Geopolymer-Based Solutions for Coal Combustion Product Solidification and Stabilization

Maria Juenger,^{1*} Lynn Katz,¹ Michelle Lacks,¹ Monday Uchenna Okoronkwo,² Gaurav Sant,² and Magdalena Balonis²

> ¹ University of Texas at Austin ² University of California, Los Angeles

* <u>mjuenger@mail.utexas.edu</u>; 512-232-3593 301 E. Dean Keeton St., C1748, Austin, TX 78712

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Executive summary

Coal combustion products (CCPs) contain heavy metals that have the potential to leach into surface and ground waters when disposed improperly. Of further concern is that, in recent years, power plants have been injecting sodium carbonate compounds such as trisodium hydrogendicarbonate dihydrate (trona) into their flue gas streams to reduce SOx emissions. Trona injection has been shown to alter the characteristics of collected fly ash and increase leaching of heavy metal compounds from the ash, posing a higher environmental threat.

Geopolymers that utilize CCPs as an aluminosilicate precursor are under consideration as an alternative to conventional portland cement for solidification/stabilization (S/S) of CCPs prior to disposal. These materials, made by activating aluminosiliceous powders (e.g. fly ash) with highly alkaline solutions, may improve stabilization of heavy metal wastes. The design of geopolymer mixtures for optimum S/S of CCPs is not straightforward, however. This study represents an advancement upon the traditional trial and error mixture design process by using thermodynamic phase equilibria models to predict the phases present in the solidified materials, including porosity, and experimentally validating these models. Characterization of the CCPs was conducted to provide parameter inputs to the thermodynamic models. Mixtures were designed for experimental testing by minimizing model predicted porosity, thereby maximizing predicted solid phase formation. Geopolymer mixtures were compared against portland cement-stabilized mixtures, and both were experimentally tested for solidification (compressive strength, phase formation, and porosity) and stabilization of heavy metals and oxyanions following EPA standard LEAF protocols at different liquid/solid (L/S) ratios and pH. Another unique aspect of this work was the comparison of the standard reagent water used for leaching tests to a simulated landfill leachate fluid that more accurately represents landfill conditions.

Thermodynamic modeling suggested testing geopolymer activating solutions for CCPs of: 4M NaOH, 8M NaOH, and 4M NaOH with added fumed silica to increase the silica modulus (SiO₂/Na₂O) of the solution to 1.5. It was found experimentally that geopolymers made with 4M NaOH had higher reactivity than those made with 8M NaOH, and increasing the silica modulus to 1.5 also somewhat increased reactivity of specimens. Portland cementbased mixtures were observed to bind oxyanions more effectively at high pH than geopolymers, but geopolymers were capable of reducing leaching for a number of elements over a broad pH range. The extent of leaching depended on the element, the geopolymer composition, and the test method used. Testing with simulated groundwater/landfill leachate indicated that leaching of copper and, to a lesser extent, selenium is affected by landfill leachate components, which could have impacts on wastes with larger quantities of these elements. A comparison of the cost of S/S strategies with their effectiveness demonstrated that CCPs activated by a 4M NaOH solution, without modification of silica modulus, provide the lowest cost solution with excellent performance. This project demonstrated that an iterative approach of thermodynamic modeling and experimental testing proved to be invaluable as the models helped in the design of the experiments and the experimental results will help inform and improve future modeling efforts. It can be concluded that S/S of CCPs using a 4M NaOH activating solution is a cost-effective strategy, providing excellent mechanical and chemical performance, which can likely be broadly applied. For example, future work could examine a 4M NaOH solution to geopolymerize combinations of CCPs and brines for plants seeking zero-liquid discharge.

Notations

ABLP	Australian Bottle Leaching Procedure
AFm	Monosulfoaluminate (Ca ₄ Al ₂ O ₆ (SO ₄) \cdot 12H ₂ O) – and related phases
AFt	Ettringite (Ca ₆ Al ₂ O ₉ (SO ₄) ₃ ·32H ₂ O) – and related phases
BA	Bottom Ash
ССР	Coal Combustion Product
COPC	Constituents of Potential Concern
C-S-H	Calcium Silicate Hydrate
EA	Economizer Ash
EDS/EDX	Energy Dispersive X-ray Spectroscopy
EPA	Environmental Protection Agency (U.S.)
FA	Fly Ash
FEP	Fluorinated Ethylene Propylene
GW	Groundwater/Simulated Landfill Leachate
HDPE	High Density Polyethylene
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
LDH	Layered Double Hydroxide
LEAF	Leaching Environmental Assessment Framework
LOI	Loss on Ignition
L/S	Liquid-to-Solid ratio
LSP	Liquid-Solid Partitioning
MPW	Millipore Water (pure reagent water)
Ms	Silica Modulus (SiO ₂ /Na ₂ O in geopolymers)
N-A-S-H	Sodium Alumino-Silicate Hydrate
NOM	Natural Organic Matter
OPC	Ordinary Portland Cement
PTFE	Polytetrafluoroethylene
SEM-EDX	Scanning Electron Microscopy
SOx	Sulfur Oxides
S/B	(Activating) Solution-to-Binder (e.g. fly ash) ratio by mass
	(in geopolymers)
SPLP	Synthetic Precipitation Leaching Procedure
S/S	Solidification/Stabilization
TCLP	Toxicity Characteristic Leaching Procedure
TEM	Transmission Electron Microscopy
Trona	Trisodium Hydrogendicarbonate Dehydrate
w/cm	Water-to-Cementitious Materials ratio by mass
WHO	World Health Organization
XRD	X-ray Diffraction

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1. Introduction

The objective of this research was to design and evaluate geopolymer mixtures made with coal combustion products (CCPs) to solidify/stabilize CCPs that cannot be beneficially reused and which present environmental hazards. Geopolymers are solid materials made by reacting aluminosiliceous powders with caustic solutions; these present an alternative to solidification/stabilization (S/S) of CCPs with portland cement with a potentially higher volume of CCP per stabilized solid.

There are many challenges involved in using geopolymers for S/S of CCPs. For one, the composition of CCPs is highly variable, and unique mixtures must be designed for each CCP source for optimum solidification and stabilization properties. Furthermore, though the literature suggests that geopolymers may provide enhanced stabilization compared to traditional portland cement-CCP mixtures, these materials have not been thoroughly assessed in the laboratory, especially under conditions that are representative of those in landfills. In this study, we took a unique approach to designing geopolymer mixtures with CCPs targeted for disposal using thermodynamic phase equilibria modeling to predict the phase assemblage and porosity in the solidified material. This "solubility-informed mixture design" method can rapidly assess a variety of mixture designs to target those with minimized porosity (i.e. minimized permeability) and maximized formation of solid reaction products that stabilize oxyanions and heavy metals. The model uses CCP composition as an input, so the materials under consideration were first thoroughly characterized. In this study, the CCPs assessed were trona-impacted fly ashes, an economizer ash, and a bottom ash. The designed mixtures were then fabricated and tested in the laboratory to validate the modeling approach. The geopolymer mixtures, made by combining the CCPs with sodium hydroxide solutions (in some cases with added silica), were compared to portland cement-CCP blends in order to determine if geopolymers indeed provide reduced leaching of heavy metals and oxyanions. The mixtures were tested following the standard leaching environmental assessment framework (LEAF) protocols (EPA, 2013) with solutions of varied pH and liquid/solid ratio using the specified reagent water. In addition, a simulated landfill leachate water was tested in order to represent realistic landfill conditions.

This report summarizes the findings of this research, presenting the mixtures designed through thermodynamic modeling, the experimental testing results from those mixtures, and the comparison between predicted performance and measured performance. Finally, recommendations are provided for mixture design processes and further testing.

2. Background

Cementitious materials have been used to solidify and stabilize heavy metals in contaminated soils, wastewater treatment byproducts, mining wastes and coal

combustion products for decades. Many studies have tested the capacity of ordinary cement (OPC) and other typical cementitious materials (lime, slag) for solidification and stabilization of these wastes (Kogbara et al., 2013; Shi & Fernández-Jiménez, 2006; Provis & van Deventer, 2009). Production methods generally entail adding a small amount of binder (OPC) to a large amount of waste in order to create a weak solid that will largely prevent leaching of contaminants (Provis & van Deventer, 2009). However, methods other than OPC have proven more successful when it comes to stabilizing heavy metal wastes. (Shi & Fernández-Jiménez, 2006).

In the 1970s, Joseph Davidovits patented geopolymers, a solid material that does not require the use of OPC for formation (Davidovits, 1994). Since their inception, geopolymers have been investigated as an alternative method for solidification and stabilization of hazardous wastes (Comrie et al., 1989). A number of studies highlight the successes of geopolymers in stabilizing a variety of contaminants including heavy metals (Provis & van Deventer, 2009; Guo & Shi, 2013; Zhang et al., 2008a). In addition, these systems contain a larger percent waste than OPC systems. Therefore, geopolymer systems are of interest to industries that produce heavy metal wastes, such as the coal power generation and mining industries.

In both OPC-based and geopolymer materials, contaminants can be physically trapped within a solid phase, can sorb onto the surfaces of phases, and can partake in chemical reactions by precipitating out as insoluble salts or becoming a chemically bound component of a newly formed phase. While the success of chemical stabilization varies by element, physical encapsulation is generally dependent on material factors such as permeability, which can similarly affect all elements. Therefore, solidification and stabilization processes involve minimization of porosity to reduce permeability and maximization of the phases that can chemically stabilize contaminants.

2.1 Leaching from CCPs

Four CCPs were considered for solidification and stabilization testing in this study: two fly ashes, one economizer ash, and one bottom ash. Bottom ash is the first to be collected from a coal power plant as it is collected at the base of the furnace. It contains larger particles than fly ash, which settle to the bottom of the furnace, and contains a large majority of the unburnt coal. Economizer ash is collected from particles that were light enough to "fly" out of the top of the furnace, but heavy enough to fall out of the air immediately after. Economizer ash also consists of larger particles than fly ash, but contains almost no unburnt coal (ACAA, 2015). Fly ash is the last to be collected, and it contains much finer particles than either bottom or economizer ash. It is generally collected in a bag house or electrostatic precipitator.

The two fly ashes used in this study were collected from coal power plants that inject trisodium hydrogendicarbonate dihydrate (trona) into their flue gas streams. Trona is a sodium carbonate compound that is used to reduce SO_x emissions from in a small number

of coal power plants. While traditional coal fly ash and trona-impacted ash contain similar heavy metal concentrations, trona-impacted ash has been shown to leach heavy metals at higher concentrations and is therefore a greater threat to the environment (Dan et al., 2013; Su et al., 2011). Contaminants in CCPs that are of interest in this study are arsenic, cadmium, cobalt, copper, chromium, nickel, lead, selenium, and zinc. The metals/metalloids are frequently segregated into two groups: those that form oxyanions in aqueous solution, and those that are typically present as cations at circumneutral or lower pH. Some metals, such as chromium form either cations (e.g. Cr^{3+}) or oxyanions (CrO_4^{2-}) depending on the redox state of the system.

Of the three types of CCPs analyzed, economizer ash is mentioned least in the literature, with a majority of the literature focusing on fly ash and sometimes bottom ash. The focus on fly ash likely stems from its wide use in concrete. Economizer ash and bottom ash do not meet ASTM requirements for use in concrete but can be used as fill in roadway embankments, for example (ACAA, 2015). Utilizing trona-impacted ashes in concrete is of concern due to the higher sulfur trioxide and soluble sodium compounds. However, stabilization of these wastes in cementitious products can provide a viable disposal pathway.

Leaching characteristics from coal fly ash have been thoroughly studied (Blissett & Rowson, 2012; Iyer, 2002; Zhang et al., 2016). Researchers have reported both the leaching of contaminants (e.g. As, Cd, Cr) and major cations (Al, Si, Ca) as increased major ion leaching can be an indicator for increased contaminant leaching (Tiruta-Barna et al., 2006). Contaminants tend to leach to a greater extent at low and high pH than at midrange pH. Factors that impact leaching include particle size, the presence or absence of specific solid phases that serve as adsorbents or co-precipitates, and the relative solubility of hydroxides, carbonate or sulfate solids as a function of pH (Blissett & Rowson, 2012; Zhang et al., 2016). Typically, fly ash does not leach heavy metals in concentrations that would render it a hazardous waste as classified by the Toxicity Characteristic Leaching Procedure (TCLP) set forth by the US EPA (EPA1311, 1992; Zhang et al., 2016). However, the two fly ashes used in this study were collected from coal power plants that inject trona into their flue gas streams. There are significantly fewer studies characterizing leaching from trona-impacted ashes, but it has been shown that leaching increases in ashes that are trona-impacted (Dan et al., 2013; Su et al., 2011). Specifically, oxyanions of arsenic and selenium have been shown to leach more at high pH in trona-impacted ashes compared to non-impacted counterparts (Su et al., 2011). In addition, results show that trona-impacted ashes have a higher natural pH than their counterparts, thus increasing the possibility of oxyanion leaching (Dan et al., 2013; Su et al., 2011). This can be explained by the composition of trona fly ashes. Trona, as a sodium carbonate compound, is highly soluble, and it is hypothesized that metals sorb onto the surface of the sodium compounds and then are then more easily released once the sodium compounds dissolve. It has been suggested that the "insoluble fraction of the trona ash lost its capability to adsorb... elements under the natural pH condition" due to competition from trona reaction products including chloride, carbonate, and sulfate (Dan et al., 2013).

2.2 CCP S/S Methods

2.2.1 Portland Cement Mixtures

CCPs can be mixed with ordinary portland cement (OPC) and water to form solids for disposal. When OPC is mixed with water it, chemically reacts to form new hydrated phases, primarily calcium silicate hydrates (C-S-H in cement chemistry notation), calcium hydroxide (Ca(OH)₂), ettringite (Ca₆Al₂O₉(SO₄)₃·32H₂O), and AFm phases (Ca₄Al₂O₆ (SO₄)·12H₂O). While most of the phases are crystalline, C-S-H is largely amorphous. The hydration process creates an alkaline (pH > 12) environment due to the release of hydroxyl (OH⁻) ions. Contaminants can chemically bond with newly formed phases or become physically trapped within a phase.

Fly ash is considered a pozzolan, or a siliceous/alumino-siliceous material that does not contain cementitious properties, but when mixed with an alkaline material will develop cementitious properties. As a pozzolan, traditional (non-trona-impacted) fly ash is often added to the OPC-water mixture as the reaction creates an alkaline environment that allows pozzolanic reactions to occur. The addition of fly ash has been shown to produce positive effects in cement pastes and concrete mixes such as increased durability and decreased shrinkage (Van Jaarsveld et al., 1997). The effects of trona-impacted ash on concrete have received less attention in the literature (Pflughoeft-Hassett et al., 2009).

Porosity and permeability (hydraulic conductivity) are two characteristics that affect a cement paste or geopolymer's ability to release contaminants. Porosity is the quantity of pore spaces within a material from nano to meso to macropores, while permeability is the ease with which a fluid can flow through the material (Glasser, 1997). The properties are related, but may not necessarily impact leaching in the same way. High permeability is an indicator that a specimen will leach more, but a highly porous material may not leach if the pores are not connected. Typically, a highly porous material also has high permeability (Roy, 1988). These properties can be affected by the water-to-cementitious material ratio (w/cm) (or activating solution/binder (e.g. fly ash) (S/B) ratio in a geopolymer) and concentrations of major ions in the matrix (e.g. calcium).

Permeability values for cementitious materials are low, making them ideal for hazardous waste stabilization (Van Jaarsveld et al., 1997). OPC systems contain a wide range of pore sizes, including nanopores, which are beneficial for stabilizing hazardous wastes as they can trap metals or significantly slow down the leaching process. However, the inclusion of wastes into cement matrices has been shown to increase the porosity, which could enhance leaching (Poon et al., 1986). High porosity increases leaching due to increased solid surface-water contact, which can accelerate contaminant leaching.

2.2.2 Geopolymer Mixtures

CCPs can be alkali-activated (i.e. mixed with a caustic solution) to form a solid through a geopolymerization process. Inorganic geopolymers are alkali-activated aluminosilicate binders whose strength derives from tetrahedral silicon-oxygen-aluminum bonds (Van Jaarsveld et al., 1997). When sodium hydroxide, or the equivalent, is mixed with fly ash, the silica and alumina bonds are dissolved, and new amorphous phases are formed.

Geopolymer properties depend heavily upon the silica modulus (Ms), defined here as the molar ratio of SiO₂/Na₂O, but which can also be defined as SiO₂/Al₂O₃. (Allahverdi et al., 2008). The silica modulus "plays an important role in both the mechanical and morphological characteristics of geopolymers" and affects the formation of new phases (De Vargas et al., 2011). A sodium silicate activating solution can be used as the activating solution, which gives a fixed silica modulus. In order to vary the silica modulus, the sodium content can be controlled using sodium hydroxide in varying concentrations and silica content can be modified by the addition of fumed silica.

Similar to cementitious materials, geopolymers have low porosity (Ryu et al., 2013), which makes them ideal for physically encapsulating wastes. The ability of a geopolymer to physically encapsulate heavy metals can depend upon its structural stability, porosity, and permeability, among other factors. Often the silica modulus is increased to create stronger, denser, and less porous materials (Allahverdi et al., 2008; Gao et al., 2014). In addition, increasing alkaline solution molarity has been shown to increase compressive strength and decrease porosity of geopolymers (Ryu et al., 2013). When calcium is present (such as from high calcium fly ash), it can reduce geopolymerization but increase the formation of calcium based amorphous compounds, which ultimately decreases porosity (Al-Zboon et al., 2011).

2.3 Chemical Stabilization

Contaminants present in CCPs include arsenic, cadmium, chromium, cobalt, nickel, lead, selenium, zinc, and mercury. The metals can be loosely grouped into two major categories: those that form *oxyanions* in aqueous environments and those that remain *cationic* in a low to mid-pH range.

Cationic metals sorb to clays and clay minerals and form hydroxide and carbonate solids, depending on the pH and composition of the system. Sorption of cations to clays and clay minerals increases with increasing pH. Solubility is also pH-dependent, and the total soluble concentration of a heavy metal cation typically decreases, reaches a minimum, and then increases with increasing pH as the dominant hydroxide species becomes anionic (e.g. Ni(OH)₃⁻).

