THE EFFECT OF pH ON THE LEACHING OF SELECTED ELEMENTS FROM COAL-FIRED POWER PLANT FLY ASH.

by

Stephen M. Smith
B. A., University of Missouri, Kansas City, 1978

Submitted to the Department of Geology
and the Faculty of the Graduate School
of the University of Kansas in partial
fulfillment of the requirements for
the degree of Master of Science.

Ernest E. Angino
Professor in Charge

David A. Grisafe

Wakefield Dort Jr.
Committee Members

Ernest E. Angino
For the Department

12/4/86
Date Thesis Accepted

TABLE OF CONTENTS

LIST OF TABLES

LIST OF PLATES

LIST OF FIGURES

ABSTRACT

The goal of this study is to determine the effect of pH on the leaching of selected elements from coal-fired power plant fly ash samples and whether these elements would be present in toxic amounts in the leachate. A modification to the Environmental Protection Agency extraction procedure was used for this study.

Three fly ash samples were separated into various size fractions. Over 40% of each sample is smaller than 5 µm and over 65% is smaller than 20 µm. Analysis of the size fractions show that Al_2O_3, CaO, MgO, P_2O_5 and SO_3 are enriched on the smallest size fractions while FeO, K_2O, Na_2O, SiO_2 and TiO_2 are distributed equally among the size fractions or are slightly depleted on the smallest fraction. These fly ashes produce slurries whose an average pH is 11.77. Acetic acid was used to maintain a pH of 8, 6 and 4 for these experiments.

Analyses of As, Ca, Cd, Cr, Fe, Na, Pb and Se revealed that the highest concentrations occur in the leachate produced at pH 4. The concentrations generally decrease rapidly at pH 6 and then more slowly as the pH increases. Cr and Fe showed an amphoteric nature as the concentrations reached a minimum at near neutral pH's and then increased slightly at strongly alkaline pH.

The Cl^- concentration was greatest at pH 4, decreased at a constant rate to pH 8 and then more slowly to pH 11.8. The SO_4^{2-} concentration was highest at pH 6 and decreased at progressively greater rates as pH increased. The lower than expected SO_4^{2-} concentration at pH 4 may be due to pretreatment of the leachate for this set of experiments prior to its analysis.

As, Cd, Cr, Pb, and Se are all present in amounts exceeding the E.P.A. toxicity criteria at pH 4. The concentrations for all but Se quickly drop to below the toxicity criteria as pH increases. Only Se remains at legally defined toxic levels at near neutral pHs.

INTRODUCTION

Coal is one of the leading sources of energy in the United States and the world. It accounted for 24% of the total energy consumed in the U.S. (1.83×10^{19} J) and approximately 33% (1.05×10^{20} J) of world consumption during 1980 (Ramage, 1983).

This amounts to a total consumption of 648 million metric tons of coal in 1980 and 670 million metric tons in 1983 for the United States (United Nations, 1985). Assuming an average of 14.2% remaining coal ash (Adriano et al., 1980), this results in the generation of 91 million metric tons of ash during 1983. Eighty-four percent of the ash produced by the electric utility industry, which consumed 73% of the coal used in 1975, is fly ash. This results in 56 million metric tons of fly ash generated in 1975 for the electric utilities alone. At present, fly ash production has dropped to less than 46 million metric tons per year (Shepard et al., 1985). However, the amount of fly ash produced annually can be expected to increase in the future.

The electric utilities reported that about 70% of the ash was sluiced to storage ponds in 1975 (Adriano et al., 1980). The remainder was trucked off. About 65% of the total ash was ultimately disposed of in landfills. Only 20.6% of the total ash was productively utilized in 1977.

This figure has dropped to approximately 17% at present (Shepard et al., 1985). The rest remains in the storage ponds.

The great quantity of coal ash represents a significant potential source of contamination to both ground and surface water. Most naturally occurring elements can be found in fly ash, albeit most of them as trace elements. However, many of these are toxic even in trace amounts. In 1978, fly ash was classified as a special waste by the U.S. Environmental Protection Agency (ibid.). This category is much less stringent than for toxic wastes, but requires that the storage ponds be sealed to prevent the leachate from contaminating local ground water. Furthermore, a ground water monitoring system must be installed on site (Kopsick and Angino, 1981). However, in 1980, the special wastes category was abandoned and fly ash was reclassified as nonhazardous. This left regulation of disposal of fly ash up to the individual states (Shepard et al., 1985).

The purpose of this study is to examine the effect of pH on the leaching of selected elements from fly ash. Numerous studies have determined that pH is one of the most important factors in controlling the leaching of fly ash. Some previous studies based their conclusions about mobilizing different elements from fly ash on analyses of leachates of different fly ashes at their naturally occurring pH (Chu et al., 1978; Kopsick & Angino, 1980). Only three studies have attempted to regulate the pH directly during the leaching process (Theis and Wirth, 1977; Phung et al., 1979; Griffin et al., 1980).

PREVIOUS STUDIES

Several studies have been performed on the leaching of fly ash, however there has been little similarity in the methodologies.

Perhaps the earliest study was performed by Jones and Lewis (1960). In this study 25 g samples of fresh fly ash from the Hams Hall power station, England, were leached in 5 cm columns under a constant head of 1 to 5 cm at a rate of approximately 1 mL/min for approximately 20 hrs (1200 mL total). The leachate was collected in 40 mL aliquots for analysis. Leaching rates for B, Ca and K were found to decrease rapidly at first and gradually level off. No P, Al or Fe were detected in the leachate. No mention was made as to whether the pH of the leachate was determined.

Theis and Wirth (1977) ran a series of experiments where 200 g samples of fly ash were suspended in one liter of distilled water for 24 hrs. The pH of the slurries were maintained at 3, 6, 9 and 12 with NaOH or $HClO_3$. They centrifuged and filtered the slurry and analyzed the supernate for As, Cd, Cr, Cu, Ni, Pb and Zn. Whole ash analyses were also done for Al, Ca, Fe, Hg, Mn, and Si in addition to those elements in the leachate study.

The results of Theis and Wirth's experiments showed that the amount of each element mobilized decreases with increasing pH. The notable exception to this is As, which shows a major increase in concentration from pH 9 to 12. This is probably due to the fact that it forms insoluble compounds with many metals and precipitates out of solution normally. However, at higher pHs the concentrations of these metals are greatly diminished and the AsO_4^{3-} anion remains in solution because its solubility product is not exceeded.

Theis and Wirth also suggest that the readily leachable trace elements are primarily associated with surface deposits of Fe, Mn or Al oxides on the fly ash particles. Association with alkali metal and alkaline earth oxides were not examined here. Elements associated with the silica-alumina glass matrix are available for leaching only after extensive weathering of the ash.

Chu et al. (1978) performed studies on several power plants operated by the Tennessee Valley Authority. The discharge water from twelve ash settling ponds received detailed chemical analyses. The pH of these samples ranged from 3.3 to 12 with the background pH of the river waters ranging from 7 to 8. The pH was correlated with the concentration ratios of Ca^{2+} to SO_4^{2-}.

Chu et al. also ran leaching studies on two fly ash samples, one low Ca (slightly acidic) and one moderately high Ca (alkaline). Samples of the fly ash were leached in thirty times their weight of river water for 24 hours at 20°C. They filtered the slurry through a 0.45 micron membrane filter and discarded the leached fly ash. They then drew off a portion of the supernate for analysis of Ag, Al, As, B, Ba, Be, Ca, Cd, Cl, CN^-, Cr, Cu, Fe, Hg, Mg, Mn, N, P, Pb, Ni, Se, Si, SO_4^{2-} and Zn. They also analyzed the river water for background levels of these elements. They repeated the process nineteen additional times using fresh fly ash, but the same supernate.

Based on their experiments, Chu et al. concluded that particle size, agitation of the slurry, pH of the slurry and temperature influence the mobilization of elements from the fly ash. The trend of the ratio of the element leached to its total concentration in the ash is Se > B > Cr > Ni > Cu > Ba > As > Zn > Al for alkaline slurries. The trend for neutral slurries is B > Cd > As > Se > Zn > Ni > Mn > Cu > Ba. They also determined that the mobilization occurs rapidly with the change in pH and specific conductance becomes relatively constant within four hours.

Phung et al. (1979) leached 0.2 to 5.0 g samples of fly ash in 24 mL of deionized water for three days. The slurries were left at their natural pH of 12.3 or were adjusted to 9.0 or 6.0 with HCl twice daily. At the end of 3 days, the slurries were diluted to 30 mL, centrifuged and filtered. The supernate was then analyzed for B, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn.

The experiments performed by Phung et al. showed that the mobilization of B, Pb, Co, Cr, Ni, and Mn increased greatly at lower pHs. Zn mobilization increased to a lesser extent. Cu and Cd mobilization increased by a relatively small amount. These and other experimental results on fly ash amended soils led them to conclude that the alkalinity of the fly ash and soil pH and texture should be considered as well as hydrology and climate when selecting disposal sites for fly ash.

Churey et al. (1979) suspended one gram of fly ash from 28 different sources in 200 mL of distilled water for two hours at room temperature. The supernate was analyzed for As (0.00 to 0.11 mmole/L), B (0.06 to 7.37 mmole/L), Mo (0.00 to 0.08 mmole/L), P (0.00 to 0.17 mmole/L) and Se (0.00 to 0.08 mmole/L). They suggest that differences in the leachate concentrations may be due to the original composition of the source coal and combustion conditions. They also refer to the importance of the predominant particle size of the ash (Davison et al., 1974) in determining the surface area of the particles available for leaching per unit mass.

Griffin et al. (1980) performed a series of experiments in which eleven coal wastes, of which one was a fly ash, were leached as 10% (weight to volume) slurries for six months. The long period of time was chosen to allow the slurries to come to complete equilibrium instead of mobilizing only the readily available surface materials.

Eight duplicate sets of each sample were leached, four under an air atmosphere and four under an argon (O_2 and CO_2 free) atmosphere. One set in each group was allowed to react under its natural pH: 4.08 under air, 4.26 under Ar. NaOH and HNO_3 were used to maintain the other three sets in each group at other pHs: 8.82, 7.97 and 2.74 under air; 9.98, 7.08 and 2.52 under Ar. The slurries were stirred daily. The supernates were then analyzed for 36 different elements or ionic species along with the chemical O_2 demand, electroconductivity and Eh. The fly ash was also analyzed for 53 elements.

Results of the experiments performed by Griffin et al. showed that in almost all cases the metal concentrations were highest in the supernate of the lowest pHs. Four metals: Al, total Fe, Mn and Zn were at elevated levels in all of the acid supernates and thought to represent the greatest environmental hazard. Ca levels were also higher than recommended, but are not believed to represent as great a threat. Sulfate was the dominant anionic species present and, along with Cl, Na and K, showed no regular trend in mobilization with pH.

Griffin et al. concluded that pH and redox potential are probably the two most important factors governing the mobilization of elements from coal solid waste. Materials with low natural pH represent the greatest potential threat to the environment. Also, of the eleven materials tested, only the fly ash leachate could be considered acutely toxic (Cd concentrations exceeded the E. P. A. primary drinking water standard by a factor of 4 at the natural pH).

Kopsick and Angino (1981) ran experiments on six fly ashes and three bottom ashes from around the country. In these experiments, 5 cm inside diameter columns were packed to a height of 46 cm with ash. Distilled, deionized water was run through the columns from the bottom and seven samples were collected over a two hour period. The process was repeated twice at one week intervals on the original samples which were kept saturated during the intervening periods. The leachate samples were analyzed for Ca, Cu, Fe, K, Mg, Mn, Na, Pb and Zn as were the source ashes.

Kopsick and Angino concluded that the various elements were not all mobilized proportionally to the composition of the whole ash. Ca, K, Mg and Na are readily mobilized while Cu, Fe, Mn, Pb and Zn were mobilized more slowly. The pH of the leachates tended to be higher for the western ashes which were enriched in Ca and Mg. Two of the three bottom ashes produced a more acidic leachate than their corresponding fly ashes.

Various studies have also been performed on the association of different elements on fly ash particles of different sizes. It has been observed that certain elements are concentrated on the smaller particles.

Natusch et al. (1974) and Davison et al. (1974) obtained fly ash samples from both the cyclone precipitator (in bulk) and the exhaust stack (using an Andersen stack sampler) of a coal-fired power plant. The precipitator samples were divided into size fractions of >74 µm and 44 to 74 µm by sieving and >40 µm, 30 to 40 µm, 20 to 30 µm, 15 to 20 µm, 10 to 15 µm, 5 to 10 µm and <5 µm by aerodynamic methods. The exhaust stack samples were also divided into size fractions of >11.3 µm, 7.3 to 11.3 µm, 4.7 to 7.3 µm, 3.3 to 4.7 µm, 2.1 to 3.3 µm, 1.1 to 2.1 µm and 0.65 to 1.1 µm by the Andersen sampler.

Chemical analyses by Natusch et al. and Davison et al. of these different size fractions revealed that As, Cd, Cr, Ni, Pb, S, Sb, Se, Tl and Zn showed pronounced trends of increasing concentration on the smaller size fractions. Al, Be, C, Fe, Mg, Mn, Si and V showed limited trends of increasing concentration on the smaller size fractions. Bi, Ca, Co, Cu, K, Sn and Ti did not show any apparent concentration trends.

Natusch et al. proposed a volatilization-adsorption (or condensation) model to explain the various observed concentration trends. Elements in the first group, primarily in the form of oxides, have lower boiling or sublimation temperatures than those in the second and third group. Thus they are more easily volatilized in the high temperatures of the power plant combustion chamber. As the gases cool, the volatilized elements condense on the surface of the fly ash particles, forming a layer of uniform thickness on the particles regardless of the particle size. Since smaller particles have a greater surface area per unit mass, assuming similar densities, than larger particles; the more readily volatilized elements will have a greater concentration in the smaller size fractions. Those elements with higher boiling or sublimation temperatures will be found in the glassy matrix of the fly ash particles and will be more uniformly distributed among the various size fractions.

The elements As, Cd, Cr, Pb, Sb, Se and Tl in the first group of Natusch et al. and Davison et al. are considered moderately to acutely toxic. The smaller fly ash particles are those most likely to escape the pollution control systems of power plants and can be respirated deeply into the lungs where the trace elements are efficiently transferred into the blood stream. Thus, the pollution control technology employed in coal-fired power plants is least effective in controlling the most potentially harmful particulate emissions.

Klein et al. (1975) analyzed the coal, slag (or bottom ash), fly ash and flue gases of a large coal-fired power plant in Memphis, Tennessee for thirty-seven elements to trace the pathways of the elements through the system. They determined that most of the elements fit into one of three classes. Class I elements: Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th and Ti are readily incorporated into both the slag and fly ash, being partitioned about equally between the two phases. Class II elements: As, Cd, Cu, Ga, Pb, Sb, Se and Zn are found primarily in the fly ash phase and with a relatively minor presence in the slag. Class III elements: Br, Cl and Hg remain almost entirely in the gas phase. Cr, Cs, Na, Ni, U and V do not readily fit into any of the three classes, but appear to be intermediate between Classes I and II.

The Class I elements of Klein et al. are not readily volatilized during the combustion of the coal. They tend to form a uniform melt and remain in the glassy matrix of both the slag and fly ash. All of the Class I elements are classified by Mason (1966) as lithophile elements, those associated with aluminosilicate minerals in the earth's crust. The two exceptions are Co and Fe which are siderophile elements, those associated with the earth's metallic core. These two also exhibit secondary lithophilic and chalcophilic affinities. Chalcophile elements are those associated with sulfide minerals in the earth's crust.

The Class II elements of Klein et al. are more readily volatilized at combustion temperatures (typically

1300 to 1500 C according to Natusch et al. (1974) and less than 1650 C according to Shannon (1982)). They escape from the slag phase with the fly ash and flue gas and, as the exhaust cools, condense or are adsorbed onto the fly ash particles. They are in close agreement with the list of elements found by Natusch el al. and Davison et al. (see above) to show pronounced trends of increasing concentration on smaller particles. The exceptions are Cu, which showed no clear trend, and Ga, which was not investigated. All of the Class II elements are classified as chalcophile elements by Mason, except for Cu which may be either a chalcophile or a lithophile element.

Of the six unclassified elements of Klein et al., Cs, Na, U and V are classified as lithophile elements by Mason. Cr and Ni may be either lithophile or chalcophile elements.

Coles et al. (1979) collected samples of the input coal and stack fly ash from a large, western power plant. The fly ash was divided into four size fractions with mass median diameters of 2.4, 3.7, 6.0 and 18.5 µm by a specially designed stack sampler. The coal, a low sulfur (0.46%), high ash (23%) type, was analyzed for 44 elements. The fly ash was analyzed for 42 elements. Forty elements were classified into three groups based on the distribution among the size fractions. Group I elements: Al, Ca, Ce, Cs, Dy, Eu, Fe, Hf, K, La, Mg, Mn, Na, Nd, Rb, Sc, Sm, Ta, Tb, Th, Ti and Yb show little or no variation among the size fractions. Group II elements: As, Cd, Ga, Mo, Pb, Sb, Se, W and Zn become increasingly more concentrated on the smaller size fractions. Group III elements: Ba, Be, Co, Cr, Cu, Ni, Sr, U and V demonstrate intermediate behavior between Groups I and II.

The Group I elements of Coles et al. are all classified as lithophile elements by Mason. These elements are primarily incorporated in the glassy matrix of the ash particles although some will react with H_2SO_4 on the surface to form various sulfate crystals, especially $CaSO_4$. The Group II elements are classified as chalcophile elements. The elements are believed to be mostly volatilized during combustion of the coal and later condense onto the particles. The Group III elements show a trend of increasing concentration on the smaller size fractions, but to a lesser extent than the Group II elements. According to Mason's scheme, Cu, Co and Ni may be found in association with both aluminosilicates and sulfides in the earth's crust. Ba, Be, Cr, Sr, U and V are all classified as lithophile elements.

Smith et al. (1979) collected fly ash samples from a coal-fired power plant in Centralia, Washington. The ash was divided into seventeen size fractions: <0.2 µm, 0.2 to 0.5 µm, 0.5 to 0.9 µm, 0.9 to 1.5 µm, 1.5 to 3 µm, 3 to 6 µm, 6 to 10 µm, 10 to 12 µm, 12 to 18 µm, 18 to 22 µm, 22 to 30 µm, 30 to 35 µm, 35 to 50 µm, 50 to 60 µm, 62 to

74 μm, 74 to 149 μm and >149 μm using an air elutriation technique for all but the two coarsest fractions which were divided by a sonic sifter. Each size fraction was analyzed for Al, As, Ba, Ca, Ce, Cr, Cu, Fe, Ga, Ge, K, La, Mn, Mo, Nb, Ni, P, Pb, Rb, S, Se, Si, Sn, Sr, Ti, V, Y, Zn and Zr by X-ray fluorescence. Br, Cd, Cl, Co, Cs, Eu, Hg, I, In, Nd, Pd, Pr, Rh, Ru, Sb, Sm, Te and U were also analyzed for, but were not found in concentrations above their detection limit.

Smith et al. determined that there are clear trends of increasing concentration on the smaller particles for As, Cr, Ga, Ge, Mo, Ni, P, Pb, S, Se, Sn and Zn with less well defined trends for K and V. The concentrations of the remaining elements were generally independent of particle size. All of the above elements showing a concentration trend are classified as chalcophile elements by Mason, except for Cu and Ni which may be either chalcophile or lithophile elements and Cr, K, P and V which are lithophile elements.

