionic radii, Ni, Mg and Zn are the elements most likely to be substituted for Fe in the iron oxide lattice. However, the ratio of Fe to the other ions is not constant in the different leachant solutions. The ratios of solubility in the two acids and in H_2SO_4 to H_2O are significantly different. Based on these data, Ni, Mg and Zn in the fly ash samples cannot be identified as substitutes for Fe in hematite or magnetite. Barium could substitute for Ca, but solubility patterns do not support this assumption. The solubility of other elements, such as aluminum, was too low to allow speculation about the solubility of alumino silicates or the presence of Al oxides.

Volumetric Solubility Functions

The rate at which metal ions are released from fly ash is a complex function of the flow rate of the leachant, the alkalinity of the ash, the distribution of elements in various chemical compounds or minerals, and characteristics of the leachant solution, particularly its pH. Discrete leaching processes occur at different rates. In this experiment, the release of cations is defined as a solubility function with respect to the volume of leachant solution. During the first leaching interval, the ashes alkalinity is neutralized, and the release of metal ions, except for Ca, is relatively low. At some point, the release of metal ions increases by one or more orders of magnitude, and remains at that level, until the readily soluble ions are released. Then the elemental release decreases, again by one or more orders of magnitude.

The solubility of an element is defined by the three volumetric functions and the median volumes for those functions. The N LF (neutralization leaching function) is describes the release of cations until the sample is neutralized (dM_N/dV_N, meq/L). The RLF (rapid leaching function) rate is the average slope of cumulative curve between inflection points (dM_L/dV_L, meq/L). The TLF (terminal leaching function) is the average slope of cumulative curve after 2nd inflection point (dM_T/dV_T, meq/L). In a natural setting, if the infiltration rate is known (L/d), the time dependent release of the elements can be estimated. Acid fly ash samples exhibit only two functions; neutralization is usually complete with the first addition of an acid leachant.

Conclusions

Based on this population of Class F PC fly ashes, cations in fly ash are only slightly soluble, and elements other than arsenic tend to be most soluble in acid solutions. The differing solubilities with respect to concentration leached and the most effective leachant indicate that the elements are present in the ash in different chemical compounds or mineral forms. and that non-silicates tend to be more soluble. The elemental solubility of different metals in fly ash can be considered independent variables.

Mineral speciation may be a controlling factor in cation solubility, but XRD data are not sufficient to determine the effect. Solubility patterns for pairs of elements of similar ionic radii and valence did not support speculation about elemental substitution in mineral lattices.

Solubility of most elements correlates more strongly to the non-silicate concentration than to the total concentration.

The average release of metal ions from fly ash can be differentiated into 2 or 3 rates related to the alkalinity of the fly ash and the concentration of various elements in the non-silicate fraction of the ash.

The results of this study are in general agreement with the previous leaching studies discussed earlier. However, this project is the most comprehensive leaching study of CCB, both in terms of the number of samples, the evaluation of the factors controlling solubility, and the ability to differentiate distinct phases of cation solubility as a function of to controlling factors.

Additional work

The data from this experiment can be used to address other topics not included in this dissertation. This discussion was limited to the results of leaching Class F PC fly ashes. A similar analysis can be applied to different types of samples, Class C ashes and FBC samples for example.

The x-ray diffraction data was not sensitive enough to relate solubility to mineral species in the fly ash. Determining elemental distributions and associations by SEM-EDX may provide additional information to relate solubility to particular chemical compounds/minerals.

Although the solubility of all the major, minor and trace cations was addressed, the elemental solubility was averaged over all the samples in the sample set or subset. More detailed analysis of individual ions, such as As or Cr, may differentiate solubility due to different valence states and determine maximum leachate concentrations.

Additional work is expected to determine the correlation between the neutralization rate and the decrease in soluble Ca concentration in the samples. The relationship between leaching rate and the change in the non-silicate concentration will provide additional information on the leaching mechanisms.

APPENDICES

Appendix A

Abbreviations, Acronyms and Units

Units of Measure

µg	microgram
d	day
g	gram
kg	kilogram
L	liter
mg	milligram
mL	milliliter
meq	milliequivalent
mt	metric ton
st	short ton
wk	week

Abbreviations

AA	Atomic Absorption
AES	Atomic Emission Spectroscopy
AMD	Acid Mine Drainage
ASTM	American society for Testing and Materials
CCB	Coal Combustion By-products
CUB	Coal Utilization By-products
C_{daf}	Carbon concentration, dry, ash free
CA WET	California Waste Extraction Test
CCP	Coal Combustion Product
daf	Dry, ash free
DI	Deionized
DOE	U.S. Department of Energy
ECN	Netherlands Energy Research Foundation
EPA	Environmental portection Agency
EPRI	Electric Power Research Institute
EPTOX	Extraction Procedure Toxicity Test
ESP	Electrostatic Precipitator
FBC	Fluidized Bed Combustion
FFCW	Fossil Fuel Combustion Wastes
FGD	Flue Gas Desulfurization
GMW	Gram Molecular Weight
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric acid
H_3BO_3	Boric acid
HAc	Acetic acid

HAPs	Hazardous air pollutants
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HNO_3	Nitric acid
ICP	Inductively Coupled Plasma
ISO	International Standards Organization
NAA	Neutron Activation Analysis
LEP	Leachate Extraction Procedure
L/S	Liquid to solid (mass) ratio, L/kg or mL/g
M	Molar = MW/L
MCL	Maximum contaminant level
MEP	Multiple Extraction Procedure
$MgCl_2$	Magnesium Chloride
MMMF	Moisture, mineral matter free
MSW	Municipal Solid Waste
MW	Gram molecular weight
N	Normal = Equivalents/L
NETL	National Energy Technology Laboratory
PC	Pulverized Coal combustion
RO	Reverse Osmosis
RCRA	Resource Conservation and Recovery Act
SEM-EDX	Scanning Electron Microscopy-Energy Disbursive X-ray micro analysis
SGLP	Synthetic Groundwater Leaching Procedure
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
XRD	X-ray disbursive analysis

Elements

Symbol	**Element**	**Atomic Weight**
Ag	Silver	107.870
Al	Aluminum	26.9815
As	Arsenic	74.9216
B	Boron	10.811
Ba	Barium	137.34
Be	Beryllium	9.0122
Cd	Cadmium	112.40
Ca	Calcium	40.08
C	Carbon	12.011
Co	Cobalt	58.9322
Cr	Chromium	51.996
Cu	Copper	63.54
Fe	Iron	55.847
Hg	Mercury	200.59
K	Potassium	39.102
Mg	Magnesium	24.312
Mn	Manganese	54.9380
Mo	Molybdenum	95.94
Na	Sodium	22.9898
Ni	Nickel	58.71
O	Oxygen	15.9994
Pb	Lead	207.19
S	Sulfur	32.064
Sb	Antimony	
Se	Selenium	78.96
Si	Silicon	28.186
Zn	Zinc	65.37

Appendix B

Chemical and Mineral Composition of Coal Ash

Elemental Distribution of Trace Elements

Although elemental composition may be reported as a percentage of the original coal, analysis is usually performed on coal ash and then back calculated to a whole coal basis. In a comprehensive study of the Argonne Premium coal samples (Curtis and Klizas, 1998), 51 elements were determined by a variety of analytical techniques. Only INAA was sufficiently sensitive to quantify 29 elements in the coal samples. For all other techniques it was necessary to ash the samples at 525 °C. For the ICP analysis major elements were determined in ash samples sintered with sodium peroxide. The ash matrix was dissolved with HCl, HNO_3, $HClO_4$ and HF for the determination of trace elements (Briggs, 1998). The combination of techniques identified the major elements in ash as silicon, aluminum, iron, magnesium, calcium, sodium, potassium, titanium, phosphorous ans manganese. Trace elements are lithium, beryllium, boron, scandium, vanadium, chromium, cobalt, nickel, copper and zinc.

The elemental composition gives no information about the mineral compound actually present in the coal or ash, although the solubility of the element, its response to coal cleaning procedures, weathering and combustion are dependent on the mineral matrix in which it exists. Using a semi-quantitative leaching procedure, Curtis et al, (1998, 1999) inferred the modes of occurrence for trace elements in 16 Appalachian coal samples. They concluded that arsenic, mercury and selenium are associated the pyrite, although mercury and selenium could be associated with the organic portion of the coal. Beryllium and chromium were associated primarily associated with silicates, and zinc, antimony, nickel, manganese and uranium are also associated with silicates. Small percentages of arsenic, thorium and cobalt are also associated with silicates, and over 50 % of the antimony, selenium, mercury, beryllium, chromium, uranium, lead, thorium, cobalt and nickel is assumed to be in the organic fraction. Manganese and calcium are in carbonates, although some manganese was detected in siderites. Thorium and uranium are believed to occur in phosphates. Lead and zinc are believed to be in monosulfides, although these elements may also be present in silicates and pyrite.