In contrast to cations, oxyanion sorption to oxides and hydroxides decreases with increasing pH. Of the contaminants listed, arsenic, chromium, and selenium are often

present in waste streams as oxyanions making them more susceptible to leaching at high pH when sorption is the primary mechanism of incorporation within the geopolymer. Formation of precipitates is dependent on the presence of the solubility products with cationic ions such as Ca^{2+} , Mg^{2+} and Fe^{3+} (e.g. $Ca^3(AsO_4)_2$). In many cases, oxyanions can co-precipitate in precipitating phases. Goldberg and Glaubig (1988) noted increased removal of As(V) onto calcite with increasing pH; however, it is not clear whether the removal mechanism was adsorption or co-precipitation. The CCPs in this study have a high natural pH (11-13), thus oxyanions have a higher potential to leach under natural conditions.

2.3.1 Oxyanions

Arsenic

Arsenic is highly toxic and has therefore been studied rigorously. It is a known carcinogen and acute arsenic poisoning symptoms can include nausea, vomiting, and diarrhea (Ratnaike, 2003). Arsenic is generally found in two oxidation states of which As(III) is a higher threat than As(V) as it is both more toxic and more difficult to remove from water (Ratnaike, 2003). Fortunately, As(V) is the dominant form in coal fly ash (Huggins et al., 2007). Even though arsenic forms oxyanions in aqueous environments, results indicate that "increased destruction of the cement matrix at low pH has more effect on the leachate arsenic concentration than the increased solubility (of arsenic mineral phases) at high pH" (Leist et al., 2003a). Thus, leaching of arsenic at both high and low pH is of concern.

Reduced arsenic leaching at mid-range pH can be caused by sorption or the formation of precipitates. Dixit and Herring (2003) showed decreased As(V) sorption onto goethite with an increase in pH, but they did not examine pH above 10. Wei et al. (2016) showed that As(V) adsorption actually increased again above pH 12, though the percent adsorbed was still low. The sorbents in these systems were goethite and titanium dioxide, which are not present in high concentrations in cement and geopolymer systems, but they show trends similar to aluminum oxides with increased adsorption at mid-range pH.

Arsenic wastes have previously been stabilized using both OPC and geopolymers. Cement hydrates such as ettringite and AFm-phases are known to incorporate anions, which can include AsO_4^{3-} , in the interlayer, contributing to their stabilization (Gougar et al., 1996). Leaching studies indicate that arsenic stabilization is dependent on a number of factors, including calcium and iron content of the stabilization matrix, as well as external factors such as pH (Provis & van Deventer, 2009). Notably, introducing waste materials (e.g. As, Cr, Se) and matrix components (e.g. Ca, Na, Fe) in different forms can generate different leaching results (Palomo et al., 2005).

Across the board, matrices with high calcium contents stabilize arsenic better than lowcalcium mixtures, and while often papers claim that OPC does not stabilize arsenic well, cement mixtures have generally outperformed geopolymers (Provis & van Deventer, 2009; Dutré & Vandecasteele, 1998; Leist et al., 2003a). This may be due to precipitation or co-precipitation of arsenic with calcium and calcite, respectively. Indeed, geopolymers made with low-calcium ashes have achieved low oxyanion stability (Álvarez-Ayuso et al., 2008); however, geopolymer mixtures can perform just as well as cements with the addition of lime or other calcium sources (Dutré & Vandecasteele, 1998). The main factor in arsenic stabilization in both cement and geopolymer specimens is likely the formation of low solubility calcium-arsenic compounds, and not binding by silica and alumina (Dutré & Vandecasteele, 1998; Leist et al., 2003b). Alexandratos et al. (2007) outline a large number of possible calcium-As(V) precipitates that could form including CaAsO₄⁻, CaHAsO₄, CaH₂AsO⁴⁺, Ca₄(OH)₂(AsO₄)₂(H₂O)₄ and others. Amongst their compounds, CaH₂AsO⁴⁺ has the highest solubility and Ca₅(AsO₄)₃OH the lowest. Recently, however, arsenic and selenium have been immobilized in a fly ash-geopolymer composite (Bankowski et al., 2004; van Deventer et al., 2007), thought to be due to the formation of layered double hydroxide (LDH) and aluminate hydrate phases, which serve as chemical residences for the oxyanions, a mechanism that is not reliant on calcium.

Dutre & Vandecasteele (1998) tested leaching of As(III) and determined that precipitation of CaHAsO₃ was occurring. Similar testing has not been carried out with As(V), though it has been shown that systems containing the highest amounts of calcium are the most effective for stabilizing arsenic trioxide, pentoxide, and arsenate (Leist et al., 2003a). Similarly, fly ash geopolymers have been shown to bind arsenic better than metakaolin (a solely alumino-siliceous material), and cement-based systems have been shown to stabilize arsenic and chromium better than fly ash-based systems (slag, cement & fly ash, fly ash & lime), further suggesting that stabilization by silica or alumina materials is not the primary mechanism for arsenic stabilization (Akhter et al., 1990; Fernández-Jiménez et al., 2005).

While increased calcium content has been clearly shown to decrease leaching of arsenic, impacts of iron content are less well defined. Iron oxides present in fly ash have been shown to adsorb arsenic, whereas iron oxides introduced separately into the system have caused no decrease in arsenic leaching (Fernández-Jiménez et al., 2005). Transmission electron microscopy (TEM) was used to verify that arsenic was sorbed onto iron particles present in fly ash, but when Fe₂O₃ particles were introduced into a metakaolin system, no arsenic was visible on the particles. It has also been shown that arsenic pentoxide and trioxide leached more in a cement matrix that included additional Fe(II), suggesting that adsorbing onto or complexing with iron is not an ideal removal mechanism for arsenic (Leist et al., 2003b).

Selenium

Selenium can be found in many forms in the environment: Se(II-), Se(0), Se(IV) and Se(VI). While arsenic is predominantly found in oxidized form, reduced selenium (Se(IV)) is predominant in coal fly ash (Huggins et al., 2007). Selenium is not a carcinogen and is not toxic to humans at low levels; it is actually recommended for consumption by the World Health Organization (WHO) at around 10-70µg/day (WHO 2011). However, at high levels

(mg/day) selenite and selenate can have adverse effects including growth retardation and reproductive effects (WHO 2011).

There are fewer studies on selenium than arsenic, and binding with OPC and geopolymers has been less successful. Results range from similar leaching in both fly ash and geopolymers, to reduced leaching in geopolymers but not by a significant amount (Álvarez-Ayuso et al., 2008; Bankowski et al., 2004; Kupwade-Patil et al., 2014). Reduced leaching of selenite and selenate in soils by binding with OPC has been somewhat effective through the precipitation of calcium selenite hydrate (CaSeO₃·H₂O) and selenite substituted into ettringite (Ca₆Al₂(SeO₄)₃(OH)₁₂·26H₂O) as shown by SEM-EDX and x-ray diffraction (XRD) (Hyun et al., 2009). However, at low pH values these precipitates dissolved, and selenium was once again present in the system.

Chromium

Chromium is a known carcinogen with toxic effects to a number of human body systems (CDC, 2011). It can be present as either a cation in its +3 oxidation state (Cr(III))) or an oxyanion in the +6 oxidation state (Cr(VI)). Hexavalent Cr(VI) is the most toxic and the most mobile (Provis & van Deventer, 2009) as it is typically present as an oxyanion. Fortunately, Cr(III) is the dominant form found in coal ash, though Cr(VI) can be found in small percentages (USGS, 2015).

Chromium has been successfully stabilized with OPC and geopolymers (Guo & Shi, 2013; Zhang, et al., 2008a). The main methods for chromium stabilization are thought to be the formation of insoluble chromium hydroxides, calcium chromium hydroxide complexes, and calcium chromate (Ca₂CrO₄), though it has been suggested that Cr(III) could be replacing aluminum in octahedrally-coordinated calcium aluminate hydrate (C-A-H) (Glasser, 1997).

As Cr(III) precipitates out more easily than Cr(VI), methods for Cr(VI) removal often entail reducing to Cr(III) first. The addition of sulfide has been shown to reduce Cr(VI) to Cr(III), which ultimately reduces chromium leaching (Glasser, 1997; Zhang et al., 2008b). A majority of leaching tests with chromium have been completed by doping OPC or geopolymer pastes with soluble chromium salts (Zhang et al., 2008a). In the presence of sulfide, more highly soluble salts result in reduced leaching as the Cr(VI) is more available to be reduced to Cr(III) by S²⁻ (Zhang et al., 2008b). In summary, Cr(III) is more readily stabilized than Cr(VI) through the formation of insoluble hydroxides, and Cr(VI) can be stabilized by first reducing to Cr(III).

2.3.2 Cations

In coal fly ash, cations (Cd, Cu, Co, Ni, Pb, Zn) are generally found in the +2 oxidation state. Metal ion concerns include toxicity (e.g. Cd), neurodevelopmental problems (e.g. Pb) and cancer (e.g Cr(VI)) (Ibrahim, 2016; CDC 2013). As cations, these elements are more effectively precipitated out in the mid pH range and higher, and they tend to behave similarly in cement and geopolymer systems. Cations typically form metal hydroxides or carbonates with pH-dependent solubility, as shown in Figure 2.1 for metal hydroxides. As shown, metal hydroxides solubility increases at both low and high pH, and the pH of least solubility varies by element. For instance, cadmium has a pH of lowest hydroxide solubility around 11, whereas copper has its lowest solubility at pH 9. For the elements of greatest concern in this study the minimum solubility occurs at relatively high pH (pH 10-11), though still lower than the pH range often found in cement and geopolymer systems (pH >12). Adsorption to solid phases and co-precipitation processes can extend the upper range of removal of cations.



Figure 2.1: Solubility Diagram for Metal Hydroxides (Reproduced from Porex, 2017)

In line with this reasoning, experiments have achieved strong stabilization of cations in both OPC and geopolymer systems at high pH, and the formation of metal hydroxides has been shown with SEM images (Akhter et al., 1990; Zhang et al., 2008a). As would be expected, studies have found low binding of cations at low pH, with metal leachate concentrations generally following the solubility profile of formed hydroxides (Kogbara, et al., 2014; Li et al., 2001).

Outside of metal hydroxides and carbonates, it is suspected that alkaline earth metal hydroxides are (e.g. Ca(OH)₂(s)) forming in OPC systems and being incorporated into the cement paste, further decreasing leaching at high pH (Diez et al., 1997). Some promising results also show that copper, cobalt, and nickel have been incorporated into a kaolinite-based geopolymer network, and zinc has been shown to bond with silica and oxygen in geopolymer-like environments (Anseau, et al., 2005; Hanzlicek & Steinerova-Vondrakova, 2006). For example, by chemical entrapment, lead is contained in geopolymers in the form of insoluble lead silicate Pb₂SiO₅ (Zhang et al., 2008a; Phair et al., 2004; Palacios & Palomo, 2004; Palomo & Palacios, 2003; Perera et al., 2005), while copper was found evenly distributed throughout the geopolymer network (Phair et al., 2004). Significantly, hydrated cement phases such as the AFm, hydrotalcite-like phases and C-S-H have been

shown capable of binding metals, by weak physisorption, or structural incorporation (Poon et al., 1985; Glasser, 1997; Berardi et al., 1998; Albino et al., 1996; Chen et al., 2009; Habib et al., 2012; Malviya & Chaudhary, 2006; Gougar et al., 1996). However, none of these results have been directly correlated to reduced leaching at low pH.

Mercury and related metals that do not form insoluble precipitates at elevated pH are thought to be held in cementitious pore solutions, such that their mobility depends largely upon physical encapsulation by the cement matrix. Thus, in cementitious systems, leachability is closely related to porosity of the final product (Poon et al., 1985; Chrysochoou & Dermatas, 2006). However, soluble HgCl₂ has been shown to be immobilized in geopolymer systems, based on alkali-activated Class F fly ash, where chemical stabilization of Hg was attributed to the formation of highly insoluble HgS₂ (Donatello et al., 2012). Mercury has also been immobilized in slag-based geopolymers, where both chemical binding and physical encapsulation have been thought to be contributing factors (Qian et al., 2003a; Qian et al., 2003b). In traditional hydrated cement systems, Hg has been reported to precipitate as slightly soluble HgO (McWhinney et al., 1990). Other studies (Serrano et al., 2012; Serrano et al., 2016) indicate that Hg can be contained in polynuclear chloromercury(II) complexes associated with ettringite, with coprecipitation of Hg as an inner-sphere complex of Hg(OH)₂ bound to Fe(III) surfaces such as in ferrihydrite (Serrano et al. 2012; Wang et al., 2012).

2.4 Leaching in Landfill Conditions

When CCPs are disposed of, they are generally deposited in landfills or ash ponds (ACAA, 2015). Many of the leaching tests that have been previously carried out on CCPs, cement pastes, and geopolymers (such as those described in the earlier sections) test leaching in reagent water at natural pH, or in reagent water plus an acidifying agent (e.g. acetic acid, nitric acid, sulfuric acid) to adjust the pH. However, in real-life scenarios CCPs would be leaching not in reagent water, but into real solutions present in the landfill, which can contain a vast number of components that could potentially affect trace metal leaching.

Landfill leachate, from municipal, commercial and mixed industrial waste, can contain bicarbonate, phosphate, sulfate, silicates, and natural organic matter (NOM) (Christensen et al., 2001; Ghosh et al., 2006). In general, it is thought that the presence of additional ions in landfill leachate could cause competition for adsorption sites onto solid materials, increase aqueous complexation and increase leaching of trace elements. To date, there are little data to support these hypotheses, as the few studies that tested leaching with background ions generally showed either no difference between de-ionized water versus solutions containing salts or less leaching in the salt solution (Zhang et al., 2008a; Zhao et al., 2017). In contrast, NOM has been shown to have greater effect on leaching from CCPs. NOM can bind with elements and form both adsorbable and non-adsorbable complexes, which can either increase leaching (As(V)) or decrease leaching (Sr, Mo, V) of different elements (Zhao et al., 2017). Dissolved organic carbon (DOC) has also been shown to increase the leaching of copper from CCPs (Van Zomeren & Comans, 2004). While there exists a large body of work detailing relationships between specific elements and NOM, relatively few papers examine how NOM affects leaching from CCPs and even fewer discuss how NOM and other landfill conditions affect leaching from cement pastes and geopolymers.

2.5 Summary

There are multiple factors affecting the leaching of trace elements from geopolymer and cement systems, so it is difficult to determine exact reasons for reduced leaching of specific elements in different systems. Metals can be precipitated as hydroxides, substituted into amorphous matrices (C-S-H, C-A-H, N-A-S-H, silica-alumina systems), physically trapped within a matrix, or sorbed onto the surface of a compound. Researchers have both speculated and shown through macroscopic experiments, thermodynamic data, XRD, SEM-EDX, and TEM that, in most cases, elements are being stabilized in multiple ways depending on the conditions of the system. pH is highly relevant to leaching in almost all systems, with low pH systems generally leaching more (even for oxyanions) than high pH systems.

A factor mentioned in many papers that appears to heavily affect trace metal leaching is the concentration of calcium. OPC systems inherently have larger calcium concentrations than geopolymer systems, and this enables the formation of insoluble calcium carbonates or calcium-metal compounds. If the pH is maintained in the mid to high range, stabilization of many species in both geopolymer and OPC systems is achieved. However, if systems are exposed to low pH, stabilization is less effective. This could be due to degradation of the cement/geopolymer matrix, allowing for metals to leach out, or due to the increased solubility of hydroxide precipitates.

A majority of leaching tests reported in previous literature have been completed following the toxicity characteristic leaching procedure (TCLP – EPA Method 1311) or similar methods put forth by non-US governments (e.g. Australian Bottle Leaching Procedure (ABLP)), and these test leaching in relatively clean environments. Tests have also been carried out in environments with background ions such as magnesium sulfate or sodium carbonate, but few if any tests have been carried out in landfill or groundwater-like conditions that include natural organic matter (NOM) (Zhang et al., 2008a). Only recently have tests including NOM been carried out with regards to leaching from fly ash, but these tests have not yet carried over to leaching from cement pastes and geopolymers (Zhao et al., 2017).

In the research presented in this report, we attempted to fill the gaps in the literature identified herein by experimentally testing geopolymer and cement-stabilized CCPs for solid phase formation, porosity, compressive strength, and leaching. In the process, we also tested the impacts of landfill-like conditions on the leaching of heavy metals from geopolymers and optimized geopolymer compositions for reduced trace metal leaching.

3. Materials

Four CCPs were obtained for testing: two trona-impacted fly ashes (FA-H and FA-B), one bottom ash (BA), and one economizer ash (EA). Upon receipt, the materials were characterized using x-ray fluorescence spectroscopy for oxide composition, quantitative x-ray diffraction for phase assemblage, loss on ignition, and laser diffraction for particle size distribution.

Oxide analysis for FA-H was provided by the supplier. The other ashes were sent to Wyoming Analytical Labs, Inc. for x-ray fluorescence spectroscopy. Results are shown in Table 3.1. Loss-on-ignition (LOI) testing was performed according to ASTM C 311 (2013), which involves heating the ash in a furnace to 105°C followed by heating to 750°C in an uncovered porcelain crucible and measuring the mass loss. Results are shown in Table 3.1. The bottom ash has a significantly higher loss-on-ignition than the other materials, suggesting a higher quantity of unburnt carbon.

