

Estimating the Potential Release of Thallium from Fly Ash Under Different Environmental Scenarios

Research Thesis

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Abstract

To date, minimal research has been conducted to determine the intrinsic characteristics of fly ash that control the leaching of thallium. The liquid-solid (L/S) partitioning of thallium leached from Cardinal fly ash as a function of pH was examined under laboratory conditions using parallel batch extraction. The aqueous phase concentration of thallium decreased with decreasing pH. The results suggest that the following three mechanisms facilitate thallium leaching from fly ash: (1) dissolution of thallium salts attached to fly ash surface sites, (2) desorption of thallium from fly ash surface sites, and (3) thallium release due to underlying surface dissolution. X-ray absorption spectroscopy (XAS) was used in order to determine the dominant mechanism facilitating the leaching of thallium. The XAS results were inconclusive and the dominant mechanism could not be determined. The L/S partitioning of thallium as a function of time was also examined under 1-D mass-transfer controlled leaching. The results suggest that the leaching of thallium from fly ash is not a simple diffusion process.

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Contents

List of Figures.....	6
List of Tables.....	7
Introduction.....	8
Objectives.....	10
Experimental Methodology.....	10
Method 1313.....	11
Method 1315.....	15
X-Ray Absorption Spectroscopy.....	19
Results.....	21
pH Analysis.....	21
Mass Transfer Analysis.....	24
X-Ray Absorption Analysis.....	27
Conclusion.....	31
Future Work.....	32
References.....	33
Appendix A.....	35

List of Figures

Figure 1: Schematic of batch extraction test (Vanderbilt University 2011) used to assess the equilibrium release of thallium under various site pH values and liquid-to-solid ratios.

Figure 2: Schematic of leachate tank test (Vanderbilt 2011) used to determine leaching when mass transfer processes control thallium release.

Figure 3: Titration curve produced by adding acid/base solutions to 20.00 ± 0.2 g dry fly ash maintaining L/S of 10 mL solution/g dry fly ash.

Figure 4: Thallium dissolution and pH dependence

Figure 5: Thallium Flux under 1-D diffusion controlled release conditions

Figure 6: Cumulative Thallium Release as a function of time

Figure 7: Particle size distribution for (a) coarse (b) medium and (c) fine particles

Figure 8: (a) Normalized (b) first derivative of Tl L(II)- XANES spectra of fly ash samples and references

List of Tables

Table 1. Extraction parameters as a function of particle size under LEAF Method 1313

(Vanderbilt, 2011)

Table 2. Resulting acid-base schedule from Pre-titration test

Table 3. Batch samples prepared only with HNO_3 solution

Table 4. Batch samples prepared only with NaOH solution

Table 5. Total mass, mass of the HDPE molds, and the mass of the fly ash for 6 different molds

Table 6. Schedule of Eluate Renewals

Table 7. Summary of results under LEAF- Method 1313

Table 8. Summary of raw data for leachate tank test

Table 9. pH values over the course of leachate tank experiment

Table 10. Results from liner combination fitting

Introduction

In the United States, approximately 130 million short tons of coal combustion byproducts (CCPs) were produced in 2011, 47% of which consisted of fly ash (ACAA 2011). While 38% of the fly ash produced was beneficially used (e.g. substitute for portland cement), the majority of the material required disposal in landfills. It is important to understand the behavior of fly ash in order to develop effective and environmentally sound management approaches.

The Tennessee Valley Authority Kingston Fossil Plant spill in 2008 drew attention to the environmental and health impacts of thallium. Approximately 5.4 million cubic yards of fly ash and bottom ash were released into the Emory River during the spill (TVA 2009). The Tennessee Department of Environment and Conservation (TDEC) and the United States Environmental Protection Agency (USEPA) investigated the effected areas to identify potential environmental and health impacts, including the suspension of fine particles, the potential accumulation of trace elements in river sediment, and the leaching of ash contaminants to surface water (Ruhl et al 2009). Water quality testing showed that water quality criteria were exceeded for the following elements: aluminum (Al), arsenic (As), cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), and thallium (Tl) (USEPA 2009; TDEC 2009). The TDEC noted that the highest number of criteria violations were for thallium (23 violations). While there has been a significant amount of research conducted on the leaching of trace elements such as arsenic, selenium, and mercury from fly ash, minimal research has been conducted to determine the intrinsic characteristics of fly ash that control the leaching of thallium.

Thallium is now considered a priority metal by the USEPA. The USEPA has established an enforceable maximum contaminant level (MCL) in drinking water of 2 µg/L and a non-enforceable MCL goal of 0.5 µg/L. The MCL represents the achievable thallium level with

consideration to both human health and cost, while the MCL goal only considers human health. The USEPA has also established an Ambient Water Quality Criteria of 0.24 µg/L for thallium and soil screening levels of 6 mg/kg for residential soil. These limits reflect that thallium is highly toxic, capable of causing gastrointestinal problems and detrimental neurological effects in humans (USEPA 2009).

Thallium is an inorganic element that naturally exists in one of two oxidation states: Tl(1) and Tl(3). In most natural aquatic systems, the predominant oxidation state is Tl(1) (Peter and Viraraghavan 2005). Thermodynamically, Tl(1) may form a number of different solids including carbonates, oxides, sulfides, and hydroxides. Weathering processes naturally introduce toxically insignificant inputs of thallium to the environment. Anthropogenic sources include potash, effluents from sulfuric acid production, and the mining and smelting of certain metals (McNeely et al. 1979). Coal combustion is one of the most significant anthropogenic sources of thallium in the environment (NRCC 1982). Thallium is believed to volatilize during coal combustion and condense on fly ash particles in the cooler parts of the boiler system (Natush et al. 1974; ATSDR 1992). Thallium tends to concentrate in the smaller size ash fractions (Natush et al 1974). The speciation of thallium in fly ash is unknown, but it is a critically important determinant of its leaching behavior.

In one of the few studies that investigated the leaching of thallium from fly ash and CCPs, the Electric Power Research Institute (ERPI 2006; Pugh et al. 2009) examined the concentration of thallium in 81 different field leachate samples. The maximum measured concentration of thallium in the samples was 17.58 µg/L and the dominant dissolved species of thallium were Tl(1) and TlSO_4^- . The study also noted that the highest levels of thallium were found at pH values less than 9 and under oxic redox conditions of +200 to +350 mV. The

primary mechanisms facilitating the leaching of thallium were hypothesized to include sulfate oxidation, oxide dissolution, and cation exchange. Another study examined the sorption of thallium to iron and manganese oxides (minerals constituents prevalent in fly ash) and found that the percent sorption of Tl(1) increased with increasing pH over a range of 4-8 (Gadde and Laitenen 1974). Nearly zero adsorption is observed in the pH range of 4-6 and approximately 15% adsorption was observed at pH 8.

Objectives

The primary objectives of this research were: (1) to understand the intrinsic characteristics of fly ash that control the leaching of thallium under a variety of conditions using the recently developed USEPA Leaching Environmental Assessment Framework (LEAF) methodology and (2) to understand the molecular-level factors and mechanisms that control the intrinsic leaching behavior of thallium from fly ash using X-ray absorption spectroscopy. Insight into the factors and mechanisms that influence thallium's leaching behavior was important in understanding how thallium was transported in the environment, which will allow engineers to develop more effective remediation techniques and solutions to minimize its release and impact to human health and the environment.

