

ENVIRONMENTAL ASSESSMENT OF INDUSTRIAL WASTE BYPRODUCTS TO  
ESTIMATE THE RELEASE OF ELEMENTS UNDER DIFFERENT DISPOSAL AND  
ENVIRONMENTAL CONDITIONS

By

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To my grandfather (Ahmed)  
To my mom and dad  
To King Abdullah  
To my wife (Haton Khayat)  
To my three kids (Alwaleed, Eliana, and Ahmed)

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## LIST OF ABBREVIATIONS

BA	Bottom Ash
CFA	Coal Combustion Fly Ash
COPCs	Constituent Of Potential Concerns
GCTLs	Groundwater Cleanup Target Levels
HTAGS	High Temperature Arc Gasification Slag
Kd	Partition Coefficient
MSW	Municipal Solid Waste
PC	Portland Cement
SCMs	Supplementary Cementitious Materials
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristics Leaching Procedure
WTE	Waste to Energy
WTRs	Water Treatment Residues

Abstract of Dissertation Presented to the Graduate School  
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ENVIRONMENTAL ASSESSMENT OF INDUSTRIAL WASTE BYPRODUCTS TO  
ESTIMATE THE RELEASE OF ELEMENTS UNDER DIFFERENT DISPOSAL AND  
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By

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The aim of this scientific research is to identify which laboratory leaching tests are most appropriate in given waste management scenarios. For example, if studying whether or not it is appropriate to use EPA TCLP for assessing the utilization of concrete mixed with fly ash in pavement applications then the setting of the laboratory-leaching test should reflect the disposal conditions. Currently, TCLP uses acetic acid to mimic disposal in a municipal landfill scenario; however, using this test to assess the leaching of concrete mixed with fly ash is not adequate. Oftentimes after the standardization of a test it will be used in disposal scenarios in which it cannot account for site-specific conditions. These tests should only be used in the site disposal conditions in which they were developed. This dissertation aims to demonstrate a proposed environmental risk assessment protocol for assessing risk associated with beneficial reuse of industrial waste byproducts (Research Task 1) and to demonstrate the difficulty of using standardized leaching tests without regard to site specific conditions (Research Task 2). Research task 3 proposes a novel approach of evaluating the reuse of high temperature plasma arc gasification slag as supplementary cementitious materials (SCMs). Additionally, the fourth

research topic investigates the chemical release mechanism within industrial waste products subjected to changes in physical integrity.

Partition coefficient ( $K_d$ ) values readily available in the literature are often used to assess the fate and transport of metal contaminants in groundwater. However, to distinguish between the potential impacts of the disposal of beneficial reuse waste byproducts and traditional waste,  $K_d$  values specific to the site under consideration could help provide relevant insights on contamination risks. In this study, contamination risk of beneficially reused byproducts to groundwater was assessed using batch leaching tests to generate leachate samples from waste to energy (WTE) bottom ash and coal combustion fly ash (CFA). The results demonstrate that soil specific  $K_d$  values can lead to accurate predictions of the potential waste contamination risk when coupled with traditional environmental impact assessments. The results of this study point to site-specific  $K_d$  values as critical parameter when modeling the fate and transport of pollutants.

Drinking water treatment residues (WTR), generated from the lime softening processes, are commonly reused or disposed of in a number of applications; these include use as a soil amendment or a subsurface fill. A study was conducted using a broad range of leaching tests, including a framework of tests recently adopted by the United States-Environmental Protection Agency (EPA) and tests that were modified to account for scenario-specific conditions, such as the presence of natural organic matter (NOM). The results of these additional leaching tests demonstrated that certain applications, including disposal in a water body with NOM or suggest placement in an anaerobic environment, showed increased leaching of elements such as Fe, and that a site specific assessment should be conducted prior to using WTR in these types of

applications. This study illustrates the importance of leaching test selection when attempting to provide an estimation of release in practice.

The third study investigates the physical and chemical properties of blended cement produced using high temperature arc gasification slag (HTAG). Results from the study demonstrated that at low replacement percentages the total heat evolution and the compressive strength of the control cement and slag-cement blends were similar. The 28 day strength of mortars produced using 5% HTAG slag was 98% of the control. Significant decreases in strength and heat were seen with higher replacement percentages (20-50%). This is likely due to a dilution of the cementitious reactants as well as the larger particle size of the slag. The slag was more than twice the mean particle size (47.7  $\mu\text{m}$ ) of the cement.

The fourth research study investigates the effect of physical integrity alteration on leaching of elements from industrial waste materials. Artificial cracking was created using the compressive strength test at two different levels (33% and 66% of the maximum strength load). A permeability test was used as a direct tool to measure the level of cracking. This study found a high release of major elements (e.g., Al,Na) and certain trace elements (e.g., Sb) at higher degree of cracking in the control and amended concrete with mine tailings. The increase is not due solely to the physical alteration, other chemical factors played a role in this increase.

## CHAPTER 1 INTRODUCTION

### **Background and Motivation**

Industrial by-products like coal, fly ash, and demolition waste materials pose environmental risks when mismanagement and thus can be costly to clean up. This has prompted the recent trend of utilizing these waste by-products as resources rather than disposing of them. Some by-products possess technical properties which make them useful for other industrial processes like road construction; and the reuse of such by-products helps reduce landfill space requirements. The by-products which remain in a landfill may be of concern because of their ability to contaminate local ground water resources. This has sparked the need for environmental groundwater assessment to determine the risk of allowing waste by-products to be disposed of in landfills. These by-products release constituents of potential concern (COPCs), including organic and inorganic compounds, over time and thus groundwater in the vicinity should be evaluated for contamination (Reid, 2000).

Assessing the risk of waste by-products releasing COPCs is a multi-step process that takes into consideration the potential effects on many stakeholders. The targets most directly at risk are ground water resources and humans who consume that groundwater. As COPCs are released they travel by routes of exposure, like air or water, and concentrations are affected by duration of exposure (Townsend et al., 2006). It is common practice for a risk assessment evaluation to be conducted on waste by-products generated from industrial activities. These by-products can be found in the form of water sludge, street sweepings, coal fly ash, and other materials. Naturally occurring materials, like those found in iron rich soil are also subjected to risk assessment evaluation because of their risk to human health and their ability to negatively impact the local environment (Wang and Mulligan, 2006).

Leaching is a term that describes the transformation of organic and inorganic COPCs transferring from the solid waste by-products or native materials into the liquid phase when in contact with water (Washington State Department of Ecology, 2003). There are several factors that affect the release of constituents into the liquid phase, such as the physical or chemical properties of the material as well as the chemical properties of the surrounding environment (Kosson et al., 2002b). For example, some inert materials contain naturally occurring elements, but depending on local conditions due to the environment or human activity those elements may leach out and become soluble. The extent of COPCs leaching are affected by several physical and chemical factors.

Leaching tests were developed to assess the release of COPCs from waste materials in many different waste management scenarios (van der Sloot, 2000a). These tests are conducted under lab controlled conditions and documented using a standardized language. The tests evaluate and classify the leaching behavior of byproducts and provide data on the accuracy of the assessment method.

Leaching tests are classified based on the nature of the test under equilibrium conditions. This allows the test to determine the maximum release of the contaminants from the solid phase to the liquid phase (van der Sloot, 1996a). The first type of leaching tests are classified as batch-leaching. Batch leaching tests are run in an end-over-end fashion while controlling for certain variables (e.g., solution, pH, liquid to solid ratio (LS)) and following a specific series of steps. Duration and particle size are also accounted for in these tests. Batch-leaching tests are fast, qualitative and inexpensive (Jackson et al., 1984). The second classification are non-static leaching tests or dynamic tests. Dynamic leaching tests provide detailed data over time (Al-Abed et al., 2008). These tests provide qualitative information in the long term and better simulate a waste management scenario and site-specific conditions.

Another type of leaching classification is based on the practice and natural disposal of the waste (van der Sloot, 1996a). These are classified as compliance and characterization tests. Compliance tests are aimed at a direct comparison with regulatory threshold values and are used by generators before disposal to the landfill to comply with environmental regulatory agencies disposal limit requirements, such as Toxicity Characteristic Leaching Procedure (TCLP) (Kosson et al., 1996). The characterization tests, such as the pH stat tests or tank leaching tests in the U.S., are designed to better simulate different waste disposal and utilization conditions.

Waste generators commonly use the TCLP test due to its popularity as a compliance leaching test in the U.S (Vann et al., 2006). This test determines if waste is hazardous or not. It simulates the disposal of waste in leachate that is typically generated from municipal solid waste (MSW) dumped in landfills. The COPCs leachate concentrations are compared with toxicity characteristics (TC) values. The TCLP test, however, was not designed to quantify the risk associated with the reuse of waste byproducts. The TCLP test can only define the characteristic release of COPCs under very limited conditions that neglect external factors. Thus, there is a need for a broader range of characterization tests and case-by-case evaluations.

The Synthetic Precipitation Leaching Procedure (SPLP) is another common approach for evaluating the release of COPCs. The SPLP test is used when waste is subject to acid rain conditions for beneficial reuse of waste (Townsend et al., 2006). These leaching procedures estimate the maximum release of COPCs in a specified LS ratio and are run under an assumption of equilibrium. However, they are limited due to their inability to account for other factors that can control the release of contaminants. The complexity of byproduct disposal necessitates special consideration of how environmental regulations affect test

procedures alongside the fundamental understanding of how different environments impact certain byproducts. It is in this regard that future leaching assessment tools should always account for varied environmental scenarios (Herrington et al., 2006).

Environmental regulation is primarily concerned with the health of the environment including human and animal exposure. This concern calls for fast and reliable assessment methods like the Environmental Protection Agency's (EPA) SPLP and TCLP tests. While these tests can help ensure the safety of a local environment, they do not provide information on the environmental impact that waste byproducts may pose. Environmental impact assessments that account for site-specific conditions should also be conducted. A column leaching test is one such test that can be used. Thus it is necessary to conduct scientific studies while modelling the leaching process under controlled conditions that account for naturally occurring leaching conditions.

After the standardization of a test it will often be used in disposal scenarios in which it cannot account for site-specific conditions. These tests should only be used in the site disposal conditions in which they were developed. This dissertation aims to demonstrate the risk of using standardized leaching tests without regard to field conditions (Research Task 1) or soil sorption mechanism (Research Task 2), and to further conduct leaching testing for a selected industrial waste byproduct focusing on the effect of physical change on leaching (Research Task 3). Additionally, a novel beneficial reuse assessment research of plasma arc slag as supplementary cementitious materials (SCMs) will be proposed in Research Task 4.

### **Objectives and Organization of Dissertation**

This dissertation presents real world disposal scenarios evaluated using standardize leaching procedures and modified for site-specific conditions, risk assessment of selected industrial waste byproducts that evaluate leaching and sorption, beneficial reuse assessment

of an industrial waste byproduct, and field leaching evaluation of selected industrial waste byproduct. The overall objective of this dissertation is to advance the field of environmental engineering (specifically the beneficial use of industrial byproducts) with site-specific parameters and by providing a feasibility study of the beneficial use of an industrial waste material in a construction application. Four distinct Specific research objectives are outlined below for each study:

Chapter 2 aims to determine the partition coefficient for different industrial waste byproducts applied in beneficial reuse applications. The objectives of this chapter are to illustrate a novel approach for calculating site specific partitioning coefficients for trace elements using waste extraction test leachates. Additionally, it provides a discussion on factors influencing the coefficients, and demonstrates the impact that these  $K_d$  can have on fate and transport modelling.

The third chapter of this dissertation is characterizing drinking water sludge in different waste management scenarios, using different developed and modified leaching tests. The objectives of this chapter are to conduct a suite of leaching tests to fully characterize drinking water sludge in order to potentially predict leaching in different reuse management scenarios.

Chapter 4 of this dissertation is assesses the use of high temperature arc gasification slag as a supplementary cementitious material. This chapter presents a novel examination of the potential for use of slag as a supplementary cementitious material, and will serve to guide researchers, slag generators, and other interested parties in evaluating its reuse opportunities.

The last research chapter of this dissertation serves to evaluate the impact of the physical integrity of encapsulated industrial byproducts focused on the leaching of elements. The major objectives of this chapter are to examine how stress, through simulated cracks,

influences the release of elements and to evaluate if the addition mine tailings results in decreased strength of the finished material.

CHAPTER 2  
DETERMINATION OF SITE SPECIFIC PARTITION COEFFICIENTS FROM  
INDUSTRIAL WASTE LEACHATES AND QUANTIFICATION OF COEFFICIENT  
INFLUENCE IN BENEFICIAL USE EVALUATION

**Background**

Industrial waste products contain chemical elements that can contaminate ground water resources. One method of reducing the environmental impact of industrial waste byproducts is through various beneficial reuse applications (Oehmig et al., 2015; Wiles, 1996). The primary method of assessing a reused byproduct's environmental risk is by evaluating its potential to leach contaminants into the surrounding groundwater (Blaisi et al., 2015; Townsend et al., 2006). This type of risk assessment couples results from leaching tests to fate and transport models that simulate the mobility of contaminants of potential concerns (COPCs) through subsurface environments. The concentrations of COPC at sensitive receptor sites can thus be predicted (Allison and Allison, 2005; Selim and Iskandar, 1999). Fate and transport models typically require inputs that quantify subsurface environments such as: infiltration rate, aquifer and vadose zone thickness, aquifer pH, soil partitioning coefficient ( $K_d$ ), receptor distance, and concentration of COPC, among others (Allegrini et al., 2015; Apul et al., 2007; EPA, 1999). All of these inputs substantially influence modeled COPC concentrations at receptor sites and most have been the subject of significant research and data compilation (François et al., 2009; Mclean and Bledsoe, 1992a).

The solid to liquid partitioning coefficient ( $K_d$ ) between a waste leachate and soil interface is one input parameter used in fate and transport modeling that has been a point of contention in the literature (Strawn and Sparks, 1999). While most beneficial use evaluations will employ leaching tests to determine specific COPC concentrations, empirical determinations of site-specific  $K_d$ 's are less frequent. Most of the risk assessment evaluation found in current scientific literature has been performed using reference  $K_d$  values or using

$K_d$  values found in empirical modeling programs (e.g., MINTEQ2) (Allison and Allison, 2005; U.S. EPA, 2014). These studies have contributed to the understanding of the elemental interactions that take place in specific solutions at precise conditions. However, using a literature derived  $K_d$  value when assessing beneficial reuse risk may not result in the most accurate contamination risk profiles, considering the range of  $K_d$  found in the literature (Sauve et al., 2000).

The objectives of this study is to demonstrate that waste- and soil-specific  $K_d$  values can be determined and used in fate and transport modeling for the risk assessment of beneficially reused industrial waste byproducts. Two industrial waste materials [waste to energy (WTE) bottom ash (BA) and coal combustion fly ash (CFA)], which are frequently evaluated for beneficial use applications, were tested. The EPA's Composite Model for Leachate Migration with Transformation Products (EPA-CMTP) was used (U.S. EPA, 2015). EPA-CMTP has been used as a modeling tool in the US at the state and federal levels for beneficial reuse assessments and was recently used as a part of the decision making efforts related to the regulatory status of coal combustion residual management (U.S. EPA, 2005). This chapter illustrates a novel approach for calculating site specific partitioning coefficients for trace elements using waste extraction test leachates. Additionally, it provides a discussion on factors influencing the coefficients, and demonstrates the impact that these  $K_d$  can have on fate and transport modelling.

## **Materials and Methods**

### **Soil and Waste Sample Collection**

Soil samples were collected from eight different locations in Florida, US. Soil samples were collected at a constant depth of 5-25 cm below the ground surface. The soil sampling locations were selected to provide a wide range of soil types which would differ in

both their chemical composition as well as their physical characteristics, so that the impact of these parameters on the  $K_d$  could be evaluated. Prior to testing, the soil was air dried at room temperature (approx.  $24 \pm 2$  °C) for three days, passed through a 2 mm sieve, and refrigerated at approx. 4 °C until time of analysis. Two grab samples of industrial waste byproducts were collected from facilities in FL, U.S. CFA was collected from a coal fired power generation unit, the samples were collected from the discharge of the facilities fabric filters and do not contain the scrubber residues associated with acid gas removal. A sample of processed WTE BA was collected from a mass burn, WTE facility, this facility subjects its bottom ash to ferrous (magnet) and non-ferrous (eddy current separation) metals recovery following combustion. To reduce heavy metal leaching from the WTE BA (commonly done prior to beneficial use applications) the material was aged for three months before sample collection and testing.

### **Soil Classification and Total Environmentally Available Element Content**

Total environmentally available concentration of elements in the soil samples of each sample were determined by EPA Method 3050b using acid digestion in six replicates. The percentage of sand, silt and clay in each of the soil samples were determined based on grain size distribution of the soil in accordance with the procedures outlined in ASTM D422. The pH and oxidation reduction potential (ORP) of each soil sample were determined in accordance with procedures outlined in EPA method 9045D. Soil moisture content was measured by determining the initial and oven dried mass in accordance with ASTM D2216. An approximation of the soil organic matter content was determined by measuring the loss on ignition (LOI) of the soils, utilizing the method described in Santisteban et al.<sup>18</sup> which reports soil organic matter as the LOI after four hours of combustion at 550 °C.

### **Batch Leaching and Soil-Liquid Partitioning Tests**

Industrial waste leachates (for soil-waste leachate partitioning testing) were generated using a modified EPA method 1316 test (at a set liquid to solid ratio (L/S) of 10 mL-reagent water/g-waste). Prior to testing the sample was first size reduced to pass a U.S #4 sieve (4.75 mm). Each waste was leached in 8 replicates, a 200 g dry mass of waste was used to generate a sufficient quantity of leachate for the soil sorption tests.

The leachate generated from the 1316 test was introduced to one of the 8 soils to conduct the soil sorption experiment (each soil sorption test was conducted in triplicate). The soil sorption testing was run in accordance with ASTM D4646 (ASTM, 2008).

### **Acid Digestion and Elemental Analysis**

All leachate samples were digested using an automated hot block digestion system in accordance with EPA acid digestion method 3010a (U.S. EPA, 1992). Soil sample digestions and waste leachate extractions were evaluated for their major and trace element content using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), in accordance with EPA method 6010B (U.S. EPA, 1996). All samples were analyzed for: Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Na, Ni, Pb, Sb, Se, V, and Zn. Leachates were also evaluated for the inorganic anions,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  using ion chromatography (IC) in accordance with EPA method 9056a (U.S. EPA, 2007).

### **Partitioning Coefficient Determinations**

The empirically determined  $K_d$ 's were calculated using waste leachate concentration ( $C_{\text{initial}}$ ) from method 1316 and the aqueous concentration following the soil sorption test ( $C_{\text{final}}$ ). The  $K_d$ 's reported in this study are all expressed in units of L/kg.

## **Example of Beneficial Use Assessment**

Often times, in regulatory decision making efforts, fate and transport models are applied to evaluate the potential for a waste product (either beneficially used or disposed of) to impact surrounding water supplies (Allison and Allison, 2005; Essington, 1997; Selim and Iskandar, 1999). Critical components to these models include: the  $K_d$ , waste leachate concentration, and the regulatory thresholds used for comparison. To illustrate the impact that the  $K_d$  can have on the outcome of a fate and transport assessment two beneficial use scenarios were evaluated using the U.S. EPA's IWEM; a detailed description of the program can be found in (U.S. EPA, 2005).

The two scenarios evaluated were: the use of WTE bottom ash as a roadway sub-base, and the use of CFA as a structural fill material; the majority of the input parameters (infiltration rate, fill volume, roadway thickness, subsurface hydrogeology) for these models were set using values developed for two previous assessments conducted by: Benson and Edil (2005) and the Electric Power Research Institute [EPRI] For each of the scenarios evaluated, the input concentrations were set at the values leached in the method 1316 test, for the CFA (structural fill) and WTE BA (road base) (EPRI, 1990; Benson and Edil, 2005).

Each of the modeling evaluations were run using three different  $K_d$ 's. The default  $K_d$  for each element (from IWEM) was used as well as the values representing the lowest and the highest calculated  $K_d$  for each element from the soil sorption testing. The default inorganic  $K_d$  in IWEM employs a non-linear sorption isotherm which is derived using the geochemical speciation model MINTEQA2. Additional information on IWEM can be found in the IWEM Model 3.1 Technical Background Document (U.S. EPA, 2005).

## Results and Discussion

### Soil Characterization

Soil characteristics for each of the 8 samples tested, including soil pH and conductivity, percentage of organic matter, total Al, Fe and Mn content, and soil classification conducted in accordance with the methodology outlined by the United States Department of Agriculture (USDA) are presented in Table 2-1. Total Al, Fe and Mn are reported since they have been previously shown to influence soil and  $K_d$  (Essington, 1997; Mclean and Bledsoe, 1992a) .

Iron concentrations in soil samples ranged from 5,800 mg-Fe/kg-soil to 167 mg-Fe/kg-soil. Soils 2,4,5 and 7 had Fe concentrations over 1,900 mg-Fe/kg-soil, while soils 1,3,6, and 8 had Fe concentrations less than 555 mg-Fe/kg-soil. Soils 2,4,5 and 7 had Al concentrations of: 11,200, 10,400, 7,500 and 8,400 mg-Al/kg-soil respectively. Al concentrations ranged from 11,200 to 906 mg-Al/kg-soil. Manganese concentrations ranged from 0.55 to 61.0 mg-Mg/kg-soil. These values were below mean values for the continental U.S. (330 mg-Mg/kg-soil) as reported by Shacklette and Boerngen (Shacklette and Boerngen, 1984) but were consistent with measured values reported in Florida (Ma et al., 1997). Aluminum and Fe total concentrations also fell below their respective continental means (4.7 and 1.8%, respectively) however they were similar to values in Florida as reported by Chen et al. (1999) (Al and Fe concentrations of  $2,200 \pm 3,000$  and  $2,300 \pm 4,500$  mg/kg ( $\pm$  SD)). Soil pH's were slightly acidic and varied from 5.00 to 6.32. Organic matter fractions for all soils were measured at or below 5.00%. Soils used in this study consisted of 80-98 % sand, 1-5 % silt, and 1-16 % clay. All soils evaluated were either sand or loam, which are characteristic of typical FL soils (Ma et al., 1997).

## **Waste Leaching and Elemental Composition**

Total environmentally available concentrations of elements in CFA and WTE BA are presented in Table 2-2. Concentrations of As, V, Se, and Ba were found to be substantially higher in the CFA while concentrations of Al, Zn, and Sb, were higher in WTE BA.

Aluminum was the most abundant in CFA, while Ca was most abundant in WTE BA.

Leached concentrations for the CFA and WTE BA are presented in Table 2-3. Mean values for post extraction leachate pH's were 9.70 and 10.4 for CFA and WTE BA respectively. To determine COPCs present in the WTE FA and CFA GCTLs were used as comparable concentration thresholds. CFA leached Al (8.39 mg/L), As (0.174 mg/L), Cr (0.125 mg/L), Sb (0.0301 mg/L), and V (0.325 mg/L) in excess of respective GCTLs. WTE BA leached Al (122 mg/L), and Sb (0.0361 mg/L) in excess of GCTLs. The reduced concentration of certain elements (most notably Pb) in the WTE BA is likely due to the material being aged prior to testing. Aging is known to impact pH, and effect the release of COPC in WTE BA (Meima and Comans, 1997).

## **Determination of Soil-Waste Leachate Partitioning Coefficients**

Leachate pH for WTE BA and CFA after determining  $K_d$  is presented in Table 2-4. In all instances, the leachate pH was found to be highly dictated by the initial pH of the waste leachate introduced into solution. All tested soils had a final alkaline pH. The pH of leachate decreased from its initial value during the 1316 test when introduced to the soil. Final pH values for CFA ranged from 9.50 (soil 1) to 8.01 (soil 2). Final pH values for the WTE BA ranged from 8.12 (soil 4) to 10.3 (soil 8). As a whole, the pH's of the WTE BA  $K_d$  extractions was found to be higher than those of CFA extractions, most likely due to the higher initial pH of WTE BA during the 1316 testing. CFA and WTE BA did not seem to follow similar trends with respect to the influence of soil type on pH. Neither WTE BA or

CFA leachate appeared to follow a consistent pH trend with respect to initial soil pH or classification. While the leachate data does not represent a wide range of pH values it does demonstrate that for these and other similar waste products (e.g., combustion residues) the pH of the soil-leachate interface may be elevated in beneficial use scenarios. As pH is known to be a significant factor controlling chemical speciation, leaching, and sorption this would be an important component for consideration when conducting a site (or area) specific beneficial use assessment.

Figure 2-1 presents the experimentally determined elemental  $K_d$  values for CFA and WTE BA for: Al, Sb, and V. These elements were measured at concentrations above detection limits in both waste materials (Table A-1); this produced 5 experimentally determined  $K_d$  for WTE BA and 6 for CFA. Means and ranges of  $K_d$  determined for each waste type and element were compared to evaluate if waste type had an impact on  $K_d$ . Experimentally determined  $K_d$  were also compared to previously reported ranges of values in the literature (Table 2-5). Soil type was also evaluated to determine if it contributed to the differences in  $K_d$ .

### **Aluminum**

$K_d$  values for Al ranged from  $7,010 \pm 926$  L/kg (Soil 2) to  $498 \pm 20.4$  L/kg (Soil 8) for CFA and  $1,990 \pm 500$  L/kg (Soil 4) to  $9.81 \pm 0.42$  L/kg (Soil 8) for WTE BA. Soil 8 produced the lowest  $K_d$  for both the WTE BA and CFA. Soil 8 was 98% sand and  $K_d$  of soil 8 was lowest for both waste streams. However, there were no discernable trends based on waste types for any of the other soil types or soil classification. Experimentally determined  $K_d$ 's for each of waste type was plotted against the total element concentration of each soil to evaluate trends that might have been present. Relationships between soil element content and  $K_d$  are displayed in Figure 2-3 if calculated  $R^2$  values were greater than 80%. Al was the only

element that demonstrated a correlation between soil content and  $K_d$ . Al concentration in soil was found to correlate linearly with Al  $K_d$  for both waste leachates ( $R^2$  values were 0.957 (CFA) and 0.954 (WTE BA)).

### **Arsenic**

Leached concentrations of As were only present in CFA leachates.  $K_d$  values for As ranged from  $2,000 \pm 72.2$  L/kg (soil 7) to  $92.5 \pm 2.84$  (soil 3). These values fell within range of previously reported  $K_d$  (Table 2-5), but previously reported values encompass several orders of magnitude. There was no correlation between soil classification and experimentally determined  $K_d$ . Partitioning of As was found to correlate relatively well ( $R^2 = 0.830$ ) with measured Fe content in the soil (Figure 2-2). This supports previous research that has demonstrated iron oxide surfaces as sorption sites for trace metals including As (Elkhatib et al., 1984).

