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Mineral Solubilization from Municipal Solid Waste Combustion Residues:

Implications for Landfill Leachate Collection Systems

by

Lisa R. Rhea

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Environmental Engineering
Department of Civil and Environmental Engineering
College of Engineering
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Keywords: ash, batch tests, clogging, deposition, precipitates, waste-to-energy

Dedication

I would like to dedicate this thesis to my family. To my husband, R. Douglas Rhea, my mother, Ruth R. Robinson and my children, Jeremiah and Elijah Van Horn. Without their support, encouragement and understanding, I would not have been able to complete this thesis.

Acknowledgements

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List of Abbreviations

BA	Bottom Ash
CE	Capillary Electrophoresis
CT	Contact Time
EC	Electric Conductivity
EDS	Electron Dispersive Spectroscopy
FA	Fly Ash
FAA	Flame Atomic Absorption
FDEP	Florida Department of Environmental Protection
H	Hillsborough
HDPE	High Density Polyethylene
L/S	Liquid to Solid
LCS	Leachate Collection System
MSW	Municipal Solid Waste
ORP	Oxidation Reduction Potential
P	Pasco
PBL	Palm Beach Leachate
PL	Pasco Leachate
SE	Sequential Extraction
SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
USEPA	United States Environmental Protection Agency
VFA	Volatile Fatty Acids
WTE	Waste-to-Energy

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ABSTRACT

Leachate collection systems consist of a series of pipes installed beneath the waste at the base of a landfill. The liquid drains toward a central location where it is pumped and then treated, discharged, or recirculated. In some landfills, solid precipitates form in the collection system resulting in clogging and malfunctions of the drainage system. The formation of the precipitates is linked to the chemical and biological stability of the leachate generated within the landfill. To control the formation of precipitates and prevent clogging of leachate collection systems, it is important to understand factors that influence leachate characteristics.

Ashes from municipal solid waste (MSW) combustion are either placed in monofills or combined with traditional solid waste, and sludges and biosolids from wastewater and drinking water treatment plants when landfilled. The ashes, depending on the type of combustion process, contain high concentrations of metals and non-biodegradable materials. As the waste degrades, oxygen in the landfill is consumed and the leachate becomes anaerobic. The reducing environment allows for greater solubility of metals.

This research tested ashes from three different Waste-to-Energy (WTE) facilities to understand better the role MSW fly ash and MSW bottom ash in the chemical make-up of landfill leachate. Two different types of batch tests were used to analyze the leaching behavior. First, a contact time batch test with a range of different contact times was used to assess the rate at which different elements reach equilibrium. This was followed by a sequential extraction batch test that predicted the total amount of soluble material in the ashes.

The chemical characteristics of the leachate produced by the ashes were understood and the leaching behaviors analyzed, dominant chemical factors that influence the formation of precipitates were identified. This data produced a better understanding of the roles of WTE ashes in the production of precipitates in leachate collection systems.

Introduction

In landfills, the interactions of rainwater and other sources of moisture with waste constituents produce leachate. The chemical composition of leachates is controlled by several factors including: waste characteristics; quantity of liquid that percolates through the landfill; biological activity; and the age of the landfill. In many areas of the country, water and wastewater treatment by-products and combustion residues are co-disposed with municipal solid waste (MSW). Residuals from water treatment facilities can contain high levels of inorganic compounds such as iron, aluminum, and calcium depending on the type of treatment process. Wastewater residuals (biosolids) tend to be high in organics, nutrients, and metals. Depending on the combustion process, incinerator ashes contain high concentrations of metals and non-biodegradable materials. The heterogeneity of the wastes contributes to the complexity of chemical and biological reactions that occur in the leachate.

Over the last thirty years, many factors have contributed to changes in the composition of municipal solid waste. Changing societal habits, including increased use of plastics, different approaches to packaging, and the proliferation of electronic devices, have resulted in increased amounts of non-biodegradable materials in landfills. In Florida, many municipalities have adopted the use of Waste-to-Energy (WTE) facilities with the main goal of reducing the net volume and mass of wastes prior to landfilling and a secondary goal of energy production (FDEP, 2000). Combining combustion residues with MSW, residuals from wastewater and water treatment plants, industrial by-products, and construction and demolition wastes in landfills affects leachate characteristics. As wastes degrade, oxygen is consumed leading to anaerobic conditions. Changes in the redox potential of the leachate influence microbial reactions, solubility, and partitioning of many constituents (Kylefors, 2003).

Leachates generated in landfills are managed in a variety of ways dictated by regulatory requirements. Leachate collection systems consist of a series of pipes installed beneath the waste. The liquid drains toward a central location where it is treated, discharged, or recirculated. It has been reported that in some landfills, solid precipitates deposit in the collection system resulting in clogging and malfunctions of the drainage system. The formation of precipitates is linked to the chemical and biological stability of the leachate generated within the landfill. To control the formation of precipitates and prevent clogging of leachate collection systems, it is important to understand factors that influence leachate characteristics.

Objectives

The purpose of this research project is to evaluate the leaching properties of WTE combustion residues that are typically landfilled. The specific objectives are:

1. Develop batch tests to evaluate leaching characteristics of bottom ash, fly ash, and mixed ashes from WTE facilities.

2. Compare leachates generated from batch tests of combustion residues to leachates produced in laboratory lysimeters simulating monofills, landfills operating as monofills, and landfills that co-dispose ashes with MSW.

3. Identify dominant chemical factors that influence the formation of deposits in leachate collection systems.

Literature Review

This section discusses the state and national regulatory requirements for the operation of WTE facilities and landfills. Another area covered by the literature, and of concern in the operation of lined landfills, is the potential clogging of the leachate collection system, leading to contamination of the surrounding environment. Finally the section discusses a review of batch tests that have been developed to help determine the chemical composition and possible toxicity of the waste materials placed in landfills.

Regulatory Requirements

Regulations for waste management and landfill design have been established to protect public health and control environmental contamination. In this section, regulatory requirements for management of ash generated in waste-to-energy facilities, and landfill design and operation are summarized. The federal regulations establish minimum standards and allow the states to make the necessary adjustment to compensate for local variations.

Waste-To-Energy in Florida

The construction and design of landfills in Florida is influenced by the topography and hydrology of the state. Because Florida is very flat with a shallow water table, the base of landfills is at the land surface with waste deposition occurring at successive elevations. In many locations, landfills are the only topographic variation in an otherwise uniform environment. To reduce the volume of waste requiring landfilling, many municipalities combust MSW in Waste-to-Energy (WTE) facilities. Typically, MSW combustion produces energy and results in a volume reduction up to 90% and a mass reduction up to 75% (USEPA, 2004). WTE facilities have become an integral part of waste management in Florida (FDEP, 2000).

There are currently 13 operating WTE facilities in the state of Florida; most of these are located near large metropolitan areas. The active WTE facilities and general information about each facility is given in Table 1. Each facility is required to meet current EPA Maximum Achievable Control Technology air quality standards (FDEP, 2000). To achieve this, many of the plants have upgraded air pollution control equipment from electrostatic precipitators to combined systems that include dry scrubbers, filter fabric gas, and nitrogen oxide controls (FDEP, 2000).

Table 1: WTE Facilities in Florida (FDEP, 2000)

Facility Location	Technology Type	Megawatts of Electricity	% by mass of Waste WTE	% by mass of Waste Landfilled
Bay	Mass Burn	12.0	44	44
Broward	Mass Burn	66.5	34	40
Broward	Mass Burn	64.0	34	40
Dade	Refuse Derived Fuel	78.5	27	50
Hillsborough	Mass Burn	29.0	25	47
Hillsborough	Mass Burn	22.0	25	47
Lake	Mass Burn	12.5	30	43
Lee	Mass Burn	30.0	37	25
Monroe	Mass Burn	4.0	25	51
Palm Beach	Refuse Derived Fuel	61.3	25	40
Pasco	Mass Burn	31.2	34	54
Pinellas	Mass Burn	75.0	40	37
Polk	Wood Waste, Tire Derived Fuel	39.6	1	62

Counties with active WTE facilities burn an average of 29%, landfill 45% and recycle 26% of the MSW. The combustion residues are either combined with other waste streams or placed in monofills in local landfills. Since 1994, when the Supreme Court ruled that ash from MSW combustion must be treated as other hazardous wastes in *City of Chicago vs. Environmental Defense Fund*, all WTE facilities have been required to test the ash using the federal Resource Conservation and Recovery Act testing requirements for hazardous waste, prior to disposal in lined landfills (FDEP, 2000).

EPA Regulations- Landfill Leachate Management

Engineered landfills are designed to protect the surrounding environment from contamination by leachate generated within the landfill. The waste characteristics, age, and extent of biological activity within a landfill influence the leachate composition

(USEPA, 1993). The volume of leachate generated by a landfill is estimated prior to construction based on the precipitation patterns for a geographical region. As a landfill ages, changes in the quantity and quality of the leachate occur due to the establishment of microbial communities and the degradation and solubilization of constituents from the waste. Regulatory requirements stipulate that all landfills receiving combustion residues must have liners and leachate collection systems to prevent the migration of leachate into groundwater systems. Design requirements specified by the USEPA are summarized in Table 2.

Table 2: Summary of Parameters for Landfill Leachate Collection System Designs

Parameter	Section	Material and Specifications	Figure 1
Composite Liner	Base	Soil with hydraulic conductivity less than 1 x 10^{-7} cm/sec; Slope > 2%	A
	Liner	Flexible membrane	B
Leachate Collection System	Drainage Layer	Placed directly over liner; material based on availability of granular material or geosynthetic net; Conductivity greater than 1 x 10^{-2} cm/sec; Slope > 2%	C
	Collection Pipes	Perforated; minimum 6 inch diameter; embedded within the drainage layer; strong enough to support waste and drainage layer	D
	Filter Layer	Geotextile and/or sand; Protects drainage layer from physical clogging	E

Adapted from EPA publication EPA530-R-93-017

The base of the composite liner, which acts as the landfill foundation, is a 2-foot soil layer with a hydraulic conductivity of less than 1 x 10^{-7} cm/sec (USEPA, 1993). Typically, clay is used to construct this relatively impermeable layer. A flexible membrane liner covers the clay layer, and provides an additional layer of protection in case cracking occurs in the underlying clay due to shifts in the soil. These layers provide a barrier that prevents the leachate from quickly traveling through the soil and into the groundwater.

If the leachate develops sufficient head, it will penetrate the composite liner. To prevent the leachate from developing sufficient head to penetrate the composite liner, a leachate collection system (LCS) is installed above the liner. Figure 1 is a diagram of the design requirements for the base of a landfill. The design parameters require the LCS maintain a leachate head of less than 30 cm (USEPA, 1993). However, during times of peak flow it is acceptable to exceed this value for short periods.

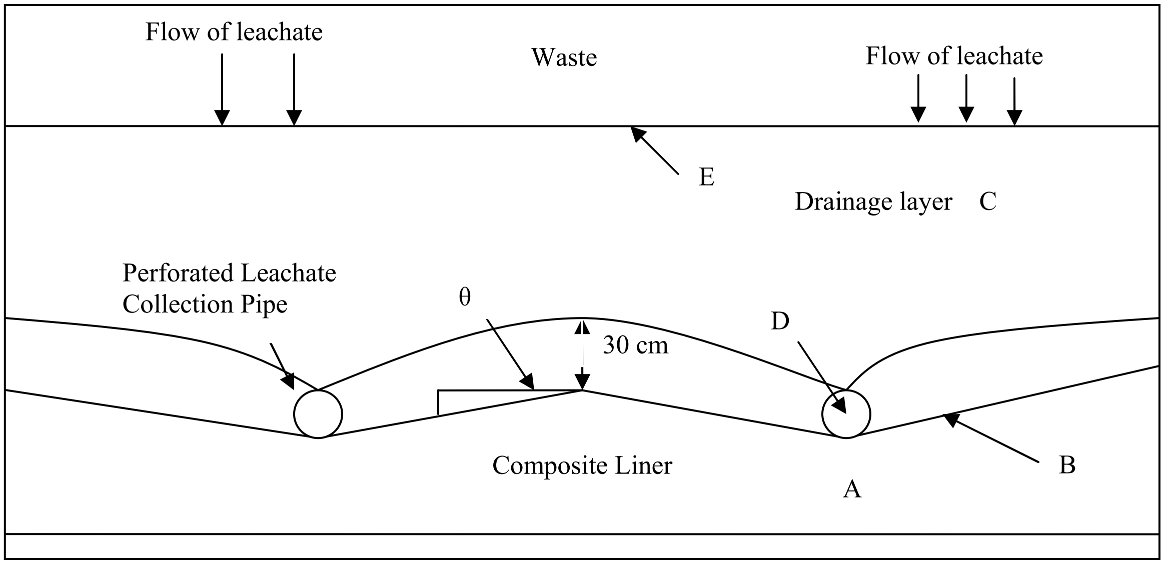

Figure 1: Diagram of the Base of an Engineered Landfill

The LCS consists of a series of perforated pipes embedded in a drainage layer. The perforated pipes are a minimum 6-inch diameter plastic pipe and are required to support the combined weight of the drainage layer and the waste when the landfill is at capacity (USEPA, 1993). If the pipes are not able to support this weight, the LCS will fail. The drainage layer material must have conductivity equal to or greater than 1×10^{-2} cm/sec, with a slope of at least 2% so that the leachate will flow towards the collection pipes (USEPA, 1993). To prevent physical clogging of the collection pipes, the drainage material diameter must be larger than the perforations in the pipe. Another measure used to prevent physical clogging is the filter layer. This layer of geotextile and sand is placed above the drainage blanket and prevents waste from traveling into the drainage layer and the collection pipes creating physical blockages in the flow.

Biological and chemical clogs can occur in the LCS pipes. To help control the formation of mineral precipitates and biofilms, clean-out access ports need to be included in the LCS. These ports must be placed at locations that allow cleaning equipment and chemicals to access the whole system. The suggested method for removal of mineral deposits is to flush the system with a liquid that contains biocides and cleaning agents (USEPA, 1993). The cleaning removes mineral precipitates and biofilm buildup in the pipes, but does not prevent the formation of future clogs.

Clogging of Leachate Collection Systems

Typically, the design life of landfills spans several decades, depending on the available space and the quantity of waste received (Fleming, 1999). Leachate collection systems that are below the layers of waste are prone to failure from several factors including clogging (Cooke, 2001).

In some landfills, evidence of clogging can be seen within 4 years of beginning operations (Rowe, 2002). The clogs are caused by the formation of biofilms and insoluble mineral deposits that fill the void spaces within the drainage layer and the perforated collection pipes (Paksy, 1998).

Drainage media has been implicated in the formation of clogs in landfill leachate collection systems (Rowe, 2000). While the initial hydraulic conductivity and porosity of different media may be similar, there are differences in the size of the pores and the available surface area for different types of media. For a given volume, smaller media provides a greater surface area, allowing for increased biofilm development that may influence the clogging rate (Rowe, 2000). Larger media provides for larger pores sizes that result in more uniform leachate flow, maintaining the hydraulic conductivity through the collection system and reducing the likelihood of clogging.

Regardless of the medium, the flow of the leachate also affects the rate at which clogs form. Clogging has been found in both saturated and unsaturated zones of leachate collection systems. In anaerobic environments, unsaturated regions have less clogging than saturated regions due to differences in available substrate for microbial activity. During times of high flow, the increased activity of the microorganisms can lead to biofilm production and the precipitation of insoluble minerals. In reality, the environment in the leachate collection system of a landfill cycles between saturated and unsaturated conditions depending on precipitation patterns. Unfortunately, deposition of precipitates is most pronounced in regions that experience changing flows, cycling between saturated and unsaturated conditions (Paksy, 1998; Rowe, 2000).

The formation of insoluble minerals presents a serious problem since it reduces the hydraulic conductivity of the leachate collection system. Analysis of the clog material removed from landfills in Canada and Great Britain identified calcite, $CaCO_3$, as the major constituent in the clog material (Manning, 1999; Rowe, 2000). Other minerals containing iron, sulfide, sulfate and carbonate were also identified in the solid. One technique used by Rowe et al (2002), to characterize the amount of calcium carbonate in the precipitate, is based on the molecular mass ratio of Ca^{2+} to CO_3^{2-}, which is equal to 0.67. If the ratio is greater than 0.67, calcium is available to precipitate with other anions. When the ratio is lower than 0.67 carbonate is available to precipitate with other cations. From this approach, it was determined that the calcium rather than the carbonate limits the formation of the calcite in leachate collection systems (Rowe, 2000).

Chemical characterization of the leachate associated with clogging material reflects the composition of the precipitate. In models of leachate chemistry, CO_3^{2-} and SO_4^{2-} are the dominant anions, regardless of the pH, and are considered supersaturated

(Manning, 1999). Typically, leachates are saturated with respect to $CaCO_3$, $FeCO_3$, $MgCO_3$, and $Ca_5(PO_4)_3OH$ (Rowe, 2002). There are also high concentrations of sodium, potassium and chloride in leachates but due to the highly soluble nature of these ions, they are not commonly found in precipitates. Supersaturated leachates provide a rich source of ions for mineral precipitation.

Leaching Tests

The types of waste that are placed in a landfill contribute to the leachate characteristics. Various tests have been developed to determine the leaching behaviors of materials (Hage, 2003). Tests used to establish the leaching characteristics of wastes include field tests, simulator tests and batch tests. A comparison of these tests is given in Table 3. The tests differ mainly in duration and the presence or absence of biological activity. The results from these tests can be used to help predict the long-term behavior of waste as it decomposes in a landfill.

Table 3: Comparison of Three Types of Tests Used to Characterize the Leaching Potential of Landfilled Materials

Category	Description	Advantages	Disadvantages
Field	Monitors the characteristics of leachates produced by wastes in an established landfill.	Established microbial communities; heterogeneity of waste constituents	Can take several years; limited access to the reacting materials; inability to determine the contribution of the various waste constituents to the characteristics of the leachate
Simulator	Waste is placed in a column, commonly called a lysimeter, and allowed to react over several months.	Allows for the establishment of microbial communities; mimics a landfill; controlled flow of leachant; access to the reacting materials in select locations	Can take months to complete; inability to determine the contribution of the individual waste constituents to the characteristics of the leachate
Batch	Individual wastes and select combinations of waste are placed in non-reactive containers with leachant for a specific length of time.	Completed in several weeks; allows for the identification of the contribution of the individual waste constituents to the characteristics of the leachate.	Missing microbial activity; limited interaction among different types of waste

Field and Simulator Tests

A field test is used to monitor characteristics of leachates produced by wastes in established landfills or in controlled test cells (Kylefors, 2003). In both types of field tests, wastes are exposed to natural weathering allowing for the establishment of microbial communities and production of leachate from natural precipitation. In a test cell, the waste can be characterized prior to landfilling, while in an established landfill this information is not readily available. In either situation, the interactions of the waste and the microorganisms are hard to monitor due to the large quantity and heterogeneity of material. This type of study can take several years to complete, and, due to the lack of access to the decomposing wastes, can leave many questions unanswered. An advantage to this type of approach is it allows for the study of all of the components of a landfill, including design and daily management.