Procedures

According to the USEPA, the Leaching Environmental Assessment Framework (Vanderbilt University 2011) consists of four elements: (1) establishing relevant real-life scenarios, (2) performing laboratory tests to determine the intrinsic behavior of a material, (3) estimating the flux of elements and long-term release of elements using modeling, and (4)

making determinations about the leaching estimates for different scenarios through comparisons with various regulatory limits. Laboratory leaching tests were used to examine how fly ash composition and solution conditions influence thallium release. Data was obtained on the intrinsic characteristics of fly ash that influence the leaching of thallium under conditions in which leaching was controlled by percolation and mass transfer. Percolation within a fly-ash landfill or infiltration through a low-permeability material represent real life scenarios of equilibrium-controlled and mass-transfer controlled thallium release, respectively.

Introduction to Method 1313: Liquid-Solid Partitioning as a Function of Extract pH Using Parallel Batch Extraction Procedure

Method 1313 uses parallel batch extraction to obtain a series of extracts of solid materials (eluates), which may be used to estimate the liquid-solid partitioning (LSP) of thallium as a function of pH under laboratory conditions (22°C). This method provides solutions with concentrations considered indicative of leachates under field conditions at comparable ranges of pH for the case when the LSP is controlled by aqueous phase saturation of the constituent of potential concern (COPC). Eluate thallium concentrations may be used in conjunction with information regarding environmental management scenarios to estimate the anticipated leaching concentrations and release rate under the conditions evaluated. When LSP is controlled by the amount of the constituent present in the solid that may dissolve (i.e., for highly soluble species), the mass released (mg/kg), rather than the concentration, is indicative of field conditions.

For the purposes of this research, Method 1313 was used to provide values for intrinsic Cardinal fly ash parameters that control leaching of thallium under an equilibrium controlled scenario at a liquid to solid (L/S) ratio of 10 mL extract/g-dry fly ash (value specified in the

method). Liquid-solid chemical equilibrium occurs when rate of thallium desorption is equal to the rate of thallium sorption to fly ash particles. This implies that the aqueous and solid phase thallium concentration gradient is balanced.

Method 1313: Preliminary Testing and Sample Preparation

Preliminary testing of the material was required to ensure the accuracy of Method 1313. The fly ash particle size was determined in order to establish the minimum dry mass (g-dry) of fly ash, the suggested vessel size to hold the fly ash sample and eluent, and contact time required to reach equilibrium as specified by LEAF Method 1313. Table 1 lists the extraction parameters as a function of particle size. Particle size reduction may be necessary to reduce the contact time required to reach liquid-solid equilibrium and to minimize mass transport through large particles. However, particle size reduction was not necessary for the Cardinal fly ash sample because 85% by weight of the material was made up of particles ≤ 0.3 mm in size. Under the direction of Method 1313 (see table below), the leaching experiment required a minimum dry mass of 20 ± 0.02 g-dry fly ash, a 250 mL vessel, and 24 hour mixing to achieve equilibrium.

Table 1. Extraction parameters as a function of particle size under LEAF Method 1313 (Vanderbilt, 2011)

Particle Size (85 wt% less than) (mm)	US Sieve Size	Minimum Dry Mass (g-dry)	Contact Time (h)	Suggested Vessel Size (mL)
0.3	50	20 ± 0.02	24 ± 2	250
2.0	10	40 ± 0.02	48 ± 2	500
5.0	4	80 ± 0.02	72 ± 2	1000

The moisture content of the fly ash was also calculated in order to provide the dry mass equivalent of the “as tested” fly ash. The moisture content of the sample fly ash was

approximately 0.001 g H₂O/g “as received” ash and therefore was considered dry.

In order to conduct the parallel batch extraction test, an acid-base schedule was formulated from a pre-titration test curve. Two solutions, 500 mL of 1 N NaOH and 500 mL of 2 N HNO₃, were prepared for the pre-titration and parallel batch extraction tests. The NaOH solution was prepared by adding de-ionized water to approximately 20.0680 g NaOH (s) until the total volume reached 500 mL. The HNO₃ solution was prepared by adding de-ionized water to approximately 46.98 mL of concentrated HNO₃ until the total volume reached 500 mL. The 5 pre-titration samples were prepared by adding approximately 20±0.02 g- dry fly ash into separate 250 mL vessels. De-ionized water and the NaOH and HNO₃ solutions were added as specified in the acid-base schedule below. Each sample was prepared at a liquid-to-solid ratio (L/S) of 10 mL extract/g-dry fly ash as specified in the method. Table 2 summarizes the pre-titration test. It contains a list of amount of fly ash, volume of acid/base added to each vessel, and the resulting leachate pH after 24 hours mixing (equilibrium attained).

Table 2. Resulting acid-base schedule from Pre-titration test

Bottle	1	2	3	4
Mass dry fly ash (g)	20.0076	20.0128	20.0063	20.0114
HNO₃ added (mL)	20	10	-	-
NaOH added (mL)	-	-	-	20
DI added (mL)	180	190	200	180
pH	1.39	2.1	8.34	12.33

Eleven target pH points ranging from 2 to 12 were selected for the parallel batch extraction tests. Like the pre-titration samples, the 11 batch test samples were prepared by adding

dry fly ash, de-ionized water, and acid/base solutions into separate 250 mL vessels. Each sample was prepared at a L/S of 10 mL extract/g-dry fly ash as specified in the method. Tables 3 and 4 show the mass of dry fly ash, volume of de-ionized water, and volume of acid/base solution added to each vessel. The amount of acid/base and deionized water added to each vessel was calculated based on the pre-titration curve. An approximate volume of acid/base necessary to achieve a target pH can be read from the curve.

Table 3. Batch samples prepared only with HNO₃ solution

Bottle	1	2	3	4	15	11
Mass dry fly ash (g)	20.0112	20.0152	20.0057	20.0149	20	20.009
HNO₃ added (mL)	10	7.5	5	2	1	0.5
DI added (mL)	190	192.5	195	198	199	200

Table 4. Batch samples prepared only with NaOH solution

Bottle	5	14	6	7	9
Mass dry fly ash (g)	20.0096	20.0033	20.0112	20.0042	20.0068
NaOH added (mL)	-	1	4	10	20
DI added (mL)	200	199	196	190	180

Method 1313: Parallel Batch Extraction Experiment

Figure 1 is a schematic of the batch leaching experiment. After preparation, the samples were mixed for 24 hours in an “end-over-end” fashion to attain equilibrium. At the end of mixing, the liquid and solid phase were separated via settling. Leachate pH measurements were taken and the liquid phase was clarified via vacuum filtration. Glass fiber filter paper (0.70 μ

pore size) was used to filter the samples. The resulting solution was collected and preserved using approximately 5 mL of HNO₃. The concentration of thallium in the solution was measured using an 880Z Atomic Absorption Spectrometer. Three standard thallium solutions (1006 ppm, 20.12 ppm, and 5.03 ppm) and a blank were made to reveal reagent impurities or equipment contamination by verifying the accuracy of atomic absorption spectroscopy (AAS) measurements.

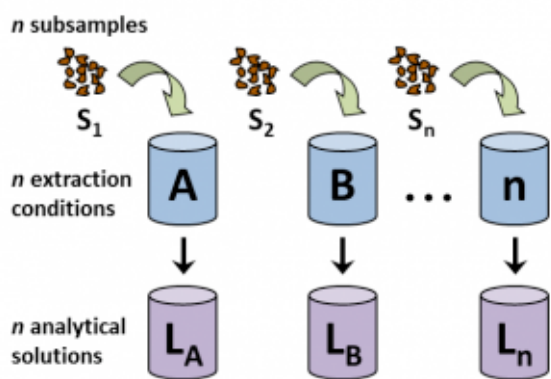


Figure 1. Schematic of batch extraction test (Vanderbilt University 2011) used to assess the equilibrium release of thallium under various site pH values and liquid-to-solid ratios.