### **Antimony**

Antimony concentrations were measured in both CFA and WTE BA leachates. In both instances Sb was found to leach approximately 5 times its GCTL. For WTE BA Sb is often times one of the elements which is of critical focus for beneficial use (Fairbrother et al., 2007). Sb  $K_d$ 's for CFA and WTE BA varied by an order of magnitude and ranged from:  $4.23 \pm 0.147$  (Soil 3) to  $44.4 \pm 10.4$  (Soil 7) L/kg for CFA and  $5.66 \pm 0.178$  (Soil 3) to  $46.2 \pm 5.83$  (Soil 7) L/kg for WTE BA. Similar to As, Soil 7 was found to produce the highest  $K_d$  for Sb in both WTE BA and CFA leachates. Both wastes followed similar trends with respect to calculated  $K_d$  and soil used (CFA  $K_d$ 's: 7, 5, 4, 2, 6, 8, 1, 3; WTE BA  $K_d$ 's: 7, 5, 4, 2, 1, 6, 8, 3). While there was no correlation between soil type  $K_d$ , Fe content was seen to be highly correlated for both leachate samples (Figure 2-2).

## **Chromium**

Leached concentrations of Cr were only present in CFA leachates.  $K_d$ 's ranged from  $10.4 \pm 1.51$  (Soil 7) to  $1.06 \pm 0.00164$  (Soil 1) L/kg. The majority of  $K_d$ 's fell on the low end of the range of reported values (125-65,600 L/kg) (Sauve et al., 2000). Partitioning of Cr was found to correlate relatively well ( $R^2 = 0.915$ ) with the measured Fe content in the soil (Figure 2-2).

## **Molybdenum**

Leached concentrations of Mo were only initially present in the WTE BA; therefore  $K_d$ 's could only be determined for the WTE BA soil-leachate interface.  $K_d$  values for Mo ranged from  $4.57 \pm 1.64$  (soil 4) to  $0.0318 \pm 0.00362$  L/kg (soil 8). The majority of the measured values fell on the low end of the range of data reported in the literature (0.631-501 L/kg) (Allison and Allison, 2005). There was no correlation between soil classification and the experimentally determined  $K_d$  for Mo. Partitioning of Mo was not found to correlate with either Al nor Fe contents.

## **Selenium**

Leached concentrations of As were only present in CFA leachates.  $K_d$ 's ranged from  $40.3 \pm 0.963$  (Soil 4) to  $7.54 \pm 1.37$  L/kg (Soil 8). Measured  $K_d$  values were within range of data reported in literature (Table 4). Partitioning of Se was found to correlate relatively well ( $R^2 = 0.960$ ) with the measured Al content in the soil (Figure 2-3). This supports previous research which demonstrates that iron oxide surfaces represent sorption sites for Se (Peak, 2006).

## **Vanadium**

Vanadium concentrations were measured in both CFA and WTE BA leachates. Calculated V  $K_d$ 's for both CFA and WTE BA varied by three orders of magnitude and ranged from:  $9.50 \pm 2.40$  (Soil 3) to  $3,690 \pm 15.2$  (Soil 7) L/kg and  $0.0879 \pm 0.00157$  (Soil 3)

to  $53.6 \pm 12.7$  (Soil 7) L/kg respectively. Similar to Sb and As Soil 7 was found to produce the highest  $K_d$  for V in the WTE BA and CFA leachates. Both wastes followed a similar trend with respect to calculated  $K_d$  and soil used (CFA  $K_d$ 's: 7, 5, 4, 2, 6, 1, 8, 3; WTE BA  $K_d$ 's: 7, 5, 4, 2, 8, 6, 1, 3). Soil type did not correlate well with  $K_d$ , and only Fe content was seen to be highly correlated with both leachates (Figure 2-2).

## **Zinc**

Leached concentrations of Zn were only present in WTE BA.  $K_d$  values for Zn ranged from  $2.07 \pm 0.660$  (soil 1) to  $73.5 \pm 2.36$  L/kg (Soil 6). The measured  $K_d$  values fell within range of reported  $K_d$  values in the literature (Table 2-5) (Allison and Allison, 2005; Sauve et al., 2000). There was no correlation between soil type and the experimentally determined  $K_d$  for Zn. Partitioning of Zn was not found to correlate with either Al or Fe content.

## **Trends and general conclusions**

Average pH values, following sorption tests when FA and WTE BA samples were mixed with soils, were  $9.00 \pm 0.501$  and  $9.80 \pm 0.735$  respectively. Speciation diagrams based on thermodynamic data and literature pH-dependent studies suggest that these elements exist in cationic forms at low pH, but within the experimental pH range these elements' anionic or oxyanionic species predominated (Cornelis et al., 2008). At oxidized state and under this study pH range, As exist in the form of arsenate As(V) and As(III), Al as  $Al(OH)_4^-$ , Cr as Cr(VI) and Cr(III), Mo as Mo(VI), Sb as Sb(III) and Sb (V), Se as Se (IV), V as V(IV) and V(V), and Zn as  $Zn(OH)_2$  (Sposito, 2008). These pH ranges may not be the pH ranges that covers all beneficial use applications, but the results obtained here emphasis again on the importance of selecting the  $K_d$  value based on the specific beneficial use scenarios. Sorption mechanism is favorable for As, V, and Zn but Cr, Se, Mo, and Sb has low sorption mechanism under this

study pH ranges. In addition to this, certain elements were retained well with Al or Fe. Al and Fe content in soils correlate linearly with measured  $K_d$  values for certain COPCs; Metal-(oxyhyd) oxides such as hydrous ferric oxides (HFOs), and hydrous aluminum oxides (HAOs) are known to be a representative scavengers of trace metals, which makes relatively strong bonding via complexation (Singh et al., 1984; Tessier et al., 1979). In Fig 2 and 3,  $K_d$  values of Sb, As, Cr, and V exhibited distinct linearity with Fe content, where that of Al, Se coupled with Al content. These different affinities towards Fe and Al oxides are presumably due to the different dielectric constants of the two solids and resulting structures of water at the interfaces (Brown and Calas, 2013). These findings have implications for operators where soil can be used as a sink for certain COPCs.

Under the investigated pH of this study, arsenic exists as arsenite As(III) or arsenate As(V), but mostly dominated by As(III) when taking into the account the final pH and the ORP (~200 mV). It is suggested that adsorption at this pH region is dominated by As(III) (Smedley and Kinniburgh, 2002). This was because  $\text{OH}^-$  results in electrostatic repulsion between As(V) and hydroxylic functional group, which is generated from the accumulation of the  $\text{OH}^-$ . Electrostatic attraction between arsenic and hydroxylic functional groups strengthen As sorption under this study pHs (Table 4) (Cornelis et al., 2008). Arsenic is known to show greater affinity towards both Fe and Mn oxides,(Elkhatib et al., 1984) however, sorption reactions appear to be weaker on aluminum oxide surfaces (Cornelis et al., 2008; Manning and Goldberg, 1997). Figure 2 presents the relationship between total iron in soil samples and calculated  $K_d$ . The correlation iron and  $K_d$  was both positive and significant ( $R^2 \sim 0.830$ ). Similar correlations were observed in Livesey et al. (1981). Arsenic sorbs strongly to iron oxide surfaces at acidic and neutral pH ranges (Traina, 1996). However, desorption of arsenic from iron oxide becomes favorable as pH becomes more alkaline (11

and higher) (Fuller and Davis, 1989; Traina, 1996). These findings were not the case with the pH values obtained in Table 4. In Table 4, the mean pH value for CFA and WTE BA were 9.00 and 9.80 respectively. Similar to other anions, As is influenced by the presence of competing ions (e.g.,  $PO_4^{3-}$  and  $SO_4^{2-}$ ) which can compete with As for sorption sites. Several studies indicated  $SO_4^{2-}$  competition with As is insignificant, while the presence of  $PO_4^{3-}$  is significant in decreasing As adsorption (Goh and Lim, 2004). However, reported that  $SO_4^{2-}$  was able to displace some of the adsorbed As(V) on an amended soil. It is not clear from this study if  $SO_4^{2-}$  caused any competition for surface sites with As. The initial  $PO_4^{3-}$  in this study was reported to be below the detection limits, which indicate that  $PO_4^{3-}$  did not compete with As for surface sites. Because iron oxide surfaces can hold large amount of arsenic, any chemical changes in the groundwater can induce desorption of arsenic in sufficient that results in exceedances of the GCTLs.

Selenium exists as selenite Se(IV) and selenate Se(VI), but mostly dominated by Se (IV) under this pH range (Cornelis et al., 2008). Toxicity of Se depends on its oxidation state. Selenite is considered to be more toxic than selenate (Zhang and Frankenberger, 2001). Adsorption reactions with soil mineral surfaces attenuate solution Se concentrations. Selenium  $K_d$  values in CFA samples (~3.30-17.5 L/kg), Se did not undergo favorable sorption under this study pH values and most likely due to the repulsion between Se and accumulated hydroxide ions found on soil surfaces (Dzombak and Morel, 1996). It is well established in the literature that aluminum and iron oxides are the most favorable surface sites for Se sorption (Peak, 2006). In addition, Se as reported in the literature may compete with other anions, such as  $SO_4^{2-}$  and  $PO_4^{3-}$ , but it is unclear if similar observation could be addressed in this study (Goh and Lim, 2004). Aluminum and iron oxides have high points of zero charge (8-9.5) which can easily attract anions to their surfaces (Peak, 2006). A

correlation between total aluminum and Se was both positive and significant ( $R^2 \sim 0.960$ ) (Fig.3).

The study found poor sorption rates above a pH of 7, and it was concluded that Mo sorption was much lower under the investigated pH range of this study. Higher pH range depresses sorption of Cr and the presence of sulfates may overcome Cr sorption to a greater degree as a result of competitive electrostatic effects (Zachara et al., 1987). WTE BA had an average  $SO_4^{2-}$  of 46.5 mg/L and Cr has a similar ionic radii and charge as  $SO_4^{2-}$ . This may be the reason that it overcomes Cr sorption. A positive correlation between Cr sorption and total Fe ( $R^2 \sim 0.962$ ) was observed (Fig.2). This trend was also found in other studies where it was also found that the magnitude of the iron oxide on the surface of the soils increases the sorption of Cr (VI) through specific site sorption (Rai et al., 1989). Zn is the only cationic element that was observed at alkaline pH values and it is probably due to elements precipitates as hydroxide at alkaline pH (Mclean and Bledsoe, 1992b). Zn behaves similarly to other cations, where its sorption and precipitation increases with pH. In addition to pH, the sorption of Zn is dependent on its initial concentration ( $\sim 0.0208$  mg/L). Zinc is expected to produce higher  $K_d$  values if the initial concentration is higher. A positive correlation was found between Zn sorption and the total iron content ( $R^2 \sim 0.902$ ) for five out of eight soil samples (Soil's 2, 3, 5, 7, and 8), which agree with observations found in Hickey et al. (1984).

The effect of a solution's ionic strength on the sorption of Al, Sb, and V was used as indirect evidence for coming to understand the type (specific or nonspecific adsorption) of anionic sorption the element has in the system, and to compare the  $K_d$  values differences in CFA and WTE BA samples. Al and V averaged  $K_d$  values that were higher in the coal FA sample when compared to the WTE BA sample (Fig.1). The ionic strength in CFA and WTE

BA were 745 and 1,340 mg/L respectively. The influence of ionic strength on Al and V sorption were much higher in WTE BA sample which resulted in a reduction of Al (average  $K_d$  ~2,600 and 467 L/kg for CFA and WTE BA respectively) and V (average  $K_d$  ~938 and 25.8 L/kg for CFA and WTE BA respectively) sorption. This observation indicated that most of Al and V may be complexed through outer-sphere complexation (Manohar et al., 2005). Vanadium sorption correlated well with total iron in the CFA sample ( $R^2$ ~ 0.840 and 0.0481 for CFA and WTE BA respectively) (Fig.2). Similar observation have been documented by Naeem et al. (2007). While Sb sorption (Fig.1) was slightly unaffected by ionic strength changes ( $K_d$ ~ 14.4 and 15.8 L/kg for CFA and WTE BA respectively) this behavior is hypothesized for inner-sphere complexation (Xi et al., 2010). Sb was correlated well with total iron (Fig.2) ( $R^2$ ~ 0.950 and 0.990 for CFA and WTE BA respectively) and manganese (Fig.4) ( $R^2$ ~ 0.942 and 0.962 for CFA and WTE BA respectively). The results obtained in this study showed an increase Sb sorption as a function of total manganese as also indicated in Thanabalasingam et al. (1990) (Thanabalasingam and Pickering, 1990). The study concluded that the affinity between Mn oxide surface sites and antimony species was high enough to overcome any repulsion effects from other elements. Similar to other oxyanion elements, sorption of Mo is significant at acidic pH values (pH of approximately 3-5) on Al and Fe hydro(oxide) surfaces, but was more profound in Fe hydro(oxide) (Jones, 1995). Sorption of Mo on Fe hydro(oxide) decreases significantly when increasing the pH above 4 (Goldberg et al., 1996). Molybdenum  $K_d$  values ranged from 0.0318 to 4.57 L/kg. This range of values is quite low. It is hypothesized that Mo competes with other anions for sorption sites. This study could not find any correlation between Mo sorption and total Al or Fe as indicated by Glodberg et al. (1996).

Average pH values, following sorption tests when CFA and WTE BA samples were mixed with soils, were  $9.00 \pm 0.501$  and  $9.80 \pm 0.735$  respectively. These pH ranges may not be representative of pH ranges that cover all beneficial reuse scenarios, but they emphasize the importance of selecting site specific  $K_d$  values. In addition, Al and Fe content in soils correlate linearly with measured  $K_d$  values for certain COPCs. These findings have implications for operators where soil can be used as a sink source for certain COPCs.

The major differences between the study derived results and the literature derived  $K_d$  values are attributed to using different types of soils, different experimental conditions (e.g., different L/S ratio or using batch or column test to determine  $K_d$  values), and using simple solutions as opposed to using leachate generated from industrial waste byproducts.

### **IWEM Modeling Results and Impact of Soil-Specific Partitioning Coefficient**

Table 2-6 shows the results following IWEM simulations. Based on Monte Carlo analysis equipped in IWEM, 90<sup>th</sup> percentile exposure concentrations compared to the benchmark thresholds (GCTL herein) were estimated for each element of interest. In case of the coal FA used in a structural fill, the 90<sup>th</sup> percentile concentrations at the location of 3.02 m were all below the GCTLs (0.01 and 0.1, 0.006, and 0.049 mg/L for As, Cr, Sb, and V respectively) regardless of the  $K_d$  values (default, minimum, or maximum) used, indicating that the coal FA is appropriate for this beneficial use scenario under broad range of soil conditions. On the other hand, when the WTE BA was used as a subbase material in roadway, an overshoot (higher 90<sup>th</sup> percentile concentration than GCTL) was observed in several cases. For example, application of minimum  $K_d$  value of Al (9.81 L/kg) leads to the exceedance of GCTL (0.2 mg/L), whereas no risk was associated with either default, or maximum  $K_d$  values. Furthermore, even introduction of maximum  $K_d$  value could not prevent the 90<sup>th</sup> percentile Sb concentration from exceeding the GCTL (0.006 mg/L) indicating poor

retention capacity of Sb and additional remediation efforts might be required especially for Sb in this case.

These examples presented serve to illustrate the importance of using site specific parameters that present in the beneficial use applications, where the coexisting ions may play a significant role over the entire process. The effect of site specific conditions on  $K_d$  values should include descriptions of those site specific conditions: pH, dissolved elements, geochemical matrix of the water in the system. Although soil heterogeneity was not accounted for, and the hydrologic and geochemical conditions used in the simulations were limited in a relatively simple conceptual cases, still the results presented in this study tells that the broad range of  $K_d$  values might arise from different types of soil, which will cause drastic differences in plume distributions as well the concentration at receptor well.

Risk-based paradigm has become more and more important in environmental regulatory, and potential risk of elements at a specific site needs to be determined by the availability of metals, not by the total concentration. From this point of view, probabilistic analysis using IWEM may contribute to decision making process regarding beneficial use evaluation by considering site-specific DAFs.

Table 2-1. Physico-chemical characteristics for each collected soil sample. Soil samples were collected from Florida with different characteristics. The soil samples were used to determine the partitioning coefficient for WTE bottom ash and coal combustion fly ash

Soil Sample	Soil #1	Soil # 2	Soil #3	Soil #4	Soil #5	Soil #6	Soil #7	Soil #8
Chemical characteristics								
pH	5.30	5.69	6.10	6.32	5.23	5.40	5.00	5.10
Conductivity ( $\mu$ S)	18.2	30.4	14.3	23.1	99.2	21.4	23.3	34.5
Organic matter (%)	2.74	1.67	1.05	3.75	2.68	1.72	4.85	1.03
Total element content (mg-element/kg-dry soil) $\pm$ StdDev								
Aluminum	2,200 $\pm$ 100	11,200 $\pm$ 2,750	906 $\pm$ 16.8	10,400 $\pm$ 2,280	7,500 $\pm$ 9 75	3,400 $\pm$ 385	8,400 $\pm$ 706	1,200 $\pm$ 230
Iron	555 $\pm$ 2.36	1,900 $\pm$ 297	167 $\pm$ 15.1	2,800 $\pm$ 423	3,500 $\pm$ 402	442 $\pm$ 109	5,800 $\pm$ 456	537 $\pm$ 63.2
Manganese	61.0 $\pm$ 0.501	7.41 $\pm$ 1.54	3.20 $\pm$ 0.244	7.81 $\pm$ 1.30	22.9 $\pm$ 3.03	0.55 $\pm$ 0.0143	21.6 $\pm$ 2.31	1.28 $\pm$ 0.652
Physical characterization (%)								
Sand	81	88	80	88	88	97	89	98
Silt	3	3	5	1	2	1	1	1
Clay	16	9	15	11	10	2	10	1
USDA classification <sup>a</sup>	Sandy loam	Loamy sand	Sandy loam	Loamy sand	Loamy sand	Sand	Loamy sand	Sand

<sup>a</sup> United States Department of Agriculture textural soil classification system (USDA, 1987)

Table 2-2. Coal FA and WTE BA total element content. The data were determined using a standardized EPA solid digestion method. The experiment was conducted in triplicate for each material

Element	Coal FA total (mg-element/kg-dry soil) $\pm$ StdDev	WTE BA total (mg-element/kg-dry soil) $\pm$ StdDev
Al	12,200 $\pm$ 150	50,000 $\pm$ 1,200
As	72 $\pm$ 1.10	2.50 $\pm$ 0.0900
Ba	650 $\pm$ 12.5	390 $\pm$ 30.6
Be	2.70 $\pm$ 0.650	0.850 $\pm$ 0.002
Ca	4,400 $\pm$ 300	60,600 $\pm$ 3,000
Cd	0.980 $\pm$ 0.01	10.5 $\pm$ 1.10
Cr	24.0 $\pm$ 1.20	245 $\pm$ 20.9
Cu	52.0 $\pm$ 3.20	1,600 $\pm$ 35.0
Fe	10,000 $\pm$ 400	66,000 $\pm$ 1,400
K	1,940 $\pm$ 30.4	1,850 $\pm$ 42.3
Mn	46.0 $\pm$ 1.30	1,000 $\pm$ 29.0
Mo	8.80 $\pm$ 0.910	8.20 $\pm$ 0.930
Na	590 $\pm$ 30.0	7,500 $\pm$ 140
Ni	20.0 $\pm$ 0.930	102 $\pm$ 10.2
Pb	12.5 $\pm$ 0.500	480 $\pm$ 5.30
Sb	0.600 $\pm$ 0.0003	16.0 $\pm$ 1.10
Se	4.20 $\pm$ 0.930	0.990 $\pm$ 0.002
V	60.0 $\pm$ 2.40	15.8 $\pm$ 0.860
Zn	28.0 $\pm$ 2.30	1,870 $\pm$ 30.0

Table 2-3. Method 1316 leachate concentrations. This method is a standardized leaching procedure adopted by the EPA and was conducted at a LS ratio of 10 and extracted for 24 and 72 hours for each the coal fly ash and WTE bottom ash

Element	Florida GCTL (mg/L)	Coal FA concentration±StdDev (mg/L)	WTE BA concentration±StdDev (mg/L)
Al	0.2**	8.39±0.147	122±0.218
As	0.01*	0.174±0.0129	<0.004
Ba	2*	<0.001	<0.001
Be	0.004*	<0.002	<0.002
Ca	-	109±1.76	258±2.42
Cd	0.005*	<0.001	<0.001
Cl	250	53.8±5.20	140±10.2
Cr	0.1*	0.125±0.001	<0.002
Cu	1.3**	<0.002	<0.002
Fe	0.3**	<0.002	<0.002
Mn	0.05**	<0.001	<0.001
Mo	0.035**	<0.004	0.0572±0.0146
Na	160,000*	17.6±0.137	211±0.350
Ni	0.1*	<0.002	<0.002
No <sub>3</sub> <sup>-</sup>	-	1.05±0.01	3.00±0.565
Pb	0.015*	<0.005	<0.005
Sb	0.006*	0.0301±0.006	0.0361±0.002
Se	0.05*	0.00846±0.001	<0.0057
SO <sub>4</sub>	250	223±30.0	46.5±5.10
V	0.049**	0.325±0.003	0.00386±0.0002
Zn	5**	<0.002	0.0208±0.002
Ionic strength,mg/L	-	745	1,340

\*Primary drinking water standard

\*\* Secondary drinking water standard

Table 2-4. pH values of the coal FA and WTE BA leachate under EPA method 1316 and sorption test. pH probe was calibrated prior to the leaching test. pH readings were taken in unfiltered leachate for both materials following the extraction test

	Coal FA (average± StdDev)	WTE BA (average± StdDev)
EPA Method 1316 <sup>a</sup>	9.70±0.265	10.4±0.0929
Soil#1 <sup>b</sup>	9.50±0.149	10.2±0.0420
Soil#2 <sup>b</sup>	8.01±0.0961	9.78±0.007
Soil#3 <sup>b</sup>	8.59±0.0682	10.2±0.007
Soil#4 <sup>b</sup>	9.45±0.0745	8.12±0.1690
Soil#5 <sup>b</sup>	9.30±0.0263	10.1±0.0212
Soil#6 <sup>b</sup>	8.99±0.0421	10.0±0.0150
Soil#7 <sup>b</sup>	9.05±0.0843	9.71±0.120
Soil#8 <sup>b</sup>	9.12±0.0362	10.3±0.132

<sup>a</sup> pH values following Method 1316, with no soil addition

<sup>b</sup> pH values following sorption test

Table 2-5. Partitioning Coefficient values from the literature. These values were gathered from different scientific studies. Partitioning coefficient values varied due to several reasons, such as using different soil types, different laboratory procedures, among others

Element	CFA $K_d$ ranges (L/kg) <sup>a</sup>	WTE BA $K_d$ ranges (L/kg)	Metal $K_d$ used in recent U.S. EPA risk assessments <sup>b</sup> (L/kg)	Allison and Allison (Allison and Allison, 2005) minimum-maximum (median) (L/kg)	Sauve et al. (Sauve et al., 2000) <sup>c</sup> minimum-maximum (mean) (L/kg)	CCR(U.S.EPA, 2014) <sup>d</sup> minimum-maximum (L/kg)
Al	498-7,010	9.81-1,990	25.0-31.0	2.00-20,000 (2,510)	-	$1.6 \times 10^{-7} - 0.450$
As	92.5-2,000	-	25.0-31.0	2.00-20,000 (2,510)	1.60-530,000 (13,100)	0 – 510
Cr	1.06-10.4	-	1,200-43,000,000	0.199-2,000 (6,000)	125-65,600 (14,900)	0- 53.0
Mo	-	0.0318-4.57	20.0	0.631-501 (12.6)	14.0-52.0 (36.0)	0 – 0.640
Sb	4.23-44.4	5.66-46.2	45.0	1.26-251 (200)	-	0 – 1.10
Se	7.54-40.3	-	2.20-18.0	0.501-251 (10.0)	1.6-600,000 (43,900)	0 -5,800
V	9.50-3,690	0.0879-53.6	1,000	12.6-501	-	0 – 320
Zn	-	2.07-73.5	62.0	0.1-100,000 (500)	1.40-320,000 (11,615)	0 – 60.0

<sup>a</sup> $K_d$  values for Ba, Be, Cd, Cu, Ni, and Pb were not included since their initial concentration in EPA method 1316 were below detection limit (Table A-1).

<sup>b</sup>Allison and Allison (Allison and Allison, 2005). Partition coefficients used in several recent U.S. EPA risk assessments were presented in the paper, but the origin of these data is generally unknown.

<sup>c</sup>Data were obtained compiled from more than 70 different studies.

<sup>d</sup>This document is a recent risk assessment of coal combustion residuals and it includes a range of  $K_d$  values produced using nonlinear isotherm model. The minimum and maximum values are the 5 and 95% percentiles of  $K_d$  respectively.