Smith et al. generally agree with the volatilization-adsorption model of Natusch et al. for the larger fly ash particles. However, they observed that even those elements that show increasing concentration on the smaller size fractions tend to level off below 2 μm. To explain this, they proposed a model for the formation of the smallest particles by the bursting of larger particles from release of gas. The resulting submicron particles then coagulate into a suite of particles of smaller than 3 µm. This process dominates the formation of particles smaller than 2 µm. If the condensation of the volatilized elements occurs prior to the completion of the coagulation, then the concentration of these elements would be largely independent of size for these particles.

Most of the studies described above used type F, i.e. high Fe and low Ca, fly ash. The study by Jones and Lewis (1960) makes no mention of the analysis of the fly ash itself. Theis and Worth (1977) published only the range of analyses of eleven fly ashes, but these suggest that they were probably type F. Chu et al. (1978) reports the analysis of only two of the fly ashes used, both of which are type F. Churey et al. (1979) obtained samples from around the United States, but does not report the analysis of the whole ash. Griffin et al. (1980) examined a type F fly ash. Kopsick and Angino (1981) examined four type F and two type C, i. e. high Ca and low Fe, fly ashes.

The studies involving the distribution of elements on different size fractions of fly ash by Natusch et al. (1974), Davison et al. (1974), Klein et al. (1975), and Coles et al. (1979) were all performed with type F ashes. Only the study by Smith et al. (1979) used a fly ash with near equal amounts of Ca and Fe.

THE JEFFREY ENERGY CENTER AND SOURCE COAL

Fly ash samples for this study were obtained from the Jeffrey Energy Center (NE$^1/_4$, Sec. 7, T9S, R12E) in Pottawatomie County, Kansas. The plant is principally owned and operated by the Kansas Power and Light Company.

The Jeffrey Energy Center consists of three identical coal-fired generating units. These units use the entrained bed system where the coal is first ground to a fine powder and then blown into the combustion chamber of the boiler with hot air. Water is circulated through a network of pipes and is converted to steam to drive the generator turbines. The flue gases and fly ash are first passed through an electrostatic precipitator, which removes 99% of the particulates, and then on to the stack gas scrubbers which remove the SO_2. The flue gases, which now consist primarily of CO_2 and water vapor with minor amounts of SO_2, N_2O, NO, NO_2 and fly ash that get past the pollution abatement systems, are exhausted through three 183 m chimneys.

The Jeffrey Energy Center uses approximately 6.8 million metric tons of coal per year (Larson, 1985). Maximum daily coal consumption for the plant is approximately 23000 metric tons and 8000 metric tons per unit. Each unit produces approximately 270 metric tons of fly ash per day.

The Jeffrey Energy Center obtains its coal from the Belle Ayr (Sec. 34, T48N, R71W) and Eagle Butte (Sec. 26, T51N, R72W) mines in Campbell County, Wyoming. Both mines are operated by the Amax Coal Company. Coal production during 1980 was 14.6 million metric tons for the Belle Ayr mine and 7.6 million metric tons for the Eagle Butte mine (Schmidt & Boyer, 1983). The operator plans to change production to 10 million and 22 million metric tons, respectively during 1986 and 12 million and 20 million metric tons, respectively during 1991.

Both the Belle Ayr and the Eagle Butte mines take coal from the Anderson-Canyon (Wyodak) seam of the Fort Union Formation of the Powder River Basin coal field. This subbituminous coal is of Paleocene age (Glass, 1975). The seam measures 22.7 m thick at the Belle Ayr mine (ibid.) and averages 21 m thick throughout the Wyoming portion of the basin (Energy Resources, 1980). The coal is described as generally banded with vitrain bands and moderately dull to moderately bright attritus (Glass, 1975). Wood grain is commonly visible in the lower 70% of the seam. Fracturing is variable. The top 0.25 m of the seam is shaly. A thin carbonaceous claystone layer is present 3.6 m from the bottom of the seam.

Belle Ayr coal generally yields 1.97×10^7 J/kg when burned and contains 0.36% sulfur and 5.33% ash (Schmidt and Boyer, 1983). Eagle Butte coal generally yields 1.93×10^7

J/kg and contains 0.44% sulfur and 5.15% ash. This is similar to an average heating value of 2.05 x 10^7 J/kg (range: 1.71 x 10^7 to 2.24 x 10^7 J/kg, based on 79 samples), an average sulfur content of 0.8% (range: 0.1 to 3.5%) and an average ash content of 6.3% (range: 3 to 16%) for the entire Powder River Basin coal field (Energy Resources, 1980). Results of a detailed chemical analysis of three samples taken from the Belle Ayr Mine are presented in Table 1.

TABLE 1. ANALYSIS OF 3 COAL SAMPLES FROM THE BELLE AYR MINE, CAMPBELL COUNTY, WYOMING (after Glass, 1975).

Major & Minor Elements (percent on a whole-coal basis).

Sample:	74-38	74-39	74-40
Ash Content	7.6	6.3	7.1
Si (XRF)	0.96	0.68	0.86
Al (XRF)	0.54	0.48	0.53
Ca (XRF)	1.00	1.00	1.00
Mg (AA)	0.140	0.150	0.150
Na (AA)	0.068	0.070	0.072
K (XRF)	0.019	0.012	0.017
Fe (XRF)	0.28	0.16	0.23
Mn (XRF)	0.0029	<0.0010	0.0013
Ti (XRF)	0.058	0.051	0.055
P (XRF)	0.0135	0.0160	0.0146
Cl (XRF)	<0.008	<0.006	<0.007

Trace Elements (parts per million on a whole-coal basis)

Sample	74-38	74-39	74-40
As (Col)	3	1	2
B (ESA)	30	50	30
Ba (ESA)	300	300	300
Be (ESA)	0.3	0.2	0.2
Cd (AA)	0.100	0.100	0.100
Co (ESA)	2.0	2.0	2.0

Table continued on the next page.

TABLE 1 cont'd. ANALYSIS OF 3 COAL SAMPLES FROM THE BELLE AYR MINE, CAMPBELL COUNTY, WYOMING (after Glass, 1975).

Trace Elements (parts per million on a whole-coal basis)

Sample	74-38	74-39	74-40
Cr (ESA)	7.0	5.0	5.0
Cu (AA)	16.4	10.7	12.4
F (SIE)	45	45	45
Ga (ESA)	2	3	2
La (ESA)	7	7	7
Li (AA)	2.4	3.0	2.6
Mn (XRF)	29	<10	13
Mo (ESA)	1.0	1.0	1.0
Nb (ESA)	2	2	2
Ni (ESA)	5.0	5.0	5.0
Pb (AA)	3.0	2.5	2.5
Sb (Col)	0.7	0.3	0.4
Sc (ESA)	2.0	2.0	2.0
Se (XRF)	0.7	6.7	1.2
Sr (ESA)	100	150	100
Th (NAA)	3.3	<2.0	<2.0
U (NAA)	0.8	0.6	<0.2
V (ESA)	20	15	20
Y (ESA)	3.0	3.0	3.0

Table continued on the next page.

TABLE 1 cont'd. ANALYSIS OF 3 COAL SAMPLES FROM THE BELLE AYR MINE, CAMPBELL COUNTY, WYOMING (after Glass, 1975).

Trace Elements (parts per million on a whole-coal basis)

Sample	74-38	74-39	74-40
Yb (ESA)	---	0.3	0.5
Zn (AA)	7.4	3.4	4.8
Zr (ESA)	15	15	15

All analyses were performed by the U. S. Geological Survey Laboratories, Denver, Colorado. Methods of analyses are given in parentheses following the element using the following abbreviations:

AA:	Atomic Absorption Spectrophotometry
Col:	Colorimetric Methods
ESA:	6 Step Emission Spectrographic Analysis (Semiquantitative Analysis)
NAA:	Neutron Activation Analysis
SIE:	Specific Ion Electrode
XRF:	X-ray Fluorescence.

METHODOLOGY

Large samples (40 to 50 kg) of fly ash were obtained from the Jeffrey Energy Center: KP&L 38 on 18 March 1982, KP&L 39 on 1 July 1983 and KP&L 40 on 13 October 1983. Samples KP&L 39 and 40 were split into smaller portions soon after sampling. A large fraction (approximately three quarters) of sample KP&L 38 has been used in other tests not related to this study. The remainder of this sample was split into portions of approximately the same size as the splits of KP&L 39 and 40. Later, these splits were microsplit into yet smaller portions of 9 to 11 g.

Each of the three fly ash samples was divided into different size fractions using an ATM Model L3 Series A Sonic Sifter equipped with a horizontal pulse attachment and various sieves. The size fractions were <5 µm, 5 to 10 µm, 10 to 20 µm, 20 to 35 µm, 35 to 45 µm, 45 to 75 µm, 75 to 150 µm and >150 µm. Each of the size fractions was analyzed for SiO_2, Al_2O_3, CaO, FeO, MgO, Na_2O, K_2O, TiO_2, SO_3 and P_2O_5 using a Kevex energy dispersive electron microprobe. Whole ash samples were also analyzed with the microprobe.

The method used in leaching the fly ash is a modification of the U.S. Environmental Protection Agency (1978) recommended methodology. The E.P.A. method calls for mixing one part solid with sixteen parts distilled, deionized water; adjusting the mixture to pH 5 with acetic acid and stirring the mixture for twenty-four hours. At the end of the leaching period, the mixture is centrifuged to separate the solid and liquid phases. The supernate is then diluted to twenty times (in mL) the initial mass of the sample (in g). A more detailed presentation of the method is given in Appendix 2.

The present study involves leaching the fly ash samples at pH 4, 6, 8 and the natural pH of the material, ±11.8, to determine the effect of pH on the leaching of selected elements. Acetic acid was added as required to keep the fly ash slurry at the desired pH (±0.1 pH units) during the twenty-four hour leaching period. This method was selected due to the cementitious nature of these fly ashes. Without constant stirring, the ash would settle and quickly set up into a solid lump with the surface area available for leaching greatly reduced in an unpredictable manner. Keeping the ash in suspension provides a more reproducible method and a worst case system for the tests.

The experimental apparatus consisted of a polyethylene beaker with a polyethylene propeller stirrer used to keep the fly ash in suspension (see Figure 1 and Plate 1). The pH of the slurry was monitored with an Orion Model 91-06 combination pH electrode and a Model 211 digital pH meter.

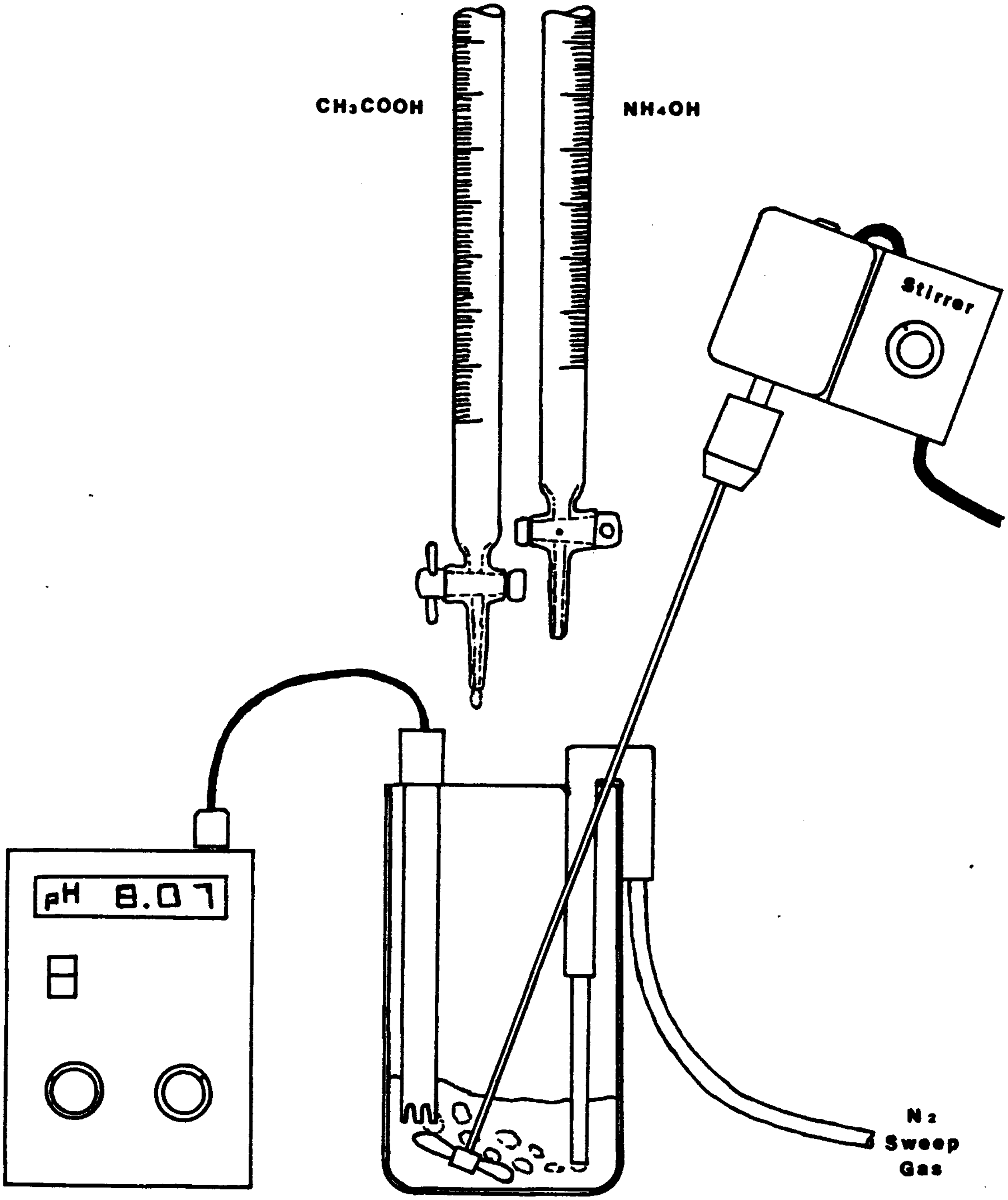


Figure 1. Diagram of Leaching Apparatus.

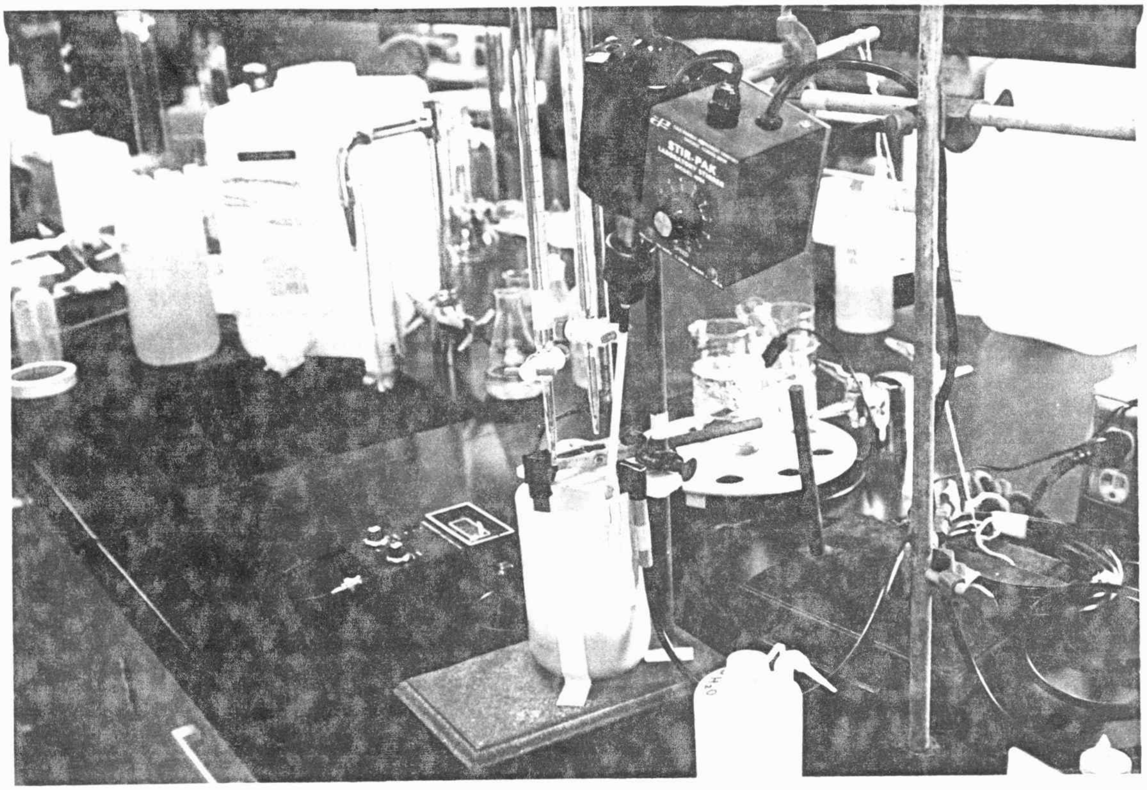


Plate 1. Leaching Apparatus.

Two burettes containing acetic acid and 10:1 dilute ammonium hydroxide were suspended above the beaker for maintaining the desired pH. Glacial acetic acid was used for the leaching runs at pH 4, 4:1 dilute acetic acid at pH 6 and 20:1 dilute acetic acid at pH 8. A polystyrene tube was also used to bubble N_2 sweep gas through the slurry during the runs at pH 8 and above to minimize the solution of atmospheric CO_2 and subsequent precipitation of insoluble carbonates.

During the first 15 to 40 seconds of the leaching run, 12.500 g of fly ash were slowly added to 140 mL of distilled, deionized water. The water was first boiled to remove dissolved CO_2 and was cooled to room temperature with N_2 sweep gas for the runs at pH 8 or higher. During this time, the strongly alkaline fly ash would cause the pH to rise to 11 or greater before any of the acetic acid could be added to bring it down to the desired pH. The desired pH would usually be obtained within the first 100 seconds, generally in less time.

The rate at which acetic acid was added reflects the rate of the leaching reaction. Acid had to be added at a rapid rate initially as the readily soluble material on the surface of the fly ash particles quickly entered solution. Depending on the ash sample and the pH of that leaching run, 40% to 60% of the total amount of acid added over the twenty-four hour period was added during the first hour. As time passed, acid was added at progressively slower rates as the remaining leachable materials responsible for the alkalinity of the fly ash became more tightly bound to the surface and/or were fixed as part of the glassy matrix of the fly ash particles.

In addition to the acetic acid added to the fly ash slurry; distilled, deionized water was used to periodically rinse spattered fly ash off the sides of the beaker, pH electrode, stirring propeller shaft and sweep gas tube. The total amount of liquid used during the leaching runs, i.e. starting liquid, acetic acid and rinse water, was typically 190 mL.

After the twenty-four hour leaching period, the fly ash slurry was transferred to three centrifuge tubes and was spun at approximately 3000 rpm (14800 m/sec^2 at the bottom of the tube) for 10 min to separate most of the fly ash from the supernate. The supernate was transferred to a volumetric flask, acidified with 3 mL of concentrated nitric acid (at pH 6 and above only) to prevent subsequent precipitation of elements prior to analysis and diluted to 250 mL with distilled, deionized water. Four 55 ml aliquots were drawn off from below the surface of the supernate to minimize transference of the hollow cenospheres, most of which floated to the surface. These aliquots were centrifuged three additional times for 10, 15 and 15 min. After this, some cenospheres still remained in suspension in the supernate. The supernate was then transferred to a polyethylene storage bottle.