Introduction to Method 1315: Mass Transfer Rates of Constituents in Monolithic or compacted Granular Materials Using a Semi-Dynamic Tank Leaching Procedure

Method 1315 of LEAF provides intrinsic material parameters for release of inorganic species under mass transfer controlled leaching conditions. This test method was used to obtain a series of eluents, which may be used to estimate the diffusivity of constituents and physical retention parameters of the solid material under specified laboratory conditions. Method 1315 can be used to test anything from a 1-dimensional (1-D) through 3-dimensional (3-D) mass transfer cases. In all cases, the sample size was at least 5 cm in the direction of mass transfer and the liquid-to-surface area ratio (L/A) was maintained at 9 ± 1 mL/cm². The solvent system used in this characterization method is de-ionized water. For the purposes of this research, Method 1315 was used to provide the mass transfer rates of thallium contained in Cardinal fly ash under

1-D diffusion controlled release conditions, as a function of leaching time.

Method 1315: Preliminary Testing and Sample Preparation

Sample preparation under Method 1315 requires fly ash to be compacted at a moisture content corresponding to 90% of the optimum packing density in order to provide a uniform approach to obtaining a sample density that approximates field conditions. The optimum moisture content refers to the mass of water in the fly ash sample ($\text{g H}_2\text{O/g sample}$) that was present at the optimum packing density ($\text{g-dry material/cm}^3$). Dr. Tarunjit Butalia, a research scientist at Ohio State University, had prior knowledge of the optimum moisture content of the Cardinal Fly ash sample (10%). The following formula was used to calculate the mass of the water added to the sample (W_w) to achieve 10% moisture content ($W_\%$): $W_\% = W_w / W_d * 100\%$ where W_d was equal to the mass of the dry fly ash sample. Approximately 1150.8 g of fly ash and 115 mL of water was added into a rectangular, plastic tub and mixed until homogeneity is achieved.

Method 1315 specifies that the sample holder be composed of an impermeable material or other material resistant to high and low pH. Fly ash samples were mechanically packed into 6 different cylindrical (3 in. diameter) high-density polyethylene (HDPE) molds. The ash was compacted to a height of 6 inches (the total weight of the holder and fly ash reached approximately 270 to 275 g). The wall thickness of the molds was such that the distance between the outside of the mold surfaces and the leaching vessel were < 0.5 cm as specified by Method 1315. The mass of each mold was measured and recorded (See Table 5).

As specified in Method 1315, 25 blows were required to achieve optimum packing density. After the samples were packed, the mass of each mold with sample was measured and

recorded (See Table 5). The mass of the fly ash in each mold was calculated by subtracting the mass of the mold from the mass of the mold with fly ash sample.

Table 5. Total mass, mass of the HDPE molds, and the mass of the fly ash for 6 different molds

Sample	Total Mass	Mass of Mold	Mass of Fly Ash
1	276.65	76.43	200.22
2	269.71	76.37	193.34
3	272.36	76.2	196.16
4	273.27	76.09	197.18
5	275.38	76.41	198.97
6	270.46	76.2	194.26

The volume of de-ionized water required for the tank-leaching procedure was determined using the following formula: $V_w = 3.14 * r^2 * (L/A)$ where r equals the radius of the sample surface area (face) exposed in cm. and (L/A) was equal to 9 mL/cm^2 . Approximately 410 mL of de-ionized water was needed for the tank-leaching procedure. A 1 L leaching vessel was used to hold the samples. The height of the sample holder (HDPE mold containing fly ash) was altered using a handsaw to correspond with the height of deionized water in the leaching vessel. The sample was placed at the bottom of the leaching vessel with the exposed face facing the top of the leaching vessel. However, 410 mL of de-ionized water was insufficient, as it did not provide the necessary distance between the top of the eluent and the solid-liquid interface. Therefore, an extra 45 mL of de-ionized water was added to the leaching vessel. Adding 45 mL of water did not exceed the $9 \pm 1 \text{ mL/cm}^2 \text{ L/A}$.

Method 1315: Leachate Tank Test

Figure 2 is a schematic of the leachate tank test. The schedule of leaching intervals and cumulative release times are listed in table 6. At the end of each interval, the sample holder was

removed from the leaching vessel and placed in another leaching vessel containing 455 mL of de-ionized water. Leachate pH measurements were taken and the liquid phase was clarified via vacuum filtration. Glass fiber filter paper (0.70 μ pore size) was used to filter the samples. Approximately 250 mL of the resulting solution was collected and preserved using approximately 5 mL of HNO₃. The concentration of thallium in the solution was measured using an 880Z Atomic Absorption Spectrometer. Three standard thallium solutions (1006 ppm, 20.12 ppm, and 5.03 ppm) and a blank were made to reveal reagent impurities or equipment contamination by verifying the accuracy of AAS measurements.

Table 6. Schedule of Eluate Renewals

Interval Label	Interval Duration (hr)	Interval Duration (d)	Cumulative Leaching Time (d)
T1	3 ± 0.5	-	0.125
T2	3 ± 0.5	-	0.25
T3	18 ± 0.5	-	1
T4	-	1 ± 0.1	2
T5	-	5 ± 0.1	7
T6	-	7 ± 0.1	14
T7	-	7 ± 0.1	21
T8	-	7 ± 0.1	28

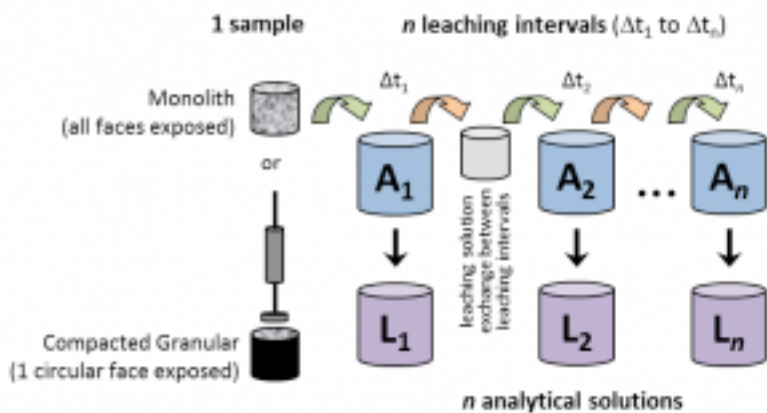


Figure 2. Schematic of leachate tank test (Vanderbilt 2011) used to determine leaching when mass transfer processes control thallium release.

X-ray Absorption Spectroscopy: X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)

In addition to determining the intrinsic leaching characters of thallium for fly ash, X-ray absorption spectroscopy was used to determine the molecular association of thallium with fly ash to gain insight into the leaching process. X-ray absorption spectroscopy is a technique used to determine the structure of matter. The process uses high energy x-rays to generate photoelectrons that induce electronic scattering interactions (C.S. KIM et al. 2000). These interactions gives rise to the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS), which were analyzed to derive the redox state, interatomic distances, oxidation state, coordination number, and identify the nearest neighbors of thallium in fly ash samples. This information can be used to understand and explain the data and model results developed by the Method 1313 and Method 1315. The data can also be used to determine if thallium associates with chloride, sulfate, carbonate, etc. in fly ash in different particle sizes.