Oxide/property	FA-H	FA-B	EA	BA
SiO ₂ (%)	30.13	30.68	39.90	40.70
Al ₂ O ₃ (%)	16.70	15.81	16.79	14.54
Fe ₂ O ₃ (%)	5.35	4.53	4.99	4.29
CaO (%)	25.00	25.39	25.45	16.57
MgO (%)	5.73	4.85	4.81	3.33
Na ₂ O (%)	8.55	6.28	1.56	1.07
K ₂ O (%)	0.43	0.37	0.33	0.35
TiO ₂ (%)	-	1.42	1.61	1.24
MnO ₂ (%)	-	0.10	0.10	0.08
P ₂ O ₅ (%)	-	0.95	0.81	0.70
SrO (%)	-	0.40	0.40	0.28
BaO (%)	-	0.66	0.60	0.46
SO₃ (%)	5.31	6.14	2.52	0.83
LOI (%)	3.99	2.43	0.14	15.57
d ₅₀ (μm)	15.6	15.5	125.4	164.7

Table 3.1: Compositions and properties of the CCPs

Particle size distributions of the ashes were determined using laser diffraction in a Mastersizer 2000. The principle behind laser diffraction particle size analysis is that different sized particles scatter an incident light at different angles, with larger particles scattering at lower angles. Isopropyl alcohol (>95% concentration by weight) was used as a dispersant to prevent hydration of particles during the test. The refractive indices of both the particles and the dispersant are required for particle size calculation. A value of 1.39 was used for the refractive index of isopropanol (Chu & Thompson, 1961). Refractive indices for fly and bottom ash can vary, and generally range between 1.5-1.7 (Jewell & Rathbone, 2009). A refractive index of 1.7 was used, as this gave a residual value of less

than 1% for all ashes. A residual of less than 1% indicates that there is a good fit between the measured and calculated data from the instrument. Ultrasonication was used for 30 s to disperse the particles, then the system was allowed to rest for a minimum of 15 minutes before measurements were taken to allow bubbles to clear and to provide even dispersion of particles. The particles and dispersant were pumped into the instrument for testing, and pump speeds used varied from 2000-2500 rpm depending upon the ash. Higher pump speeds were used on ashes with larger particle sizes (the bottom and economizer ashes) to keep the larger particles suspended in the dispersant. Five measurements were recorded for each sample and the average distributions are shown in Figure 3.1. The results are summarized in Table 3.1 through a value reported for median particle diameter (d_{50}).



Figure 3.1: Particle size distributions of CCPs

Two ashes, the bottom ash and the economizer ash, had particles of size greater than $1000\mu m$, which is the highest size accurately measured by the instrument. To correct for this, the ashes were sieved through a No. 18 sieve (1mm) before running the test. Any ash that was greater than $1000\mu m$ was then passed through a series of sieves and weighed to determine a general particle size distribution for the larger particles. Results are summarized in Table 3.2.

	Table 3.2: F	Particle size	distribution	of larger	particles
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Douticle Size (mm)	Percentage by Weight					
Particle Size (mm)	Economizer Ash	Bottom Ash				
< 1	75.3%	77.1%				
1-2	8.6%	11.1%				
2-2.8	6.1%	4.3%				
>2.8	9.9%	7.5%				

Both qualitative and quantitative x-ray diffraction (XRD) analyses were run on each ash to determine the individual solid phases (crystalline minerals and amorphous glasses)

present in each sample as well as the relative weight percent of each phase. Preparation of two samples was completed for each ash, one for qualitative analysis and one for quantitative. To begin sample preparation for both analyses, slightly more than 1 g of ash was crushed using a ceramic mortar and pestle and sieved through a #325 sieve (45μ m). Any amount that did not pass through the sieve was re-crushed until the entire sample passed through the sieve. The entire sample was crushed to ensure that all crystalline phases were included in the sample. For quantitative analysis, a specific amount of reference material was introduced into the sample. For these analyses, zincite (ZnO) was included at 10% by mass. The powders were mixed in an agate mortar and pestle and a small amount of ethanol was added to mix the two together evenly. Samples were then dried in an oven.

After crushing, samples were placed into glass slides for analysis in a Rigaku Miniflex 600 XRD Analyzer. The glass slides have an indented portion (approximately 0.5 mm deep) in which the samples were placed. There are several possibilities for error in sample preparation for XRD, including preferred orientation and peak shifting. To prevent preferred orientation, a razor blade was used to cut across the sample in perpendicular directions after which a flat glass plate was used to press down on the sample without twisting. Samples were run with a 20 range of 4-70°, a step size of 0.02°, and at 1.5-2 degrees per minute. Qualitative analysis was completed using Jade and the PDF 2015 database after which quantitative analysis was completed using PDXL2 software.

Quantitative analysis provides the percentage of each known crystalline phase, as well as the percentage of amorphous phases based upon a known zincite percentage of 10%. PDXL2 cannot quantify amorphous phases, and therefore, if the sample contained amorphous phases, the percentage of zincite appeared as greater than 10%. The amorphous phase is present in the x-ray output as a lump in the background in the 20 range of approximately 10-20°. The percentages of all phases were adjusted down proportionally so that the zincite percentage equaled 10%, and the remaining percentage was the amorphous content of the sample.

The results are shown in Figure 3.2 (and in Appendix B). As expected, the fly ashes have higher amorphous contents than the bottom and economizer ashes, which is what makes them generally more favorable for beneficial reuse in portland cement concrete.

Raw CCPs were digested to determine trace metal contents according to EPA method 3050b. A 1 g sample (dry weight) was added to a pre-weighed 250 mL fluorinated ethylene propylene (FEP) bottle and heated in a mixture of nitric acid (HNO₃, 67-70% w/w, trace metal, Fisher) and hydrogen peroxide (>30% H₂O₂, trace metal, Sigma Aldrich) for a total of approximately four hours. After four hours, the remaining liquid was filtered to 20 μ m using Whatman^R No. 41 filter paper into 100mL volumetric flasks and then diluted with Millipore water to 100mL. For all CCPs some solids remained undissolved. Samples were analyzed using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS).



Figure 3.2: Phase distributions identified by XRD in CCP samples



Figure 3.2 (continued): Phase distributions identified by XRD in CCP samples

Average trace metal content of the raw CCPs determined by digestion are shown in Table 3.3. FAH trona-impacted fly ash generally had the highest mass of trace metals with the exception of copper. Cadmium was present at the lowest concentrations for all CCPs with concentrations in the 1 mg/kg range. Samples were completed in triplicate for FAH and FAB, and in duplicate for the economizer ash (EA) and bottom ash (BA). Trace element contents are similar to those found in trona-impacted ashes in the literature and generally fall within the range of typical coal fly ash trace element compositions (Blissett & Rowson, 2012a; Su et al., 2011).

Element	FAH	FAB	EA	BA	OPC
As (mg/kg)	28.9	13.3	9.8	4.5	16.0
Cd (mg/kg)	1.2	1.0	2.0	0.3	0.3
Co (mg/kg)	17.3	18.0	14.8	9.0	43.2
Cu (mg/kg)	124.8	140.6	108.4	65.4	6.1
Cr (mg/kg)	74.1	56.5	41.9	22.9	31.6
Ni (mg/kg)	50.7	42.7	33.5	20.1	26.7
Pb (mg/kg)	26.7	20.9	18.0	5.9	19.2
Se (mg/kg)	18.1	13.6	0.2	1.5	0.8
Zn (mg/kg)	134.0	52.7	36.1	37.7	123.5

Table 3.3: Trace metal content of CCPs and OPC determined by digestion

4. Solubility-Informed Mixture Design

Immobilization of contaminants in solidified materials can be accomplished by chemical or physical processes, as discussed earlier. Therefore, mixture design was approached from the following two perspectives:

- Stabilization: where the phase assemblage is modeled to identify systems that produce reaction products with the greatest potential for stabilizing heavy metals by structural incorporation, complexation, or sorption.
- Solidification: where the phase assemblage is modeled to identify mixtures that will yield the lowest porosity and lowest diffusion coefficients for heavy metals.

4.1 Evaluation of the hydrated phase assemblage

To evaluate the effect of activation solution and binder (CCP) composition on the matrix mineralogy, first detailed simulations were carried out for activated fly ash materials while varying the concentration of NaOH and the silica modulus of the activation solution. Thermodynamic simulations of phase balance and aqueous chemical speciation were computed using the Gibbs Energy Minimization Software (GEMS, version 2.3), a broadpurpose geochemical modeling platform developed by Kulik et al. (2003, 2013) and Wagner et al. (2012). The GEMS software uses Gibbs energy minimization criteria to compute equilibrium phase assemblages and ionic speciation in a complex chemical system from its total bulk elemental composition. The software applies a convex programming approach based on the Interior Points Method (Mehrotra, 1992) in conjunction with information of the thermodynamic properties of phases (i.e. solids, liquid and air) to calculate material balances. Chemical interactions involving solid phases, solid solutions and the aqueous electrolyte(s) are considered simultaneously. The thermodynamic properties of all the solid and the aqueous species were sourced from the default GEMS-PSI database (Thoenen & Kulik, 2003; Johnson et al., 1992; Hummel et al., 2002), with additional data for the cement hydrates sourced from the cemdata07 database (Lothenbach & Winnefeld, 2006; Lothenbach et al., 2008; Matschei et al., 2007),

and data relevant to alkali activated fly ash compounds sourced from elsewhere (Gomez-Zamorano et al., 2017; Myers et al., 2015). The standard molar thermodynamic properties of relevant hydrated phases at T = 25 °C and p = 1 bar as used in the thermodynamic calculations are presented in Appendix A. The Truesdell-Jones modification of the extended Debye-Hückel equation (Equation 4.1) (Helgeson et al., 1970), was used to account for the effects of solution non-ideality due to the presence of dissolved salts:

$$\log \gamma_{j} = \frac{-Az_{j}^{2}\sqrt{I}}{1+B\alpha_{j}\sqrt{I}} + bI + \log_{10}\frac{x_{jw}}{X_{w}}$$
 Equation (4.1)

where, γ_j is the activity coefficient of jth ion (unitless); z_j is the charge of jth ion; α_j is the ion-size parameter (i.e. effective hydrated diameter of jth ion, Å); A (kg^{1/2}·mol^{-1/2}) and B (kg^{1/2}·mol^{-1/2}·m⁻¹) are T,P-dependent Debye-Hückel electrostatic parameters (Hummel et al., 2002); b is a semi-empirical parameter that describes short-range interactions between charged aqueous species in an electrolyte solution (representing the predominant electrolyte in the system)); I is the molal ionic strength of the solution (mol·kg⁻¹); x_{jw} is the molar quantity of water, and X_w is the total molar amount of the aqueous phase. Constant values of α (3.31 Å) and b (0.098 kg/mol) are taken to represent the average ion size and common short-range interactions of charged aqueous species in a NaOH-dominated solution (Helgeson et al., 1981). It should be noted that the applied solution phase model is accurate only for ionic strengths \leq 2.0 mol/L, beyond which, its accuracy is reduced (Kulik et al., 2003). Hence, while the trends are correct, the absolute values feature some uncertainty that arises in direct proportion to the ionic strength of the starting "activation solution".

The equilibrium phase assemblage was calculated for activated FA-B and FA-H. The activation solutions consisted of: (a) 2-10 M NaOH and (b) separate mixtures of 4M NaOH + SiO₂ and 8M NaOH + SiO₂ (silica modulus, SiO₂/Na₂O = 0 - 2). The simulations were carried out across a range of water-to-binder ratios (w/b, representing water-to-fly ash mass ratio in these cases, excluding the NaOH and added SiO₂) ranging from 0.34 to 0.69 at 25 °C and 1 bar. In each case, special focus was placed on quantifying the solid hydrates present and the capillary porosity of the system, i.e., the ratio of the pore fluid volume to the total volume. Assuming that the systems are sufficiently mature, the fly ash component in the mixture was assumed to be 60% reacted (Durdziński et al., 2015). The phase assemblages calculated for both fly ashes, FA-B and FA-H, as a function of the concentration of NaOH and silica modulus of activation solutions (8M NaOH+SiO₂), are shown in Figures 4.1 and 4.2.



Figure 4.1: The hydrated phase assemblage as a function of the molarity of NaOH activator for (a) FA-B, and, (b) FA-H that were activated for w/b = 0.50 to produce geopolymers. For the sake of clarity, this example assumes that that the fly ashes are 60% reacted. The amount of ferrihydrite and hydrotalcite-like compounds formed are linked to the Fe and Mg contents of the fly ash, respectively. Since these quantities remain invariant they are not shown here.

In general, as seen in Figure 4.1, increasing the NaOH concentration enhances the quantity of C-S-H (calcium-silicate-hydrate (Myers et al., 2015)), and $C_2ASH_8^1$ (strätlingite (Okoronkwo & Glasser, 2016)) formed, while reducing the porosity of the matrix. The observed increase in C-S-H is significant as it enhances mechanical strength, while reducing the transport of ions through the matrix (e.g., as relevant for the immobilization of metal oxyanions (Chrysochoou & Dermatas, 2006)). The increase in the C-S-H content is due to the progressive rise in pH caused by an increase of the NaOH concentration, which promotes the dissolution of the fly ash, and the consequent release of [Ca] (Ben Haha et al., 2011). Ettringite ($C_6As_3H_{32}$) is predicted to form at low NaOH concentrations, around 2 M NaOH, while, SO₄-AFm (i.e., C₄AsH₁₂) formation is favored at higher concentrations (Matschei et al., 2007). However, the low quantities of these compounds formed suggest limited potential for the chemical encapsulation of oxyanions (Gougar et al., 1996; Chrysochoou & Dermatas, 2006). Interestingly, the amount of N-A-S-H (sodiumalumino-silicate-hydrate) formed decreases with increasing NaOH concentration. This is traceable to the stability properties of N-A-S-H which is greatly influenced by pH and Ca content of the system (Gomez-Zamorano et al., 2017; Myers et al., 2014; Garcia-Lodeiro et al., 2011). Thus, the Ca-rich nature of the fly ash promotes the formation of the more stable strätlingite and C-S-H solids at equilibrium (Garcia-Lodeiro et al., 2011).

The pH of the aqueous phase (pore solution) increases with activator concentration, which would encourage the precipitation of insoluble hydroxides, aluminosilicates, and salts of cationic metals (Phair & Van Deventer, 2001). Such precipitation reactions, which consume [OH]-, and the sorption of alkalis, would, in time, reduce the pH of the solution

¹ Cement chemistry notation is used in this section, where single letters represent oxides: C=CaO, S=SiO₂, A=Al₂O₃, Fe=Fe₂O₃, s=SO₃, M=MgO, and H=H₂O

(Glasser, 1997). Nevertheless, the high pH environment imparts a net negative charge to the fly ash solids and reaction products (Yousuf et al., 1995) (e.g., C-S-H (Nonat, 2004; Viallis-Terrisse et al., 2001)). This encourages the repulsion and desorption of oxyanionic species (e.g. $H_2AsO_4^-$ or $HAsO_4^{2-}$), while facilitating the sorption and precipitation of cationic species (Ghosh et al., 2006). This is significant, as while the high pH environment offers a means to suitably immobilize cationic contaminants, (purely) NaOH-activated fly ash may not offer a robust environment to encapsulate oxyanions, unless their uptake into the AFt/AFm can be ensured (Gougar et al., 1996; Zhang, 2000; Chrysochoou & Dermatas, 2006).

In contrast to phase development seen in the presence of (solely) NaOH-based activator, the addition of "SiO₂" to the system, i.e., to increase its silica modulus (see Figure 4.2b), increases the amount of N-A-S-H formed. Simultaneously, the quantity of C-S-H formed shows a slight decrease, passing through a minimum at Ms =1.0, with a subsequent increase thereafter. The increase in N-A-S-H with an increasing Ms of activation solution indicates that the pore solution in a purely NaOH activated system is somewhat deficient with respect to dissolved silica. While this increase in aqueous silica, with increasing Ms, is important for immobilizing cationic metals that form insoluble silicates, e.g. lead (Pb), which is stabilized as lead silicate Pb_2SiO_5 (Phair et al., 2004; Palacios & Palomo, 2004; Palomo & Palacios, 2003; Zhang et al., 2008; Perera et al., 2005), it is more important for stabilizing oxyanions, owing to the decreased pH (Ghosh et al., 2006) and decreased porosity. The amount of hydrotalcite-like M₄AH₁₀, which can intercalate anions, and ferrihydrite $(1/2FH_3)$ formed are related to the Mg and Fe contents of the fly ash, respectively, and remain unchanged (Lothenbach & Winnefeld, 2006).



a.

Figure 4.2: The hydrated phase assemblage as a function of the silica modulus for: (a) FA-B, and, (b) FA-H that were activated for w/b = 0.50 to produce geopolymers. For the sake of clarity, this example assumes that that the fly ashes are 60 % reacted. The amount of ferrihydrite and hydrotalcite-like compounds formed are linked to the Fe and Mg contents of the fly ash, respectively. Since these quantities remain invariant they are not shown here.

4.2 The influence of the porosity on contaminant transport

The release of contaminant species from the coal combustion products, or any stabilized material, is critically influenced by the porosity of the material (Oh & Jang, 2004). For this reason, it is important to evaluate the porosity of matrix in order to assess its suitability for waste immobilization. The effective diffusion coefficient of a porous material can be expressed as a function of the relationship between pore structure parameters, including porosity and tortuosity, following the Nernst-Einstein relation (Einstein, 1905), as shown in Equation (4.2) (Epstein, 1989; Currie, 1960; Troeh et al., 1982; Fick, 1995):

$$D_e = D_0 \left(\frac{\phi}{\tau}\right)$$
 Equation (4.2)

where D_e is the effective (ionic) diffusivity of a porous material (m²/s), Ø is the capillary porosity (i.e., the ratio of the pore solution to the total volume of the system; see Figures 4.1-4.2), τ is the tortuosity (unitless, i.e., inverse pore connectivity often represented as β (Ghanbarian et al., 2013)), and, D_0 is the diffusivity of ions in bulk water.



a. D. Figure 4.3: (a) The evolution of the capillary (coarse) porosity as a function of the extent of fly ash reacted in an alkali activated FA-B and FA-H system produced using 8 M NaOH solutions at w/b = 0.50, (b) The evolution of the capillary (coarse) porosity as a function of the molarity of NaOH activator and its silica modulus (M_s). The fly ash is assumed to be 60% reacted (Durdziński et al., 2015).

The tortuosity is defined as a function of the porosity and is (empirically) related to the peak capillary pore diameter (Nakarai et al., 2006; Maekawa et al., 2003) as shown in the Equation (4.3):

$$\tau = -1.5 \tanh[8.0(\phi - 0.25)] + 2.5$$
 Equation (4.3)

As such, the transport response of these materials can be estimated as a function of the residual coarse (capillary) porosity in these systems (Nakarai et al., 2006; Hillel, 2004).

Generally, it is accepted that, in each system, increasing the w/b increases the porosity and facilitates contaminant transport (Hillel, 2004). In the activated fly ash systems (Figure 4.3a), the extent of fly ash reaction strongly influences capillary pore volume. Thus, it is likely necessary to achieve at least 50 % fly ash reaction, before the capillary porosity decreases substantially and suitable mechanical properties are realized (Ben Haha et al., 2011). It is important to point out that both fly ashes, FA-H and FA-B showed very similar reductions in their porosity with increasing reaction (Figure 4.3a).

