RELEASE OF MERCURY DURING LEACHING OF FLY ASH

An Honors Thesis

Presented in Partial Fulfillment of the Requirements for

Graduation with Distinction in the

College of Engineering at The Ohio State University

By

Ellen Regennitter

The Ohio State University 2007

Honors Thesis Examination Committee:

Approved by

Dr. Harold Walker, Advisor

Dr. Linda Weavers

 Harold Walker Adviser Undergraduate Program in Engineering

ABSTRACT

Fly ash created in the generation of energy contains mercury. Currently, the most accepted use for fly ash is as an inexpensive alternative to Portland cement in concrete mixtures. Because of new mercury-air standards, determining the affect of mercury within concrete structures is important. Analyzing the make-up of the fly ash, then, is used in this research concept to gain an understanding of the impact of the chemical make-up of fly ash on a concrete structure. Pinpointing the fly ash - concrete interaction and synthesizing the characteristics demonstrated in a concrete containing fly ash ultimately leads to a perception of the release of mercury from these materials in their final state. Leachate tests were preformed to simulate the release of mercury from fly ash samples in Municipal Solid Waste Landfills and Construction Landfills. The results of these analyses led to the determination of the limited short and long-term release of mercury from the samples and these conclusions lead to a basic understanding of the impact fly ash sample release of mercury can have on concrete structures.

Dedicated to my family

ACKNOWLEDGMENTS

I wish to thank my adviser, Dr. Hal Walker, for guidance, support, encouragement and patience for allowing me to gain time management experience and emphasizing the importance of learning in a hands-on environment.

I thank Dan Golightly for introducing me to work in the laboratory and initially developing my comfort level in this working area.

I am grateful to Ryan Mackos for spending long hours helping me to finish all research analysis. Without his help, none of these conclusions could have been reached.

VITA

PUBLICATIONS

Not Applicable

FIELDS OF STUDY

Major Field: Structural Engineering

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

Coal fly ash is produced as a byproduct of energy generation. As coal-fired boilers generate electricity, fly ash and flue gas desulfurization byproducts are created. In the process of energy generation, mercury is volatized and converted to elemental mercury at the very high temperatures located within coal-fired utility boilers (EPA, 2000). A portion of this mercury is re-oxidized as the flue gas is cooled. As conversion from gaseous elemental mercury to HgC_{ξ} and HgO occurs, the mercury is effectively captured in fly ash material (EPA, 2000). HgC_{ξ} is effectively captured during this process with $SO₂$ control, but because some mercury forms that are created are more difficult to remove, it is important to understand the effect of their volatility and limited solubility. Once formed, fly ash can be utilized as an inexpensive alternative to Portland cement in concrete, as it has been found to enhance certain desirable properties in freshly prepared and hardened concrete.

Electrical power generator production of fly ash is approximately 15% of the fly ash that is incorporated into structural concretes and grout (American Coal Ash Association, 2002). Once included in the concrete mix, fly ash reduces the water

requirements of the concrete mixture. A concrete made with fly ash also has increased workability, reduced heat of hydration and a reduced air content. After the concrete has cured, it has an increased compressive strength as a product of the reduced water content. Typically, the fly ash concrete will have lower absorption and permeability and generally improved defense against sulfate attack. Concrete is a porous material and mercury bound to fly ash ultimately may be released following concrete placement. In addition to the prolonged threat of mercury release is an initial potential for release through the mixing, pouring, curing and temperature increase of concrete. In any of these processes, the temperature of fly ash could increase the volatization and release of mercury from the concrete material.

Recently, the presence of mercury in fly ash material has been a topic of great importance based on the announcement of the Clean Air Mercury Rule. The rule, which is expected to come into effect in 2007, will significantly impact the reuse initiatives of coal combustion byproducts. Because fly ash contains mercury, especially when activated carbon injection is used as a means to achieve greater mercury reductions in generation, it is important to understand the impact of mercury levels in fly ash concrete applications. As mercury emissions controls are brought on-line, an increase in the amount of mercury contained in fly ash is expected, and because concrete is a porous material, the mercury bound to fly ash may ultimately be released to the atmosphere.