Using a similar method, Huggins et al (2000) found that in bituminous coals approximately 50 pct of chromium is associated with the organic macerals as an amorphous fine-particle oxyhydroxide. Most of the remaining chromium is associated with the silicate illite. All of the chromium was present as the trivalent ion; detectable amounts of hexavalent chromium were not found in the four coals tested. Hower et al (1997) associated As and Pb with pyrite in two Kentucky coals.

In a study of one subbituminous and three bituminous and coals, Senior et al (2000b) determined that quartz, kaolinite, illite composed approximately 30 pct of the mineral fraction. Miscellaneous silicates constituted another 30 pct. The concentration of pyrite varied from 1 to 30 pct. Siderite, calcite and other carbonates made up from 1 to 6 pct of the minerals. Phosphates were present only in one bituminous sample and the subbituminous coal. Measurable quantities of K-feldspar and montmorilonite were detected only in the subbituminous sample. Iron is usually associated with pyrite, and other elements (Ni, As, Se, Zn, Hg) form sulfides or are incorporated in the pyrite structure. Like iron, these elements may be present in silicates and associated with the organic matter. However, although Fe was associated with carbonates, oxides and sulfates, the trace elements were not detected in these fractions. Pyrite was associated with high density, larger particles. Quartz and silicates tended to be concentrated in smaller particles.

Ten Carboniferous-Permian coal samples, a Tertiary brown coal and a Quaternary peat sample were collected in China (Zhang et al, 1998). There was significant enrichment of the alkali and alkaline earth elements. The peat and brown coal also had higher concentrations of As, Cr, and Co. Although Ba and Sr concentrations were higher in the higher rank coals, there was no apparent distribution with rank.

Minerals in Coal and Ash

In a study of 35 coal samples from 8 countries, Vassilev and Vassileva (1996) identified approximately 100 minerals. The minerals were characterized as major (> 1% by wt), minor (.1><1% by wt), and trace (<0.1 % by wt). On a semi-quantitative basis, the mineral groups in decreasing order of importance are: silicates > carbonates > oxyhydroxides > sulfides > sulfates > phosphates > others. Quartz and kaolinite, illite, plagioclase, and K-feldspar are the primary silicates. Calcite and dolomite are the primary carbonates, and pyrite and marcasite are the most common sulfide minerals. Gypsum and iron oxyhydroxides may also be found in coal. Other minerals are present in minor to trace amounts. The pyrite and marcasite are believed to be syngenetic minerals formed in the reducing environment of the coal swamp, although some epigenetic sulfides may be precipitated from low-temperature hydrothermal solutions. Silicate and oxyhydroxide minerals are primarily detrital minerals or weathering products of other minerals in coal. Quartz is the most common mineral in coal. Gypsum is commonly associated with pyrite and may be a weathering product of sulfide and carbonate minerals. Alumino-silicate volcanic glass, possibly deposited from volcanic ash during the peat forming process, is the primary component of the amorphous mineral phase in coal.

In another study of 41 coals, Vassilev et al (1996) relate mineral assemblages to rank of the coal. The coals were divided according to rank, based on dry ash free carbon concentration (C_{daf}). The lower rank coals are enriched in mineral matter, including calcium and magnesium oxides. The highest rank coals have increased contents of silica, aluminum, iron, potassium, sodium, and titanium. Coals of intermediate rank have higher concentrations of silica and sodium. The formation of pyrite, gypsum and apatite may occur during diagenetic processes. Quartz constitutes about 27 % of the ash in low rank coals, 40 % of medium rank coals and about 31% in high rank coals. Several other minerals (kaolinite, plagioclase, K-feldspar) have a maximum concentration in medium rank coals, while other minerals (corundum, calcite, pyrite and apatite) reach a minimum relative concentration in the medium rank coals. The relative concentrations of illite, montmorilonite biotite, hematite and zeolite are comparable in all three rank groups, although the concentration of mineral matter in the coal samples is significantly different. The alkali, alkaline earth and weakly bound elements are easily mobile and may be leached from the detrital silicates. Other elements, particularly potassium, may be added to coal sediments by percolating solutions. Organically bound, ion exchanged and pore water elements can crystallize to minerals during lithification.

Analysis of the minerals in 40 samples of a Powder River Basin (PRB) coal, revealed predominantly well crystalized kaolinite and quartz (Brownfield et al, 1999). The quartz was primarily detrital, but trace amounts of β-form quartz, with apatite and zircon, was attributed to air-fall and reworked volcanic ash deposited in the peat swamp. Dissolution and alteration of pyroxenes, feldspars, and amphiboles, common in volcanic ash, may have contributed to the authigenic kaolinite, anatase, and calcite. The PRB coal contained higher amounts of Ba, Ca, Mg, Na and Sr than eastern bituminous coals. These elements are associated with hydrated alumino-phosphates and clay minerals, as well as with calcite, barite , biotite and apatite. The Ca and Mg-rich mineral phases in the coal and resultant ash were attributed to volcanic minerals.

In a study of Gulf Coast lignites, the concentration of As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, Se, and U was determined in 250 coal samples (Warwick et al, 1997). Enrichment of some elements was attributed to proximity to igneous rocks or to deposition of volcanic ash. There was a high degree of lateral and vertical variability of elemental concentrations even within a single bed.

The original mineral composition of the coal seam can also be modified by post-coalification circulation of geothermal fluids. Pyrite from 14 samples from the lower Pennsylvanian coals of northwestern Alabama were examined by ion microprobe/SEM (Kolker, 1999). Epigenetic pyrite was found to be enriched with arsenic. Arsenic rich coals are prevalent in fault zones, and Kolker implies that post coalification hydrothermal fluids were limited to fault zones. Daniels et al (1990) collected 15 coal samples from the anthracite fields of Pennsylvania; minerals within the coal matrix include NH_4-illite and kaolinite, representing a mixture of detritus and authigenic phases. Systematic cleat sets are well mineralized and contain kaolinite and quartz, as well as tosudite ($Na_{0.5}(Al,Mg)_6(Si,Al)_8O_{18}(OH)_{12}\bullet 5H_2O$), sudoite ($Mg_2(Al,Fe^{3+})_3Si_3AlO_{10}(OH)_8$), rectorite ($(Na,Ca)Al_4(Si,Al)_8O_{20}(OH)_4\bullet 2(H_2O)$) and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). These minerals were assumed to replace kaolinite at high temperatures, the different minerals were attributed to differences in the composition of fluids during late stage diagenesis.

Based on their boiling points and the phase change temperature of their oxides, several authors have described the partitioning of trace elements in CCB (Germani and Zoller, 1988, Meij, 1989; Yokoyama et al, 1991). The first group of elements, which are concentrated in bottom ash or equally distributed between bottom ash and fly ash, includes typically lithophile elements: Ba, Mg, Mn. In a second group, trace elements, enriched in the fine particulate fraction are usually chalcophile elements such as As, Cd, Pb, Se, and Zn. Group 3 includes volatile elements which remain in the vapor state, Hg, Br. Several elements partition between groups.

Davison et al (1974) studied the trace element partitioning of 25 elements in fly ash. The concentration of the elements, Pb, Sb, Cd, Se, As, Ni, Cr, and Zn increased with decreasing particle size. The concentration of the elements Fe, Mn, V, Si, Mg, C, Be, and Al was found to increase with decreased particle size only for particles with a diameter less the 11 µm. These elements showed no size dependence for larger particles. The concentrations of Bi, Sn, Cu, Ti, Ca and K showed no dependence on particle size. The size dependence was attributed to volatilization of elements or compounds with lower boiling points during combustion, followed by condensation or adsorption on entrained particles. However, the model they propose indicates that the surface adsorption or condensation is a direct function of the surface area and inversely related to particle mass. This would indicate that large, lower weight particles would be favored as adsorption sites.

Vaporization and condensation form an ultrafine aerosol during PC combustion (Senior et al, 2000a). Factors such as residence time, temperature history and level of turbulence control the size and morphology of the aerosol particles. Fly ash particles with aerodynamic diameters less than 0.4 µm were attributed to condensation. Non-volatile elements, such as Fe, were found to concentrate in larger ash particles. Between 10 and 30 pct of the volatile elements, As, Sb, Se, and Zn, are in the condensed fly ash particles. Arsenic and Sb are soluble in silicate glass and may be retained by glassy particles that form by coalescence of minerals. Correlations between the concentrations of arsenic and calcium in fly ash are assumed to indicate the formation of calcium arsenate.

Chemical composition

EPRI (1987a) conducted a study of the composition of 39 fly ash samples and 40 bottom ash samples, from power plants in the U.S. Total elemental composition was determined by energy disbursive x-ray fluorescence analysis (XRF). The major element concentrations of fly ash and bottom ash were very similar. The trace element composition indicated that more volatile elements (As, B, Cl, F, S and Se) were preferentially partitioned to the fly ash. The trace element concentration tended to be higher in fly ash derived from bituminous coal.