From a compositional perspective, increasing the pH (i.e., NaOH concentration) of activator and its silica modulus (M_s) both decreases the porosity (see Figure 4.3b). This is a consequence of the increased quantity of hydrated solids formed, which are boosted as a result of the rising NaOH concentration and M_s (see Figure 4.1 & 4.2). This indicates that a near-linear decay in D_e is expected with the increasing NaOH concentration. The influences of M_s on ion-diffusion are more complex. For example, the porosity (and hence the effective diffusion coefficient of ions) passes through a maximum at $M_s = 1.0$ before declining thereafter (see Figure 4.3b). This is also reflected in the hydrated phase assemblages (see Figure 4.2), wherein the lowest solid content, and hence highest porosity, is realized at $M_s = 1.0$. Against the observation that, most often, the porosity of the sodium silicate activated formulations is lower than that of the corresponding NaOH-activated material, this suggests that these systems may offer a superior immobilization solution due to their improved strengths (Ben Haha et al., 2011) as compared to solely NaOH-activated fly ash formulations.

4.3 Guidelines and recommendations

Based solely upon physical characteristics described in Section 3, the economizer and bottom ash could be expected to be less reactive and therefore form weaker cements pastes and/or geopolymers than the two fly ashes. Fly ash H (FAH) had slightly finer particles and larger surface area than fly ash B (FAB), but the differences were small enough that the two could be expected to perform similarly without further information.

Examining chemical characteristics furthers the conclusion that the economizer and bottom ash are less suitable for geopolymerization than the two fly ashes. The bottom ash had a large LOI (Table 3.1), indicating a high unburnt carbon content, which hinders reactivity, and both the economizer and bottom ash had lower amorphous content than the two fly ashes. In addition, they contained lower concentrations of almost every trace element of concern than the two fly ashes (Table 3.3), meaning that stabilization is less of an issue for these ashes. The two fly ashes (FA-H and FA-B) are likely significantly more reactive and contained higher metal contents, so the focus of the majority of the experimental testing was on these materials.

Based on the observed phase assemblages and the evolution of porosity (which correlate to effective diffusion coefficients) described earlier, the guidelines and recommendations in Table 4.1 have been constructed. It is important to note that these only consider

solidification, i.e., an emphasis on physical encapsulation. This approach focuses on maximizing the binder mechanical integrity; i.e., a robust analogue of physical encapsulation potential. Chemical stabilization is more complex, but evidence in literature indicates that systems with higher pH are better suited for stabilizing cationic metals, while systems containing alumino-ferrite tri-substituent (AFt, i.e., ettringite) and/or alumino-ferrite monosubstituent (AFm, e.g., monosulfoaluminate and strätlingite) compounds will improve the stabilization of oxyanions (Poon et al., 1985; Provis & van Deventer, 2009; Ioannidis & Zouboulis, 2005; Wieland et al., 2006; Chrysochoou & Dermatas, 2006). Also, isovalent metallic ions may substitute Ca in C-S-H (Díez et al., 1997; Pomiès et al., 2001; Żak & Deja, 2015). While recommendations are based mainly on solidification at the time of design, the data obtained from performance testing and phase analysis of the materials made in this study are compared to predictions of phase assemblages from the models and chemical stabilization suggestions from the literature to validate predictions.

Table 4.1: Recommendations regarding activation solution composition for enhancing fly ash reactions in geopolymer systems. This example considers w/b = 0.45 and a degree of fly ash reaction of about 60 %.

Activation solution	Phase balance	Ion diffusivity
	• Systems should be high in C-S-H (for	
≥ 4 to 8 M NaOH	Ca-rich precursors)	Low
	AFm compounds should be present	
M _s <1.0; M _s > 1.0	• Systems should be high in C-S-H and	
(≥ 4 to 8 M NaOH +	AFm compounds	Low
SiO ₂)	• N-A-S-H compounds should be present	

Based on these recommendations, a preliminary testing matrix was developed. In order to compare geopolymer mixtures to a standard method of solidification/stabilization, it was determined that mixtures should be made with the CCPs combined with portland cement and water, using mixtures that contain 30 % and 60 % CCP by mass and water-tobinder (CCP) ratios of 0.40-0.45. Geopolymer mixtures should be made using 4M and 8M NaOH. In some mixtures M_s should be adjusted to 1.5. Based on results of testing, mixture proportions should be adjusted for workability and adequate solidification.

5. Solidification Testing

Chemical characterization of the CCPs presented in Section 3 identified the mineralogy of the fly ashes and quantified the concentrations of hazardous contaminants within each ash as well as in the portland cement used. These results served as a baseline for assessing the changes in mineralogy resulting during solidification. Physical characterization of the solidified mixtures was performed to evaluate the relative solidification of the materials (strength, porosity etc.), which provides an indication of the potential for diffusion of contaminants from the matrix.

Of the four CCPs obtained for testing, it was found that the two trona-impacted ashes had higher contaminant contents and were of higher concern for stabilization than the economizer ash and bottom ash (Table 3.3). Therefore, most of the experimental testing for solidification/stabilization was completed on fly ash-based mixtures. The performance of geopolymers made with the fly ashes was compared to more traditional mixtures containing portland cement and fly ash.

5.1 Mixtures

Section 4 outlined mixture design suggestions based on thermodynamic modeling for both portland cement-fly ash blends and geopolymers. The actual cement-fly ash blends tested followed these design suggestions and contained CCP, ordinary portland cement (OPC), and de-ionized water, as shown in Table 5.1. CCP/OPC ratios and water-tocementitious material (w/cm) (by weight) were first varied, trial-mixed, and tested to create workable mixture designs. The workability of mixtures was measured through mini-slump testing, with results reported in Table 5.1 (Kantro, 1980). A mixture is considered to have acceptable workability if the mini-slump area is greater than 1500 mm². Very high values of mini-slump area can indicate that a mixture will become inhomogeneous after casting due to settling, but there is no defined value for this limit. CCP characteristics varied, and therefore different mixture designs were chosen for different CCPs in order to optimize workability.

Geopolymer mixture designs also followed suggestions presented in Section 4, and a similar trial-mixture testing was completed with varying NaOH molarity, solution-tobinder (S/B) ratio, and silica modulus (M_s , molar ratio of SiO₂/Na₂O, adjusted by adding fumed silica), resulting in the proportions shown in Table 5.2. In S/B, the solution is defined as the combined solution of water and activator (sodium hydroxide and silica), while the binder is the CCP. All of the mixtures shown in Tables 5.1 and 5.2 have acceptable workability, with the 60% bottom ash/40% cement mixture having only marginally acceptable workability.

Once a mixture design was established, mixtures were made (one or two at a time) and cast into cylinders following ASTM standards C305 (2004) and C192 (2016). The cylinder size from ASTM C192 was modified to a 50mm x 100mm cylinder. Enough cylinders were cast to allow for compression testing at 7 days and 28 days and to complete all leaching and characterization tests. Specimens were cured for 28 days at 100% relative humidity, at 38°C for the first 24 hours and 23°C thereafter. After compression testing, the samples were crushed to less than 2mm and stored in a vacuum desiccator to slow down or stop hydration. All further characterization and leaching tests were completed on 28-day specimens in order to have a standard curing period. Specimens cured for shorter or longer time periods would show different results than those provided in this study.

Sample designation	ССР	% Water (of total by mass)	% CCP (dry weight)	% OPC (dry weight)	w/cm	Mini-Slump Area (mm²)
30% FAH	Fly Ash H	31%	30%	70%	0.45	2,994
60% FAH	Fly Ash H	31%	60%	40%	0.45	2,454
30% FAB	Fly Ash B	29%	30%	70%	0.40	*
60% FAB	Fly Ash B	26%	60%	40%	0.35	*
30% EA	Economizer Ash	29%	30%	70%	0.40	5,614
60% EA	Economizer Ash	29%	60%	40%	0.40	9,507
30% BA	Bottom Ash	25%	30%	70%	0.35	2,717
60% BA	Bottom Ash	26%	60%	40%	0.35	1,465

Table 5.1: Cement paste mixture design and mini-slump area results

*Mini-slump data not available as testing was not completed on these specimens. Mini-slump testing was only completed after it was established that each mix would require a different w/cm.

Sample Designation	Ash	NaOH Concentration	Silica Modulus (M _s)	S/B	Mini-Slump Area (mm²)
4M FAH	Fly Ash H	4M	0	0.55	2,432
4M FAH	Fly Ash H	4M	0.15	0.55	8,317
M _s =0.15					
4M FAH	Fly Ash H	4M	1.5	0.55	15,199
Ms=1.5					
8M FAH	Fly Ash H	8M	0	0.65	2,204
4M FAB	Fly Ash B	4M	0	0.45	2,162
8M FAB	Fly Ash B	8M	0	0.55	1,928

Table 5.2: Geopolymer mixture design and mini-slump area results

5.2 Strength

The US EPA has varying solidification requirements for hazardous waste disposal depending upon the waste being solidified, but for treatment of typical wastes under the Resource Conservation and Recovery Act (RCRA) they require a minimum strength of 50 psi (345 kPa) (EPA, 1996). The UK Environment Agency and Environment Canada have minimum 28-day stabilization requirements of 1 MPa and 440 kPa, respectively, for non-reactive hazardous wastes (Kogbara et al., 2014). While often the goal for geopolymers and cement pastes is to create a solid with high compressive strength so that it can be utilized in construction, the specimens made in this study were made for disposal. Therefore, the goal for solidification in this study was to create specimens with low compressive strength with minimum values in the 500 kPa-1 MPa range.

Strength results for cement pastes and geopolymers are shown in Figures 5.1 and 5.2. Cement pastes had compressive strengths in the 15-20 MPa range, while geopolymers had compressive strengths typically in the 1-10MPa range. Cement pastes were

significantly stronger than geopolymers, which was not surprising since there is a relatively high proportion of cement in these mixtures compared to those used for soil stabilization. Renew et al. (2016) used only 10% OPC by mass, with 60% CCP, and 30% liquid. A higher amount of cement was used in this study to improve stabilization (reduce leaching) rather than for increasing strength. In addition, higher strength of cement pastes could be partially due to the lower w/cm as compared to the geopolymers' S/B. The low compressive strengths of geopolymers more closely align with the requirements for landfill disposal, while cement pastes were much stronger than requirements. All geopolymer specimens had average 28-day compressive strengths of 1 MPa or greater which meets US, UK, and Canadian disposal requirements.

For the results shown in Figures 5.1 and 5.2, two specimens were broken at 7 days, and either two or three were broken at 28 days, with average values shown and the error bars representing the range of results. The mixtures with adjusted silica modulus were replicated, and Figure 5.2 includes results from both sets of tests. It would be expected for the specimens to be stronger at 28 days than at 7 days, but this was not always the case. The discrepancy is likely due to specimen preparation and the low strength of geopolymers. Specimens were prepared in 50 mm x 100 mm cylinders, and the tops were leveled off during casting. The tops of the cylinders were not always level, but neoprene pads were used during compression testing to compensate for this. Compression testing carried out on cylinders with uneven surfaces can yield lower results as load will not be dispersed evenly throughout the cylinder causing it to break faster. In addition, it was found that, due to the low strength of geopolymers, often the edges on the top and bottom of the cylinder would crumble during testing before the main body of the geopolymer actually cracked. Therefore, the strengths are likely artificially low.



Figure 5.1: 7-day and 28-day average compression test results for FAH and FAB cement paste specimens with varying percent fly ash. Error bars indicate range of measured results.



Figure 5.2: 7-day and 28-day average compression testing results for FAH and FAB geopolymer specimens with varying activating solution compositions. Error bars indicate range of measured results.

Amongst geopolymer specimens, 4M NaOH geopolymers were stronger than 8M NaOH geopolymers, and 4M FAB yielded the highest compressive strength, which is correlated with the lowest S/B at 0.45. Increasing the silica modulus has unclear results on compressive strength, as a M_s of 0.15 decreased strength for the 4M FAH, while the effect of M_s=1.5 at 28 days is unclear due to the wide variability in measured results. Therefore, it appears that decreasing the S/B had a larger impact on strength than increasing the M_s. The thermodynamic modeling did not account for varying S/B, but did suggest that 4M NaOH and 8M NaOH-activated systems, with and without added silica, would have adequate strength for solidification, and this prediction was validated by the experimental data.

5.3 Porosity

Increased porosity is generally correlated with increased leaching due to increased permeability as well as a lower degree of reaction resulting in less binding of contaminants in reaction products. Porosity was calculated based upon a difference in weight between specimens saturated with water and isopropanol and dry weight. Samples were completed in duplicate and average values are shown in Table 5.3. Data were only collected for FAH specimens. The data suggest that cement pastes and the 4M $M_s = 1.5$ geopolymer had lower porosity than did 8M geopolymer and the 4M $M_s = 0.15$ geopolymer. However, the measured values are all quite similar, and, as such, are not likely to have a noticeable impact on leaching behavior.

Sample	Porosity (mL/g)
60% FAH Cement Paste	0.40 ± 0.0002
4M M _s = 0.15 FAH	0.54 ± 0.0091
4M M _s = 1.5 FAH	0.40 ± 0.0036
8M FAH	0.55 ± 0.0040

Table 5.3: Porosity results for FAH cement pastes and geopolymers (average of two specimens and range of results shown)

5.4 X-Ray Diffraction

Crystalline phases and amorphous content obtained from XRD for geopolymers and cement pastes can be compared to those found in the raw CCPs and cement to help determine changes responsible for reduced leaching. FAH geopolymer results are shown in Figure 5.3 and Table 5.4, while cement paste and FAB geopolymer results are included in Appendix B. Qualitative and quantitative analyses were completed using Jade and PDXL2 software, respectively. Qualitative analysis determines the phases present in the sample, and quantitative analysis determines the percent of each phase. PDXL2 uses Rietveld analysis to determine phase percent. Some phases present in the raw ashes were also present in geopolymers such as quartz, periclase, calcite and ye'elimite. Quartz and periclase are both insoluble, and their presence in both CCP and geopolymers indicates that they did not react. Quartz and periclase have been found in raw fly ash and reacted geopolymers by others as well (Bankowski et al., 2004; Swanepoel & Strydom, 2002). Calcite concentrations increased from raw CCPs to geopolymers, but the lime peak present in CCPs is absent in the geopolymers. The NaOH used to make geopolymers likely contained carbonate due to dissolution of atmospheric CO₂, so the increase of calcite is not unexpected. Both calcite and C-S-H have peaks at approximately 29.4° 2θ , but the calcite peak would be expected to be much sharper as C-S-H is mostly x-ray amorphous (Scrivener et al., 2015). A portion of the calcite peak could be attributable to C-S-H, but here it is assumed that the whole peak is calcite.

The thenardite present in CCPs is absent after geopolymerization, and a new sodiumbearing phase, sodalite, is present. Sodalite contains chloride, which was expected to be present in the system only at low concentrations. It is possible that the sodalite peaks are a different sodium-bearing phase that does not contain chloride, however chloride could potentially be present in the system as trona is known to react with HCl in flue gas streams. In addition to having a higher sodalite content than other geopolymers, the 8M geopolymer had a higher katoite content as well.

The geopolymer with M_s =1.5 had a higher amorphous content than other geopolymers, which can be associated with its higher strength because the amorphous content is assumed to be the strength-providing N-A-S-H geopolymer phase. The geopolymer with M_s =0.15 had a composition different than that of other geopolymers. It had a large peak at approximately 11° 20, which is attributed to hydrocalumite, but could be hydrotalcite,

AFm solid solution, or a C-A-H phase, though the hydrocalumite peak fits best (Scrivener et al., 2015). Similar to sodalite, hydrocalumite contains chloride and it is likely that chloride is available at such low quantities that forming hydrocalumite would be infeasible. The phase was also present in 4M geopolymers without a silica modulus adjustment, and 8M geopolymers to a lesser extent. Replicate specimens of the Ms=0.15 and Ms=1.5 mixtures confirmed the results shown in Figure 5.3.



Figure 5.3: FAH geopolymer XRD diffractograms at 28 days

5.5 Loss on Ignition

Loss on ignition (LOI) is an indicator of reaction as it can be an approximation of the amount of chemically bound water, i.e. water bound in the reaction products (Fagerlund, 2009). Cement paste and geopolymer samples were heated to 100°C, weighed, then ignited to 1000°C; the mass after ignition was compared to that at 100°C to differentiate bound water from evaporable (free) water. Samples were completed in triplicate, and average values and range of results are shown in Table 5.5. The percentage of bound water in all systems was in the range of 10%. The geopolymer with the highest silica modulus had the largest LOI and cement pastes with 60% CCP had the lowest LOI. All values were somewhat low, with reported literature values around 20-40% for cement pastes (Fagerlund, 2009).

Phase Name	Phase Formula	FAH Phase %	4M FAH Phase %	8M FAH Phase %	4M FAH M _s = 0.15 Phase %	4M FAH M _s = 1.5 Phase %
Amorphous C-S-H/ N-A-S-H	N/A	65.1	61.6	60.8	47.9	70.2
Anhydrite	CaSO ₄	1.6	-	-	-	-
Calcite	CaCO₃	2.3	10.7	10.8	11.5	15.2
Katoite	$Ca_3Al_2(SiO_4)_{(3x)}$ (OH) _{4x}	-	5.7	13.1	-	-
Hydrocalumite	Ca ₂ Al(OH) ₆ [Clx (OH) _x]-3H ₂ O	-	3.8	1.5	13.8	-
Lime	CaO	2.3	-	-	-	-
Merwinite	Ca₃Mg(SiO₄)₂	8.6	3.6	2.1	-	-
Periclase	MgO	4.0	3.2	2.8	4.0	2.6
Quartz	SiO2	9.3	4.2	4.4	11.2	7.7
Sodalite	NaAlSiOCl₂	-	3.0	2.6	-	-
Thenardite	Na ₂ SO ₄	4.1	_	-	-	-
Ye'elimite	Ca4(AIO2)6SO4	2.7	4.3	1.8	-	4.3

Table 5.4: FAH and FAH-geopolymer XRD phases and phase contents at 28 days

Data quality including Rwp, Rp, and Chi² values are shown in Appendix B.