Because mercury is a well known neurotoxin, it is important to determine the fate of mercury in concrete. Therefore, the objectives of this research analysis are to identify the analyte makeup of typical fly ash samples and to determine the extent to which leaching releases mercury from fly ash to the atmosphere. In previous work, the gaseous

release of mercury during curing of concretes was determined. In this study,

investigation continues to examine the leaching of mercury to water during disposal and reuse of fly ash. The project centered around identifying the sample characteristics of fly ash specimens and analysis of their effects on mercury release. Leaching data was modeled using geochemical speciation methods to develop a better understanding of the roles of different solid phases in controlling the solution of chemistry of the leachate. The observations can then be correlated to the effects of fly ash utilized in concrete applications. Using two specific leach testing methods, fly ash samples were tested for reactions in landfills and reactions under acid rain conditions.

First, five different samples of fly ash were selected. Each sample of fly ash was created in a generation facility from a different location which could have had an affect on the level of mercury in the sample. The different fly ashes were then used in typical leachate testing procedures to synthesize the natural affects of rain water and landfill acid on the sample. The fly ash - leachate solutions were then analyzed using a Varian SpectrAA to determine the mercury in each sample. The solutions were also subjected to an Inductively Coupled Plasma Atomic Emissions Spectrometry test to determine the additional analyte make-up of the samples. In the end, the data collected from these tests were manipulated to determine if the effects of the mercury and additional analyte material in the fly ash could pose a threat to health if released through naturally occurring leaching.

This report is organized as a thorough investigation of fly ash, the elemental composition of the samples, the mercury content in the concrete ingredients and the result of that elemental makeup. The leaching test procedures are then discussed as an example

3

of two ways that fly ash elemental makeup can leach into the water supply. The discussion will also serve as an attempt to prove the adequacy of this analysis for assessment of environmental impact. Finally the test methods and test results for the experiments are discussed and conclusions are drawn from the data collected.

CHAPTER 2

TEST METHODS

2.1 Concrete and Fly Ash

As one of several coal combustion by-products, fly ash is the finely divided mineral residue resulting from the combustion of coal in electric generation plants. Because fly ash is an inorganic incombustible matter present in the coal, it becomes fused during combustion into an amorphous structure. Once burned, fly ash becomes suspended in exhaust gas as a solidified material and typically is collected by electrostatic precipitators. Generally, fly ash particles are cylindrical and range in size from .4 micrometers to 100 micrometers. Fly ash particles are comprised mostly of aluminum oxide, silicon dioxide, and iron oxide. Because they are pozzolanic, they react to form cementious material. In 1996, America's coal-fired power plants produced 53 million tons of fly ash. Although the chemical and physical properties of coal ash make it ideal for a variety of engineering applications, it must compete against other inexpensive bulk materials like sand and gravel. As a result, there are only certain areas where it is economically advantageous to transport and handle the fly ash. About three-quarters of the fly ash produced in the United States is not recycled for commercial use. Instead, the fly ash is placed in a specifically designed landfill. To prevent environmental impacts, landfill sites are carefully chosen to avoid flood plains and wells are typically installed around the site so that the quality of the surrounding water can be routinely inventoried.

Fly ash that is recycled is utilized in several different ways. Power plant fly ash is used in autoclaved aerated concrete blocks, liquid fixation, blasting grit, highway ice control, masonry blocks, concrete admixture, as material in lightweight alloys, roadway and runway construction, flowable fill material, roofing granules, grouting and structural fill. Fly ash is used as a high-performance substitute for Portland cement and sometimes as an addition to the clinker which is ground to form Portland cement. The material can replace up to 50% of Portland cement by mass in concrete and changes the chemical make-up of the concrete mix in several different ways which can lead to higher final strength and reduced risk of chemical corruption. Replacing Portland cement with fly ash also decreases the greenhouse gas signature of concrete by reducing carbon dioxide production. Coal fly ash has been used around the world as an ingredient of concrete for 60 years and many United States suppliers routinely use fly ash in concrete mixtures. The ash is processed into pellets that make it more readily utilized as an aggregate in concrete as well.