The supernate was analyzed for Ca, Cd, Cr, Fe, Na and Pb by atomic absorption spectrophotometry using a Perkin-Elmer Model 2380 with an air-acetylene nebulizer burner according to Standard Methods (Greenberg et al, 1980) and Analytical Methods (Perkin-Elmer, 1982). An Instrumentation Labs Video 22 atomic absorption spectrophotometer with a hydride generation system was used for determining As and Se. A Technicon AutoAnalyzer II was used to analyze Cl by the ferric thiocyanate method and SO_4 by the methylthymol blue method according to Techniques of Water-Resources Investigations (Skougstad et al., 1979).

RESULTS

As mentioned previously, the fly ash used in this study is derived from a low sulfur, subbituminous coal mined in the Powder River Basin near Gillette, Wyoming. The ash samples were obtained from the conveyor system from the electrostatic precipitator of Unit 2 of the Jeffrey Energy Center in Pottawatomie County, Kansas.

Size Distribution

The size distributions of the three fly ash samples are presented in Table 2. Most of the ash particles are found in the smallest size fractions. Sample KP&L 38 follows a unimodal division among the size fractions even though the range of the fractions increases with the coarser sieves. The range of size fractions selected was in part due to the availability of the sieves on hand. Samples KP&L 39 and KP&L 40 exhibit a trimodal size distribution, however. The minor increase in the 45-75 μm fraction over the 35-45 μm fraction may be due solely to the fact the range covered by this set is three times greater than the preceding one. The great increase in the 10-20 μm fraction over the 5-10 μm in KP&L 39 and 40 cannot be so easily explained. The mass of the fly ash in the <5 μm and 5-10 μm fractions are down by 9% when compared to the corresponding fractions of sample KP&L 38

TABLE 2. SIZE DISTRIBUTIONS OF FLY ASH SAMPLES.

Size Frac. (µm)	KP&L 38 (wt. %)	KP&L 39 (wt. %)	KP&L 40 (wt. %)	Average (wt. %)
< 5	51	41	42	45
5 – 10	15	7	6	9
10 – 20	12	18	21	17
20 – 35	9	15	16	13
35 – 45	5	6	5	5
45 – 75	4	7	6	6
75 – 150	3	5	3	4
> 150	1	2	1	1
Total	100	101	100	100

while the mass of the 10-20 µm and 20-35 µm are up by about 7%. The reason for this is not known.

There are numerous factors involved in the combustion of coal that could affect the formation and size distribution of the fly ash particles. The different samples were obtained at different times of the year. Varying seasonal demands for electricity causes the power plant to burn coal at differing rates. The speed with which the coal is blown into the combustion chamber, the amount of air used to burn the coal, the temperature of combustion and the water content and chemical composition of the coal all affect combustion and thus the chemical composition, mineralogy, and particle size distribution of the fly ash. Given the number of variables involved, the variation of the fly ash from the same unit of the power plant is not surprising.

Major Element Analysis of the Whole Ash

Major element analysis of the inorganic portion of the fly ash samples is presented in Table 3. The analyses were normalized to total 100% by weight for these species. Complete skanning of the spectrum using the electron microprobe indicated that no other species were present in greater than trace quantities. Analyses of both the whole ash and the <5 µm size fraction are given to demonstrate the tendency of certain elements to be concentrated in the

TABLE 3. NORMALIZED CHEMICAL ANALYSES OF INORGANIC PORTION OF FLY ASH SAMPLES.

Oxide	KP&L 38		KP&L 39		KP&L 40		Average	
	< 5μm (wt.%)	Whole (wt.%)	< 5μm (wt.%)	Whole (wt.%)	< 5μm (wt.%)	Whole (wt.%)	< 5μm (wt.%)	Whole (wt.%)
CaO	35.3	30.9	38.6	33.7	41.6	34.4	38.5	33.0
SiO_2	21.1	29.1	20.4	28.4	18.7	31.0	20.0	29.5
Al_2O_3	19.5	17.3	18.9	17.0	17.9	15.5	18.8	16.6
MgO	7.7	6.6	7.4	6.7	7.1	5.8	7.4	6.4
FeO	4.3	5.4	5.2	5.5	6.0	5.2	5.2	5.4
Na_2O	2.1	2.5	2.8	2.3	1.9	2.2	2.3	2.3
TiO_2	1.8	1.9	2.0	2.2	1.8	1.7	1.9	1.9
K_2O	0.4	0.4	0.2	0.2	0.3	0.3	0.3	0.3
SO_3	4.7	3.6	3.0	2.8	2.9	2.7	3.5	3.0
P_2O_5	3.2	2.4	1.5	1.2	1.8	1.3	2.2	1.6
Total	100.1	100.1	100.0	100.0	100.0	100.2	100.1	100.0

smaller size fractions of the ash. The high Ca to Fe ratio designates this as a type C fly ash.

Of the ten oxides analyzed, only SiO_2 showed a clear affinity for the whole ash. FeO was generally more concentrated in the whole ash, but was enriched in the <5 μm fraction of sample KP&L 40. These elements are thought to exist primarily in the glassy matrix phase of the fly ash. Si is classified as a lithophile element by Mason (1966) and Fe as a siderophile element with secondary lithophilic and chalcophilic affinities. Lithophile elements are those associated with the aluminosilicate minerals in the earth's crust. Siderophile elements are those associated with the earth's metallic core. Chalcophile elements are those associated with sulfide elements in the earth's crust.

Al_2O_3, CaO, MgO, P_2O_5 and SO_3 are all enriched in the <5 μm size fraction relative to the whole ash. Al, Ca, Mg and P are all classified as lithophilic by Mason, while S is chalcophilic.

K_2O, Na_2O and TiO_2 all displayed an equal or mixed partitioning between the <5 μm size fraction and the whole ash. All three are classified as lithophilic by Mason.

The volatilization-adsorption model originally proposed by Natusch et al. (1974) and elaborated on by Davison et al. (1974) explains the enrichment of certain elements on the smaller particles by a mechanism where the more volatile elements and elemental oxides first escape from the combustion chamber as a gas and then, as the exhaust cools, are adsorbed onto the surface of the fly ash particles which escaped as tiny droplets of molten glass. If one assumes that the fly ash particles are of uniform density regardless of size (excluding the hollow, bubble-like cenospheres), then the smaller size fractions will have a greater amount of surface area per unit mass for the volatile elements to condense on. Thus the elements which are more volatile will appear to be more concentrated per unit mass of the fly ash sample on the smaller size fractions.

Although this model was initially developed from data derived from type F fly ashes, it should be generally applicable to all types of fly ash. However, considerable variation in the combustion processes as to temperature, rate of combustion, fuel to air ratio, and other factors as well as variation in the composition of the source coal may contribute to deviations from the model.

Of the five elements examined here (Al, Ca, Mg, P and S) that were more concentrated on the <5 μm size fraction, only S was described by Natusch et al. (ibid.) as having a strong affinity for the smaller size fractions. Al and Mg were described as having limited affinities. Ca, which is much more concentrated on the <5 μm size fraction in this study, showed no clear trend in the study of Natusch and P was not examined. Al, Ca and Mg were all found to exhibit no concentration trends with size by Coles et al. (1979), contrary to the results of this study. P and S were not examined. Smith et al. (1979) observed clear trends for the concentration of P and S on the smaller size fractions, in agreement with the present study. However, they did not observe such trends for Al and Ca. Mg was not examined.

The other five elements examined here (Fe, K, Na, Si and Ti) are either more or equally concentrated in the whole ash samples. These elements also showed limited or no affinity for the smaller size fractions in the study by Natusch et al. (ibid.). Na was not examinied. Similarly, these elements exhibited little or no variation among size fractions in the study by Coles et al. (ibid.). Smith et al. (ibid.) also found that the concentration of Fe, Si and Ti were independent of particle size. In that study, K exhibited a slight trend for increased concentration on the smaller particle size fractions and Na was not examined.

Of the ten elements examined in this study, five fail to follow the results predicted by the volatilization-adsorption model. Al_2O_3, CaO and MgO are all refractory materials which the model predicts would be contained in the glassy matrix of the fly ash particles and thus be independent of particle size. Yet these oxides are found enriched in the <5 μm size fraction. K_2O and Na_2O are relatively volatile materials which the model predicts would condense on the surface of the fly ash particles and thus be enriched in the <5 μm size fraction. However, these oxides occur independent of particle size.

Detailed study of the reasons for the anomalous behavior of these species is beyond the scope of this study. However, some possible explanations may be offered.

The Al in the source coal probably occurred primarily in clay minerals. Some of these clay sized particles may have remained separate from the molten glass droplets that formed the fly ash particles. During the sieving of the ash these particles would have easily passed through the 5 μm sieve into the smallest fraction. Natusch et al. (1974) also reported a limited trend for Al to be enriched on the smaller size fractions.

Ca and Mg present more of a problem. These elements probably occurred as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4 \cdot 2H_2O$) and/or epsomite ($MgSO_4 \cdot 7H_2O$) mixed in with the coal. The carbonate minerals decompose into CO_2 and CaO or MgO at less than 900° C and the sulfate minerals into SO_3 and CaO or MgO at less than 1150° C, well below typical combustion temperatures of 1300° to 1600° C (Natusch et al., 1974). These highly refractory oxides would still be in solid form at these temperatures. None of the previous studies cited reported any trend for these elements to be more concentrated on the smaller size fractions.

The Al, Ca and Mg problem may in fact be an artifact of the method of analysis. The fly ash itself was analyzed with an electron microprobe which can only penetrate approximately 10 μm into the material. Thus the beam would not penetrate into the larger particles where the model predicts these elements would be more concentrated. This explanation is questionable because Si and Fe are behaving as expected by the model and were analyzed by the same technique.

Na and K pose the opposite problem. Both the metals (unlikely to exist under these conditions) and their oxides are volatile at combustion temperatures. The model predicts that they would tend to be adsorbed on the surface of the cooling fly ash particles and thus be enriched in the smaller size fractions, but no such trend is observed. In this case, this study is in agreement with the previous studies cited which also failed to observe any such trend. Only Smith et al. (1979) reported a poorly defined trend for K to be enriched in the smaller size fractions. However, both species are fairly mobile and can enter a glass structure under these high temperature conditions.

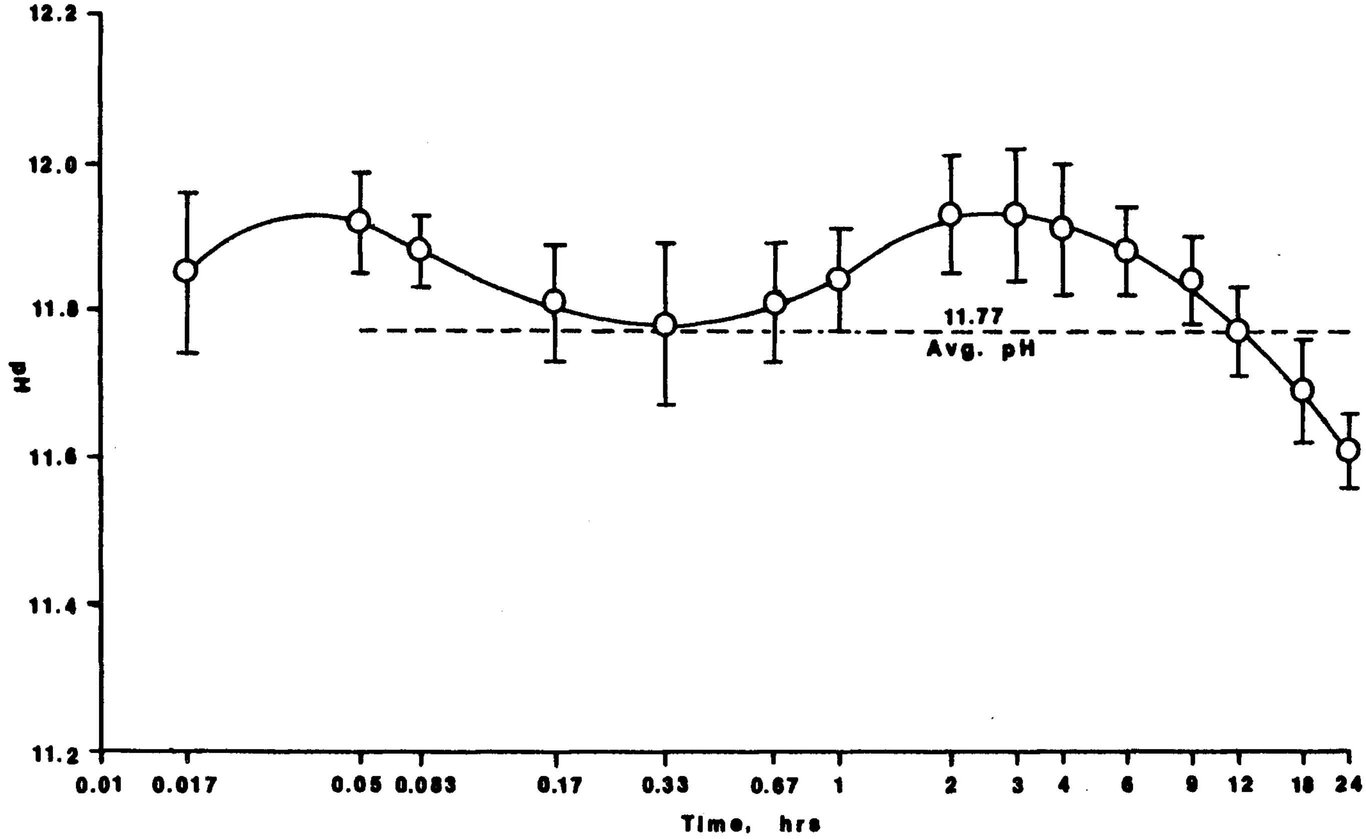
X-ray diffraction data (Grisafe, 1986) provide some additional support of the enrichment of Ca and Al absorbed on the surface of the fly ash particles. Lime (CaO), anhydrite ($CaSO_4$) and gehlenite ($Ca_2Al_2SiO_7$, tentative identification, and possibly some other silicate minerals with a similar structure to gehlenite and/or a solid solution series) are commonly identified in a number of fly ash samples obtained from the Jeffrey Energy Center. When the fly ash is hydrated, ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O$) is commonly found. This indicates that Ca and Al are present in a form that is readily available to produce new minerals. Although this does not constitute direct proof, it suggests that that these elements are adsorbed on the surface of the glassy fly ash particles.

pH of Fly Ash Slurries

No attempt was made to control the pH of the fly ash slurries for one set of leaching experiments. The pH of these slurries was recorded with time during the course of the experiments to determine the natural pH of each of the ashes. The results are summarized in Table 4 and shown in Figure 2. As can be seen, the pH rose rapidly to greater than 11.7 and reached a relative maximum of 11.92 ± 0.07 average after 0.05 hr had elapsed. The pH then began to decrease to a relative minimum of 11.78 ± 0.11 average after 0.33 hr average. At this time the pH again began to increase to an average maximum of 11.93 ± 0.09 after 2 to 3 hr had elapsed. After this the pH would again slowly

TABLE 4. AVERAGE pH OF FLY ASH SLURRIES.

Time (hr.)	Average pH KP&L 38	KP&L 39	KP&L 40	Average	95% C. I.
0.017	11.72	11.89	11.94	11.85	±0.11
0.050	11.85	11.96	11.96	11.92	±0.07
0.083	11.84	11.89	11.91	11.88	±0.05
0.17	11.70	11.85	11.89	11.81	±0.08
0.33	11.62	11.83	11.89	11.78	±0.11
0.67	11.67	11.86	11.89	11.81	±0.08
1.00	11.74	11.88	11.89	11.84	±0.07
2.00	11.81	12.01	11.98	11.93	±0.08
3.00	11.80	12.03	11.96	11.93	±0.09
4.00	11.79	12.00	11.93	11.91	±0.09
5.00	11.78	11.98	11.90	11.88	±0.09
6.00	11.82	11.95	11.87	11.88	±0.06
9.00	11.77	11.89	11.85	11.84	±0.06
12.00	11.72	11.81	11.79	11.77	±0.06
18.00	11.61	11.72	11.72	11.69	±0.07
24.00	11.58	11.63	11.63	11.61	±0.05
Average	11.71	11.81	11.80	11.77	±0.05


12.2
12.0
11.8
11.6
11.4
11.2
pH
0.01
0.017
0.05
0.083
0.17
0.33
0.67
1
2
3
4
6
9
12
18
24
Time, hrs
11.77
Avg. pH

decrease to an average of 11.71 ± 0.05 after 24 hr had elapsed. The pH may have continued to decrease, but the experiments were stopped at that point. The greatest pH observed was 12.07 for sample KP&L 39-2 after 2 hr had elapsed. The lowest pH observed after the fly ash had been added to the distilled, deionized water was 11.52 for sample KP&L 38-3 at the end of the 24 hr period. The average pH for each of the three fly ash samples was obtained by averaging the recorded pH at 0.05, 6, 12, 18 and 24 hr.

The overall pH of the fly ash slurry is controlled by the species released during the leaching. An example of this is the reaction:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^-.$$

Although all of the species involved contribute to the control of the pH, Chu et al. (1978) proposed that the relative concentrations of Ca^{2+} and SO_4^{2-} dominate the process. Chemical analysis of the waters of fourteen ash storage ponds operated by the Tennessee Valley Authority revealed a rough correlation between the ratio of Ca^{2+} to SO_4^{2-} and pH. The average $Ca^{2+}:SO_4^{2-}$ ratio for this study is 2.16 (ranges from 1.55 to 3.05, however no close correlation was observed over this narrow range of pHs). These ratios are much higher than any value reported by Chu et al.: a maximum of 1.36 at pH 11.3.

A possible mechanism for the bimodal curve of pH versus time is a two stage release of basic oxides. When the fly ash was initially added to the water, there was a rapid dissolution of the material deposited on the surface of the glassy matrix material. This material was leached from the fly ash particles within the first few minutes. The pH then began to gradually decrease, possibly due to removal of alkaline earths by reaction with atmospheric CO_2 to form insoluble carbonates and free H^+ or the slower, but more steady release of SO_3 to form H_2SO_4. Although the water used for these experiments was first boiled and a N_2 sweep gas system was used, the system was open to the atmosphere and some CO_2 could have become dissolved in the slurry. At the high pH of this system (>10.3) any dissolved CO_2 would exist primarily as CO_3^{2-}. After 0.15 to 0.30 hr had elapsed, the rate of leaching of basic oxides would again increase to overtake whatever mechanism was causing the pH to drop. Whether this leaching is of adsorbed material more tightly bound to the core of the fly ash particles or was the result of etching of the glassy matrix itself is not known. The result is the gradual increase of the pH to a level approaching and often exceeding that of the initial relative maximum. The second maximum would generally occur after 2 to 3 hr had elapsed, but could take up to 4 hr to occur. After this, the pH reducing mechanism would then become dominant again and the pH would slowly decrease for the remainder of the experiment. Despite the reduction of pH, it is thought the leaching continues throughout the entire 24 hr period, but at greatly reduced rates. This is based on the necessity to continue to add dilute acetic acid to maintain a constant pH 8 at the end of 24 hr (see below).

Rates of Acid Addition to Control pH

The rate at which acetic acid was added to maintain constant pH was recorded for these three series of experiments. Although the leaching rates for each individual species may vary, it is thought that the rate of acid addition generally reflects the overall leaching rate of the fly ash. The rates of acetic acid additions are summarized in Table 5.