X-ray Absorption Spectroscopy: Sample Preparation

For the purposes of this research, X-ray absorption spectroscopy was used to (1) determine what thallium species (chloride, sulfate, carbonate, etc.) were associated with different particle sizes of fly ash and (2) determine which species of thallium leached. Therefore, three different particle-size samples were prepared via sedimentation. A 10 ft high PVC pipe was filled with de-ionized water. To hinder leaching during sedimentation, a fly ash solution (pH 12.68) was prepared by adding base and de-ionized water as in Method 1313. The fly ash solution was poured into the PVC pipe and the solution was left to settle. A solution containing “coarse” particles was collected after 5 minutes of settling, a solution containing “medium”

particles was collected after 60 minutes of settling, and the remaining solution collected contained the “fine” particles. The fly ash particles were separated via vacuum filtration and oven dried at 105°C. The particle size distribution of the three fly ash samples were analyzed using Mastersizer. In addition to the three fly ash samples, an “as received” and “pH 2 leached” sample were prepared to investigate which species of thallium leached. The “pH 2 leached” sample was prepared as specified by Method 1313. After 24 hours of mixing, the fly particles were separated via vacuum filtration and oven dried at 105°C.

X-ray Adsorption Near Edge Spectroscopy (XANES)

Thallium L(II)-XANES spectrum was collected using Beamline 20-ID-B with insertion device at the X-ray Science Division of Advanced Photon Source at Argonne National Laboratory, Argonne, IL. The electron storage ring at APS provided energy of 7.0 GeV with a topup fill status. Beam energy was calibrated by the adsorption edge of TiCl at 14707 eV. The XANES spectra were collected in fluorescence mode with one solid-state 4-element detectors under ambient temperature. A Si(111) monochromator was used for energy selection with an energy resolution (DE/E) of 1.4×10^{-4} (eV/eV). Except for the leached sample, each sample was scanned 50 times. In addition to the five fly ash samples, five Tl references, i.e., Tl_2CO_3 , Tl_2SO_4 , TlCl , TlCl_3 , and Tl_2O_3 (ACS reagent grade; Sigma-Aldrich, Milwaukee, WI), were also included. These 5 specific references were chosen based upon the likelihood of formation during the combustion process due to the presence of Cl_2 , CO_2 , and SO_2 in flue gas. Each reference was scanned three times. The XAS data process software, ATHENA, was used to analyze the Tl XAFS spectra. Data reduction, including background subtraction, normalization, and averaging, was done in a standard manner.

Results

pH Dependence Analysis

Figure 3 is a plot of the leachate equilibrium pH (post-mixing) as a function of the amount of acid/base added to the sample. In Figure 4, the aqueous phase concentration of thallium is plotted as a function of pH. Table 7 is a summary of the batch leaching results. All values less than limit of detection ($0.130 \mu\text{g/L}$) were recorded as “< 0.130”. The concentration of thallium decreased at a decreasing rate as the pH of the leaching solution became more basic. The thallium fraction in the fly ash available for dissolution also decreased at a decreasing rate as pH increased. Previous elemental analyses determined that the concentration of thallium in the sample fly ash was 12 ppm by mass. The calculated maximum and minimum available fractions of thallium in the fly ash were 17.9% (at pH 2.05) and 0.00% (at pH 12.68), respectively.

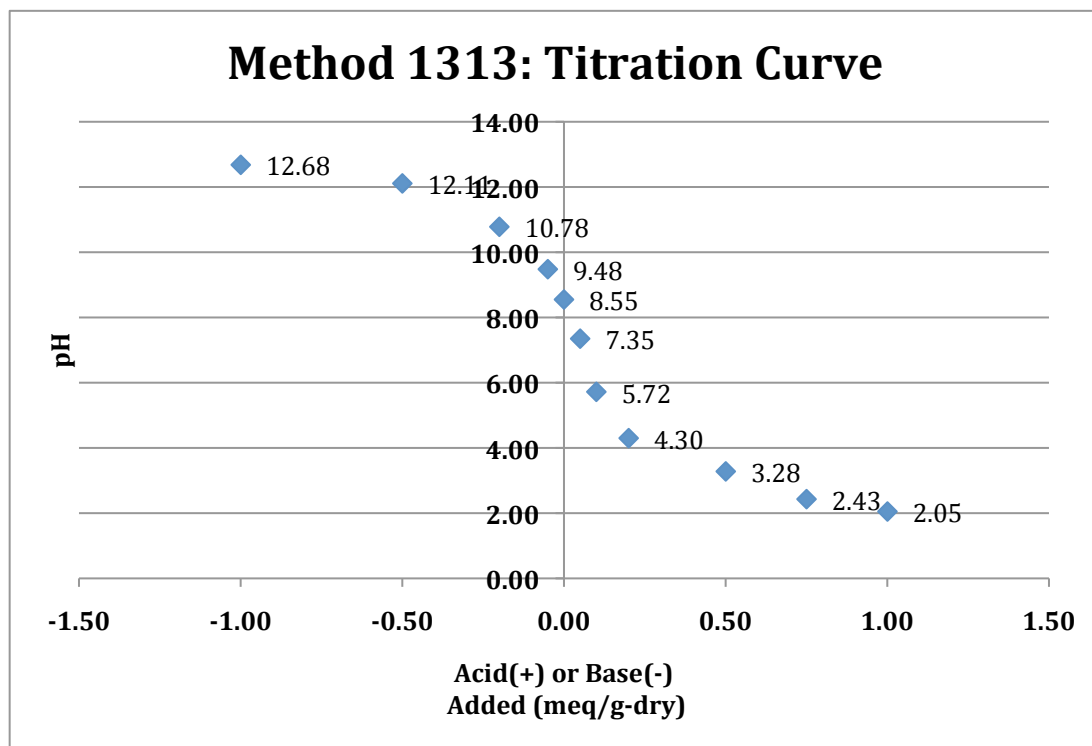


Figure 3. Titration curve produced by adding acid/base to 20.00 g dry fly ash, L/S 10 mL solution/g dry fly ash.