Most health-related fly ash concerns focus on the potential health risk of inhalation, ingestion, direct contact or exposure to trace elements. Coal fly ash particles are essentially insoluble aluminosilicate glasses, however trace substances on the ash surface may still be soluble. Water, acid rain and other liquids can percolate through ash and dissolve, or leach, trace elements from the ash. The analyte make-up could then potentially reach a drinking water source such as groundwater, rivers or lakes. Suspended particles would be removed from the water through filtration at water treatment plant; however, the dissolved elements would not be removed through this process.

6

Recycling fly ash in products and construction carries many benefits – and the focus of this study has been to rule out potential hazards from this recycling process so that barriers to re-use of fly ash are minimized. Using coal ash as cement can mean that the process consumes less energy and limestone than production of conventional cement – and avoiding electricity production lessens overall emissions. In addition, carbon dioxide emissions from cement kiln firing are reduced in direct proportion to the amount of ash substituted in a concrete mix.

Figure 2.1: Fly ash beads at the microscopic level

CCP Production & Beneficial Use (1966 - 2004)

Figure 2.2: Usage of Coal Combustion Products

Figure 2.3: Production and Usage of Coal Combustion Products

Figure 2.4: Potential Uses of Coal Ash By-products

2.2 Fly Ash Elemental Composition, Samples and Mercury Content in Concrete Elements

Five different coal fly ash samples were utilized in this research study. The fly ash was classified as Class F and it originated from eastern bituminous coal combusted electrical utilities. Class F fly ash is characterized for the content, specific surface area and loss of ignition values. As required by ASTM, Class F fly ash should have an LOI less than 6%. The concentrations of SiO_2 , $Fe₂O₃$ and $Ab₂O₃$ must be greater than 70%. In a previous study, the elemental composition of the fly ash was verified using Cold Vapor Atomic Adsorption Spectrometry and Cold Vapor Atomic Fluorescence Spectrometry in determining the mercury and inductively coupled plasma – atomic emission spectrometry to verify the concentrations of silicon, iron, aluminum and sulfur.

Elemental Composition	Concentration (%)
Aluminum	15.1
Barium	0.3
Calcium	2.4
Iron	2.3
Magnesium	0.7
Potassium	1.5
Silicon	26.9
Sodium	0.7
Sulfur	0.1
Zinc	0.1
Arsenic	16.6
Cadmium	2.5
Cobalt	34.8
Chromium	129
Copper	127
Lead	27.2
Lithium	197
Manganese	129
Mercury	0.117
Molybdenum	15.1
Nickel	84.7
Phosphorus	930
Selenium	18.8
Strontium	75

Table 2.1: Elemental Composition of Fly Ash Samples

As the demand for finer, more accurately sized fly ash grows, classification methods for fly ash ingredients have become more sophisticated. Generally speaking, most powders are the result of a comminution process that creates a combination of fly ash samples which dictate characteristic hardness or abrasive nature of the material.

There are a range of machines available for the comminution process and each has its own particular ability to break compounds through compression, impact or attrition. Therefore the classification of dry powders using conventional sieving techniques becomes progressively more important. For a given classified sample, the specific gravity of materials and the separation or cut size moves the sample up or down the classification scale. There are many reasons to classify the fly ash produced through electrical generation and the criterion can range from simply the size of the largest particle to the decorative finish or surface coating of the materials. Because the ASTM codes have a very heavy emphasis on the chemistry of fly ash and the chemistry of fly ash is highly dependent on the mineralogy and particle size, it is therefore important to understand this classification process and the impact of the particle size.