The simulator test requires less time then a field test but can still take several months to complete. The design and placement of the reactors, commonly called lysimeters, depends on the purpose of the study and can influence the results. In a laboratory, the results may not correlate with field tests due to differences in temperature, time and water to solid contact frequency (van der Sloot, 1998). Lysimeter design parameters from published studies are compared in Table 4. Typically, wastes, or other materials, are placed in a reactor and allowed to react for a specific time period, during which liquid is circulated through the system, gas production is monitored and leachate is produced. The gas and leachate are sampled regularly and tested for a predetermined set of parameters.

Table 4: Select Design Parameters for Lysimeters

Geometry of Lysimeters	Material of Lysimeters	Packing Material	Reference:
Columns: Diameter= 50mm Length= 700mm	Schedule 40-PVC	6-mm diameter glass beads	Rowe, R.K., VanGulck, J. and Millward, S. (2002)
Boxes: 0.25m x 0.6m x 0.7m	PVC	clear stone used for drainage blanket, 5-10yr old waste sep. by geotextile	Fleming, I.R., Rowe, R.K. and Cullimore, D.R. (1999)
Boxes: 3.12 m^2 x 1.06m deep	Brick and concrete	lined with HDPE, 100-mm gravel, waste	Blight, G.E., Fourie, A.B., Shamrock, J., Mbande, C. and Morris, J.W.F. (1999)
Columns: Diameter= 230mm Length= 900mm	MDPE/HDPE	limestone / Thames gravel, 4-5 yr old waste	Paksy, A., Powrie, W., Robinson, J.P. and Peeling, L. (1998)

Lysimeter tests allow for a complete characterization of wastes prior to start-up and careful control of moisture in the system. However, the environment within the reactors allows for the establishment of microbial communities. The impact of waste characteristics on the quality of the leachate can be observed. In many ways lysimeters are black boxes, since the ability to determine a direct relationship between individual materials and leachate characteristics is unknown.

Batch Test

Batch Tests, also called compliance tests, can be used to determine leaching characteristics of individual wastes. An overview of batch tests, mostly developed to regulate industrial waste disposal, is given in Table 5. The tests fall into three main categories: shake tests, pH-stat test, and sequential extractions. The shake test allows waste to be exposed to a specific amount of leachant for a predetermined length of time. After the time interval has been completed, the leachate is analyzed for select chemical parameters, usually designated by a regulatory agency (van der Sloot, 1998). The pH-stat tests are used to determine how a material will behave in a given environment (Hage, 2003). The leachant is monitored to ensure that the pH remains constant throughout the period of contact. Once the leachate is removed, it is tested for a set of chemical parameters that vary depending on the goals of the test. Sequential extractions tests are used to determine the depletion of solubilizable constituents in a material. In this test, the leachant is removed and replaced until the levels of the parameters of interest are below detection limits.

Table 5: Overview of the Three Main Categories of Batch Tests

Batch Test Category	Description
Shake Test	This test allows wastes to be exposed to a specific amount of leachant for a predetermined length of time.
pH-Stat Test	The pH-stat tests are used to assess how materials behave under constant pH for a fixed exposure time. The pH of leachant is monitored continuously.
Sequential Extraction Test	This test is used to determine the amount of solubilizable constituents in wastes. After a specific amount of time, the leachant is replaced until the parameters of interest fall below the detection limits.

The main variables among the tests are the liquid to solid mass ratio (L/S), the leaching medium, temperature, contact time, and separation technique. A comparison of batch tests that have been used to assess waste leachability is given in Table 6. By following the procedure from any of the assorted tests, it is possible to determine the behavior of waste as it is exposed to a leachant. The results can be used to help predict the long-term behavior wastes within a landfill in the absence of microbial activity.

Table 6: Comparison of Select Batch Leaching Tests Protocols

Test	Liquid / Solid Ratio (mass)	Leaching Medium	Temp	Agitation Time	Contact Time	Separation Technique
Toxicity Characteristic Leaching Procedure USEPA Method 1311 (USEPA, 1996)	20 / 1 ratio	The leaching fluid used is a function of the alkalinity of the solid phase	Ambient	18 hrs	18 hrs	Filtration using a 0.6μm glass filter
pH-Stat Test European CEN, 2000 (Hage, 2003)	9 / 1 ratio	pH regulated with dilute nitric acid and dilute sodium hydroxide at pH= 4, 5.5, 7, 8, 9, 10, 11, 12	Ambient	Not stated	24 hrs	Filtration using a 0.45 μm filter
ASTM Water Leach Test D-3987-85 (Bagchi, 1990)	20 / 1 ratio Ex. 70 g solid to 1400 mL of liquid	Distilled Water	18 - 27°C	18 hrs	24 hrs	Decanting or pipetting
Shaking Leaching Test DIN 38414 (Kylefors, 2003)	10 / 1 ratio	Distilled Water	Ambient	24 hrs	24 hrs	Decanting or pipetting
Aqueous Extracts of Soil Samples, Methods of Soil Analysis 2nd Edition (American Society of Agronomy, 1982)	1 / 1 or 5 / 1	Distilled Water	Ambient	1 hrs	1 hr	Filtration using a highly retentive paper
Shaking Leaching Test, European CEN, 2002 (Hage, 2003)	1st interval: 2 / 1 2nd interval: 8 / 1	Distilled Water	Ambient	1st interval: 6 hrs 2nd interval: 18 hrs	1st interval: 6 hrs 2nd interval: 18 hrs	Filtration using a 0.45μm filter
Method for Accelerated Leaching of Solidified Waste USDOE BNL 52268 (Department of Nuclear Energy, 1990)	Liquid volume will be 100 times the surface area of the solid	Distilled or Deionizer water, the leachant can be replenished until the solid is depleted	Maximum temp. of 50°C	None	13 intervals 2 hrs, 5 hrs, 17 hrs, 1-11 days	Decanting or pipetting

Experimental Methodology for Batch Test Leaching Study

Two different types of batch tests were developed to characterize the leaching potential associated with combustion residues: contact time tests and sequential extraction tests. The contact time test provides an estimate of the time necessary to mobilize minerals from solid wastes. This test also provides insight into the sequence of dissolution, allowing for the identification of readily soluble species, thus providing a static view of the interaction between the leachant and the waste material. The sequential extraction test provides a dynamic view of the material's behavior as it encounters fresh leachant at regular time intervals. This test allows for simulation of the sequential changes in leaching mechanisms that occur as fresh water interacts with the waste material. A comparison of the information that can be obtained from each batch test is presented in Table 7.

Table 7: Comparison of Information Learned from Contact Time and Sequential Extraction Batch Tests

Batch Test	Time	Stability	Potential Solubility
Contact Time	Predetermined cumulative time series	Equilibrium	Initial solubility
Sequential Extraction	Fixed leachate replacement intervals	Flow equivalent extraction	Total soluble material

In this project, combustion residues from three different WTE facilities were subjected to contact time and sequential extraction tests. Test methodology was adapted from the Method for Accelerated Leaching of Solidified Waste (Department of Nuclear Energy, 1990). To assess the efficiency of using batch tests to predict leachate characteristics and the potential for clogging of leachate collection systems, batch test results were compared to leachates from laboratory lysimeters containing combustion residues and landfill leachates. The sources of the combustion residues and leachates are listed in Table 8

Table 8: Sources of Combustion Residues and Leachates Tested

Source	Material	Code	Processing Method	Tests Run
West Palm Beach County	Bottom Ash	BA	RDF Facility	Contact Time, Sequential Extraction
	Fly Ash	FA	RDF Facility	Contact Time, Sequential Extraction
	Leachate	PBL	Landfill cell- Co-disposal of bottom ash, fly ash, MSW, and treatment plant residuals	Analysis of inorganic constituents
	Clogging material from leachate collection system	C	Landfill cell- Co-disposal of bottom ash, fly ash, MSW, and treatment plant residuals	Elemental Analysis of solid phase
	Laboratory lysimeter	RA	80% bottom ash 20% fly ash	Analysis of inorganic constituents
Pasco County	Mixed Ash	P	Mass Burn	Contact Time, Sequential Extraction
	Leachate	PL	Landfill cell- Ash monofill	Analysis of inorganic constituents
Hillsborough County	Mixed Ash	H	Mass Burn	Contact Time, Sequential Extraction

The WTE residues were collected in 1-liter LDPE bottles or 5-gallon plastic containers and upon arrival, were stored at 4°C until the batch tests were started. The batch tests were usually started within a week of acquiring each sample. In addition to the batch tests, a preliminary characterization of the material was performed, using a scanning electron microscope coupled with energy dispersive spectroscopy. Due to the larger particle sizes in the bottom ash, some of the material was ground in an electric grinder prior to starting the batch tests.

Experimental Design

This project was developed to evaluate the role of combustion residues in clogging of leachate collection systems. Typically, ash produced at WTE facilities is disposed either in a monofill or in combination with other waste materials. As moisture filters through landfills, leachate is produced. Unstable leachates may lead to clogging of the collection system. In this project batch tests were developed to simulate liquid/solid interactions that occur in landfills receiving combustion residues. Distilled water was used as a leachant to mimic the chemical composition of rainwater. The relationship of the batch test, lysimeter tests, and field tests is shown in Figure 2. The experimental design for each type of batch test is presented in this section including test optimization, initial set-up of tests, daily operations, leachate analysis, and data management.

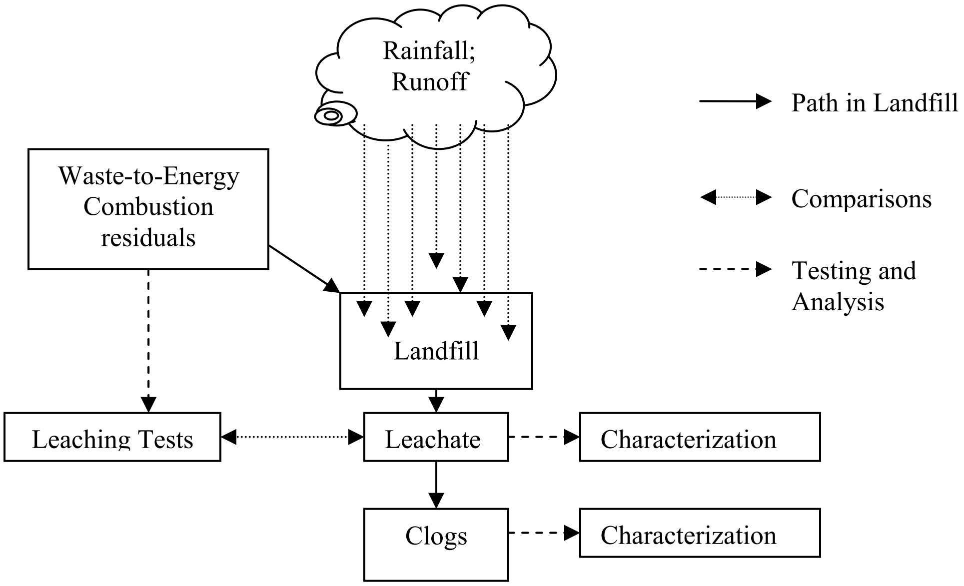

Figure 2: Diagram of the Interactions Occurring in Landfills and the Relationship to Batch Tests

Batch Test Optimization

Preliminary batch tests were conducted to optimize the liquid to solid (L/S) mass ratios of distilled water to ash and the duration of the contact intervals . An overview of the approach used during the initial tests is shown in Figure 3. The preliminary tests were designed to assess the quantity of leachate produced, the concentrations of the leached constituents, and the need for pre-treatment of the solid material. The first study focused on determining the contact time intervals necessary for diffusion to occur, while providing adequate volume to conduct leachate characterization tests. The leachates from the preliminary batch tests were characterized and the data from these initial tests was used to develop a final protocol for the testing of the combustion residue samples.

Batch Test Development

Protocols for the batch tests conducted in this project were adapted from the Method for Accelerated Leaching of Solidified Waste (Department of Nuclear Energy, 1990). All tests were conducted using Nalgene amber high-density polyethylene (HDPE) wide mouth bottles. The HDPE bottles are non-reactive with the leachant and leachate, and do not absorb the released ions (Department of Nuclear Energy, 1990). To ensure a uniform environment, in which the temperature does not change by ±1°C and to simulate the higher temperatures found in landfills, the containers were placed in a 35°C incubator for the reaction period.

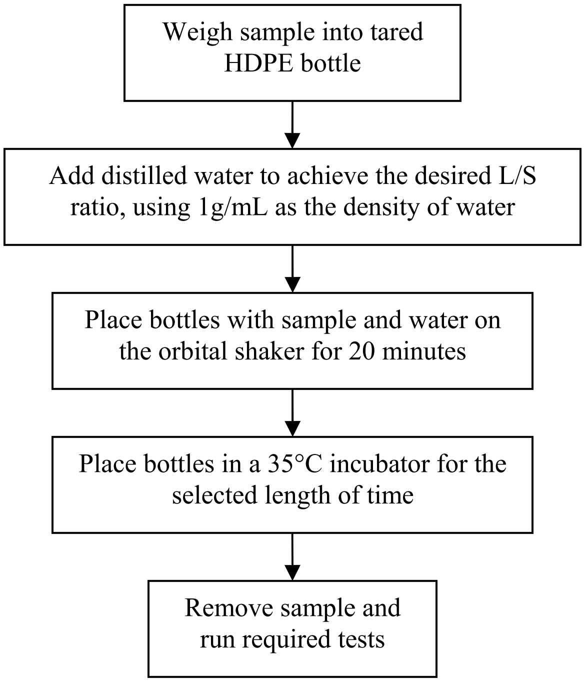

Figure 3: Overview of Approach Used for Preliminary Batch Tests

Preliminary Contact Time Tests

The first preliminary batch tests, designed to determine the contact time requirements of the solids and the leachant, were conducted using an L/S ratio of 10. This ratio was selected based on the EPA Toxicity Characteristic Leaching Procedure (TCLP) protocol that states that at L/S ≥ 10, the waste can be considered 100% solid and any residual water in the material can be disregarded in the calculation of leachant waste relationships (USEPA, 1996). Three aliquots of each of two ash samples- BA and FA- were placed in individual HDPE bottles and treated according to the scheme shown in Figure 3. Distilled water was added until an L/S ratio of 10 was reached for all six bottles based on an average density of 1 g/mL for distilled water. The contact times ranged from 24 to 120 hours, as shown in Table 9. At the end of the assigned time interval, the leachate was removed and tested for a limited number of parameters including, pH, conductivity, alkalinity, total organic carbon, total solids, and the dissolved metals: calcium, potassium, magnesium, sodium and aluminum. Since not all tests could be run on the first day, the samples were preserved and stored at 4°C for future analysis. Based on the results, it was concluded each system approached equilibrium by 48 hours. Therefore, shorter time intervals were needed at the initiation of the leaching reactions.

Table 9: Time Intervals Used for Initial Batch Tests

Type of Waste	FA	BA
Number of bottles	3	3
Respective contact times	24 hours 48 hours 120 hours	24 hours 48 hours 120 hours

Preliminary Sequential Extraction Tests

The second set of trial batch tests was designed to assess the difference in leaching based on the L/S ratio. Using FA as the solid and distilled water as the leachant, batch tests were set up as shown in Table 10. As before, the removed leachate was tested for a limited number of parameters. However, upon removing the leachate at the end of 48 hours, an equal amount of distilled water was used to replenish the leachant, thus maintaining a constant L/S ratio in the bottle but increasing the total L/S ratio over time. This was continued through four cycles, allowing for observation of the role of the L/S ratio in the depletion of soluble materials in the waste. The L/S of 4 and 6 did not provide sufficient leachate for analysis, while the L/S of 20 was too dilute. Based on this information, the actual batch tests were designed based on an L/S value of either 8 or 10.

Table 10: Fly Ash and Distilled Water at Various L/S Ratios

Bottle Number	Bottle 1	Bottle 2	Bottle 3	Bottle 4	Bottle 5
L/S ratio	4	6	8	10	20
Contact Time	48 hours	48 hours	48 hours	48 hours	48 hours
Number of Replenishments	4	4	4	4	4

The results from the preliminary batch tests were used to set basic parameters for the contact time and sequential extraction batch tests. The establishment of equilibrium at approximately 48 hours influenced the time intervals used in both types of batch tests. The L/S =10 was determined to be the best option since sufficient leachate was produced for analysis and the solid required no pretreatment.

Contact Time Batch Tests

The contact time batch test was designed to yield a static view of the interaction between the waste material and the leachant. From this information, the readily soluble materials could be identified and the length of time needed for the establishment of complete equilibrium could be determined. To insure a broad view of the interaction between ash and leachant the tests were set up for 21 days with three replicates per time interval as detailed in Table 11.

Table 11: Time Intervals for Contact Time Batch Tests

Contact Time Group Number	1	2	3	4	5	6	7	8	9
Contact Time Hours	2	7	72	144	216	288	360	432	504
Reaction Containers	3	3	3	3	3	3	3	3	3

The initial set-up for all batch tests was identical; 125 mL amber HDPE bottles were pre-cleaned by soaking in an acid bath of 1% nitric acid for 24 hours. The bottles were then rinsed five times with Nanopure™ water and allowed to air dry for two to three days. Once completely dried, the bottles were placed on an analytical balance, tared, and approximately 13.5 grams of ash was added to each bottle. The exact mass was recorded and sufficient distilled water was added to achieve an L/S = 10. The volume added was usually slightly more then 135 ml, which completely fills the bottle, eliminating headspace. The bottles were then treated as shown in Figure 4. At the end of each time interval, the three bottles were removed from the incubator and the leachate was removed by filtration. The leachate was divided into three volumes, one for immediate testing and the other two were preserved for chemical characterization.