In all cases, the rate of acid addition proceeded rapidly at first and then gradually slowed. When the amount of acetic acid added was plotted versus the logarithm of time, linear relationships are obtained (see Figures 3 and 4). Linear regression of the average rates of all three fly ash samples produced the following equations:

$$\text{pH 8:}\quad A = 0.0090\,log(t) + 0.011$$

$$dA/dt = 0.00030/t$$

$$\text{pH 6:}\quad A = 0.013\,log(t) + 0.027$$

$$dA/dt = 0.00043/t$$

Text continued on page 51.

TABLE 5. RATE OF ACETIC ACID ADDITIONS TO MAINTAIN CONSTANT pH OF FLY ASH SLURRY PER GRAM OF ASH.

pH	Time	Acetic Acid (equivalents)				
	(hrs)	KP&L 38	KP&L 39	KP&L 40	Average	95% C. I.
8	0.25	0.00046	0.00058	0.00075	0.00060	±0.00010
	0.50	0.00055	0.00072	0.00092	0.00068	±0.00014
	0.75	0.00061	0.00083	0.00103	0.00083	±0.00015
	1.0	0.00067	0.00092	0.00113	0.00091	±0.00016
	2.0	0.00082	0.00114	0.00136	0.00111	±0.00019
	3.0	0.00091	0.00127	0.00149	0.00122	±0.00021
	4.0	0.00098	0.00137	0.00158	0.00131	±0.00021
	5.0	0.00103	0.00144	0.00166	0.00138	±0.00022
	6.0	0.00107	0.00151	0.00172	0.00143	±0.00023
	12	0.00126	0.00177	0.00196	0.00166	±0.00025
	18	0.00140	0.00195	0.00212	0.00182	±0.00026
	24	0.00153	0.00210	0.00227	0.00196	±0.00027
6	0.25	0.0014	0.0018	0.0020	0.0018	±0.0002
	0.50	0.0016	0.0020	0.0022	0.0019	±0.0002
	0.75	0.0017	0.0021	0.0023	0.0020	±0.0002
	1.0	0.0018	0.0022	0.0024	0.0021	±0.0002
	2.0	0.0019	0.0024	0.0026	0.0023	±0.0002
	3.0	0.0021	0.0026	0.0027	0.0025	±0.0002
	4.0	0.0022	0.0027	0.0029	0.0027	±0.0002
	5.0	0.0023	0.0029	0.0030	0.0028	±0.0002
	6.0	0.0024	0.0030	0.0031	0.0029	±0.0002

Table continued on the next page.

TABLE 5, cont'd. RATE OF ACETIC ACID ADDITIONS TO MAINTAIN CONSTANT pH OF FLY ASH SLURRY PER GRAM OF ASH.

pH	Time (hrs)	Acetic Acid (equivalents) KP&L 38	KP&L 39	KP&L 40	Average	95% C. I.
6	12	0.0027	0.0035	0.0037	0.0033	±0.0003
	18	0.0030	0.0038	0.0039	0.0036	±0.0003
	24	0.0031	0.0039	0.0041	0.0038	±0.0003
4	0.25	0.0096	0.0103	0.0133	0.0110	±0.0010
	0.50	0.0123	0.0156	0.0197	0.0160	±0.0018
	0.75	0.0167	0.0206	0.0249	0.0208	±0.0020
	1.0	0.0198	0.0249	0.0292	0.0246	±0.0023
	2.0	0.0278	0.0353	0.0384	0.0338	±0.0027
	3.0	0.0318	0.0398	0.0422	0.0379	±0.0027
	4.0	0.0338	0.0405	0.0435	0.0393	±0.0025
	5.0	0.0356	0.0422	0.0454	0.0411	±0.0025
	6.0	0.0370	0.0435	0.0463	0.0423	±0.0024
	12	0.0422	0.0469	0.0495	0.0462	±0.0019
	18	0.0446	0.0488	0.0512	0.0482	±0.0019
	24	0.0470	0.0499	0.0527	0.0499	±0.0018

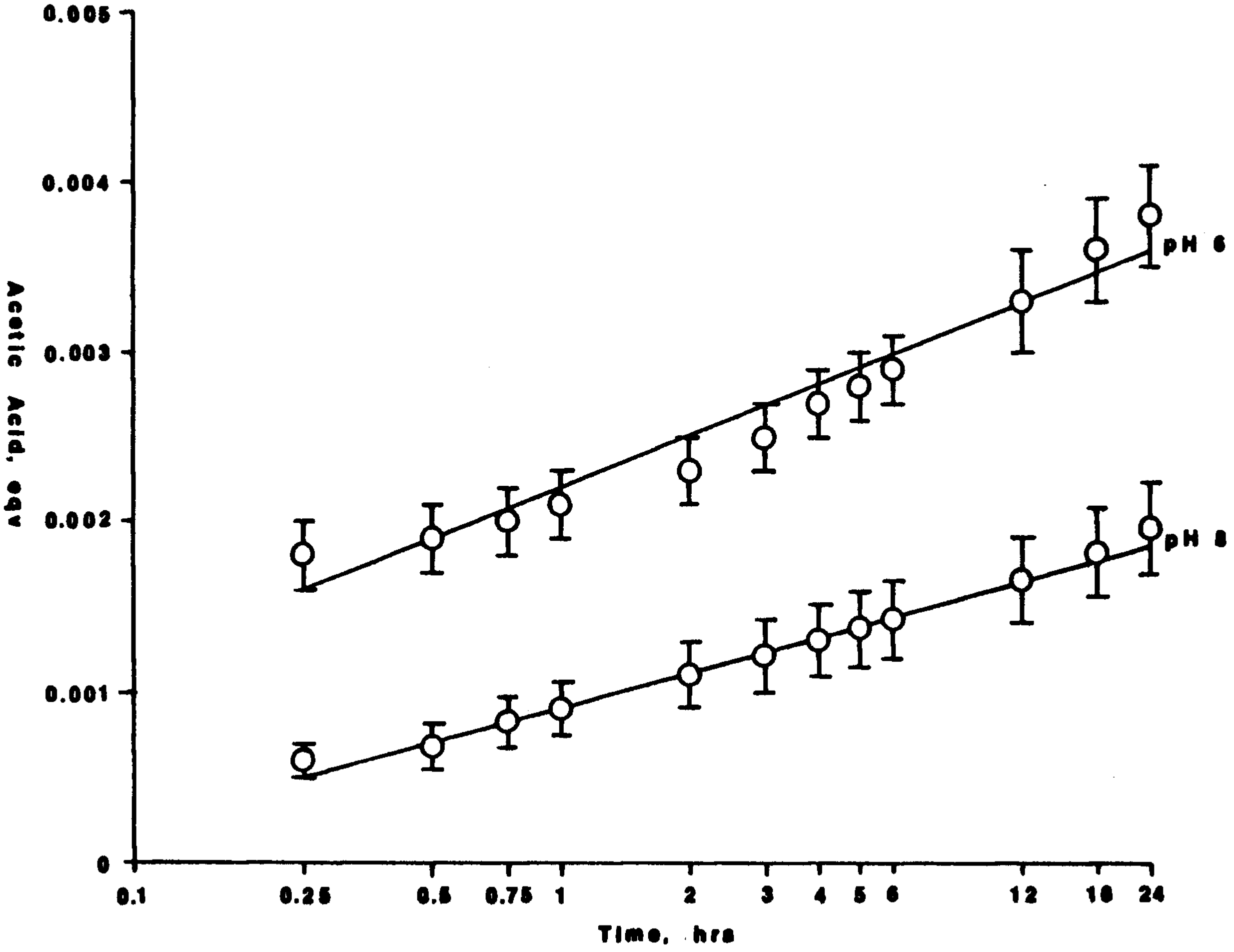


Figure 3. Rate of Acetic Acid Additions to Maintain Constant pH 8 and pH 6 of Fly Ash Slurries per Gram of

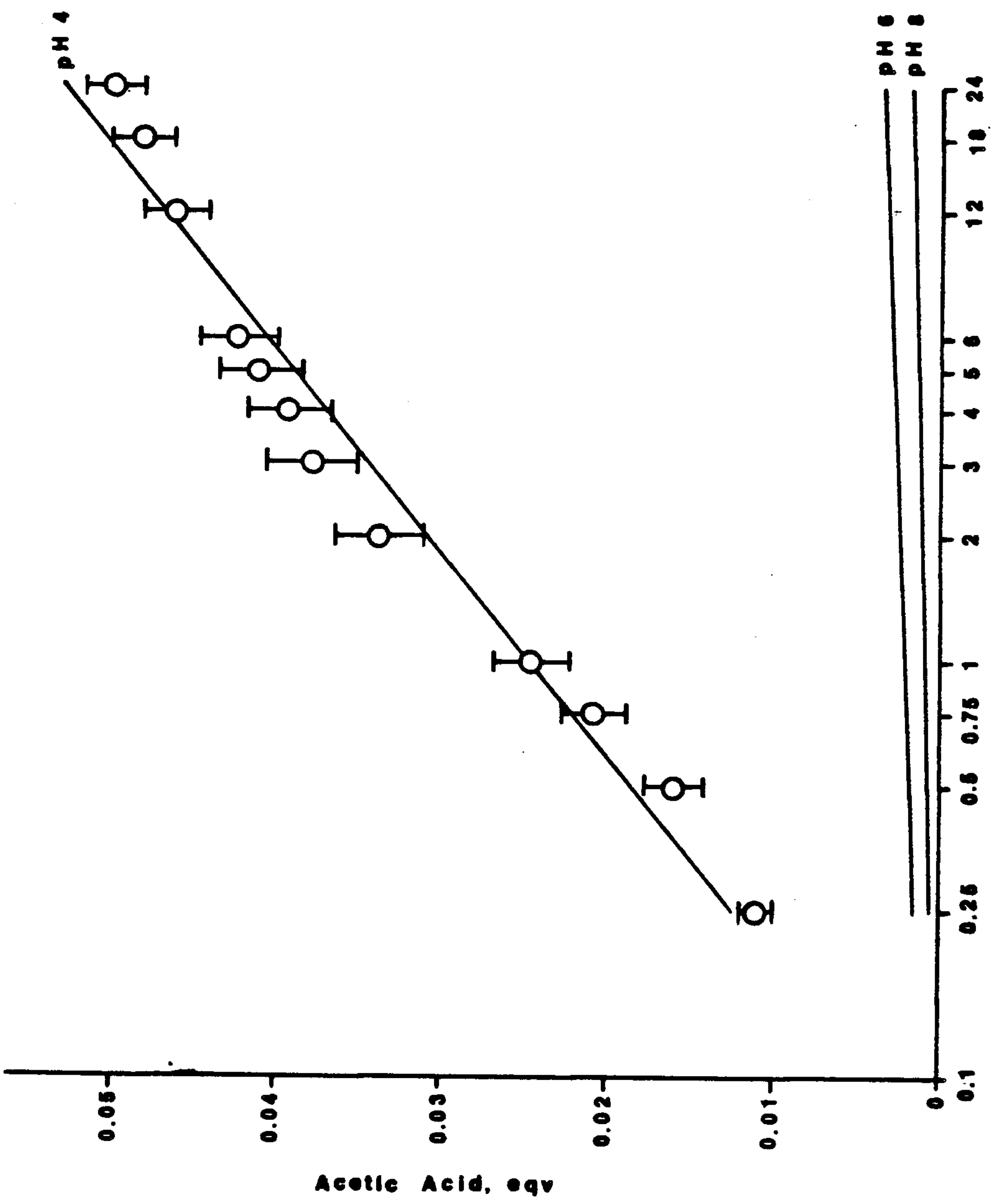


Figure 4. Rate of Acetic Acid Additions to Maintain Constant pH 4 of Fly Ash Slurries per Gram of Ash.

$$\text{pH 4:}\quad A = 0.257\,log(t) + 0.309$$

$$dA/dt = 0.00890/t$$

where A is the average amount of acetic acid added (in equivalents per g of fly ash) and t is the elapsed time (in hours).

The fit of the line to the data for the experiments performed at pH 8 is quite good. However, the data for the experiments performed at pH 6 and pH 4 deviate from the line somewhat. For the pH 6 experiments, the rate of acid addition proceeds more slowly than the calculated rate from 0.5 hr to 12 hr and then more rapidly for the last 12 hr. The best fit line does remain within the 95% confidence interval of the data throughout the 24 hr period. The deviation for the pH 4 experiments is much more pronounced. The rate of acid addition proceeds more slowly than the calculated rate for the first hour, then more rapidly until 10 hr have elapsed. The rate then slows again for the last 14 hr. At 0.25 to 0.5 hr, 2 to 3 hr and 18 to 24 hr, the best fit line falls outside the 95% confidence interval.

It is interesting to note that the rate of acetic acid addition data for the pH 4 experiments oscillate around the best fit line in the same manner that the average pH varies from a constant (compare Figures 2 and 4). However, the data for the pH 6 and pH 8 experiments oscillate in the opposite manner, albeit with a lesser amplitude (compare Figures 2 and 3).

The rate of the acid addition between the different sets of experiments also did not increase as fast as might be expected. The change from pH 8 to pH 6 represents a two orders of magnitude increase in the hydronium ion (H_3O^+) concentration, yet the rate of acetic acid addition for the pH 6 experiment is only 140% of the pH 8 rate. The difference from pH 8 to pH 4 represents a four orders of magnitude increase, yet the rate is only 2970% of the pH 8 rate.

The Environmental Protection Agency extraction procedure (U.S.E.P.A.', 1978) calls for the leaching slurry to be maintained at pH 5.0 ± 0.h with up to 4 mL 0.5 *N* acetic acid solution per gram of sample. This corresponded to a maximum of 0.002 equivalents of acetic acid per gram of sample. The great alkalinity of these fly ash samples would have quickly consumed this amount of acid. Although no experiments were performed at this pH, it was bracketed. This amount of acetic acid was generally used in less than five minutes to maintain the slurry at pH 4. However, 0.002 equivalents of acetic acid per gram was sufficient to maintain the slurry at pH 6 for an average of forty-five minutes (0.25 hr for sample KP&L 40 and 0.5 hr for for sample KP&L 39, but 2.5 hr for sample KP&L 38). This amount was more than adequate to maintain sample KP&L 38 at pH 8, but would maintain sample KP&L 39 for about 20 hr and sample KP&L 40 for about 13 to 14 hr.

Chemical Analysis of the Leachate

The results of the chemical analyses for As, Ca, Cd, Cl^-, Cr, Fe, Na, Pb, Se and SO_4^{2-} are summarized in Table 6 and plotted in Figures 5 through 14. The figures are plotted for the average concentration of each of the species in the leachate for all three fly ash samples. These values are given in Table 6 under the designation "All". The error bars give the 95% confidence interval of the analyses calculated from the standard deviations. The interpolated line between the data points is an intuitive fit drawn with a flexible spline curve by the author. The analyses are of ten selected species and should not be considered comprehensive for all the species present in the leachate. Such a comprehensive analysis was beyond the scope of this study.

The general trend for the species observed is for the highest concentrations to occur in the leachate maintained at pH 4. The average concentrations of the metallic elements at pH 6 would drop to less than 40% of the average that was obtained at pH 4, sometimes to less than 1%. The concentrations of these elements would then continue to drop, albeit at a slower rate, as the pH increased. The two exceptions to this are Cr and Fe where the concentra-

Text continued on page 72.

TABLE 6. RESULTS OF CHEMICAL ANALYSES OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
As	KP&L 38	4	1.3	± 0.1	0.026
	KP&L 39	4	1.1	± 0.1	0.022
	KP&L 40	4	1.2	± 0.2	0.024
	All	4	1.2	± 0.1	0.024
As	KP&L 38	6	0.04	± 0.01	0.0007
	KP&L 39	6	0.03	± 0.03	0.0006
	KP&L 40	6	0.05	± 0.03	0.0009
	All	6	0.04	± 0.01	0.0008
As	KP&L 38	8	0.02	± 0.01	0.0003
	KP&L 39	8	0.01	± 0.01	0.0002
	KP&L 40	8	0.01	± 0.02	0.0001
	All	8	0.01	± 0.01	0.0002
As	KP&L 38	11.7	0.00(1)	± 0.00(2)	0.0000(2)
	KP&L 39	11.8	0.00(3)	± 0.00(4)	0.0000(6)
	KP&L 40	11.8	0.00(3)	± 0.00(4)	0.0000(7)
	All	11.8	0.00(3)	± 0.00(2)	0.0000(5)
Ca	KP&L 38	4	6280	±760	126
	KP&L 39	4	6190	±350	124
	KP&L 40	4	8450	±300	169
	All	4	6970	±640	139

Table continued on the next page.

TABLE 6, cont'd. RESULTS OF CHEMICAL ANALYSIS OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
Ca	KP&L 38	6	2400	±110	47.9
	KP&L 39	6	2800	±100	56.0
	KP&L 40	6	3060	± 20	61.2
	All	6	2780	±170	55.6
Ca	KP&L 38	8	1580	±130	31.6
	KP&L 39	8	2040	± 70	40.8
	KP&L 40	8	2230	±180	44.6
	All	8	1950	±230	39.0
Ca	KP&L 38	11.7	170	± 30	3.4
	KP&L 39	11.8	220	± 40	4.3
	KP&L 40	11.8	230	± 50	4.5
	All	11.8	200	± 30	4.1
Cd	KP&L 38	4	0.19	± 0.01	0.004
	KP&L 39	4	0.17	± 0.02	0.003
	KP&L 40	4	0.17	± 0.02	0.003
	All	4	0.18	± 0.01	0.004
Cd	KP&L 38	6	0.04	± 0.01	0.001
	KP&L 39	6	0.06	± 0.03	0.001
	KP&L 40	6	0.06	± 0.02	0.001
	All	6	0.06	± 0.01	0.001

Table continued on the next page.

TABLE 6, cont'd. RESULTS OF CHEMICAL ANALYSES OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
Cd	KP&L 38	8	0.02	± 0.01	0.000(4)
	KP&L 39	8	0.02	± 0.01	0.000(4)
	KP&L 40	8	0.02	± 0.01	0.000(5)
	All	8	0.02	± 0.01	0.000(4)
Cd	KP&L 38	11.7	0.01	± 0.02	0.000(2)
	KP&L 39	11.8	0.00(3)	± 0.01	0.000(1)
	KP&L 40	11.8	Less than detection limit.		
	All	11.8	0.00(4)	± 0.01	0.000(1)
Cl^-	KP&L 38	4	6	± 0	0.1
	KP&L 39	4	4	± 0	0.08
	KP&L 40	4	5	± 0	0.1
	All	4	5	± 1	0.1
Cl^-	KP&L 38	6	5	± 4	0.1
	KP&L 39	6	2	± 2	0.05
	KP&L 40	6	4	± 0	0.08
	All	6	4	± 1	0.08
Cl^-	KP&L 38	8	4	± 2	0.07
	KP&L 39	8	3	± 2	0.05
	KP&L 40	8	3	± 0	0.06
	All	8	3	± 1	0.06

Table continued on the next page.