With LOI as an indicator of reaction it would be expected that a higher reaction would be correlated with higher strength. Thus, it was not surprising that 30% fly ash cement pastes were stronger and had a larger LOI than 60% fly ash pastes. In addition, the geopolymer with M_s =1.5 had the highest LOI and had one of the highest strengths, and 4M geopolymers had higher LOI and higher strengths in both cases. However, 4M FAB had the highest strength of all the geopolymers, and it had a lower LOI than 4M FAH. It is possible that a similar amount of solution reacted with geopolymers and cement pastes, but that the phases formed in cement had higher strength than those formed in geopolymers.
Sample	% LOI
30% FAH	10.8 ± 0.05%
60% FAH	9.1 ± 0.05%
30% FAB	10.3 ± 0.52%
60% FAB	9.2 ± 0.14%
4M FAH	11.2 ± 0.18%
4M FAB	10.6 ± 0.24%
8M FAH	10.7 ± 0.15%
8M FAB	9.3 ± 0.44%
4M FAH M _s = 0.15	9.3 ± 0.80%
4M FAH M _s = 1.5	12.9 ± 0.09%

Table 5.5: Geopolymer and cement paste loss on ignition results (average of three specimens and range of results shown)

5.6 Solidification Summary

All geopolymers met the US landfill strength requirements, and XRD and LOI testing suggest that raising the silica modulus to 1.5 increased reactivity compared to the other geopolymers. Results also indicated that 4M geopolymers had a more complete reaction than 8M geopolymers, as indicated by their increased LOI and higher strength. Similar results have been found in the literature for high calcium fly ash-based geopolymers, such as the ones studied here, where it has been shown that increasing the NaOH concentration beyond what is required for dissolution of the fly ash leads to a decrease in compressive strength (Winnefeld et al., 2010, Williamson et al., 2016).

In general, it is expected that a high degree of reaction in cement pastes or geopolymers is beneficial with respect to leaching (i.e. results in less leaching of contaminants) due to the greater potential to form new phases that can physically or chemically bond with contaminants in the ash. Based on the results reported here, geopolymers made with 4M NaOH would therefore be expected to stabilize elements better than geopolymers made with 8M NaOH, and the geopolymer made with 4M NaOH with M_s=1.5 would be expected to perform the best. Following this reasoning, the 30% CCP cement pastes would be expected to outperform the 60% CCP cement pastes due to the higher proportion of cement which ultimately leads to greater reactivity.

The results from geopolymer experimental testing validate the ability of the thermodynamic models to suggest appropriate material proportions for solidification, as all systems tested provided adequate mechanical properties. The models were not able to predict that 4M NaOH-activated CCPs show improved performance over 8M NaOH-activated CCPs, likely because the models are developed for a fixed degree of reaction (at equilibrium) and the experimental samples have different degrees of reaction than those modeled.

6. Stabilization Testing

The test methods used for determining the leaching potential of CCP-based geopolymers and cement pastes are based on the testing protocol developed by researchers at Vanderbilt University in collaboration with the Energy Centre of the Netherlands, the Danish Hydraulic Institute (DHI) and the US EPA (Kosson et al., 2002). The leaching environmental assessment framework (LEAF) includes a series of US EPA SW-846 methods (Methods 1313-1316) that characterize (i) the liquid–solid partitioning (LSP) of contaminants as a function of pH (US EPA Method 1313), (ii) the LSP of contaminants as a function of liquid-to-solid ratio (L/S) using either an up-flow percolation column (EPA Method 1314) or parallel batch extractions (US EPA Method 1316), and (iii) the mass transport rate of contaminant from monolithic or compacted granular materials (US EPA Method 1315) (Garrabrants et al., 2010; EPA, 2013).

The LEAF methods were developed to address concerns for typical single-pH leaching tests such as the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP) that may not represent leaching in realistic environments (Hattaway et al., 2013). The TCLP measures leaching only at a low pH (3-4), while the leachate pH from specimens used in this study can be extremely basic (pH > 12). Due to the high natural pH of the CCPs, cement pastes, and geopolymers, the LEAF testing makes particular sense in this study. The pH variant test was completed on all specimens, followed by the variant L/S testing. Select-flow percolation column dynamic tests were also carried out to gain an understanding of how contaminants leached over time.

In the literature, concentrations of contaminants in landfill leachate are generally compared to the TCLP regulatory levels for determining a hazardous waste (Table 6.1). Materials that leach at concentrations greater than the TCLP regulatory levels are classified as hazardous waste, and are then subject to further restrictions. It should be noted that TCLP only tells you if a material is hazardous or not and does not reflect the real leachate concentrations in landfills, especially for CCPs. It should also be noted that the LEAF test methods do not compare directly to the TCLP test methods. For instance, the L/S used in the TCLP method is 20, while the pH variant test (EPA Method 1313) in the LEAF methodology uses an L/S of 10. Results are presented with the TCLP requirements in mind, as current regulations have not yet been updated to reference testing methods other than the TCLP.

Leaching test results are presented using different formats for varying pH and liquid/solid (L/S) testing. Results are presented in Appendix C as raw concentrations, with the resulting elemental concentrations plotted against either pH or L/S. Results are also normalized by total metal concentration in the ash and cement (Table 3.3) to show percent leaching. Several elements were present in the OPC at high enough concentrations to affect the results, and impacts are mentioned where relevant. The normalization is important because, without it, results would be biased toward systems that did not contain as much of the contaminants in the original mixture.

Element	TCLP Regulatory Level (mg/L)		
Arsenic	5.0		
Barium	100.0		
Cadmium	1.0		
Chromium	5.0		
Lead	5.0		
Mercury	0.2		
Selenium	1.0		
Silver	5.0		

Table 6.1: TCLP leachate concentration regulatory limits for an L/S of 20

6.1 pH and L/S Testing Methodology using LEAF protocol

The goal of applying EPA Method 1313 was to determine the leaching of different constituents of potential concern (COPCs) in a pH range of 2-13. 125 mL high-density polyethylene (HDPE) bottles were used for pre-titration and 250 mL HDPE bottles were used for the full scale batch test. Nitric acid (HNO₃, 67-70% w/w, Trace Metal, Fisher) was used to adjust the pH in each bottle. Two blanks were run with each test. One blank was run with pure reagent water (MPW or simulated landfill leachate) and one with reagent water plus the maximum amount of nitric acid required to reach the lowest pH. Tests were run with a liquid/solid (L/S) ratio of 10.

For a particle size of <2 mm, the method calls for a total of 360 mg (dry weight) per test. Given the large number of samples in our matrix, the method was modified to use 180 mg (dry weight) per test to save raw CCPs and to reduce the amount of material required to be crushed. The L/S ratios were maintained; the amount of material and eluent were reduced proportionately. Thus, the results should be equivalent.

Samples of 20 g (dry weight) were added to pre-weighed and labeled bottles, followed by reagent water (MPW or simulated landfill leachate) and nitric acid. Reagent water was added by weight assuming a density of 1.0 g/mL, and nitric acid was added by pipette under a fume hood. Bottles were weighed after the addition of each new component.

Bottles were placed into a rotator at 38 ± 2 rpm for 48 ± 2 hours. Note that the leaching time used in our experiments conducted under EPA Method 1313 were longer than the TCLP equilibration time of 18 ± 2 hours. Thus, there is potential for increased leaching over the longer time period. The 48 hour clock was begun when the rotator was turned on. After 48 ± 2 hours, bottles were removed from the rotator and allowed to settle for 10-15 minutes before testing and sample collection.

The goal of EPA Method 1316 testing was to assess leaching from different COPCs for various liquid/solid (L/S) ratios. For a particle size of <2 mm, the method calls for a total of 1.5 kg (dry weight) per test. This protocol was again modified; we did not perform a

test with L/S of 0.5 and added a test with L/S of 20. The latter test was conducted to match the TCLP test, and the 0.5 L/S was excluded because the mixtures adsorb a significant amount of water, which limits extractable water. This change resulted in reducing the amount of material required per test compared to the standard Method 1316. It should be noted that only one of the five samples per test was modified, for which a minimum dry weight of 10 grams was used versus 20 grams. Thus, a total of 370 mg (dry weight) were required per test. Tests were run with L/S ratios of 1, 2, 5, 10, and 20. One blank was run with pure reagent water (MPW) for each test.

Cement paste and geopolymer specimens were added to pre-weighed and labeled fluorinated ethylene propylene (FEP) bottles, followed by reagent water (MPW). Both 250 L and 1L FEP bottles were used depending upon the amount of specimen required. Reagent water was added by weight, assuming a density of 1.0 g/mL. Bottles were weighed after the addition of each new component.

Bottles were placed into a rotator at 38 ± 2 rpm for 48 ± 2 hours. The 48 hour clock was begun when the rotator was turned on. After 48 ± 2 hours, bottles were removed from the rotator and allowed to settle for 10-15 minutes before testing and sample collection.

6.2 Leaching of Major lons

From the oxide composition data in Table 3.1, the major components of the cement and geopolymer systems are known to be aluminum, silicon, and calcium. The presence of these ions is therefore expected in solution after a leaching test. While these major ions are unregulated, and their leaching is not considered harmful to the environment, tracking the concentrations of these ions can provide an understanding of how the leaching conditions break down reaction products in the cement pastes and geopolymers. For example, dissolution of mixed or co-precipitates containing major ions and heavy metals could lead to increased leaching and phase transformations, whereas reduced concentrations of major ions are indicative of formation, transformations, and changes in crystallinity of precipitates.

Figure 6.1 shows measured calcium and aluminum leachate concentrations with varying pH, and Figure 6.2 shows calcium, aluminum, and silicon leachate concentrations with varying L/S for the different geopolymers tested. Calcium concentrations can be seen to dramatically increase with a slight decrease in pH, and then mostly level off, while aluminum leached at high concentrations at both low and high pH, reaching a minimum around pH 7. The leveling off of calcium is likely an indication that most available calcium had leached into the system by around pH 8, and below pH 8 there was either no remaining calcium or it was strongly bound into a phase. The change in aluminum concentrations with pH closely follows typical aluminum solubility diagrams, and is, therefore, what would be expected. At low pH, the increase in aluminum concentration is an indication of the breakdown of geopolymer matrices and, thus, a corresponding

increase in leached metal ions is expected. Conclusions are applicable only to geopolymers tested and not to cement pastes.



Figure 6.1: Calcium (a) and aluminum (b) in aqueous solution versus pH with an L/S of 10 for FAH and FAB geopolymers with 4M and 8M activating solution

Major ion concentrations were determined for both pH and L/S testing. One sample in each of these tests was conducted under similar conditions to assess repeatability. This is the sample with an L/S of 10 and no acid added. Since the L/S is the same in both tests, the ultimate pH and leachate concentrations would also be expected to match. Table 6.2 shows that similar leachate concentrations of aluminum and calcium were obtained when extracted from samples with comparable L/S and pH values. These results support the validity of these test methods and confirm our hypothesis that reducing the masses used in the pH testing did not impact the results.

6.3 Leaching of Oxyanions

The three elements that may possibly form oxyanions that leach from geopolymers are Cr, As and Se. However, under oxidizing conditions it is expected that Cr will be present as Cr(III), which is more likely to be found as a cation in aqueous phases formed from dissolution of fly ash. Thus, the focus of investigation of oxyanions was on As and Se species.

6.3.1 Arsenic

As discussed in Section 2, As(V) is the dominant form of arsenic in coal fly ash (Huggins et al., 2007). Even though arsenic forms oxyanions in aqueous environments and is expected to leach at high pH, results indicate that "increased destruction of the cement matrix at low pH has more effect on the leachate arsenic concentration than the increased solubility (of arsenic mineral phases) at high pH" (Leist et al., 2003a). Thus, leaching of arsenic at both high and low pH is of concern.



Figure 6.2: Calcium (a), aluminum (b) and silicon (c) in aqueous solution versus L/S at natural pH (ranging 12-13) for FAH and FAB geopolymers with 4M and 8M activating solution (note that y-axes are different between plots to better visualize the data). Vertical lines represent the L/S for which pH variable leaching tests (EPA Method 1313) were carried out.

Geopolymer	Collected Values	1313 (pH Testing)	1316 (L/S Testing)
4M FAH	L/S	9.0	10.0
4M FAH	рН	12.69	12.55
4M FAH	Al (mmol/L)	8.20	5.24
4M FAH	Ca (mmol/)	0.23	0.34
4M FAB	L/S	9.4	11.0
4M FAB	рН	12.41	12.52
4M FAB	Al (mmol/L)	5.06	3.44
4M FAB	Ca (mmol/)	0.62	0.45
8M FAH	L/S	10.6	10.7
8M FAH	рН	12.40	12.28
8M FAH	Al (mmol/L)	2.71	2.04
8M FAH	Ca (mmol/)	0.18	0.18
8M FAB	L/S	10.7	10.8
8M FAB	рН	12.53	12.58
8M FAB	Al (mmol/L)	3.05	2.08
8M FAB	Ca (mmol/)	0.27	0.29

Table 6.2: Comparison of aluminum (mmol/L) and calcium (mmol/L) concentrations at similar pH and L/S values from two different tests (EPA Method 1313 and 1316)

Figure 6.3 shows arsenic concentrations in leachate from FAH ash, geopolymer and cement paste specimens versus pH and L/S. Graphs for FAB specimens are included in Appendix C and are similar to those for FAH. The main difference between FAH and FAB specimens was that FAH specimens leached more than FAB specimens, and this is attributed to the higher arsenic concentrations in FAH as determined from digestion (Table 3.3).

Figure 6.3 clearly shows that arsenic leached at both high (>12) and low (<5) pH, and it also shows that the highest concentrations were obtained with a low L/S, and lowest concentrations were obtained at mid-range pH (6-10). The raw ash in particular produced high leachate concentrations at low L/S, while the geopolymers and cement pastes were able to reduce leaching in this scenario. The raw ash exceeded the TCLP limit of 5.0 mg/L for arsenic put forth by the US EPA at low L/S (a more stringent condition than the TCLP L/S of 20), but the limit was never exceeded by geopolymer or cement pastes even under stringent conditions (Figure 6.3). Yet when viewed as percent leached, the 8M geopolymers actually leached a higher percent of the total As present compared to the raw ash (Appendix C). Conversely, 4M geopolymers and cement pastes performed better than raw ash, even when viewed as percent leached. This ties back to indications from experimental results (LOI and strength results in Section 5) that the 4M geopolymers had higher reactivity than 8M geopolymers so that reduced heavy metal leaching would occur in 4M geopolymers.



Figure 6.3: Arsenic concentrations in leachate from FAH cement paste and geopolymer specimens with an L/S of 10 versus pH (a) and at natural pH versus L/S (b) (note that y-axes are different between plots to better visualize the data). Graphs (c) and (d) show arsenic concentrations in leachate as percent of the total arsenic present in the system. The horizontal and vertical dotted lines represent the arsenic TCLP limit and the L/S for which the TCLP limit applies, respectively.

Notably, cement pastes performed significantly better than all tested geopolymers at high pH for both FAH and FAB specimens. As discussed in Section 2, matrices with a high calcium content have been shown to stabilize arsenic better than low-calcium mixtures, and cement mixtures have generally outperformed geopolymers (Provis & van Deventer, 2009; Dutré & Vandecasteele, 1998; Leist et al., 2003a). The main factor in arsenic stabilization in both cement and geopolymer specimens is likely the formation of low solubility calcium-arsenic precipitates as opposed to binding to silica and alumina (Dutre & Vandecasteele, 1998; Leist et al., 2003b). While both FAH and FAB had high calcium contents for coal fly ash (approx. 25% CaO), the OPC had over twice this concentration at 62.5% CaO, and subsequently it is not surprising that cements outperformed geopolymers at high pH.

6.3.2 Selenium

Selenium is typically found in reduced form as Se(IV) in coal ash (Huggins et al., 2007). Figure 6.4 shows selenium concentrations in leachate from FAH and FAB raw ash, geopolymer, and cement paste specimens versus pH. Graphs showing concentration versus L/S are included in Appendix C with similar trends in performance of the mixtures as shown in Figure 6.4 (e.g. the mixture with $M_s = 0.15$ reduced leaching the most in both tests). For FAH specimens, it is apparent that geopolymers and cement pastes reduced leaching as compared to the raw ash across a wide pH range. For FAB specimens, geopolymers reduced leaching at mid and low pH, but leached more at high pH than did the raw ash. However, at high pH and low L/S (Figure 6.4 (e) and (f)), geopolymers were again able to reduce leaching as compared to the raw ash. It was only under the high L/S, high pH condition that geopolymers performed worse than the raw ash. It is unclear why geopolymers were successful in stabilizing selenium across the board in FAH specimens but not in FAB specimens.

With regards to regulations, the 1.0 mg/L TCLP limit for selenium was exceeded by raw ashes and most specimens under the more stringent conditions used in this research, but at the TCLP L/S of 20, none exceeded the limit (Appendix C and Figure 6.4 (e) and (f)).

Similar to arsenic, cement pastes stabilized selenium at high pH better than geopolymers. Results in the literature for selenium stabilization range from similar leaching in both fly ash and geopolymers, to reduced leaching in geopolymers, but not by a large amount (Álvarez-Ayuso et al., 2008; Bankowski et al., 2004; Kupwade-Patil et al., 2014). In high calcium systems (e.g. OPC), reduced leaching of selenite and selenate has been found in soils through the precipitation of calcium selenite hydrate (CaSeO₃·H₂O) and selenite substituted into ettringite (Ca₆Al₂(SeO₄)₃(OH)₁₂·26H₂O) as shown by SEM-EDX and XRD (Hyun et al., 2009). Reducing leaching in high calcium systems (i.e. cement paste systems) is therefore in accordance with the literature, and geopolymer results in this study are promising, as FAH specimens were able to reduce selenium leaching across a wide pH range.



Figure 6.4: Selenium concentrations in leachate from FAH (a) and FAB (b) raw ash, cement paste and geopolymer specimens with an L/S of 10 versus pH. Graphs (c) and (d) show selenium concentrations in leachate as a percent of the total selenium in the system. The selenium TCLP limit is 1.0mg/L (or 1000 μ g/L using units shown in the plot).: Graphs (e) and (f) shown selenium concentrations in leachate with varying L/S.