EPRI (1987b,c) also conducted an extensive literature search on the inorganic and organic constituents of fossil fuel combustion residues (EPRI, EPRI,. They concluded that the inorganic composition was highly variable. Some non-volatile elements were evenly distributed between fly ash and bottom ash, while volatile elements tended to be concentrated in fly ash. They concluded that data available at that time was insufficient to predict leachate composition.

The Council of Industrial Boiler Owners (CIBO) conducted a survey of operators of FBC units, requesting information on the physical and chemical characteristics of FBC fly ash. Information was received from 39 facilities. The major difference between ashes in the two groups is that FBC ashes contain higher concentrations of Ca, due to the injection of limestone as a sorbent to control SO_2. The major constituents in the ash are oxides of silicon, aluminum, iron and calcium. Trace elements were found to be concentrated in the smaller ash particles.

The Pennsylvania Department of Environmental protection (PADEP) requires that mining companies placing fly ash in surface mines apply for a modification of their mining permit (Module 25 and Module 25A). DOE personnel were allowed to copy the Module 25 applications and reports (Kim and Cardone, 1997). The information from 37 operators included analyses of 218 ash samples, of which 99 were clearly identified as fly ash. In addition to Si, the major elements were Al, Ca and Fe. Although values for Fe and Al were reported in approximately 90 pct of the analyses, values for Ca were reported in only 10 pct of the analyses. The trace elements, As, Cr, Cu, and Ni were reported in about 80 pct of the analyses, while Sb, Cd, and Ag values were given for 20 pct of the samples. In this type of data, it is uncertain whether missing values indicate values below the analytical detection limit or were not included in the analysis.

Volatilization, melting, decomposition and the formation of new minerals, as well as oxidation are the mechanisms that transform the minerals in coal. There is a significant difference between the minerals in coal and those in the ash produced from the same coals When the coals studied by Vassilev and Vassileva (1996) were ashed at 815 °C, the minerals were primarily oxyhydroxides and silicates with lesser amounts of sulfates, carbonates, and phosphates. They also note an increase in amorphous minerals. .

Minerals in CCB are usually not considered particularly hazardous. The inclusion of heavy metals or hazardous air pollutants (HAPs)in the ash and their solubility are the primary determinants of toxicity. Concentration is not the only factor; volatility, toxicity and solubility determine the potential for health and environmental effects. All of these factors are functions of speciation within the ash. The speciation of Cr, As, Se and Ni were investigated by Huggins et al (1997). They estimated that toxic Cr(VI) generally constituted less than 5 % of the chromium in coal ash. Arsenic is found almost entirely as As(V) in fly ash samples. It is also found as As(V) in most bottom ash samples, but some bottom ashes contain as much as 25% As(III), probably as a result of high temperature and oxygen lean combustion conditions. Although abundant Fe interfered with the its precise determination, Ni was present as Ni^{2+}, with no evidence of nickel sulfides in coal ash. In two samples prepared under the same conditions, Se was present in different forms. One sample contained elemental Se or a selenide while the other was predominantly selenate.

The transition of minerals in coal to those found in combustion by-products is related to the high temperature oxidation and to the rate of cooling of the inorganic melt. Thompson and Argent assumed that at 2000°K, a completely molten slag was at equilibrium. Above 1300°K, mullite, iron oxides and silica are predicted to be formed. Below 1300°K, sodium and potassium sulfates separate from the melt. Variability in the cooling characteristics of the melt is believed to contribute to variability in ash composition. The removal of sulfur as sulfur dioxide during combustion also contributes to the formation of iron oxides. The authors conclude that ash formation in combustion is a complex process and is affected by mineral content ans speciation.

Ashes from high sulfur, high iron coals have a variety of iron-bearing phases, including magnetite, hematite, goethite (Hower et al, 1999). Spinel, mullite and silicates may also contain iron. The iron bearing minerals were characterized in class F fly ash that was sized and magnetically separated. The SiO_2 concentration is higher in the non-magnetic fractions, but it also constitutes a substantial portion of the magnetic fractions. The inclusion of the non-magnetic glass particles in the magnetic fractions may be sue to the presence of mixed particles or to the presence of trace magnetic minerals on the larger glass particles. Magnetite and hematite are the iron oxide phases, enriched in the magnetic fractions. Chromium and nickel follow similar patterns, possibly due to substitution for iron in the spinel structure.

A classification system for fly ash was proposed, based on the modal and normative mineral phases (O'Connor, 1997). It was developed to characterize preferential retention sites for environmentally sensitive elements, assuming that different mineral species should differentially incorporate ions of different sizes. It was noted that some minerals are unchanged in the combustion system, showing little evidence of pyro-metamorphism. These are primarily quartz, K-feldspar and mica. Fly ash grains are generally heated to temperatures at which the minerals fuse. Quick cooling may favor the simple end member ternary phases in silicate glasses. The bulk fly ash is a collection of mineral species, and impurities may be incorporated in crystals or adsorbed on surfaces.

In a study of fly ash from high and low sulfur coals burned at the same power plant, the concentration of As was 170 ppm in the high sulfur ash, as opposed to an average concentration of 54 ppm in ash from low sulfur coal (Finkelman et al, 1997). Microprobe analysis of individual fly ash grains indicated that the arsenic concentration was generally near the limit of detection. Although the microprobe analysis showed no surface enrichment, selective leaching indicated that the As occurred primarily as a condensate on ash particle surfaces. Separation studies indicated that Cr was enriched in the Fe-oxide phases, such as spinel. The leaching experiments showed 70 pct of Cr to be in the glassy silicate portion of the ash. Similar results were found for Ni and Co. Both Sb ans Zn were also found to be present in more than one ash phase.

Appendix C

Leaching Methods

The most frequently referred to leaching procedures are those developed for characterizing the toxicity of hazardous solid waste: Toxicity Characteristic Leaching Procedure (TCLP), Extraction Procedure Toxicity Test (EPTOX), Synthetic Precipitation Leaching Procedure (SPLP) and the American Society for Testing and Materials Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM-D3987). These methods and similar tests have also been applied to a variety of non-hazardous materials.

Batch Methods

Batch leaching methods can be approximately described as those in which a sample is placed in a given volume of leachant solution for a period of set period of time. Most of the methods require some type of agitation to insure constant contact between the sample and the leachant. At the end of the leaching period, the liquid is removed and analyzed.

Toxicity Characteristic Leaching Procedure (TCLP)

The Toxicity Characteristic Leaching Procedure (TCLP) was developed to determine the mobility of organic and inorganic species in liquid, solid and multi-phasic wastes placed in a sanitary landfill. It is used to characterize the soluble and volatile components of a waste material. The presence of any one of 40 toxic constituents, 8 of which are metals, in concentrations equal to or greater than that specified under the Resource Conservation and Recovery Act (RCRA), the material is considered hazardous based on toxicity.

TCLP uses one of two leaching fluids based on the alkalinity of the sample. If the pH of the samples is less than 5, a sodium acetate buffer with a pH of 4.93 ± 0.05 is used. For materials with a pH greater than 5, an acetic acid solution with a pH of 2.88 ± 0.05 is the liquid medium. The diameter of the sample particles must be < 9.5 mm and the minimum sample size is 100 g for materials that do not contain volatile compounds. The method specifies that the weight of the leachant solution as 20 times the weight of the solid sample (20/1). If it is assumed that the density of the leachant solutions is approximately 1, this ratio is frequently given as 20 mL of leachant per gram of sample (20 mL/g). The method specifies end over end rotation at 30 rpm for a period of 18 ± 2 hr. Ambient temperature is to be maintained at 23 ±2° C during the extraction procedure. If , under these conditions, the concentration of a constituent exceeds the regulatory limit, the sample is considered hazardous.

Extraction Procedure Toxicity Test (EPTOX)

The extraction procedure, EPTOX, was also developed to determine characteristic toxicity under sanitary landfill conditions. EPTOX was in use prior to the adoption of TCLP. The sample particle size must be < 9.5 mm in diameter and sample size is 100 g. The L/S is 16, and if the pH is >5, 0.5 N acetic acid is used to adjust the pH to 5.0 ± 0.2. No more than 4 mL of acid per g of sample should be added. The pH should be monitored and adjusted during the procedure. At the end of the extraction period, water is added to adjust the L/S to 20 The mixture should be agitated for 24 hr at an ambient temperature between 20 and 40° C. Method 1310 A also included a procedure for determining the structural integrity of solid materials.

Synthetic Precipitation Leaching Procedure (SPLP)

Synthetic Precipitation Leaching Procedure (SPLP) is another EPA method originally designed to evaluate the mobility of organic and inorganic constituents of liquids, soils and wastes. The leachant fluid is intended to mimic the acidity of acid rain; water is adjusted to an appropriate pH with a 60/40 mixture by weight of sulfuric and nitric acids. For soil samples collected east of the Mississippi River , the pH is adjusted to 4.20 ±0.05; west of the Mississippi River the pH is adjusted with the sulfuric acid/nitric acid mixture to 5.00 ± 0.05. If the sample is a waste, the leachant is the pH 4.2 solution. The particle diameter should be < 9.5 mm; 100 g is the minimum sample size, and the L/S is 20. The sample is placed in an extraction vessel for end over end rotation at 30 rpm for 18 ± 2 hr. Ambient temperature is to be maintained at 23 ± 2°C. Except for the leachant fluid, the procedure is very similar to TCLP.

Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM-D3987)

The American Society for Testing and Materials (ASTM) procedure is intended to rapidly generate a leachate from solid waste. It is not intended to simulate conditions in the field. Reagent water is the leaching fluid, and the method does not require particle size reduction. It calls for rotary agitation about a central axis at a rate of 29 rpm for 18 hours. The sample size is 70 g, and L/S is defined a volume in milliliters that is 20 times the weight of the sample in grams. Ambient temperature should be between 18 and 27 ° C. EPA's methods were developed assuming a co-disposal of 95 % municipal solid waste and 5 % industrial waste. The ASTM method was developed as a more appropriate alternative for monofill industrial waste sites.

California Waste Extraction Test (CA WET)

As a human health issue, the California Department of Health Services developed the Waste Extraction Test (WET) to determine if extractable constituents can be leached to groundwater from material in a sanitary landfill (CCR, 1984). WET uses a citrate buffer with a pH of 5 to extract metallic and other constituents from waste. If the waste is not capable of generating acidic leachate, deionized water can be substituted for the citrate buffer. The citrate buffer is a 0.2 M sodium citrate, prepared by titrating citric acid in deionized water with 4.0 N sodium hydroxide. A fifty gram sample, with particles less than 2 mm, and 500 mL of the extraction solution are placed in a flask. To remove oxygen, the flask is flushed with nitrogen gas for 15 minutes. The flask is sealed and vigorously agitated on a table shaker or other apparatus for 48 hours. Temperature should be maintained between 20 and 40 ° C. The extractant fluid is then filtered and acidified with nitric acid. The procedure can be used to extract all metals except hexavalent chromium. The concentration of soluble constituents are reported as mg/L or as mg/ kg of solid waste.

Availability Test for Granular Materials (NEN 7341)

Van der Sloot et al (1994) have worked extensively on the development of Dutch Standard Leaching Tests to characterize all type of granular waste. The Availability Test (NEN 7341) assesses the fraction of an element that could become available under extreme environmental conditions. Particle size is less than 125 μm and L/S is 100 L/kg. Samples are leached at pH 4 and at pH 7, continuously agitated for 3 hrs. The pH 4 extraction is assumed to represent the lowest natural pH and the neutral pH 7 is assumed to release oxyanionic species.

Synthetic Groundwater Leaching Procedure

The Synthetic Groundwater Leaching Procedure developed by Hassett (2000) uses a leaching solution that is intended to simulate leachate anticipated in field conditions. The procedure allows fro changes in leachability related to the formation of hydrated secondary phases and new minerals over extended periods of time. The solid sample and synthetic groundwater solution are agitated for 60 days or more with sampling at regular intervals. He synthetic groundwater leaching solution is intended to mimic groundwater that could contact the material. If it is to be placed above the water table, and will be contacted only by rainwater, DI water can be used as the leaching solution. If the material will be in contact with highly mineralized water, either the water itself or a synthetic mixture of similar composition and pH should be used. The procedure suggests that a 10 g sample and 220 mL of leaching solution be added to a series of 250 mL polysulfone bottles. Samples are taken after 18 hr, at the end of one week, one month and 2 months. Longer sampling intervals can be added.

Leachate Extraction Procedure (LEP)

The Leachate Extraction Procedure (LEP, 1985) was developed for use in Ontario, Canada. It was subsequently adopted accepted by the Canadian General Standards Board (CGSB, 1987)to identify materials that posed a toxicity risk to the environment. The LEP is similar to EPTOX, specifying the same particle size, L/S and leachant solution. The primary differences are that in the LEP the sample size is 50 g and end over end rotation at the rate of 10 rpm for 24 hr is required.

Serial Batch Methods

In serial batch methods, a sample of waste is leached successively with fresh aliquots of the same leaching fluid. This method is intended to eliminate the effect of concentration on solubility and to simulate long-term exposure to the leachant solution.

Multiple Extraction Procedure (MEP)

The Multiple Extraction Procedure (MEP)is designed to simulate repetitive leaching that a waste could undergo in an improperly designed sanitary landfill. It is intended to produce the highest concentration of a constituent that can be extracted in a natural environment. Samples are leached according to the EPTOX method. Then the solid sample is re-extracted nine times according to the SPLP method. Each leachate is analyzed separately. If the concentration of a regulated constituent increases in the 7th, 8th or 9th extraction, the procedure is repeated until the concentration remains constant or decreases. The initial and final pH of each fluid extract is recorded, and the concentration of the constituents in each extract is reported.

Standard Test Method for Sequential Batch Extraction of Waste with Acidic Extraction Fluid (ASTM D 5284)

The release of constituents from a waste containing at least 5% dry solids is estimated with this procedure, although it is not intended to simulate the leachate under site leaching conditions. The pH of the leachant solution should reflect the actual pH of precipitation of the geographic region in which the waste is to be disposed. It is prepared by adding a 60/40 mixture of sulfuric and nitric acids to DI water until the desired pH is obtained. To a sample containing 100 g of waste on a dry weight basis, sufficient extraction fluid is added so that the final L/S is 1:20. The sample is agitated continuously for 18 hr at 18 to 27 °C. The waste/leachant solution is then transferred to a pressure filtration vessel and filtered under pressure with nitrogen or other inert gas. The total dissolved solids of the filtrate is determined and then it is preserved for analysis. The solid sample, including the filter, is transferred from the filter back to the original extraction vessel. Less than 500 g of leachant solution is used to transfer the sample and rinse the filtration devise, including the amount used to rinse the filter as it is removed. Leachant solution is added to achieve the original L/S ratio. This procedure is repeated for a total of ten leaching cycles. The leachate from each step is analyzed independently.

Standard Test Method for Sequential Batch Extraction of Waste with Water (ASTM D 4793)

This method has follows the same general procedure as ASTM D5824, except that Type IV reagent water is the leaching solution. The final pH of the leachates is intended to reflect the interaction of the leachant with the buffering capacity of the waste, as when the waste controls the final pH of the leachate. As described above, the sample should contain 100 g of solids on a dry weight basis, the L/S ratio is 20, the agitation period is 18 hr and the procedure is repeated 10 times.

Column Tests

Column leaching tests are considered as simulating the flow of percolating groundwater through a porous bed of granular material. The flow of the leaching solution may be in either down-flow or up-flow direction and continuous or intermittent. The flow rate is generally accelerated when compared to natural flow conditions. However, it should be slow enough to allow leaching reactions to occur. A basis assumption in column leaching is that the distribution of the leaching solution is uniform and that all particles are exposed equally to the leachant solution. Precipitation or sorption within the column may affect the results.

Standard Test Method for Leaching Solid Material in a Column Apparatus (ASTM D-4874)

This test method is intended to generate aqueous leachate from solid materials in a column apparatus. It is intended to maximize the leaching of metallic species from a solid. The aqueous fluid passes through particles of known mass in a saturated up-flow mode. The column is constructed of glass, 300 mm long with an inside diameter of 100 mm. Stainless steel end plates are attached with rods or any method that ensures a leakproof seal with a chemically inert gasket. A flow distribution disk of sintered stainless steel with a nominal pore diameter of 70 μm fits inside the bottom of the column. The leaching fluid is contained in a pressurized reservoir with pre-purified nitrogen or argon at a headspace pressure less than 275.8 kPa. The maximum particle size is 10 mm (1/10 of the inside diameter of the column) and the size distribution is representative of that expected in field placement. The column is completely filled and the mass of sample determined. The sample is saturated with water, then the leachant solution flow upward through the sample so that the equivalent of one void volume passes through the sample in a 24 hr period. At a minimum, Void volumes 1,2,4 and 8 are analyzed.

Dutch Standard Column Test (NEN 7343)

This test is a regulatory test to simulate leaching from mineral waste that would occur in less than 50 yr. The height of the column is 20 cm with a diameter of 5 cm; the diameter of the waste particles must be less than 4 mm. The leachant is demineralized water adjusted to pH 4 with nitric acid in an up-flow application. Seven leachate fractions are collected within a period of approximately 21 days; the L/S ratio is between 0.1 and 10.

Nordtest Column Method (NORDTEST)

This method in use in the Nordic countries is similar to the Dutch Column test, except that column dimensions are optional**.** The minimum column diameter is 5 cm, and the minimum height is 20 cm. The flow rate is 0.03 to 0.1 L/S per 24 hours, and only four to five leachate fractions are collected.