TABLE 6, cont'd. RESULTS OF CHEMICAL ANALYSES OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
Cl^-	KP&L 38	11.7	3	± 2	0.05
	KP&L 39	11.8	2	± 0	0.04
	KP&L 40	11.8	2	± 0	0.04
	All	11.8	2	± 1	0.04
Cr	KP&L 38	4	3.4	± 0.3	0.067
	KP&L 39	4	2.2	± 0.4	0.044
	KP&L 40	4	2.7	± 0.3	0.055
	All	4	2.8	± 0.3	0.055
Cr	KP&L 38	6	0.1	± 0.1	0.002
	KP&L 39	6	Less than detection limit.		
	KP&L 40	6	Less than detection limit.		
	All	6	0.0(3)	± 0.0(2)	0.000(6)
Cr	KP&L 38	8	0.1	± 0.1	0.002
	KP&L 39	8	0.1	± 0.1	0.001
	KP&L 40	8	0.0(2)	± 0.1	0.000(4)
	All	8	0.1	± 0.1	0.001
Cr	KP&L 38	11.7	0.1	± 0.1	0.002
	KP&L 39	11.8	0.1	± 0.1	0.001
	KP&L 40	11.8	0.1	± 0.1	0.002
	All	11.8	0.1	± 0.1	0.002

Table continued on the next page.

TABLE 6, cont'd. RESULTS OF CHEMICAL ANALYSES OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
Fe	KP&L 38	4	870	±160	17.3
	KP&L 39	4	790	±120	13.7
	KP&L 40	4	610	± 90	12.3
	All	4	720	±100	14.4
Fe	KP&L 38	6	1.8	± 0.6	0.04
	KP&L 39	6	3.6	± 2.4	0.07
	KP&L 40	6	3.1	± 2.2	0.06
	All	6	2.9	± 1.0	0.06
Fe	KP&L 38	8	1.0	± 0.5	0.02
	KP&L 39	8	2.1	± 4.5	0.04
	KP&L 40	8	1.2	± 0.5	0.02
	All	8	1.4	± 0.9	0.03
Fe	KP&L 38	11.7	2.2	± 1.1	0.04
	KP&L 39	11.8	9.2	± 5.0	0.18
	KP&L 40	11.8	8.3	± 1.9	0.17
	All	11.8	6.6	± 2.9	0.13
Na	KP&L 38	4	280	± 50	5.5
	KP&L 39	4	280	± 30	5.5
	KP&L 40	4	230	± 60	4.7
	All	4	260	± 30	5.2

Table continued on the next page.

TABLE 6, cont'd. RESULTS OF CHEMICAL ANALYSES OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
Na	KP&L 38	6	120	± 10	2.4
	KP&L 39	6	100	± 20	1.9
	KP&L 40	6	80	± 10	1.5
	All	6	100	± 20	1.9
Na	KP&L 38	8	100	± 10	2.0
	KP&L 39	8	100	± 10	2.0
	KP&L 40	8	80	± 10	1.7
	All	8	90	± 10	1.9
Na	KP&L 38	11.7	70	± 10	1.5
	KP&L 39	11.8	80	± 10	1.6
	KP&L 40	11.8	60	± 10	1.1
	All	11.8	70	± 10	1.4
Pb	KP&L 38	4	2.7	± 0.6	0.054
	KP&L 39	4	2.6	± 0.3	0.052
	KP&L 40	4	2.6	± 0.3	0.053
	All	4	2.7	± 0.2	0.053
Pb	KP&L 38	6	0.2	± 0.1	0.004
	KP&L 39	6	0.2	± 0.3	0.003
	KP&L 40	6	0.2	± 0.3	0.003
	All	6	0.2	± 0.1	0.003

Table continued on the next page.

TABLE 6, cont'd. RESULTS OF CHEMICAL ANALYSES OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
Pb	KP&L 38	8	Less than detection limit.		
	KP&L 39	8	0.1	± 0.1	0.001
	KP&L 40	8	0.1	± 0.1	0.002
	All	8	0.1	± 0.1	0.001
Pb	KP&L 38	11.7	Less than detection limit.		
	KP&L 39	11.8	Less than detection limit.		
	KP&L 40	11.8	Less than detection limit.		
	All	11.8	Less than detection limit.		
Se	KP&L 38	4	0.49	± 0.17	0.010
	KP&L 39	4	0.66	± 0.17	0.013
	KP&L 40	4	0.76	± 0.25	0.015
	All	4	0.64	± 0.11	0.013
Se	KP&L 38	6	0.27	± 0.08	0.005
	KP&L 39	6	0.19	± 0.04	0.004
	KP&L 40	6	0.22	± 0.04	0.004
	All	6	0.23	± 0.03	0.005
Se	KP&L 38	8	0.12	± 0.06	0.002
	KP&L 39	8	0.08	± 0.03	0.002
	KP&L 40	8	0.14	± 0.10	0.003
	All	8	0.11	± 0.03	0.002

Table continued on the next page.

TABLE 6, cont'd. RESULTS OF CHEMICAL ANALYSES OF FLY ASH LEACHATE.

Element	Sample	pH	Conc. (mg/L)	95% C. I. (mg/L)	Proportion (mg/g ash)
Se	KP&L 38	11.7	0.02	± 0.01	0.000(3)
	KP&L 39	11.8	0.02	± 0.01	0.000(4)
	KP&L 40	11.8	0.02	± 0.01	0.000(5)
	All	11.8	0.02	± 0.01	0.000(4)
SO_4^{2-}	KP&L 38	4	720	± 40	14
	KP&L 39	4	670	± 60	13
	KP&L 40	4	660	±120	13
	All	4	680	± 40	14
SO_4^{2-}	KP&L 38	6	1010	± 0	20
	KP&L 39	6	960	± 80	19
	KP&L 40	6	920	± 20	18
	All	6	960	± 40	19
SO_4^{2-}	KP&L 38	8	890	± 70	18
	KP&L 39	8	730	± 20	15
	KP&L 40	8	650	± 80	15
	All	8	790	± 60	16
SO_4^{2-}	KP&L 38	11.7	70	± 40	1
	KP&L 39	11.8	120	± 40	2.3
	KP&L 40	11.8	100	± 30	2.0
	All	11.8	100	± 20	1.9

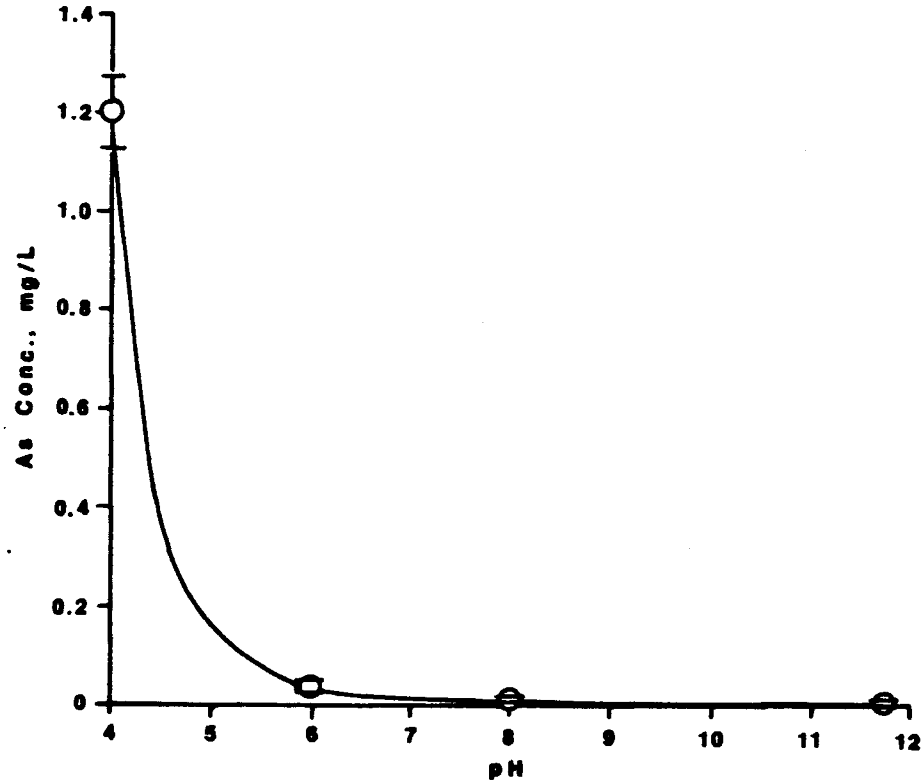


Figure 5. Arsenic Concentration in Fly Ash Leachate vs. pH.

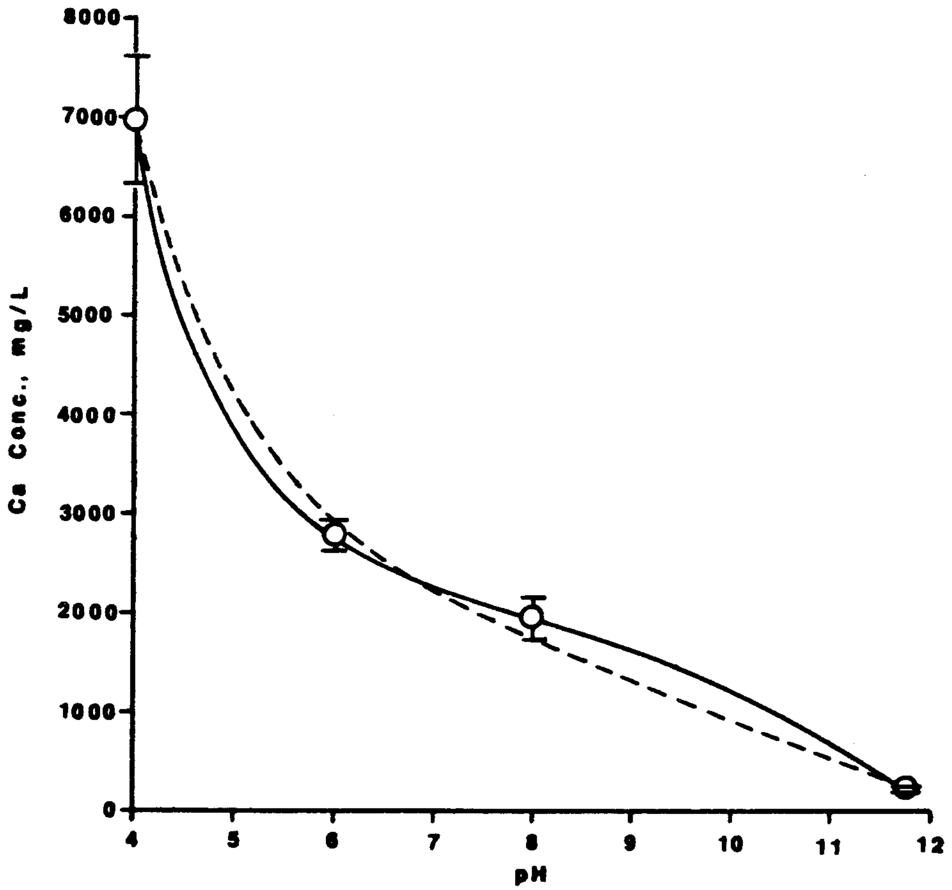


Figure 6. Calcium Concentration in Fly Ash Leachate vs.

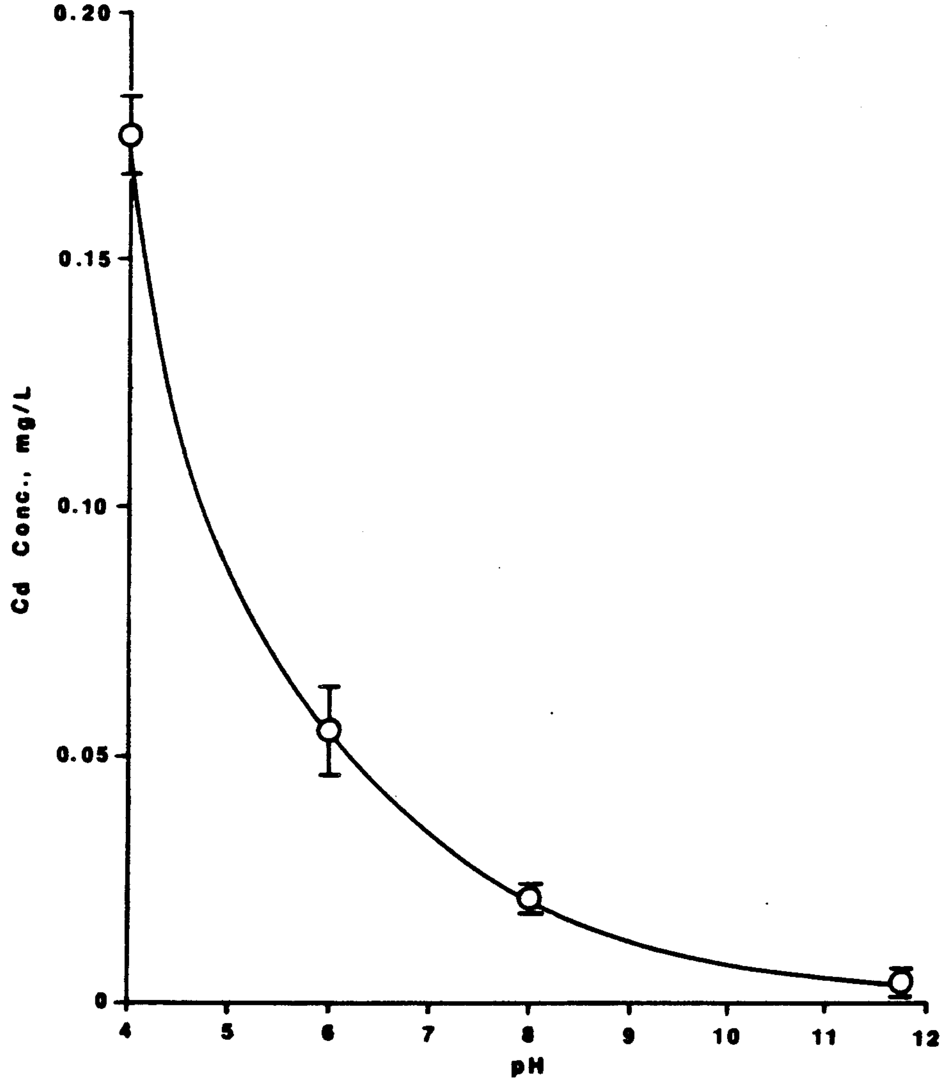


Figure 7. Cadmium Concentration in Fly Ash Leachate vs. pH.

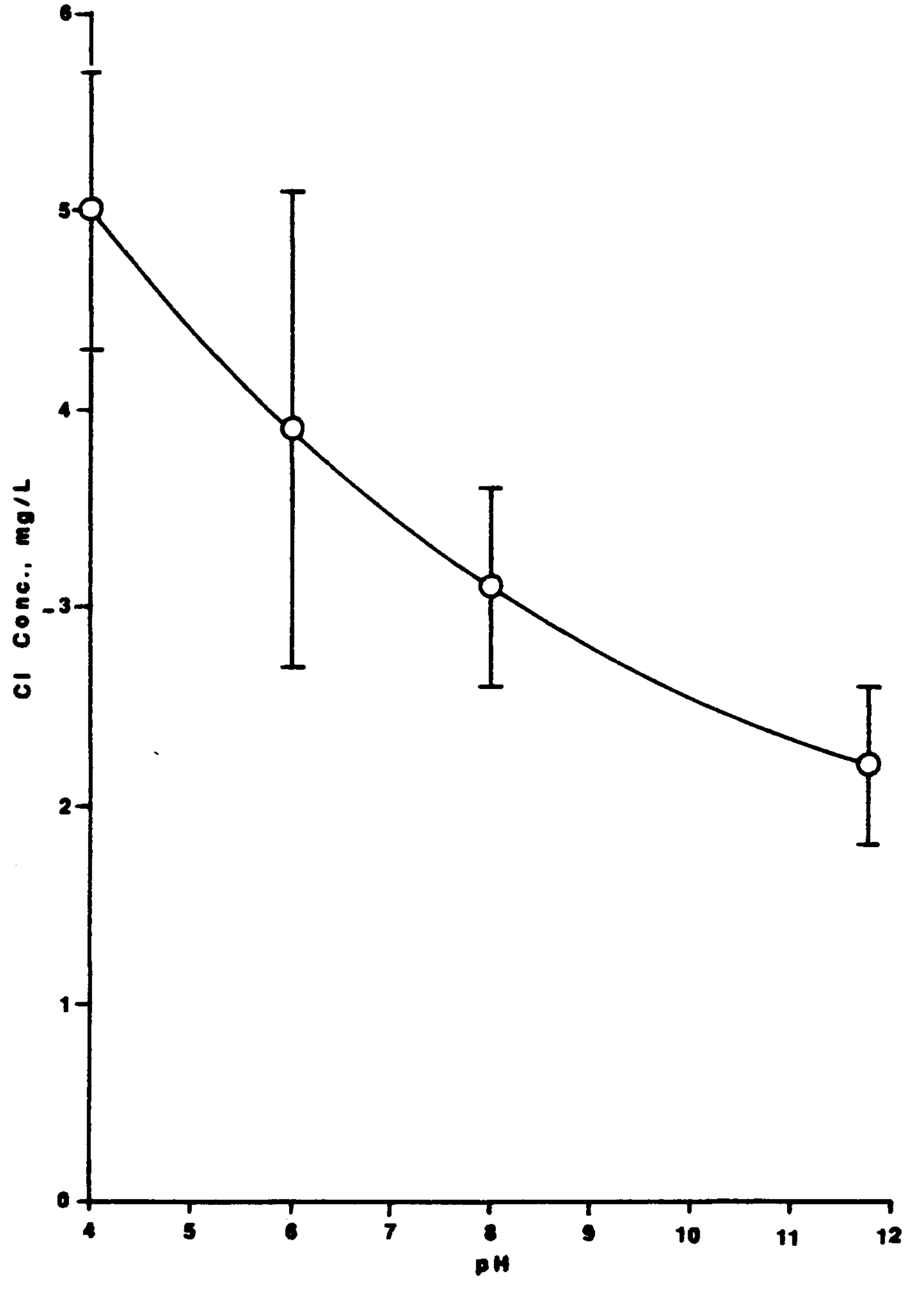


Figure 8. Chloride Concentration in Fly Ash Leachate vs. pH.