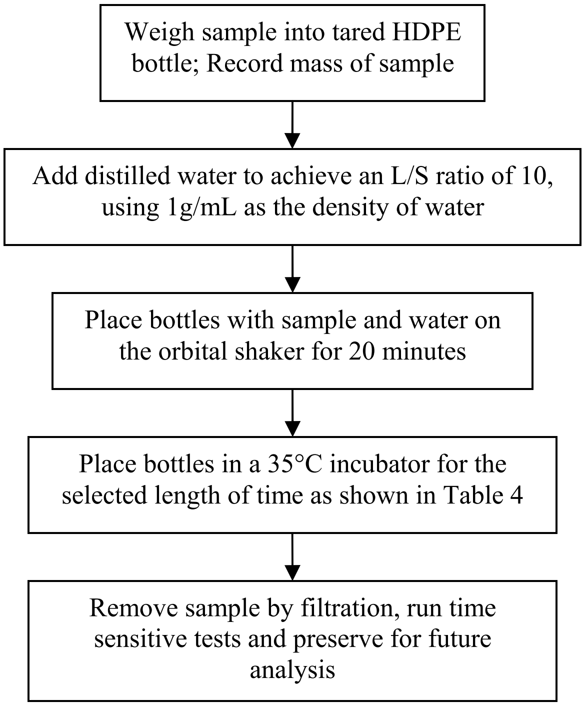

Figure 4: Overview of Contact Time Batch Tests

Sequential Extraction Batch Tests

The sequential extraction batch test was designed to provide a dynamic view of the interaction between solids and leachants. The identity of the more soluble constituents was seen in the preliminary tests; however, over time the contributions of less soluble materials to the leachate became obvious. The time interval between extractions was set at 72 hours, to allow apparent equilibrium to be reached while providing adequate time to test each sequential step. The duration of the sequential extraction tests was determined by the L/S ratio, which increased with each subsequent extraction, in most cases the process lasted 3 months. The HDPE reaction containers are shown in Figure 5 and the steps taken in the sequential extraction batch test are shown in Figure 6.

Figure 5: Sequential Extraction HDPE Reaction Containers

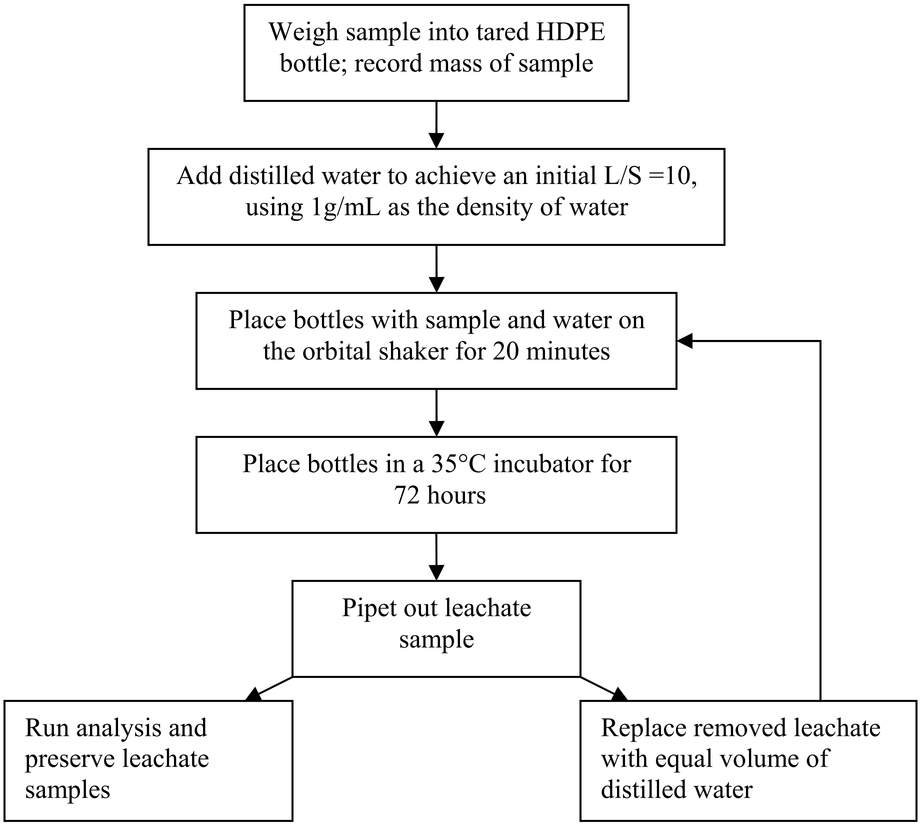

Figure 6: Overview of Sequential Extraction Tests

The subsequent removal of leachate and replenishment with distilled water started at an L/S of 10 and continued, with full chemical analysis, until the cumulative L/S ratio reached 100. By this point, a clear picture of the leaching trends of the ash was available; however, the ash was still releasing ions into solution. From L/S = 100 through L/S =200 the leachate was removed and replenished as before but the leachate was only tested for pH, temperature and conductivity. The final extraction at an L/S = 200 was preserved and fully analyzed.

Quality Assurance Methods

To reduce the possibility of contamination during the production and removal of leachate from the batch tests, several precautions were implemented. The leaching containers were made from HDPE, a material that does not interact with the leachate or the leachant and will not absorb materials released by the ash (Department of Nuclear Energy, 1990). The bottles and lids were pre-cleaned by soaking in a 1% nitric acid bath for 24 hours, removed, rinsed five times with Nanopure™ water, and allowed to air dry for several days. This process reduced the likelihood of the container contaminating the sample.

After each time interval, the leachate was removed by either pipetting or filtration. 25-50 mL disposable serological pipettes were used to remove the leachate from the sequential extraction batch tests. A new tip was used for each extraction and then disposed. The contact time batch test samples were filtered through Whatman 6 Qualitative filter paper, which retains particles larger than 3µm, using funnels that had been cleaned with Sparkleen 1 (Fisherbrand) and rinsed with Nanopure™ water.

A set of 24 Erlenmeyer flasks were initially acid washed in 1% nitric acid and rinsed thoroughly with Nanopure™ water. These flasks were dedicated for use in this project and isolated from the general laboratory equipment. Upon the removal of the leachate from each batch test, it was placed in one of these flasks. After the completion of the initial chemical analyses, the remaining leachate was transferred to Fisherbrand Disposable Sterile Centrifuge tubes for storage and preservation.

Leachate Characterization

The chemical characterization of the leachate produced by each batch test, laboratory lysimeters simulating ash monofills, landfills operating as monofills and landfills that co-deposit ashes with MSW included the use of several techniques. The procedures used in each test were based on Standard Methods for the Examination of Water and Wastewater, 20th Edition (1998). A list of the tests conducted for this project is shown in Table 12 and detailed protocols are given in Appendix A. For this project, characterization tests were grouped into two categories, those that were time sensitive and those that could be preserved for future analysis.

Table 12: Chemical Characterization Tests Used for Evaluation of Leachate

Test	Standard Methods, 20th Edition-number and description	Storage and Preservation	Detection Limits
pH	4500-H+ B. Electrometric Method inoLab pH probe, calibrated at pH=4, 7, 10	Test immediately	pH of 0-14
Conductivity	2510 B. Laboratory Method inoLab conductivity probe	Test immediately	1μS/cm – 2 S/cm
Dissolved Metals: Calcium, Copper, Iron, Magnesium, Manganese, Potassium, Sodium, Zinc	3111 B Direct Air-Acetylene Flame Method using a PerkinElmer Flame AA	Preserve by adding 5mL of concentrated nitric acid to 1 L of sample. Good for up to 6 months. Prior to use adjust to pH=4.	Lower limit= 0.1 mg/L to 0.01 mg/L depending on the metal
Total Hardness	2340 B. Hardness by Calculation	Based on metals preservation	Lower limit= 1 mg/L as $CaCO_3$
Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate, Sulfate	4140 B Capillary Ion Electrophoresis with indirect UV Detection. Using Beakman Capillary Electrophoresis	Refrigerate at 4°C and process as soon as possible	For 30s sampling time, lower = 0.1 mg/L
Carbonate	Calculated value from Alkalinity Titration	Store at 4°C and analyze within 6 hours	Lower limit = 12 mg/L
Alkalinity	2320 B Titration Method	Store at 4°C and analyze within 6 hours	Lower limit =20 mg/L as $CaCO_3$
Aluminum	3500-Al B. Eriochrome Cyanine R Method	Acidify with concentrated nitric acid to pH=2, good for 6 months	0.00 mg/L to 0.250 mg/L
Solids (TDS)	2540 C Total Dissolved Solids	Store at 4°C and begin test within 3 days	Lower limit= 10 mg/L
TOC	5310 C. Persulfate-UV Method using a SIEVERS 800 Portable Total Organic Carbon Analyzer	If the sample can not be analyzed immediately, it needs to be acidified to pH=2 with sulfuric acid	Lower limit= 0.01 mg C /L
Total Nitrogen	4500-N C. Persulfate Method	Acidify to pH< 2 using concentrated sulfuric acid and store at 4°C for up to 28 days	0-25 mg/L
Total Phosphorous	4500-P C. Vanadomolybdophosphoric Acid Colormetric Method	Acidify to pH< 2 using concentrated sulfuric acid and store at 4°C for up to 28 days	0-25 mg/L
Silica	4500-SiO2 Molybdosilicate Method	Store at 4°C in a plastic bottle for up to 7 days	0-100.0 mg/L

Time Sensitive Tests

Due to the instability of some constituents, it was important to complete some tests immediately after sample collection. The sample holding times ranged from immediate analysis to seven days. The time sensitive tests and the time ranges that were considered acceptable are listed in Table 13. If the tests could not be completed within the specified amount of time, the results obtained were considered questionable due to chemical reactions that occurred in the leachate.

Table 13: Summary of Time Sensitive Chemical Analysis

Time	Storage	Tests
Test Immediately	None	pH, Conductivity, Oxidation-Reduction Potential, Temperature
Within 6 hours	4°C	Alkalinity
Start within 3 days	4°C	Total Dissolved Solids
Within 7 days	4°C in plastic	Silica
As soon as possible	4°C	Anions (Cl^-, Br^-, NO^{2-}, SO_4^{2-}, NO_3^-, F^-, PO_4^{3-})

The four tests that needed to be completed immediately were done using probes, which made it possible to complete the analysis within 30 minutes of sample collection. Alkalinity titrations were conducted in triplicate for each sample, so each set of extractions required nine individual titrations. Generally, this could be completed within one hour of extracting the leachate. The solids analyses were also started on the same day as the leachate was extracted; a measured volume was filtered into a pre-weighed ceramic dish and placed in the oven to evaporate off the water. The final determination of the total dissolved solids took several days to complete due to the weighing, drying and cooling cycles required by the method. The remaining two time sensitive tests were completed as soon as possible, usually within seven days of sampling. The silica content was measured using wet chemistry, and the anion concentrations were determined by Capillary

Electrophoresis (CE). During the lag time between extractions and tests, the leachate was stored at 4°C.

Preserved Tests

After proper preservation, leachate samples were stored for analysis of metals and nutrients. The pH was lowered by adding a small volume of concentrated acid allowing these samples to be stored for up to six months at 4°C. For metal analyses preservation, 5 mL of concentrated nitric acid was added to each liter of sample. The reason for using nitric acid in the preservation of metals was that the nitrate ions released by the acid do not form precipitates with the metal cations. Concentrated sulfuric acid was used to preserve for total nitrogen, total phosphorous and total organic carbon. One interesting side effect of this preservation technique was the formation of calcium sulfate precipitates upon the addition of the sulfuric acid. An overview of the tests and the appropriate preservation techniques is given in Table 14.

Table 14: Summary of Preserved Tests

Time	Preservation	Storage Temperature	Tests
6 months	5 mL HNO_3 to 1 L sample	4°C	Al, Ca, Cu, Fe, Na, K, Mg, Mn, Zn
28 days	pH=2 by addition of H_2SO_4	4°C	Total Nitrogen, Total Phosphorous, Total Organic Carbon

Flame Atomic Absorption (FAA) was used to determine the concentration of dissolved metals in each leachate. The samples from each individual extraction were preserved and all samples from each test were analyzed as a group. The only exception was aluminum, this concentration was determined using Eriochrome Cyanine R. The SIEVERS 800 Total Organic Carbon Analyzer was used to determine the TOC. The remaining two tests, Total Nitrogen, and Total Phosphorous were colorimetric tests, requiring digestion.

Hardness, a chemical test that measures the multi-valent cations in a solution, can be determined by EDTA titration or by measurement of dominant multi-valent cations. In the analysis of leachate, the presence of large quantities of metals interferes with the color change of the indicator, making it impossible to detect the endpoint of the titration. Since the dominant cations in hardness are calcium and magnesium, the hardness was calculated using the following formula: Total Hardness (mg $CaCO_3$/L) = 2.497 $[Ca^{2+}]$ + 4.118$[Mg^{2+}]$ (Standard Methods, 1998). The calcium and magnesium concentrations were measured using the FAA.

Chemical Analysis Quality Assurance

To ensure the accuracy of the chemical parameters measured during leachate characterization tests, specific quality assurance practices were adopted. Depending on the type of equipment involved, these tests involved re-calibrating, testing standards, running blanks, running replicates or spiking the sample with a known ion. On occasion, to verify the accuracy of results multiple checks were employed.

The pH probe and FAA required regular re-calibration. The pH probe was recalibrated every three to four days using Arcos brand buffer solutions with pH = 4, 7, 10. To eliminate any cross contamination, the probe was thoroughly rinsed with Nanopure™ water and dried with a Kimwipe™ between testing each sample. The FAA required calibration each time it was turned on or the lamp was changed. At least five standards were used to create a calibration curve, with the middle concentration used to re-slope the curve. A graph of the calibration curve was printed at the beginning of each run to verify the accuracy of the calibration. The concentrations of the standards used in calibrating depended on the metal tested. Calcium, sodium and potassium required high range calibration curves, while iron, magnesium and manganese were low range calibrations. Since the samples were preserved at the time of extraction, all of the leachate produced by the batch tests was analyzed using the same calibration curve. To avoid contamination, the sampling capillary was rinsed with Nanopure™ water between each sample. Three replicates were run on each sample and to insure consistency in the readings, the FAA was re-sloped after every ten samples.

The CE calibration was also based on a standard curve; however, the accuracy of the curve was verified periodically instead of recalibrating the system. This verification was accomplished by processing a solution of known concentration every two weeks and analyzing the results. At times, questions came up about the identity of a peak on the electropherogram, and to verify the identity of the ion producing the peak, the sample was spiked and rerun. If the peak in question increased in size, then its identity was verified. If a new peak appeared, then its location helped identify the peak since they always appeared in the same order.

Testing a standard solution was the method used to insure the validity of the conductivity and ORP probes. Two solutions were prepared following the procedures in Standard Methods; these were 0.01 M KCl solutions for testing conductivity and a Light's solution for ORP (Standard Methods, 1998). The probes were placed in the appropriate solutions every two weeks and allowed to equilibrate. The reading on the conductivity probe was usually within 2% of the expected value of 1412 μS/cm, indicating the accuracy of the measurements. According to the ORP probe information, the Light's standard should read between 400 and 500 mV. When tested, the ORP probe was between 430-460 mV, which indicated it was valid in an oxidized solution. Unfortunately, most of the results from the leachate were reduced and it was impossible to verify the accuracy in a reduced environment since a standard for this range was not available.

One of two approaches, running replicates or processing a standard, verified the remaining tests. For the tests verified by running replicates, the average and the standard deviation were calculated and recorded. Some of the tests were very labor intensive, so completing multiple runs was impractical; instead a standard with the concentration comparable to the expected results was run in parallel with the sample.

Data Validation and Analysis

To keep all of the data organized, data from each WTE facility was stored electronically in a separate directory; within the folder was an Excel workbook for each batch test. Data from individual results were entered into the appropriate spreadsheet and the significant figures verified. Since all batch tests were run in triplicate, the results were averaged and the standard deviation was calculated. Any results that deviated from the average were re-examined and if needed the test were repeated.

Data Validation

To validate the comprehensiveness of the analyses of the leachates, three internal checks were performed: measured TDS to conductivity ratio, measured TDS = calculated TDS, anion-cation balance. These approaches are described in the Data Quality section of Standard Methods (Standard Methods, 1998).

The TDS test measures the mass of dissolved solids in the leachate, while conductivity measures the ability of the leachate to conduct an electrical current. TDS to conductivity ratios between 0.55 and 0.7 were considered acceptable and were calculated by dividing the TDS (mg/L) by the conductivity (µS/cm) (Standard Methods, 1998). Values that fell outside of the acceptable range indicated that one or both of the measurements were suspect and the tests needed to be repeated. An additional technique for examining the relationship between these two pieces of discrete data was to graph the TDS versus conductivity and add a trend line. The slope of the trend line was positive, indicating an increase in conductivity with an increase in TDS. To determine the "nature and strength" of the relationship between these two parameters the Pearson Product-Moment Correlation coefficient was calculated (Blair, 1999). This allowed for a definitive determination of the positive correlation and the degree to which the relationship was linear.

A comparison of the measured TDS and the calculated TDS was used to ensure that most of the dominant constituents were identified. The measured TDS was determined by evaporation of the water from an aliquot of filtered leachate while the calculated TDS was arrived at by summing the concentrations of the measured constituents. In theory, if all constituents had been identified, the ratio of calculated TDS to measured TDS would be 1 (Standard Methods, 1998). The acceptable ratio range for calculated TDS to measured TDS was between 0.8 and 1, values outside of the range were considered suspect and required further analysis.

The final validation step focused on the ions in the leachate. Since solutions are electrically neutral, the positive charges have to equal the negative charges. The concentrations of the measured constituents were converted from mg/L to meq/L that allowed for a comparison of the relative charges rather than that of the masses. The formula used, taken from Standard Methods, 20th edition, for the cation-anion balance was:

$$\% \text{ Difference} = 100\,\frac{\Sigma \text{ cations (meq/L)} - \Sigma \text{ anions (meq/L)}}{\Sigma \text{ cations (meq/L)} + \Sigma \text{ anions (meq/L)}}$$

The acceptable difference for solutions of high ionic concentration was 5 percent or less (Standard Method, 1998).

Analysis

Several statistical and chemical techniques were employed to evaluate batch test results and to compare results from different tests. Statistical techniques were used to organize and summarize the data. The chemical techniques provided insight into the relationships of the different elements in the leachate and the stability of the leachate. The statistical analysis is explained first, followed by the chemical analysis.