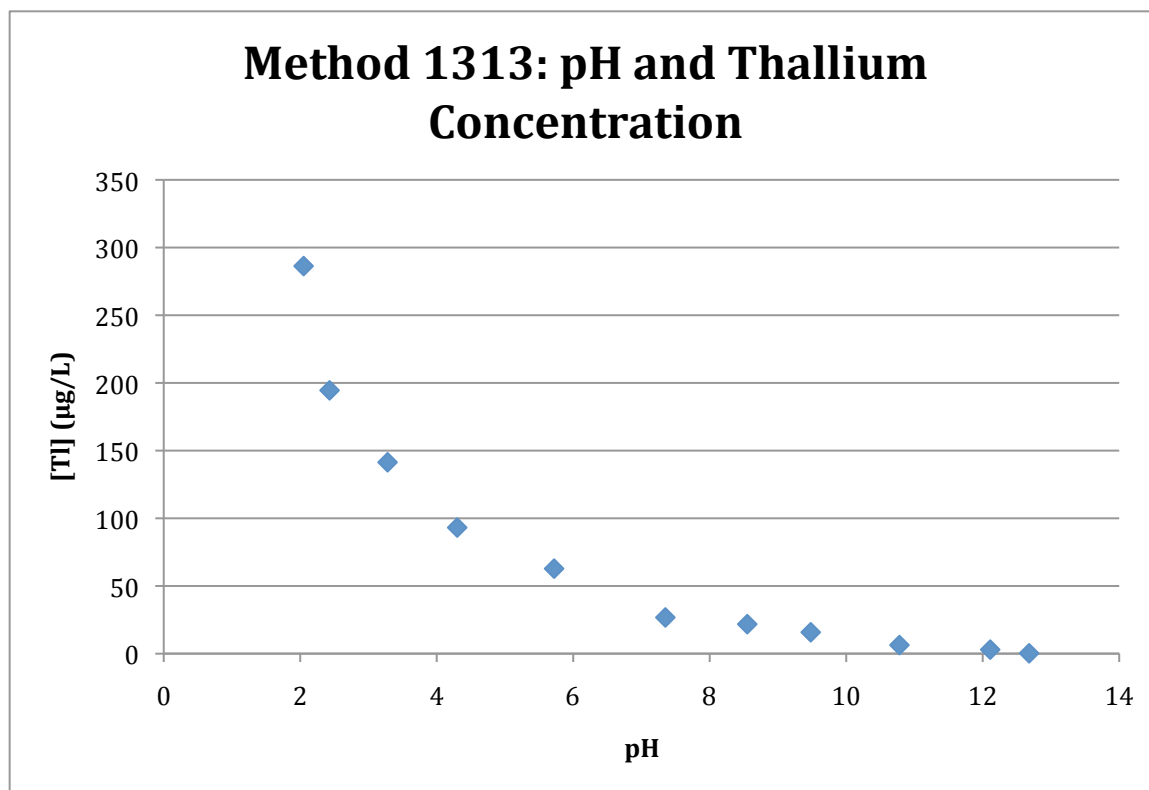


Figure 4. Thallium dissolution and pH dependence

Table 7. Summary of results under LEAF- Method 1313

pH	concentration (µg/L)	mass	ug/g	available fraction (%)
2.05	286.32	20.0112	2.1103	23.8
2.43	194.502	20.0152	1.9435	16.2
3.28	141.382	20.0057	1.4134	11.8
4.3	93.169	20.0149	0.9310	7.8
5.72	62.823	20	0.6282	5.2
7.35	26.762	20.009	0.2675	2.2
8.55	21.801	20.0096	0.2179	1.8
9.48	15.813	20.0033	0.1581	1.3
10.78	6.37	20.0112	0.0637	0.5
12.11	3.001	20.0042	0.0300	0.3
12.68	0.292	20.0068	0.0029	0.0

Leaching results show a strong dependence on solution pH, reflecting the importance of the following three mechanisms in facilitating the leaching of thallium from fly ash: (1) dissolution of thallium salts attached to fly ash surface sites, (2) desorption of thallium from fly ash surface sites, (3) thallium release due to underlying surface dissolution.

The relationship between pH and the dissolution of thallium salts attached to fly ash surfaces can be explained by equilibrium chemistry. In solution, salts will dissolve and reform. The system (salt in solution) reaches equilibrium when the rate of salt formation is equal to the rate of salt dissolution. The solubility of a salt (the quantity of salt that can dissolve in acid/base solution) is dependent on the anion or cation affinity for excess H^+ or excess OH^- , respectively. For example, the solubility of Tl_2CO_3 ($Tl_2CO_3 = 2Tl^{1+} + CO_3^{2-}$) under acidic conditions is dependent on the affinity of CO_3^{2-} for H^+ . Under acidic conditions, excess H^+ will compete with Tl^+ to interact with CO_3^{2-} and more Tl^+ will be left in solution. Therefore, the solubility of the thallium salt increases with decreasing pH. Dissolved thallium salts leach from fly ash surface sites and leach into the liquid phase. The aqueous phase thallium concentration of thallium will increase as the anion or cation affinity for excess H^+ or excess OH^- (respectively) increases. The aqueous phase concentration of thallium increased under increasingly acidic conditions and decreased under increasingly basic conditions, which may reflect the high solubility of thallium salts under acidic conditions and low solubility of thallium salts under basic conditions. These observations are consistent with research conducted by Ryzhenko and Mironenko (1994), who observed that the dissolution rates of carbonates and sulfates increased as pH decreased below 5.

The relationship between pH and desorption of thallium from fly ash surfaces can also be explained by equilibrium chemistry. The leaching process occurs to balance the thallium concentration gradient between the aqueous and solid phase. To achieve equilibrium, the rate of thallium desorption approaches the rate of thallium sorption to fly ash constituents. However under acidic conditions, thallium competes with protons for adsorption sites. Therefore, the concentration of thallium in the aqueous phase will be greater than the concentration of thallium under neutral or basic conditions. The aqueous phase concentration of thallium increased under

increasingly acidic conditions, which may reflect thallium desorption from fly ash surfaces under acidic conditions. This is consistent with research conducted by Gadde and Laitinen (1974), who found that desorption of thallium from iron and manganese oxides (minerals constituents prevalent in fly ash) decreased with increasing pH over a range of 4-8.

The results also reflect that the fraction of thallium available for leaching (and ultimately the aqueous phase thallium concentration) increases as conditions become more acidic. As fly ash surface groups dissolve, the underlying matrix is exposed and previously trapped fractions of thallium become exposed and available to leach. At low pHs, excess protons catalyze the dissolution of surface groups (e.g. iron oxides and aluminum silicates). Protons attach to oxygen in the surface groups, removing electron density and decreasing the strength of metal-oxygen bond. As a result, the surface groups are released and the underlying matrix becomes exposed to the solution.

Mass Transfer Analysis

Table 8 contains the aqueous phase thallium concentration for two separate trials at the end of each cumulative time interval. All values less than limit of detection (0.130 µg/L) were recorded as “< 0.0130”. In figure 5, the thallium flux is plotted against the mean interval time.

Thallium flux (F) in mg/m² is calculated using the following formula:

$$F = ([\text{TI}] * V) / (A * (t_i - t_{i-1}))$$

where [TI] is the aqueous phase concentration of thallium in mg/L, V is the volume of de-ionized water added to the leaching vessel (0.455 L), A is the fly ash surface area exposed to the eluate (0.00456 m²), t_i is the cumulative time (s) at the end of the current leaching interval, and t_{i-1} is the

cumulative time (s) at the end of the previous leaching interval. The mean interval time (T) was calculated using the following formula:

$$T = (\sqrt{t_i} + \sqrt{t_{i-1}}) / 2$$

where t_i is the cumulative time (s) at the end of the current leaching interval, and t_{i-1} is the cumulative time (s) at the end of the previous leaching interval.

In figure 6, the cumulative mass of thallium is plotted against the cumulative leaching time. Over the course of the first day, the thallium flux decreased. Therefore, the rate of thallium entering the aqueous phase appears to approach the rate of thallium entering the solid phase. Over time, the rate of thallium transfer from the ash to the aqueous solution (flux) decreases and the rate of thallium transfer from the aqueous solution to the ash increases until the system has reached chemical-solid equilibrium and the rates of transfer are equal.