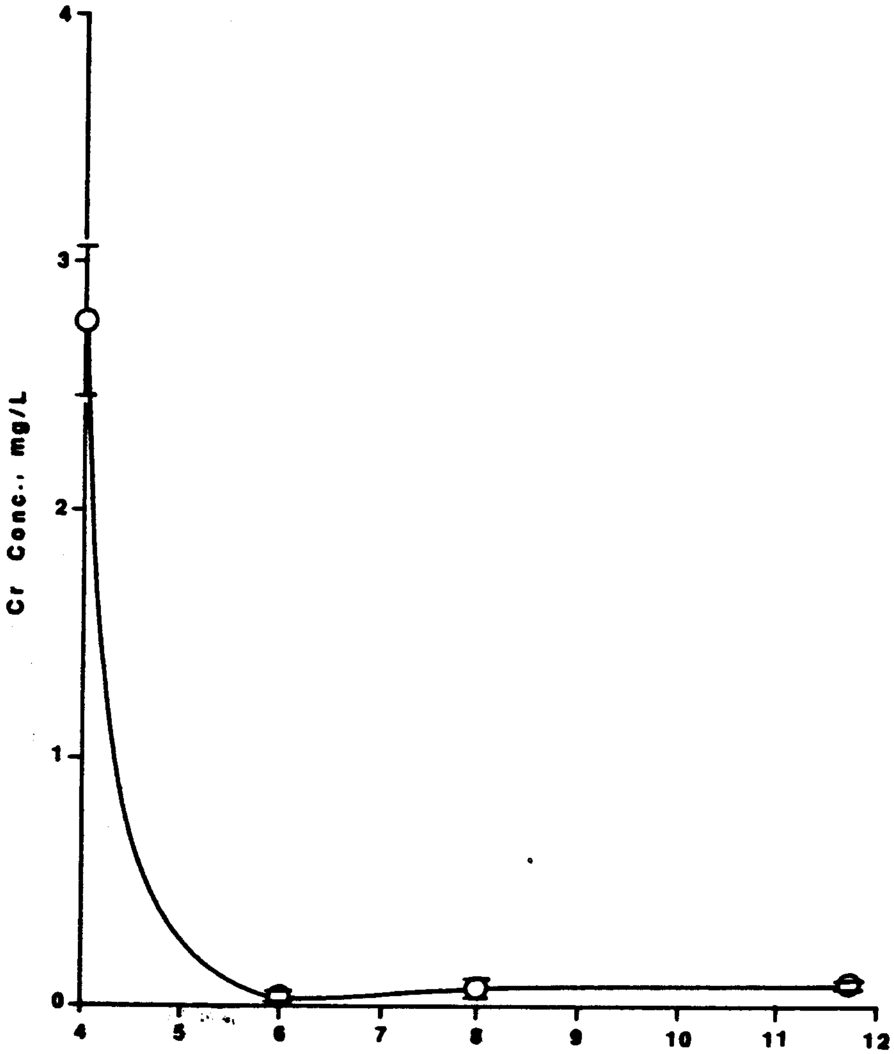


Figure 9. Chromium Concentration in Fly Ash Leachate vs. pH.

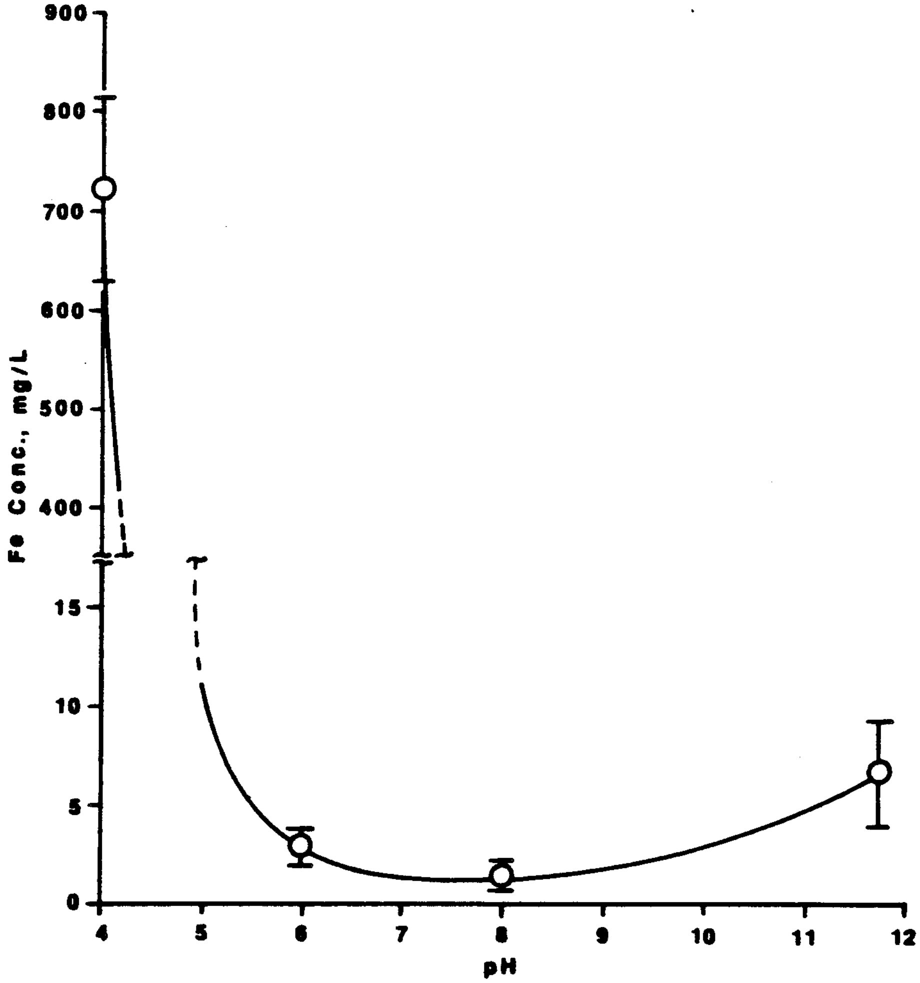


Figure 10. Iron Concentration in Fly Ash Leachate vs. pH.

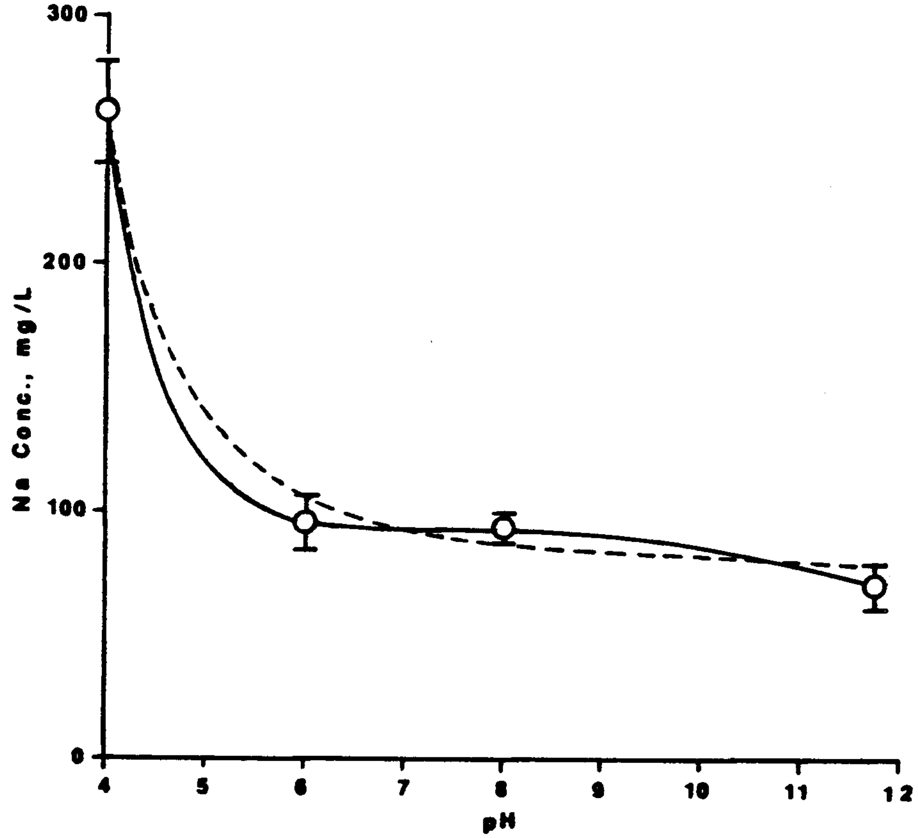


Figure 11. Sodium Concentration in Fly Ash Leachate vs. pH.

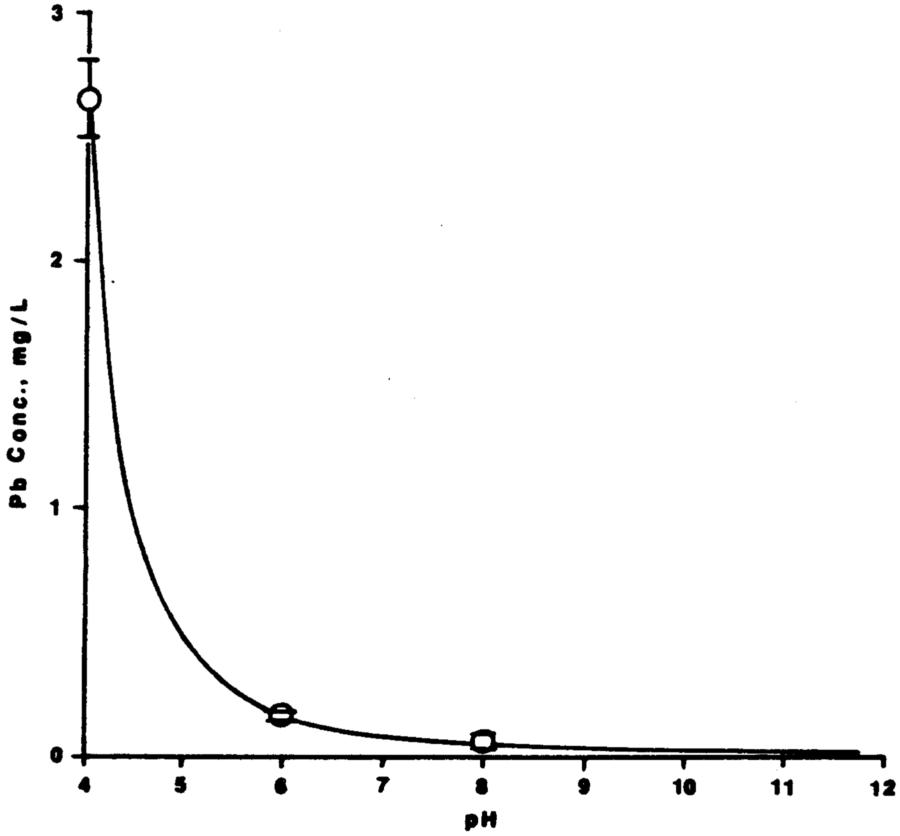


Figure 12. Lead Concentration in Fly Ash Leachate vs. pH.

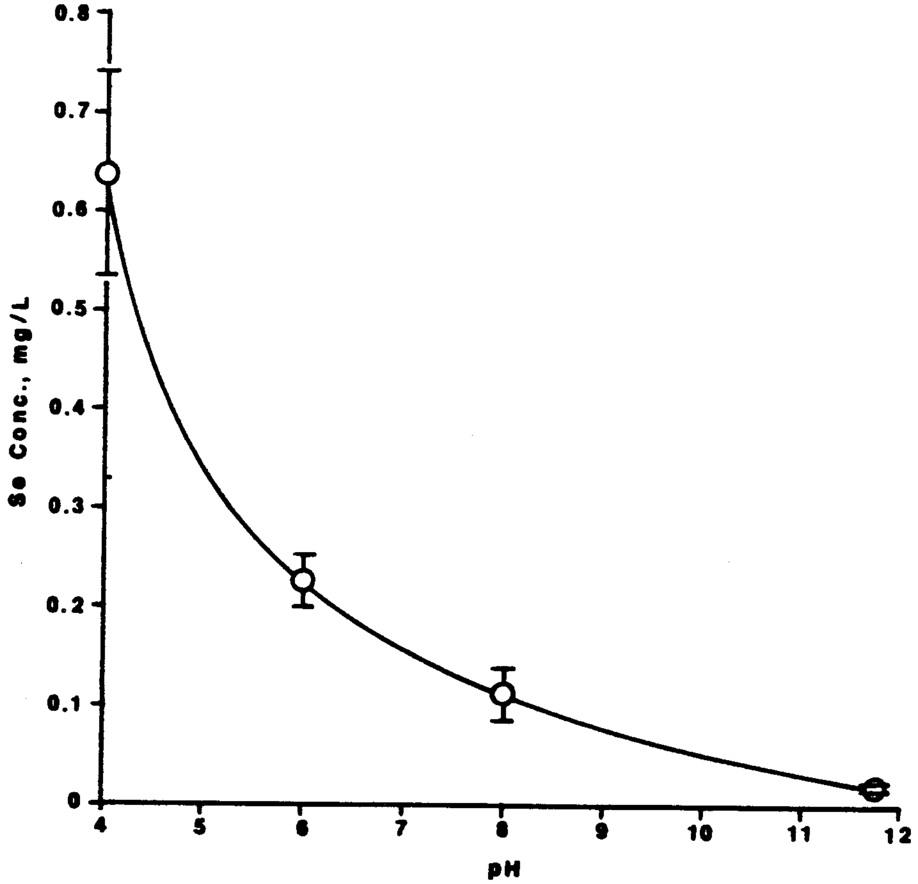


Figure 13. Selenium Concentration in Fly Ash Leachate vs. pH.

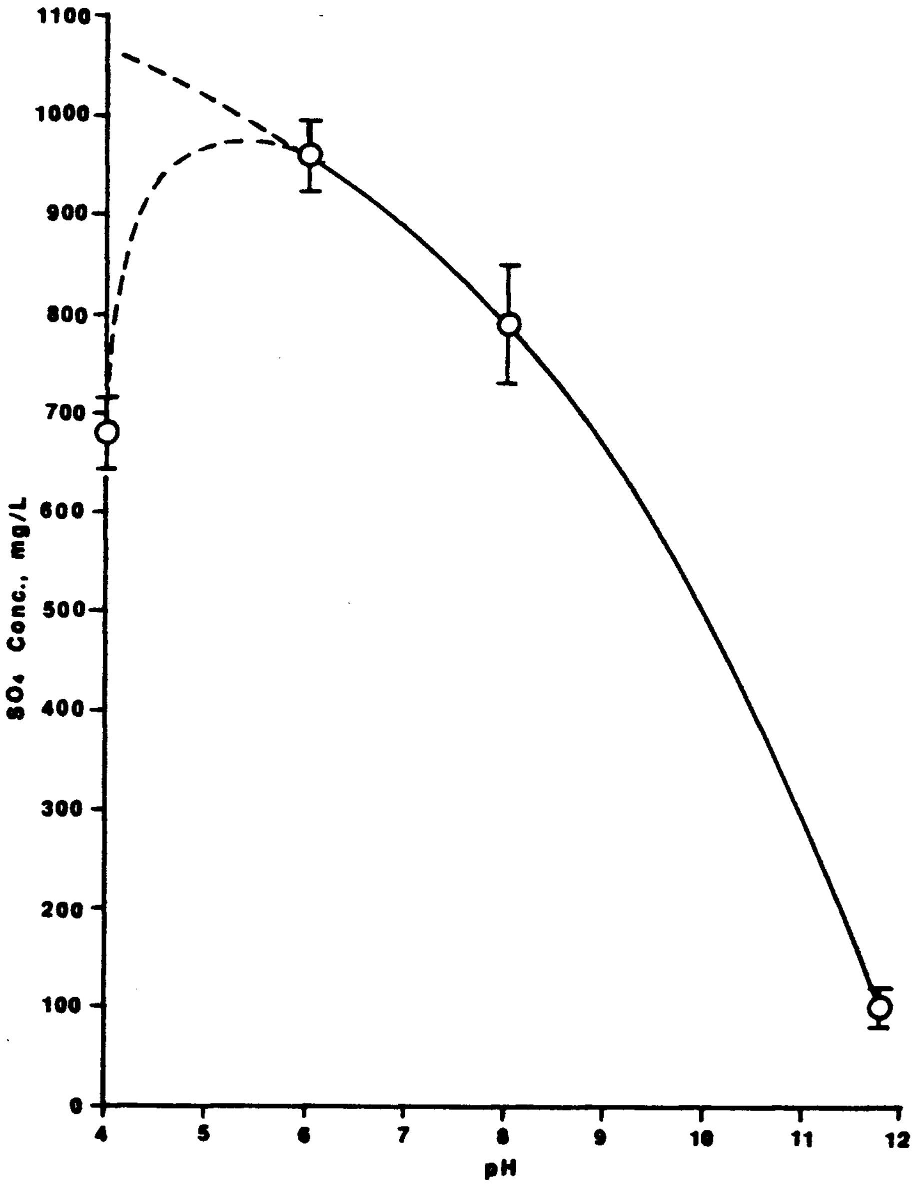


Figure 14. Sulfate Concentration in Fly Ash Leachate vs.

tions decreased rapidly at first as the pH increased, but then began to increase slightly again. The nonmetallic species behave somewhat differently. The Cl^- concentration follows a steady decrease from pH 4 to pH 8 at a slower rate than any of the metallic elements examined and then at a slower rate to pH 11.8. The SO_4^{2-} concentration actually rises from pH 4 to pH 6 and then decreases at an increasing rate. This last point will be discussed further below.

This study is in agreement with the previous studies of Theis and Wirth (1977), Chu et al. (1978), Phung et al. (1979) and Griffin et al. (1980) that the pH of the slurry is of major, if not primary, importance in the mobilization of elements from fly ash. The increase in the concentrations of the species from the experiments performed at the natural pH of the slurry to those maintained at a constant pH 4 ranged from a 200% increase for Cl^- in sample KP&L 39 to a 110,000% increase for As in sample KP&L 38.

Arsenic

Arsenic concentrations ranged from 0.001 to 0.005 mg/L at the natural pH of the slurry to 1.01 to 1.35 mg/L at pH 4. The relative difference between the concentrations of sample KP&L 38 at the natural pH of the slurry and pH 4 is the greatest observed in this series of experiments. The concentration at pH 4 is in excess of the maximum permissible levels of the Environmental Protection Agency Drinking Water Standards (E.P.A.D.W.S.) of 0.05 mg/L by more than a factor of ten (Federal Register, 1978). By this criteria, the fly ash should be considered a toxic waste. However, 23.5 or more times the maximum amount of acetic acid allowed by the E.P.A. leaching methodology (ibid.) was used to maintain the slurry at this pH. The As concentrations for the remainder of the experiments were below the E.P.A.D.W.S. The average As concentration dropped below 0.5 mg/L at pH 4.3 and continued to drop as pH increased (see Figure 5). This continuous decrease in concentration as pH increases differs from the study by Thies and Wirth (1977) where the As concentration decreased rapidly from pH 3 to 6, leveled off and then increased from pH 9 to 12.

Calcium

Calcium is present in the leachate at higher concentrations than any other species examined. This is not surprising as CaO has the greatest concentration in weight percentage of any of the major species in the analysis of the fly ash samples (see Table 3) and is known to exist as crystalline lime (CaO) in the solid ash. The concentrations ranged from 160 to 240 mg/L at the natural pH of the slurry to 5440 to 8700 mg/L at pH 4. There is no E.P.A.D.W.S. for calcium. As can be seen in Figure 6, the concentration of the Ca decreases rapidly from pH 4 to pH 6, decreases more slowly from pH 6 to pH 8, but then the curve begins to decrease somewhat more rapidly to pH 11.8. This may be due to the loss of some of the Ca as relatively insoluble calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and/or ettringite ($Ca_4Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O$) at the higher pH. As mentioned earlier in this section, despite the initial boiling of the water and use of a N_2 sweep gas system, some atmospheric CO_2 may have become dissolved in the water where it dissociated into CO_3^{2-} and combined with the Ca^{2+}. The SO_4^{2-} concentration also dropped rapidly from pH 8 to pH 11.8 (described later in this section). However, a solely concave curve (decoy curve) may be drawn within the 95% confidence interval bars.

Cadmium

Cadmium ranged from less than the detection limit of 0.002 mg/L to 0.01 mg/L at the natural pH of the slurry to 0.15 to 0.20 mg/L at pH 4. The concentration at pH 4 exceeded the E.P.A.D.W.S of 0.01 mg/L by greater than a factor of ten, so under these conditions the fly ash could be considered a toxic material. However, this is again under conditions more severe than the E.P.A. standard leaching methods by more than an order of magnitude. The Cd concentrations for the remainder of the experiments were below the criteria for toxicity classification. The average Cd concentration dropped below 0.1 mg/L at pH 4.8 and continued to drop at a gradually decreasing rate as the pH increased (see Figure 7).