There are two parameters that determine the reactivity of fly ash – mineralogy and particle characteristics. Particles are mostly glassy, solid, and spherical in shape and there may also be unburned carbon present depending on burn efficiency. Particles of fly ash range in size from 1 to 10 microns and regardless of the type of classification, the ash will contribute to the 7 and 28 day strengths of concrete.

To determine element al concentrations of the samples before leaching tests were preformed, a solution of fly ash was prepared in a microwave-heated digestion method of a closed vessel containing 300mg of fly ash and an acid mixture of nitric, hydrochloric and hydrofluoric acids. (EPA 2000) The Varian VISTA was calibrated using matrix matched sample solutions and the concentrations of each test produced backgroundcorrected relative intensities for the 9 spectral lines that correlate with aluminum, iron and silicon for a simultaneous available emissions of 1.2kW plasma.

12

The classification of fly ash is important in the selection of ash that is used in concrete mixtures and each different classification can mean something different for the mercury content of the samples. Fly ash is most beneficially used as a plasticizer, and the charged cement particles tend to break bonds and flocculate. This action is different than the normal effect of cement in concrete which disperses through cement particles and tends to adsorb to surfaces and act as a repellent. Certain types of reactive fly ash particles act as a very powerful repellent which because of their charges and dependent on the presence of reactive crystalline phases in the ash.

Figure 2.5: Summary of processes for classification of fly ash

Previous experiments were designed to determine the background mercury concentration in Portland cement. The analysis was conducted using a Varian Hot Block and samples were digested and then transferred to high-density polyethylene bottles and

subjected to Cold Vapor Atomic Adsorption Spectrometry and Cold Vapor Atomic Fluorescence Spectrometry testing. The intent of this project was to submit the fly ash to a similar test to determine the extent of release of mercury, iron, silicon and sulfur, which is found in the chemical makeup, to the environment during leaching.

2.3 Experimental Setup and Leaching Testing

Leaching tests serve to quantify the source terms for fate and transport modeling. The purpose of the testing is to obtain aqueous phase concentrations of constituents which are released from solids when placed in a land disposal unit. The underlying assumption is that if the constituent does not leach from the waste, then land disposal of that constituent is not a threat to groundwater. Toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) have been widely used to generate leachate concentrations for all types of solids for both organic and inorganic constituents. The assumption is that potentially hazardous wastes comprise at most 5% of the volume of the material deposited in municipal solid waste landfills. The municipal waste is assumed to degrade and produce an acidic liquid to which the waste is exposed. Thus, a 5%/95% relationship leads to the specific composition of the acetic acid solution used in the TCLP test.

To separate forms of leaching, test procedures exist that are applicable to a study focusing on the effects of fly ash in the environment. The toxicity characteristic leaching procedure (TCLP) works to determine the mobility of organic and inorganic analytes in solid wastes. The TCLP test method is utilized in this project when the liquid fractions of the TCLP extract indicated a regulated compound was present. In this method, the fly

ash samples are subjected to 18 hour and 7 day interaction with the leaching solution. For liquids containing .5% solids, the liquid was separated from the solid phase using a filtration device and then stored for analysis. The leaching solution in this method is a mixture of glacial $CH₃CH₂OOH$, reagent water, and NaOH. The solution is diluted to a volume of 1 liter and made to have a pH of 4.93. This method also places requirements on the minimal size of the field sample, depending on the physical state of the waste. Immediately after TCLP extracts are extracted, the samples were prepared for analysis as specified in the procedure. Samples are allowed to be refrigerated, and were refrigerated in this project following preparation for analysis. After all samples were gathered for analysis, the ICP-AES and SpectrAA analyses were utilized. The method was completed in duplicate.