Table 2-6. IWEM 90<sup>th</sup> calculated percentile concentration. IWEM software is an approved EPA risk assessment model and has been used in several risk assessment studies. The two examples shown below are real life waste management examples. The rationale for showing the default, minimum and maximum partitioning coefficient is to illustrate the differences when using different  $K_d$  values, which may result in different outcomes

Using coal FA as a structural fill				
	Initial concentration	Default $K_d$ <sup>a</sup>	Minimum $K_d$	Maximum $K_d$
As (mg/L)	0.174	0.0128	0.0252 <sup>b</sup>	$5.23 \times 10^{-13c}$
Cr	0.125	0.0169	0.0181	0.0181
Sb	0.0301	0.00410	0.00440	0.0014
V	0.325	0.0436	0.0470	0.000
Using WTE BA as a subbase material in roadway				
Al <sup>d</sup>	122	0.00340	42.2 <sup>e</sup>	$2.50 \times 10^{-14f}$
Mo	0.0572	0.0197	0.0200	0.0200
Sb	0.0361	0.0124	0.00820	$5.05 \times 10^{-4}$

<sup>a</sup>  $K_d$  default values were calculated using MINTEQ2 program. The actual  $K_d$  values are not shown during the simulation

<sup>b</sup> As, Cr, Sb, and V minimum  $K_d$  values were 92.5, 1.06, 4.23, and 9.50 L/kg respectively for coal FA

<sup>c</sup> As, Cr, Sb, and V maximum  $K_d$  were 2,000, 10.4, 44.4, and 3690 L/kg respectively

<sup>d</sup> Even though Al was above the GCTL in the coal FA leachate, IWEM program analyze Al only under roadway application

<sup>e</sup> Al, Mo, and Sb minimum  $K_d$  values were 9.81, 0.0318, and 5.66 L/kg respectively

<sup>f</sup> Al, Mo, and Sb maximum  $K_d$  values were 1990, 4.57, and 46.2 L/kg respectively

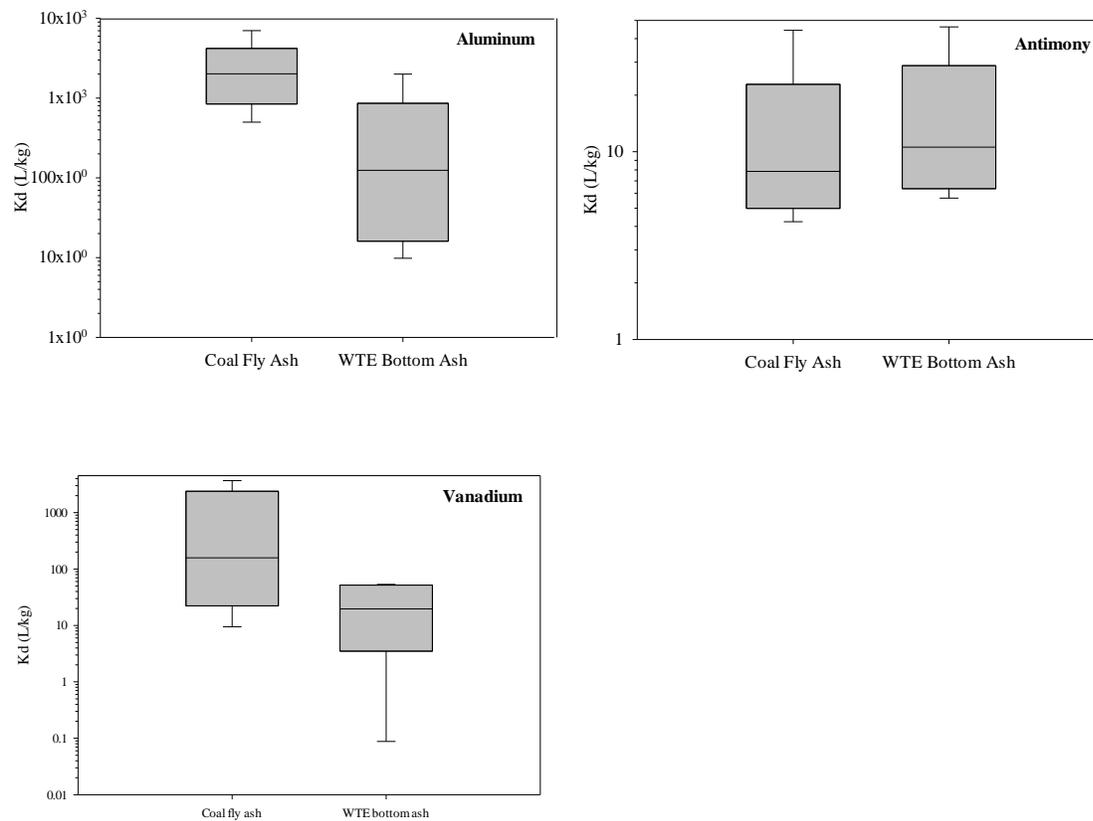


Figure 2-1. Ranges of partition coefficient values ( $K_d$ ) for aluminum (Al), antimony (Sb), and vanadium (V) for coal fly ash (CFA) and waste to energy bottom ash (WTE BA). Leachates were generated using a modified EPA's method 1316 and equilibrated with each of the 8 tested soils in sorption experiments in accordance to ASTM D4646

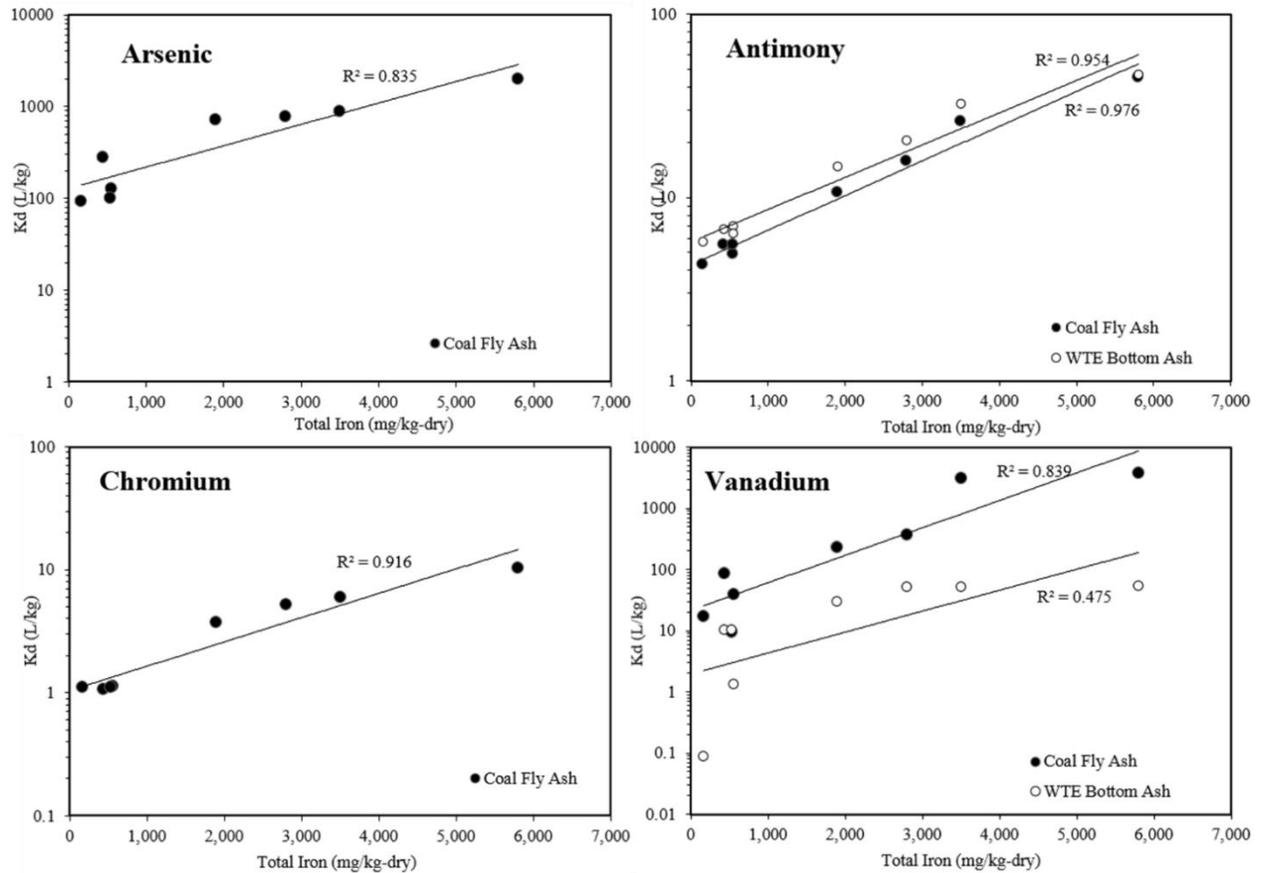


Figure 2-2. Partition coefficients from the tested soils using leachates generated from coal fly ash and WTE bottom ash for As, Cr, Sb, and V as a function of total iron concentrations. Results are averages of 3 replicates (n=3) and the line was determined through regression analysis. Only elements with calculated  $R^2 > 0.80$  are included in this figure

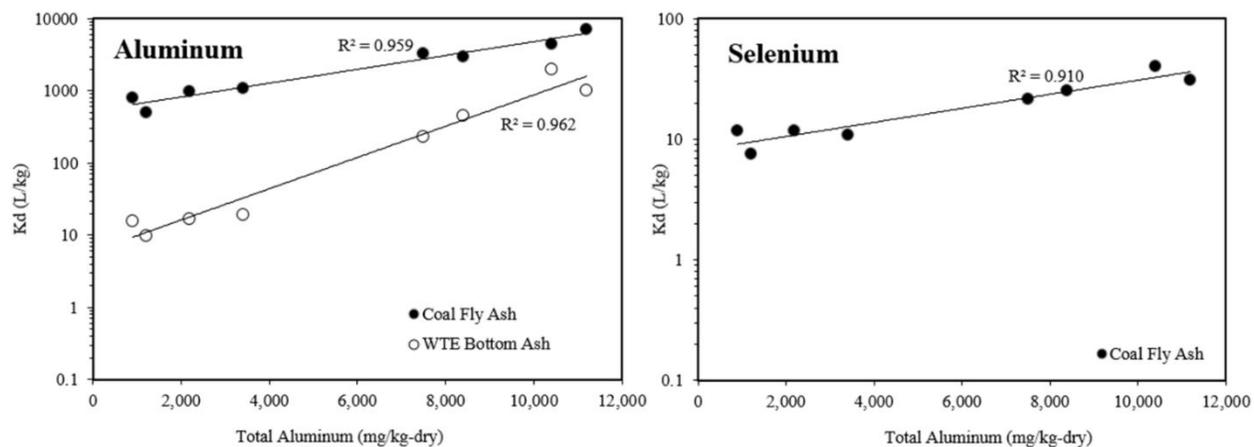


Figure 2-3. Partitioning coefficient for Al and Se as a function of soil total aluminum content. These elements were the only elements with a good correlations. Total content was determined using total digestion method as described in details in the methodology section of this chapter

CHAPTER 3  
EVALUATION OF THE IMPACT OF LIME SOFTENING WASTE DISPOSAL IN  
NATURAL ENVIRONMENTS

**Background**

Water treatment residues (WTR) are solid wastes from the lime softening of drinking water and often contain trace elements as a result of the constituents removed and the treatment chemicals added (e.g., polymers, alum, ferric coagulants). Water treatment residues can be recycled through land application and offer a number of potential benefits, including a reduction in the nutrient loading of surface water bodies (Ippolito et al., 2011). A recent study examined the characteristics of lime softening WTR in Florida, and found that for the most part, trace element concentrations did not vary dramatically among lime WTR when Al and Fe salts were used as a supplement to conventional lime softening (Cheng et al., 2014). This suggests that existing policies related to the beneficial use of lime WTR would apply equally to lime WTR that use small quantities of additional treatment chemicals (alum and ferric salts) to help to improve other water quality parameters (such as the removal of the organic compounds responsible for color). These experiments did find, however, that certain elements (Al, Fe, Mn) were released to a greater extent under chemically-induced reducing conditions (in comparison to the same test where a reducing agent was not utilized).

While the results of the previous work provided guidance to the regulatory community and the utilities producing the WTR, they were conducted using standard practices for assessing the beneficial use of waste materials (e.g., batch leaching tests), and thus trace element behavior under several potential reuse applications remains uncertain. For example, some generators have proposed to use lime-softening WTR as clean fill below the water table, an application that has been demonstrated to have beneficial properties in controlling nutrient loading (Maszkowska et

al., 2013). Numerous conditions that would be expected to occur under such a management scenario may not be adequately reflected using standardized batch tests, including the development of anaerobic conditions, lower liquid to solid ratios (L/S), and the presence of naturally-occurring organic matter (NOM).

The presence of organic matter in natural water bodies has been demonstrated to affect trace element release from soils. Leaching of a number of waste materials has been shown to be highly dependent on concentrations of organic matter, either contained as a fraction of the waste itself, or mobilized by landfill leachate or other means. In many areas of south Florida, the surficial aquifer is known to contain high concentrations of NOM, if WTR are to be disposed of as a subsurface fill, it is likely that the water in contact with the material would be elevated in NOM content (with respect to the typical extraction fluids used in leaching tests). Therefore, leaching tests designed to evaluate disposal in these types of conditions need to be modified to account for these factors.

The objective of this study is to further examine the leaching of trace elements from lime softening WTR by utilizing experimental procedures that better assess element behavior in the natural environments of question. Several of the procedures employed are from a new suite of leaching protocols developed for the United States Environmental Protection Agency (US-EPA), and patterned after European leaching tests (van der Sloot, 1996b). As these protocols do not address some conditions that may be encountered in the natural environment [e.g., anaerobic conditions, the presence of NOM], the authors examine possible modifications to standardized protocols to address use-specific conditions. Although this paper provides value to the specific waste reuse question at hand, perhaps of even more importance is the evaluation of how existing leaching protocols can best be applied to the beneficial use, risk assessment process. This paper

highlights how the broader suite of recently adopted leaching tests can be used to generate a more thorough assessment of leaching risk, but also identifies limitations within these tests. The use of modified leaching procedures illustrates to the reader additional opportunities for refinement of leaching tests to address site-specific conditions and allow for a better interpretation of results.

## **Materials and Methods**

### **Facility Description and Sample Collection**

Water treatment residues were collected from five potable water treatment facilities in Florida, US; samples were collected from locations representing the most recently produced WTR available for sampling at each facility. Composite samples were generated by sampling from conveyors or belt presses for a 20-minute period, or taking 6 to 10 subsamples from sludge piles or drying lagoons. After collection, samples were stored for 48 hours after which the free water was removed, and the samples were further air dried for three days at an ambient room temperature of  $24 \pm 3$  °C. Following drying, samples were homogenized through repeated mixing. Moisture content was measured in accordance with ASTM D2216 and verified throughout the course of the experiments.

### **Leaching Tests**

Environmental Protection Agency methods 1312, 1313, and 1314 (US-EPA, 2014) were conducted on the WTR samples; these methods were altered slightly to accommodate the characteristics of the samples tested. Method 1313 is a batch leaching test ( $L/S = 10$ ) that evaluates leaching as a function of pH. Method 1314 is an up-flow percolation column test using reagent water as the leaching solution and a flow rate set between  $0.75 \pm 0.25$  L/S per day.

To assess the impact of anaerobic conditions on trace element release from WTR, method 1314 was repeated in a glove box under a nitrogen atmosphere. Prior to conducting the

experiment, the reagent water used in the test was purged with nitrogen gas inside of the controlled chamber for 30 minutes. Water treatment residues were first placed into columns outside of the controlled environment and then transferred through an airlock into the glove box, where the column was again purged with nitrogen gas for ten minutes to eliminate the presence of oxygen. The presence of anaerobic conditions were verified by monitoring the oxygen level in the glove box (using a portable oxygen meter (LandTec GEM-500) (and maintaining that level at less than 0.1% oxygen throughout the course of the test). The initial measured ORP values in the column tests (which were 150-200 mV lower than the measured values for the aerobic tests) also indicated the presence of anaerobic conditions. Column leachates were collected and filtered using a 0.45-um polypropylene syringe filter inside the nitrogen environment.

The synthetic precipitation leaching procedure (SPLP: EPA method 1312) is a batch leaching test conducted at a L/S of 20 mL of extraction fluid per gram of “as received” sample (meaning that the actual L/S would almost always  $\geq 20$  and would be a function of the sample moisture content). The leaching solution is made from a mixture of dilute sulfuric and nitric acids which are mixed with reagent water until a pH of  $4.20 \pm 0.5$  is obtained (done prior to sample addition). The equilibration time for method 1312 is  $18 \pm 2$  hours. Results from SPLP testing have been used in a number of beneficial use assessments (Townsend et al., 2006). To examine differences between SPLP and what might likely occur in certain reuse applications, both the SPLP and a modified SPLP test were performed on the 5 WTR samples in triplicate. The SPLP test was conducted in accordance with the method outlined above. The modified test was performed in a similar fashion, but the leaching solution was replaced with surface water samples taken from three freshwater locations throughout Florida. The water samples are described by a visual observation of the darkness of the water, which was meant to reflect the

NOM content. The total organic carbon (TOC) content was analyzed by high temperature combustion on TOC analyzer (Shimadzu 5000 Total Organic Carbon Analyzer). The samples analyzed for TOC represent a series of grab samples taken at each location during a separate sampling event, but were used as a relative indicator of the TOC content of the water used in the natural solution leaching test. The collected water samples are referred to as low (SW#1), medium (SW#2), and high (SW#3) in color respectively. The concentrations of trace metals contained in the raw water samples were assessed prior to use the experiment.

### **Total Concentration Analysis**

A total environmentally available, microwave-assisted digestion was conducted on the WTR in accordance with EPA method 3051A. This method involves the addition of  $9 \pm 0.1$  mL concentrated  $\text{HNO}_3$  and  $3 \pm 0.1$  mL HCL to a 0.5 g sample of the WTR. The sample is then heated in a microwave for a period of 10 min and a maximum temperature of  $175^\circ\text{C}$ . A total environmentally available digestion is designed to assess the maximum concentrations of elements that would be released into the environment, certain refractory minerals such as quartzes, silicates, aluminates and other oxides may not be fully dissolved during this test method and these minerals may contain other bound analytes within their matrix. Therefore measured values in this test many differ from the total elemental concentration of the waste material (if the sample contains substantial amounts of these insoluble minerals), however these bound elements are considered immobile in the environment and excluded from most aqueous transport mechanisms. In this instance, the WTR were dissolved completely following the digestion procedure.

## **Chemical and Trace Elemental Analysis**

Conductivity and pH were measured for all samples using a multi-parameter meter (Thermo Electron Corporation; Orion 5 Star). The oxidation reduction potential (ORP) was assessed with a handheld ORP meter (Oakton ORPTestr 10). Leachate samples were digested in accordance with EPA Method 3010A. All leachate samples were analyzed for Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Se using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) in accordance with EPA Method 6010C.

## **Risk Assessment Approach**

When assessing the management options for the beneficial use of a waste material, many U.S. state and federal regulatory agencies use a risk-based approach. Often times, risk-based groundwater thresholds are developed by relating health effects (both carcinogenic and non-carcinogenic) from epidemiological studies to an acceptable level of risk (e.g., 1 in 1,000,000), based on an ingestion dose. From there, concentration thresholds are developed and used, among other things, as part of a beneficial use assessment. In the state of Florida, the Florida Groundwater Clean-Up Target Levels (GCTLs) are used in this fashion (Townsend et al., 2006). Leachate concentrations in this study are compared to the GCTLs, as this is a common mechanism that has been used by U.S. state and federal regulatory agencies when assessing a wastes potential for beneficial use. Direct comparison of leachate concentrations to groundwater risk thresholds does not take into account pathways for element dilution and attenuation such as sorption within the vadose zone or dilution of contaminants as they enter the surficial aquifer. However the direct comparison practice is still commonly used by many regulators and comparison to the GCTLs provides a frame of reference for the relative concentrations of detected elements (so that constituents of potential concern can be identified and further

evaluated). The Florida GCTLs are predominantly federal primary and secondary drinking water standards and the risk based concentration thresholds used in this manuscript would likely be very similar to those used in other states and countries.

## **Results and Discussion**

### **Leaching as a Function of pH**

pH has been shown to be a major factor influencing the leaching of waste materials and is an important component for consideration when evaluating contaminant release in the natural environment (Kosson et al., 2014). The results of method 1313 are presented first in order to demonstrate the impact of pH on trace element release from WTR, and so that the data may be used to explain the results present in subsequent sections. For all of the five facilities, variation between the sample replicates was minimal. Ag, Cd, Pb, Mo, and Se were not found to be above method detection limits at any of the measured pH values. For all of the detected elements, the maximum concentrations were shown to leach at low pH values (pHs 2 and 4). Al and Ba were detected at all of the pH values evaluated, in all of the facilities tested; leaching trends did not vary between facilities. Aluminum (Figure 3-1) displayed an amphoteric leaching trend with increased leaching at high (10-13) and low (2-4) pHs. Concentrations of Ba (Figure 3-1), Mn, and Ni were found to decrease from a maximum at a pH of 2, to below the method detection limits at a pH of  $\approx 9$ ; concentrations of Mn were found to be above GCTLs for pH values  $< 7-8$  (depending on the facility evaluated). As and Cr were detected only in the low pH range. Cu was detected in leachates from all facilities at a pH value of 2.0; two (facilities 4 and 5) out of five facilities displayed Cu leaching in the high range of the pH values tested. Fe release from the WTR was similar to Cu in that all five facilities were shown to leach detectable concentrations of Fe from a pH of 2 to a pH of either 5.5 or 7 and that two (facilities 2 and 4) of the facilities tested

did show Fe leaching in the high pH range. Of all of the elements evaluated only Mn and Al fell above their respective GCTLs at a pH value higher than 5.5. 5.5 can be considered a conservative low pH threshold for the reuse scenarios being examined here as the highly alkaline WTR would likely produce pH values in the neutral or basic pH range. As, Cr, Ni, and Ba were found to exceed GCTLs in WTR in certain facilities at pH values of 2 and 4. Fe concentrations were measured in exceedance of its GCTL at pH values of 5.5 and above.

Table 3-2 displays the results of the SPLP tests, as well as a comparison to the concentrations measured at the natural pH (pH immersed in water at a L/S of 10) of the WTR in method 1313. The mean (average of the 5 facilities) Al and Ba SPLP concentrations and corresponding pH values are also indicated in Figure 4-1. The natural pH was selected for comparison to the SPLP as it represents a data set (from a batch leaching test) that could potentially be used in a risk based decision making scenario. Only Al and Ba were detected in the SPLP leachates, this could potentially be attributed to the depletion of the mobile, surface available elements and the subsequent dilution by the larger L/S (than method 1313) used in the SPLP test. SPLP pH values ranged from 9.63 to 10.7. In method 1313, Al was detected in three out of five facilities (at the natural pH) all in lower concentrations than the SPLP; method 1313 pH values ranged from 9.08 to 10.1. Barium concentrations were below method detection limits for all WTR tested in method 1313, but were detected in SPLP tests from all 5 facilities at a mean concentration of 0.0694 mg/L. This value was over three times the method detection limit of 0.02 mg/L. Concentrations of both of the detected elements (Ba and Al) in the SPLP were elevated above the 1313 values at the natural pH in all instances. Although the SPLP extraction solution does incorporate a small amount of dilute acid, the minuscule volume of acid added is

hypothesized to not be substantial enough to overcome the pH differences created by the increased L/S.

The final pH of the leachate was hypothesized as the main factor that produced concentrations of Al in the SPLP which were elevated with respect to the method 1313 test (at the natural pH). Figure 1 demonstrates that leached concentrations of Al increase as the pH of the leaching solution becomes more alkaline, therefore it would be expected that the SPLP, with the higher solution pH (on average 0.7 pH units above method 1313) would leach more. Differences in pH between the SPLP and method 1313 can be explained by the L/S of the tests. The SPLP is conducted at an “as-is” L/S of 20:1 which does not account for the moisture content of the sample (a moisture content of 0.2 or 20% would correspond to a L/S of 25); method 1313 is conducted at a L/S of 10. Column testing (method 1314) on the WTR (Figure 3-2) displayed an increasing pH with increasing L/S.

Differences in Ba leaching (between SPLP and the natural pH) were not hypothesized to be driven by pH, as the leached concentrations in the SPLP test (mean pH – 10.23) were higher than the leached concentrations for method 1313 at the natural pH (mean pH – 9.53). Barium exists as a cation and its solubility is likely to decrease with increasing pH. This is supported by the data in Figure 3-1, as the leaching of Ba was below method detection limits from a pH of 9 to a pH of 13. There are a number of other possible factors that could explain the increased concentrations of Ba in the SPLP. The filters used for method 1313 are polypropylene with a 0.45 um pore size; SPLP requires an “effective” pore size of 0.6 – 0.8 um, and the filters are made from glass fibers. It’s possible that the SPLP filters allow more Ba into the filtrate, resulting in higher concentrations. Additionally, colloidal formation with Al (measured in increased concentrations in the SPLP test) or other elements present in the leachates could have

resulted in the decreased Ba concentrations seen, as these are particularly sensitive to pore size. Colloidal formation of one or more elements most commonly Al have been observed in leachates from 25 different waste materials. Other factors which could have produced the elevated concentrations in the SPLP test are the leaching solution used (SPLP contains dilute  $\text{H}_2\text{SO}_4/\text{HNO}_3$  added to produce a solution pH of  $4.20 \pm 0.05$ ), and differences in the L/S of the test. The authors cannot point conclusively to one mechanism creating differences in the tests, and it is likely that several may have played a role, however the data are provided so that the reader can understand the differences between the methods and how they may impact other beneficial use assessments.

Comparing values from the method 1313 (natural pH) and SPLP, to the selected risk thresholds (FL-GCTL) elucidates the importance of the minor differences in the test results with respect to a beneficial use assessment. For method 1313, Al concentrations exceeded the GCTL, for all five facilities, at high (12-13) pH values. The concentrations of Al in the SPLP test (Table 3-2) exceeded the GCTL for three out of the five facilities (facilities 3,4, and 5). In the natural pH - method 1313 test Al concentrations exceeded the GCTL in one out of five facilities (facility 5). The average concentrations of all five facilities for SPLP and method 1313 tests (natural pH) were 0.231 mg/L and 0.150 mg/L, respectively.

The results above demonstrate that the use of different leaching tests (e.g., using the natural pH values for comparison to target levels or using SPLP) could cause a regulatory risk assessment to produce two different outcomes, even if a confidence interval or other statistical method was employed. SPLP concentrations, which were over the GCTL for Al, were found to be below the respective threshold in method 1313 (at the natural pH). Method 1313 results illustrate that Al leaching decreased in the pH range typical for most reuse scenarios that would

be encountered (a consistent observed decrease in Al release from a pH of 12 to a pH of 7). These results would provide regulators with important information as many proposed reuse or disposal applications for WTR (e.g, soil amendment, clean lake fill) would likely result in a pH lower than the natural (or SPLP) pH of the material, and consequently reduce the potential for Al leaching.

Although Ba concentrations from method 1313 (natural pH) and SPLP were below their GCTL, values of Ba from the SPLP were more than 3 times higher. The large differences in the measured values demonstrate that a scenario could arise for other elements (when conducting a beneficial use assessment on a waste material) where SPLP concentrations were elevated above a risk threshold, and method 1313 concentrations were not. Similarly, factors such as differences in L/S could result in values from method 1313 being above SPLP, as a number of wastes have been demonstrated to leach in higher concentrations at lower L/S, due in part to the loss of the initial surface available elements and/or the depletion of mineral forms during leaching and the dilution of these constituents at higher L/S (Pawlowska, 2007). If a beneficial use assessment of lime WTR had been conducted using solely SPLP, it may have been concluded that this material would not be suitable for beneficial use (based on SPLP concentrations of Al elevated above its GCTL). With the additional information provided by method 1313, specifically, the lowered leaching of Al related to the decreased pH values seen in the natural pH leachates (when compared to SPLP), regulators and generators of WTR would likely have more comfort in reusing the material, as they could now demonstrate (through the use of method 1313) that leaching risk would be expected to be limited when placed in the natural environment (where reuse pH values would typically be lower than seen in the SPLP test).

## Up-flow Percolation Column Testing

In addition to pH changes, there are other drivers that facilitate trace element release from WTR, including the L/S and the atmosphere in which the WTR is placed in. Method 1314, an up-flow percolation column test, was conducted on the WTR in order to better assess what might occur in a reuse or disposal scenario where water is percolating through a mass of WTR (were low L/S conditions might be expected to develop). Often times, prior to beneficial use or disposal, WTR are stored in large piles or lagoons. Percolation testing would be better representative of the pore water concentrations of this and other scenarios. Column testing under anaerobic conditions was done to evaluate the effects of redox changes on trace element leaching from WTR, as proposed use applications for WTR include use as a quarry or lake fill, or placement in other hypolimnetic environments where anaerobic or low oxygen conditions may develop (Cheng et al., 2014). These applications are sometimes proposed for WTR to reduce nutrient loading in water bodies or as a low cost alternative to disposal of WTR in a lined landfill.

Aluminum was the only measured element (Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Se) that was detected in the column tests under aerobic conditions. Figure 3-2 presents data from Facilities 1 and 5 under aerobic and anaerobic conditions; the measured leachate pH values for aerobic and anaerobic column tests from Facilities 1 and 5 are presented in Figure 3-3. Under aerobic conditions, concentrations of Al from all facilities increased with increasing L/S, from a minimum of <0.02 mg/L to a maximum concentration of 0.926 mg/L (L/S 10). The maximum concentrations from the column tests were elevated above both the SPLP and method 1313 natural pH values for four out of five facilities (facilities 1, 2, 4, 5). The mean leachate pH ranged from  $8.26 \pm 0.25$  to  $9.14 \pm 0.044$  (Ave  $\pm$  StdDev).