The average, also called the arithmetic mean, measures the central tendency and standard deviation measures the variability in the data (Blair, 1999). These calculations provided insight into the precision of the data. The average was calculated for each CT group (Table 11) and SE extraction set, allowing for a comparison within the groups. The average and standard deviation were calculated for each parameter in the completed CT tests.

The one-way ANOVA F-test allowed for the comparison of results between different batch tests. With $\alpha = 0.05$, the ANOVA tested the null hypothesis, H_o: $\mu_1 = \mu_1 = \mu_1 = \mu_1$, against the alternative hypothesis, H_1: not all μ_i are equal. The calculations were performed using Microsoft® Office Excel 2003, which provided the statistical analysis in the form of a table as shown in Table 15.

Table 15: Sample ANOVA Results from Microsoft ® Office Excel 2003

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
H	27	37990	1407.037	32837.04
P	27	34605	1281.667	68544.23
FA	27	16550	612.963	6475.499
BA	27	41493	1536.778	44741.1

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	13694293	3	4564764	119.6547	1.37E-33	2.691979
Within Groups	3967545	104	38149.47			
Total	17661838	107				

The first analysis compared the results from H, P, FA, and BA contact time tests. The same analysis was used on the H, P, FA, and BA sequential extraction tests. The second comparison subdivided the batch test results into two categories based on the WTE facility technology, comparing H to P and FA to BA. When comparing the CT results to the SE results, the ANOVA test was not useful due to large changes that occurred with each subsequent extraction in the SE tests. Instead, a two-sample unequal variance t-test was used to compare the first four SE results to the CT results.

Parameters with high degrees of variability required the use of several additional techniques. The use of trend lines and linear regressions provided information about the correlation of data. The generated equation indicates whether the correlation was positive or negative and allowed for possible predictions of future changes. The coefficient of determination, r^2, indicated the strength of the model (Blair, 1999). In the SE results, the clearest interpretation of the data was provided by the percent decrease in concentration over a set number of extractions.

Several techniques were used to analyze chemical data. First the concentrations were converted to mol/L by dividing the mass concentrations by the molar mass of the measured element. Using balanced chemical reactions and chemical formulas, a quick comparison of the molar ratios was possible. However, in concentrated solutions, the molar concentrations are insufficient in determining the behavior of the ions. The charges and concentrations of the ions in solution can influence the ionic interactions and therefore it is important to include activity corrections.

First the ionic strength of the leachate was calculated and used to calculate activity coefficients for the individual ions. The formula used to calculate ionic strength was $I = \frac{1}{2} \Sigma c_i z^2$ (Benjamin, 2002). The activity coefficients were calculated using the Davies equation, $\log \gamma_{DAVIES} = -Az^2[(I^{0.5}/1-I^{0.5})-0.2I]$, which is applicable for solutions with $0.1 < I < 0.5$ (Benjamin, 2002). The Davies equation provides activity coefficients based on the ionic charge. Once the molar concentrations were corrected for activity, the potential for precipitate formation was analyzed using saturation indices.

A saturation index is the ratio of the reaction quotient, Q, to the solubility product, K_{sp}. The reaction quotient is the product of the molar concentrations of the ions in the mineral, adjusted for activity. The K_{sp} value is an equilibrium constant and changes depending on the temperature of the system. The K_{sp} value was adjusted from 25°C to 35°C using the Arrhenius equation (Benjamin, 2002). The relationships between Q, Ksp and the saturation index are presented in Table 16.

Table 16: Relationship of Q, Ksp and Saturation

Q, K_{sp} Relationship	Saturation Index value	Level of Saturation
$Q < K_{sp}$	< 1	Unsaturated
$Q = K_{sp}$	= 1	Saturated, equilibrium
$Q > K_{sp}$	> 1	Supersaturated

Results

The results from the batch tests, lysimeter studies, and field samples are presented in this section. A comparison of selected results from the contact time (CT) tests and the sequential extraction (SE) tests is provided and compared to characteristics of leachates from laboratory lysimeters and field samples. Batch test results are used to identify the dominant chemical factors influencing the formation of precipitates.

Comparison of Contact Time and Sequential Extraction Batch Tests

In this section results obtained from the CT and SE tests are compared. The ash samples used in the batch tests were obtained from three different WTE facilities: Hillsborough (H), Pasco (P) and Palm Beach (FA and BA).

pH, Alkalinity, and Conductivity

Leachates from all ash samples had relatively high levels of pH regardless of source or leachate extraction method. The pH values for the leachate produced using the CT test ranged from pH = 11.3 to 12.0.while the SE results ranged from pH = 10.5 to 12.0. Alkalinity is a measure of the buffering capacity of a solution, and the alkalinity results differ depending on the type of batch test used to produce the leachate and the source of the ash. The alkalinity results were more variable than the pH results with CT test standard deviations ranging from 60 to 250 mg/L as $CaCO_3$. During the first six extractions SE alkalinity values decreased by 18% to 83% (Table 20). The alkalinity and pH results for the CT tests are presented in Figure 7, and the SE test results are presented in Figures 8 – 11.

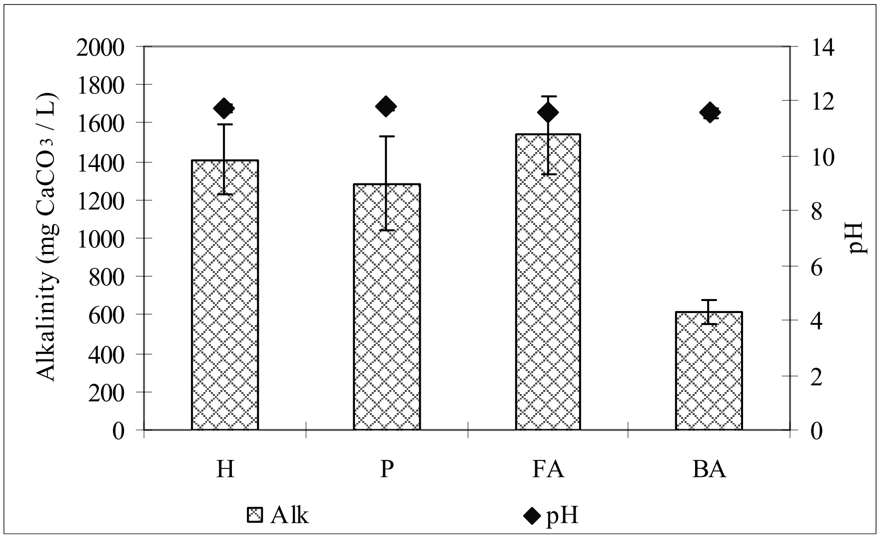

Figure 7: Comparison of pH and Alkalinity for Leachates Produced Using Contact Time Batch Tests

In the SE tests, after encountering a mass of water equal to 100 times the initial mass of ash, the pH values had standard deviations of less than 0.4, and trend lines added to the pH values on Figures 8 - 11 having slopes of less than 0.1. An ANOVA analysis comparing the pH to the L/S ratios showed the slopes of the lines did not deviate significantly from zero. Thus, even though there was a reduction in alkalinity, the buffering capacity of the leachate was still adequate to resist a change in pH. The final alkalinity values were similar to those of typical groundwater ranging from 60 to 110 mg $CaCO_3$ /L.

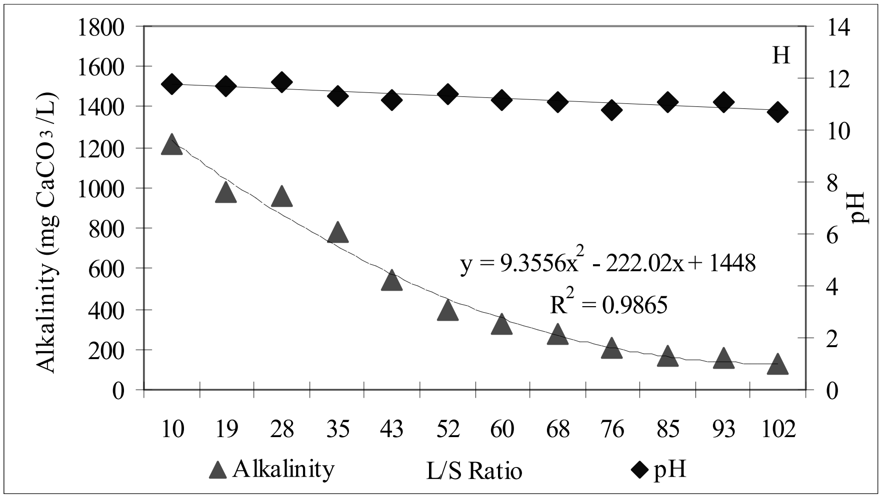

Figure 8: Sequential Extraction Alkalinity and pH Results for Hillsborough Ash

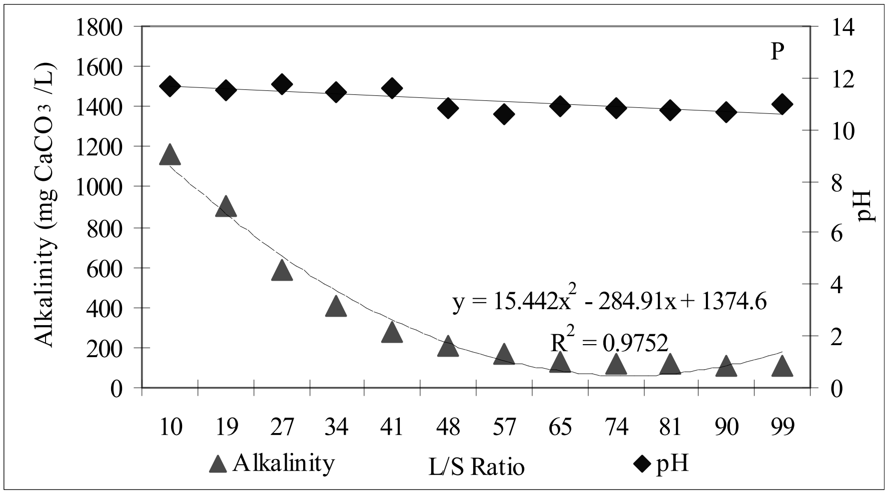

Figure 9: Sequential Extraction Alkalinity and pH Results for Pasco Ash

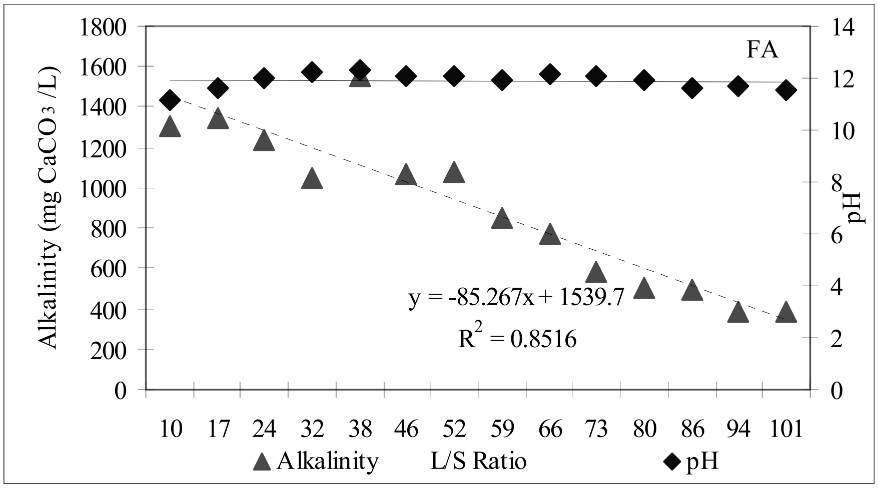

Figure 10: Sequential Extraction Alkalinity and pH Results for Fly Ash

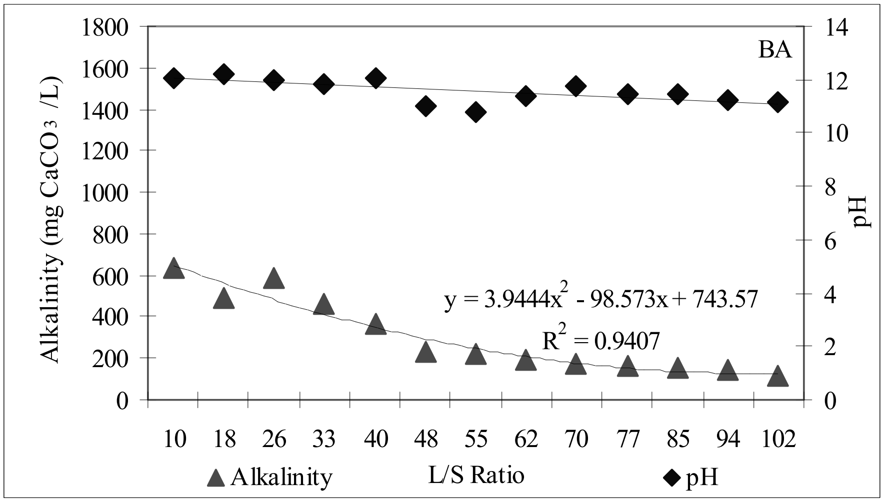

Figure 11: Sequential Extraction Alkalinity and pH Results for Bottom Ash

A one-way ANOVA, with $\alpha = 0.05$, tested the null hypothesis, H_o: $\mu_1 = \mu_1 = \mu_1 = \mu_1$, against the alternative hypothesis, H_1: not all μ_i are equal. The results showed $F > F_{critical}$ when comparing all four samples for alkalinity and pH, causing H_o to be rejected. However, grouping the samples according to WTE technology used at the facility changed the F statistic. ANOVAs of H and P leachates showed no significant difference in pH, with $F < F_{critical}$. H_o was rejected for the H and P alkalinity CT results but the SE results failed to reject H_o. An ANOVA of the CT results for FA and BA pH results showed no significant difference. The other ANOVAs used to analyze FA and BA showed large differences between the alkalinities and pHs of these two samples, causing a rejection of H_o. A summary of the ANOVA results for alkalinity and pH is presented in Table 17.

Table 17: ANOVA Table for Batch Test Alkalinity and pH Values

Sample	Type of Batch Test	df	F (alkalinity)	$F_{critical}$	F (pH)	$F_{critical}$
H, P, FA, and BA	CT	107	119.67	2.69	18.97	2.69
H and P	CT	53	4.19	4.03	2.15	4.03
FA and BA	CT	53	449.91	4.03	0.45	4.03
H, P, FA, and BA	SE	55	10.67	2.82	10.94	2.78
H and P	SE	27	1.04	4.30	0.22	4.23
FA and BA	SE	27	34.74	4.30	5.50	4.23

A one-way ANOVA was used to compare the alkalinity and pH from the CT and SE leachates. There was a significant difference between the two batch tests. When the samples were subdivided as before, there were significant differences between H, P and FA, while BA had an $F < F_{critical}$. A summary of this analysis is presented in Table 18.

Table 18: ANOVA Results Between CT and SE for Alkalinity and pH Results

Sample	Type of Batch Test	df	F (alkalinity)	$F_{critical}$	F (pH)	$F_{critical}$
H, P, FA, and BA	CT and SE	95	42.53	2.12	13.14	2.10
H	CT and SE	23	39.41	4.30	29.20	4.23
P	CT and SE	23	32.67	4.30	33.73	4.23
FA	CT and SE	23	43.64	4.26	11.57	4.23
BA	CT and SE	23	24.81	4.26	1.99	4.23

Because an ANOVA tests requires equal numbers of samples, a two-sample unequal variance t-test compared the first four SE results to the CT result. This analysis showed no significant differences in pH during the first four extractions. A summary of the t-test results is presented in Table 19. An obvious decrease in alkalinity with each subsequent extraction precluded the use of this comparison.

Table 19: Two-Tail T-Test of pH for First Four SE Results and Complete CT Results

Samples	P(T<=t) two-tail	t Critical
H: CT and SE	0.009	2.262
P: CT and SE	0.157	3.182
FA: CT and SE	0.489	4.303
BA: CT and SE	0.002	2.776

Conductivity is a measure of a solution's ability to conduct an electrical current and an indirect measure of the dissolved ions in a solution. TDS values directly relate to conductivity. Generally, the TDS/EC ratio for a solution is between 0.55 and 0.7 (Standard Methods, 1998). Given this relationship, the TDS results are expected to mirror the conductivity results. The conductivity and TDS results for the CT batch tests are presented Figure 12. The SE results for these two parameters are presented in Figures 13 – 16.