6.3.3 Oxyanion Summary

Arsenic and selenium leaching varied across pH and L/S. Arsenic tended to leach at both low and high pH while selenium leached noticeably more at high pH than at low pH. FAH geopolymers were able to reduce selenium leaching across the entire pH range compared to raw fly ash, and both FAH and FAB geopolymers reduced arsenic leaching at low L/S values. Specifically, geopolymers were able to keep arsenic levels below the TCLP limit at low L/S values, where the raw ash exceeded the limit. 4M geopolymers tended to outperform 8M geopolymers for both elements, and thus they are the preferred option for oxyanionic wastes. While cement pastes bound both arsenic and selenium better at high pH compared to geopolymers, geopolymers are the preferable matrix as OPC systems incorporate less fly ash into the resulting solid, which ultimately takes up more space in the landfill. The improved performance of cement systems at high pH was expected based upon the literature, as high calcium systems have been shown to bind oxyanions better due to the formation of insoluble calcium compounds (Provis & van Deventer, 2009; Dutré & Vandecasteele, 1998; Leist et al., 2003b). Ultimately, geopolymers were successful at reducing arsenic and selenium leaching from the fly ashes under a number of conditions.

6.4 Cations

A number of cationic heavy metals are present in fly ashes including Cd, Cu, Co, Ni, Pb, Zn and Cr. The most common oxidation state of these elements is Me(II) with the exception of Cr(III). In addition, all of these elements tend to form hydroxide, carbonate and sulfide precipitates with pH dependent solubility. Thus, it is not surprising that the trends in behavior of these elements was found to be similar.

6.4.1 Chromium

Chromium can be present in either of two major oxidation states, Cr(III) and Cr(VI), of which hexavalent Cr(VI) is the most toxic and the most mobile (Provis & van Deventer, 2009). The majority of chromium expected to be present in the fly ashes is Cr(III), which is a cation (USGS, 2015). Chromium is a known carcinogen with toxic effects to a number of human body systems (CDC, 2011). Fortunately, Cr(III) is the dominant form found in coal ash, though Cr(VI) can be found in small percentages (USGS, 2015).

Figure 6.5 shows that the raw ash leached chromium at both low and high pH, whereas tested geopolymer and cement specimens only leached at low pH. Leaching at low pH is expected as $Cr(OH)_{3(s)}$ dissolution occurs at low pH, chromium sorption is reduced at low pH, and aluminum phases dissolve at low pH. However, if a chromium hydroxide phase were controlling the concentrations, mg/L concentrations of Cr would be expected at pH 5 for the amorphous hydroxide phase. Results from these tests suggest that dissolution is either slower or a more crystalline or mixed phase precipitate is present in the raw fly ash. It can easily be seen that all tested specimens reduced chromium leaching at high

pH. In particular, the raw ash exceeded the 5.0 mg/L TCLP limit at low L/S, whereas geopolymer and cement specimens did not come close to the limit. The same results were obtained for FAB specimens (Appendix C). At mid-range pH (6-10), very little leaching occurred for all specimens. From Figure 6.1, both calcium and aluminum concentrations in geopolymer leachate were higher at low pH than at high pH, so the potential breakdown of a mixed phase precipitate within the fly ash or geopolymer could be partly responsible for increased chromium leaching at low pH.



Figure 6.5: Chromium concentrations in leachate from FAH ash, cement paste and geopolymer specimens with and L/S of 10 versus pH (a) and at natural pH versus L/S (b). Graphs (c) and (d) show chromium concentrations in leachate as a percent of the total chromium in the system. The horizontal and vertical dotted lines represent the arsenic TCLP limit and the L/S for which the TCLP limit applies, respectively.

Cement pastes and geopolymers performed similarly across pH and L/S ranges, and unlike arsenic and selenium, 8M geopolymers tended to slightly outperform 4M geopolymers, though the difference was small. In the literature, chromium has been successfully stabilized with OPC and geopolymers (Guo & Shi, 2013; Zhang et al., 2008a). The main methods proposed in the literature for chromium stabilization are thought to be the

formation of insoluble chromium hydroxides, calcium chromium hydroxide complexes, and calcium chromate (Ca₂CrO₄), though it has been suggested that Cr(III) could be replacing aluminum in octahedrally-coordinated calcium aluminate hydrate (C-A-H) (Glasser, 1997). The main take-away is that all geopolymers and cement pastes were able to significantly reduce chromium leaching at high pH as compared to the raw ashes, especially at low L/S.

6.4.2 Other Cations

In coal fly ash, the majority of heavy metal cations (Cd, Cu, Co, Ni, Pb, Zn) are generally found in the 2+ oxidation state. As cations, these elements are more effectively precipitated out in the mid to high pH range and were found to behave similarly in cement and geopolymer systems as shown in Figure 6.6 and cation graphs in Appendix C.

Figure 6.6 shows cadmium as an example cation where leaching increased below pH 7. For some elements the pH was lower than 7 before any significant leaching occurred. Table 6.3 shows the approximate pH at which each element showed an increase in leaching. For each element FAH and FAB specimens gave similar results, and additional graphs are included in Appendix C. In general, geopolymers and cement pastes leached less at low pH than did the raw ash, which is considered a successful stabilization. Different geopolymers performed better for some elements than others, but especially at high pH, concentrations were low enough to consider all geopolymers successful.

Figure 6.6 shows cadmium concentrations as a percent of total cadmium in the system (total cadium concentrations are documented in Table 6.4). The OPC used for cement pastes contained many of the cations tested, as indicated in Table 3.3, and this became clear at low pH. In many cases, the cement pastes were leaching at higher concentrations than would be possible if the OPC did not contain any metals. To account for this, concentrations of elements within the OPC were included in the normalized graphs to show percent leaching.

Element	pH of Increased Leaching
Cd	<7
Со	<7
Cu	<5
Ni	<7
Pb	<4
Zn	<6

Table 6.3: pH of increased leaching for cations



Figure 6.6: Percent cadmium leached from FAH (a) and FAB (b) raw ash, cement paste and geopolymer specimens with an L/S of 10 versus pH. The cadmium TCLP limit is 1.0mg/L.

Table 6.4: Total cadmium in cement paste and geopolymer specimens from which
percentages for Figure 6.6Error! Reference source not found. are calculated

FAH Specimen	Total Cadmium	FAB Specimen	Total Cadmium
	(µg)		(µg)
30% FAH Cement	4.8	30% FAB Cement	4.5
Paste		Paste	
4M FAH	24.1	60% FAB Cement	5.9
		Paste	
8M FAH	21.0	4M FAB	20.2
4M FAH Ms=0.15	21.7	8M FAB	17.3
4M FAH Ms=1.5	21.5		

In the literature, experiments have achieved strong stabilization of cations in both OPC and geopolymer systems at high pH, agreeing with the results of this study (Akhter et al., 1990; Zhang et al., 2008a). As would be expected, studies have found low binding of cations at low pH, with metal leachate concentrations generally following the solubility profile of formed hydroxides (Kogbara et al., 2014; Li et al., 2001).

The literature also suggests that mixed calcium metal hydroxides are forming in OPC systems and being incorporated into the cement paste, further decreasing leaching at mid and high pH (Diez et al., 1997). Some promising results also show that copper, cobalt, and nickel have been incorporated into a kaolinite-based geopolymer network, and zinc has been shown to bond with silica and oxygen in geopolymer-like environments, but these results have not been directly correlated to reduced leaching at low pH (Anseau et al., 2005; Hanzlicek & Steinerova-Vondrakova, 2006).

6.5 Dynamic Testing

In addition to the pH and L/S variant tests described earlier, a few up-flow column tests (EPA Method 1314) were performed on crushed cement pastes over a period of approximately two weeks. Four 5 cm x 30 cm borosilicate glass columns with polypropylene filters covering either end were connected to a Cole Parmer Masterflex pump via 1/16 in polytetrafluoroethylene (PTFE) tubing. PTFE tubing was connected to 0.89 mm Viton tubing at the pump head via PTFE adaptors. Teflon tape was used over adaptors to prevent leaking.

Cement pastes were sieved to 1-2.38 mm to obtain a column diameter to particle diameter ratio of 20. 300 g (dry weight) of material was added to the column with a layer of silica sand at the bottom and top to fill remaining space. PTFE tubing was attached to the top of the column and led into 1L or 250 mL FEP bottles. The entire set up was placed in a fume hood.

Eluent was either Millipore water or simulated landfill leachate and was pumped at a rate of approximately 0.16 mL/min. Components of the simulated landfill leachate are outlined in the next section.

Results from the dynamic tests indicate how quickly contaminants are released from the pastes into the environment. However, it should be noted that these tests were conducted with crushed materials which could accelerate the leaching process. Monolith tests such as EPA 1314 were not conducted as part of this research. Results were obtained for FAH, FAB and bottom ash cement pastes. These tests were conducted using Millipore water or a simulated landfill leachate as the source water. Thus, there was little buffering of the water and the pH of the water increased to above 12 as it passed through the column.

Figure 6.7 shows selenium and chromium concentrations in leachate collected from the up-flow column over time. Two typical trends were noticed among the graphs: 1) when initial leachate concentrations were high, they dropped off quickly, 2) when initial concentrations were low, they were maintained at this level for a larger cumulative L/S. The first trend is noticeable for selenium leaching from the 60% FAH paste, and the second trend is noticeable in chromium leaching from the 60% FAH paste. Most elements followed the trend of highest concentration at low L/S, to lowest concentration at high cumulative L/S, which was expected as the contaminants leached out over time until there was no more left to leach. The bottom ash cement pastes had notably less leaching of oxyanions (selenium and arsenic) than did the fly ash based pastes. Plots for additional elements are shown in Appendix C.



Figure 6.7: Selenium (a) and chromium (b) total concentrations in collected leachate from an up-flow column set up versus cumulative L/S with either Millipore water (MPW) or the simulated landfill leachate (GW) as the source water (note that y-axes are different between plots to better visualize the data and that the data for chromium here are in µg while in Figure 6.5 the chromium data are in mg)

Comparing the results in Figure 6.7 to those from the batch tests for selenium and chromium in Figures 6.4 and 6.5, respectively, it is clear that the concentrations are much lower in the dynamic tests than in the batch tests. Dynamic tests more accurately simulate the hydrodynamics of field scenarios, and contact times between the water and solid particle surfaces can be significantly lower in flow through experiments. The use of 1-2.38 mm particles in these experiments represents a conservative approach, as the area for water/surface contact is greater than would be expected compared to the stabilized masses that would be produced during solidification/stabilization. Further studies using undisturbed, consolidated blocks (per EPA method 1315) could provide more realistic conditions and may be worth pursuing now that optimal preparation conditions have been identified.

6.6 Leaching in Simulated Landfill Leachate

The results outlined in sections 6.1-6.5 were completed using reagent water (Millipore Water, MPW). Leaching tests were also completed with a simulated landfill leachate to more accurately emulate leaching in a landfill environment. Simulated landfill leachate components were based upon (Ghosh et al., 2006) who examined typical municipal landfill leachate extracts. There are wide range of typical values, so median values were chosen, shown in Table 6.5.

A majority of the elements examined in this study did not show any differences in leaching between reagent water and the simulated landfill leachate. However, selenium, and more notably copper, tended to leach more in the landfill leachate than in the reagent water, which could be a concern for wastes with high concentrations of these elements.

Component	Concentration (mmol/L)	Source
Bicarbonate	30	NaHCO₃ (Sigma-Aldrich, ACS grade, 99.7%)
NOM	400 mg/L (as TOC)	Aldrich Humic Acid [™]
Hydroxylamine Hydrochloride	0.4	NH ₂ OH-HCl (Aldrich, 99.999% trace metal)
Silicate	0.3	Silicic Acid (Sigma-Aldrich, 99.9%, 20μm)
Mg	4.1	MgCl ₂ -6H ₂ O (Amresco, ACS grade)
Са	2.5	CaCl ₂ (Spectrum, FCC grade, Anhydrous)
Phosphate	0.02	NaH ₂ PO ₄ (Fisher, >99%, Anhydrous)
Sulfate	2.6	Na ₂ SO ₄ (Fisher, ACS grade, Anhydrous)
Background ions (Ionic Strength = 0.1M)	42.3	NaNO₃ (Sigma-Aldrich, ReagentPlus, >99.0%)

Table 6.5: Landfill leachate composition

Figure 6.8 shows the percent selenium leached from FAH geopolymer systems in reagent water and the simulated landfill leachate. Selenium appeared to leach slightly more in the simulated landfill leachate than reagent water at high pH. The trend shown in Figure 6.8 is more obvious in geopolymers that contained a higher silica modulus (Figure 6.8 (a)) than those where the silica modulus was not adjusted (Figure 6.8 (b)).

Landfill leachate can contain bicarbonate, phosphate, sulfate, silicates, and natural organic matter (NOM) (Christensen et al., 2001; Ghosh et al., 2006). In general, it is thought that the presence of additional ions in landfill leachate could cause competition for adsorption sites onto solid materials, increase aqueous complexation and increase leaching of trace elements. However, the few studies that have tested leaching with background ions generally showed either no difference between de-ionized water versus solutions containing salts, or less leaching in the salt solution (Zhang et al., 2008a; Zhao et al., 2017). In contrast, NOM has been shown to have greater effect on leaching from CCPs. NOM can bind with elements and form both adsorbable and non-adsorbable complexes, which can either increase leaching (As) or decrease leaching (Sr, Mo, V) of different elements (Zhao et al., 2017). Dissolved organic carbon (DOC) has been shown to increase leaching of copper from raw CCPs (Van Zomeren & Comans, 2004), which is consistent with the results of this work.



Figure 6.8: Percent selenium leached in reagent water and simulated landfill leachate from FAH geopolymer specimens with $M_s>0$ (a) and $M_s=0$ (b) with an L/S of 10 versus pH Among cations, copper showed increased leaching in simulated landfill leachate in all tests and across a wide pH range. Figure 6.9 shows the percent copper leached from FAH and FAB specimens in reagent water versus the simulated landfill leachate. It can clearly be seen that more copper leached in the landfill leachate than in reagent water. Studies have shown that copper binds with NOM, and it is expected that the copper in the fly ash was complexing with NOM keeping it dissolved in solution (Wang et al., 2015; Holm 1990).



Figure 6.9: Copper in reagent water and simulated landfill leachate from FAH (a) and FAB (b) geopolymer specimens with an L/S of 10 versus pH

As there were many components in the simulated landfill leachate, it was difficult to determine effects of a single component on the leaching of various elements. However, the simulated landfill leachate did not drastically change leaching results as compared to reagent water. The difference in selenium leaching was minimal, and while the change in

copper leaching was more significant, total copper leaching at mid-range pH was low at less than 2%.

6.7 Summary

Of the four examined CCPs, the two trona-impacted ashes (FAH and FAB) contained the highest contaminant content and therefore stabilization of these ashes was a higher concern than for the economizer and bottom ash. Thus, the fly ashes were used to make a majority of the geopolymer and cement specimens tested.

Results from leaching tests are summarized here. It should be noted that the contaminant levels assessed in leachates were normalized by the original amounts in the constituent materials, including OPC, so as to not unfairly bias results for samples containing different amounts of fly ash.

- 4M geopolymers reduced arsenic leaching more than 8M geopolymers at high pH and low L/S.
- FAH geopolymers reduced selenium leaching across the entire pH range. FAB geopolymers reduced selenium leaching in mid-range pH and at low L/S.
- All geopolymers successfully stabilized chromium at high pH, and none performed significantly better than another.
- 4M and 8M geopolymers tended to perform equally well for divalent cations, with 4M geopolymers performing better in some cases and 8M geopolymers performing better in others. All concentrations for cations tended to be low, including concentrations in leachate from raw CCPs. In many cases, such as for Pb, the concentrations across the pH range were well below those predicted by hydroxide solubility.
- While increasing the silica modulus to 1.5 made the geopolymer less porous, no consistent differences were found in leachate from 4M geopolymers where the silica modulus was not adjusted versus that where $M_s = 1.5$.
- At high pH, cement pastes outperformed geopolymers for leaching of arsenic and selenium.
- Contaminant concentrations in dynamic tests were lower than in static tests, suggesting that even lower concentrations of contaminants would be released in the field than were measured in the static tests.
- Aqueous copper concentrations were higher in simulated landfill leachate than in reagent water, suggesting aqueous complexation with NOM moieties. Selenium concentrations were also slightly increased at high pH values.

7. Assessment of Solubility-Informed Design Methodology

7.1 Microstructure characteristics of the geopolymer systems

The experimental data show qualitative agreement with some aspects of the predictions from thermodynamic calculations. However, such agreement (or lack thereof) should be examined in the context of the role of: (i) reaction kinetics, which are not considered in the thermodynamic calculations, and, (ii) the role of carbonation and alkali binding, such can alter the pH and induce phase transformations in hydrated geopolymer systems.

7.1.1 Reaction Kinetics

The "equilibrium" nature of thermodynamic calculation makes no consideration of reaction rates (i.e., of the rates at which the precursors may react to form hydrated solids, the rate of hydrated solid dissolution, the rate of microstructural degradation, or any other kinetic processes). The x-ray diffraction analysis of the geopolymer samples at 28 days displays substantial unreacted ye'elimite, quartz, merwinite and periclase (Figure 5.3, Table 5.4). While, it may not be surprising to detect unreacted 'low reactive' minerals such as quartz, the presence of high amount of unreacted ye'elimite, a fairly reactive mineral phase (Hargis et al., 2014), indicates that the degree of reaction of the fly ash is likely less than the 60% that has been assumed for the thermodynamic simulations (Section 4.1). The loss on ignition data in Table 5.5 provides insight on the relative degree of reaction of the fly ash, but the actual percentage of fly ash reacted cannot be extracted based on current assessments.