Synthetic Precipitation Leaching Procedure (SPLP) is designed to simulate a monodisposal of waste and reveal the soluble phases of a sample being tested. The test aids in predicting the geochemical effect of a "flush" on a material and the extraction liquid used in this method is similar to the TLCP method; however, it mirrors the effects of precipitation leaching rather than municipal landfill leachate. Static leaching tests, like these, are short term tests and involved agitating samples using a rotator device and then sampling the resulting solution. The SPLP test is a method designed to predict and determine the potential for leaching metals into ground and surface waters and uses a 1:20 liquid to solid ratio. There is a rigorous leach of the material (for 18 hours and 7 days) and the extraction fluid is intended to simulate precipitation which occurs naturally east of the Mississippi river as a fluid slightly acidic to reflect industrialization and air pollution impacts on precipitation.

Figure 2.6: Rotator Device for TCLP and SPLP testing

2.4 Inductively Coupled Plasma Atomic Emissions Spectrometry (ICP-AES)

Flame spectroscopy, the distinctive optical colors that are produced when compounds of certain metals are vaporized in flames, is a highly sensitive and specific means of identifying minute quantities of certain elements in materials. Optical emission spectrometry developed into a powerful method of chemical analysis and in these developments, the concentration of a specific element in a sample can be related to the intensity of lines in its optical spectrum. Modern inductively coupled plasma atomic emissions spectrometry relies on the same principles as flame spectrometry and determines minute amounts of a very wide range of elements even in the presence of much greater quantities of other elements. In analyzing samples, the inductively coupled plasma atomic emissions spectrometry machine relates the chemical solution samples to a set of calibrating standard. Each standard contains an accurately known concentration of analyte element and a range of concentration for each element in the set is chosen to

include the expected concentration of that element in the sample solutions. The calibrating solutions and sample solutions are sprayed into the plasma which is created in the machine using Argon, and the intensities of appropriate emission lines are recorded. The concentrations of the element in each sample solution are determined from the calibrating graphs.

The plasma used in this method for analysis is simply a gas whose properties are influenced by the presence of a significant concentration of ions and electrons. These exist in approximately equal numbers over the volume of the plasma, so overall electrical neutrality is maintained. ICP instrumentation relies on the used of the tesla coil to ignite the plasma and then inject the sample flow into the base of the plasma. The bench top ICP-AES is the third generation of ICP instrumentation and coordinates usage of computer control, innovative optical design and lower argon and power consumption over the life of the machine. The sample introduction system transports the analytes of interested to the excitation source that causes the sample to undergo desolvation and excitation resulting in emission of characteristic radiation. Due to the high temperature of the ICP, singly charged ions dominate and the spectrometer separates the radiation of interest so that the detection system measures the intensity of the selected radiation as compared to the standard.

2.5 Varian SpectrAA Testing

Samples were also analyzed by the Varian SpectrAA 880Z Zeeman Atomic Absorption Spectrometer (AAS). Because all atoms can absorb light in certain wavelengths, these wavelengths can identify an atomic spectra based on characteristic spectroscopic lines. Wavelengths are sharply defined and when a range of wavelengths is surveyed and compared, lines which originate in the ground state atom are most often of interest in atomic absorption spectroscopy and are called resonance lines. With particular spectroscopic characteristics, each element comprises a number of discrete lines. Using atomic absorption spectroscopy in conjunction with the analysis of this experiment therefore allows analyte elements in a leachate solution to be compared spectroscopic ally to calibration solutions enabling the concentration of analyte to be defined for a given sample. Using the Beer-Lambert Law to define a relationship between analyte concentration and light absorption, it can be seen that increased sensitivity can be achieved in electrothermal atomization – in the case of this experiment, allowing the mercury concentration in a sample of fly ash to be more highly detected.

Graphite furnace atomic absorption has become a field of analytic chemistry focused on determining very low levels of trace metals in a variety of sample types. In this form of analysis, molecules and compounds are broken down to atoms and ions. Because light absorption or emissions is in discrete energy packets, the different in energy between the energy levels is inversely proportional to the wavelength of emitted light. Using a hollow cathode lamp, a furnace creates and contains atoms in the light path. Atom population is then exposed to HCL emission at the resonance wavelength and the light transmission is measured and absorbance is calculated. The detection limit for CVAAS is .1 parts per billion.