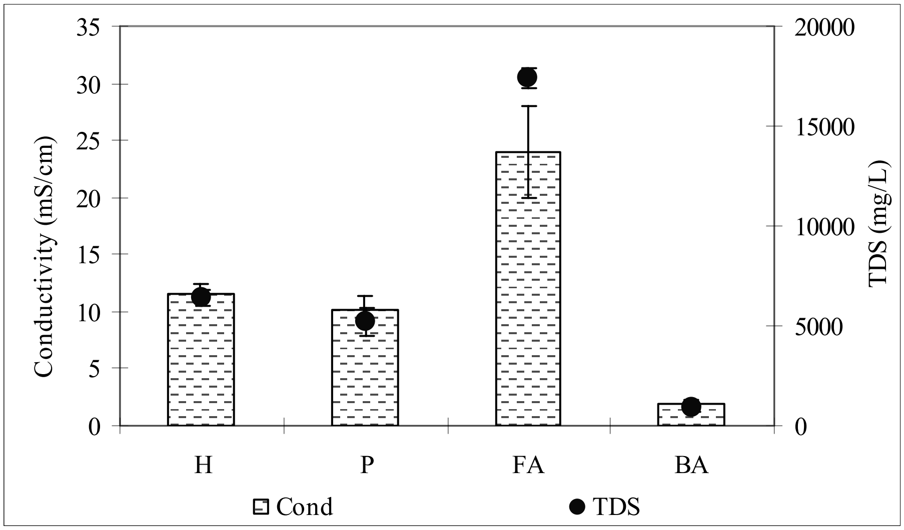

Figure 12: Conductivity and TDS for Contact Time Batch Tests

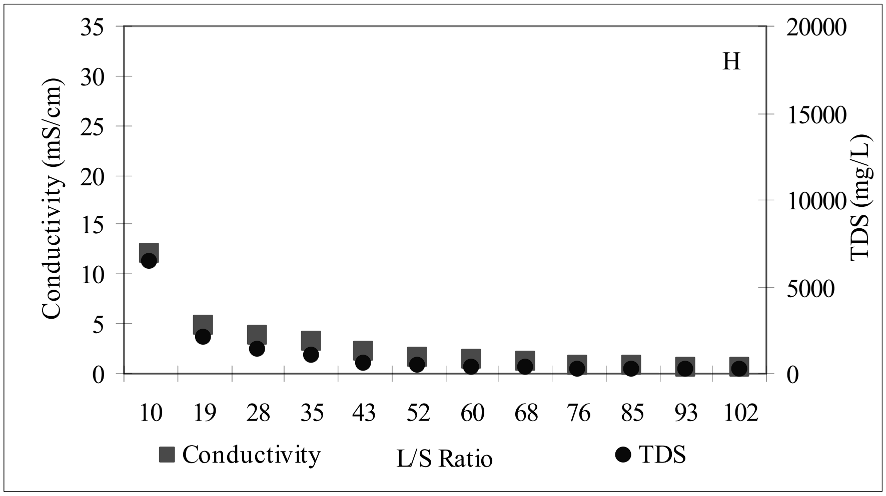

Figure 13: SE Conductivity and TDS Results for Hillsborough Ash

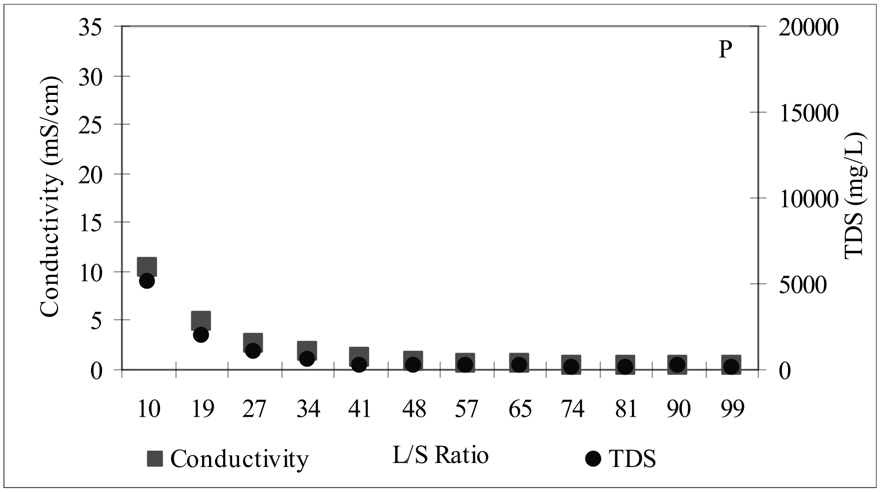

Figure 14: SE Conductivity and TDS Results for Pasco Ash

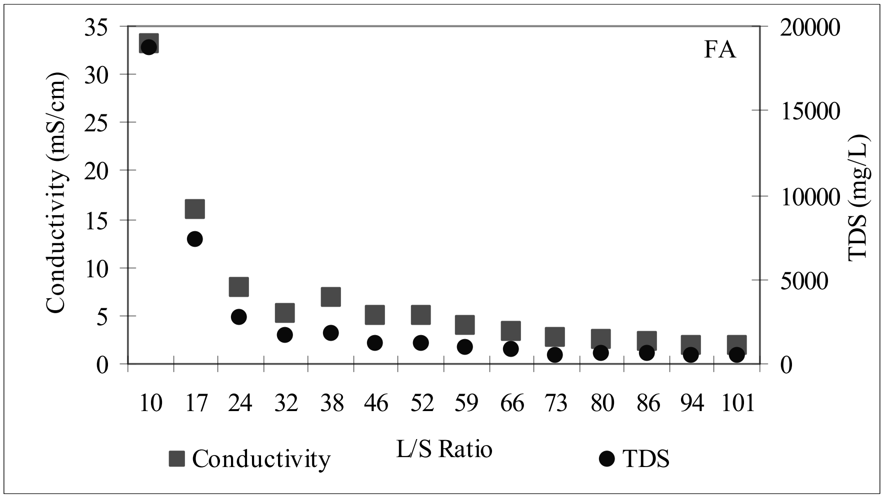

Figure 15: SE Conductivity and TDS Results for Fly Ash

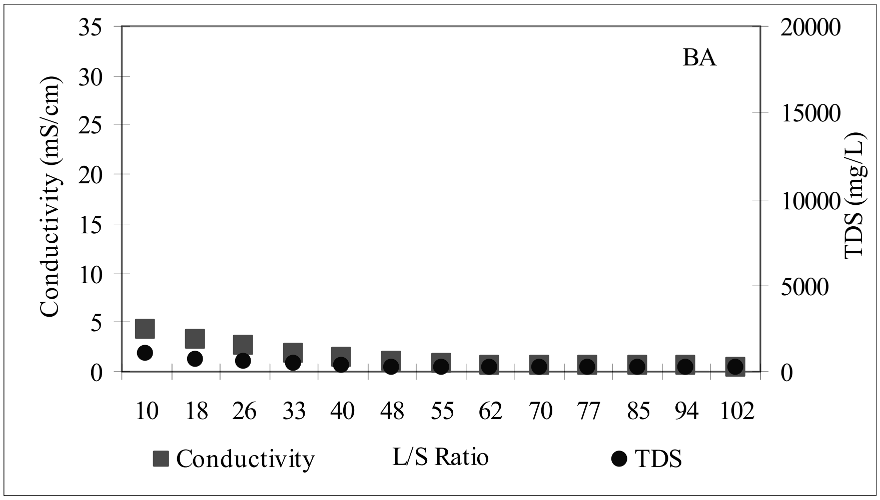

Figure 16: SE Conductivity and TDS Results for Bottom Ash

The CT batch test for H, P and BA had lower conductivity and TDS results than FA (Figure 12). The H and P ashes were quenched at the WTE facility prior to landfilling. This initial rinse removed some of the readily soluble minerals, reduced the ability of the ash to release ions and in turn lowered the conductivity. The BA had the lowest conductivity due to the insoluble nature of the minerals found in the ash.

During the SE test, for all samples, the greatest decrease in conductivity and TDS occurred during the first three extractions. Suggesting that the readily soluble ions were washed out of the ash quickly, leaving behind less soluble constituents. Most of the samples had a decrease greater than 85% from the initial conductivity, and 93 % from the initial TDS values after six extractions. The bottom ash was the exception, dropping 76% and 78% respectively. A possible explanation is due to the lower concentration of soluble ions in the original bottom ash sample. The percent decrease for each sample after six extractions is presented in Table 20.

Table 20: Summary of Percent Decrease in Alkalinity, Conductivity, and TDS During the First Six Sequential Extractions

	H % Decrease	P % Decrease	FA % Decrease	BA % Decrease
Alkalinity	67	83	18	63
Conductivity	86	92	85	77
TDS	93	94	93	78

It should be noted that conductivity measurements were not reliable during part of the study making the data questionable. This could be considered a minor deviation given that the TDS results mirror the conductivity results.

Major and Minor Ions

In general, the results for the other tested parameters follow the same patterns as seen above; the CT tests established equilibrium while the SE tests showed a reduction in concentration during the first six extractions. The dominant ions in the batch tests leachates were calcium, potassium, sodium, carbonate, chloride and sulfate.

The sodium, potassium and chloride ions are readily soluble and not usually found in LCS clog materials. However, an abundance of these ions does influence the ionic strength of the leachate, changing the activities of the precipitate-forming ions. The concentrations of these three ions from CT tests are presented in Figure 17.

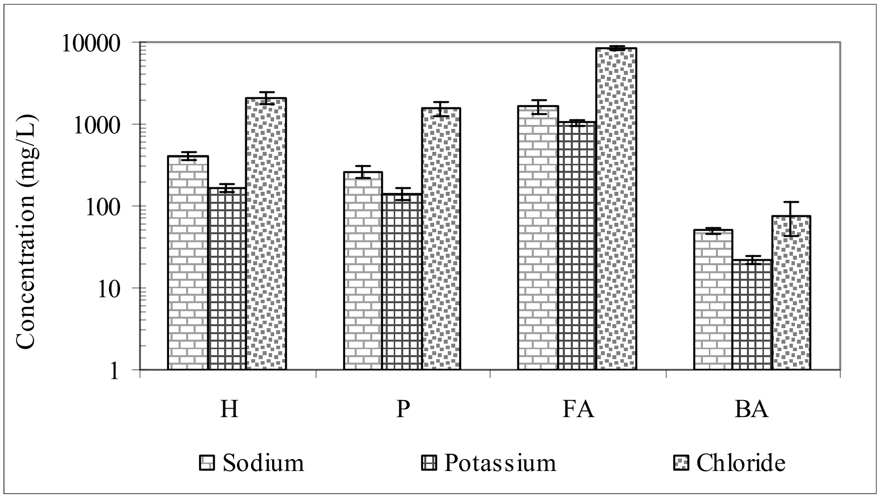

Figure 17: Log Scale Concentrations of Sodium, Potassium, and Chloride from CT Batch Tests

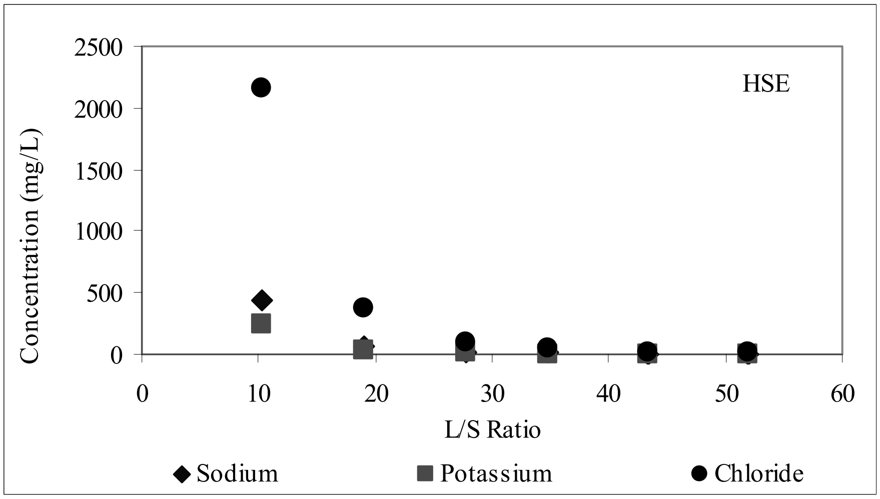

Figure 18: Extractions 1 - 6 Sodium, Potassium, and Chloride Results for H Leachate

The SE test concentrations for sodium, potassium, and chloride are presented in Figure 18 for H leachate over an L/S ratio of 10-60. These same trends were observed in all the ash samples and by the second extraction; the impact of these ions on the ionic strength of the leachate was no longer significant. The concentrations of these ions for the first six extractions of P, FA, and BA leachate are presented in Table 21 and the percent decreases are presented in Table 23.

Table 21: Extractions 1 - 6 Sodium, Potassium, and Chloride Results for P, FA, and BA Leachates

Sample	Ion	L/S 10 Conc. (mg/L)	L/S 20 Conc. (mg/L)	L/S 30 Conc. (mg/L)	L/S 40 Conc. (mg/L)	L/S 50 Conc. (mg/L)	L/S 60 Conc. (mg/L)
P	Na^+	256	41	12	7.6	5.5	3.7
	K^+	150	28	7	4.0	3.1	1.5
	Cl^-	1460	203	60	41.9	23.3	7.6
FA	Na^+	1834	553	159	58.7	35.6	20.7
	K^+	1164	301	68	28.1	20.2	11.6
	Cl^-	7652	3051	666	207.2	144.9	49.6
BA	Na^+	61	12	6	2.9	2.9	3.1
	K^+	51	15	6	2.6	1.9	1.2
	Cl^-	35	17	10	13.4	5.5	3.4

Calcium, carbonate and sulfate were the dominant ions found in the precipitates that clog LCS. The H, P, and FA ash samples had high concentrations of calcium, ranging from 1476 mg/L to 4273 mg/L. These concentrations were at least double those of carbonate or sulfate. The BA sample had the lowest concentrations, and the calcium concentration was lower than the carbonate concentration. These relationships are presented in Figure 19.

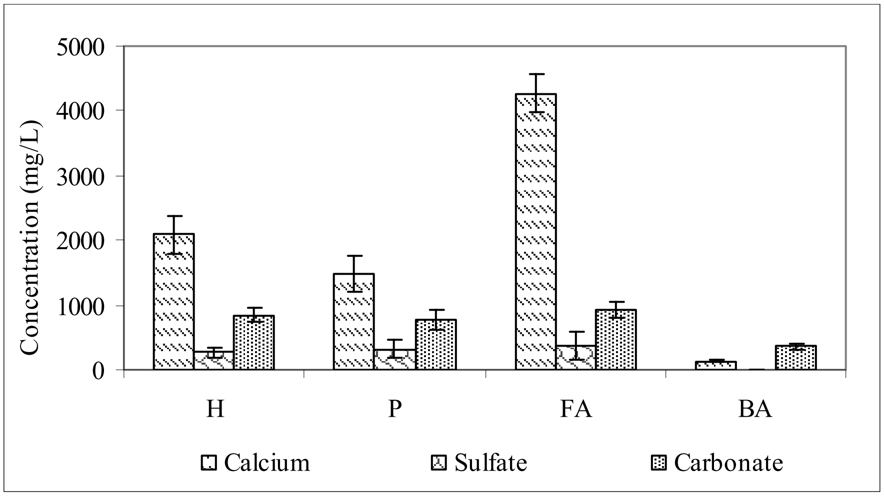

Figure 19: CT Test Calcium, Carbonate and Sulfate Results for H, P, FA, and BA Leachates

With the exception of BA sulfate concentrations, the SE batch test for calcium, carbonate and sulfate followed the same pattern. The concentrations decreased with each subsequent extraction. The initial six extractions of the Hillsborough ash are presented in Figure 20, and a summary of the P, FA and BA results are presented in Table 22. The percentage decrease of calcium, potassium, sodium, carbonate, chloride, and sulfate ions are presented in Table 23. Since the calcium, carbonate, and sulfate were less soluble, the percent decrease was less than that of potassium, sodium and chloride.

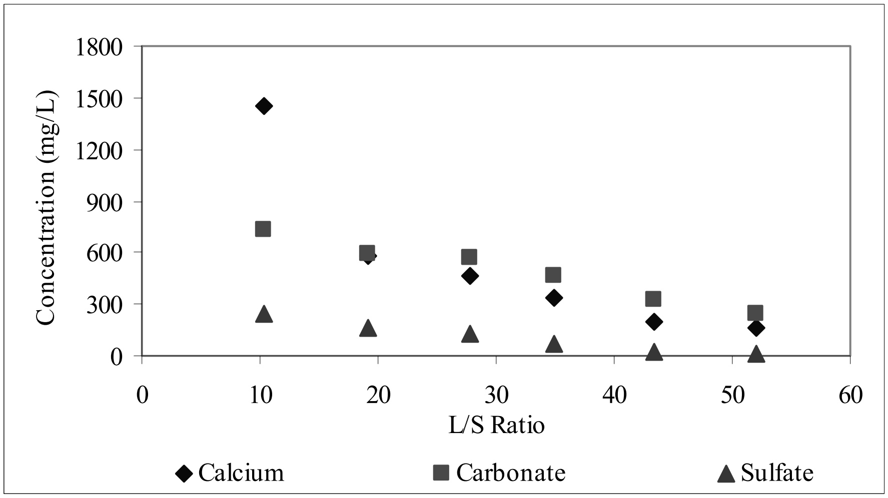

Figure 20: SE Test Calcium, Carbonate and Sulfate Results for H Leachate

Table 22: Extractions 1 - 6 Calcium, Carbonate and Sulfate for P, FA, and BA Leachates

Sample	Ion	L/S 10 Conc. (mg/L)	L/S 20 Conc. (mg/L)	L/S 30 Conc. (mg/L)	L/S 40 Conc. (mg/L)	L/S 50 Conc. (mg/L)	L/S 60 Conc. (mg/L)
P	Ca^{+2}	1167	505	283	188	123	71
	CO_3^{-2}	700	544	352	244	168	128
	SO_4^{-2}	320	167	114	68	46	36
FA	Ca^{+2}	5637	2179	892	562	539	545
	CO_3^{-2}	782	806	740	628	934	640
	SO_4^{-2}	512	210	30	16	8	7
BA	Ca^{+2}	411	308	267	210	151	97
	CO_3^{-2}	382	294	350	276	218	140
	SO_4^{-2}	16	25	34	28	30	26

Table 23: Summary of Percent Decrease in Calcium, Potassium, Sodium, Carbonate, Chloride, and Sulfate for H, P, FA, and BA Leachates

Ion	H % Decrease	P % Decrease	FA % Decrease	BA % Decrease
Calcium	89	94	90	76
Potassium	99	99	99	98
Sodium	99	99	99	95
Carbonate	67	82	18	63
Chloride	99	99	99	90
Sulfate	93	89	98	N/A*

*BA did not show a decrease in sulfate concentration.

For the other tested parameters, concentrations were either near or below the methods detection limits. In general, these constituents followed the same patterns presented above, with two exceptions: CT zinc and SE aluminum. The CT zinc concentrations for H, P, and FA, even though extremely low, were highest in the first time interval of two hours and decreased as presented in Figure 21. This behavior implies that the zinc originally bonded to a more soluble anion and quickly dissolved. Once in solution, the zinc precipitated out of the leachate. The other minor cations in the CT test did not exhibit any discernable patterns.

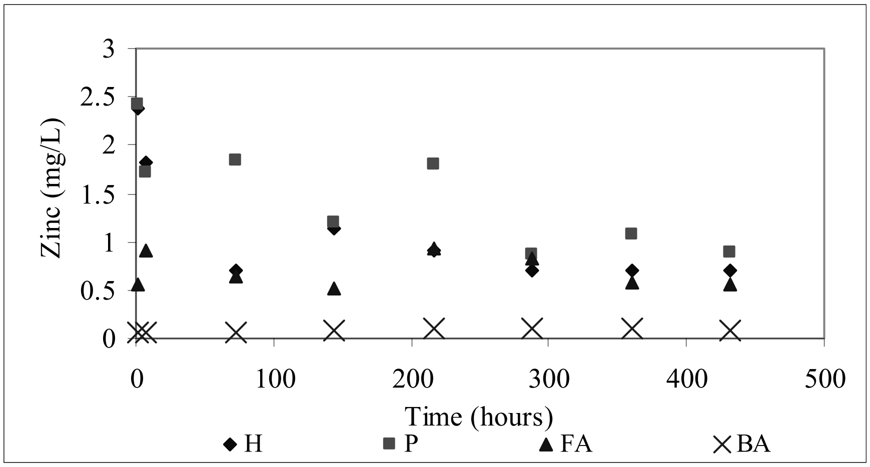

Figure 21: Contact Time Results for Zinc Concentrations

The aluminum ions in the SE tests did not exhibit the same behavior pattern as the other ions. Over time, the concentrations of aluminum in the leachates increased as presented in Figure 22. One explanation for this behavior was that the aluminum, which had a low solubility, was bonded to an anion that washed out during the extractions and the solubility equilibrium shifted to enable dissolution. Another possibility was the samples had pieces of aluminum metal that may have been oxidized to Al^{+3} as the leachate changed with each subsequent extraction. The pieces of aluminum metal were visible in the bottom ash samples.