Gravity Flow Columns

The up-flow column procedures are designed to insure that the leachant solution is equally distributed throughout the column, i.e., that all particles are equally exposed to the leachant. However, gravity flow columns can also be used to study leaching of porous media. Column experiments more closely approximate the flow conditions, particle size distribution and pore structure, leachant flow and solute transport found in the field (Zachara and Streile, 1990). Column experiments can be conducted in both saturated and unsaturated conditions. Unsaturated conditions are usually intended to mimic vadose zone placement. Intermittent addition of a given volume of leachant solution at the top of the column can provide uniform distribution of the fluid and approximate a constant fluid front moving through the unsaturated column. Saturated columns are obtained by a constant fluid flux, and allowing the fluid to pond at the top of the column. Variables, such as leachate collection, sampling frequency, leachant flow rate, and duration of the experiment, are determined by the experimental objectives.

Sequential Leaching Tests

Sequential leaching tests use a single sample that is leached by a series of different leaching fluids. The constituents extracted with a particular leachant are associated with a particular mineral phase or chemical species. Speciation is considered one of the controlling factors in the potential release of cations to the environment.

Palmer's Sequential Leaching Method (USGS)

The USGS sequential leaching method was developed as a rapid indirect method of determining the modes of occurrence of trace elements in coal (Palmer et al, 1999). Duplicate 5 g samples (-60 mesh) are sequentially leached with 35 mL of a leachant solution at room temperature for 18 hr. The leachant solutions are 1 N ammonium acetate to remove exchangeable cations, 3 N hydrochloric acid to extract cations associated with carbonates and monosulfides. Concentrated hydrofluoric acid dissolves silicates and 2 N nitric acid releases cations in disulfides. Residual elements are believed to be associated with the organic matrix. The sample and leachant fluid are placed in a 50 mL polypropylene tube and shaken in a motorized wrist shaker.

Short Sequential Procedure

A short sequential procedure uses two steps to assess the lability of heavy metals in soil particles (Maiz et al, 2000). Mobile elements are extracted by agitating the sample for 2 hr in 0.01 M calcium chloride solution. The L/S is 10, and tests were conducted at room temperature. The sample is centrifuged and the supernatant removed. The residue is rinsed and then leached with a solution of 0.005 M diethylenetriaminepentaacetic acid (DPTA), 0.01 M calcium chloride, and 0.1 M triethanolamine (TEA) at pH 7.3; L/S is 2. Agitation for 4 hr at room temperature releases mobilisable elements. The mobile elements are those that are soluble under normal weathering conditions. The mobilisable elements are the exchangeable and chelated fractions.

Tessier’s Sequential Leaching Method

Like the later USGS sequential extraction procedure, Tessier (1979) uses a series of extractant fluids to dissolve metals associated with particular ligand phases in a complex sample. A sample (0.5 g) is weighed into an acid washed polycarbonate centrifuge tube. After addition of the appropriate reagent, the sample is shaken at room temperature to ensure continuous suspension of the sample. The supernatants were separated by centrifugation at 10,000 rpm for approximately 25 min. The residue was washed with 10 mL of DI water between steps. The reagents used in the Tessier procedure are summarized in Table C-1.

Table C-1. Summary of Tessier's sequential extraction method.

Reagent	Volume	Concentration	pH	Reaction time	Target
Magnesium Chloride	8 mL	1 M	7	1 h	extractable metals
Acetic acid/ sodium acetate	8 mL	1 M	5	5 h	carbonates
Hydroxlamine hydrochloride in acetic acid	20 mL	0.04 M	2	6 H @ 96°C	Fe & Mn oxides
Hydrogen peroxide ammonium acetate nitric acid	27% 3.2 M 20%				Organically bound metals
HF/HNO_3[1]					Residual metals

[1] A modified Tessier procedure uses aqua regia (4 M nitric acid and concentrated nitric acid) in place of the hydrofluoric/nitric acid mixture (Raksasataya et al, 1996)

BCR Sequential Leaching Method

A three step sequential extraction procedure was developed by the commission of the European Communities Bureau of Reference (BCR). In this procedure (Quevavller et al, 1994), the first extractant is 0.11 M acetic acid, pH 3 to remove exchangeable metals and carbonates. Hydroxylamine hydrochloride (0.1 M, pH 2) is used next to solubilize metals bound to Fe and Mn oxides. The third step A solution of 27 % hydrogen peroxide and 1 M ammonium acetate at pH 2 oxidizes metals bound to organic species. This method has also been modified (Raksasataya et al, 1996) to include aqua regia digestion of the residual material.

Monolithic Leaching Methods

Monolithic leaching methods are used to evaluate the release of elements from a material that normally exists as a massive solid, cement for example. Monolithic tests are frequently used to characterize the release of pollutants from stabilized waste materials. The release of an element is a function of the exposed surface area as opposed to the mass. Flow around systems relate solubility to the surface area of a particular volume. Flow through systems also consider the internal pore surface. And some systems take into account the rate of diffusion of the leachant solution into the pores.

Static Tests

In static monolithic leaching, a particle of regular geometry and known surface area is immersed in a volume of leachant solution. The same leachant solution is sampled at defined intervals and replaced with fresh solution (Hoberg et al,2000). According to van der Sloot et al (1989), the elemental flux, J, in this type of test is described by the equation:

$$J = \sum_{i=1}^{n} (C_i - C_0) / A * t \qquad \textbf{(18)}$$

where C is the concentration of the element in the leaching solution, A is the surface area and t is the contact time, and n is the number of cycles.

Flow Through Leaching Test

The flow through leaching test (Poon et al, 2000) is used to characterize leaching from a waste that is more permeable than the surrounding material. In the flow through leaching test, the solid sample is placed in a flexible wall permeameter. The leaching solution is DI water at a mean flow rate of .0166 mL/min at a pressure of 400 kPa.

Core Leaching System

In this system, a reactions cell, slightly larger that the diameter of the core, is constructed of acrylic pipe (Paulsen and Kuhlman, 1989). The sides of the core are coated with epoxy to ensure that the core will not disintegrate during testing and that all leachant flows through the core. After the core is placed in the cell, o-ring caps form a seal at each end of the sample. A sulfuric acid solution is the leachant, introduced in the bottom of the cell at a pressure of 30 psi. Similar cells constructed of PVC pipe and stainless steel can be used to leach core samples at substantially higher pressures.

Flow Around Leaching Tests

In a flow around leaching system, the external surface of a solid sample is in contact with the leachant.

Bulk Leaching

Bulk leaching generally refers to leaching large samples, either in a large column or in heaps. They are either industrial systems or used in a research setting to leach a non-homogeneous sample with a large particle size. Bulk leaching methods are not particularly applicable to fly ash.

Heap Leaching

Heap leaching is used in the hydro-metallurgical industry, particularly for the cyanide leaching of gold and silver ores (Fleming, 1999). The purpose is to obtain a “pregnant” solution from which a metal can be recovered. A large ore sample is placed on a constructed pad that incorporates a leachate collection system. The heap is constructed to maximize permeability and minimize channeling. Mechanical sprays are used to apply the leachant solution at a rate of less than .01 L/s/m^2. Fine particles are unstable in heaps, and may passivate ore surfaces, reducing the efficiency of the leaching system. Heaps have also been used for the oxidative leaching of pyrite from coal (Cathles and Breen, 1983). In this case, the convection of air throughout the heap is as important as the equal distribution of the liquid leachant.

Trickle Bed Reactor

A trickle bed reactor is a large column (>25 cm ID) containing more than 100 kg of solid sample (Dalverny et al, 1996). The leachant solution is sprayed on the top of the sample in order to distribute it throughout the mass of the sample. Plugging with fines and channeling are problems in this type of leaching apparatus.

Combined Methods

The International Ash Working Group (IAWG) has designed a leaching protocol to quickly determine the total leachable elements in a material and to estimate metal release in a normal environmental setting (van der Sloot et al, 1994; van der Sloot, 1998). An availability test is based on the extraction of fine-grained material at a L/S of 100 at a controlled pH of 4, which is assumed to be a lower pH limit found in natural environments. A second test at a pH of 8 is used to determine leachability of oxyanionic species. From the total acid consumption, the acid neutralization capacity of the material is estimated. Total elemental release as a function of time is estimated by leaching at different L/S values in a serial batch test. The release of contaminants is usually expressed in mg/kg leached against the L/S ratio.

Comparison of Leaching Methods

Several studies have attempted to compare different leaching methods, either to correlate data from disparate techniques or to determine optimum suitability for a given material/conditions/objective. Most comparisons were based on comparative release of particular elements by 2 or more specific procedures. They generally did not consider differences in such factors as test objective, leachant volume, sample size, and test duration.

DOE/LASL

In 1981, researchers at the Department of Energy/Los Alamos Scientific Laboratory (DOE/LASL) compared EPTOX with a procedure used at the laboratory (Heaton, et al, 1981). The samples were coal preparation wastes. The LASL static leach procedure was similar to EPTOX except that it used a L/S of 5. The release of RCRA elements was found to be comparable with both procedures. An evaluation of longer term tests noted that the differences between one day and longer term tests were not large.