Method 1314 was then performed inside a glove box, in a nitrogen atmosphere, to assess the effects of anaerobic conditions on trace element release from WTR. Aluminum and Fe were detected in the column test under anaerobic conditions. In four out of the five facilities the leachate pH increased throughout the experiment; the mean leachate pH began at  $8.40 \pm 0.17$  (Ave  $\pm$  StdDev) and peaked at  $8.75 \pm 0.80$  (L/S 10). The exception to this trend was facility 5, (end aerobic leachate pH - 9.14, end anaerobic leachate pH - 7.32). For four of the five facilities the pH values seen were similar to the pH values for the column tests done under aerobic conditions. The ORP of the leachates under anaerobic conditions ranged from 0 to -120 mV and decreased throughout the course of the tests in all instances.

In comparison to column tests under aerobic conditions, Al concentrations varied widely in the data set under anaerobic conditions. The cumulative mass release (mg-constituent leached/kg-sample) at a L/S of 10 was used as a tool for comparison of the two data sets. Facilities 1 and 2 did not leach Al at any L/S under anaerobic conditions; their pH values were similar to those under aerobic conditions. Facility 4 leached concentrations within 25% of conventional method 1314s values (44.3 mg-Al/kg-WTR) under anaerobic conditions (33.7 mg-Al/kg-WTR). Cumulative mass release from facility 3 was found to be 86% higher under anaerobic conditions (10.7 mg-Al/kg-WTR) than in an aerobic environment (5.75 mg-Al/kg-WTR). Cumulative mass release from facility 5, where the final pH of the column tests was more than 1.5 pH units apart, and the largest difference would have been expected based on pH alone, was less than 2.5% different between the two tests (aerobic - 50.8 mg-Al/kg-WTR, anaerobic 52.0 mg-Al/kg-WTR). Fe, not present in aerobic column leachates, was detected in two facilities under anaerobic conditions (Facilities 4, 5). For both facilities leached Fe values increased up to a L/S of 1. Fe concentrations from Facility 5 decreased continuously following L/S 1. After a L/S

of 1, Fe leaching from facility 4 decreased initially, and then experienced a slight rebound at a L/S of 5 (Figure 4-4).

The total concentration of WTR were assessed to evaluate if Fe and Al release from method 1314 was influenced by the total amount of Fe/Al in the WTR, these values are presented in Table 3-3. Total concentrations of Al were all within the same order of magnitude and the leaching under aerobic and anaerobic conditions was not found to correlate to the total concentrations present. Although total Fe concentrations did vary (the largest total Fe value corresponding to the facility where the largest dose ferric salts was used), there was again no correlation between total Fe concentration and Fe release under anaerobic conditions; neither of the two facilities that used ferric salts as an additive saw Fe release in either scenario.

The results of the column testing demonstrate the importance of using the appropriate leaching test when conducting a beneficial use evaluation. Concentrations of Al in method 1314 leachates were elevated above those in the batch tests, as well the Al GCTL. Factors such as L/S are known to influence leached concentrations and these results demonstrate that further care needs to be taken with respect to reuse of WTR in low L/S, percolation-controlled scenarios. Changes in the atmospheric environment were found to influence Al leaching, although concentrations did not increase dramatically.

Iron leaching was not seen in the aerobic column test, but was observed (for two facilities) during the anaerobic experiment (measured values were below the Florida regulatory threshold (0.3 mg/L)). Limited Fe release in the anaerobic column tests could potentially be attributed to the relatively small amount of ferric salts used as a treatment additive (in comparison to a water treatment plant where ferric salts are used as the chief coagulant) or the fact that the Eh-pH state measured in the anaerobic column tests did not fall within the range that

would result in Fe reduction into its soluble Fe(II) state. Examining a Pourbaix diagram for Fe in water indicates that for the reduction of Fe to occur at a pH of 7 (the lowest pH value measured in the column tests) an Eh of approximately -0.1 V would need to be present (this corresponds to an ORP of -344 mV using the Ag/AgCl type ORP electrode), this value increases to an Eh of < -0.2 V at a pH of 8 (Roy et al., 1991).

Because of the basic nature of the WTR and the relatively low ORP required to reduce Fe in these pH environments, Fe release from WTR would likely be limited in an anaerobic environment (provided that the pH and Eh values measured were similar to those measured here). Batch tests used in a previous study by the authors did illustrate the release of Fe under more aggressive chemically induced reducing conditions (Cheng et al., 2014). Mechanisms that could have facilitated Fe release from two of the facilities (4 and 5) include microbial activity and the presence of organic matter (Wang and Mulligan, 2006), which could have assisted in driving release under the anaerobic conditions. Microbial activity and organic content in the WTR were not assessed and are again suggested as potential controlling factors to be examined in future beneficial use assessments. Although the reduction potential present in the anaerobic column tests was not found to be in the Eh range favorable of facilitating Fe release, these results still provide valuable data as to the measured ORP for WTR in an anaerobic environment. For the two facilities (4 and 5) that did exhibit Fe release, the co-release of other elements was not observed, suggesting that disposal in hypolimnetic environments should not be of any additional concern if similar pH and redox conditions (to those evaluated here) are present.

### **Natural Water Leaching Test**

To assess the impacts of disposal of WTR into natural water bodies, surface water samples were used to conduct the natural water leaching test; the water samples used were

visually characterized and classified by their TOC content. Table 3-4 presents the trace element concentration, TOC, and pH data on the natural waters used in the experiment, along with the mean final pH after the WTR was added.

The measured TOC content for the three surface water samples were 17.0 (SW#1), 13.6 (SW#2), and 8.89 mg/L (SW#3). Determined TOC concentrations were much lower way below the mean value for other water bodies, such as Suwannee River (33.8 mg/L), groundwater (0.1-15.0 mg/L) (Leenheer et al., 1974). Al, Ba, Fe, and Mn were the only measured elements that were detected in any of the samples. Concentrations of Mn were below 0.005 mg/L for all of the surface water samples after the addition of the WTR. It is important to note that some of the natural water solutions used initially contained concentrations of trace metals that were elevated above SPLP values seen for the WTR. In addition, the leachate pH, following WTR addition, increased for all five facilities (mean pH of water samples – 7.16, pH following WTR addition - 8.26); this was hypothesized to have resulted from the alkaline nature of the WTR.

Figure 3-5 presents a comparison of the SPLP results and the results that were obtained in the natural water leaching test, results are presented in a box and whisker type plot using the data generated for all of the facilities. Concentrations of Al in the natural water test were: 0.0969 (SW#3), 0.0528 (SW#2), 0.0318 mg/L (SW#3). The mean leachable concentrations of Al in the SPLP test were higher than Al concentrations in the natural water extraction solutions. Al concentrations increased as the measured TOC decreased. The leachate concentration of Al for the WTR that was mixed with the high TOC natural water was lower (mean – 0.032 mg/L) than the value measured when the water was initially tested (0.231 mg/L); this demonstrates that the WTR decreased the concentrations of Al in the natural water, despite a pH increase that would be hypothesized to facilitate increased leaching (based on the results of method 1313). Formation

and the subsequent removal through precipitation/filtration of Al-NOM colloids can be cited as one of the potential reasons for the observed decrease. Al is known to form complexes with humic acids and other NOM types often present in surface waters (Schädler, 2009).

The concentrations of Fe present in the natural water test followed a trend similar to that of Al, with increasing concentrations of Fe in leachates related to decreasing NOM (these values varied by over an order of magnitude). Again raw water concentrations of the high TOC water were reduced following the addition of the WTR. The mean concentrations of Fe in the natural waters (listed from low to high TOC) were: 0.381, 0.307, 0.0529 mg/L. These concentrations of Fe were greater than the values from the SPLP test, which were less than instrument detection limits (0.03 mg/L) in all cases. Ba did not follow the same trend as Fe/Al, as leaching increased with higher values of TOC. The low (Ba - 0.0292 mg/L) and medium (Ba - 0.0399 mg/L) TOC natural water tests fell below the mean SPLP value (Ba - 0.694 mg/L) while the high TOC sample was slightly above (Ba - 0.110 mg/L).

There are a number of factors that could have influenced element release in the natural water tests. The first factor evaluated was pH; it is hypothesized that the values from the SPLP tests were elevated above the Al concentrations in the natural water experiments due to the sample pH. Leachates from the SPLP test yielded an average pH of 10.2 compared to 8.27 in the natural water test. Based on method 1313 (Figure 3-1), this pH difference would explain the higher concentrations seen in the SPLP. Ba found as a cation, and shown in WTR to decrease in leaching with increasing pH (Figure 3-1), would have been more likely to be released from the WTR at a pH of 8 than at a pH of 10. This could have contributed to the elevated concentration seen in the high TOC test; however, based on the observed trend with TOC and Ba, other mechanisms are hypothesized to have been more likely to drive Ba release. Iron was not found to

leach above detection limits (0.03 mg/L) in the pH range of the natural water tests (8-10) during the method 1313 testing again pointing to additional factors facilitating Fe release.

Organic carbon plays an important role in controlling the solubility of organophilic metals in water bodies. The presence of NOM in the natural water samples clearly influenced the leaching of trace elements from the WTR. For Fe/Al, measured values from the raw water with the high TOC were found to be reduced when the WTR was added. This phenomena could be related to the addition of Ca (from the WTR) to NOM-particulate systems (surface waters). This addition has been demonstrated to facilitate colloid destabilization and particle aggregation in water samples, potentially providing a mechanism for removal of trace metals (in this instance Fe and Al). As the amount of TOC in the waters decreased, or the types of TOC present changed, this effect could have been lessened, resulting in the increasing concentrations (with decreasing TOC) of Fe and Al seen. For Fe and Ba, values measured in some or all of the natural water tests were elevated above the SPLP and method 1313 results. Therefore, NOM must have played some role in increasing the leached concentrations. Without further analysis the exact mechanisms driving this release cannot be determined; however, this experiment serves to illustrate the importance of assessing not only the presence but the type of NOM that might be encountered in a beneficial use scenario.

Leached quantities of Al from the WTR were decreased in the natural water tests when compared to the SPLP. All Al and Ba values from natural water tests were below their GCTLs. The decrease in pH (in relation to the SPLP) when placing the WTR in a real world submerged usage application, would be likely to facilitate decreased Al release, something that would not have been uncovered using a standardized leaching test. Conversely, concentrations of Fe (not present in the SPLP) were seen to be above the GCTL (0.3 mg/L) in some instances; this varied

over an order of magnitude, based on the type of water sample used (and the TOC of the sample). A site-specific assessment of the impacts of the NOM (from the water body where the material was to be placed) would likely represent the most appropriate approach when disposing of WTR as subsurface fill. Use of a standardized leaching methodology could have resulted in the under or over prediction of the impacts of WTR addition to water bodies based on the site-specific conditions present.

Table 3-1. Chemical characteristics of WTR. These data were obtained from the operator of each facility. Moisture content was determined using a standardized method at 105 °C. Dry and wet weight were recorded for each WTR

Facility	Lime (kg/day)	Ferric salts (kg/day)	Other (kg/day)	Moisture content (%)
1	527	N/A	N/A	41.4
2	297	10.0	0.788 (Polymer)	43.8
3	216	1	0.0360 (Chem-Floc)	26.9
4	319	N/A	N/A	28.6
5	83.7	N/A	N/A	14.5

Table 3-2. SPLP and EPA method 1313 leachate concentrations for aluminum and barium. SPLP and method 1313 were conducted for each WTR following the procedure explained in the methodology section. Natural method 1313 test used only the WTR with no acid or base addition since it is widely used in several risk assessment studies. The leachable concentrations for both tests were compared to determine any differences and to illustrate the importance of selecting the correct method when conducting a leaching test

Facility	SPLP pH	Natural pH method 1313	Aluminum concentration mg/L (StdDev)		Barium concentration mg/L (StdDev)	
			SPLP	Natural pH method 1313	SPLP	Natural pH method 1313
1	10.7	9.59	0.0667 (0.003)	< 0.05	0.087 (0.001)	< 0.02
2	10.4	10.1	0.0923 (0.0051)	0.0775 (0.0013)	0.074 (0.016)	< 0.02
3	10.6	9.63	0.204 (0.009)	0.155 (0.008)	0.061 (0.002)	< 0.02
4	9.82	9.25	0.235 (0.0089)	< 0.05	0.065 (0.0052)	< 0.02
5	9.63	9.08	0.557 (0.02)	0.422 (0.019)	0.060 (0.001)	< 0.02

Table 3-3. Total environmentally available concentrations of aluminum and iron in WTR samples. A standardized total digestion method was used to determine the total contents for Al and Fe in dry basis. Al and Fe were selected to determine if the addition of Al and Fe as an additives during the treatment process has any effect in leaching of trace elements

Facility	Aluminum concentration (mg/kg-dry)	Iron concentration (mg/kg-dry)
1	582	296
2	688	7,660
3	573	1,860
4	432	2,640
5	799	749

Table 3-4. Natural water classification for each surface water samples. Water samples were collected from Florida to illustrate to the operator the effect of natural organic matter on leaching of trace elements from WTR. Natural water had detectable concentrations of four elements. Surface water samples were classified according to their total organic carbon concentrations and ranged from high to low

classification	TOC (mg/L)	Natural water pH <sup>a</sup>	pH following WTR addition	Al (mg/L)	Ba (mg/L)	Fe (mg/L)	Mn (mg/L)
High	17.0	7.6	8.25	< 0.022	0.0101	0.175	<0.001
Medium	13.6	6.99	8.19	< 0.022	0.0201	0.12	<0.001
Low	8.89	6.82	8.15	0.231	0.131	0.453	0.0023

<sup>a</sup>The pH of the natural water when collected, prior to the addition of the WTR

<sup>b</sup>The pH of the natural water and WTR following sample rotation

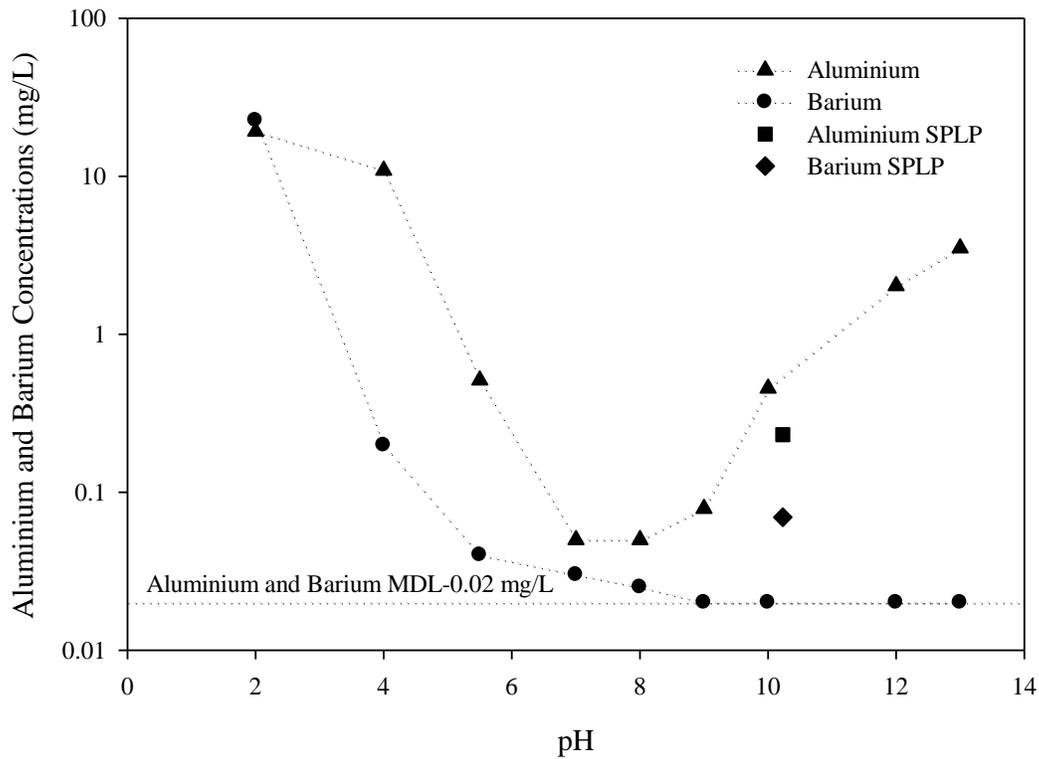


Figure 3-1. Leaching of WTE as a function of pH- mean values for the five facilities tested. Acid or base were added at specified volume until the desired pH was obtained. SPLP test data for Al and Ba were included in the same plot to show any concentration differences, which may change the outcome of risk assessment decision making process

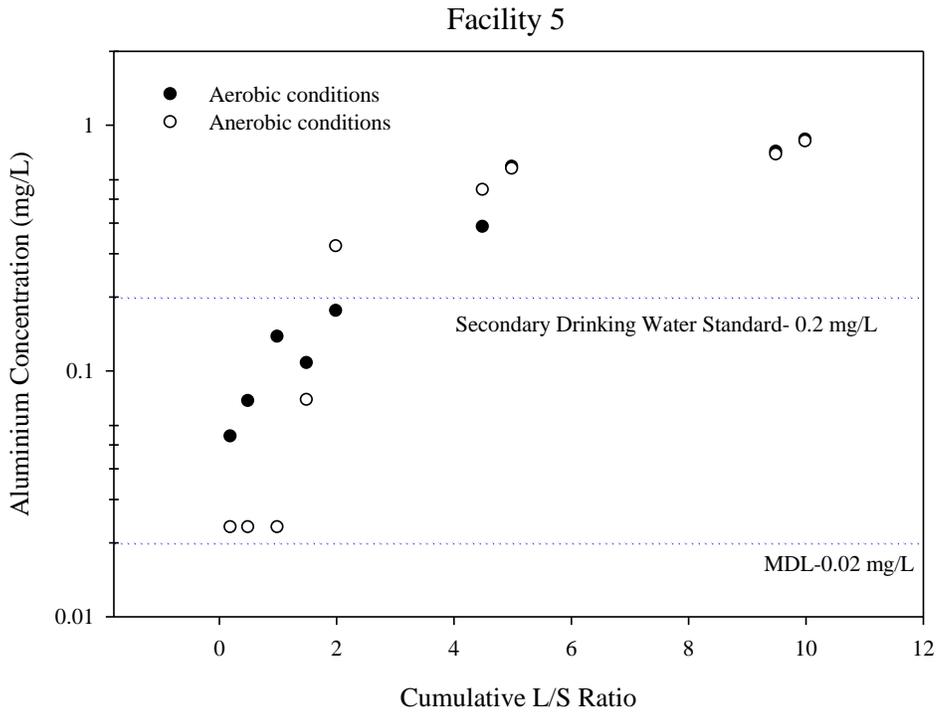
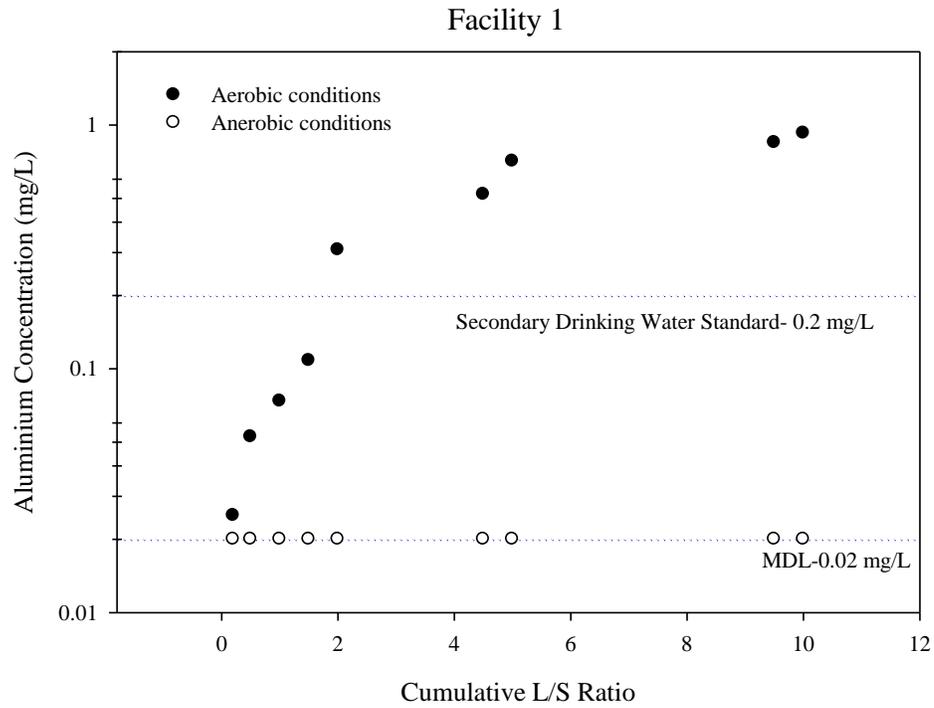


Figure 3-2. Aluminum release as a function of L/S under aerobic and anaerobic conditions (method 1314- facilities 1 and 5). Aluminum was detected in other facilities, but only two facilities were showing here. The test was conducted using oxygen free environment

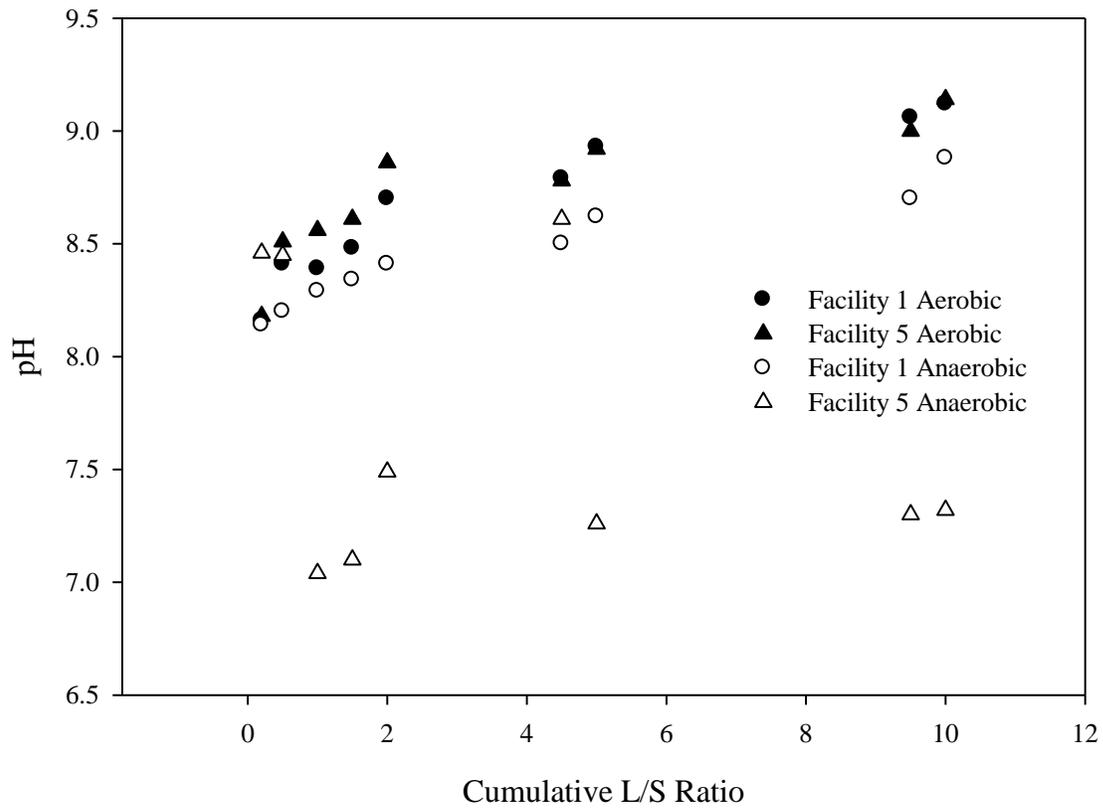


Figure 3-3. pH data for method 1314 tests conducted under aerobic and anaerobic conditions for facilities 1 and 5. pH readings were recorded following each collection time for both facilities under aerobic and anaerobic conditions

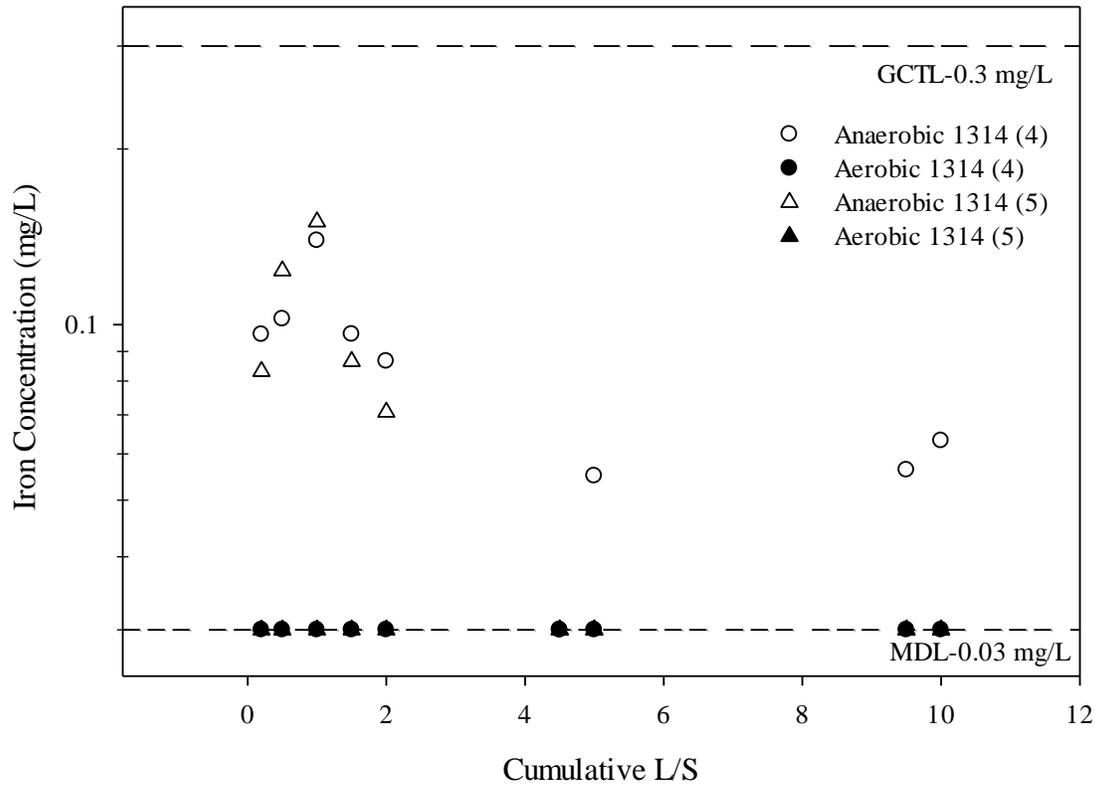


Figure 3-4. Iron release as a function of L/S under aerobic and anaerobic conditions (method 1314 – facilities 4 and 5). Fe was only detected in two out of five facilities under anaerobic conditions. The concentrations were below the GCTLs, but still were detected. These findings illustrate to the reader the importance of conducting a risk assessment for the specific facility in question, as well as the selecting the appropriate leaching procedure