Although thermodynamic calculations do not assess the mechanical integrity of potential immobilization solutions systems, they offer a reasonable means to estimate relevant parameters, such as the porosity, which are influential in estimating both mechanical behavior (strength) and transport response (Mai & Cotterell, 1985; Chen et al, 2013; Provis et al., 2014). The limited porosity data from experimental results (Table 5.3) show similar trends to the calculated data (Figure 7.1a), wherein porosity decreases with increasing alkalinity and silica modulus (M_s) of the alkali activation solution. While the values are different at low M_s, better agreement is noted at high M_s, wherein the higher abundance of reactive silica ensures improved progress of reactions. As shown in Figure 7.1b, however, since the extent of fly ash reaction strongly influences capillary pore volume, it is likely necessary to achieve about 50 % fly ash reaction before the capillary porosity diminishes substantially enough to improve mechanical properties (Ben Haha et al., 2011). While this aspect is not addressed herein, it requires an assessment of the period (i.e., the chemical reactivity of the fly ash (Oey et al., 2017)) that needs to elapse before this extent of reaction occurs.



Figure 7.1: (a) The coarse porosity as measured experimentally (Table 5.3) and estimated by thermodynamic calculation. Expectedly, porosity decreases with an increase in M_s of the activation solution, due to enhanced formation hydrated compounds (Hillel, 2004). The values are different at low Ms, but, better agreement is noted at high Ms, wherein the higher abundance of reactive silica ensures improved progress of reactions. (b) The evolution of the capillary (coarse) porosity as a function of the extent of fly ash reacted in an alkali activated fly ash system produced using 4 M and 8 M NaOH solutions at w/b = 0.50

7.1.2 Role of Carbonation

As seen in the x-ray analysis (Figure 5.3, Table 5.4), the geopolymer samples are partially carbonated, since no attempts are made to exclude CO₂ contamination during the handling of hydrated cementitious systems (Taylor, 1997), hence the observed differences in calculated phase assemblage under CO_2 -free conditions (Figure 7.2a). As seen in Figure 5.3, the quantity of calcite increased and 'hydrocalumite-like' carboaluminate phase formed in the geopolymer samples, due to partial carbonation. Figure 7.2 (b) illustrates the influence of CO_2 -contamination on the phase assemblage: the siliceous hydrocalumite-like phase, C_2ASH_8 (i.e. strätlingite (Okoronkwo & Glasser., 2016a), Figure 7.3a) is readily replaced by the stable member, $(C_4ACH_{11}/CAc_{0.5}H_{12})$ (carboaluminate hydrate (Matschei & Glasser, 2010), Figure 7.2b) of the same family; this has been identified as hydrocalumite in the XRD patterns of the geopolymer samples (Figure 5.3). The C-S-H is partially decomposed and the excess silica re-enters into reaction to form more N-A-S-H (sodium-alumina-silicate hydrate) gel and siliceous hydrogarnet (Okoronkwo & Glasser, 2016b), identified as katoite in Figure 5.3. Siliceous katoite is usually suppressed during thermodynamic calculation in GEMS (Gibbs Energy Minimization Software, used for the simulations) to enable acceptable convergence (Lothenbach, 2010). While, CO₂-contamination could be undesirable in cementitious systems, especially for structural applications involving the use of steel reinforcing bars (Talakokula et al., 2016), it appears to be beneficial for high calcium alkali-activated fly ash system, like those used in this study due to its role in enhancing solid volume (Shi et al., 2006).



Figure 7.2: The hydrated phase assemblage of simulated systems with: (a) negligible carbonation, and, (b) exposure to significant carbonation. This example, and the calculated volume balances assume that the fly ash is 60 % reacted as is reasonable for a mature alkali activated formulation (Provis & Rees, 2009; Rees et al., 2007). The minerals are labeled following standard cement chemistry notation: $A = Al_2O_3$, $c = CO_2$, C = CaO, $F = Fe_2O_3$, $H = H_2O$, M = MgO, $N = Na_2O$, $s = SO_3$, $S = SiO_2$

7.2 Resistance of geopolymer matrix to degradation during leaching

To assess the relative resistance of the geopolymer systems to dissolution, the solid phase assemblages were exposed to simulated leaching, following EPA's LEAF 1313 and 1316 protocols (Kosson et al., 2002; EPA, 2013), similar to the experimental tests. The geopolymer systems were first subjected to simulated leaching as a function of the liquid (leachant)-to-(reactant) solid (I/s) ratio. In general (Figure 7.3a), at a critical dilution level (I/s), the internal pH of the system decreases abruptly, and solid phases begin to rapidly dissolve. For example, for an 8 M NaOH-activated system, C-S-H begins to dissolve rapidly at l/s \approx 0.1 ml/g, and dissolved ions react with each other to form new phases (e.g. N-A-S-H; not shown). No new phases are formed for the alkali-silicate-activated system (Figure 7.3a), in spite of the rapid decomposition of the C-S-H, which starts at $1/s \approx 0.03$ ml/g. Figure 7.3c displays the release of Ca resulting from the dissolution of the hydrated phases from various geopolymer systems, formulated with various silica modulus (M_s), as a function of I/s. In general, the resistance of the matrix increases with increasing silica modulus of the activating solution used for the formulations. Indeed, this suggests that in terms of "structural integrity" (i.e., but not necessarily ion retention), the (NaOH + SiO₂)based alkali-activated formulation is expected to be superior to the purely NaOHactivated fly ash formulation. Despite, the limiting factors of kinetics and carbonation, discussed earlier, the thermodynamic calculations show substantial agreement to aspects of the experimental data (e.g. Figure 6.2). However, due to the destabilization (nonformation) of hydrocalumite-like phases at $M_s \ge 1.0$, (Figure 5.3, Table 5.4, and Figure 7.3b), alkali-silicate based activated fly ash formulations with $M_s < 1.0$, are expected to stabilize contaminants better, especially the oxyanions (Gougar et al, 1996; Bankowski et al., 2004; Zhang, 2000). This explains why the formulation with $M_s = 0.15$, in general, outperformed formulations with $M_s = 1.5$, in all the experimental leaching tests.



Figure 7.3: (a) The effects of leaching on the solid phase assemblages as a function of the liquid (leachant)-to-(hydrated) solid (l/s) ratio for an alkali-silicate ($M_s = 0.5$) activated fly ash formulation, (b) The hydrated phase assemblages of an alkali activated fly ash formulation as a function of the silica modulus (SiO₂/Na₂O, molar ratio, Ms.), and (c) The evolution of aqueous Ca as a function of the function of the liquid (leachant)-to-(hydrated) solid (l/s) ratio for an alkali-silicate ($M_s = 0.5$ -to-1.5) activated fly ash formulations. This example, and the calculated volume balances assume that the fly ash is 60 % reacted as is reasonable for a mature alkali activated formulation (Provis & Rees, 2009; Rees et al., 2007).

Calcium, aluminum and silicon are the most abundant cations/oxyanions that form the major solid phases in cementitious systems (Taylor, 1997). Thus, the dissolution of solid phases containing such ions serves as an indicator of the release of any contaminants that are physically or chemically contained in such compounds (Poon et al., 1985). Therefore, following EPA's LEAF 1313 protocols (Kosson et al., 2002; EPA, 2013) the geopolymer systems were also subjected to leaching as a function leachant pH (i.e., using dilute HNO₃ and NaOH as the leachants to condition the pH). Figure 7.4 shows: (i) a constant level of Ca in the aqueous leachate solution across pH levels ranging from 2-to-13, for alkaliactivated fly ash formulations, an indication of stability of the hydrated solid phases containing Ca, in the system, and, (ii) an increase in aqueous Si at pH \geq 12; for alkaliactivated fly ash formulations that suggests the dissolution of Si-bearing phases in the system.

As an example, when interpreted in the context of pH dependent stability, the simulations suggest that the system noted in Figure 7.4 ($M_s = 0.5$) would encapsulate insoluble precipitates (e.g., hydroxides) of cationic contaminants (i.e., Cr(III), Cd, Co,Cu, Ni, Pb and Zn) across the whole range of pH tested, and, contain insoluble precipitates of oxyanionic

contaminants (i.e., As and Se) for pH < 12. This implies that the increased leaching of the cationic and oxyanionic metals at moderately acidic pH, as observed in the experimental data (Table 6.2 and Figure 6.2) is likely on account of transport/porosity controlled egress from dissolving hydroxides of these metal contaminants (Li et al., 2001; Kogbara et al., 2014). However, the increased leaching of oxyanions is ascribed to both matrix degradation (i.e., dissolution of hydrated phases hosting such species) and time dependent egress from their dissolving hydroxides (Gougar et al., 1996; Bankowski et al., 2004; Zhang, 2000; Li et al., 2001; Kogbara et al, 2014; Dutré & Vandecasteele, 1998).



Figure 7.4: The effect of the pH of the leachant on matrix stability. The figure shows Ca and Si release into the leaching solution (for l/s = 10 ml/g) for an 8 M (NaOH+SiO₂) activated fly ash formulation. The pH of the leachant was conditioned by the addition of either HNO₃ or NaOH to create acidic or alkaline conditions.

In summary, thermodynamic calculations can effectively be used to assess the: (i) evolution of hydrated phase assemblages and porosity that are relevant to select host matrices which display the best characteristics for physical and chemical stabilization of contaminants, and, (ii) which also offer the best matrix stability in terms of their resistance to dissolution under leaching exposure. In addition, it can also be concluded that:

- Alkali activated fly ash formulations, once they have achieved a suitable extent of fly ash reaction show good potential to serve as a stabilization solution for metallic contaminants across a wide range of pH conditions.
- While, OPC-based systems, in general, show high stability in high pH environments, alkali activated fly ash formulations show superior stability at slightly acidic conditions.
- In terms of minimizing porosity and hence maximizing structural integrity, the (NaOH+SiO₂) based alkali silicate activated fly ash formulation are superior to purely NaOH-activated fly ash formulations especially for M_s < 1.0 (Gougar et al., 1996; Bankowski et al., 2004; Zhang, 2000).

8. Conclusions and Recommendations

In this research, thermodynamic phase equilibria models were used to design geopolymer mixtures for solidification/stabilization of CCPs. The designed mixtures were made in the laboratory and compared against portland cement-stabilized mixtures. Overall, geopolymers met the strength requirements for landfilling and were able to reduce leaching for a number of contaminants across a wide pH and L/S range. Especially at low L/S, geopolymers reduced concentrations in leachate noticeably for the more challenging elements: arsenic, selenium, and chromium. Testing at low L/S values is important as it can be indicative of conditions in a landfill where large quantities of the ash or geopolymer are present in one area. 4M geopolymers were typically more successful than 8M geopolymers, and this is attributed to a higher percent reaction in 4M geopolymers as shown through LOI and compressive strength results. Lastly, leaching in a simulated landfill leachate increased leaching of copper and selenium at high pH as compared to leaching in reagent water which could impact leaching for wastes with high concentrations of these elements. The success of the solubility-informed mixture design was demonstrated through a comparison of predicted phase assemblages and porosity to the experimentally-determined properties.

With respect to implementation of this work, the best design of a mixture for S/S of CCPs will be dependent on which contaminants are of most concern and what conditions are present in the landfill. For examples, at high pH portland cement mixtures have reduced leaching compared to geopolymer mixtures, but the opposite is true at low pH. 4M NaOH is an appropriate activating solution concentration for making geopolymers with CCPs. Adjustment of the silica modulus may provide some improvement, but would not merit the additional cost, as shown in Table 8.1. Cost assessments on the S/S mixtures were made by considering the cost of the constituent materials, not including fly ash and water, and proportioning the materials as done in this study. The cost of portland cement was assumed to be \$111/metric ton. The cost of sodium hydroxide was assumed to be \$380/metric ton. The cost of sodium hydroxide was assumed to be \$380/metric ton, depending on the purity of the source. The 4M NaOH geopolymer provides the most cost-effective solution, especially given the high stabilization performance. This solution also takes up the least volume of landfill, allowing more fly ash to be disposed per unit volume.

Mixture	Cement (kg)	NaOH (kg)	Fumed silica (kg)	Approximate Cost per kg CCP
60% fly ash/40% cement	67	0	0	\$7.40
4M NaOH geopolymer	0	5.3	0	\$2.00
4M NaOH geopolymer with Ms = 1.5	0	5.3	5.56	\$11-\$29

Table 8.1: Cost of S/S mixtures per 100 kg CCP (not accounting for cost of CCP or water)

This project demonstrated that an iterative approach of thermodynamic modeling and experimental testing proved to be invaluable as the models helped in the design of the experiments and the experimental results will help inform and improve future modeling efforts. It can be concluded that S/S of CCPs using a 4M NaOH activating solution is a cost-effective strategy, providing excellent mechanical and chemical performance.

It is very likely that S/S using a 4M NaOH activating solution to make geopolymers can be applied more broadly, beyond the materials tested in this project. Identification of candidate CCPs for S/S through geopolymerization can be done on the basis of examining oxide analysis and particle size distribution. While the geopolymers tested in this study performed well in leaching tests, future long term testing following EPA method 1315 could also provide relevant data with respect to leaching of contaminants. Furthermore, it would be interesting to extend this work to combinations of CCPs and brines, to demonstrate the applicability of this strategy toward S/S of wastes for plants seeking zero-liquid discharge.

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Appendix A

Supplementary information: Geopolymer-Based Solutions for Coal Combustion Product Solidification and Stabilization

Maria Juenger,^{1*} Lynn Katz,¹ Michelle Lacks,¹ Monday Uchenna Okoronkwo,² Gaurav Sant,² and Magdalena Balonis²

1 University of Texas at Austin

Table A1. St	andard the	armodynami	c propertie	s at 25 °C · TI	hermodynan	nic data fo	r comonts	"comdat	22007" ^{1, 2}
Table AL. 50					Termouynan	lic uata iu		Centual	la2007
	log K _{so}	Δ _f G° [kl/mol]	Δ _f H° [kl/mol]	S° [I/K/mol]	a ₀ [I/K/mol]	a1	a₂	a ₃	V° [cm³/mol]
(Al-)ettringite (C ₆ As ₃ H ₃₂)	-44.9	-15205.94	-17535	1900	1939	0.789			707
Tricarboalum- inate $(C_6Ac_3H_{32})$	-46.5	-14565.64	-16792	1858	2042	0.559	-7.78e6		650
Fe-ettringite	-44.0	-14282.36	-16600	1937	1922	0.855	2.02e6		717
C ₃ AH ₆	-20.84	-5010.09	-5540	419	292	0.561			150
$C_3AS_{0.8}H_{4.4}$	-29.87	-5368.01	-5855	369	109	0.631	-1.95e6	2560	143
C ₃ FH ₆	-25.16	-4116.29	-4640	439	275	0.627	2.02e6		155
C ₄ AH ₁₃	-25.40	-7326.56	-8302	700	711	1.047		-1600	274
C ₂ AH ₈	-13.56	-4812.76	-5433	440	392	0.714		-800	184
C ₄ AsH ₁₂	-29.26	-7778.50	-8750	821	594	1.168			309
C ₄ AcH ₁₁	-31.47	-7337.46	-8250	657	618	0.982	-2.59e6		262
$C_4Ac_{0.5}H_{12}$	-29.13	-7335.97	-8270	713	664	1.014	-1.30e6	-800	285
C ₂ ASH ₈	-19.70	-5705.15	-6360	546	438	0.749	-1.13e6	-800	216
C_4FH_{13}	-29.4	-6430.94	-7395	737	694	1.113	2.02e6	-1600	286
C ₂ FH ₈	-17.6	-3917.38	-4526	476	375	0.780	2.02e6	-800	194
C_4FsH_{12}	-33.2	-6882.55	-7843	858	577	1.234	2.02e6		322
$C_4Fc^-H_{12}$	-35.5	-6679.20	-7637	737	612	1.157	-5.73e5		290
$C_4Fc_{0.5}H_{12}$	-33.1	-6440.19	-7363	749	648	1.080	7.24e5	-800	296
C ₂ FSH ₈	-23.7	-4809.53	-5453	583	422	0.815	8.91e5	-800	227
M ₄ AH ₁₀	-56.02	-6394.56	-7196	549	-364	4.21	3.75e6	629	220
M ₄ AcH ₉	-51.14	-6580.15	-7374	551	-382	4.24	4.32e6	629	220
M_4FH_{10}	-60.0	-5498.84	-6289	586	-381	4.27	5.78e6	629	232
C _{1.67} SH _{2.1} (jen.; C-S-H)	-13.17	-2480.81	-2723	140	210b	0.120	-3.07e6		78
C _{0.83} SH _{1.3} (tob.; C-S-H)	-8.0	-1744.36	-1916	80	85	0.160			59
portlandite	-5.20	-897.01	-985	83	187	-0.022		-1600	33
H ₂ O	-14.00	-237.18	-286	70	75				18

2 University of California, Los Angeles

	log K _{so}	Δ _f G°	Δ _f H°	S°	a ₀	a1	a2	a ₃	V°
		[kJ/mol]	[kJ/mol]	[J/K/mol]	[J/K/mol]				[cm³/mol]
Anhydrite	-4.36	-1322.12	-1435	107	70	0.099			4
Calcite	-8.48	-1129.18	-1207	93	105	0.022	-2.59e6		37
Brucite	-11.16	-832.23	-923	63	101	0.017	-2.56e6		25
Al(OH)3(am)	0.24	-1143.21	-1281	70	36	0.191			32
Al2O3	1.64	-1568.26	-1662	51	115	0.012	-3.51e6		26
Fe(OH)₃(mic)	-4.60	-711.61	-844	88	28	0.052b			34
Fe ₂ O ₃	-14.08	-739.53	-821	88	98	0.078	-1.49e6		30
C ₃ S		-2784.33	-2931	169	209	0.036	-4.25e6		73
C ₂ S		-2193.21	-2308	128	152	0.037	-3.03e6		52
C ₃ A		-3382.35	-3561	205	261	0.019s	-5.06e6		89
C ₄ AF		-4786.50	-5080	326	374	0.073			130
NASH 1	-9.05	-2453.72							
NASH 2	-6.58	-1848.00							

 a_0 , a_1 , a_2 , a_3 are the empirical coefficients of the heat capacity equation: $C_{\rho}^{\circ} = a_0 + a_1T + a_2T^{-2} + a_3T^{-0.5}$; no value = 0.