EPRI (1986)

The Electric Power Research Institute (EPRI) sponsored a round robin evaluation of TCLP and EPTOX (Mason and Carlile, 1986). The study intended to evaluate the reproducibility of the TCLP and compare the results to those obtained with EPTOX. Seven CCB samples were sent to each of three laboratories which performed duplicate determinations with both TCLP and EPTOX. In the TCLP tests, four samples were leached with the sodium acetate buffer and three with acetic acid. For the individual procedures, most of the variability was related to consistent differences in the results from one of the three laboratories. When comparing the methods, the TCLP and EPTOX concentrations of 14 elements were comparable for approximately 60 pct of the determinations. Eighty-three pct of the concentrations determined with TCLP were equal to or greater then those determined with EPTOX.

EPRI (1990)

In a report to EPRI (Zachara and Streile, 1990), Static (batch) and dynamic (column) methods were compared. Based on a review of the literature, batch systems were determined to be suited to determining specific geochemical reactions in leaching and attenuation processes. Column studies could be used to identify the effect of physical factors, generally related to porosity, and time-dependent leaching and attenuation. Multi-solute systems, in which major ions and trace elements may react under different geochemical conditions, are better studied in columns. Batch methods tend to be inexpensive and simple; and they generate chemical data for mechanistic applications. Column methods are more expensive and more operationally complex, but they generate results which reflect real systems subject to fluid flow and solute transport.

ECN

The Netherlands Energy Research Foundation (ECN) compared regulatory test procedures used in the US, Canada, Germany, France, Switzerland and the Netherlands (van der Sloot et al, 1991). They concluded that tests which report results as a leachate concentration (mg/L) were less descriptive of the potential for long term release than leached quantity (mg/kg). The maximum leachability of different elements was fund to be a function of the L/S, and a test conducted at one L/S was unlikely to predict the long term leachability of all elements. And although the effect of pH on release is established, the effects of changes in redox potential and the concentration of complexing agents, as well as the effect of temperature differences , have not been established.

CEN/TC292

The European Commission on Normalization through its technical committees is addressing the integration of leaching methods for various materials. The committee on waste materials (CEN/TC292) addresses issues related to disposal of wastes and also to by-products or secondary raw materials intended for reuse (van der Sloot et al, 1997). This committee recognizes three types of leaching tests: basic characterization, compliance, and field verification. For both types of tests, a distinction is made between process control (percolation, diffusion) and leaching mechanism (shake or column tests, monolithic tests). Currently, the group is working on a compliance test for granular materials, using DI water and L/S of 2 and 10. A vacuum accelerated monolithic test is also being developed. A basic characterization test and a pH static leach test are to be developed. All of the current tests apply only to inorganic components.

Appendix D

Previous Studies of the Release of Metals from CCB

The results of laboratory experiments and field studies are briefly described. A summary of the results of regulatory leaching tests is also included.

Laboratory Studies

Batch and column leaching tests were also used to characterize the co-disposal of FBC ash and coal slurry solids (Dreher et al, 1990). The combined material was to be used in place of a soil cover over a reclaimed coal slurry impoundment. The leaching experiments demonstrated the oxidation of pyrite in the coal slurry solids in the alkaline solution generated by the FBC ash. Boron, Ni, Mo, Se and Sr were the trace elements reported in the leachate.

Long term natural leaching of fly ash in field lysimeters was compared to batch and column leaching tests (Hjelmar, 1990). Soluble Na and K are initially leached from the ash in the lysimeters; Ca and SO_4 dominate the long term composition. Only As, Cr, Mo, Se, and V which form oxyanions are leached in the alkaline environment of the lysimeter. In the column tests, the concentration of Ca, SO_4, K, Na, Mg, As, B, BA, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, V, Zn decreased with increased L/S. Similar results were found for the batch tests. The cumulative amount of an element leached versus the L/S ratio showed reasonable agreement for the lysimeter and laboratory tests.

In a comparison of acid and alkaline leaching, Teixeira et al (1992)found Ca and Mg to be the most soluble major elements in both methods. Although less soluble than Ca and Mg, Na and K were slightly more soluble in the alkaline solutions. They suggest that the major elements were present as soluble oxides or sulfates. The trace elements, Mn, Ni, Co, and Cu, were more soluble in acid solution. The elements forming oxyanions, Mo, Cr, and V, were more soluble in alkaline leachates. The solubility of all the trace elements measured was less than 20 %. They associated the solubility of the trace elements with concentration on the surface of the fly ash particle.

Paul et al (1994) compared the results of shake tests (TCLP and ASTM) with column leaching to estimate the release of metals from CCB to be used as backfill in an abandoned surface mine. Three materials were tested: a type F fly ash from Illinois coal, an unoxidized scrubber sludge; and an oxidized scrubber sludge. The column leaching solution was natural groundwater obtained from an upgradient well near the site. They determined that the concentration of Ag, As, and B and Cr were comparable in the shake tests and the column leaching test. More Mo was released in the column test than in the shake tests, and the concentration of several elements in the leachate was less than that in the groundwater applied to the column samples. The shake tests were not well correlated with the column leaching results, which was assumed to be more representative of field leaching conditions.

The acid-leachable concentration of Cd, Cr, An, Pb, Hg and Ag from coal fly ash was compared to that from MSW ash (Fleming et al, 1996). For both materials, an increase in the concentration of the metals was correlated to a decrease in the pH of the leachant. The oxide mineralogy of the ash, the spatial distribution of the oxides and the diffusion of hydrogen ions into the ash, as well as the concentration of metals in the ash are believed to control the concentration in the leachate.

Metals in sulfuric acid solution at pH of 4 or 1 were equilibrated with samples of fly ash, fluidized bed ash and hydrated fly ash (Karapanagioti and Atalay, 1996). Metals normally present in AMD (Fe, Mn, Zn, Al, and Mg) were preferentially adsorbed on the alkaline CCB material while the pH of the solution was above 4. Adsorption, which was attributed to interaction with layer silicates and oxides of Fe , Al and Mn, was not significant when the solution pH was 1. At low pH, adsorbed Fe was released into solution and other cations were released into solution. The buffering capacity of PC fly ash and FBC ash was related to the concentration of Ca in the ash. The release of Na, Ni, Mg, Pb, Mn, Cu, Zn, Al, Fe, and Cr were usually below detection levels until the buffering capacity of the sample was exceeded. The release of Ca wan not pH dependent, but was believed to be related to the concentration of Ca in solution.

A 4-year column study of coal ash blended with coal refuse determined the long term effect of alkaline ash on acid formation (Stewart, 1996; Stewart et al, 1997). The purpose of blending the materials was to determine if the fly ash could buffer the acidity normally produced from the coal refuse. The pH of the leachate from the columns containing both materials was between 6 and 8 for the duration of the trial. In contrast the pH of the unamended refuse was below 2 within 3 months. The concentration of heavy metals in the leachate from the blended sample was generally less than 10 % of that from the control. In a similar study with a larger column, Stewart (1995) related the effectiveness of the fly ash co-disposal with mine spoil to the amount of ash needed to maintain an alkaline environment. Sufficient alkalinity could limit the oxidation of pyrite in the coal refuse. Metal release was related to low pH leachate.

Fly ash collected at different points in the exhaust gas stream was designated as an “upstream” and “downstream” sample (Fishman et al, 1997). The upstream samples contained more coarse material but had less sulfur that the downstream samples. After 18 hr leaching tests, the pH of the downstream leachate was lower, and the concentrations of Al, and K higher. The downstream ash spheres were observed to have a thicker coating of soluble poorly crystalline aluminum potassium sulfate (APS). It was hypothesized that the increase in APS coatings was related to the decrease in temperature between the two sampling sites. The lower temperature allowed for a greater condensation of aerosols in the exhaust gas stream.

Steenari et al (1997) studied fly ash samples from the combustion of 3 fuels in a circulating fluidized bed (CFB). Quartz and minor amounts of feldspar were present in the ash. Ca was present as an oxide, sulfate and carbonate. Hydration reactions may produce ettringite, portlandite and calcite. They found over 80 % of the Ca to be soluble in acid, but less Ca was leached from ash that had been wetted prior to leaching, possibly due to the formation of ettringite. Less than 20 % of the K was leached from the fly ash samples, and it was slightly more soluble in water than in acid. The lower solubility of alkali metals was attributed to their occurrence in clay minerals.

Water soluble components from samples of Turkish lignite fly ashes were used to improve the removal of sulfur from unburned lignites (Yaman & Kucukbayrak, 1997). Five or 40 g samples of fly ash were extracted in an autoclave with 200 mL of distilled water. The extract was added to a 5 g lignite sample which was also heated in an autoclave. The fly ash extract increased the removal of sulfur from 41.8 % to 50.4 % of the total sulfur. The alkaline fly ash extract apparently neutralized the sulfuric acid normally produced in the oxydesulfurization procedure.