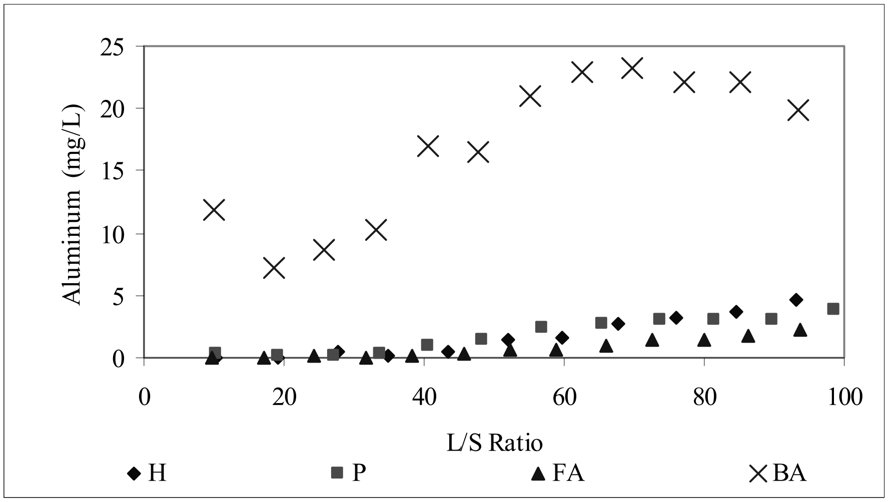

Figure 22: Sequential Extraction Results for Aluminum

As shown, the CT and SE batch tests present different information about the leaching characteristics of the samples. The CT test provided information about the readily soluble minerals present in the ash and the time needed to establish equilibrium. Whereas, the SE test provided a more dynamic view of the leaching behavior, providing insight into the changes in leaching patterns as the waste encountered fresh leachant.

Comparison of Batch Tests, Lysimeters and Field Samples

In this section, CT batch leachates are compared to leachates from lysimeter and landfills. The reason for using the CT results in the comparison with the lysimeter monofill results (R1 and R5), provided by Cardoso (2004), is that leachate was recirculated through the lysimeter and the system had an L/S < 10. The landfill leachate was a grab sample generated by ashes of different ages and L/S ratios. The FA and BA results are compared to lysimeter leachates (R1 and R5) and Palm Beach landfill leachates (PBL). The landfill receiving the FA and BA ashes co-deposits the ash with MSW and water and wastewater treatment sludges. The H and P ashes are compared to

R1, R5 and Pasco landfill leachate (PL). The Pasco landfill deposits the P ash received from the neighboring WTE facility in a monofill.

The major elements found in LCS clog material are calcium, carbon, and sulfur. The pH and concentration of ions influences the rate of precipitate formation. Because of this, the following section focuses on these select parameters: pH, calcium, carbonate, and sulfate. Carbonate levels for the landfill leachates were estimated from alkalinity measurements using a conversion factor of 0.60.Unfortunately, this approach overlooks the impact of volatile fatty acids (VFA) on the measured alkalinity.

Carbonate is a weak diprotic acid that acts as a buffer in natural systems. The disassociation reactions and pKa's for the carbonate system at 25°C are as follows (Kotz, 1991):

$$H_2CO_{3\,(aq)} \leftrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)} \quad pKa_1 = 6.38$$

$$HCO_3^-{}_{(aq)} \leftrightarrow H^+_{(aq)} + CO_3^{-2}{}_{(aq)} \quad pKa_2 = 10.32$$

The species of carbonate present in leachate depend on the pH of the leachate. A comparison of the carbonate concentrations and pH values of the leachates is presented in Figures 23 and 24.

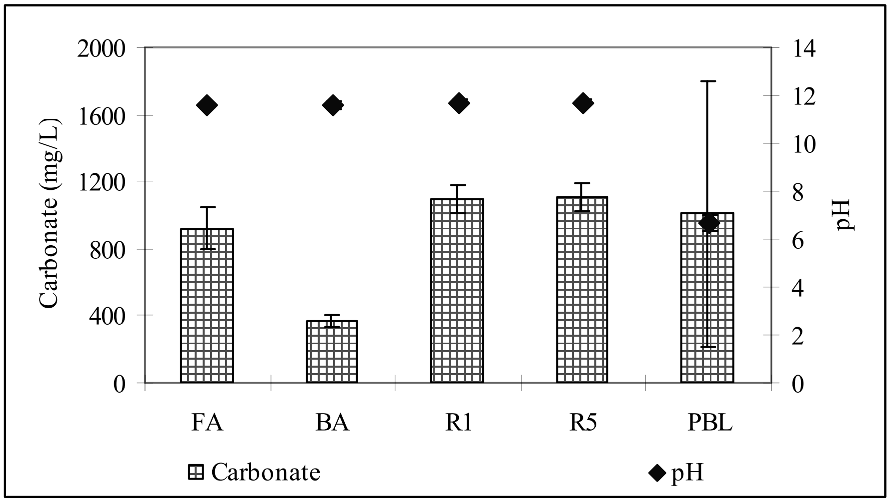

Figure 23: Comparison of Carbonate and pH for FA, BA, R1, R5 and PBL Leachates

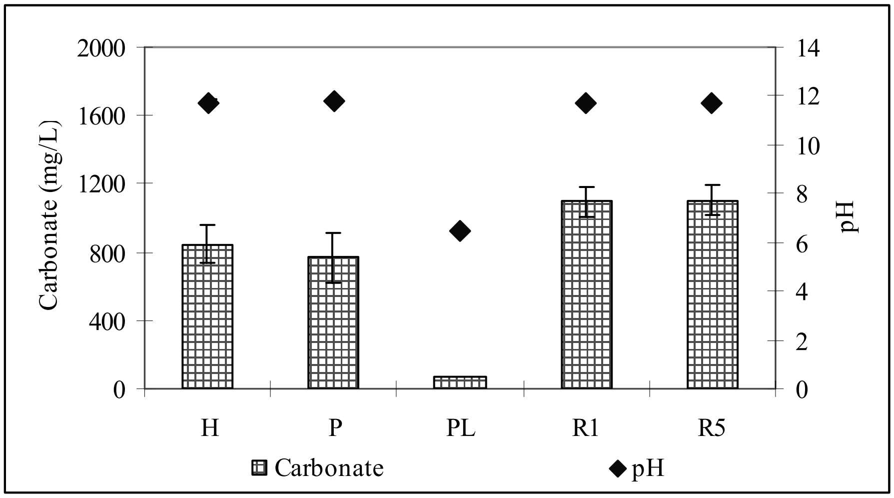

Figure 24: Comparison of Carbonate and pH for H, P, PL, R1 and R5 Leachates

The leachate produced in the laboratory had a high pH indicating that the majority of the carbonate ions were present as carbonate. The landfill leachates had lower pH values, so the dominant species for the carbonate ions was most likely bicarbonate. The PBL leachate appears unusual in this comparison, the low pH and high carbonate values seem contradictory. Since the landfill that generated this leachate co-deposits ash with other waste materials, a high VFA concentration probably caused the discrepancy.

The calcium, carbonate, and sulfate ion concentrations for the laboratory and landfill leachates are presented in Figures 25 and 26. The concentration of calcium was higher than 1000 mg/L in all samples except BA which average 133 mg/L.

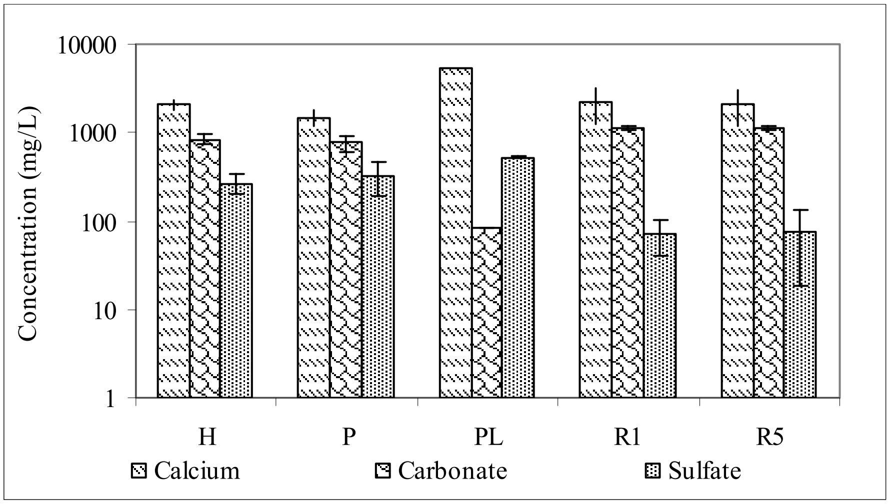

Figure 25: Comparison of Calcium, Carbonate, and Sulfate for H, P, PL, R1 and R5 Leachates

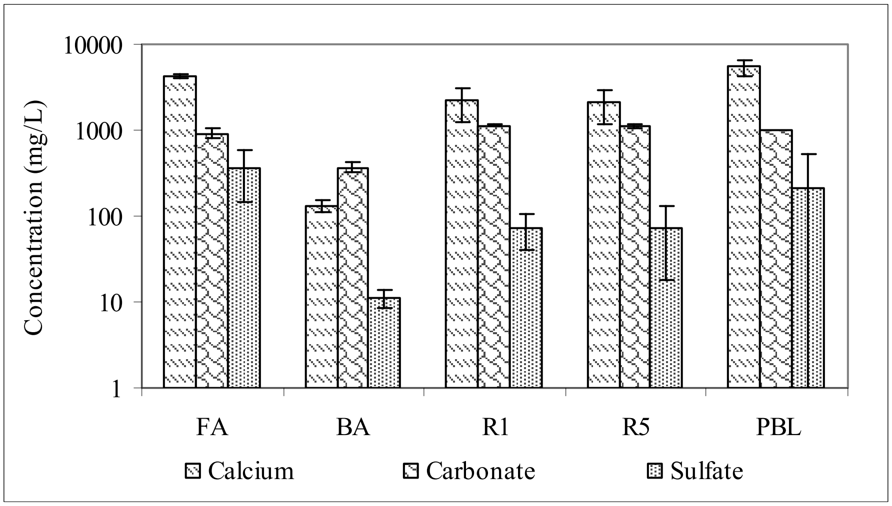

Figure 26: Comparison of Calcium, Carbonate, and Sulfate for FA, BA, R1, R5 and PBL Leachates

A direct comparison of mass concentrations is deceptive since different elements have different molecular weights. Another approach, suggested by Rowe, et al. (2000), compares the ratio of calcium ions to carbonate ions. If the ratio is greater than 0.67, calcium is in excess and available to precipitate with other ions. Table 24 presents the Ca^{+2}/CO_3^{-2} mass ratios for each of the solutions.

Table 24: Calcium / Carbonate Ratios for H, P, PL, FA, BA, RA1, RA5, and PBL Leachates

	H	P	PL	FA	BA	R1	R5	PBL
Ca^{+2} (mg/L)	2093	1476	5384	4273	133	2182	2071	5429
CO_3^{-2} (mg/L)	844	769	84	922	368	1127	1131	1008
Ratio	2.48	1.92	64	4.63	0.36	1.94	1.83	5.39

With the exception of the BA leachate, the leachate samples had excess calcium. Calcium precipitates easily with several ions, including carbonate, sulfate and hydroxide. Another way of presenting this information involves a comparison of molar concentrations. The ions in calcite ($CaCO_3$) and gypsum ($CaSO_4$) precipitates have one-to-one molar relationships. The molar concentrations of calcium, carbonate and sulfate are presented in Figures 27 and 28.

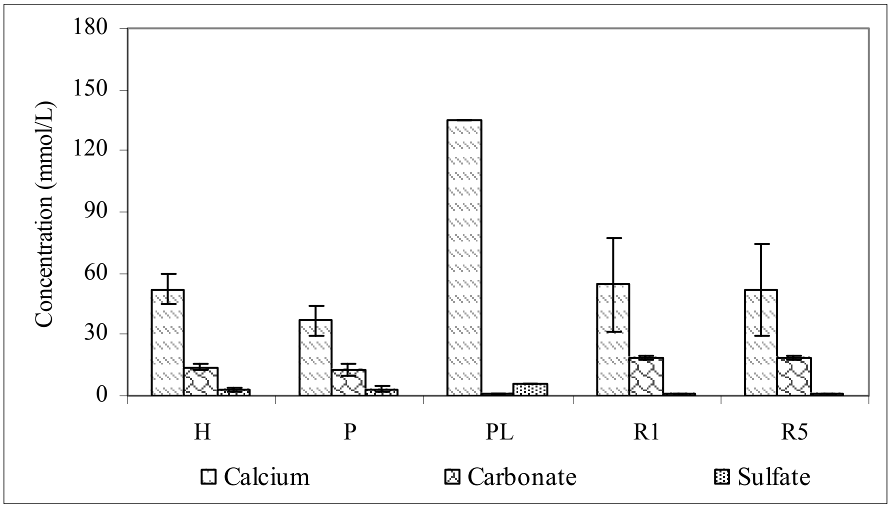

Figure 27: Molar Concentration of Calcium, Carbonate, and Sulfate in H, P, PL, R1 and R5 Leachates

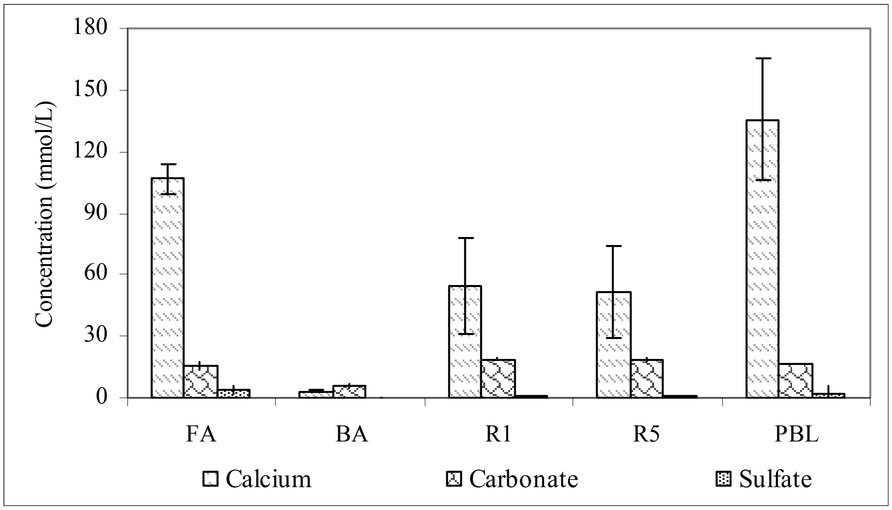

Figure 28: Molar Concentrations of Calcium, Carbonate, and Sulfate in FA, BA, R1, R5 and PBL Leachates

A one-way ANOVA showed significant differences between the concentrations of calcium, carbonate, and sulfate in the laboratory and landfill leachates. However, the laboratory tests correctly identify the identities of the dominant ions and the relative proportions. The differences in the concentrations may have been due to the microbial activity in the landfill, which was not present in the batch tests and different L/S ratios.

Chemical Factors Influencing Precipitate Formation

The formation of a precipitate is not only dependent on the molar ratio of the ions in the leachate, but on the solubility product, K_{sp}. The K_{sp} value is the product of the molar concentrations, adjusted for temperature and ionic activity. In dilute systems, the activity of ions are often ignored but the leachate produced in the laboratory and in landfills precludes this omission. The following reactions describe three common precipitates found in LCS clog material and the corresponding K_{sp} values in Table 25 (Benjamin, 2002).

Calcite: $Ca^{+2}{}_{(aq)} + CO_3{}^{-2}{}_{(aq)} \leftrightarrow CaCO_{3\ (s)}$

Aragonite: $Ca^{+2}{}_{(aq)} + CO_3{}^{-2}{}_{(aq)} \leftrightarrow CaCO_{3\ (s)}$

Gypsum: $Ca^{+2}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)} \leftrightarrow CaSO_{4\ (s)}$

Table 25: Ksp Values for Calcite, Aragonite and Gypsum (Benjamin, 2002)

Mineral	K_{sp} at 25°C	K_{sp} at 35°C
Calcite, $CaCO_{3\ (s)}$	$10^{-8.48}$	$10^{-8.66}$
Aragonite, $CaCO_{3\ (s)}$	$10^{-8.36}$	$10^{-8.43}$
Gypsum, $CaSO_{4\ (s)}$	$10^{-4.85}$	$10^{-1.61}$

If the reaction quotient (Q) is compared to the K_{sp} the relative degree of saturation can be assessed. The saturation indices for calcite are presented in Figures 29 and 30.