Chloride

Chloride concentrations ranged from 2 mg/L to 3 mg/L at the natural pH of the slurry to 4 mg/L to 6 mg/L at pH 4. This was the smallest relative difference in concentration between the extremes of pH observed and thus the species least affected by the change of pH. These concentrations are all well below the recommended E.P.A.D.W.S. of 250 mg/L. The average concentration gradually decreases from pH 4 to pH 11.8 at a slowly decreasing rate (see Figure 8). An anomaly did occur for sample KP&L 39 where the Cl^- concentration decreased particularly rapidly from pH 4 to pH 6, rose slightly to pH 8 and then decreased to the minimum observed pH at 11.8. This behavior was not observed for the other two fly ash samples.

Chromium

Chromium concentrations ranged from less than the detection limit of 0.02 mg/L to 0.14 mg/L at pH 6 to 1.78 to 3.63 mg/L at pH 4. The concentrations exceeded the E.P.A.D.W.S. of 0.05 mg/L Cr by greater than a factor of ten only under the conditions required to maintain the pH at 4. The concentrations remained below this criteria for toxicity classification for the other experiments. The average Cr concentration dropped below 0.5 mg/L at pH 4.7 and reached a minimum at pH 6 (see Figure 9). The average Cr concentration then began to increase very slightly as the pH increased. This increase is apparent for the average concentrations of all three fly ash samples averaged together, but becomes less well defined when individual experiments are examined. Maximum Cr concentrations of 0.14 mg/L were measured at both pH 6 and pH8. The maximum concentration measured at the natural pH of the slurry is 0.13 mg/L. Nonetheless, this indicates that Cr does have a slight amphoteric nature, possibly due to oxidation of Cr^{III} to Cr^{VI}, for the fly ash samples examined in this study.

Iron

Iron concentrations ranged from 0.9 to 4.2 mg/L at pH 8 to 380 to 970 mg/L at pH 4. The E.P.A.D.W.S. has a recommended maximum concentration of 0.3 mg/L for Fe, but this is a recommendation for aesthetics of taste rather than for a toxicity threshold. Except for the relative difference of As concentrations for sample KP&L 38 between the natural pH of the slurry and pH 4, Fe concentrations showed the greatest relative differences between the lowest average at pH 8 and the highest at pH 4. The Fe concentrations decreased rapidly from pH 4 to pH 6 and then much more slowly from pH 6 to pH 8 (see Figure 10). However, the concentrations then began to increase significantly as the pH increases to 11.8. The increase is fairly small for sample KP&L 38, but is greater than 400% for sample KP&L 39 and greater than 600% for sample KP&L

40. Along with Cr, Fe was the only species examined which showed an amphoteric nature by becoming more soluble at both extremes of pH. This may possibly be due to the oxidation of Fe^{II} to Fe^{III} or to the formation of a soluble complex of Fe with excess OH^- radicals. The leachates produced at pH 4 have an orange coloration that is absent from those produced at higher pH. This is thought to be the result of an Fe acetate complex of some sort. An early experiment using dilute nitric acid to maintain the pH at 4 produced a colorless leachate.

Sodium

Sodium concentrations ranged from 53 to 83 mg/L at the natural pH of the fly ash slurry to 185 to 327 mg/L at pH 4. This was the smallest relative difference in concentration between the extremes of pH observed for cations and thus the least affected by change of the pH. There is no E.P.A.D.W.S. for Na. Although Na is the least dependent on pH of the cations examined here, it is not unaffected. The concentration decreased rapidly from pH 4 to pH 6, then remained nearly constant from pH 6 to pH 8 (see Figure 11). From pH 8 to pH 11.8 the concentration decreased again, as it did for Ca. Unlike Ca, a partial precipitation mechanism at high pH cannot be postulated as Na has no common insoluble salts. However, like Ca, a solely concave curve (decoy curve) can be drawn within the 95% confidence interval bars.

Lead

Lead concentrations range from less than the detection limit of 0.05 mg/L at the natural pH of the slurry to 2.1 to 3.1 mg/L at pH 4. The Pb concentrations exceed the E.P.A.D.W.S. of 0.05 mg/L by greater than a factor of ten only at pH 4. The concentrations are less than the criteria for toxicity classification for the other experiments. The average Pb concentration drops below 0.5 mg/L at pH 5 and continues to decrease as the pH increases at a reduced rate (see Figure 12).

Selenium

Selenium concentrations range from 0.013 to 0.023 mg/L at the natural pH of the fly ash slurry to 0.34 to 0.93 mg/L at pH 4. The concentrations exceed the E.P.A. D.W.S. OF 0.1 mg/L by more than a factor of ten at pH 4, pH 6 and nearly half of the experiments at pH 8. The average Se concentration does not drop below 0.1 mg/L until pH 8.3 (see Figure 13). The amount of acetic acid used to maintain the pH at both 4 and 6 exceeds the maximum amount allowed by the E.P.A. leaching methodology, but the average amount used to maintain the pH at 8 was very close to the 0.002 equivalents per gram of solid sample specified. Although the procedure used here differs enough from the E.P.A. methodology to prevent the unequivocal declaration of samples KP&L 38 and KP&L 40 as toxic based on the leachability of Se, it suggests that this may be the case. It is not presently possible to perform the E.P.A. tests as specified due to the lack of the proper equipment. At the natural pH of the fly ash slurry, the Se concentration is well below the toxicity criteria.

Sulfate

Sulfate concentrations ranged form 60 mg/L to 130 mg/L at the natural pH of the slurry to 910 mg/L to 1010 mg/L at pH 6. Sulfate displayed the most anomalous behavior by increasing from pH 4 to pH 6 and then decreasing at an increasing rate to pH 11.8 (see Figure 14). This final loss may be due to the precipitation of relatively insoluble gypsum ($CaSO_4 \cdot 2H_2O$) and/or ettringite ($Ca_4Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O$). The SO_4^{2-} concentrations exceed the maximum recommended E.P.A.D.W.S. for all of the controlled pH experiments and the average concentration does not drop below 250 mg/L until pH 11.2. This standard is a recommendation only and does not constitute a toxicity criterion.

The low SO_4^{2-} concentration at pH 4 may be due to preliminary processing of the leachate prior to its analysis. An amorphous gel had formed in the storage bottles of all of the pH 4 leachates following the initial separation of the fly ash from the supernate. Because the anions examined in this study were analyzed by visible light spectrophotometric techniques, it was necessary to first centrifuge the leachate to remove this gel which would have caused erroneously high readings by scattering the light beam. Some of the SO_4^{2-} may have been removed with the gel. This processing occurred prior to analysis of chloride, but apparently had little or no effect due to the high solubility of Cl^- salts. The experiments performed at pH 6, pH 8 and the natural pH did not have any such gel form and received no additional centrifuging. An intuitive extrapolation to pH 4 based on the data from the experiments performed at higher pH is also plotted on Figure 14. Even with the extrapolated extension, this is the the only curve with a convex upward profile.

CONCLUSIONS

This study confirms that for the metallic elements, As, Ca, Cd, Cr, Fe, Na, Pb and Se, pH is a major factor in controlling the mobility of elements leached from fly ash. The highest concentrations of these elements were found in the leachates generated at pH 4. The concentrations decrease to less than 40% (less than 1% in the case of Fe) of the pH 4 values by pH 6 and continue to decrease at a progressively slower rate as the pH increased. The two exceptions were Cr and Fe which showed a slight amphoteric tendency. The Cr concentration dropped to a minimum at pH 6, rose slightly at pH 8 and then remained steady as the pH increased. The Fe concentration followed the standard decreasing curve until pH 8 and then increased slightly at the natural pH of 11.8. The amphoteric nature of these two species may due to a change in the oxidation states. Further study of the electric potential versus the pH may clarify this observation.

The anionic species examined here, Cl and SO_4, are also influenced by pH, but in a different manner. Instead of the rapid initial decrease in concentration followed by a progressively slower rate of decrease as the pH increased, as demonstrated by the metallic elements, Cl concentration decreased at a slower, steady rate until pH 8 was reached and then at a yet slower rate. The SO_4 concentration increased from pH 4 to pH 6 and then decreased at an increasing rate as the pH increased. The low SO_4 concentration at pH 4 may be due to pretreatment of the leachate required for the analysis of this species at this pH. However, even if the concentration is extrapolated back from the data at pH 6 and greater, this is the only species examined in this study where the curve of concentration versus pH is convex upward.

Thus the presence of acid protons attacking the ash particles and displacing the heavier and less chemically active species greatly affect the mobility of these species. According to the volatilization-adsorption model discussed previously, there is a coating of various species on the surface of the glassy matrix of the fly ash particles that is fairly soluble even without the presence of acid protons. However, the presence of the acid protons greatly increases the mobility of these species. The increase in the concentration of the species examined in this study between the natural pH of the slurry at 11.67 to 11.89 to the slurries maintained at pH 4 ranged from a low of 200% for Cl (KP&L 39) to 110,000% for As (KP&L 38). Whether the increase is due to the removal of adsorbed material bound more tightly to the surface of the glassy core of the fly ash particles or to etching of the glassy core itself is not known. This represents an area for further study.

The five elements examined in this study for which the Environmental Protection Agency (1978) has established toxicity levels: As, Cd, Cr, Pb and Se, are all present in toxic amounts at pH 4. However, the conditions to maintain this low pH are much more extreme than specified by the E.P.A. methodology, nor are they likely to be encountered in the natural world. Such extremely acidic conditions do occur, but are relatively rare. The concentrations of four of these elements quickly drop below the levels established for toxicity criteria as the pH increases to 5. Even under these less stringent conditions, a considerable amount of acid is still required. However, Se remains quite mobile. The average Se concentration for all three of the fly ash samples examined does not drop below the toxicity criterion of 0.1 mg/L until pH 8.3. Although a significant amount of acid is required to keep the highly alkaline fly ash at this pH, it is not beyond the amount specified by the E.P.A. The methodology of this study is sufficiently different from that of the E.P.A. to prevent the unequivocal classification of these samples as toxic due to the leachability of Se, but it suggests that this may be so. At the natural pH of the slurries, all five elements were found to be less concentrated in the leachate than the toxicity criteria levels. Further study of the selenium problem is suggested.

The natural pH of the fly ash slurries was observed to follow a consistent pattern. The pH initially rose to 11.6 or greater within the first minute of the addition of the fly ash and continued to a relative maximum of 11.8 to 12.0 within 3 to 5 min. It then decreased to a relative minimum of pH 11.6 to 11.9 after 10 to 40 min had elapsed. The pH then increased again to a second relative maximum of 11.8 to 12.1 after 1 to 5 hr, typically 2 to 4 hr, had elapsed and then continued to decrease for the remainder of the experiments to a final pH of 11.5 to 11.7. The pH would probably continue to drop, but the experiments were halted after 24 hr. The reason for this bimodal behavior is not well understood.

Rates of leaching are thought to correlate to the rate at which the acetic acid was added to maintain a constant pH. Linear relationships are observed when the amount of acid used to maintain the pH is plotted against the logarithm of time. The linearity of the plot is quite good for the experiments performed at pH 8, but grows less precise as the pH decreases. The deviation of the data from a straight line for the pH 4 experiments, the least linear series, mimics the deviation of the natural pH of the slurries from a constant value with time. The slopes of the best fit lines determined for each of the three series of experiments increases only slightly from 0.0007 at pH 8 to 0.0010 at pH 6, but then takes a major increase to 0.0205 at pH 4. Still the amount of the increase of the slopes is less than expected considering that the difference of two pH units between each series of experiments represents an one hundred fold increase in the acidity of the slurry.

Size fractionation studies of the fly ash indicate that over 40% of the particles are less than 5 μm in diameter and over 65% are less than 20 μm in diameter. X-ray microprobe analyses of ten major elements were performed on the different size fractions. CaO, SiO_2 and Al_2O_3 make up over 75% of the inorganic portion of the fly ash. The volatilization-adsorption model for the formation of fly ash predicts that at combustion temperatures the more volatile species will be enriched on the smallest particles due to the greater surface area per unit mass of the particles. SiO_2, FeO, TiO_2, SO_3 and P_2O_5 all behave as expected by the model. However, The nonvolatile CaO, Al_2O_3 and MgO were all found enriched in the smallest size fraction while the volatile Na_2O and K_2O displayed no particular trend in enrichment among the various size fractions. Further study of these discrepancies is also suggested.

Fly ash is a chemically and physically complicated material. The chemical composition of the source coal and the variation in combustion conditions of temperature, rate of combustion and other factors resulting from the changing demand for power with time can produce great variations in the chemical and physical properties of the fly ash. Even though great care was taken to split the bulk samples obtained from the same source over a range of time, considerable variation was commonly noted between similar experiments performed on splits obtained from the same sample as well as between different samples. Still, clear trends are observed when the results are averaged together. Based on these data, the conclusions discussed herein are presented with reasonable confidence.

BIBLIOGRAPHY

Adriano, D. C., A. L. Page, A. A. Elseewi, A. C. Chang and I. Straughan, 1980, Utilization and Disposal of Fly Ash and Other Coal Residues in Terrestrial Ecosystems: A Review: Journal of Environmental Quality, Vol. 9, No. 3, pp. 333-344.

Chu, Tien-Yung J., Richard J. Ruane and Peter A. Krenkel, 1978, Characterization and Reuse of Ash Pond Effluents in Coal-Fired Power Plants: Journal of the Water Pollution Control Federation, Vol. 50, pp. 2494-2508.

Churey, Dorothy J., Walter H. Gutenmann, Alina Kabata-Pendias and Donald J. Lisk, 1979, Element Concentrations in Aqueous Equilibriates of Coal and Lignite Fly Ashes: Journal of Agricultural and Food Chemistry, Vol. 27, No. 4, pp. 910-911.

Coles, David G., Richard C. Ragaini, John M. Ondov, Gerald L. Fisher, David Silberman and Bruce A. Prentice, 1979, Chemical Studies of Stack Fly Ash from a Coal-Fired Power Plant: Environmental Science and Technology, Vol. 13, No. 4, pp. 455-459.

Davison, Richard L., David F. S. Natusch, John R. Wallace and Charles A. Evans, Jr., 1974, Trace Elements in Fly Ash: Dependence of Concentration on Particle Size: Environmental Science and Technology, Vol. 8, No. 13, pp. 1107-1113.

Energy Resources Co., Inc., 1980, *Low-Rank Coal Study: National Needs for Resource Development*, Vol. 1, Walnut Creek, CA, 64 p.

Glass, Gary B., 1975, *Analyses and Measured Sections of 54 Wyoming Coal Samples: Report of Investigation No. 11:* Geological Survey of Wyoming, Laramie, WY, 219 p.

Greenberg, Arnold E., Joseph J. Connors, David Jenkins and Mary Ann H. Franson, editors, 1980, *Standard Methods for the Examination of Water and Wastewater:* American Public Health Association, Washington, DC, 1134 p.

Griffin, R. A., R. M. Schuller, J. J. Suloway, N. F. Shimp, W. F. Childers and R. H. Shiley, 1980, Chemical and Biolgical Characterization of Leachates from Coal Solid Wastes: Environmental Geology Notes, No. 89, Illinois State Geological Survey, Champaign, IL, 99 p.

Grisafe, David, 1986, State Geological Survey of Kansas, Lawrence, KS, personal communication.

Jones, L. H. and A. V. Lewis, 1960, Weathering of Fly Ash: Nature, Vol. 185, No. 4710, pp. 404-405.

Klein, David H., Anders W. Andren, Jeul F. Emery, Cyrus Feldman, William Fulkerson, William S. Lyon, Jack C. Ogle, Yair Talmi, Robert I. Van Hook and Newell Bolton, 1975, Pathways of Thirty-seven Trace Elements Through Coal-Fired Power Plant: Environmental Science and Technology, Vol. 9, No. 10, pp. 973-979.

Kopsick, Deborah A. and Ernest E. Angino, 1981, Effect of Leachate Solutions from Fly and Bottom Ash on Groundwater Quality: Journal of Hydrology, Vol. 54, pp. 341-356.

Larson, J. Dale, 1985, Kansas Power and Light Co., Topeka, KS, personal communication.

Mason, B., 1966, Principles of Geochemistry: John Wiley and Sons, Inc., New York, NY, 329 p.

Natusch, David F. S., John R. Wallace and Charles A. Evans, Jr., 1974, Toxic Trace Elements: Preferential Concentration in Respirable Particles: Science, Vol. 183, pp. 202-204.

Perkin-Elmer Corp., 1982, Analytical Methods for Atomic Absorption Specrophotometry, Norwalk, CT, 416 p.

Phung, H. T., L. J. Lund, A. L. Page and G. R. Bradford, 1979, Trace Elements in Fly Ash and Their Release in Water and Treated Soils: Journal of Environmental Quality, Vol. 8, No. 2, pp. 171-175.

Ramage, Janet, 1983, Energy, A Guidebook: Oxford University Press, Oxford, Eng., 366 p.

Schmidt, Jack C. and James Boyer, 1983, An Overview of Coal Leasing, Mine Development, and Future Production in the Powder River Coal Basin, Montana and Wyoming: *Coal Development: Collected Papers*, Vol. 1, Scott Fisher, Project Coordinator, U. S. Dept. of the Interior, Bureau of Land Management, Washington, DC, pp. 123-156.

Skougstad, Marvin W., Marvin J. Fishman, Linda C. Friedman, David E. Erdmann and Sandra S. Duncan, editors, 1979, *Techniques of Water-Resources Investigations of the U. S. Geological Survey, Chapter A1: Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Book 5: Laboratory Analysis:* U. S. Government Printing Office, Washington, DC, 626 p.

Shannon, Robert H., 1982, *Handbook of Coal Based Electric Power Generation*: Noyes Publications, Park Ridge, NJ, 372 p.

Shepard, Michael, Dean Golden, Ralph Komai and Thomas Morasky, 1985, Utility Solid Waste: Managing the By-Products of Coal Combustion: Electric Power Research Institute Journal, Vol. 10, No. 8, pp. 20-35.

Smith, Richard D., James A. Campbell and Kirk K. Nielson, 1979, Concentration Dependence upon Particle Size of Volatilized Elements in Fly Ash: Environmental Science and Technology, Vol. 13, No. 5, pp. 553-558.

Theis, Thomas L. and John L. Wirth, 1977, Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems: Environmental Science and Technology, Vol. 11, No. 12, pp. 1096-1100.

United Nations Dept. of International Economic and Social Affairs, Statistics Office, 1985, *Energy Statistics Yearbook 1983*: United Nations Publishing Division, New York, NY, 475 p.

United States Environmental Protection Agency, 1978, Extraction Procedure: Federal Register, Vol. 43, No. 243, Monday, 18 December, pp. 58982-58957.