Table A2: Standard partial molal thermodynamic properties of the aqueous species used in the									
Ca Snecies	$\Delta_{\rm H}^{\rm Calculations of solubility constants References} = Species \Delta_{\rm H}^{\rm Calculations of solubility constants References} = Species (1/mol \cdot K) = Cn^{\circ} (1/mol \cdot K)$								
Species			5 (5/1101 K)						
Al ³⁺	- 483.7	- 530.6	- 325.1	- 128.7					
$AIO^{+} (+ H_2O = AI(OH)_2^{+})$	- 660.4	- 713.6	- 113.0	- 125.1					
AIO_2^- (+ 2H ₂ O = AI(OH) ₄ ⁻)	- 827.5	- 925.6	- 30.2	- 49.0					
AlOOH° (+ 2H ₂ O = Al(OH) ₃ °)	- 864.3	- 947.1	20.9	- 209.2					
AIOH ²⁺	- 692.6	- 767.3	- 184.9	56.0					
AlHSiO ₃ ²⁺	- 1540.5	- 1634.3	- 25.0	- 215.9					
(+ H ₂ O = AlSiO(OH) ₃ ² +)									
AlSiO4 ⁻	- 1681.4	- 1833.9	11.12	- 4.57					
(+ 3H₂O = AlSiO(OH)6 [−])									
Ca ²⁺	- 552.8	- 543.1	- 56.5	- 30.9					
Ca(HSiO₃)⁺	- 1574.2	- 1686.5	- 8.3	137.8					
$(+ H_2O = CaSiO(OH)_3^+)$									

Species	Δ _f G° (kJ/mol)	Δ _f H° (kJ/mol)	S° (J/mol∙ K)	Cp° (J/mol · K)
Na ⁺	- 261.9	- 240.3	58.4	38.1
NaOH°	- 418.1	- 470.1	44.8	- 13.4
NaHSiO₃°	-128.8	-140.7	41.84	102.95
$HSiO_3^{-}$ (+ $H_2O = SiO(OH)_3^{-}$)	- 1014.6	- 1144.7	20.9	- 87.2
SiO2°	- 833.4	- 887.9	41.3	44.5
SiO_3^{2-} (+ H ₂ O = SiO ₂ (OH) ₂ ²⁻)	- 938.5	- 1098.7	- 80.2	119.8
OH⁻	- 157.3	- 230.0	- 10.7	- 136.3
H⁺	0	0	0	0
H ₂ O°	- 237.2	- 285.9	69.9	75.4
N2°	18.2	- 10.4	95.8	234.2
O2°	16.4	- 12.2	109.0	234.1

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Appendix B – Characterization Results

B.1 UNUSED SUPPLEMENTARY CEMENTITIOUS MATERIALS XRF RESULTS

Oxide	Lafarge Slag	Calcium Aluminate Cement
SiO ₂	36.27%	5.08%
Al ₂ O ₃	9.23%	50.52%
Fe ₂ O ₃	0.33%	2.25%
CaO	38.70%	36.89%
MgO	11.50%	0.57%
Na ₂ O	0.46%	0.08%
K ₂ O	0.45%	0.30%
TiO ₂	0.41%	2.08%
Mn ₂ O ₃	0.26%	0.04%
P2O5	0.01%	0.14%
SrO	0.05%	0.06%
BaO	0.05%	0.00%
SO ₃	2.18%	0.02%

Table B.1: Slag and Calcium Aluminate Cement XRF Results

B.2 CCP XRD RESULTS



Figure B.1: FAH, FAB, EA, and BA XRD Diffractograms

Phase Name	Phase Formula	PDF#	FAH Phase Percent (%)	FAB Phase Percent (%)
Amorphous	N/A	-	65.1	59.6
Anhydrite	CaSO ₄	37-1496	1.6	13.1
Calcite	CaCO ₃	5-586	2.3	2.3
Gehlenite	Ca ₂ Al(AlSiO ₇)	37-755	-	6.3
Lime	CaO	37-1497	2.3	2.3
Merwinite	Ca ₃ Mg(SiO ₄) ₂	35-591	8.6	27.2
Periclase	MgO	45-0946	4.0	5.7
Quartz	SiO ₂	33-1161	9.3	4.5
Thenardite	Na_2SO_4		4.1	1.9
Ye'elimite	Ca4(AlO ₂) ₆ SO ₄	33-0256	2.7	1.7
Rwp			8.43	11.8
Rp			6.49	8.77
Chi ²			1.23	1.67

Table B.2: FAH and FAB Quantitative XRD Results

Phase Name	Phase Formula	PDF#	EA Phase Percent (%)	BA Phase Percent (%)
Amorphous	N/A	-	39.9	52.5
Anhydrite	CaSO ₄	37-1496	4.3	-
Anorthite	CaAl ₂ Si ₂ O ₈	01-086-1705	3.8	2.8
Augite	Ca(Fe,Mg)Si ₂ O ₆	24-0201	12.1	2.4
Calcite	CaCO ₃	5-586	-	3.6
Gehlenite	Ca ₂ Al(AlSiO ₇)	37-755	19.4	9.6
Hematite	Fe ₂ O ₃	33-664		1.2
Lime	CaO	37-1497	0.4	-
Maghemite	Fe ₂ O ₃	39-1346		1.8
Merwinite	Ca ₃ Mg(SiO ₄) ₂	35-591	10.9	.15
Periclase	MgO	45-0946	1.7	-
Quartz	SiO ₂	33-1161	7.4	12.8
Thaumasite	Ca ₃ Si(OH) ₆ (CO ₃)	01-074-3266	-	1.4
	$(SO_4) \cdot 12H_2O$			
Ye'elimite	Ca4(AlO2)6SO4	33-0256	-	1.7
Rwp			13.54	13.58
Rp			10.15	10.51
Chi ²				2.47

	Tał	ole	В	.3:	ΕA	and	BA	Qua	ntita	tive	XRD	Resul	lts
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B.3 FAH GEOPOLYMER XRD RESULTS



Figure B.2: 4M $M_s = 0$, 0.15, 1.5 and 8M $M_s = 0$ FAH Geopolymer XRD Diffractograms

				4M FAH Ms 4M FAH Ms		
Phase Name	Phase Formula			= 0.15 Phase = 1.5 Phase		
		Phase %	Phase %	%	%	
Amorphous C-S-H	N/A	61.6	60.8	47.9	70.2	
Calcite	CaCO ₃	10.7	10.8	11.5	15.2	
Katoite	Ca ₃ Al ₂ (SiO ₄) ₍₃₋ _{x)} (OH) _{4x}	5.7	13.1	-	-	
Hydrocalumite	Ca ₂ Al(OH) ₆ [Cl- x(OH) _x]-3H ₂ O	3.8	1.5	13.8	-	
Merwinite	Ca ₃ Mg(SiO ₄) ₂	3.6	2.1	-	-	
Periclase	MgO	3.2	2.8	4.0	2.6	
Quartz	SiO ₂	4.2	4.4	11.2	7.7	
Sodalite	Na ₈ Al ₆ Si ₆ O _{2 4} Cl ₂	3.0	2.6	-	-	
Ye'elimite	Ca4(AlO ₂) ₆ SO ₄	4.3	1.8	0.0	4.3	
Rwp		8.75	9.46	9.22	8.84	
Rp		6.72	7.16	7.16	6.69	
Chi ²		1.07	1.75	2.14	1.97	

Table B.4: 4M $M_s = 0, 0.15, 1.5$ and 8M $M_s = 0$ FAH Geopolymer XRD Phases and Phase Percent

B.4 FAH CEMENT PASTE XRD RESULTS



Figure B.3: 30% and 60% FAH Cement Paste XRD Diffractograms with Zincite

Phase Name	Phase Formula	PDF#	30% FAH Phase Percent (%)	60% FAH Phase Percent (%)
Amorphous	N/A	-	51.1	63.5
Alite	Ca ₃ SiO ₅	42-551	4.6	6.0
Belite	Ca ₂ SiO ₄	23-1042	6.5	1.3
Calcite	CaCO ₃	5-586	14.9	9.3
C3A	Ca ₃ Al ₂ O ₆	38-1429	1.4	1.1
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (O H) ₁₂ (H ₂ O) ₂₆	41-1451	2.5	1.5
Gehlenite	Ca ₂ Al(AlSi)O ₇	35-755	0.6	3.8
Gibbsite	Ca ₃ Mg(SiO ₄) ₂	01-070-2038	8.1	8.3
Gypsum	CaSO ₄ -2H ₂ O	33-311	3.9	2.9
Portlandite	Ca(OH) ₂	4-733	4.9	-
Quartz	SiO_2	33-1161	1.6	2.3
Rwp			11.5	11.8
Rp			8.82	8.93
Chi ²			3.72	2.65

Table B.5: 30% and 60% FAH Cement Paste Crystalline Phases and Phase Percent

B.5 FAB GEOPOLYMER XRD RESULTS



Figure B.4: 4M and 8M FAB Geopolymer XRD Diffractograms

Phase Name	Phase Formula	PDF#	4M FAB Phase Percent (%)	8M FAB Phase Percent (%)
Amorphous	N/A	-	68.4	48.9
Brucite	Mg(OH) ₂	7-239	1.3	-
Calcite	CaCO ₃	5-586	7.5	9.1
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ (H ₂ O) ₂₆	41-1451	1.1	-
Hydrocalumite	Ca ₆ Al ₄ (OH) ₂₄ (C O ₃) Cl ₂ (H ₂ O) _{9.6}	42-558	5.2	1.4
Katoite	Ca ₃ Al ₂ (OH) ₁₂	01-074- 3031	-	13.0
Lime	CaO	37-1497	-	-
Merwinite	Ca ₃ Mg(SiO ₄) ₂	35-591	2.9	12.6
Periclase	MgO	45-0946	2.5	4.1
Quartz	SiO ₂	33-1161	5.6	6.0
Sodalite	Na ₈ Al ₆ Si ₆ O _{2 4} Cl ₂		-	4.9
Rwp			9.62	9.20
Rp			7.36	7.10
Chi ²			1.30	1.57

Table B.6: 4M and 8M FAB Geopolymer Crystalline Phases and Phase Percent

B.6 FAB CEMENT PASTE XRD



Figure B.5: 30% and 60% FAB Cement Paste XRD Diffractograms without Zincite

Phase Name	Phase Formula	PDF#	30% FAB Phase Percent (%)	60% FAB Phase Percent (%)
Amorphous	N/A	-	55.8	71.2
Alite	Ca ₃ SiO ₅	42-551	10.2	9.8
Dolomite	CaMg(CO ₃) ₂	33-628	1.1	0.6
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ (H ₂ O) ₂₆	41-1451	7.6	2.7
Gibbsite	Ca ₃ Mg(SiO ₄) ₂	01-070- 2038	13.8	8.8
Gypsum	CaSO ₄ -2H ₂ O	33-311	1.7	1.3
Merwinite	Ca ₃ Mg(SiO ₄) ₂	35-391	3.5	2.3
Portlandite	Ca(OH) ₂	4-733	5.2	-
Quartz	SiO ₂	33-1161	1.2	3.5
Rwp			13.47	15.80
Rp			10.18	11.96
Chi ²			3.26	4.78

Table B.7: 30% and 60% FAH Cement Paste Phases and Phase Percent

Appendix C – Trace Metal Leaching Test Results

C.1 FAH, ARSENIC



Figure C.1: Raw Arsenic Concentrations in Leachate from FAH specimens versus pH. Arsenic TCLP limit is 5.0mg/L.



Figure C.2: Percent Arsenic Leached from FAH specimens versus pH



Figure C.3: Raw Arsenic Concentrations in Leachate from FAH Specimens versus L/S. Arsenic TCLP limit is 5.0mg/L.



Figure C.4: Percent Arsenic Leached from FAH Specimens versus L/S

C.2 FAB, ARSENIC



Figure C.5: Raw Arsenic Concentrations in Leachate from FAB Specimens versus pH. Arsenic TCLP limit is 5.0mg/L.



Figure C.6: Percent Arsenic Leached from FAB Specimens versus pH



Figure C.7: Raw Arsenic Concentrations in Leachate from FAB Specimens versus L/S. Arsenic TCLP limit is 5.0mg/L.



Figure C.8: Percent Arsenic Leached from FAB Specimens versus L/S



Figure C.9: Raw Cadmium Concentrations in Leachate from FAH Specimens versus pH. Cadmium TCLP limit is 1.0mg/L.



Figure C.10: Percent Cadmium Leached from FAH Specimens versus pH



Figure C.11: Raw Cadmium Concentrations in Leachate from FAH Specimens versus L/S. Cadmium TCLP limit is 1.0mg/L.



Figure C.12: Percent Cadmium Leached from FAH Specimens versus L/S



Figure C.13: Raw Cadmium Concentrations in Leachate from FAB Specimens versus pH. Cadmium TCLP limit is 1.0mg/L.



Figure C.14: Percent Cadmium Leached from FAB Specimens versus pH



Figure C.15: Raw Cadmium Concentrations in Leachate from FAB Specimens versus L/S. Cadmium TCLP limit is 1.0mg/L.



Figure C.16: Percent Cadmium Leached from FAB Specimens versus L/S



Figure C.17: Raw Cobalt Concentrations in Leachate from FAH Specimens versus pH



Figure C.18: Percent Cobalt Leached from FAH Specimens versus pH



Figure C.19: Raw Cobalt Concentrations in Leachate from FAH Specimens versus L/S



Figure C.20: Percent Cobalt Leached from FAH Specimens versus L/S



Figure C.21: Raw Cobalt Concentrations in Leachate from FAB Specimens versus pH



Figure C.22: Percent Cobalt Leached from FAB Specimens versus pH



Figure C.23: Raw Cobalt Concentrations in Leachate from FAB Specimens versus L/S



Figure C.24: Percent Cobalt Leached from FAB Specimens versus L/S



Figure C.25: Raw Copper Concentrations in Leachate from FAH Specimens versus pH



Figure C.26: Percent Copper Leached from FAH Specimens versus pH



Figure C.27: Raw Copper Concentrations in Leachate from FAH Specimens versus L/S



Figure C.28: Percent Copper Leached from FAH Specimens versus L/S



Figure C.29: Raw Copper Concentrations in Leachate from FAB Specimens versus pH



Figure C.30: Percent Copper Leached from FAB Specimens versus pH



Figure C.31: Raw Copper Concentrations in Leachate from FAB Specimens versus L/S



Figure C.32: Percent Copper Leached from FAB Specimens versus L/S



Figure C.33: Raw Chromium Concentrations in Leachate from FAH Specimens versus pH. Chromium TCLP limit is 5.0mg/L.



Figure C.34: Percent Chromium Leached from FAH Specimens versus pH



Figure C.35: Raw Chromium Concentrations in Leachate from FAH Specimens versus L/S. Chromium TCLP limit is 5.0mg/L.



Figure C.36: Percent Chromium Leached from FAH Specimens versus L/S



Figure C.37: Raw Chromium Concentrations in Leachate from FAB Specimens versus pH. Chromium TCLP limit is 5.0mg/L.



Figure C.38: Percent Chromium Leached from FAB Specimens versus pH


Figure C.39: Raw Chromium Concentrations in Leachate from FAB Specimens versus L/S. Chromium TCLP limit is 5.0mg/L.



Figure C.40: Percent Chromium Leached from FAB Specimens versus L/S



Figure C.41: Raw Nickel Concentrations in Leachate from FAH Specimens versus pH



Figure C.42: Percent Nickel Leached from FAH Specimens versus pH



Figure C.43: Raw Nickel Concentrations in Leachate from FAH Specimens versus L/S



Figure C.44: Percent Nickel Leached from FAH Specimens versus L/S



Figure C.45: Raw Nickel Concentrations in Leachate from FAB Specimens versus pH



Figure C.46: Percent Nickel Leached from FAB Specimens versus pH



Figure C.47: Raw Nickel Concentrations in Leachate from FAB Specimens versus L/S



Figure C.48: Percent Nickel Leached from FAB Specimens versus L/S



Figure C.49: Raw Lead Concentrations in Leachate from FAH Specimens versus pH. Lead TCLP limit is 5.0 mg/L.



Figure C.50: Percent Lead Leached from FAH Specimens versus pH



Figure C.51: Raw Lead Concentrations in Leachate from FAH Specimens versus L/S. Lead TCLP limit is 5.0 mg/L.



Figure C.52: Percent Lead Leached from FAH Specimens versus L/S



Figure C.53: Raw Lead Concentrations in Leachate from FAB Specimens versus pH. Lead TCLP limit is 5.0 mg/L.



Figure C.54: Percent Lead Leached from FAB Specimens versus pH C28



Figure C.55: Raw Lead Concentrations in Leachate from FAB Specimens versus L/S. Lead TCLP limit is 5.0 mg/L.



Figure C.56: Percent Lead Leached from FAB Specimens versus L/S

C.15 FAH, SELENIUM



Figure C.57: Raw Selenium Concentrations in Leachate from FAH Specimens versus pH. Selenium TCLP limit is 1.0mg/L.



Figure C.58: Percent Selenium Leached from FAH Specimens versus pH



Figure C.59: Raw Selenium Concentrations in Leachate from FAH Specimens versus L/S. Selenium TCLP limit is 1.0mg/L



Figure C.60: Percent Selenium Leached from FAH Specimens versus L/S



Figure C.61: Raw Selenium Concentrations in Leachate from FAB Specimens versus pH. Selenium TCLP limit is 1.0mg/L



Figure C.62: Percent Selenium Leached from FAB Specimens versus pH



Figure C.63: Raw Selenium Concentrations in Leachate from FAB Specimens versus L/S. Selenium TCLP limit is 1.0mg/L



Figure C.64: Percent Selenium Leached from FAB Specimens versus L/S



Figure C.65: Raw Zinc Concentrations in Leachate from FAH Specimens versus pH



Figure C.66: Percent Zinc Leached from FAH Specimens versus pH



Figure C.67: Raw Zinc Concentrations in Leachate from FAH Specimens versus L/S



Figure C.68: Percent Zinc Leached from FAH Specimens versus L/S



Figure C.69: Raw Zinc Concentrations in Leachate from FAB Specimens versus pH



Figure C.70: Percent Zinc Leached from FAB Specimens versus pH



Figure C.71: Raw Zinc Concentrations in Leachate from FAB Specimens versus L/S



Figure C.72: Percent Zinc Leached from FAB Specimens versus L/S



Figure C.73: Arsenic concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.74: Cadmium concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.75: Cobalt concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.76: Copper concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.77: Chromium concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.78: Nickel concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.79: Lead concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.80: Selenium concentrations in leachate collected from an up-flow column over time versus cumulative L/S



Figure C.81: Zinc concentrations in leachate collected from an up-flow column over time versus cumulative L/S