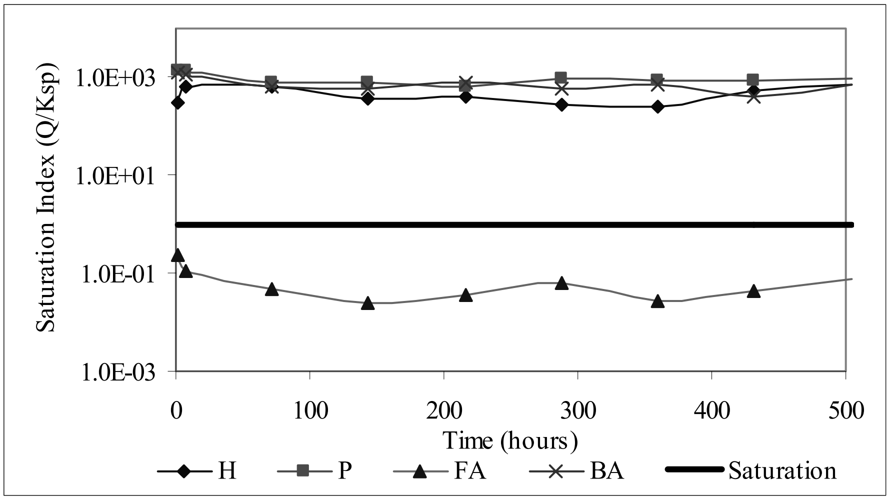

Figure 29: CT Leachate Saturation Index for Calcite

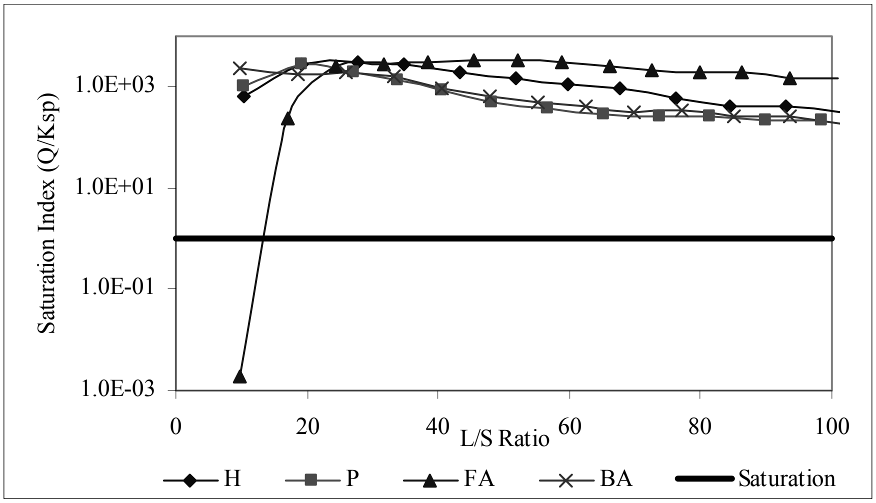

Figure 30: SE Leachate Saturation Index for Calcite

The H, P and BA leachates were all saturated with respect to calcite, regardless of the extraction technique. The FA leachate was unsaturated for the CT test and the initial extraction of the SE test, after which it became saturated. The high ionic strength of the FA leachate caused the activity of the calcium and carbonate ions to be considerably lower than the molar concentrations. Subsequent extractions flushed the more soluble ions out of the system decreasing the ionic strength and creating a supersaturated solution. Aragonite, another calcium carbonate mineral, followed the same trend. The saturation indices for aragonite are presented in Figures 32 and 33. A scanning electron micrograph of calcium carbonate formed in the unpreserved BA batch leachate is shown in Figure 31.

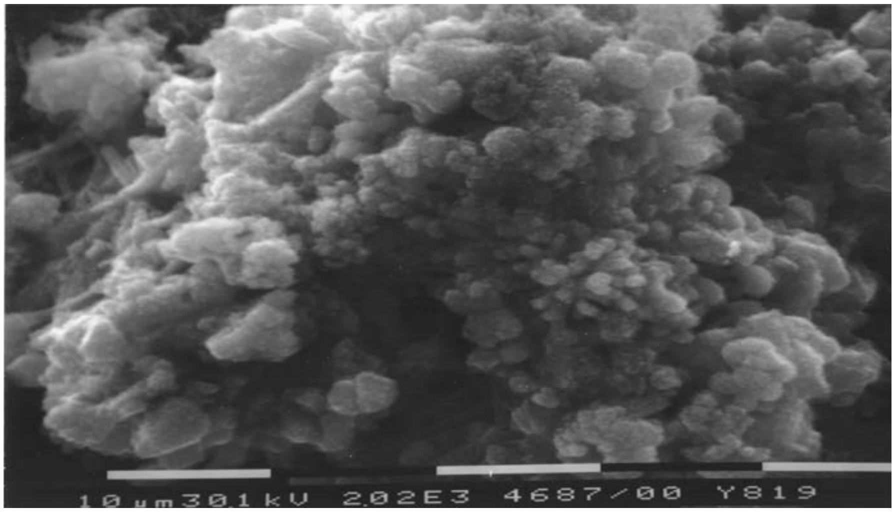

Figure 31:SEM Micrograph of Calcium Carbonate Crystals from Bottom Ash Leachate Samples

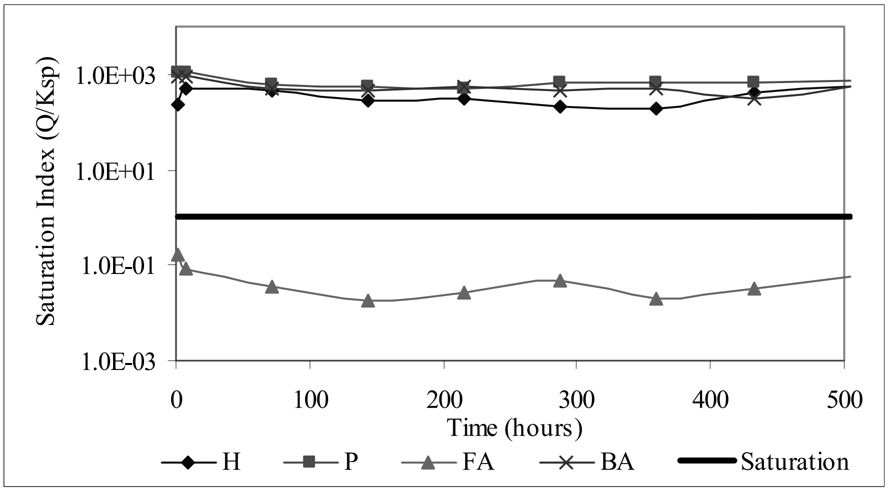

Figure 32: CT Leachate Saturation Index for Aragonite

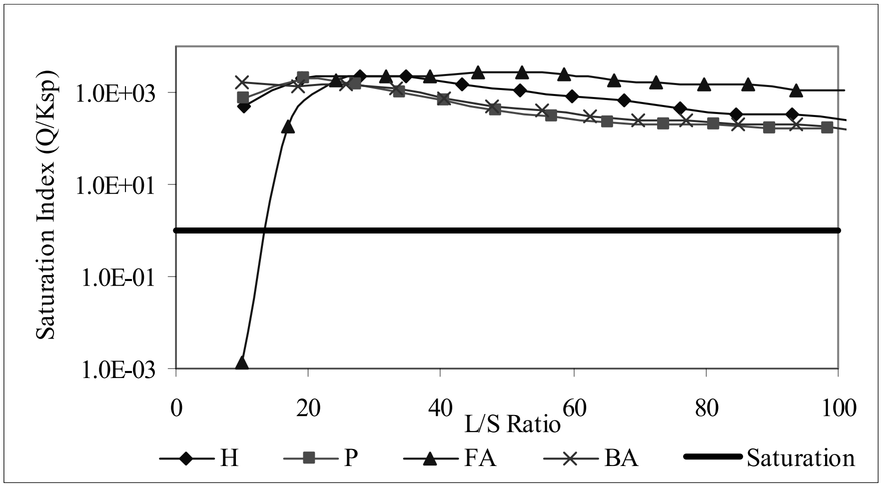

Figure 33: SE Leachate Saturation Index for Aragonite

The gypsum was unsaturated for the CT and SE test leachates and results are presented in Figures 34 and 35. Since the calcium concentrations were high for all the leachates, the sulfate concentrations caused the small gypsum reaction quotient. The addition of sulfuric acid for sample preservation demonstrated this imbalance. A scanning electron micrograph showing the calcium sulfate crystals formed upon the addition of sulfuric acid is shown in Figure 36.

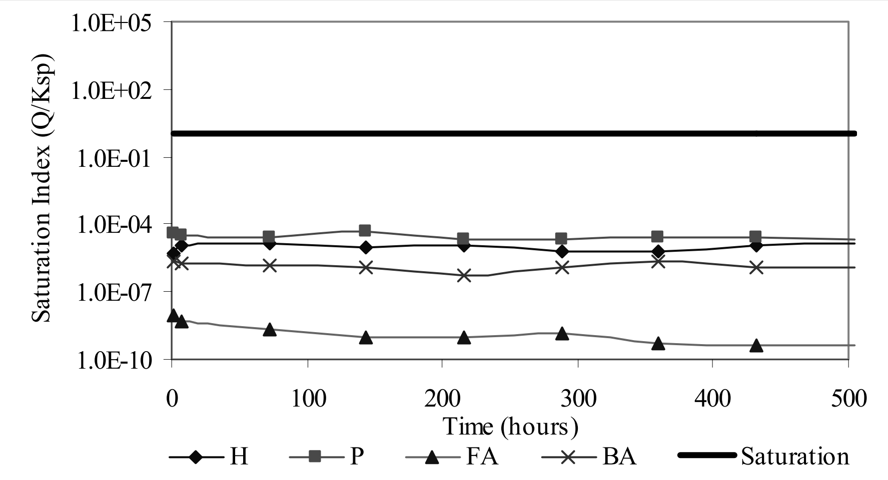

Figure 34: CT Leachate Saturation Index for Gypsum

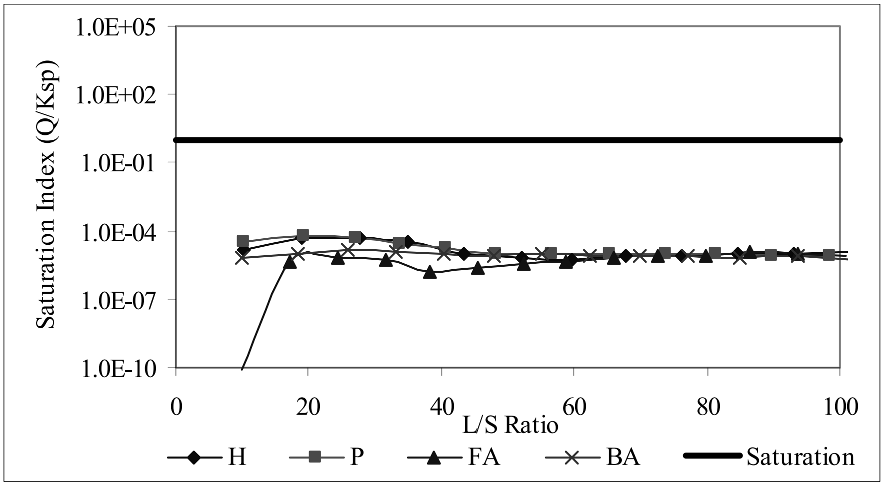

Figure 35: SE Leachates Saturation Index for Gypsum

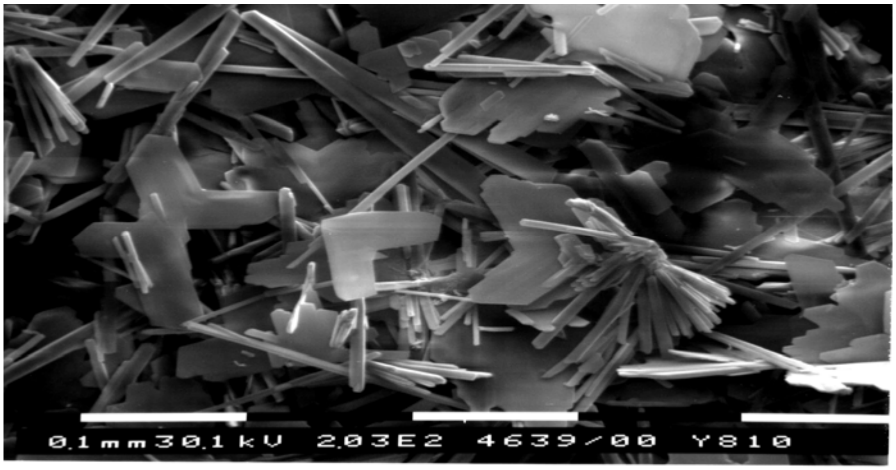

Figure 36: SEM Micrograph of Calcium Sulfate Crystals from Preserved Fly Ash Sample

All of the leachates examined during this study had high concentrations of calcium ions, one of the main cations in LCS clog material. The sulfur and carbon constituents limited the formation of precipitates in ash leachates. The supersaturated ash leachates form a delicate system that can be easily disrupted by other waste materials and microbial activity.

Discussion

Two different types of batch tests were applied to assess the leaching potential of WTE combustion residues. In this section the strengths and weaknesses of these tests are discussed and the relevance of the information provided by the batch tests is analyzed. The ability to predict the potential for precipitate formation is presented.

Comments on Batch Tests

Batch tests were used to analyze ash samples from three different WTE facilities. Two of the samples, fly ash and bottom ash, were provided by the same WTE facility. The fly ash, pictured in Figure 37, was homogenous in appearance and contained fine particles. These small particles had a larger surface area, exposing more minerals to the leachant and increasing the solubility. The bottom ash contains a wide variety of particle sizes and is pictured in Figure 38. Some of the materials in the bottom ash were identified as glass, tile, or metal. The ashes from Hillsborough and Pasco counties, which were mixtures of fly and bottom ash, physically resembled the bottom ash but the leaching characteristics reflected the combined nature of the source of the ash.

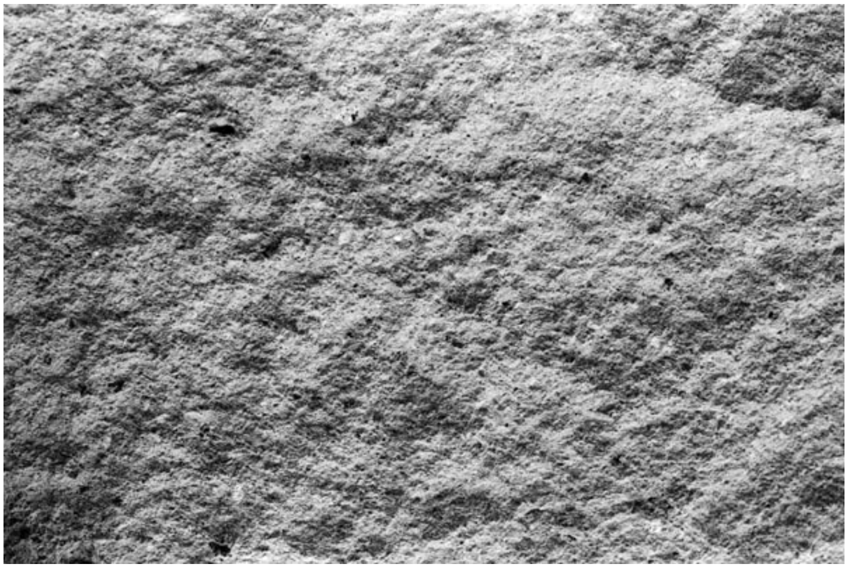

Figure 37: Picture of Fly Ash from Palm Beach County, Spring 2004

Figure 38: Picture of Bottom Ash from Palm Beach County, Spring 2004

The batch tests developed for this research fell into two categories: contact time and sequential extraction. The contact time test provided a static view of the leachate produced by the ash, since the leachant remained in contact with the same material long enough to establish equilibrium. The readily soluble materials leached out of the ash and become part of the leachate. The sequential extraction test provided a dynamic view of the leaching properties of ash as fresh leachant encountered the material. Each test proved to be useful for understanding the leaching characteristics of the material being analyzed, and its potential behavior in a landfill.

The CT test provided consistent information about the readily soluble material in the ash. The results proved to be reliable and reproducible, allowing for a complete analysis of the initial leaching capacity of the ash. The time interval variations provided insight into the stability of the leachate as it remained in contact with the ash. However, the moisture that enters a landfill does not stay in one place; instead, it flows down through the layers of waste. Modifying the CT test by shortening the initial time intervals from hours to minutes would model the contact time of water flowing through waste materials.

The first extraction from the SE batch test produced results similar to the CT test results. The difference between the two tests became apparent as the number of extractions increased. The concentrations of the ions in solution dropped substantially during the first four extractions, and then appeared to level off. Unfortunately, each subsequent extraction increased the possibility of error. The accidental removal of ash during extraction could have changed the dynamics of the system. By modifying the SE test, this source of error could be reduced. Since the majority of the soluble ions washed out of the ash during the first four extractions, the total number of extractions could be reduced. If larger L/S ratios are needed, the initial ratio could be increased.

Batch tests provide a clear picture of the chemical leaching properties of the waste material. This allows for the determination of potential interactions that favor the production of clogs. Unfortunately, the batch tests do not examine the role of microbiological activity on the leachate composition, neglecting an important part of landfill activity.

Comments on Clog Formation

In the analysis of traditional MSW landfill leachates, the calcium ion has been reported to limit the formation of precipitates (Manning, 1999; Rowe, 2000). The microbiological activity consumes the biodegradable materials, thereby increasing the carbonates and making the leachate supersaturated with carbonate and sulfate. According to Rowe et al. (2000), over 50% of the clog material is calcite. In the precipitate, calcium is the dominant cation and carbonate and sulfate are the dominant anions.

The analysis of the LCS clog material agreed with the literature. The dominant elements in the Palm Beach clog material were calcium, carbon and sulfur. Other elements, such as iron, copper, magnesium, manganese and phosphorous were present, but in much lower amounts. SEM micrographs of clog material from Palm Beach County are shown in Figure 39 and Figure 40. SEM analysis indicated the elemental composition of the clog material mirrored the chemical composition of the leachate from the batch tests, lysimeters and field samples.