APPENDICES

APPENDIX 1: CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 38 Leaching Experiment: 2 pH: 4
As: 1.4 Fe: 970
Ca: 6960 Na: 330
Cd: 0.19 Pb: 3.1
Cr: 3.4 Se: 0.70
Cl^-: 6 SO_4^{2-}: 720

Sample: KP&L 38 Leaching Experiment: 3 pH: 4
As: 1.3 Fe: 920
Ca: 6340 Na: 280
Cd: 0.19 Pb: 3.1
Cr: 3.1 Se: 0.44
Cl^-: 6 SO_4^{2-}: 710

Sample: KP&L 38 Leaching Experiment: 4 pH: 4
As: 1.3 Fe: 940
Ca: 6700 Na: 280
Cd: 0.18 Pb: 2.4
Cr: 3.6 Se: 0.46
Cl^-: 6 SO_4^{2-}: 740

Sample: KP&L 38 Leaching Experiment: 5 pH: 4
As: 1.3 Fe: 840
Ca: 5950 Na: 220
Cd: 0.20 Pb: 2.8
Cr: 3.5 Se: 0.51

Sample: KP&L 38 Leaching Experiment: 6 pH: 4
As: 1.3 Fe: 660
Ca: 5440 Na: 270
Cd: 0.18 Pb: 2.1
Cr: 3.2 Se: 0.34

Sample: KP&L 39 Leaching Experiment: 1 pH: 4
As: 1.1 Fe: 800
Ca: 6100 Na: 262
Cd: 0.17 Pb: 2.6
Cr: 2.1 Se: 0.56
Cl^-: 4 SO_4^{2-}: 700

Appendix continued on next page.

APPENDIX 1, cont'd. CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 39 Leaching Experiment: 2 pH: 4
As: 1.1 Fe: 750
Ca: 6090 Na: 280
Cd: 0.17 Pb: 2.7
Cr: 2.3 Se: 0.88
Cl^-: 4 SO_4^{2-}: 660

Sample: KP&L 39 Leaching Experiment: 3 pH: 4
As: 1.2 Fe: 640
Ca: 5810 Na: 250
Cd: 0.17 Pb: 2.5
Cr: 2.5 Se: 0.67
Cl^-: 4 SO_4^{2-}: 660

Sample: KP&L 39 Leaching Experiment: 4 pH: 4
As: 1.0 Fe: 380
Ca: 6460 Na: 290
Cd: 0.15 Pb: 2.3
Cr: 1.8 Se: 0.65

Sample: KP&L 39 Leaching Experiment: 5 pH: 4
As: 1.0 Fe: 850
Ca: 6480 Na: 290
Cd: 0.17 Pb: 2.9
Cr: 2.2 Se: 0.55

Sample: KP&L 40 Leaching Experiment: 1 pH: 4
As: 1.3 Fe: 710
Ca: 8500 Na: 190
Cd: 0.16 Pb: 2.4
Cr: 3.0 Se: 0.89
Cl^-: 5 SO_4^{2-}: 640

Sample: KP&L 40 Leaching Experiment: 2 pH: 4
As: 1.3 Fe: 580
Ca: 8050 Na: 270
Cd: 0.15 Pb: 2.4
Cr: 2.8 Se: 0.67
Cl^-: 5 SO_4^{2-}: 710

Appendix continued on next page.

APPENDIX 1, cont'd. CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 40 Leaching Experiment: 3 pH: 4

As:	1.3	Fe:	640
Ca:	8480	Na:	190
Cd:	0.16	Pb:	2.7
Cr:	2.8	Se:	0.86
Cl^-:	5	SO_4^{2-}:	620

Sample: KP&L 40 Leaching Experiment: 4 pH: 4

As:	1.0	Fe:	590
Ca:	8700	Na:	260
Cd:	0.19	Pb:	2.9
Cr:	2.6	Se:	0.46

Sample: KP&L 40 Leaching Experiment: 5 pH: 4

As:	1.1	Fe:	540
Ca:	8510	Na:	260
Cd:	0.18	Pb:	2.8
Cr:	2.6	Se:	0.93

Sample: KP&L 38 Leaching Experiment: 2 pH: 6

As:	0.04	Fe:	2.0
Ca:	2440	Na:	120
Cd:	0.04	Pb:	0.2
Cr:	0.08	Se:	0.34
Cl^-:	4	SO_4^{2-}:	1010

Sample: KP&L 38 Leaching Experiment: 3 pH: 6

As:	0.04	Fe:	1.2
Ca:	2400	Na:	120
Cd:	0.04	Pb:	0.2
Cr:	0.07	Se:	0.26
Cl^-:	5	SO_4^{2-}:	1010

Sample: KP&L 38 Leaching Experiment: 4 pH: 6

As:	0.03	Fe:	2.0
Ca:	2440	Na:	120
Cd:	0.04	Pb:	0.2
Cr:	0.14	Se:	0.25
Cl^-:	7	SO_4^{2-}:	1010

Appendix continued on next page.

APPENDIX 1, cont'd. CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 38 Leaching Experiment: 5 pH: 6
As: 0.04 Fe: 1.9
Ca: 2300 Na: 120
Cd: 0.05 Pb: 0.2
Cr: 0.02 Se: 0.23

Sample: KP&L 39 Leaching Experiment: 1 pH: 6
As: 0.05 Fe: 4.0
Ca: 2820 Na: 90
Cd: 0.07 Pb: 1.6
Cr: <0.02 Se: 0.17
Cl^-: 2 SO_4^{2-}: 930

Sample: KP&L 39 Leaching Experiment: 2 pH: 6
As: 0.04 Fe: 5.2
Ca: 2870 Na: 90
Cd: 0.07 Pb: 1.5
Cr: <0.02 Se: 0.19
Cl^-: 2 SO_4^{2-}: 990

Sample: KP&L 39 Leaching Experiment: 3 pH: 6
As: 0.04 Fe: 5.4
Ca: 2880 Na: 90
Cd: 0.08 Pb: 1.3
Cr: <0.02 Se: 0.17
Cl^-: 3 SO_4^{2-}: 970

Sample: KP&L 39 Leaching Experiment: 4 pH: 6
As: 0.02 Fe: 1.5
Ca: 2740 Na: 110
Cd: 0.04 Pb: 0.2
Cr: <0.02 Se: 0.24

Sample: KP&L 39 Leaching Experiment: 5 pH: 6
As: 0.01 Fe: 1.7
Ca: 2700 Na: 110
Cd: 0.04 Pb: 0.2
Cr: <0.02 Se: 0.19

Appendix continued on next page.

APPENDIX 1, cont'd. CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 40 Leaching Experiment: 1 pH: 6

As:	0.07	Fe:	3.5
Ca:	3040	Na:	70
Cd:	0.07	Pb:	1.7
Cr:	<0.02	Se:	0.21
Cl^-:	4	SO_4^{2-}:	920

Sample: KP&L 40 Leaching Experiment: 2 pH: 6

As:	0.06	Fe:	5.1
Ca:	3050	Na:	70
Cd:	0.07	Pb:	1.7
Cr:	<0.02	Se:	0.25
Cl^-:	4	SO_4^{2-}:	910

Sample: KP&L 40 Leaching Experiment: 3 pH: 6

As:	0.06	Fe:	4.2
Ca:	3070	Na:	80
Cd:	0.07	Pb:	1.6
Cr:	<0.02	Se:	0.25
Cl^-:	4	SO_4^{2-}:	920

Sample: KP&L 40 Leaching Experiment: 4 pH: 6

As:	0.03	Fe:	1.2
Ca:	3080	Na:	80
Cd:	0.04	Pb:	0.2
Cr:	<0.02	Se:	0.19

Sample: KP&L 40 Leaching Experiment: 5 pH: 6

As:	0.02	Fe:	1.3
Ca:	3070	Na:	80
Cd:	0.05	Pb:	0.1
Cr:	<0.02	Se:	0.22

Sample: KP&L 38 Leaching Experiment: 1 pH: 8

As:	0.02	Fe:	0.9
Ca:	1570	Na:	100
Cd:	0.02	Pb:	<0.1
Cr:	0.14	Se:	0.14
Cl^-:	4	SO_4^{2-}:	880

Appendix continued on next page.

APPENDIX 1, cont'd. CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 38 Leaching Experiment: 2 pH: 8
As: 0.02 Fe: 0.9
Ca: 1540 Na: 100
Cd: 0.02 Pb: <0.1
Cr: 0.11 Se: 0.13
Cl^-: 4 SO_4^{2-}: 870

Sample: KP&L 38 Leaching Experiment: 3 pH: 8
As: 0.01 Fe: 1.2
Ca: 1640 Na: 100
Cd: 0.02 Pb: <0.1
Cr: 0.12 Se: 0.10
Cl^-: 3 SO_4^{2-}: 920

Sample: KP&L 39 Leaching Experiment: 1 pH: 8
As: 0.01 Fe: 4.2
Ca: 2040 Na: 100
Cd: 0.02 Pb: 0.1
Cr: 0.06 Se: 0.08
Cl^-: 2 SO_4^{2-}: 730

Sample: KP&L 39 Leaching Experiment: 2 pH: 8
As: 0.01 Fe: 1.1
Ca: 2010 Na: 100
Cd: 0.02 Pb: 0.1
Cr: 0.06 Se: 0.09
Cl^-: 3 SO_4^{2-}: 740

Sample: KP&L 39 Leaching Experiment: 3 pH: 8
As: 0.01 Fe: 1.1
Ca: 2070 Na: 100
Cd: 0.02 Pb: 0.1
Cr: 0.09 Se: 0.07
Cl^-: 3 SO_4^{2-}: 730

Sample: KP&L 40 Leaching Experiment: 1 pH: 8
As: 0.01 Fe: 1.4
Ca: 2150 Na: 80
Cd: 0.02 Pb: 0.1
Cr: 0.04 Se: 0.17
Cl^-: 3 SO_4^{2-}: 710

Appendix continued on next page.

APPENDIX 1, cont'd. CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 40 Leaching Experiment: 2 pH: 8
As: 0.01 Fe: 1.2
Ca: 2250 Na: 80
Cd: 0.02 Pb: 0.1
Cr: <0.02 Se: 0.14
Cl^-: 3 SO_4^{2-}: 760

Sample: KP&L 40 Leaching Experiment: 3 pH: 8
As: <0.01 Fe: 1.1
Ca: 2290 Na: 90
Cd: 0.03 Pb: 0.1
Cr: <0.02 Se: 0.09
Cl^-: 3 SO_4^{2-}: 770

Sample: KP&L 38 Leaching Experiment: 1 pH: 11.8
As: <0.01 Fe: 2.2
Ca: 160 Na: 70
Cd: 0.01 Pb: <0.1
Cr: 0.13 Se: 0.01
Cl^-: 2 SO_4^{2-}: 90

Sample: KP&L 38 Leaching Experiment: 2 pH: 11.7
As: <0.01 Fe: 1.7
Ca: 180 Na: 70
Cd: <0.01 Pb: <0.1
Cr: 0.11 Se: 0.01
Cl^-: 3 SO_4^{2-}: 60

Sample: KP&L 38 Leaching Experiment: 3 pH: 11.7
As: <0.01 Fe: 2.6
Ca: 170 Na: 70
Cd: 0.01 Pb: <0.1
Cr: 0.10 Se: 0.02
Cl^-: 3 SO_4^{2-}: 70

Sample: KP&L 39 Leaching Experiment: 1 pH: 11.9
As: <0.01 Fe: 10.1
Ca: 220 Na: 80
Cd: <0.01 Pb: <0.1
Cr: 0.06 Se: 0.02
Cl^-: 2 SO_4^{2-}: 100

Appendix continued on next page.

APPENDIX 1, cont'd. CHEMICAL ANALYSES OF FLY ASH LEACHATE SAMPLES (mg/L).

Sample: KP&L 39 Leaching Experiment: 2 pH: 11.8

As:	<0.01	Fe:	10.6
Ca:	230	Na:	80
Cd:	<0.01	Pb:	<0.1
Cr:	0.06	Se:	0.02
Cl^-:	2	SO_4^{2-}:	120

Sample: KP&L 39 Leaching Experiment: 3 pH: 11.8

As:	<0.01	Fe:	7.0
Ca:	200	Na:	80
Cd:	0.01	Pb:	<0.1
Cr:	0.05	Se:	0.02
Cl^-:	2	SO_4^{2-}:	130

Sample: KP&L 40 Leaching Experiment: 1 pH: 11.8

As:	<0.01	Fe:	7.4
Ca:	210	Na:	60
Cd:	<0.01	Pb:	<0.1
Cr:	0.11	Se:	0.02
Cl^-:	2	SO_4^{2-}:	90

Sample: KP&L 40 Leaching Experiment: 2 pH: 11.8

As:	<0.01	Fe:	8.7
Ca:	240	Na:	60
Cd:	<0.01	Pb:	<0.1
Cr:	0.07	Se:	0.02
Cl^-:	2	SO_4^{2-}:	110

Sample: KP&L 40 Leaching Experiment: 3 pH: 11.8

As:	<0.01	Fe:	8.8
Ca:	220	Na:	50
Cd:	<0.01	Pb:	<0.1
Cr:	0.11	Se:	0.02
Cl^-:	2	SO_4^{2-}:	100

APPENDIX 2. U. S. ENVIRONMENTAL PROTECTION AGENCY EXTRACTION PROCEDURE

From the Federal Register, Vol. 43, No. 243--Monday, Dec. 18, 1978, pp. 58956-58957.

(d) *Toxic waste.* (1) *Definition*--A solid waste is a hazardous waste if, according to the methods specified in paragraph (2), the extract obtained from applying the Extraction Procedure (EP) cited below to a representative sample of the waste has concentrations of a contaminant that exceed any of the following values:

Contaminant:	*Extract level, milligrams per liter*
Arsenic	0.50
Barium	10.0
Cadmium	0.10
Chromium	0.50
Lead	0.50
Mercury	0.02
Selenium	0.10
Silver	0.50
Endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octhydro-1,4-endo,endo-5,8-dimethanonaphthalene	0.002
Lindane (1,2,3,4,5,6-hexachlorocyclohexane gamma isomer)	0.040
Methoxychlor ((1,1,1-trichloroethane)2,2-bis(p-methoxyphenyl))	1.0
Toxaphene ($C_{10}H_{10}Cl_8$-technical chlorinated camphene, 67-69 percent chlorine)	0.050
2,4-D (2,4-dichlorophenoxyacetic acid)	1.0
2,4,5-TP Silvex (2,4,5-trichlorophenoxypropionic acid)	0.10

Note: Extract levels specified for the above substances equal ten times the EPA National Interim Primary Drinking Water Standards for these substances. These standards are being revised. Extract levels specified above will be changed to reflect revisions to these standards. Also, EPA is considering use of the Water Quality Criteria under the Clean Water Act as a basis for setting extract levels, in addition to the EPA National Interim Primary Drinking Water Standards.

(2) *Identification method.* (i) *Extraction procedure.* (A) Take a representative sample (minimum size 100 gms) of the waste to be tested and separate it into its component phases using either the filtration method or the centrifugation method described in this section. Reserve the liquid fraction under refrigeration at 1-5°C (34-41°F) for use as

described in paragraph (F) of this section.

(*1*) Filtration Method. (This section describes a procedure not used in this study.)

(2) Centrifugation Method.
Equipment: Centrifuge (e.g. Damon-IEC catalog no. 7165, Damon-IEC Corp., Needham Heights, MA, or equivalent) equipped with a rotor for 600 ml to 1 liter containers (Damon-IEC catalog 976, or equivalent). For flammable material containing wastes, explosion proof equipment if recommended.

GLASS CENTRIFUGE BOTTLES

Procedure: 1. Centrifuge sample for 30 minutes at 2300 rpm. Hold temperature at 20-40°C (68-104°F).
2. Using a ruler, measure the size of the liquid and solid layers, to the nearest mm (0.40 inch). Calculate the liquid to solid ratio.
3. Repeat 1 and 2 above until the liquid:solid ratio calculated after two consecutive 30 minute centrifugations is within 3%.
4. Decant or siphon off the layers and extract the solid as described in paragraph B.

(B) Take the solid portion obtained in paragraph (i), and prepare it for extraction by either grinding it to pass through a 9.5 mm ($^3/_8$") standard sieve or by subjecting it to the following structural integrity procedure.

Structural Integrity Procedure

Equipment: Compaction tester having a 1.23 inch diameter hammer weighing 0.73 lbs. and having a free fall of 6 inches (one suitable device is the Associated Design and Manufacturing Co., Alexandria, Va., catalog no. 125).
Procedure: 1. Fill the sample holder with the material to be tested. If the waste sample is a monolithic block, then cut a representative sample from the block having the dimensions of a 1.3" dia. x 2.8" cylinder.
2. Place the sample holder in the Compaction Tester and apply 15 hammer blows to the sample.
3. Remove the now compacted sample from the sample holder and transfer it to the extraction apparatus for extraction.

(C) Take the solid material from paragraph (B), weigh it and place it in the extractor. A suitable extractor will not only prevent stratification of the sample and extraction fluid but also insure that all sample surfaces are continuously brought into contact with the well mixed extraction fluid. (When operated at greater than 40 rpm, one suitable device is available as Part No. 3736 by the Associated Design and Mfg. Co., Alexandria, Va. 22314.)

(D) Add to the extractor a weight of deionized water equal to 16 times the weight of solid material added to the extractor. This includes any water used in transferring the solid material to the extractor.

(E) Begin agitation and adjust the pH of the solution to 5.0 ± 0.2 using 0.5N acetic acid. Hold the pH at 5.0 ± 0.2 and continue agitation for 24 ± 0.5 hours. If more than 4 ml of acid for each gm of solid is required to hold the pH at 5, then once 4 ml of acid per gm has been added, complete the 24 extraction without adding any additional acid. Maintain the extractant at 20-40°C (68-104°F) during extraction. It is recommended that a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, OR 97123, or equivalent, be used for controlling pH. If such a device is not available then the following manual procedure can be employed.

Manual pH Adjustment

1. Calibrate pH meter in accordance with manufacturer's specifications.
2. Add 0.5N acetic acid and adjust pH of solution to 5.0 ± 0.2. If more than 4 ml of acid for each gm of solid is required to hold the pH at 5, then once 4 ml of acid per gm has been added, complete the 24 hour extraction without adding any additional acid. Maintain the extract at 20-40°C (68-104°F) during extraction.
3. Manually adjust pH of solution at 15, 30, and 60 minute intervals moving to the next longer interval if the pH did not have to be adjusted more than 0.5 pH units since the previous adjustment.
4. Continue the adjustment procedure for a period of not less than 6 hours.
5. Final pH after a 24 hour period must be within the range of 4.9-5.2; unless 4 ml of acid per gram of solid has already been added.
6. If the conditions of 5 are not met, continue pH adjustment at approximately one hour intervals for a period of not less than 4 hours.

(F) At the end of the 24 hour extraction period, separate the material in the extractor into solid and liquid phases as in paragraph (A). Adjust the volume of the resulting liquid phase with deionized water so that its volume is 20 times that occupied by a quantity of water at 4° C equal in weight to the initial quantity of solid material charged to the extractor (e.g., for an initial weight of 1 gm, dilute to 20 ml). Combine this solution with the original liquid phase from paragraph (A). This combined liquid, and any precipitate which may later form, is the

Extraction Procedure Extract.

(ii) *Analysis*--Analyses conducted to determine conformance with Section 250.13(b)(1) shall be made in accordance with the following or equivalent methods:

(A) *Arsenic*--Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," pp. 95-96, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(C) *Cadmium*--Atomic Absorption Method, "Standard Methods for the Examination of Water and Waste Water," latest edition, or "Methods for Chemical Analysis of Water and Wastes," pp. 101-103, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(D) *Chromium*--Atomic Absorption Method, "Standard Methods for the Examination of Water and Waste Water," latest edition, or "Methods for Chemical Analysis of Water and Wastes," pp. 112-113, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(E) *Lead*--Atomic Absorption Method, "Standard Methods for the Examination of Water and Waste Water," latest edition, or "Methods of Chemical Analysis of Water and Wastes," pp. 112-113, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(G) *Selenium*--Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," p. 145, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.