Table 8. Summary of raw data for leachate tank test

Cumulative Time Interval (d)	Concentration (µg/L)	Concentration (µg/L)
0.125	4.656	5.731
0.25	4.073	4.089
1	18.046	19.216
2	41.211	43.032
7	181.699	183.793
14	160.68	171.281
21	94.812	108.952
35	67.524	74.94

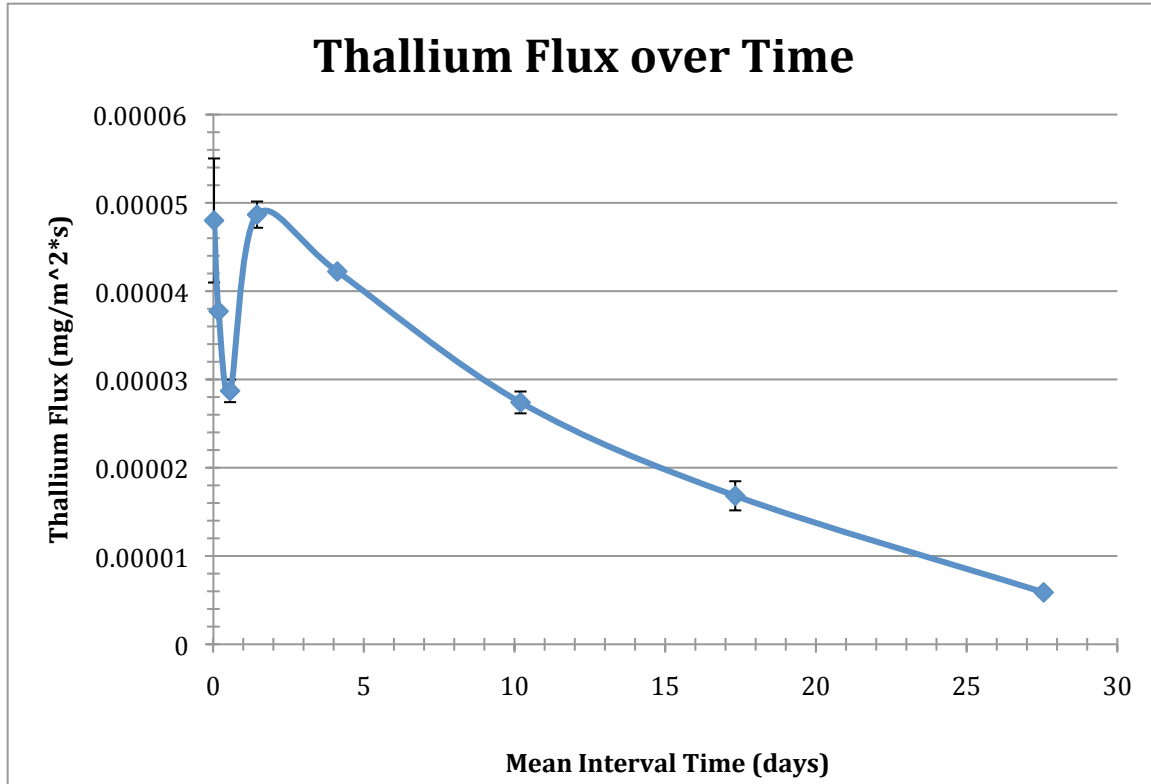


Figure 5. Thallium Flux under 1-D diffusion controlled release conditions

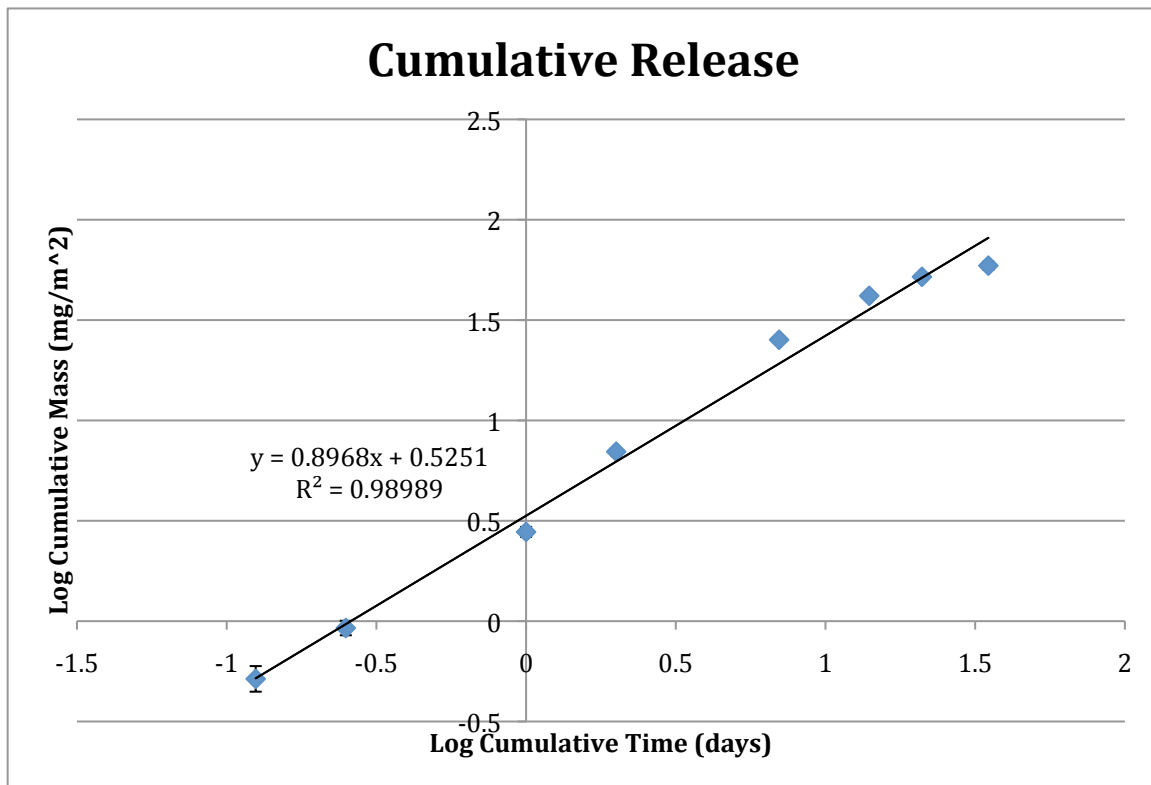


Figure 6. Cumulative Thallium Release as a function of time

It is important to note that the pH of the eluate varied from 4.02 to 4.75. Table 9 lists the pH values and the corresponding cumulative leaching interval. Based on the pH dependence analysis, the pH of the eluate solution was expected to be approximately 8.55 and the variations in pH are likely to have an effect on the chemical-solid equilibrium conditions.

Table 9. pH values over the course of leachate tank experiment

Cumulative Leaching Interval (d)	Trial 1 pH	Trial 2 pH
0.125	4.62	4.62
0.25	4.71	4.75
1	4.72	4.66
2	4.47	4.5
7	4.19	4.1
14	4.08	4.05
21	4.02	4
35	4.08	4.09

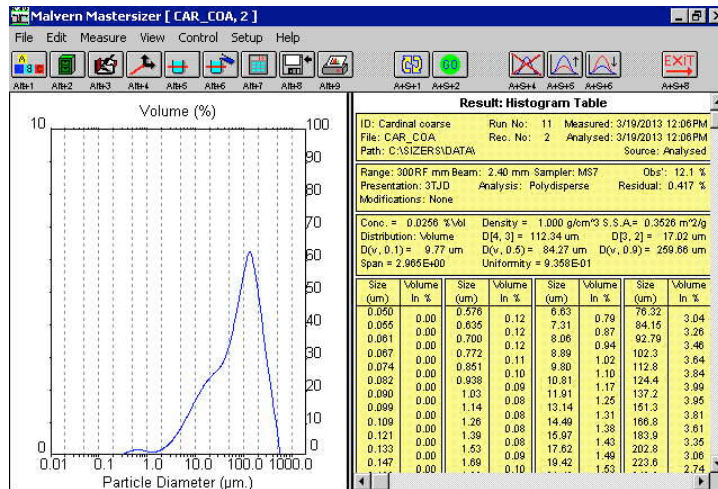
A diffusion coefficient could not be calculated using Crank's simple diffusion model. Under Crank's model, the logarithm of the cumulative release plotted versus the logarithm of time plot is expected to be a straight line with a slope of 0.5 ± 0.15 . The two plots generated using the experimental results have an average slope of 0.8968. The results reflect that Crank's assumptions were not valid for thallium leaching from fly ash. Therefore, thallium leaching from fly ash was not a simple diffusion process. The thallium flux results may provide insight into the rates of the three mechanisms hypothesized to facilitate the leaching of thallium from fly ash. The dissolution of thallium salts and desorption of thallium from fly ash surface sites may be faster than the dissolution of the surface groups.