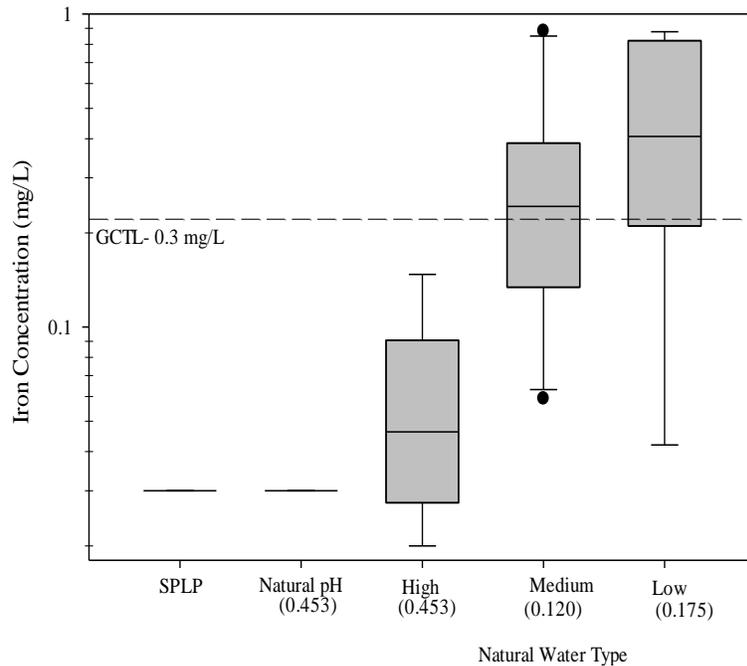
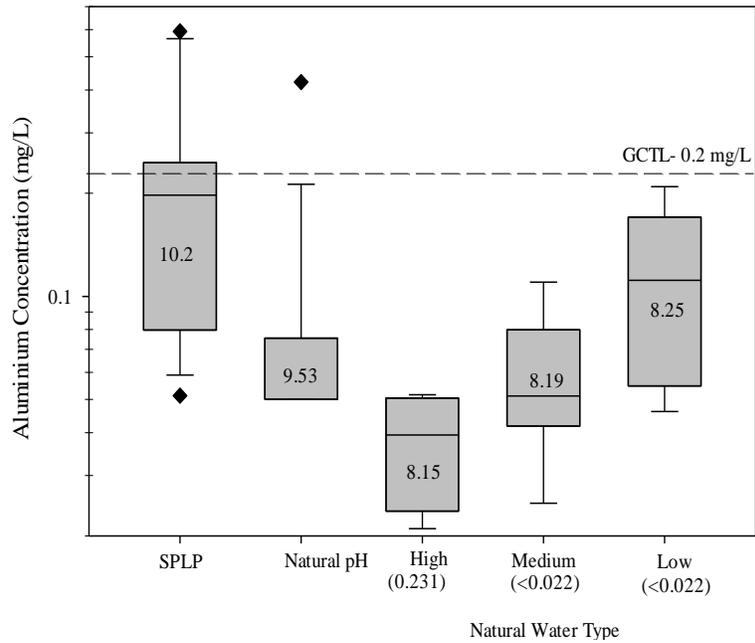


Figure 3-5. Comparison of element concentrations in SPLP, natural water pH and natural water leaching tests. Data from each leaching test was included here to illustrate the importance of selecting the appropriate leaching procedure that mimic the disposal scenario in question. The water samples were classified according to their total organic carbon concentration and ranged from high to low

CHAPTER 4  
BENEFICIAL REUSE ASSESSMENT OF HIGH TEMPERATURE PLASMA ARC SLAG AS  
A SUPPLEMENTARY CEMENTITIOUS MATERIAL (SCM)

**Background**

High temperature arc gasification (HTAG), is being explored as one emerging technology for the thermal treatment of municipal solid waste (MSW) (Gomez et al., 2009). Jung et al. (2005) reported that HTAG is an economically feasible technology that can be used to generate electricity while also producing byproducts that can be beneficially used as construction materials. The high temperatures required for this gasification process result in the creation of a waste product, vitreous slag, composed of the residual metals and silicates that originate from the MSW (Saffarzadeh et al., 2009). This slag is relatively inactive chemically when in an unprocessed state, however research has yet to explore its potential for reuse as a supplemental cementitious material (SCM) when ground to a fine powder. Due to HTAG slag's similar elemental composition to other pozzolanic materials (e.g., fly ash), and its generation in a high energy thermal process, use of HTAG as an SCM merits further exploration.

One of the most common questions posed when constructing a waste processing facility is how the generated residuals will be managed. To date, only a limited number of functional MSW HTAG facilities are currently operating throughout the world, with the large majority in Eastern Asia (Ojha et al., 2012). This has resulted in a scarcity of research related to HTAG slag and its beneficial reuse options; the majority of the work examining the beneficial use of MSW HTAG slag has focused on its environmental characterization or the use of the HTAG slag as an aggregate (Moustakas et al., 2012; Roessler et al., 2014). While limited data is available on MSW HTAG slag, slag generated from the vitrification of waste to energy ashes has been explored for use as an SCM. Lin (Lin et al., 2003) evaluated the influence of slag generated from the vitrification of MSW waste to energy fly ash when ground and used as an SCM at up to a

40% replacement of cement. Lin found that the addition of the slag delayed setting times and retarded early age strength (Lin et al., 2003).

Supplementary cementitious materials (SCMs) are gaining widespread popularity for use as an addition in cements and are also being used separately to produce geopolymers and other portland cement (PC) alternatives (Paris et al., 2016). Because of the large greenhouse gas footprint of portland cement production, SCMs serve to provide both a cost benefit (by using a low cost material that would otherwise be disposed) and an environmental advantage (Sarfo-Ansah et al., 2014). Other byproducts that have been generated from various industrial processes, such as ground granulated blast furnace slag (GGBFS) and class F coal fly ash (CFA) have been successfully utilized as SCMs (Lothenbach et al., 2011). Both of these industrial waste materials have been proven to enhance the strength and durability of portland cement concrete through reactions which facilitate the creation of a more dense microstructure and increase particle packing (Shao et al., 2000). These industrial waste byproducts set a strong precedent for the investigation of use of MSW HTAG slag as an SCM in PC mixtures.

The belief that HTAG slag can be reused is often a selling point of plasma based waste treatment technologies. This is in part due to the economic value associated with beneficial reuse (landfill diversion and perhaps sale) of these waste residuals. The research conducted herein serves to build upon efforts conducted by the authors as part of a previous study. Previous research by Roessler et al.(2016) demonstrated that the chemical composition of the MSW HTAG slag (used in both this and the previous study) contained high percentages of Ca, Al, and Si and could have a potential benefit as an SCM. An assessment of MSW HTAG, its elemental and mineralogical composition, and its potential for use as SCMs are presented here. A series of physical and chemical tests were conducted to study the pozzolanic activity of HTAG slag.

Strength development was assessed using compressive strength tests on slag-cement mortars. This data was also used to determine the activity index of the HTAG slag-cements. Isothermal conduction calorimetry was used to measure the short term heat of hydration of the slag-cements. In each of the tests control PC samples were tested as a reference for comparison. This chapter presents a novel examination of the potential for use of HTAG slag as an SCM, and will serve to guide research, slag generators, and other interested parties in evaluating its reuse options.

## **Materials and Methods**

### **Facility Description and Sample Collection**

MSW HTAG slag samples were collected from a pilot scale HTAG system located at Hurlburt Field air force base in FL, US. The Hurlburt Field unit handled approximately 11 tons of MSW per day and utilized the waste from the surrounding military base as a feedstock. Molten slag was periodically removed from the system and, approximately 200 kg of slag was collected from the facility during two separate sampling events over the course of six months. The material was first size was reduced by passing it through a 9.5mm (3/8") US sieve. Subsequent to size reduction, the sample was homogenized through repeated mixing and placed in polypropylene containers. To prepare the HTAG slag for testing as an SCM a sample (10 kg) of slag was pulverized using a disk pulverizer (BICO 242-53) that houses grinding plates made from chrome-alloy steel (UA-2000S/R). The powdered slag was then kept in sealed 5 gallon buckets (with desiccant added to prevent moisture intrusion) until time of testing.

### **Particle Size Distribution**

Particle size distribution analysis (PSD) was performed on the powdered HTAG slag by using laser light scattering (Horiba LA-950 Laser Particle Analyzer) in accordance with the procedure outlined in ASTM B822 (ASTM, 2010). The slag was dispersed using the liquid

dispersion method where lasers in the red and blue wavelengths were scattered through ethyl alcohol (200 proof) in an effort to determine particle size distribution.

### **Specific Gravity and Specific Heat Capacity**

The specific gravity ( $G_s$ ) of the slag was obtained through gas pycnometry (Quantachrome Ultrapys 1200e) in accordance to the procedure outlined in ASTM D5550 (ASTM, 2014a). A 6.25 g sample of HTAG slag was placed into a helium pycnometer which uses sample cells of known volumes for calibration purposes; this experimental procedure was repeated 10 times. A differential scanning calorimeter (TA Instruments Q20 DSC) was used to determine the specific heat capacity of HTAG slag. Based on the heat flow measured by the DSC instrument, the specific heat capacity was determined by following ASTM E1269 testing standard (ASTM, 2011). Perkin Elmer U-type aluminum pans (No. 02190041) were used as sample pans. The specific heat of the HTAG sample was measured and the temperature was then ramped up to 55 °C at a fixed heating rate of 20 °C/min. The independence of measurements was ensured by using separate samples and aluminum pans when obtaining sample line, standard, and base measurements. The DSC was calibrated prior to each sample measurement using Indium (melting point of 156 °C). The results indicate that the mean melting point of Indium is 156 °C, which is well within the range of acceptable temperatures  $156 \pm 2$  °C.

### **Mortar Specimen Preparation, Compressive Strength Testing, and Strength Activity Index**

The test specimens were cast in 5 separate batches of mortar: one control and four mixtures where a portion of the cement was replaced with the powdered HTAG slag in different percentages (5, 20, 35, and 50%). Type I/II cement and sand conforming were used which conformed to the requirements for portland cement and graded standard sand in ASTM C150 (ASTM, 2015a) and ASTM C778 (ASTM, 2013) respectively. Cubic mortar specimens (50× 50

× 50 mm) were produced and the mixture employed a water/cementitious ratio by mass (w/cm) of 0.50. The full mixture designs are presented in Table 4-1.

The mortar specimens were produced in accordance with ASTM C109. Mortar specimens were demolded 24 h after creation and stored in a lime water solution at a temperature  $23 \pm 2$  °C. Compressive strength testing was performed (in triplicate) on the PC and the slag-PC blends at 7, 28, and 56 days to determine the effect that HTAG addition had on the mortars mechanical strength. The 28 day compressive strength of the slag can be used to calculate the slag activity index. The slag activity index is calculated by dividing the compressive strength value of the 50% slag: 50% PC mortar by the compressive strength of the control mortar (100% PC) and reporting the value as a percent. For example a slag/PC mixture which yielded the same 28 day compressive strength as the control would have an activity index of 100. Based on the activity index of the slag it is graded into three strength categories for use in accordance with ASTM C989 (ASTM, 2014b).

### **Isothermal Conduction Calorimetry**

The heat of hydration of cement test was conducted in accordance with ASTM C186 (ASTM, 2015b) on each slag/PC mixture (as well as the PC control) using a TAM-Air Isothermal Calorimeter. This test measures the amount of heat that is evolved from cement hydration over the course of 7 days. Each sample is composed of 4.000 g of mixed powder (slag/PC) with 2.000 g of pure water in syringes; these samples are then placed in a calorimeter that is held a constant temperature of  $23 \pm 0.05$  °C. The samples were then equilibrated and allowed to hydrate in order to measure heat evolution.

## Results and Discussion

### Physical Properties

Particle size distribution of the powdered slag and PC were determined by laser particle size analysis and are presented in Figure 4-1. The particle size analysis showed that the slag was ground have a coarser particle in comparison to the PC. The mean particle size ( $\mu\text{m}$ ) for the HTAG slag and PC were 11.8 and 5.7 respectively. The specific gravity ( $G_s$ ) of the HTAG slag ranged from 3.13 to 3.14, with an average value of 3.13 and a coefficient of variation of 0.12%. The mean  $G_s$  of the slag was higher than that of conventional SCMs such as coal combustion fly ash (which can range between 1.9 and 2.8), and GGBFS (which can range from 2.85 to 2.95) (PCA, 2011). The mean  $G_s$  of HTAG was comparable to that of the PC (3.15). The results of X-Ray Fluorescence (XRF) analysis performed on the same MSW HTAG slag in a previous study conducted by Roessler et al.(2016) are presented in Table 4-2.

### Heat of Hydration

Heat flow and heat evolution during the 168 hour calorimetry measurement period (at  $23^\circ\text{C}$ ) are shown in Figures 4-2 and 4-3 for each of the slag-PC blends respectively, as well as the control PC sample.

The hydration process for both materials exhibit similar hydration tendencies. Typical PC hydration can be divided into five main stages (Neville, 1981). The first stage, the initial reaction, is associated with the first peak and it is related to the hydration of  $\text{C}_3\text{A}$  and  $\text{C}_3\text{S}$  with water. Stage one occurs minutes after mixing and results in a large amount of heat released due to the initial wetting and dissolution of minerals found in the mixture. The second stage is the induction stage or “dormant period” and occurs when a protective layer temporarily forms around the  $\text{C}_3\text{S}$  particles preventing any reaction from occurring (Mostafa and Brown, 2005). The third stage, the acceleration stage, is when silicates undergo hydration. This stage begins

when alkalis penetrate the protective layers and begin reacting with raw materials resulting in heat evolution and the formation of reactant products (Mostafa and Brown, 2005). This is when the resultant strength of concrete is most malleable. The fourth stage, the deceleration stage, begins when the thickness of hydrated particles reduces the amount of diffusion that takes place in the material (Mostafa and Brown, 2005). The result is a reduction of heat evolution. The fifth and last stage is the slow-continued stage. The slow-continued stage accounts for the strength of blended cements and occurs when hydration rates are at their lowest (Scrivener et al., 2015).

The peaks of the evolved heat from HTAG slag blended cements were lower than that of the PC control. Figure 4-2 and 4-3 clearly demonstrate the effect that HTAG slag substitution has on heat evolution in the blended cements. This effect can be attributed to pozzolanic reactivity and cement dilution (Mostafa and Brown, 2005; Thongsanitgarn et al., 2014). This contributes to slower hydration and heat evolution rates, as well as an overall reduction of the cumulative evolved heat (Han et al., 2015). The pozzolanic nature of HTAG slag is hypothesized to decrease heat output by reducing the rate at which hydration reactions occur in the presence of calcium hydroxide and tricalcium aluminat (Lothenbach et al., 2011). In addition, the dilution effect of the HTAG slag (replacing PC) decreases heat output because cementitious compounds, such as  $C_3S$  (a main component of hydration reactions) are lowered in concentration in comparison to the control (and also insulated by a protective HTAG slag layer that prevents these reactions from occurring) (Han et al., 2015; Kolani et al., 2012). An inverse relationship between peak exothermic activity and the relative concentration of the HTAG slag in the blended cement mixtures is shown in Figure 4-2. Overall, it was found that peak heat of the PC hydrated faster and with more heat flow than when the HTAG slag was added as a partial replacement.

Previous research has shown similar decreases in heat evolution when SCMs are added as a partial replacement of PC (Alhozaimy et al., 2015; Nocuń-Wczelik, 2001; Rahhal and Talero, 2004; Thongsanitgarn et al., 2014). Total heat evolution has been found to decrease with increasing SCM addition as well as increased material particle size (Alhozaimy et al., 2015; Nocuń-Wczelik, 2001; Rahhal and Talero, 2004; Thongsanitgarn et al., 2014). Rahhal and Talero (2004) found that the total heat evolved when coal fly ash was added as a partial replacement of cement decreased from that of controls and that the initial heat evolution was retarded (Rahhal and Talero, 2004). The same phenomena was observed when powdered limestone and scoria rock were used as natural pozzolans in conjunction with PC (Alhozaimy et al., 2015; Thongsanitgarn et al., 2014). In the experiment conducted by Alhozaimy et al.(2015) the decreased total heat evolution (with increasing addition of the powdered scoria) was also found to correspond to a decrease in the compressive strength of mortar specimens (measured 56 day strength values were between 80-65% of the control) (Alhozaimy et al., 2015). Thongsanitgarn et al.(2014) found that the total heat evolution of the hydrated material and the compressive strength of mortar specimens produced using PC, coal fly ash, and powdered limestone were reduced significantly when the particle size of the powdered limestone was increased from 5  $\mu\text{m}$  to 20  $\mu\text{m}$ . 28 day compressive strength values of mortars composed of 70% - PC, 20% fly ash, and 10% powdered limestone (either 5  $\mu\text{m}$  or 20  $\mu\text{m}$ ) were decreased from 40.32 MPa (5  $\mu\text{m}$ ) to 37.39 (20  $\mu\text{m}$ ) when the limestone particle size was increased (Thongsanitgarn et al., 2014).

The results observed when testing the HTAG slag blended cements support the conclusions of previous studies, the increasing addition of the HTAG slag resulted in a decrease in the heat evolution of the hydrated products. Overall, Figure 4-3 demonstrates that as the concentration of HTAG in PC samples increases, the heat of hydration decreases. The hydration

kinetics of the addition of HTAG in PC are best understood when comparing heat of hydration values of HTAG PC mixtures against that of pure 100% PC at 164 hrs. At low replacement percentages the cumulative heats of hydration were similar. The 5% HTAG slag blended cement had a total cumulative heat evolved of 333 j/g, 96.5% of the control cement (345 j/g).

The reduction in heat is likely attributed to several factors, one key component of which is the absence of reactants (contained in the PC) (Kolani et al., 2012; Lange et al., 1997). Furthermore, the slag used in the experiment was added at a mean particle size of 11.8  $\mu\text{m}$ , significantly larger than the PC used (mean particle size 5.7  $\mu\text{m}$ ). Further size reduction of the slag could result in increased heat evolved during the hydration process. In addition, the HTAG slag contained a higher content of MgO (12.3%) than conventional PC cements. MgO has been reported to play a substantial role in delaying heat evolution (Zheng et al., 1992). Zheng et al. (1992) found that increasing MgO content in PC retards the hydration of cement due to the formation of a protective layer of “Mg(OH)<sub>2</sub> precipitates” (Zheng et al., 1992). Altun and Yilmaz (2002) tested blended cements made with steel slag containing an elevated content of MgO (approximately 14%) and found that blended cements containing 15–30% steel slag develop 66–83% of the control sample strength after 2 days, 72–88% of the control sample strength after 7 days and 80–92% of the control sample strength after 28 days (Akin Altun and Yilmaz, 2002). The amorphous fraction of the slag could have been an additional factor which resulted in delayed and reduced heat evolution, a trend reported for other slags containing an appreciable amorphous fraction (Zheng et al., 1992). While these latter three phenomena may certainly play a role the decreased total heat evolution, the data provides evidence that the HTAG slag is less reactive than PC to some degree.

## **Compressive Strength**

Compressive strength tests were conducted in triplicate on the control PC and blended cement mortars. The results of the 7, 28, and 56 day compressive strength tests on the blended cements are presented as a percentage of the control in Figure 4-4. The measured strength values for the 5% HTAG slag addition were similar to that of the controls at all of the time periods evaluated. The 5% HTAG slag blended cement had compressive strength values of 107%, 98% and 99% of that of the controls at 7, 28 and 56 days respectively. The measured strengths of the blended cement mortars decreased significantly after the 5% slag addition. This corresponds to the substantial decrease in total heat evolution which was also observed. The 20% HTAG slag addition had compressive strength values ranging between 80 to 82% of controls while the 30% and 50% HTAG slag additions ranged between 55-62% and 31-39% respectively.

ASTM C989 Standard Specification for Slag Cement for Use in Concrete and Mortars is commonly used as a grading mechanism for slag-cements in the United States (ASTM, 2014b). The 28 day strength values of a 50% slag: 50% PC mortar are compared to a control mortar produced using PC. The minimum strength requirement for the lowest grade of cement is set at 70% of the control strength. For the HTAG slag blended cements the 50% slag: 50% PC sample was well below this value at 28 days (35%). Other lower percentage replacements (5 and 20% slag) did exceed over 70% strength at 28 days. This data indicates that use of HTAG slag processed using similar produces to those here would not be likely to meet applicable compressive strength thresholds at high percentage replacements (Table 4-5).

Table 4-1. Mix design used for each mixture. This mix design was used for other laboratory analysis, including the compressive strength and heat of hydration tests.

Code	Replacement (%)	Cement (g)	Slag (g)	Sand (g)	Water (g)	W/C
Control	0	3,180	0	8,710	1,590	0.50
5% HTAG	5	3,020	159	8,710	1,590	0.50
20% HTAG	20	2,550	635	8,710	1,590	0.50
35% HTAG	35	2,070	1,120	8,710	1,590	0.50
50% HTAG	50	1,590	1,590	8,710	1,590	0.50

Table 4-2. Chemical analysis results of HTAG. These data were determined from Roessler et al. (2016) and suggest that HTAG slag can be used as a SCMs due to high contents of Al, Ca, and Si. These phases contribute the pozzolanic activity found in portland cement. These values obtained using XRF analysis

Oxide phases	wt% of	Solid	Granulated blast furnace slag (Siddique and Khan, 2011)	Class F fly ash (Siddique and Khan, 2011)
	HTAG	PC		
Al <sub>2</sub> O <sub>3</sub>	22.6	5.10	10-15	13.3-21.3
SiO <sub>2</sub>	30.8	20.2	35-40	23.1-50.5
TiO <sub>2</sub>	0.500	0.220	-	-
Fe <sub>2</sub> O <sub>3</sub>	2.00	2.70	0.3-2.5	3.7-22.5
MnO	0.100	0.114	-	-
MgO	12.3	2.50	8.0-9.5	1.5-7.5
CaO	22.0	63.2	30-42	11.6-29.0
Na <sub>2</sub> O	1.10	0.700	0.0-1.4	1.0-2.1
K <sub>2</sub> O	nd <sup>a</sup>	0.830	0.0-0.3	0.4-1.9

<sup>a</sup>Not detected

Table 4-3. Isothermal calorimetry data for HTAG and PC mixes. The data were obtained using isothermal calorimetry instrument and detailed data can be found in the next plots

Sample ID	Maximum rate of heat evolution (mW/g)	Time of maximum rate of heat evolution (hours)	Total heat evolved during 7 days (j/g)	Heat of hydration relative to 100% PC
100% PC	3.73	10.3	345	100
5% HTAG	3.54	10.5	333	96.5
20% HTAG	3.06	10.6	295	85.5
35% HTAG	2.34	10.6	239	69.3
50% HTAG	2.23	10.9	205	59.4

Table 4-4. Normalized percentage difference from the control sample at 28 days. ASTM C989 standard specification for slag cement for use in concrete and mortars is commonly used as a grading mechanism for slag-cements in the United States

	Percentage differences compared with the control
5% HTAG	98
20% HTAG	84
35% HTAG	56
50% HTAG	35

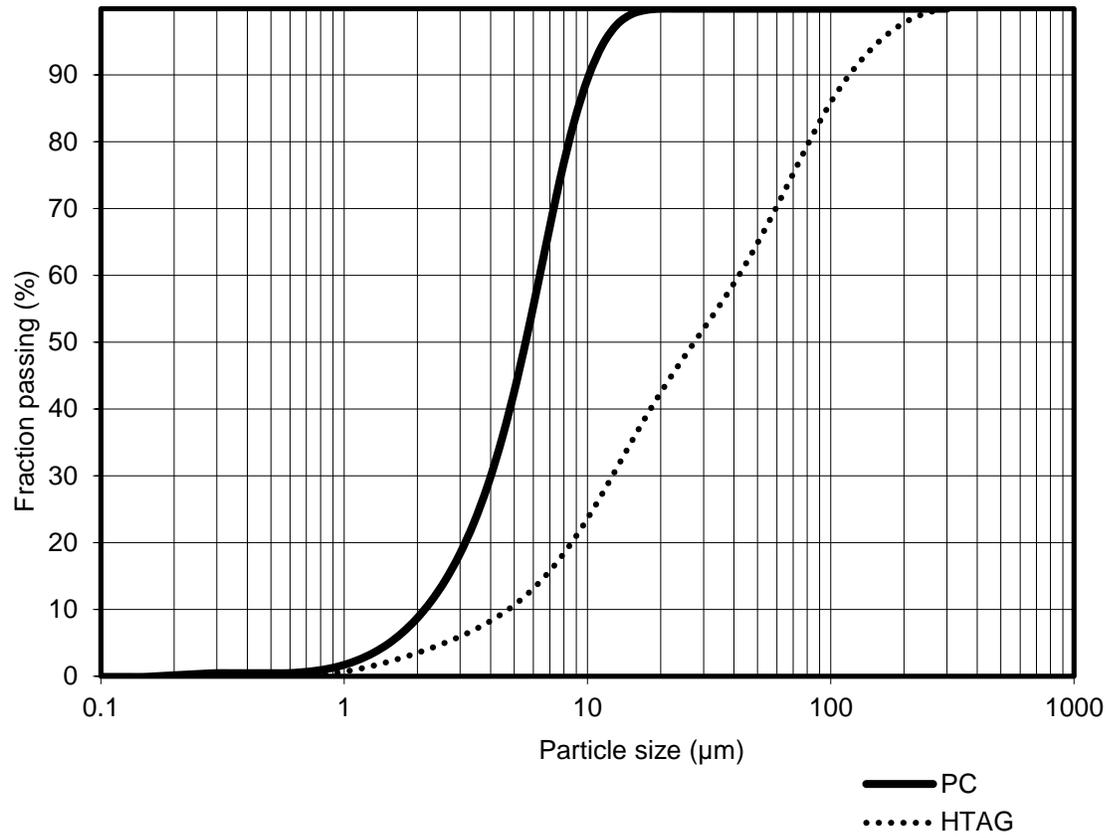


Figure 4-1. Particle size distribution of PC and HTAG slag using a laser particle size analyzer. The average particle size for the PC and HTAG slag were 5.7 and 47.7 µm. This means that PC is finer than the HTAG slag sample