The mechanism and kinetics of aluminum and iron dissolution from fly ash were studied by Seidel and Zimmels (1998). The amount of soluble Al and Fe was related to the amount of fly ash in the leaching solution, but the rate of dissolution decreased with time in a static leaching system. Less than 30 % of the Al and Fe in the ash was leached during the 12 day test, and the amount leached decreases with increased amounts of fly ash in the solution. They described the leaching of coal fly ash particles as a shrinking core model in which the formation of a porous layer of calcium sulfate inhibits solubility. Diffusion through this layer becomes the rate controlling step. In acidic leaching of coal fly ash, the leached concentration of Al, Fe, Si, and Ti reached a maximum within one hr. Approximately 70 % of the Fe and Mg in the ash was leached, but less than 30 % of the Al and Si was dissolved from the ash. Over 90 % of the calcium and the trace elements, As, Cd, Cr, Cu, Hg, Pb and Zn were extracted from the ash at a pH of less than 1. Less than 20 % of the trace elements were extracted during 3 months in water, and the concentration of these elements was below detection limits during extended leaching of the residual acid leached ash.

The ability of FBC ashes and an FGD material to reduce the solubility of heavy metals in hazardous waste was evaluated (Pritts et al, 1999). The by-products contained a minimum of 10% unreacted lime. Mixtures of ash, waste and water were prepared; the release of heavy metals from the mixtures was evaluated with TCLP. For almost all the 50/50 mixtures of waste and CCB, the concentration of RCRA metals in the leachate was below the detection limit. The effectiveness of the stabilization was attributed to pH control, metal precipitation, micro-encapsulation or surface passivation.

The leaching of trace elements from coal and CCB have been related to kinetically rapid reactions such as hydrolysis of oxides, dissolution of surface coatings, and precipitation of oxyhydroxides (Rice et al, 1999). Slow reactions are dissolution of minerals, such as clays and quartz. The release of Ca and sulfate from coal was related to the presence of pyrite, sphalerite and calcite. Trace element leachability was attributed to their association with sulfide minerals. The pH of the leachate was the controlling factor, as was the presence of a aluminum potassium sulfate (APS) coating on some fly ash particles. The coating is adsorbed on glassy particles and is readily soluble. Sulfuric acid, produced in flue gas from the reacion of SO_2 and H_2O, reacts with the surface of the glassy spheres to produce the APS. The trace elements, Cd, Co, Cu, Mn, Ni, Pb, and Zn were acid leachable, while As, Mo, and V were more soluble in leachates with a more alkaline pH.

In a kinetic experiment, (Seidel et al, 1999), the dissolution of Al from fly ash was shown to be slower than the dissolution and precipitation of calcium sulfate. Precipitation on the surface and within the pores of the particle inhibit the solubility of Al; pre-leaching with HCl to remove soluble Ca was found to increase the solubility of Al.

Querol et al (2001)compared the extraction of water soluble major and trace elements in open and closed systems for 6 fly ash samples from Spain. They assumed that heavy metals would be more mobile in open leaching systems than in closed leaching systems due to the loss of alkalinity in open systems. At equivalent volumes, the extraction yields appear to be similar for both systems. With continued leaching in the open system, the extraction yields increase for most elements. The results were considered consistent with the dissolution of small solid particles or with coatings on particle surfaces rather than the dissolution of a homogeneous glass phase.

Leaching experiments were conducted on fly ash collected from an ESP and the results compared to trace element concentrations in influent and effluent surface water at a coal-fired power plant (Dreesen et al, 1977). More than 30 pct of the As, B, Cd, F, Mo, and Se was extracted in the strongly acid solutions. From 10 to 30 pct of the Cr and V was extracted and between 1 and 10 pct of the Be, Cu, and Zn in the acid solutions. Only Mo was released at greater than 10 pct in the basic solution. The concentrations of As, B, F, Mo, SE, and V were elevated in the ash pond effluent compared to the intake water.

Theis and Wirth (1977) suggested that crystalline compounds, such as mullite, hematite and magnetite, on the surface of amorphous ash particles controlled the release of trace metals. Ammonium oxalate was used to extract trace metals associated with amorphous oxides of iron, aluminum and manganese from the fly ash particles. Hydroxylamine hydrochloride at a pH of 3, was selective for manganese oxides. Based on the amount extracted with either of the leachant solutions, As, Cr, Cd, and Zn were associated with the Fe oxides. The ions Cd and Ni were associated with manganese oxides and Pb was associated with both. Since the leachants used solubilize only surface metals, comparison with a HF/aqua regia digestion was used to characterize the fraction of metals concentrated on the fly ash surface. On average, 93 pct of the As was on the surface, but less than 50 pct of Cd, Cr, Cu, Pb, Ni and Zn were believed to sorbed on the surface oxides. In an experiment in which the ash samples were placed in water at various pH values, all of the trace metals, except As, were more soluble in acid solutions.

Samples of FA from an ESP and from an ash pond were leached for up to 6 months in distilled water (Talbot et al, 1978). The initial pH of all samples was between 10 and 12. In an open system it decreased to about 8.5 within 1 week and remained stable for the duration of the month experiment. Under a nitrogen atmosphere to exclude CO_2, the pH was above 11 for at least one month. The concentrations of dissolved Al, Si, Fe Cd, P, Ca, and Na were relatively constant (10^{-3} M or less) for all samples for the duration of the experiment. The concentration of Mg increased by more than an order of magnitude at a constant rate, and the concentration of K increased sharply toward the end of the experiment. There was no apparent difference between the ponded and fresh samples. Most of the elements were assumed to be oxides or carbonates on the surface of ash particles that dissolved immediately, while MgO was relatively inert. The major elements, Fe, Al, and Si, were most soluble at low pH, although Al and Si showed increased solubility at high pH. The solubility of Ca, Mg and Na showed little dependence on pH below a value of 10. At the isoelectric pH of ~7.55, hydrous oxides of Al and Fe, with the aluminosilicate matrix control the surface characteristics of the FA particle. The solubility of Ca and Mg is believed to be controlled by carbonate and oxide phases. Dissolved K and Na appear to be controlled by a feldspar or mica-type solid phase. The relationship with solid phases formed on the surface of the ash particle under metastable equilibrium conditions controls the dissolved components.

In a long term leaching experiment, fly ash samples were placed in small cylinders and continuously leached for up to two years (Dudas, 1981). In the initial leaching period, maximum concentrations of dissolved Ca, Na, SO_4, and OH were observed at high pH. Levels of dissolved Al, Mg and K were initially low. The solubility profile of SO_4 approximated that of Ca; levels of OH, HCO_3, and CO_3 ions reflected the decrease in pH. Ca, B, Sr, and V were found to be preferentially leached from the fly ash. The concentration of Fe, Cd, Co, Pb and Zn in the ash showed relatively little change during the leaching experiment. The initial release of ions was attributed to the dissolution of simple inorganic salts, followed by the slow dissolution of the glassy ash matrix.

Fly ash samples derived from Illinois Basin coals were equilibrated with DI water to simulate the conditions in ash pond environments (Roy and Griffin, 1984). In both acid and alkaline solutions, anhydrite solubility dominated the Ca concentration. Aluminum was found to be in equilibrium with both mullite and insoluble aluminum hydroxide phases. Aqueous silica concentrations were controlled by mullite and matrix silicates. The pH of acidic FA solutions was related to the formation and adsorption of sulfuric acid. The pH of the alkaline ash solutions was above 10 throughout the experiment due to the hydrolysis of matrix oxides.

In a review by Mattigod et al (1990), batch extractions with water were found to mobilize < 10 pct of major elements except for Ca, Na and S. The pH of the extracting fluid changed over time, tending to a circum neutral pH at equilibrium. Column studies of FA samples indicate that Ca, Na, K and S (as sulfate) are released initially at high concentrations that decline rapidly to a steady state value. Other elements, like Al, may exhibit delayed leaching. Negligible amounts of Fe, Mg, Si and also Al, are released, even in acidic leachants. However, the data are highly variable and cannot be used to predict field leachate concentrations.

In a similar review of minor elements (Eary et al, 1990), found that these tended to be more soluble in acid than in water. They attributed this to the distribution of minor elements in primary oxides which are more soluble in acids. Elements predicted to exist as soluble oxides and salts on particle surfaces (B, Cd, Cu, Mo, Se and Zn) appear to be more readily leached. In aqueous solutions, the pH, a function of the alkali and alkaline earth oxides in the ash, was the master variable that controlled the leaching characteristics of the FA. Many of the minor elements may exist in more than one oxidation state, and both the oxidation state and the ligand in a secondary solids were expected to affect the solubility of minor elements in FA.

Field Tests

Power plant fly ashes were placed in mined out areas of the Wujek mine in Silesia (Cempiel et al, 2000). In static tests, stored ashes contained approximately 5 % soluble chlorides and sulfates. The weathered ash contains 10 times more soluble components than the original ash, apparently adsorbed from the mine water. Similar results were obtained when the ashes were leached by a dynamic method. The concentration of Zn, Pb, Ni and Cr in the leachate was greatest on the first day of leaching. Concentrations of Cd and Cu were below detection limits in all leachate samples. The concentration of these elements is higher in the unamended mine water. When the mine water was used to leach the ash from the mine, the concentration of trace elements in the leachate decreased, although the concentration of major cations and anions increased.