X-ray Absorption Spectroscopy Analysis

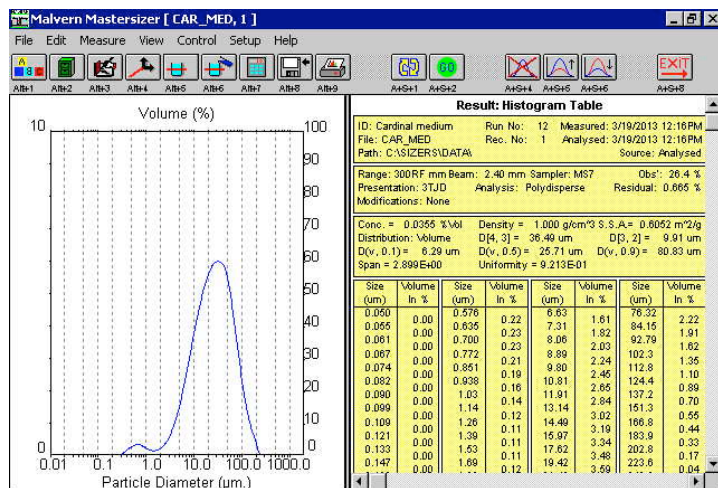
Figure 7 contains graphs/tables showing the particle size distribution for the "coarse", "medium", and "fine" particles collected via sedimentation. The median diameters (by volume)

are 84.27 μm , 25.71 μm , and 15.15 μm for the “coarse”, “medium”, and “fine” particles, respectively.

(a)



(b)



(c)

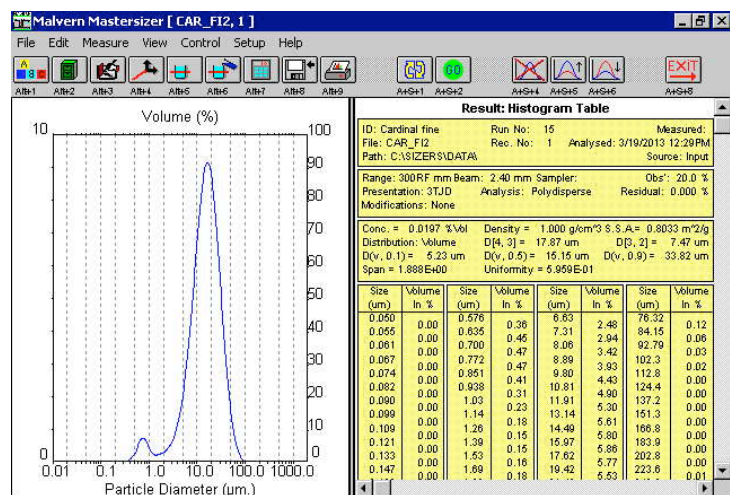


Figure 7. Particle size distribution for (a) coarse (b) medium and (c) fine particles

Figure 8 is the normalized and the first derivative of Tl L(II)- XANES spectra of fly ash samples and references. The shoulder at the pre-edge of the “as received” spectrum seems to be a combination of Tl(III) oxide and Tl(I) carbonate. The right shoulder at the adsorption edge of the “as received” spectra is similar to Tl(I) carbonate. The feature of the “as received” spectrum after the adsorption edge is similar to Tl(I) sulfate but seems to be more complex, which suggests the presence of Tl(I) sulfate and other Tl compounds, such as chlorides and carbonate. The spectrum of the “coarse” sample has a feature similar to “as received” at the pre-edge region, indicating the presences of Tl(I) carbonate and possibly Tl(III) oxide. The “as received” and “medium” samples have very similar features at the right shoulder of the adsorption edge, which suggests Tl(I) sulfate may also be present in the “medium” sample. The presences of thallium chlorides in the ash samples are not clear.

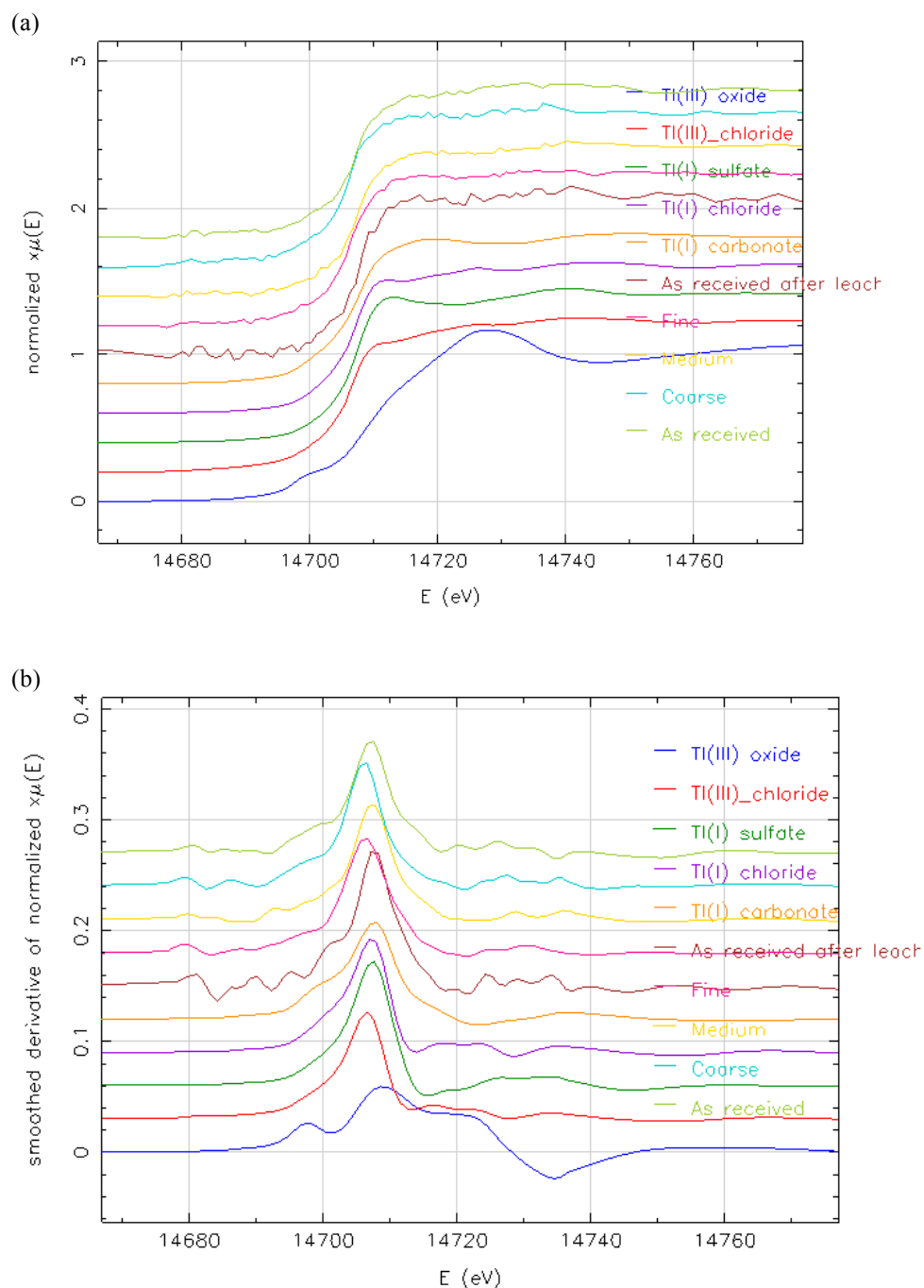


Figure 8. (a) Normalized (b) first derivative of Ti L(II)- XANES spectra of fly ash samples and references