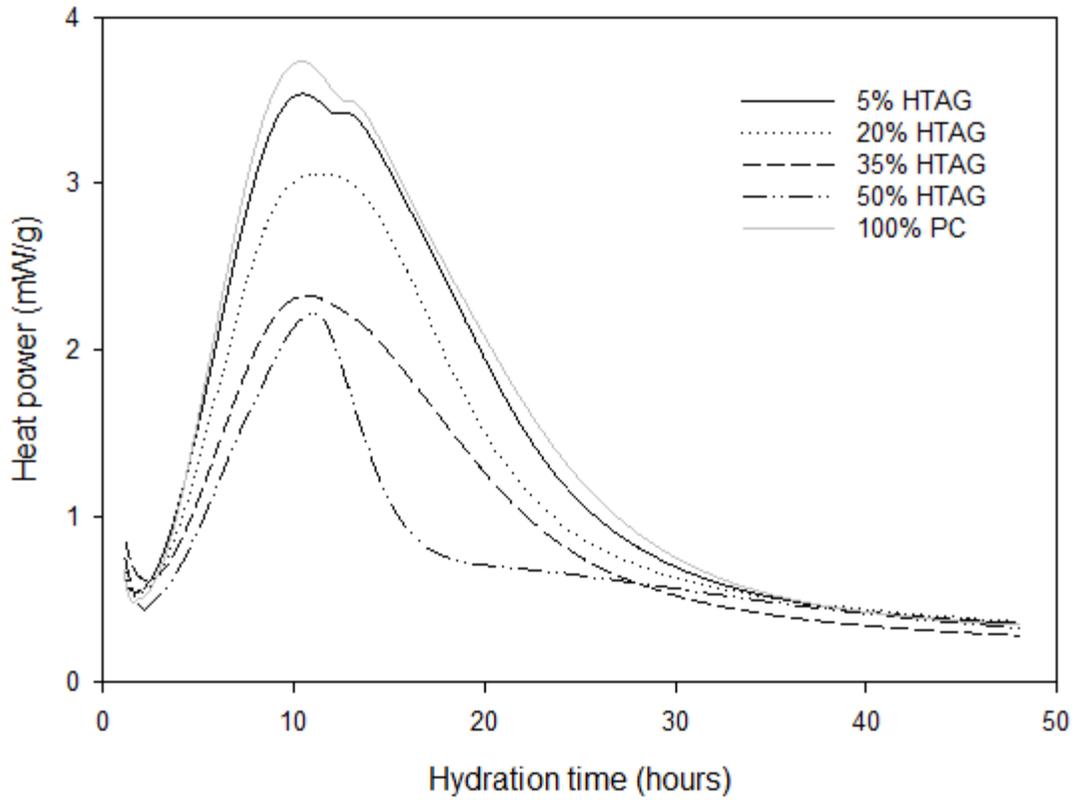


Figure 4-2. Heat power during hydration of HTAG slag and PC at 23 °C. The test were run for seven days, but the hydration time was narrowed to 48 hours. PC released the highest heat power, followed by the lower replacement percentages due to the dilution effect and higher particle size of the slag

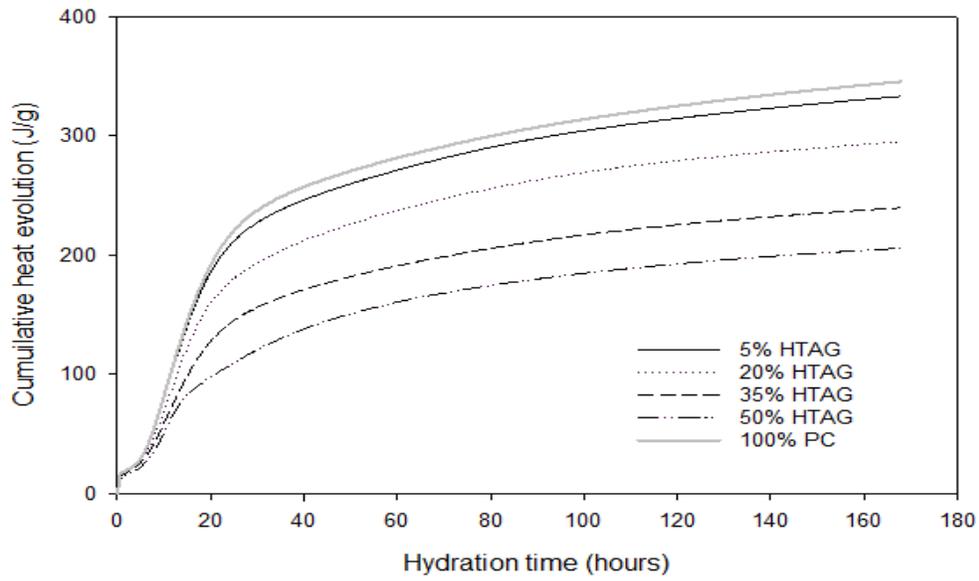


Figure 4-3. Cumulative heat evolution during hydration of HTAG slag and PC at 23 °C. The cumulative heat evolved were shown here to make it easier for comparison between the mixers. No difference was found between 100% PC and 5%

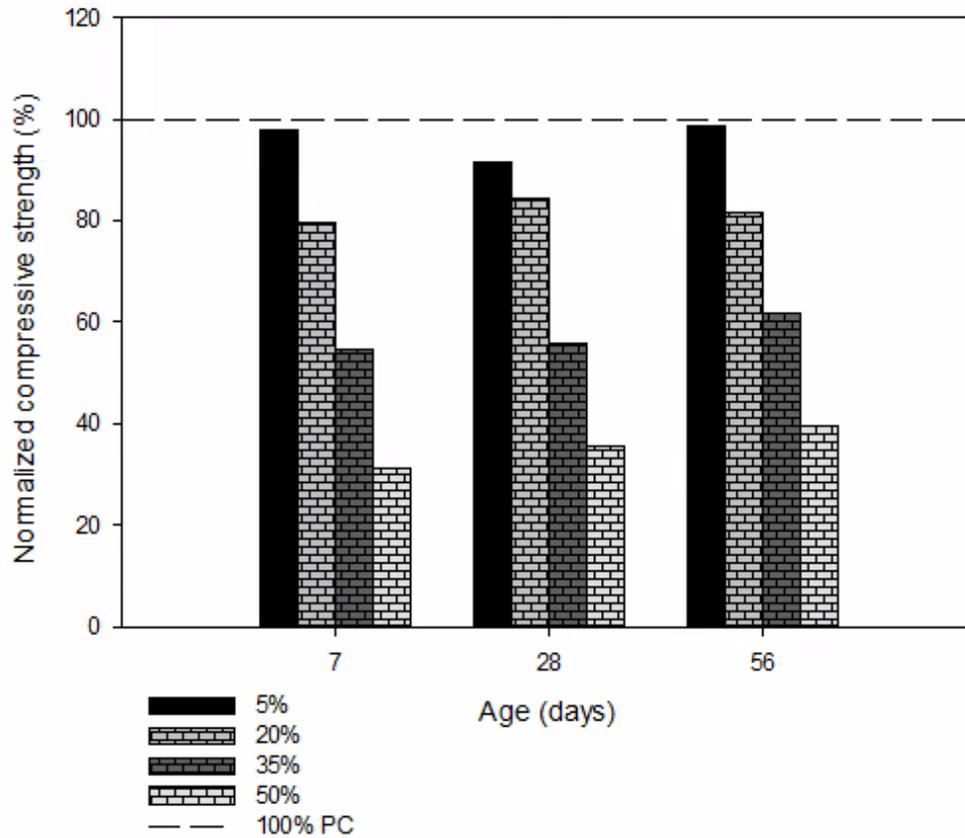


Figure 4-4. Normalized compressive strength for HTAG slag for comparison purposes. Higher replacement percentages had much lower compressive strength gain due to several reasons, including dilution effect, as well as higher particle size of the slag

CHAPTER 5  
LEACHING ASSESSMENT OF CONCRETE MADE FROM MINE TAILINGS:  
EVALUATION OF THE IMPACT OF PHYSICAL INTEGRITY ALTERNATION

**Background**

Encapsulating industrial waste byproducts is a way to minimize and contain the release of elements into the environment (Breslin and Roethel, 1995). Encapsulation can occur by using waste products as an ingredient in concrete with the exception that the waste meets the concrete standard requirements. The benefit is that encapsulating industrial waste byproducts results in a reduction of the leaching of elements (van der Sloot, 2000b). A low percentage of the water percolates through the encapsulated materials and travels to the soil beneath them. However, the leaching of pollutants in these materials is also slow and controlled by the mass transport of the pollutants through the pore's solid phase as it moves into the liquid phase. There is some evidence that environmental (e.g., acid attack) and civil ( e.g., shrinkage or heavy truck loads) conditions (Kosson et al., 2009), where concrete experiences different degrees of cracking, can lead to physical changes of the encapsulated materials which in turn may increase the risk of leaching (Kluge et al., 2014).

A number of studies have focused on the leaching of encapsulated industrial materials and industrial waste byproduct in the field or using a conventional leaching tests. A majority of these studies have focused on comparing and validating field and laboratory-based leachability of bottom ash. Schreurs et al.(2000) evaluated the relation between field-laboratory leaching from MSWI bottom ash by examining the pore water concentration of the waste itself and the accumulation of pollutants in the underlying soil. The study examined the differences between aged and fresh bottom ash leaching. Another study examined the run-off leaching of inorganic and organic compounds from concrete and asphalt surfacing materials under controlled laboratory conditions (Kayhanian et al., 2010). The main objective of this study was to determine

if pavement materials (i.e. concrete and asphalt) are the contributing sources of pollution in highway runoff. It was found that only Cr and V were released from the pavement material which contained portland cement binders. This practice is popular because it results in porous pavement which results in less pollutants and runoff draining into the storm collection system (M and W, 1995; Reem, 1994). The study demonstrated a lower concentration of trace elements in the storm collection system and a higher concentration in the percolating water.

Another study evaluated the porosity of low permeable concrete overtime under extreme immersion conditions (Liu et al., 2014). This study demonstrated that the porosity of concrete was higher as result of calcium hydroxide leaching. Another study investigated the permeability of cracked concrete to water (Picandet et al., 2009; Wang et al., 1997). Sequential crack patterns with different crack widths were analyzed. The study indicated that crack opening accelerated water flow through the concrete. Cracking in other research papers investigated heavily on the concrete durability aspect in lab and field scales, such as the effect of field conditions (e.g., carbonation shrinkage, humidity, and weathering) on durability of concrete (Banthia and Grace, 2012; Kersten et al., 1997; Yang et al., 2005).

Few research exists regarding the environmental impacts of cracking on elements release using a conventional leaching test in a laboratory scale. While changes of the physical form may play an important role in the amount of water that percolates through encapsulated materials other environmental factors may still play an important role. Apart from physical aspects, an important factor is governing the release via chemical mechanisms (Galvín et al., 2014). Some chemical factors dictate the pore water composition that controls the leachability of trace elements (Heasman et al., 1997). Therefore chemical factors may be just as important as physical ones when assessing the concentrations at which trace elements can leach through encapsulated

materials. This includes factors like the pH of a solution which is a crucial parameter in the solubility of chemical species that are currently in study at the field site of industrial waste byproducts.

The aim of the present study is to evaluate the release of trace elements from industrial waste byproducts subjected to a different degree of cracks using a test method that have been developed to assess leaching of elements from a encapsulated form; these tests allow the user to determine release of elements and diffusivity of each element. In addition, this chapter is aimed to examine how stress, through simulated cracks, influences elements release from encapsulated material over time. In addition to the leaching test, permeability of each specimen was determined using a standard procedure, since permeability coefficient is an indirect measure of cracking level. This research chapter highlights the importance of considering the long term impact that may encounters to encapsulated materials in the long term (e.g., cracking). The findings of this chapter can be used to generate more thorough assessment of elements release at different conditions, which may change the outcomes of decision making.

## **Materials and Methods**

### **Facility Description and Sample Collection**

Mine tailing samples were collected from the Pride of the West TSF in Silverton, CO and were used for analysis in the proposed research protocol. The samples were sourced from the Southern inactive storage area which is physically separated from an inactive storage area by an active storage area. A nearby stream was observed to have a yellow-orange color which was attributed to a high concentration of iron (III) hydroxide precipitates.

Sampling plots consisted of seven 10' x 10' cordoned off areas and random sampling took place through the use of a blind throw of a stone over the shoulder. Plots were spaced accordingly so that the particle sizes of mine tailings changed over the entire distance of plots

sampled. When the stone landed within the plot area it was first removed and then a shovel (stainless steel, acid washed) full of tailings was collected. If the stone landed in a previously excavated area of the plot then the stone was thrown over the shoulder again. This process was repeated until an acid washed, five gallon bucket was full of tailings which typically required 8 to 10 throws of the stone. After sampling all seven plots, the shovel (acid washed, stainless steel) was placed in a breathable sampling bag. Buckets were washed following the sampling procedure and allowed to air dry. An identical process was used to wash the shovels and lids used in the sampling process. The acid wash of laboratory equipment was done using nitric acid, sulfuric acid, and deionized water.

Samples then underwent a sieving process at the CSM campus. 3' x 3' sieves were constructed out of wood slats, screen mesh (1.5 mm x 2 mm) and screws. Following sample collection, each 5 gallon bucket underwent the sieve process and was mixed by hand with the previously mentioned small stainless steel shovel in order to homogenize samples.

Homogenization was conducted in cleaned, concrete mixer drums. Following homogenization tailings were placed back into their respective buckets.

### **Concrete Mix Design**

Mine tailings, coarse sand, and portland cement were used to make concrete. Two types of mixtures were used in this study: (1) control mixture with no mine tailings (Control) and (2) 28% replacement of fine aggregate with mine tailings (28% MT). The percent of fine aggregate replaced by mine tailings was 28% and this percentage was used in a previous study (Bray, 2013). The mix design was similar to the mix design used in a previous study, with minor modifications. The mixing procedure followed the procedure outlined in ASTM C192 Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory. Table 5-1 shows the mix design for the control and 28% MT. Following the production of specimens, they were

placed in rectangular molds ( $102 \times 203\text{mm}$ ) and wrapped with plastic sheeting to eliminate moisture loss and cured for 24h at room temperature. Following the 24h curing period, each specimen was demolded and placed in a vacuum sealed plastic sheet and cured for an additional 28 days prior to the conduction of permeability and leaching tests. Specimens for each mixture were taken out at 7, 28, and 56 days for compressive strength determination. The compressive strength test followed the procedure outlined in ASTM C39 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens.

### **Crack Creation**

Generating artificial crack patterns in concrete is a challenging procedure since there is no standardized procedure to do so in a laboratory scale. In addition, a limited number of research currently exists examining the permeability of cracked concrete (Aldea et al., 1999). Several of the studies examining permeability and cracking effects have been focused on the modeling portion of analysis (Gérard et al., 1996). A prior permeability test has been performed, using feedback from a controlled splitting test (i.e. Brazilian test) to induce controlled cracks in concrete specimens (Aldea et al., 1999; Wang et al., 1997). The Brazilian test is one method used to estimate the tensile strength of concrete through indirect tension tests. This study reported on the advantage of using this test to generate controlled crack widths, as well as proved the dependence of permeability on the value of the crack width opening. However, the test breaks concrete specimens in half and does not easily create microcracks. Therefore, compressive strength tests were used to create artificial cracks using the maximum load as a base parameter. Three different degree of cracks were created: 0% (specimen was not subject to any artificial crack, 33% of the maximum load, and 66% of the maximum load.

## Permeability Test

The permeability test followed the pressure head procedure outlined in Soongswang et al., (1988) for the control and 35% MT. Portion of the control and 35% MT specimens were taken following 28 days of curing and subjected to the same crack procedure outlined in the *Crack Creation* section at 0%, 33% and 66% of the maximum load. Following this procedure, specimens was cut to 2 inches high to fit the test apparatus using a wet saw method (electric ceramic tile saw wet cutter). Following the cutting procedure, the test specimens were wire brushed and then 1-in layer of epoxy (Sikadur 32, Hi-Mod) was cast around the side of the test specimen to fit the 6 inches diameter permeability apparatus. The specimen was placed into the permeability apparatus as described in Soongswang et al., (1988) and 90 psi pressure was applied throughout the test for a total duration of 14 days. A study state condition was reached within 10-14 days and the pressure head was recorded daily for 14 days. The permeability coefficient was calculated following equation:

$$K = \delta \frac{H}{P} \frac{Q}{A} \quad (\text{Eq. 5 - 1})$$

Where, K is the permeability coefficient in in/sec,  $\delta$  is the density of water in lb/in<sup>3</sup>, H is the length of the test specimen in inches, P is the water pressure in psi, Q is the net rate of inflow in in<sup>3</sup>/sec, and A is the cross sectional area of the test specimen in in<sup>2</sup>.

## Total Metal Analysis

Total elemental analysis was conducted following the procedure outlined in EPA method 3050b for concrete specimens (control and 28% MT). Each test was conducted in triplicate at a constant heating temperature of  $95 \pm 5$  °C with the addition of nitric, hydrochloric and hydrogen peroxide acids at constant volumes.

## Leaching Tests

Leachate samples were digested in accordance with the EPA Method 3010A. Batch leaching test SPLP (EPA method 1312) was performed on each material, following a 28 day curing period, in triplicate. Prior to performing EPA method 1312, a portion of the control and 28% MT specimens were size reduced with a jaw crusher in order to pass a 9.5 mm sieve, following the size protocol outlined in EPA method 1312. The reduced sample for each material was used to run the SPLP test. The SPLP test employs a liquid to solid ratio of 20:1 mL reagent water/g-dry sample and a rotation time of  $18 \pm 2$  hours at a constant speed of 28 rpm. Following  $18 \pm 2$  hour extraction, the samples were filtered using a vacuum filtration apparatus (EMD Millipore XX1504700) and a borosilicate glass fiber filter with 0.7 micrometer pore size (Whatman; GF/F). To allow for separation during filtration, some samples were centrifuged when a high suspended solid content was observed. In such cases a centrifuge set at  $4000 \pm 100$  rpm for 10 minutes was used (Beckman; J2-HS Centrifuge). Intact specimens were kept for the monolithic leaching experiment (EPA method 1315).

Method 1315 is a tank-leaching test that involves renewing the leaching fluid at nine intervals (0.08, 1.0, 2.0, 7.0, 14, 28, 42, 49, and 63 days). A monolith sample, cylindrical in shape, was used in this experiment with a 3-dimensional configuration. The cylindrical mold was made from polyvinyl chloride (PVC). The dimensions of the vessel were 19.1 cm high, and a diameter of 12.9 cm for both materials. The volume of reagent water added was proportional to the liquid to exposed surface area ratio of  $9 \text{ mL/cm}^2$ .

Cumulative mass release, cumulative mass flux, and observed diffusivity were calculated following the approach used by other researchers (Kosson et al., 2002a, 2002b; Sanchez et al., 2002). These parameters were used to evaluate pollutants from encapsulated materials and to determine where mobility is controlled by diffusion mechanisms. The equations used to calculate

the cumulative mass release and mass flux parameters were addressed in Roessler et al.(2015) and detailed in EPA method 1315 protocol. The observed diffusivities were calculated following the analysis outlined by Crank (Crank, 1975) using an infinite bath model. The Leachability Index (LI) is a parameter proposed and used by researchers to identify the degree of mobility of certain elements and is calculated by taking the  $-1 \times \log_{10}(D_i^{obs})$ , where  $D_i^{obs}$  is the observed diffusivity. As indicated by (Dermatas et al., 2004; Roessler et al., 2015; Singh and Pant, 2006), if the LI is  $< 6.5$  the element has a high mobility, if  $LI > 8.0$  the element has a limited mobility, and if  $6.5 < LI < 8.0$  the element has moderate mobility.

### **Environmental Analysis**

Leachate samples were digested prior to any analysis following acid digestion as outlined in EPA method 3010a. Following the digestion, samples were analyzed for major and trace elements, including Al, As, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ti, V, and Zn using an Inductively Coupled Plasma- Atomic Emission Spectrometer (ICP-AES) (Thermo iCAP 6200 Atomic Emission Spectrometer) following EPA Method 6010C.

## **Results and Discussion**

### **Compressive Strength Results**

The compressive strength test was determined after 7, 28, and 56 days of curing, and the compressive strength test was conducted for each of the samples. Figure 5-1 shows the results of the compressive strength test for the control and MT samples. The compressive strength for the control mixture was higher than the MT mixture, and it was hypothesized that the produced C-H was not sufficient due to diluting of the PC matrix with 28% MT in the mixture. The MT mixture showed results similar and not significantly different from the control sample at 7, 28, and 56 days of aging. In early aging (7 days), the compressive strength for the MT sample was slightly higher than the control sample but not significantly different. The improvement of compressive

strength is due to micro filling, the continuous addition of CSH gel, and pozzolanic activity became more significant at a later curing age (Chopra and Siddique, 2015; Saleh Ahari et al., 2015). The American Concrete Institute Building Code 318 (ACI 318) specifies a minimum compressive strength at 28 days for material used as a replacement to fine aggregates, depending on the application land use. The compressive strength results for the MT met the minimum compressive strength at 28 days (2500 psi) for driveways and various other types of applications (ACI, 2007). Further civil engineering testing is necessary to evaluate long the term durability of MT inclusion in the PC mixture.

### **Permeability Test Results**

The permeability coefficient was calculated for the control and MT samples following 28 days curing (0, 33, and 66% samples), and shown in Figure 5-2. It is observed that the permeability coefficient for the control and the MT decreases with the increase of the degree of cracking. There are limited data in the literature relating the permeability coefficient with cracked PCC, but it supports the hypothesis that increasing the degree of cracking results increasing the value of permeability coefficient. Li et al. (2016) evaluated the permeability of PCC as a function of different volume fractions of aggregates (i.e. impermeable or less pervious aggregates) and found an overall reduction of the permeability of PCC. Studies have investigated the permeability coefficient of cracked concrete to water (Picandet et al., 2009; Wang et al., 1997). Sequential crack patterns with different crack widths were analyzed. The studies showed that cracked concrete slabs increase the permeability coefficient of the material of interest and allow water to infiltrate easier. Also, depending on the width or the thickness of the crack, the conductivity values will vary (Kassim T, 2005). For example, Wang et al.(1997) who used the splitting test to create different level of cracking, and showed that concrete slabs with higher crack width increases the permeability coefficient values. Furthermore, the study found that

permeability coefficient of uncracked concrete were  $10^{-10}$  to  $10^{-9}$  cm/s compared with crack openings of 300 to 400  $\mu\text{m}$  and  $10^{-3}$  to  $10^{-2}$  cm/s (Wang et al., 1997). The study indicated that crack openings less than 50 microns is negligible and only influence minor changes to the permeability coefficient. The values of the permeability coefficient increased substantially when the PCC was subjected to higher degree of cracking. As anticipated, 0% samples for the control and the MT samples have the lowest permeability coefficient values as the concrete became more impervious and the microstructure was untacked by any load. In this stage, the amount of CSH phase increased which contribute to the impervious property (Naik et al., 1996). The additional C-S-H reduces the porosity of concrete by filling the capillary pores thus improving the microstructure of concrete in bulk paste matrix and transition zone leading to increased compressive strength (Chopra and Siddique, 2015). A decrease of MT-0% exhibited lower permeability than the control PCC sample, and it is hypothesis that is due to pore microstructure reduction when MT is included in the mixture. Other industrial wastes have been used in PCC mixture to improve the property of the concrete (Juenger and Siddique, 2015). Fly ash for instance, reduces the pore spaces in PCC resulting in a lower permeability coefficient (Fraay et al., 1989; Saleh Ahari et al., 2015). From the results in Figure 5-2 it was observed that MT sample with respect to the control sample, the permeability increases by increasing the level of cracking, except in MT-33% sample which its permeability is higher than the control sample. The permeability coefficient values in the control sample for 0, 33, and 66% were 30, 24.5, and 5.92% higher than the MT samples (0, 33, and 66% respectively).

### **SPLP Leaching Test**

The SPLP results for the size reduced control and MT samples following 28 days of curing are presented in Table 5-2; Al (1.45/1.50 mg/L) and Mo (0.0610/0.0667 mg/L for the Control/MT) showed concentrations above the GCTLs and were identified as COPC along with

Sb. Al concentration in the MT sample (1.50 mg/L) was slightly higher than the control sample (1.45 mg/L), indicating that MT contributed to this concentration. Mo concentration in MT was found to leach at concentrations (0.0667 mg/L) similar to the control sample (0.0610 mg/L). Similar to Mo, Sb leached at a concentration lower than the GCTLs for the control (<0.003 mg/L) and MT (0.005 mg/L) samples. The mean pH's of the SPLP leaching tests were 12.2 and 12.0 for the control and MT samples; indicating that components in the portland cement (PC) contributed to the elevated pH shown in control and MT samples. In addition, the alkalinity of the PC components influences the final pH of the SPLP leachate for the control and the MT leachate, as indicated from the fact that the final pH for the control and the MT were slightly identical.

Total environmentally available contents of Al, Mo, and Sb are presented in Table 5-3. Total contents in the MT samples for Mo and Sb were slightly higher when compared to the control samples, this is supported by the addition of 28% (by mass) MT in the concrete mixture which contributed to the higher concentrations. However, Al was higher in the control sample compared to the MT sample, indicating a lower Al concentration in the MT. Total content analysis for the MT itself showed a value of 1600 mg/kg-dry.

Mo and Sb are two elements found naturally in MT, and found to be higher in the MT sample. Higher contents for these elements may result in higher leachable concentrations (Table 5-2). On the other hand, Al is known to be present in PC in abundant quantities, and resulted in higher leaching of this element (Table 5-2). Prior studies (Blaisi et al., 2015; Roessler et al., 2015) have reported the speciation of Al and other elements with observed final pH's in SPLP tests (Table 5-2) while total quantities facilitate the solubility of Al, Mo, and Sb. The final pH of the SPLP solution (pH ~12) played an important role on the release of highly pH dependent

elements (e.g., Al), as this pH range favors leaching of Al. Alternatively, Sb and Mo leaching are typically more favorable at a lower pH range (Izquierdo and Querol, 2012; Kosson et al., 2014). Based on this, there are other factors which facilitated leaching of Sb and Mo in the control and MT samples. The chemical reactivity of MT, when mixed as an ingredient in PC, has not been reported on in many studies, however Bray (Bray, 2013) reported a greater release of several COCPs at higher concentrations than their respective thresholds (e.g., Cd and Pb) in the SPLP leaching test. A number of other authors have reported that reactivity of certain industrial wastes used as ingredients in PC mixtures (e.g., bottom ash) with known COCPs (e.g., Pb which is favorably leached at pH of 12) remained bound within the PC mixture (Roessler et al., 2015).

The SPLP test conducted in this study was found to leach certain COCPs (Al, Mo, Sb) above their respective thresholds. Examining the results of the batch test would provide, as proposed by other authors, a conservative estimate or “worst case scenario” approach when assessing the risk of industrial waste,(Blaisi et al., 2015; Garrabrants et al., 2010; Kosson et al., 2002a) especially when the waste material is intended to be used in a crushed manner during disposal. However in other reuse applications, appropriate leaching test should be considered when assessing risk. For example, Roessler et al. (2015) indicated that factors such as the weathering of pavements may result in minor cracking and potential increase to the surface area. These types of scenarios would result in the use of monolithic leaching assessment as a more appropriate leaching procedure.

### **Element Release from Monolithic Leaching Test**

Method 1315 is based on the Semi-infinite model of diffusion. This test provides information on the cumulative mass release rates through monolithic formed materials. Several parameters were quantified after running this test: (i) cumulative mass release ( $M_{\text{cumulative}}$  in mg/kg-dry), (ii) identify the release mechanism in cracked and uncracked samples for the control

and MT samples (i.e. dissolution, diffusion, or depletion) and (iii) determine the LI for COPCs in both materials.