In Illinois, Colorado and Ohio, test cells were constructed to hold 700 to 1000 t of by-products from Clean Coal Technology processes. Relatively high precipitation and the porosity of the CCB compared to the low permeability of surrounding soil facilitated leaching within the cells. There was no apparent change in the chemical composition of the ash with time, but anhydrite was apparently converted to gypsum in a short period of time. Over a 4 year period, the amount of gypsum decreased and the amounts of thaumasite and ettringite increased. The concentration of Na, K, Cl, SO_4 decreased with time in the cell pore water. The Ca concentration remained relatively constant. The pH and K concentration increased approximately 50 cm below the interface between the cell and the soil. The concentration of all the listed elements decreased with depth in the cell.

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 fly ash grout was injected into subsurface areas believed to be zones of acid production (Ackman et al. 1996). At these three sites, when mining was completed, overburden spoil was covered with a variable thickness of soil, then planted with grass. However, water, either from precipitation or infiltrating groundwater, apparently reacted with buried pyrite to produce AMD. The injection of the alkaline fly ash grout was tried as a relatively simple method to neutralize existing acid and to reduce the rate of acid formation. The objective at all three sites was to determine if this method was applicable as a single permanent treatment for AMD control.

Water samples were collected at outflows, from boreholes within injection areas, and from boreholes in ungrouted control areas for a year or more before the injection of the grout, 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.

The Bognanni site is a 14.6 ha reclaimed strip mine in Greene County, PA (Kim & Ackman 1994). 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 (Ackman & Cohen 1994) 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. Additional monitoring points are the Inflow and the discharge point, labeled the Seep. The seep is outside the target area and drains portions of the reclaimed mine that were unaffected by grout injection. At the Bognanni site, the grout was prepared with water from the AMD treatment system and AMD treatment sludge or lime waste (which consists of about 30 pct unused lime). Three fly ashes were used, two from conventional power plants and one 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, and the 192 m^3 of fly ash is equivalent to less than 5 pct of the estimated pore volume in the 1.2 ha section. The fly ash grout was pumped to refusal at a maximum pressure of 3.5 kg/cm^2. The water entering the

Bognanni site 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 (Kim & Ackman, 1995). The pH of the water decreased to 5 where it entered the reclaimed area (Inflow), then decreased to almost 3 within the spoil. Prior to grouting, the water at the seep had a pH of 3.2. In 3 years after grouting, the pH of water at the seep increased to 3.3, slightly higher than the pH in the ungrouted area. The concentrations of ferrous and total iron, calcium, magnesium, aluminum, sodium and manganese tended to be higher in the grouted area than in the control area. The increase in the concentrations of calcium, magnesium and aluminum in the spoil area after grouting may be due to the presence of lime and AMD sludge in the grout. In the grouted area, the average total iron concentration remained almost constant before and after grouting, but the proportion of ferrous iron decreased. At the seep, the concentrations of ferrous and total iron decreased after grouting, but the proportion of ferrous iron remained constant. The concentrations of ferrous and total iron, magnesium, aluminum, and manganese at the seep all decreased by approximately 35% after grouting. Trace element analysis indicated that barium (Ba), present in the incoming water, was not detected at the seep . Only the concentrations of cobalt (Co), nickel (Ni), selemium (Se)and zinc (Zn) were greater than 1 mg/L. The difference in the concentrations in areas grouted with CCB or FBC fly ash was less than 0.5 mg/L. At the seep, the concentration of these metals were less than average concentrations in the ungrouted control area.

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 in the pit floor. Forty-two monitoring wells were drilled on and adjacent to the site. Water samples were also collected at surface discharges 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). At the Fran site, a grout of fluidized bed combustion (FBC) ash and water (1 m^3/800 L) was injected into pods of refuse in order to divert water from the acid-producing materials. The same grout mixture, which formed a low-strength cement, was used to cover the piles of buried 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 total of 3440 m^3 of injected grout is the equivalent to 4 % of the total volume of voids. 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 more 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 in 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. In 1994, average concentrations of arsenic, cobalt, copper, nickel and zinc were higher in the injection area than in background areas. However, the concentrations in downdip and discharge samples were closer to those in the ungrouted spoil.

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. 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. 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. 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. Only the concentrations of cobalt, nickel and zinc exceeded 0.2 mg/L; all values were less than freshwater aquatic life criteria.

The porewater from borehole samples of fly ash in the unsaturated zone of a disposal mound was analyzed to investigate the long term natural weathering (Lee and Spears, 1997).

The concentration of Al, Na, Ca, SO_4, B, Co, Cr, Li, Mo, Ni, Pb ans Sr increased with depth, a result considered to be consistent with continued FA weathering. The pH of the porewater was between 7.88 and 8.94, but showed no consistent variation with depth. The concentration of Ba was almost constant and was thought to have achieved equilibrium with the a sulfate phase. The Ca and S in the FA was depleted near the surface. The concentrations of Cu, Mn, Ni, Pb, and Zn are lower near the surface. No significant change was detected in the mineralogy of the samples.

Appendix E

Methods of Analysis

Each fly ash sample in this experiment was sent to a commercial laboratory for total solid analysis. The fly ash samples were dissolved by triple acid digestion in HF, HNO_3 and H_3BO_4. The laboratory indicated that the major and minor elements were determined according to ASTM D3682, and trace elements were analyzed according to ASTM D 3683, except for Se which was determined by ASTM 4606. However, in these methods, the analysis is by AA; the actual analysis was performed with ICP-AES.

The leachate samples were sent to an on-site contractor laboratory for analysis. Their QA/QC Methods are essentially those in Standard Methods for the Examination of Water and Waste Water, APHA. For each set of 7 samples, 1 method blank,1 method standard, 1 duplicate sample, 2 calibration standards ,and 1 known addition are run. Values of standards must agree within 2% of the known values.

The samples were also analyzed at the NETL on-site laboratory. They were digested according to EPA 3051, microwave digestion in HNO_3, and EPA 3052, microwave digestion in HF, and analyzed by ICP-AES. The 3052 analysis is considered the total concentration, including silicate compounds, while the 3051 analysis give the non-silicate concentration. Microwave digestions were performed in triplicate, and the average of the three analytical values is the concentration in the solid. At the time the microwave digestions, some of the samples had been consumed in previous tests. Blank lines in these tables indicates that sufficient sample was not available for the digestion and analysis. Concentrations below the detection limit are indicated as “<IDL”. Limits of detection are listed in Table E-1

The fly ash samples were sent to a commercial laboratory for x-ray diffraction (XRD) analysis. According to their data, the sum of the major mineral phases is approximately 100 % for most samples. This result seems odd for fly ash samples which are known to contain about

40 - 60 % amorphous material that would not be detected by XRD. The laboratory explained that they quantified the mineral concentration by adding the intensities of the strongest peak for each mineral and then calculating the mineral phase as the intensity of the peak for each mineral divided by the total. They effectively normalized the data to the percentage of the mineral phase instead of the percentage of the sample. This approach was confirmed when the laboratories data was compared to raw and normalized data for several samples that had been analyzed at NETL. XRD of samples like fly ash is inherently imprecise because of the high amorphous content. It was known that XRD would not detect minerals that were present in concentrations of less than 2 % , and that substitutions of trace elements in crystal lattices of major minerals could not be detected. This analysis is therefore considered a qualitative indication of the presence of certain minerals.

The samples were also analyzed for size distribution, specific gravity, and organic carbon content. The average physical properties of the class F PC fly ash samples for this project are summarized in Table E-2.

Table E-1. Limits of Detection

Element	Solid, mg/kg ASTM 3683	Leachate, mg/L ICP-AES
As	<50	<0.08
Ba	<50	<0.015
Be	<0.05	<0.002
Cd	<1	<0.006
Co	<10	<0.006
Cr	<100	<0.006
Cu	<50	<0.006
Ni	<100	<0.010
Pb	<1	<0.080
Sb	NA	<0.080
Se	<1	<0.200
Zn	<1	<0.018

NA: Not analyzed

Table E-2. Physical properties of class F PC fly ash samples used in this test.

	Moisture	SpGravity	Organic C	Particle Size Distribution				D_{50}
	%		%	gravel, %	sand, %	silt, %	clay, %	µm
Mean	5.33	2.32	4.57	0.00	15.95	74.78	9.27	32.70
Median	0.31	2.32	3.34	0.00	11.95	76.45	7.15	22.80
Maximum	43.80	2.56	16.72	0.00	76.50	87.90	21.20	217.00
Minimum	0.00	2.01	0.00	0.00	3.40	21.50	0.30	13.70

Gravel: >2 mm
Sand >0.05 mm
Silt: >.0002 mm
Clay: <0.002 mm
D_{50} median particle size, determined for each sample

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