CHAPTER 3

TEST RESULTS AND DISCUSSION

3.1 Fly Ash Characterization: Sampling, Sample pH testing, Total Dissolved Solids Test

Testing procedures, including quality control, were conducted in accordance with EPA Test Methods 1131 and 1132. First, fly ash samples were analyzed to ensure that the particle size was less than 1.0cm. Two different leaching solutions were used to complete the experiment. In this method, the fly ash samples were subjected to 18 hour and 7 day interaction with the leaching solution. To do this, 100g of fly ash was combined with 2 L of leaching solution to achieve an acceptable liquid-to-solution ratio. The initial pH of the mixture was then determined to ensure the method requirements were met. The leaching solution in the TCLP method is a mixture of glacial CH3CH2OOH, reagent water, and NaOH. The solution is diluted to a volume of 1 liter and made to have a pH of 4.93. In the SPLP method, the solution is sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3 . To create the solution, 60 g of concentrated sulfuric acid is cautiously mixed with 40 g of concentrated nitric acid.

Figure 3.1: Initial Leachate Data for TCLP Method

Figure 3.2: Initial pH Data for SPLP Method

The test utilized the rotation device to mix the samples for 18 hours and 7 days – tests were conducted in duplicate and samples were taken as specified in the EPA procedures. As stated in the method, samples for both tests may be refrigerated unless refrigeration results in irreversible physical change to the waste. The samples were collected in "store" type containers and refrigerated. Once ready for evaluation, extreme acre was taken to minimize the loss of volatiles. Samples were collected and stored in a manner intended to prevent the loss of volatile analytes and therefore the waste samples were collected in Teflon-line capped vials. The extracts for metallic analyte determinations were acidified with nitric acid to a pH less than 2. Immediately after sampling and prior

to this storing technique, the liquid was separated from the solid phase using a filtration device. The solution was then tested for pH and total dissolved solid content.

Figure 3.3: 18 Hour Total Dissolved Solids Data for TCLP

Figure 3.4: 18 Hour Total Dissolved Solids Data for SPLP

Figure 3.5: 7 Day Total Dissolved Solids Data for TCLP

Figure 3.6: 7 Day Total Dissolved Solids Data for SPLP

Figure 3.7: 18 Hour pH Data for TCLP

Figure 3.8: 18 Hour pH Data for SPLP

Figure 3.9: 7 Day pH Data for TCLP

Figure 3.10: 7 Day pH Data for SPLP

3.2 Sample Analysis

To analyze the concentration of mercury and other analyte elements, the Atomic Fluorescence spectroscopy method was used in addition to the Inductively Coupled Plasma-Atomic Emissions Spectrometry technique as discussed earlier in this report. Both of these experimental analysis procedures can be completed utilizing Minteq A2 computer modeling programs to compare experimental results and determine the importance of different solid phases in controlling solution composition.

The ICP-AES utilizes a diffraction grating fixed in space at the far end of the spectrometer. Rotation of the diffraction grating sequentially moves each wavelength into the detector. The computer control ensures that the detector is synchronized with the

grating so that the intensity at the detector at any given time is correlated with the wavelength being diffracted by the grating. Using standard spectroscopic techniques, sequential ICP-AES can provided extremely flexible and rapid analysis of a number of chemical elements. The spectrometer was flushed with N_2 gas to improve the detection limits of elements and to ensure quality with emission wavelengths that are severely compromised by interference with air. This N_2 flush, which is constantly maintained in the instrument regardless of whether such elements are being analyzed, also protects the optics from the corrosive aspects of the atmosphere, which are particularly acute at sea. First, the machine was allowed to warm up for 30 minutes. Next, a zero-order check was conducted. Zero-order is the term used to define when the grating within the spectrometer behaves as a mirror, reflecting incoming light rather than refracting it into several wavelengths. A zero-order check physically moves the diffraction grating to its zero position, where all light is reflected. An *autosearch* is preformed next to allow the spectrometer to identify an acceptable reference peak. The machine is calibrated using standards and finally the test was completed. The TCLP leachate concentration of the AEP fly ash sample and the SPLP leachate concentration of the MER0357 fly ash sample provide examples of typical ICP-AES results for this experiment.