The pH of the leachate at the end of each collection period was measured. The pH of the control specimens in EPA method 1315 tests started at an average value of 9.75, 10.3, and 9.31 for the control-0%, control-33%, and control-66% and decreased throughout the course of the experiment to final average pH of 8.70, 8.88, and 8.90 for the control-0%, control-33%, and control-66% samples respectively. A different trend was observed in the MT samples, where the pH started with an average of 9.40, 9.34, and 9.41 and increased at the end of the experiment (after 63 days) to 11.9, 11.9, and 11.7 for MT-0%, MT33%, and MT66% respectively. Table 5-4 showed the average pH values for the control and MT specimens along with the leachable concentration for two selected COPCs. Leachable concentration of Mo was below detection limits throughout the course of EPA method 1315 experiment in the control and MT specimens, indicating that Mo is encapsulated within the PC matrix. Mo was detected in the SPLP test, suggesting that size reduction of the sample in the SPLP test (which increases the exposed surface area) and encapsulation are two major reasons for this trend. However, Al leachable concentration was above its respective thresholds (GCTLs ~0.2 mg/L) for the majority of the collection points of EPA method 1315 for the control and MT samples (cracked and uncracked specimens).

Throughout the course of the EPA method 1315 test, Al concentration was much lower than in the SPLP test with respect to the monolithic leaching test. The alkaline pH observed in the SPLP test may have facilitated the release of Al at higher leachable concentrations than EPA method 1315 test. For the majority of the test intervals, Al concentration was significantly higher in the cracked specimens (5/9-control-33% and 66%), however 4/9 intervals were not

significantly higher than the control-0% specimens, rather, their concentrations were slightly lower for the control-33% and 66%. For the majority of the test intervals, Al concentration was significantly higher in MT-66% specimens (8/9-MT66%), however 5/9 intervals were not significantly higher than the MT-0% specimens or in the MT-33% specimens (4/9 intervals were significantly higher than MT-0%). Overall, leachable concentration in the control samples was much higher than in the MT samples. The total amount of Al contained in the MT samples was much lower than PC, and it supports the previous hypothesis that leachability of Al is driven by the final pH of the leachate, as well as the natural occurrence of Al contained in PC (Total concentration of Al in the MT and control are 1600 and 4200 mg/kg-dry).

A leachable concentration of Sb was detected in the MT samples and was below the detection limit in the control specimens, indicating that Sb leaching was generated from the MT itself. Concentration of Sb was mostly below the GCTLs, except for a few leaching intervals. Sb concentration, for most leaching intervals, increased from 0.0055, 0.0027, and 0.006 mg/L to 0.0063, 0.0063, and 0.0056 mg/L for MT-0%, 33%, and 66% specimens. Leachable concentration for the majority of the leaching intervals (7/9 for MT-33%, 8/9 for MT-66%) were much higher than the MT-0% specimens. For a better comparison of COPCs between cracked and uncracked specimens, the cumulative release in EPA method 1315 test will be discussed further in the next section.

### **EPA Method 1315 Cumulative Release**

The cumulative release of two COPCs (Al and Sb) are shown in Figure 5-3 and 5-4 for control and MT specimens. The cumulative mass release of Al in the control specimens increased in order with the increasing degree of cracking from 3.49, 7.27, and 12.3 mg-Al/kg-dry for Control-0%, 33%, and 66%. In comparison with the SPLP test conducted, the  $M_{\text{cumulative}}$  for the SPLP test was 29.2 mg-Al/kg-dry which is much higher than any of the control specimen

mass release of Al. The mass release of Al in the MT sample followed the same pattern as the control samples; mass release increases when increasing the degree of cracking from 3.28, 5.49, and 6.23 mg-Al/kg-dry for MT-0%, 33%, and 66%. MT results support the hypothesis that leaching of Al is a primary component of PC and not the addition of MT in the mixture.

Cumulative release of Sb was only detected in MT specimens. The cumulative release increased when increasing the degree of cracking from 0.0799, 0.0893, and 0.0910 mg-Sb/ kg-dry, indicating an effect of increasing the surface area on the leaching of Sb in the monolithic leaching test. Comparing the  $M_{\text{cumulative}}$  obtained from the EPA method 1315 test with respect to the SPLP test indicates that SPLP has a  $M_{\text{cumulative}}$  of 0.122 mg-Sb/kg-dry which is still less than the  $M_{\text{cumulative}}$  highest value (0.0910 mg-Sb/kg-dry). Even though the pH of the monolithic test in the early interval were favored for Sb leaching at higher concentrations than the SPLP test, it was concluded that monolithic form material substantially reduces element release when compared to the SPLP test.

### **EPA Method 1315 Release Mechanism for Al and Sb**

To determine the dominant leaching mechanism in the Semi-infinite model of diffusion, a model suggested by De Groot and van der Sloot was used in this analysis.(Dermatas et al., 2004) The logarithm of the cumulative release ( $\text{mg}/\text{m}^2$ ) was plotted against the logarithm of cumulative time (days). After plotting the logarithm of the cumulative release on the y-axis and the logarithm of cumulative time on the x-axis, the slope may be calculated. The slope is used as an indicator to determine the release mechanism of the control and MT specimens. Diffusion release mechanisms employ a slope between 0.35 and 0.65. Depletion release mechanisms employ a slope less than 0.35, while dissolution release mechanisms employ a slope greater than 0.65.

A Log-log comparison, using the procedure described above, to determine the release mechanism is shown in Figure 5-5, 5-6, and 5-7. In each figure, the slope and the  $R^2$  are shown;

$R^2$  for the majority of the samples was above 0.9 indicating a good regression fit. The release mechanism for Al for the control sample (Figure 5-4) indicated a diffusion mechanism for the 0% specimen ( $0.35 < \text{slope} < 0.65$ ). As indicated by other authors, controlled concrete is governed by diffusion mechanisms and this phenomena is the major release mechanism for encapsulated PC materials.(Roessler et al., 2015) However, increasing the degree of cracking for the control specimens modified the release mechanism, which supports the hypothesis that cracked encapsulated materials results in different release mechanisms. Depletion mechanism was the dominate form of release for Al in the control specimen for 33% and 66% specimens (slope  $< 0.35$ ), which suggests that a source in PC matrix in control- 33% and 66% are washed off quickly during the initial interval and depleted overtime. This observation is supported by the LI analysis, as the LI of these specimens has a limited release of Al (LI  $> 8$ ).

The release mechanism in the MT sample for Al was governed by depletion. The control sample in the MT specimen behaved differently from the PC control sample, indicating that the release of Al in MT is governed by the PC matrix. Diluting the PC in the MT specimen by 28% resulted in the reduction of a major source of Al in the matrix. This was supported by the depletion release mechanism indicated in Figure 5-6. Similar to the control samples, MT- 33 and 66% had similar release mechanisms and are governed by depletion mechanism (Figure 5-6). The results shown here illustrate that the inclusion of MT in the PC mixture reduces Al release. Therefore increasing the degree of microcrack does increase the release of COPCs and MT inclusion in the matrix release substantially effects Al concentrations.

The release of Sb was governed by depletion mechanism for all MT samples, indicating a depletion of the Sb source in the PC matrix. The results shown here for Sb are different from Roessler et al.(2015) who evaluated the leaching of Sb using bottom ash in HMA. Their study

found that release of Sb was governed by diffusion, unlike the MT-0% sample which was governed by depletion. This point illustrates the difference of release mechanism when using different materials which may behave differently and should be assessed as a separate study. The mean, minimum, and maximum LI values were calculated from the observed diffusivity and are presented in Table 5-5 for control and MT samples. The LI ranged, for Al, from 9.03 to 13.2 and 9.01 to 14.7 for the control (0%, 33%, and 66%) and MT samples. Using the modeling values of LI to determine release behavior the LI values for all samples are classified as limited release (LI > 8). Therefore, the mobility of COPCs in this study are low in mobility to the environment, even though some specimens are subject to an external load (i.e. different degree of cracking), which illustrates that the methodology to generate cracking was not strong enough to create cracks larger than microcracks. Even though the mass release of Al, Mo, and Sb were higher in the cracked samples, their mobility to the environment was limited to some extent if they were encapsulated well and not subjected to higher degrees of cracking. Differences were observed between the LI values in control and MT samples. These differences may be attributed to different mass release values shown in Figure 5-2.

### **EPA Method 1315 Release Mechanism for Na and Major Findings**

Major elements (e.g., Na) was investigated in this chapter and found a similar trends as Al and Sb. These findings were consisted with the results found in the previous section; the higher the degree of cracking the higher release of Na. Sample with mine tailings addition (40 mg/kg) had less cumulative mass release than the control samples (92 mg/kg) (Fig 5-8 and 5-9). This trends has been investigated further to determine if these differences are related to the physical alteration or it could be other chemical factors may played a role with these changes. Based on the permeability data found in Fig 5-2, mine tailings and control samples permeability were close and no big differences were found between mine tailings and control samples (Fig 5-

2). In addition, compressive strength data in 28 days curing period showed no differences between the mine tailings and the control samples. The strength data were close and showed no significant difference. Therefore, it is indicated from Fig 5-2 that Al, Sb, and Na release differences between MT and controls were not related to the permeability changes or the physical alteration, but rather other chemical factors played a role in these changes. It is clear from the permeability and the cumulative release of major and trace elements that physical alteration did change increase the release of elements at a higher degree of cracking for the control and mine tailings samples. However, when comparing the control with the mine tailings samples, their permeability or compressive strength did not has any effect rather other chemical alteration played the role. Overall, physical alteration did change the magnitude of release, which may lead to generating different risk assessment outcomes.

Table 5-1. Concrete mix design in one cubic yard. The mix design was adopted from a previous study with a minor modification.

Type	ID	w/c	Cement (lb)	Water (lb)	Sand (lb)	Coarse aggregate (lb)	Mine tailings (lb)
Control	C	0.52	625	300	820	2138	0
Mine tailings	MT	0.52	625	302	590	2138	227

Table 5-2. SPLP concentrations for the control and MT samples. The test was run according to the procedure outlined in SPLP. The test was conducted following 28 days of curing and after crushing the specimen using a hammer. These are the only the elements that were detected which pose a great environmental concern

Avg± StD (mg/L)	Al	Mo	Sb	Final pH
Control	1.46 ± 0.18	0.01 ± 0.005	<0.003	12.0 ± 0.12
MT	1.50 ± 0.096	0.0668 ± 0.001	0.0061 ± 0.0008	12.2 ± 0.03
GCTL	0.2	0.035	0.006	

Table 5-3. Total environmentally available of three selected elements. The test was ran according to the procedure outlined in solid digestion. Other elements were detected under this test, but only elements with great environmental concern in SPLP test is shown here

Total environmentally available contents (mg/kg-dry $\pm$ StD)		
Element	Control	MT
Al	4200 $\pm$ 220	3660 $\pm$ 150
Mo	24.0 $\pm$ 3.90	50.0 $\pm$ 6.00
Sb <sup>a</sup>	0.900 $\pm$ 0.140	1.05 $\pm$ 0.200

<sup>a</sup> Total content in the control and MT samples for Sb are not significantly different, meaning that Sb is derived from the natural ingredients of the sample and not from the MT



Table 5-5. List of selected elements with their dominate release mechanisms. The release mechanism is used in several studies to dominant the form of release of encapsulated materials. Crank model was used in each of these studies

Element	Dominate chemical release mechanism	Waste type	Reference
Al	Diffusion	Control concrete	(Roessler et al., 2015)
	Diffusion	Control asphalt	
	Diffusion	Bottom ash asphalt	
	Diffusion	Bottom ash concrete	
Mo	Depletion	Control concrete	(Galvín et al., 2014)
	Depletion	Bottom ash concrete	
	Depletion	Concrete made from recycled coarse aggregate	
K	Diffusion	Concrete with concentrated magnesium potassium phosphate cement	(Torras et al., 2011)
	Diffusion	Concrete made from solidification of hazardous sludge from steel processing	(van der Sloot et al., 2002)
Ca	Dissolution	Concrete containing phosphoric acid gypsum and 15% coal fly ash	(De Groot and van der Sloot, 1992)
	Dissolution	Concrete made from solidification of hazardous sludge from steel processing	(van der Sloot et al., 2002)
Ba	Diffusion	Concrete containing phosphoric acid gypsum and 15% coal fly ash	(van der Sloot et al., 2002)
	Diffusion	Concrete made from recycled coarse aggregate	(Galvín et al., 2014)

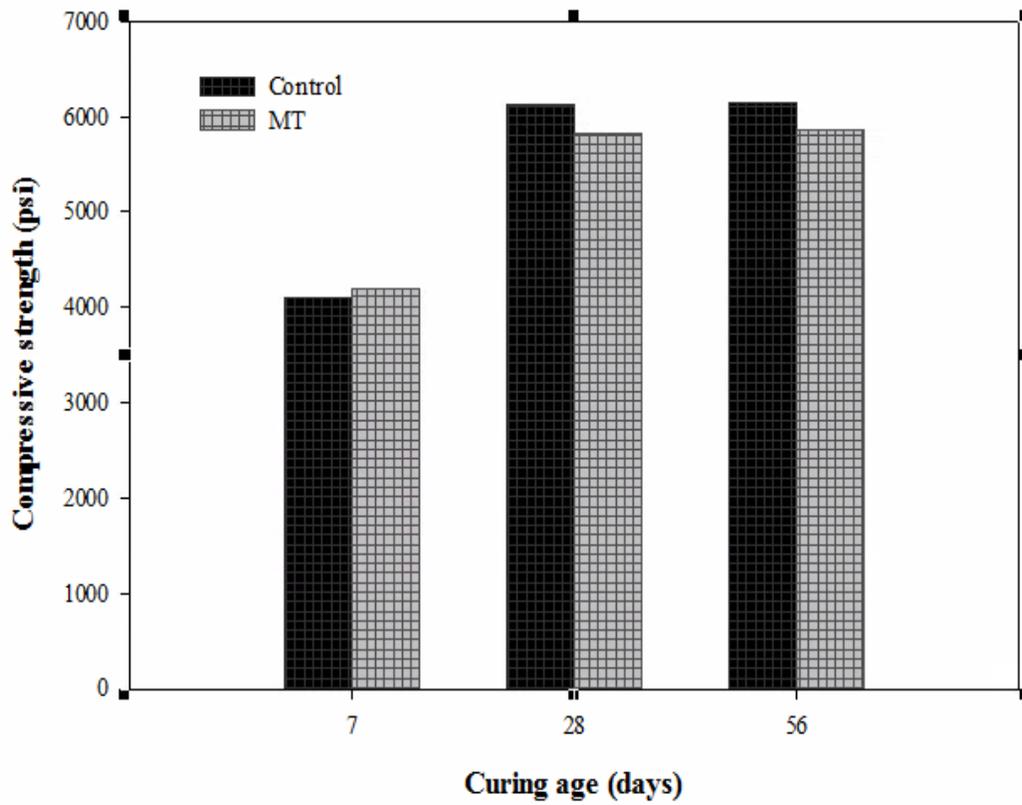


Figure 5-1. Compressive strength results for the control and MT samples. The compressive strength data were run in triplicates and ran after three time intervals (7, 28, and 56 days) in accordance to ASTM C39

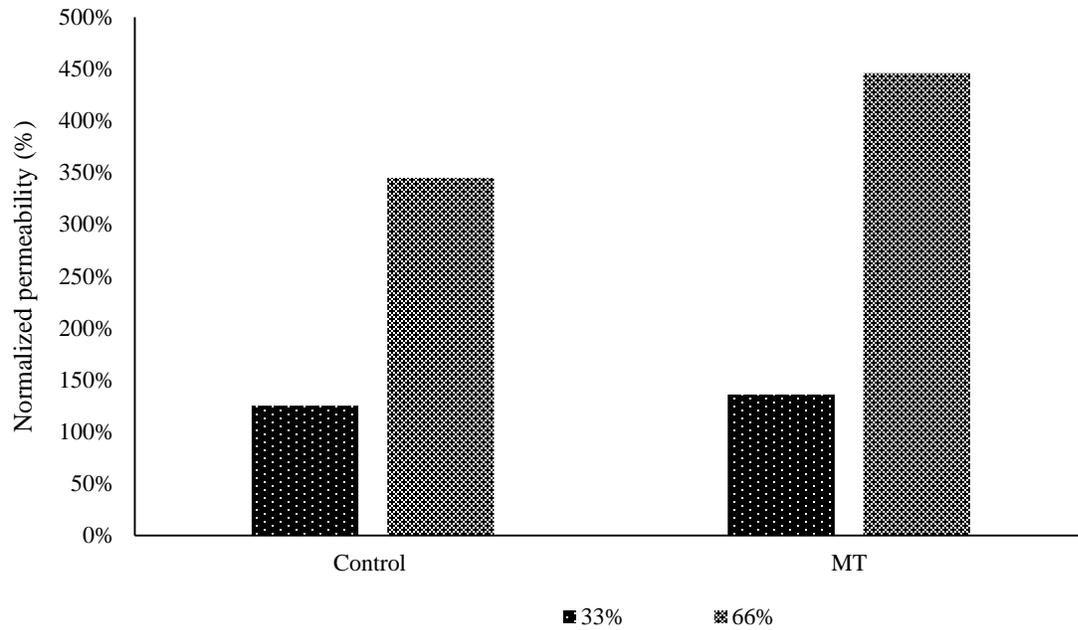


Figure 5-2. Permeability coefficient values for the control and MT samples. Cracking was simulated using the compressive strength test. 33 and 66% of the maximum load were used to create an artificial crack. The permeability coefficients were calculated using head flow pressure test for a control and mine tailings samples following 28 day curing time

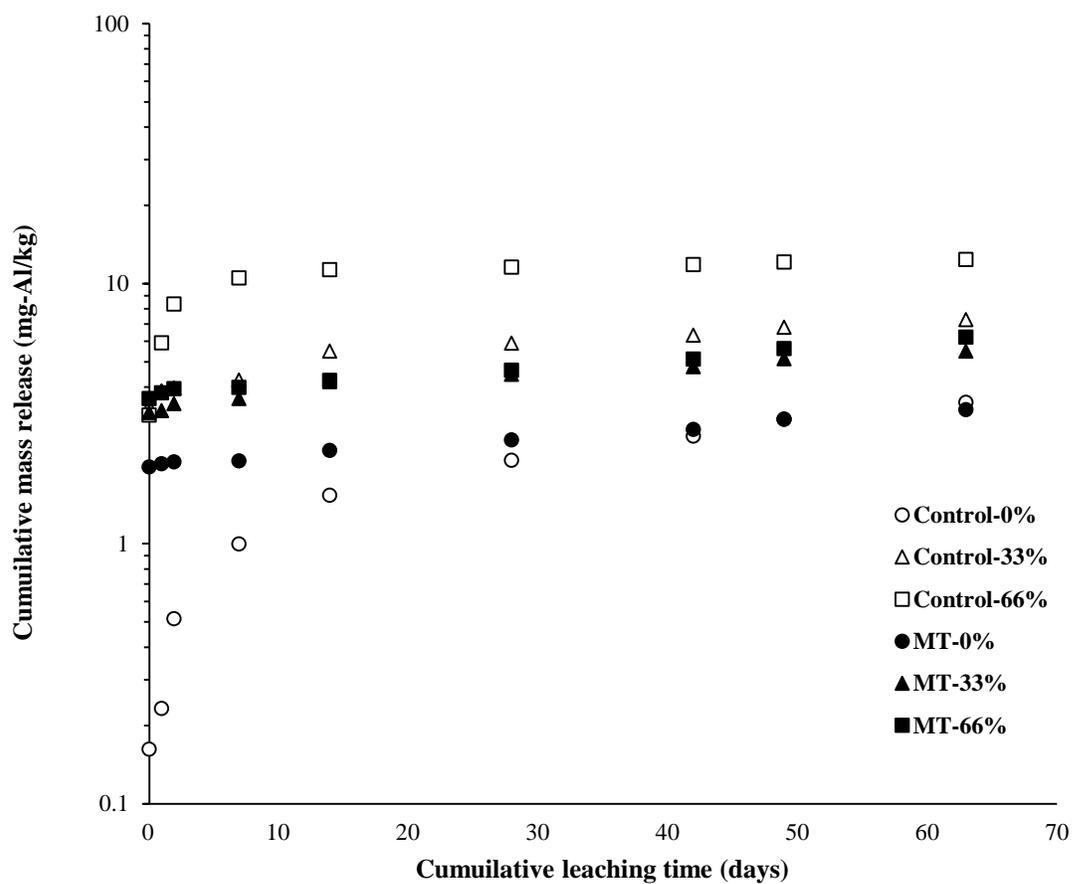


Figure 5-3. Aluminum cumulative mass release in EPA method 1315. Cumulative mass release was calculated in duplicates to show the differences between the samples. Higher cracking in the samples correlated to higher mass release. The data were consistent with major element release (e.g., Na)

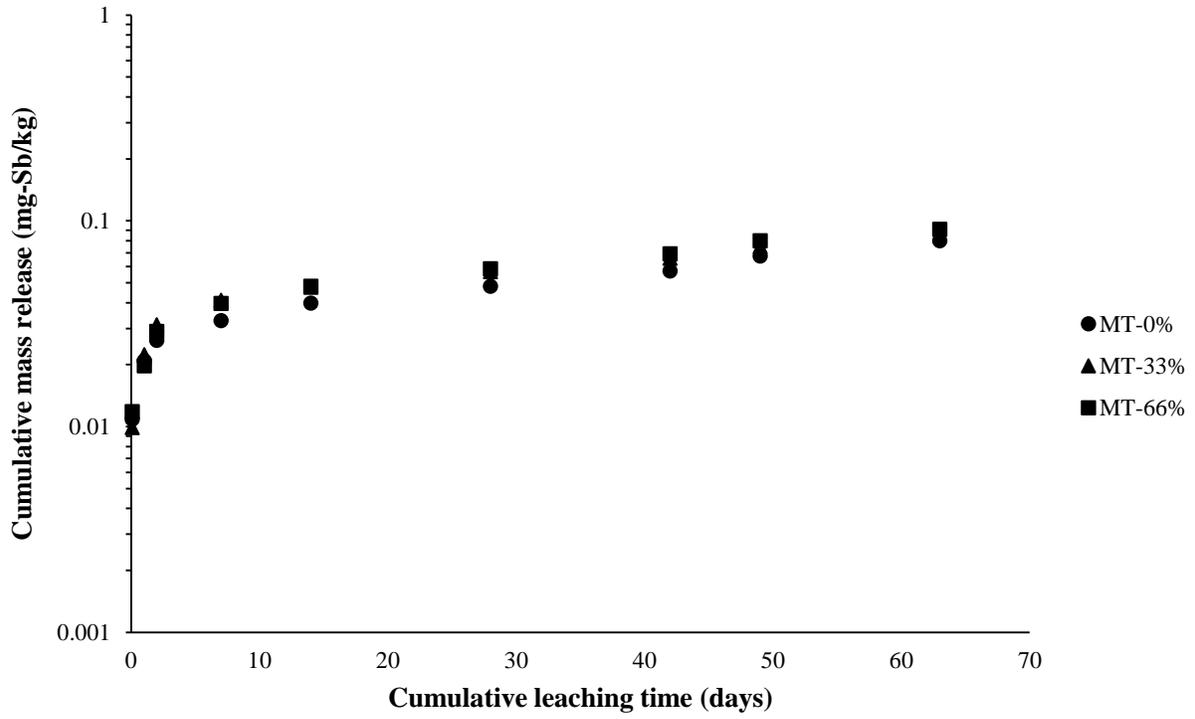


Figure 5-4. Antimony cumulative mass release in EPA method 1315. Antimony was not detected in any of the control samples. Similar mass release behavior is shown here ; the higher the crack opening the higher the mass release

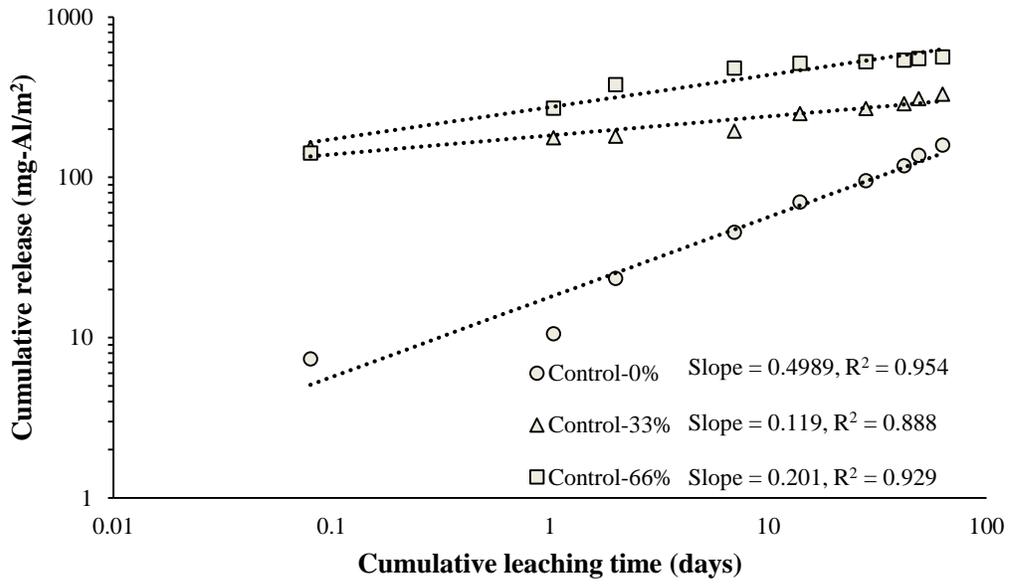


Figure 5-5. Aluminum log-log compression in the control specimens. Log-log scale was calculated in both axes to determine the dominant release mechanism. The procedure followed the Crack model that explained the chemical release in monolithic formed material, which are governed by diffusion, dissolution, and depletion

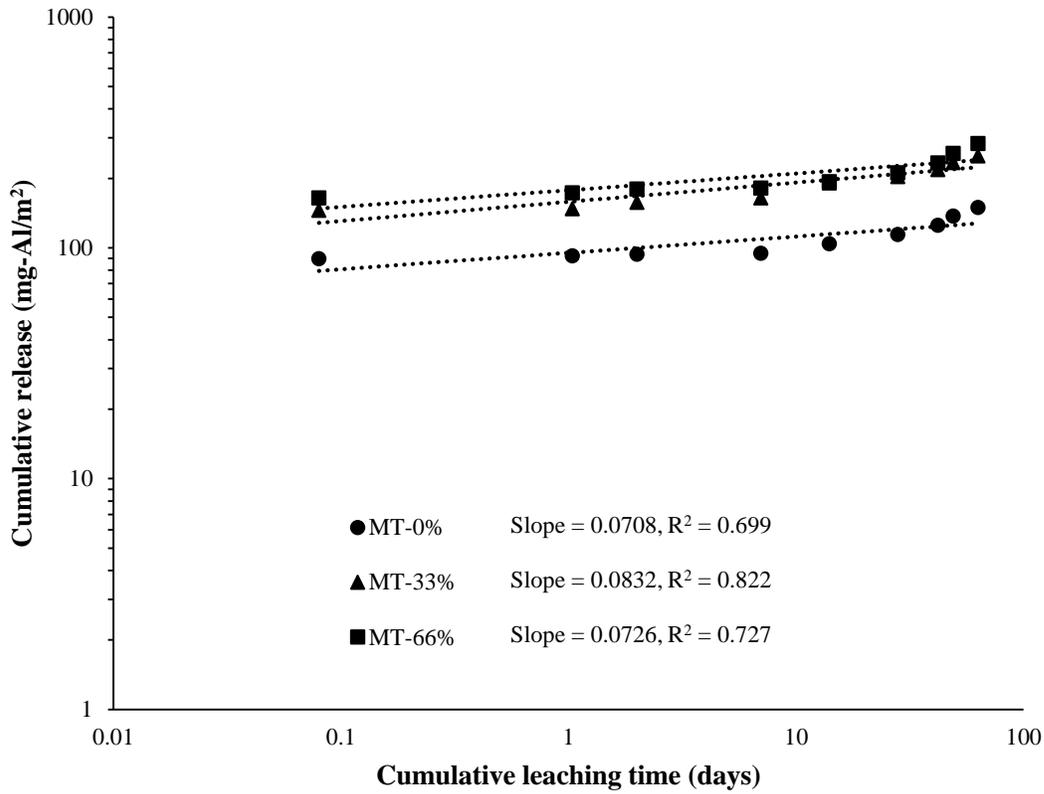


Figure 5-6. Aluminum log-log compression in the MT specimens. Log-log scale was calculated in both axes to determine the dominant release mechanism. The procedure followed the Crack model that explained the chemical release in monolithic formed material, which are governed by diffusion, dissolution, and depletion