The linear combinations of standard spectra to the five ash spectra were fitted using the ATHENA software to determine the presence of thallium species in the fly ash sample. Table 10 contains the results from linear combination fitting. The fits were processed using the first

derivative of normalized $\mu(E)$ spectra. The fitting results indicate that Tl might present in the “as received” fly ash in the form of carbonate, chloride, sulfate, and oxide. Carbonate and sulfate were likely the dominant species. More thallium presented in the coarse fraction of the fly ash in its chloride form. There was no significant difference between the medium and fine fractions. No chloride was observed after leaching.

Table 10. Results from liner combination fitting

	Tl(I) carbonate	Tl(I) chloride	Tl(I) sulfate	Tl (III) chloride	Tl(III) oxide	R factor	Reduced c2	Sum
As received	0.188	0.134	0.477	0	0.214	0.080	7.28E-05	1.013
Coarse	0.211	0.457	0.311	0	0.027	0.147	1.54E-04	1.006
Medium	0.570	0	0.385	0	0.083	0.059	5.54E-05	1.038
Fine	0.387	0.098	0.463	0	0.067	0.090	8.72E-05	1.015
Leached	0.428	0	0.613	0	0.12	0.240	3.69E-04	1.161

Conclusion

The evaluation of thallium release as a function of pH suggests that the following three mechanisms facilitate the leaching of thallium from fly ash: (1) dissolution of thallium salts attached to fly ash surface sites, (2) desorption of thallium from fly ash surface sites, (3) thallium release due to underlying surface dissolution. The X-ray absorption spectroscopy results did not provide any concrete insight into the dominant mechanism facilitating the leaching of thallium from fly ash. However, they reflect that thallium may associate with chloride, oxide, sulfate, and carbonate in fly ash and that Tl(I) chloride may leach at pH 2. Thallium mass transfer results suggest that thallium leaching from fly ash was not a simple diffusion process and that the dissolution of thallium salts and desorption of thallium from fly ash surface sites may be faster

than the dissolution of surface groups.

Future Work

The XAFS results could be improved by performing more scans to increase the signal to noise ratio and including more thallium references. This would likely produce more distinguishable results, allowing for improved determination of what thallium species were associated with different particle sizes of fly ash and which species of thallium leached. Also, sedimentation may not have been the best choice to separate the different particle sizes, as it may have caused geopolymerization and changed the surface chemistry of the fly ash. Separation via sieve would be effective and would not expose the fly ash to conditions that may change the surface chemistry of the fly ash.

The leachate tank experiment under Method 1315 could be improved by performing the experiment immediately after sample preparation. In this research, the tank test was performed approximately 2.5 weeks after sample preparation due to the trip to Argonne National Lab, which may have been enough time for changes to occur in the chemical form of the fly ash.

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Appendix

Table A-1. Raw data for pH Analysis Method 1313

Bottle	pH	Concentration (µg/L)	Mass
1	2.05	286.32	20.0112
2	2.43	194.502	20.0152
3	3.28	141.382	20.0057
4	4.3	93.169	20.0149
5	8.55	21.801	20.0096
Check [5]	-	4.766	-
6	10.78	6.37	20.0112
7	12.11	3.001	20.0042
11	7.35	26.762	20.009
14	9.48	15.813	20.0033
15	5.72	62.823	20
Check [5]	-	5.216	-
9	12.68	0.292	20.0068

Table A-2. Raw data for Mass Transfer Analysis Method 1313

Cumulative Time Interval (d)	concentration (T1)	concentration (T2)	mass (ug) (T1)	mass (ug) (T2)
0.125	4.656	5.731	2.11848	2.607605
0.25	4.073	4.089	1.853215	1.860495
1	18.046	19.216	8.21093	8.74328
2	41.211	43.032	18.751005	19.57956
7	181.699	183.793	82.673045	83.625815
14	160.68	171.281	73.1094	77.932855
21	94.812	108.952	43.13946	49.57316
35	67.524	74.94	30.72342	34.0977
Check [5]	5.141	4.745	-	-

Table A-3. Limit of Detection Data

Trial	Concentration
Check Standard [5]	4.515
Check Standard [5]	5.141
Check Standard [5]	4.536
Check Standard [5]	5.024
Check Standard [5]	5.022
Check Standard [5]	4.978
Check Standard [5]	4.096
Check Standard [5]	4.745
Check Standard [5]	4.103

Table A-4. Calculated flux under Method 1315

Mean Interval (d)	Flux (T1)	Flux (T2)	Avg. Flux	STD DEV
0.03125	4.30349E-05	5.2971E-05	4.8003E-05	7.02589E-06
0.182138348	3.76463E-05	3.77942E-05	3.77203E-05	1.04571E-07
0.5625	2.77995E-05	2.96019E-05	2.87007E-05	1.27446E-06
1.457106781	4.76136E-05	4.97175E-05	4.86656E-05	1.48769E-06
4.120828693	4.19856E-05	4.24695E-05	4.22276E-05	3.42145E-07
10.19974747	2.65205E-05	2.82702E-05	2.73954E-05	1.23723E-06
17.3232141	1.56489E-05	1.79827E-05	1.68158E-05	1.65027E-06
27.55544171	5.57248E-06	6.18449E-06	5.87848E-06	4.32758E-07

Table A-5. Calculated cumulative mass of thallium over time

Cumulative Interval (d)	Cumulative Mass µg (T1)	Cumulative Mass µg (T2)
0.125	0.46477715	0.572087167
0.25	0.871357334	0.980264522
1	2.672768084	2.8984685
2	6.786584911	7.194063503
7	24.92437345	25.54088197
14	40.96397666	42.63871168
21	50.42842064	53.51465671
35	57.1688872	60.99541265

Table A-6. Calculated LOG values of cumulative time and cumulative mass as specified under Method 1315

LOG Cumulative Time (d)	LOG Cumulative Mass µg (T1)	LOG Cumulative Mass µg (T2)	AVG LOG Cumulative Mass µg	STD DEV
0.903089987	0.332755231	0.242537794	0.287646513	0.063793361
0.602059991	0.059803709	0.008656715	0.034230212	0.036166387
0	0.426961277	0.462168585	0.444564931	0.024895326
0.301029996	0.831651287	0.856974267	0.844312777	0.017906051
0.84509804	1.39662425	1.40723589	1.40193007	0.007503563
1.146128036	1.61240211	1.629804074	1.621103092	0.012305047
1.322219295	1.702675367	1.728472744	1.715574055	0.0182415
1.544068044	1.757159739	1.785297174	1.771228456	0.019896171