Figure 3.11: TCLP Analyte Concentration for AEP Mountaineer Fly Ash Sample

Figure 3.12: SPLP Analyte Concentration for MER 0357 Fly Ash Sample

A lamp of desired wavelength and a PMT detector provide absorbance values based on the amount of the element present. When compared to a generated standard curve, the element of interest can be quantified. Detection limits for the instrument vary according the element under consideration, but for the analysis of mercury content in fly ash leachate samples the detection limits test returned a 99% confidence rating that the Hg concentrations reported were are less than 0.2ppb as recorded in the tables below. The data collected through this method gave a standard deviation of .012246.

Figure 3.13: Mercury Concentration for TCLP Extraction #1

Figure 3.14: Mercury Concentration for TCLP Extraction # 2

Figure 3.15: Mercury Concentration for SPLP Extraction #1

Figure 3.16: Mercury Concentration for SPLP Extraction #2

TCLP #1						
	Mass	Initial	18 Hour			7 Day
	(grams)	pH	TDS	18 Hour pH	7 Day TDS	pH
AEP						
Mountaineer	100	4.932	325	5.315	338	5.47
MER 0357	100	4.931	467	11.64	564	11.934
MER 032	100.1	4.928	433	11.57	593	11.98
NRT ID 1017	100.1	4.93	497	11.9	547	12.156
Coal Creek	100.1	4.93	416	11.49	502	11.2
Standard	N.A.	4.93	196	5.1	299	4.9
TCLP #2						
AEP						
Mountaineer	100	4.93	329	5.28	326	5.13
MER 0357	100.1	4.932	445	11.489	554	11.5
MER 032	99.9	4.929	429	11.57	585	12.3
NRT ID 1017	100	4.93	497	11.79	492	12.17
Coal Creek	100	4.931	498	11.56	476	11.806
Standard	N.A.	4.93	2.8	5.06	2.7	5.3
SPLP #1						
	Mass	Initial	18 Hour			7 Day
	(grams)	pH	TDS	18 Hour pH	7 Day TDS	pH
AEP						
Mountaineer	99.8	4.22	231	9.97	240	9.56
MER 0357	99.9	4.23	1559	11.75	1858	11.91
MER 032	100.1	4.23	1335	11.75	1563	11.68
NRT ID 1017	100	4.2	1077	11.66	1495	11.66
Coal Creek	100.1	4.22	1463	11.74	1558	11.67
Standard	N.A.	4.19	19.05	9.24	15	8
SPLP #2						
AEP						
Mountaineer	100	4.22	229	9.71	278	9.76
MER 0357	100.1	4.22	1134	11.66	1985	12.24
MER 032	100.1	4.2	1307	11.82	1529	11.92
NRT ID 1017	100	4.19	1227	11.74	1567	11.99
Coal Creek						
	100.1	4.22	1469	11.81	1640	11.91

Table 3.1: TCLP and SPLP Data for Fly Ash Leachate Samples

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

Data from these laboratory experiments on fly ash samples suggests that release of mercury from fly ash subjected to leachate solutions such as those found in municipal landfills and natural precipitation is low and almost undetectable through modern testing technology. Mercury release from samples subjected to both SPLP and TCLP testing methods returned negative results through atomic absorption analysis and this phenomenon exists only when mercury levels in samples are so low that the analysis is barely sensitive enough to detect the element. The additional analyte elements identified in the ICP-AES analysis of data ensures that fly ash material used in concrete, once subjected to leaching, are not harmful. This study has shown that even where some leaching of fly ash has occurred, its effects do not pose public health risks. The study has proven that the fly ash ingredient utilized in several concrete applications does not add potential mercury leaching to the concrete mix. In fact, the level of mercury in leachate from fly ash material is so low that it is nearly undetectable. The importance of using valid leaching protocols when evaluating complex inorganic materials was taken into

account throughout the study and complex chemical reactions that could occur were restricted before they could have an impact on the generation of leachate.