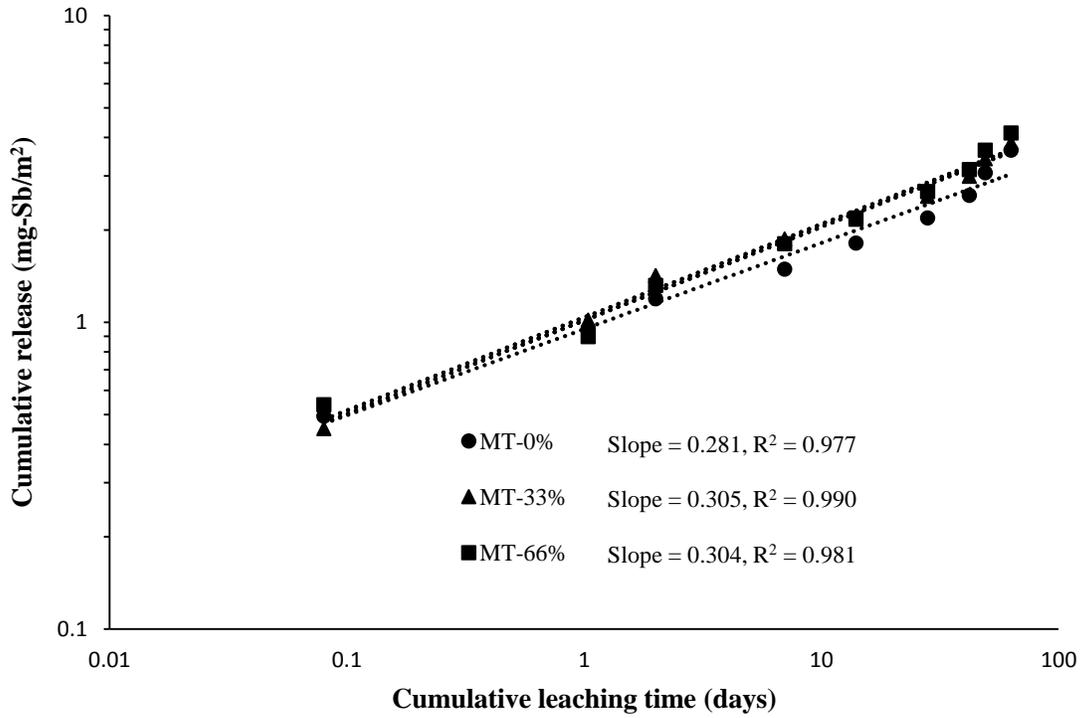


Figure 5-7. Antimony log-log compression in the MT specimens. Log-log scale were calculated in both axis to determine the dominate release mechanism. The procedure followed Crack model that explained the chemical release in monolithic formed material, which are governed by diffusion, dissolution, and depletion

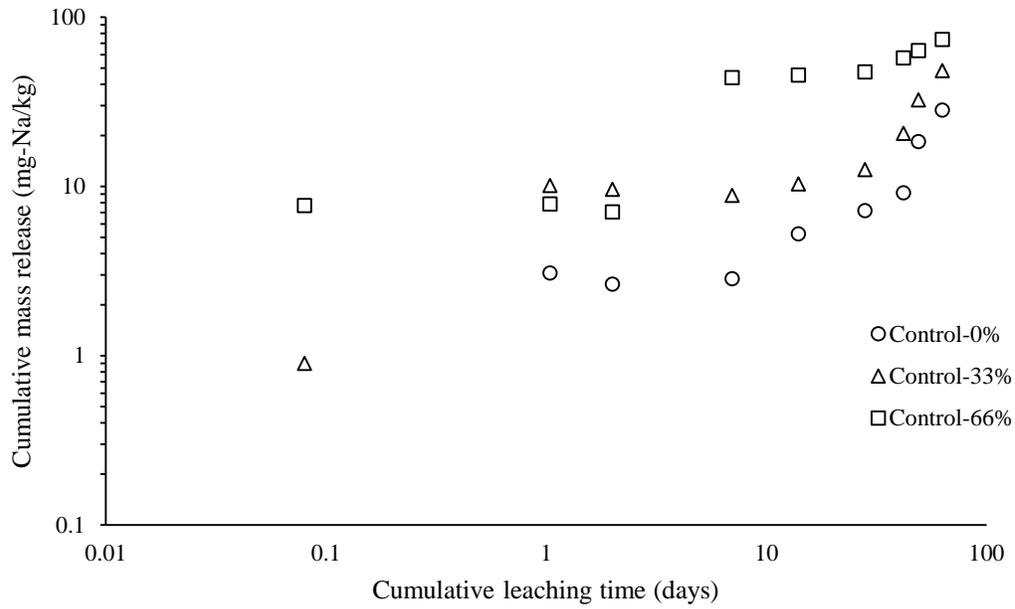


Figure 5-8. Sodium cumulative mass release in EPA method 1315 for the control sample. Similar mass release behavior is shown here; the higher the crack opening the higher the mass release

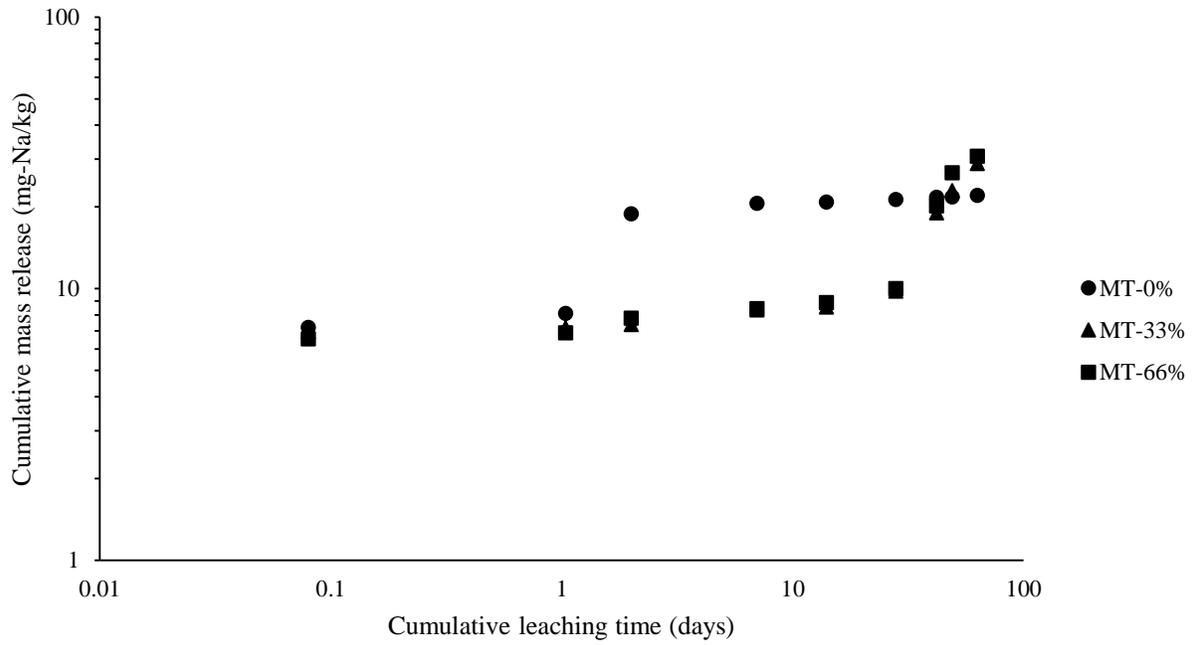


Figure 5-9. Sodium cumulative mass release in EPA method 1315 for the mine tailings sample. Similar mass release behavior is shown here; the higher the crack opening the higher the mass release

## CHAPTER 6 SUMMARY

### **Summary of Research**

This dissertation presents a novel approach to utilizing standard leaching tests to better simulate beneficial use scenarios of waste products and to assess potential risk posed by waste materials under conditions more representative of applications in the field. In addition, this dissertation demonstrates the importance of collaboration between solid waste management researchers and other related disciplines (e.g., civil engineering) by providing a case study investigating the beneficial use of an industrial waste material (high temperature gasification slag) in an engineering application (as a supplementary cementitious material).

The first research task covers determination of a site-specific partitioning coefficient for two industrial waste materials (coal fly ash and WTE bottom ash). This study demonstrates the importance of examining the effect that site specific conditions have on fate and transport models. Leachate mobility was evaluated by determining the partitioning coefficients of elements through a variety of soils. The partitioning coefficients were then used in environmental risk analyses. This chapter presents data that show that  $K_d$  selection is important and that the determination of the values to be used in simulations should not be necessarily just the default value or the mean for a particular contaminant found in literature. The IWEM simulation results demonstrate that concentrations of elements found in the coal FA samples were below the 90<sup>th</sup> percentile of GCTL regardless of the  $K_d$  value that was used in the simulation. When WTE BA was subject to IWEM analyses for use as subbase materials in roadways several trial runs led to greater than concentrations of elements overshooting the 90<sup>th</sup> percentile concentrations of accepted GCTL. IWEM simulations are dependent on  $K_d$  values that accurately reflect site-specific conditions in which industrial waste byproducts have been proposed for reuse. These

scenarios specific parameters provide more representative approach and valuable predictions when results are applied in real world applications.

The second study utilized a broader set of leaching tests on lime WTR demonstrated the importance of understanding the intended reuse or disposal scenario and tailoring the testing approach to the intended application. The suite of new leaching test methods developed by the EPA allowed for a more detailed characterization of the WTRs, and demonstrated that certain parameters such as L/S and equilibrium pH played a dramatic role in controlling element leaching. Better understanding these parameters allowed for a more educated beneficial use assessment in several cases. However these methods were limited in appropriately characterizing leaching for all of the disposal scenarios examined.

The third study demonstrated that at low replacement percentages HTAG slag could potentially be a viable candidate for use in PC as a SCM. Compressive strength and evolved heat values were similar for the PC control and 5% HTAG slag – PC blend. A substantial decrease in total evolved heat and compressive strength was seen at higher replacement percentages. This is likely due to both a lack of reactants (dilution of available cement) as well as several other chemical phenomena related to the nature of the slag. Factors such as the amorphous nature of the slag and the presence of elevated levels of MgO (in comparison to PC) could have contributed to the decreased strength/heat as well as the delay in hydration that was observed during the isothermal calorimetry. Further processing of the HTAG slag to a finer particle size would likely result in better performance of the HTAG slag in blended cements. Testing of full scale concrete specimens to evaluate longer term strength performance as well as durability would be essential areas of further research if this material is going to be incorporated as a SCM in

PC. The results of this study demonstrate that at low replacement percentages HTAG slag could potentially be a viable candidate for use in PC as a SCM.

The fourth study supported previous studies indicated the effectiveness of encapsulating industrial materials in minimizing COPCs released to the environment. MT material used in this study indicated a comparable compressive strength to the control sample at a later curing time and a lower release of Al than the control samples. Cracking the samples changed the release mechanism in the cracked sample to be governed by depletion of the source of release, instead of the common diffusion mechanism for PC, resulting in a higher mass release due to a continuous release of COPCs from the solid media to the aqueous phase.

### **Major Findings**

From the experimental results the following conclusion can be made:

- The correlation and interaction of  $K_d$  values and elemental compositions obtained from the leachate were a trivial finding of this study.
- Risk-based models have become more important in environmental regulations.
- This study demonstrates the importance of examining the effect that site specific conditions have on fate and transport models.
- These findings have implications for operators where soils can be used as a sink source for certain pollutants.
- Utilizing a broader set of leaching tests demonstrated the importance of understanding the intended reuse or disposal scenario.
- Conventional batch tests (SPLP) do not adequately predict leaching of pollutants.
- The results of this study could alter the outcome of decision making.
- Site specific evaluation of the reuse scenario at question is more adequate.

- A substantial decrease in total evolved heat and compressive strength was seen at higher replacement percentages.
- Low replacement percentages HTAG slag could potentially be a viable candidate for use in PC as a SCMs.
- When the specimens were subjected to cracking, element of concerns were not observed.
- Cracking did facilitate increased release of major elements.
- Differences in leaching between control and mine tailings amended concrete.

### **Future Work**

Future research avenues should investigate the following:

- Further processing of the HTAG slag to a finer particle size would likely result in better performance of the HTAG slag in blended cements.
- Testing of full scale concrete specimens to evaluate longer term strength performance as well as durability would be essential areas of further research.
- Partitioning coefficients should be examined while the WTE bottom ash is subjected to intensive carbonation.
- Soils used as a subbase in real world applications should be examined to determine  $K_d$  values.
- Examination of concrete amended industrial waste that is subjected to other external conditions (e.g., sulfate attack) is necessary in terms of leaching of elements.

## APPENDIX SUPPLEMENTARY INFORMATION

### **Method 1313**

Method 1313 is a batch leaching test that evaluates leaching as a function of pH, at a total of 9 pH points (2.0, 4.0, 5.5, 7.0, 8.0, 9.0, 12.0, 13.0 and the natural pH of the material) (US-EPA, 2014). Method 1313 is conducted at a static liquid to solid ratio (L/S) of 10 mL-leaching solution/per gram dry sample. In method 1313, sample mass and rotation time are specified as a function of particle size; twenty four hours was identified as the appropriate extraction time as all of the samples were able to pass a US #50 Sieve (0.297 mm). However, because of the high absorptivity of the WTR samples, and the inability to obtain a sufficient volume of liquid following rotation, the sample mass was increased to 80 grams. Additions of 1N nitric acid (Fisher Brand Trace Metal Grade) and sodium hydroxide (1.0 N ACS Reagent Grade) were used to achieve the target pH points. All method 1313 tests were conducted in triplicate.

### **Method 1314**

Leachate is collected at nine L/S (0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, and 10.0 mL/g-dry). The column's sample height and inside diameter are 28 and 5 cm, respectively; to avoid sample loss a 1-cm thick layer of washed quartz sand was placed at the top and bottom of each column. With the exception of the method 1314 tests conducted under a reducing atmosphere, all method 1313, 1314 and 1315 samples were filtered using a vacuum filtration apparatus and a 0.45-um membrane filter (PAL GHP).

### **Total Concentration**

Method 3051A involves adding 9 mL HNO<sub>3</sub> (Fisher Brand Trace Metal Grade) and 3 mL of HCL (Fisher Brand Trace Metal Grade) to 0.5 grams of sample. This is then heated in a

microwave (CEM MarsX) to  $175 \pm 5 \text{ C}^\circ$  in 5.5 min and held at  $175 \pm 5 \text{ C}^\circ$  for 4.5 min. Samples are then filtered with Qualitative filter paper (Fisher brand) and diluted to 100 mL for analysis.

Table A-1. Method detection limits for elements evaluated in study. The detection limits were calculated using a standardized statistical procedure and used as a basis for this entire dissertation

Element	Method detection limit [MDL] (mg/L)
Ag	0.005
Al	0.022
As	0.006
Ba	0.02
Be	0.002
Cd	0.001
Cr	0.0015
Cu	0.002
Fe	0.03
Mn	0.001
Mo	0.004
Ni	0.001
Pb	0.005
Se	0.008

Table A-2. Characteristics of the column test under aerobic conditions for facility 1. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.16	160±33.2	186	0.0256	0.03
0.5	8.41	142±2.65	210	0.0498	0.03
1	8.39	106±3.36	230	0.0621	0.03
1.5	8.48	101±6.32	240	0.103	0.03
2	8.70	96.3±9.10	232	0.293	0.03
4.5	8.79	90.4±0.963	261	0.4962	0.03
5	8.93	65.5±1.52	275	0.688	0.03
9.5	9.06	60.7±2.34	280	0.801	0.03
10	9.12	51.3±7.26	296	0.921	0.03

Table A-3. Characteristics of the column test under aerobic conditions for facility 2. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	7.98	54±3.45	191	0.0357	0.03
0.5	8.24	76.8±0.123	245	0.0526	0.03
1	8.38	116±0.489	277	0.0737	0.03
1.5	8.61	36.5±3.21	210	0.108	0.03
2	9.31	57.6±6.62	201	0.308	0.03
4.5	8.54	54.3±4.56	224	0.520	0.03
5	8.92	51.2±3.36	264	0.711	0.03
9.5	9.01	48.6±4.39	270	0.847	0.03
10	9.11	45.9±1.29	285	0.927	0.03

Table A-4. Characteristics of the column test under aerobic conditions for facility 3. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.65	227±55.0	143	0.022	0.03
0.5	8.62	123±40.2	194	0.0304	0.03
1	8.74	78.8±13.1	222	0.0287	0.03
1.5	8.88	58.9±1.49	234	0.0548	0.03
2	8.81	52.3±2.02	235	0.0351	0.03
4.5	9.32	44.7±10.3	168	0.0376	0.03
5	9.07	52.4±5.20	100	0.0765	0.03
9.5	9.11	37.0±6.36	88	0.0807	0.03
10	9.22	26.9±4.21	76	0.0888	0.03

Table A-5. Characteristics of the column test under aerobic conditions for facility 4. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.35	120±15.2	143	0.0594	0.03
0.5	8.44	66.3±5.36	404	0.133	0.03
1	8.34	133±1.01	340	0.192	0.03
1.5	8.83	62.9±8.10	241	0.209	0.03
2	8.88	56.4±0.56	248	0.283	0.03
4.5	9.13	44.1±1.65	156	0.383	0.03
5	8.65	38.4±3.21	91	0.405	0.03
9.5	9.02	36.5±2.32	96	0.655	0.03
10	9.12	32.0±1.15	103	0.627	0.03

Table A-6. Characteristics of the column test under aerobic conditions for facility 5. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.18	155±50.1	191	0.023	0.03
0.5	8.51	94.6±12.8	215	0.023	0.03
1	8.56	90.1±30.3	270	0.023	0.03
1.5	8.61	70.1±2.62	280	0.0758	0.03
2	8.86	53.9±1.67	210	0.319	0.03
4.5	8.78	51.9±5.56	258	0.542	0.03
5	8.92	38.7±3.17	183	0.661	0.03
9.5	9.00	51.2±6.65	287	0.756	0.03
10	9.14	54.3±2.36	290	0.854	0.03

Table A-7. Characteristics of the column test under anaerobic conditions for facility 1. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.16	160±33.2	-12	0.02	0.03
0.5	8.20	142.3±2.65	-18	0.02	0.03
1	8.29	106.3±3.36	-23	0.02	0.03
1.5	8.34	100.5±6.32	-29	0.02	0.03
2	8.41	96.3±9.10	-36	0.02	0.03
4.5	8.50	90.4±0.963	-42	0.02	0.03
5	8.62	65.5±1.52	-45	0.02	0.03
9.5	8.70	60.7±2.34	-46	0.02	0.03
10	8.88	51.3±7.26	-52	0.02	0.03

Table A-8. Characteristics of the column test under anaerobic conditions for facility 2. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.64	160	0	0.02	0.03
0.5	8.84	149	-2	0.02	0.03
1	8.94	44.1	-50	0.02	0.03
1.5	7.78	30.3	-110	0.02	0.03
2	8.96	19.2	-18	0.02	0.03
4.5	9.21	13.4	-20	0.02	0.03
5	9.25	10.3	-26	0.02	0.03
9.5	9.25	8.60	-28	0.02	0.03
10	9.26	6.21	-32	0.02	0.03

Table A-9. Characteristics of the column test under anaerobic conditions for facility 3. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.34	131	-5.1	0.0272	0.03
0.5	8.42	83.1	-7.2	0.0338	0.03
1	7.93	29.4	-8.4	0.0331	0.03
1.5	8.73	20.3	-10.9	0.0748	0.03
2	8.76	18.6	-20.5	0.0832	0.03
4.5	9.23	18.0	-45.3	0.118	0.03
5	8.96	15.6	-55.6	0.126	0.03
9.5	8.70	12.6	-70.1	0.142	0.03
10	9.01	10.6	-75.3	0.149	0.03

Table A-10. Characteristics of the column test under anaerobic conditions for facility 4. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.42	141	0	0.023	0.0962
0.5	8.63	138	-5	0.023	0.102
1	8.75	72.2	-15	0.0337	0.139
1.5	8.79	57.1	-25	0.0537	0.0963
2	8.81	44.2	-50	0.096	0.0866
4.5	8.85	35.2	-65	0.267	0.0227
5	8.90	31.5	-78	0.335	0.055
9.5	9.00	26.0	-100	0.523	0.0563
10	9.05	25.1	-120	0.695	0.0632

Table A-11. Characteristics of the column test under anaerobic conditions for facility 5. The chemical characteristics were measured following each collection time

L/S	pH	TDS (mg/L)	ORP (mV)	Al concentration (mg/L)	Fe concentration (mg/L)
0.2	8.46	242	-2	0.023	0.0832
0.5	8.45	76.2	-9	0.023	0.124
1	7.04	38.1	-14	0.023	0.150
1.5	7.1	26.3	-29	0.0758	0.0865
2	7.49	25.0	-36	0.320	0.0708
4.5	8.61	19.8	-50	0.543	0.03
5	7.26	16.1	-65	0.662	0.03
9.5	7.3	12.2	-78	0.756	0.03
10	7.32	10.5	-100	0.855	0.03

## **Batch Leaching and Soil-Liquid Partitioning Tests**

Industrial waste leachates (for soil-waste leachate partitioning testing) were generated using a modified EPA method 1316 test (at a set liquid to solid ratio (L/S) of 10 mL-reagent water/g-waste). Prior to testing the sample was first size reduced to pass a U.S #4 sieve (4.75 mm). Each waste was leached in 8 replicates, a 200 g dry mass of waste was used to generate a sufficient quantity of leachate for the soil sorption tests. To facilitate the extraction, the sample was rotated in an end over end fashion at a  $28 \pm 2$  rpm for a period of 72 hours. Following rotation, the sample was first centrifuged (for a period of 10 min at  $4,000 \pm 100$  rpm) and then filtered using a vacuum filtration apparatus and a  $0.45 \mu\text{m}$  polypropylene filtration membrane. An aliquot of each of the replicates was collected for chemical analysis (elemental concentration, pH, conductivity, and ORP), and the remaining leachate was introduced as the aqueous solution in the soil sorption test.

The leachate generated from the 1316 test was introduced to one of the 8 soils to conduct the soil sorption experiment (each soil sorption test was conducted in triplicate). The soil sorption testing was run in accordance with ASTM D4646.(ASTM, 2008) A 20:1 L/S and a 20 g-dy mass of soil were used in all of the soil sorption tests. The soil and leachate were rotated for  $24 \pm 0.5$  hours (at  $28 \pm 2$  rpm) and filtered using a vacuum filtration apparatus and a  $0.45 \mu\text{m}$  polypropylene filtration membrane. An aliquot of the filtered leachate was collected to measure pH, conductivity and ORP. The remaining leachate was then preserved for elemental analysis through acidification to a  $\text{pH} < 2$  using ultra high purity nitric acid.

## **US EPA's IWEM**

IWEM provides a simplified screening level analysis for a series of waste reuse and disposal scenarios, it employs a Monte Carlo type simulation to determine a probabilistic

distribution of groundwater concentrations based on variation in the input parameters; the value reported represents the 90<sup>th</sup> percentile groundwater concentration. Inputs values used for the two waste management scenarios for CFA (Structural fill) and WTE BA (road base) is presented in Tables A-12 and A-13.

Table A-12. IWEM Inputs Values for CFA. Detailed explanation of each input can be found in the background IWEM document

CFA	
Distance to well (m)	30
Structural fill depth (m)	1.8
Structural fill area (m <sup>2</sup> )	15,000
Depth of base of the SF below ground surface (m)	1.8
Effective bulk density (g/cm <sup>3</sup> )	1.47
Effective hydraulic conductivity (m/year)	3.16
Volume fraction occupied by leachable materials	1
Ground water pH value <sup>a</sup>	-
Depth to water table (m)	4
Aquifer hydraulic conductivity (m/year) <sup>a</sup>	-
Regional hydraulic gradient	0.035
Aquifer thickness (m) <sup>a</sup>	-
Site specific infiltration (m/year)	0.17
Recharge rate (m/year)	0.083

<sup>a</sup>Refer to IWEM technical background document section 6.4.2 for details.

Table A-13. IWEM Inputs Values for WTE BA. Detailed explanation of each input can be found in the background IWEM document

CFA	
Width of paved area (m)	10.4
Number of layers for the paved area <sup>a</sup>	4
Distance between the roadway edge and the monitoring well (m)	24.8
Angle between roadway and groundwater flor (degrees)	90
Ground water pH value <sup>b</sup>	-
Depth to water table (m) <sup>b</sup>	-
Aquifer hydraulic conductivity (m/year) <sup>b</sup>	-
Regional hydraulic gradient <sup>b</sup>	-
Aquifer thickness (m) <sup>b</sup>	-
Site specific infiltration (m/year)	0.0949
Recharge rate (m/year)	0.14

<sup>a</sup>Layer#1 (subbase) has a thickness, hydraulic conductivity, and bulk density of 0.84 m, 254 m/year, and 2.28 g/cm<sup>3</sup> respectively. Layer#2 (base) has a thickness, hydraulic conductivity, and bulk density of 0.14 m, 254 m/year, and 2.19 g/cm<sup>3</sup> respectively. Layer#3 (base) has a thickness, hydraulic conductivity, and bulk density of 0.115 m, 254 m/year, and 2.64 g/cm<sup>3</sup> respectively. Layer#4 (base) has a thickness, hydraulic conductivity, and bulk density of 0.125 m, 254 m/year, and 2.85 g/cm<sup>3</sup> respectively.

<sup>b</sup>Refer to IWEM technical background document section 6.4.2 for details.

Table A-14. Compressive strength test results for HTAG slag and control. These are the actual measured data for each specimen. The normalized data were calculated by dividing the measured value in HTAG slag by the control

	Compressive strength (psi)		
Curing time			
(days)	7.0	28.0	56.0
Control	6137	7779	8272
5%	6000	7132	8157
20%	4885	6578	6745
35%	3347	4336	5124
50%	1920	2755	3260

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