4.2 Recommendations

Several additional studies have found similar results to the analysis of this research experiment. Leaching studies conducted at a structural fill site in Minnesota and an embankment in Illinois indicated that even though some groundwater contamination had occurred, only very small localized changes in trace element concentration were detected off site after 8 years. Similarly, nearly 15 years after ash was used to construct a highway overpass embankment, sampling and analysis of groundwater, soils and vegetation in another study showed only slightly elevated levels of some constituents related to fly ash. A University of Pittsburg study conducted environmental and physical testing of concrete made from fly as and concluded that in all areas, leachate compositions of 17 different elements show fly as materials to be nonhazardous and likely environmentally benign.

Throughout the course of this research study, questions about the utilization accuracy of the TCLP and SPLP methods have been uncovered. One study suggested that the solutions used to simulate the leachate were highly inadequate. Another study concluded that the solid to liquid ratio requirement from the EPA test methods were in accurate. These issues could negatively effect the results of this study $-$ if the solutions were inadequate in leaching the fly ash material, an incorrect measurement of the elements in the leachate could be reported.

It is recommended that fly ash in concrete be continually monitored for future mercury leachate. A study focusing on the long term effects of leaching on fly ash is also suggested as a means to determine the degenerative effect of time on the samples. Though fly ash samples can only simulate the actions of the fly ash materials in concrete, the results from this study can be extended to provide insight into the overall contribution of fly ash to concrete structures. In the end, this study recommends that fly ash utliziation is an economical alternative to Portland cement that will not cause environmental or public harm.

CHAPTER 5

REFERENCES

American Concrete Pavement Association, Pavement Technology, January, 2006.

American Coal Ash Association, Coal Combustion product Production and Use, 2002.

Cannon, R.W.; *Concrete Institute,* 1968.

Electric Power Research Institute, Mercury Emissions From Concrete Containing Fly Ash and Mercury-Loaded Powdered Activated Carbon, December, 2003.

Galbreath, K.C.; Zygarlicke, C.J. Mercury Transformations in Coal Combustion Flue Gas. *Fuel Processing Technol.,* 2000, 65-66, 289.

Gibb, W. H.; Clarke, F.; Mehta, A. K. The Fate of Coal Mercury During Combustion. *Fuel Processing Technol*., 2000, 65-66, 365.

- Garboczi, E.J., and D.P. Bentz, "Fundamental Computer Simulation Models for Cement-Based Materials", 1990.
- Goldman, A., and Bentur, A., "Bond Effects in High- Strength Silica-Fume Concretes", 1989.
- Hansen, T.C.; Cement Concrete Res. 1990.
- Roberts, L.R., "Microsilica in Concrete I", in Materials Science of Concrete Vol. 1, 1989.
- Sybertz, F., "Comparison of Different Test Methods for Testing the Pozzolanic Activity of Fly Ashes", ACI SP 114-22, Fly Ash, Silica Fume, and Natural Pozzolans in Concrete, 1989.
- U.S. Environmental Protection Agency, Analysis of Emissions Reduction Options for the Electric Power Industry, March, 1999.

Zhang, M-H; *American Concrete Institute Materials Journal*, 2001.

Uchikawa, H., "Similarities and Discrepancies of Hardened Cement Paste, Mortar, and Concrete from the Standpoint of Composition and Structure", 1988.

Zimbelman, R., "A Contribution to the Problem of Cement-Aggregate Bond", 1985.

APPENDIX

Mercury Concentration Sample Data

Analyte Element Concentration