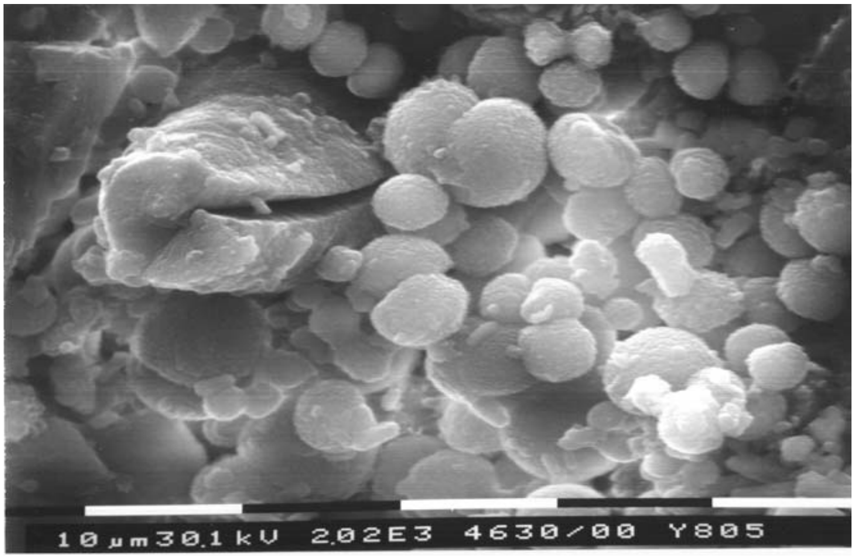

Figure 39: SEM Micrograph of Clog Material Containing Calcium, Chloride, Phosphorous, and Sulfur from Palm Beach County

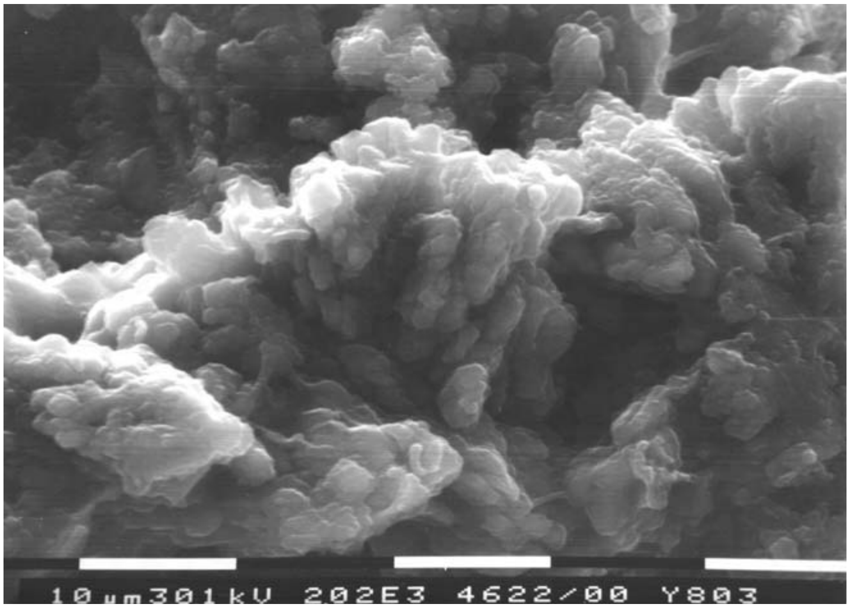

Figure 40: SEM Micrograph of Calcium Clog Material from a Palm Beach Pump Station

The combustion process at WTE facilities consumes the biodegradable materials, reducing the organic carbon in the residuals deposited in the landfill. The total organic carbon in the ash leachates ranged from 1.5mg/L to 61.1 mg/L as carbon, much lower than leachates from other waste streams that range from 500 to 5000 mg/L as carbon (Levine, 1989). The increased calcium concentration and the high pH are due in part to the addition of lime used to prevent the formation of acid rain pre-cursers during combustion. Once in the landfill, the calcium in the ash becomes soluble as water percolates through the waste. The low organic carbon concentration in the ash provides a limited substrate for microbiological activity. The presence of nanobacteria in ash monofill leachate can be seen in Figure 41. In ash monofills, as demonstrated by the batch tests, lysimeter studies and monofill leachate analysis, the calcium ions were present in abundance, and carbon and sulfur ions limit the formation of precipitates.

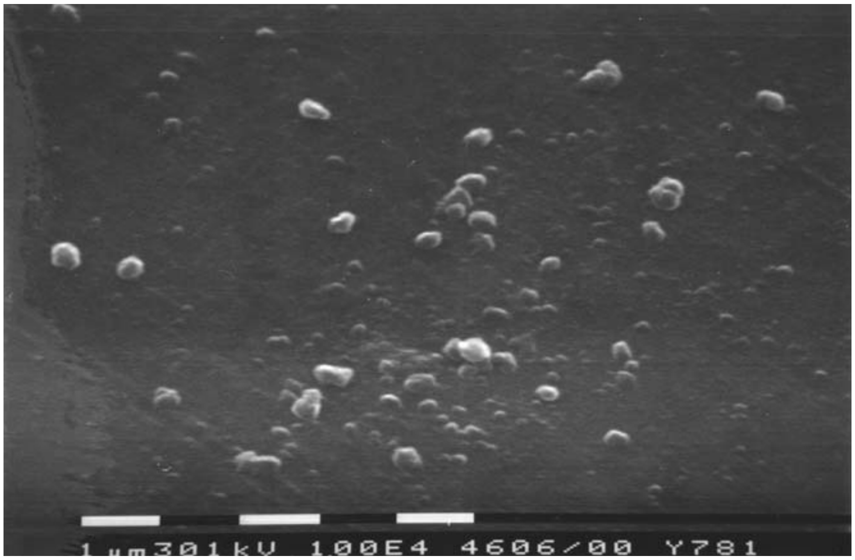

Figure 41: Bacterial Particles Identified in Leachate from an Ash Monofill

In landfills that co-deposit ash with MSW, the leachate equilibrium is different and appears to favor the formation of precipitates. The ash introduces a source of calcium ions, while the biological activity in the MSW increases the formation of carbonate. A comparison of the calcium and carbonate concentrations in the Palm Beach and Pasco leachates is presented in Table 26. Both leachates had very high concentrations of calcium- above 5000 mg/L. However, there is a tremendous difference in the carbonate values. The Palm Beach landfill combines the ash with other waste streams that are high in carbon, providing a source of carbonate. The Ca^{+2} / CO_3^{-2} ratio of the Palm Beach leachate was 5.38, indicating an excess calcium ion concentration. The Pasco landfill is a monofill, therefore the amount of carbon available for biological activity is limited and the formation of carbonate is suppressed. The Ca^{+2} / CO_3^{-2} ratio for Pasco was considerably higher (64) than the Palm Beach ratio, indicating a large amount of calcium but a limited amount of carbonate, limiting the formation of calcite.

Table 26: Comparison of Calcium and Carbonate in Two Landfill Leachates

Leachate Source	Calcium (mg/L)	Carbonate (mg/L)	Ca^{+2} / CO_3^{-2} ratio
Palm Beach	5429	1008	5.39
Pasco	5384	84	64

The concentrations of most of the ions were higher in the landfill leachate than in the batch tests, suggesting the L/S ratio in the landfill was lower than the one used in the laboratory. A lower L/S ratio would make the leachate more concentrated. Even with this discrepancy, the batch tests correctly predicted the high calcium ion concentrations found in the ash leachates and the supersaturated nature of the leachate as shown in Figure 42. The identities of the dominant ions were established, and the potential for precipitate formation confirmed.

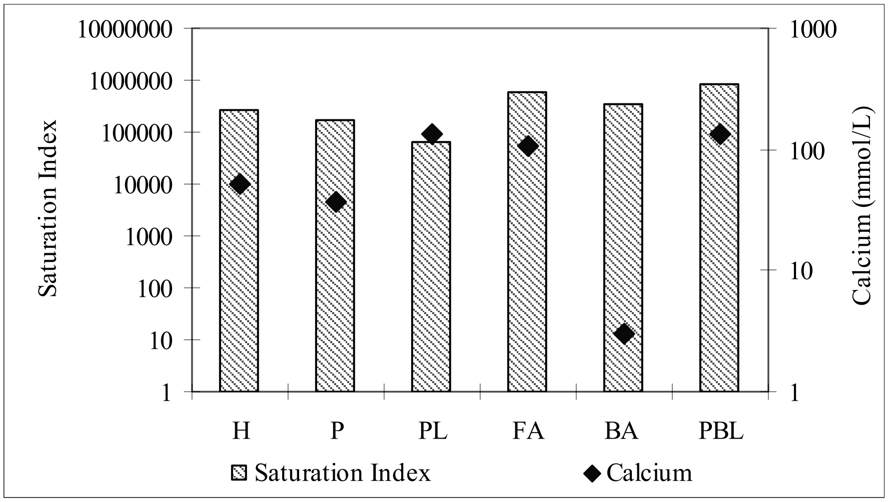

Figure 42: Comparison of Saturation Index and Calcium Concentration for Batch Tests and Leachates

Conclusions

Ash from three different WTE facilities, two mass burn and one refuse derived fuel, were characterized using batch tests adapted from the Method for Accelerated Leaching of Solidified Waste (Department of Nuclear Energy, 1990). The goal of the characterization tests was to provide a means for predicting the contributions of different waste streams to potential clog formation in landfill leachate collection systems. The major conclusions from this project are:

1. The contact time (CT) and sequential extraction (SE) tests developed for this project were useful for assessing the degree of leaching that may occur from exposure of combustion residues to landfill environments.

2. The CT test provided insight into the dominant solubilizable components of waste materials and the chemical stability of leachates generated by combustion residues.

3. The SE test provided a means to quantify the leaching behavior of combustion residues resulting from sequential exposure to rainwater as it percolates through a landfill. The ash leachates from batch and lysimeter tests contained high concentrations of calcium, potassium, sodium, carbonate, chloride, and sulfate. The sodium, potassium, and chloride ions were highly soluble and did not directly contribute to the formation of precipitates. These ions increased the ionic strength of the leachate, thereby reducing the activity of the less soluble ions in the leachate. The relationships between calcium and carbonate were used to compute saturation indices for calcium carbonate precipitation.

4. When compared with leachates from laboratory lysimeters and landfills, the batch tests correctly predicted the identities of the dominant ions and the supersaturated nature of the leachate.

5. Calcium, carbonate and sulfate ions were the major constituents identified in solidified materials isolated from a landfill leachate collection system.

6. If combustion residues are disposed in monofills, the potential for formation of precipitates appears to be limited by the anions, carbonate and sulfate.

7. Leachates generated in landfills receiving MSW tend to have higher concentrations of carbonate and sulfate than combustion residue monofills. However, in MSW leachate the low concentration of calcium limits precipitate formation and the likelihood of LCS clogging.

8. Co-disposal of combustion residues from WTE facilities with MSW in landfills provides high levels of calcium from the combustion residues and high levels of carbonate and sulfate from biological activity in the MSW, thereby increasing the potential for precipitate formation and clogging of landfill leachate collection systems.

9. The chemical composition of solid precipitates formed in landfill leachate collection systems reflects supersaturation of leachates due to excess calcium, carbonate, and/or sulfate. Incidental changes in redox conditions in leachate collection systems may help to initiate the formation of precipitates.

Engineering Implications

Landfills are designed to prevent contamination of the surrounding environment. The covering and lining of landfills and leachate collection systems are integral components of landfill management. As combustion and recycling increase, the proportion of biodegradable material disposed in landfills decreases.

This research has demonstrated the need for improved understanding of the leaching behavior of waste materials. The two main options for MSW ash disposal are monofilling or co-depositing the ash with other waste materials in landfills. When the ash is monofilled, the consistent environment allows the leachate to develop an equilibrium, keeping the supersaturated ions in solution. The co-disposal of ash with other materials changes the dynamics of the system. As leachate moves through different types of waste, the chemical equilibrium is disturbed and precipitates form. In addition, the reducing conditions within landfills increases the solubility of the ions. LCS that fluctuate between reduced and oxidized conditions have a higher chances of precipitate formation. Keeping the LCS under pressure would help maintain a reduced environment and prevent precipitate formation.

Monofills appear to be the best disposal option for MSW combustion residues, unless the chemical and biological interactions of the waste materials are taken into account. This practice would prevent two supersaturated leachates from interacting and producing precipitates. Ash leachate is high in calcium, while MSW's leachate is high in carbonate; this supersaturated chemical combination has the potential of forming calcite. Calcite, a hard mineral, clogs the LCS, preventing the collection of the leachate thus increases the leachate head on the liner.

The waste materials have the potential of producing highly reactive leachates. The materials used in the construction of the liner and LCS need to be able to withstand this reactive environment. Characterization of the leachate produced by the expected waste materials in batch tests can be used as a guide for the selection of the appropriate for landfill construction.

Additional Research

Recommendations for further research of the impacts of current combustion technologies and ash handling protocols on the leaching characteristics of ash produced at WTE facilities.

1. Research the effects of different air pollution control devices on leaching properties of fly ash. The addition of chemicals to control the emissions of acid rain pre-cursers may affect the leachable mineral content. Determining if a relationship exists could provide a basis for developing improved ash management practices.

2. Examine the impact of quenching the ash in water prior to landfilling on the initial soluble mineral content of combustion residues. This initial rinse appears to play a role in the leaching behavior of ash as demonstrated by this thesis. To determine if the initial rinse has a significant impact on the leaching behavior of the ash, pre and post quenching ash samples should be analyzed in parallel using batch and lysimeter tests.

3. Examine the changes in leaching characteristics as WTE ashes are exposed to periods of wetting and drying. It is possible that the changing moisture and redox conditions influence the leaching properties of the ash. Using the SE batch test approach, the ash could be dried at ambient conditions for a couple of days between leachate replenishments. Running this test in parallel with traditional SE tests would answer this question.

4. Determine the role of increasing temperatures on the leaching behavior of WTE combustion residues. By running identical CT batch tests at different temperatures, a relationship between the temperature and the leachate characteristics can be established.

5. Perform a statistical analysis of the waste disposal practices and the incidences of clog formation in leachate collections systems. This could be achieved by conducting a large scale survey of Class I landfills in the United States and comparing the disposal practices, co-disposal of ash and MSW versus monofilling, and the formation of precipitates in LCS.

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Appendices

Appendix A: Chemical Characterization Tests

Metals: Flame AA

Calcium, Copper, Iron, Magnesium, Manganese, Potassium, Sodium, Zinc

Source: *Standard Methods for the Examination of Water and Wastewater*, 20th edition, 3111 B Direct Air-Acetylene Flame Method

Equipment: PerkinElmer AAnalyst 100, Atomic Absorption Spectrometer

Time Frame: 6 months with preservation, store at 4°C.

Preservation of Sample: Preserve by adding 5mL of concentrated nitric acid to 1 L of sample and the sample can be stored for up to 6 months (EPA Method 3005).

Preparation of Reference Standards: Make up at least three standards. The first should be below the expected concentration, the second should be near the expected concentration and the final standard should be above the expected concentration. The middle standard will be used to re-slope. Prepare by adding the appropriate amount of reference standard to reagent grade water.

Preparation of Sample: If there are large amounts of particulate matter the sample needs to be filtered. If not, there is no preparation required.

Appendix A (continued)

Table A 1: Conditions from Analytical Methods for Atomic Absorption Spectrometry, 2000. PerkinElmer

Metal	Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentrations (mg/L)	Characteristic concentration checks (mg/L)	Linear Range (mg/L)
Ca	422.7	0.7	1.00	0.092	4.00	5.0
Cu	324.8	0.7	1.00	0.077	4.00	5.0
Fe	248.3	0.2	1.00	0.110	6.00	6.0
Mg	285.2	0.7	1.00	0.008	0.30	0.5
K	766.5	0.7	1.00	0.043	2.00	2.0
	769.9	0.7	1.40	0.083	4.00	20.0
Na	589.0	0.2	1.00	0.012	0.50	1.0
	330.2	0.7	0.63	1.700	80.00	---
Zn	213.9	0.7	1.00	0.018	1.00	1.0

Recommended Flame: Air-acetylene, oxidizing (lean, blue)

Anions: Capillary Ion Electrophoresis

Chloride, Bromide, Nitrate, Nitrite, Sulfate, Fluoride, o-Phosphate

Source: *Standard Methods for the Examination of Water and Wastewater*, 20th edition, 4140 B: Capillary Ion Electrophoresis with Indirect UV Detection

Equipment: Beckman P/ACE 5000 Series Capillary Electrophoresis System
eCap Capillary Tubing in cartridge: 375 µm O.D., 75 µm I.D., 50 cm L

Preparation: The samples need to be filtered if it contains a high concentration of suspended solids. Once completed the sample may need to be diluted.

Analytical Parameters

Table A 2: Detailed List of Analytical Tests, Methods, Storage and Preservation, and Detection Limits

Test	Standard Method, 20th Edition-number, description	Storage and Preservation	Detection Limits
pH	4500-H+ B. Electrometric Method inoLab pH probe, calibrated at pH=4, 7, 10	Test immediately	pH of 0-14
Conductivity	2510 B. Laboratory Method inoLab conductivity probe	Test immediately	1 µS/cm – 2 S/cm
Dissolved Metals: Calcium, Copper, Iron, Magnesium, Manganese, Potassium, Sodium, Zinc	3111 B Direct Air-Acetylene Flame Method using a PerkinElmer Flame AA	Preserve by adding 5mL of concentrated nitric acid to 1 L of sample. Good for up to 6 months. Prior to use adjust to pH=4.	Lower limit= 0.1 mg/L to 0.01 mg/L depending on metal
Total Hardness	2340 B. Hardness by Calculation	Based on metals preservation	Lower limit= 1 mg/L
Bromide, Chloride, Fluoride, Nitrate, Nitrite, Phosphate, Sulfate	4140 B Capillary Ion Electrophoresis with indirect UV Detection. Using Beakman Capillary Electrophoresis	Refrigerate at 4°C and process as soon as possible	For 30s sampling time, lower = 0.1 mg/L
Carbonate	Calculated value from Alkalinity Titration	Store at 4°C and analyze within 6 hours	Lower limit = 12 mg/L
Alkalinity	2320 B Titration Method	Store at 4°C and analyze within 6 hours	Lower limit =20 mg/L as $CaCO_3$
Aluminum	3500-Al B. Eriochrome Cyanine R Method	Acidify with concentrated nitric acid to pH=2, good for 6 months	0.00 mg/L to 0.250 mg/L
Solids (TDS)	2540 C Total Solids	Store at 4°C and begin test within 3 days	Lower limit= 10 mg/L
TOC	5310 C. Persulfate-UV Method using a SIEVERS 800 Portable Total Organic Carbon Analyzer	If the sample can not be analyzed immediately, it needs to be acidified to pH=2 with sulfuric acid	Lower limit =0.01 mg TOC /L
Total Nitrogen	4500-N C. Persulfate Method	Acidify to pH< 2 using concentrated sulfuric acid and store at 4°C for up to 28 days	0-25 mg/L
Total Phosphorous	4500-P C. Vanadomolybdophosphoric Acid Colormetric Method	Acidify to pH< 2 using concentrated sulfuric acid and store at 4°C for up to 28 days	0-25 mg/L
Silica	4500-SiO2 Molybdosilicate Method	Store at 4°C in a plastic bottle for up to 7 days	0-100.0 mg/L

Appendix B: Procedures for Batch Tests

Sequential Extractions Batch Tests

Contact Time of 72 hours

Procedure:

1. Prepare four High Density Polyethylene (HDPE) bottles for use by washing with Sparleen 1, rinsing thoroughly, and soaking in a 1% nitric acid bath for 24 hours. Upon removal, rinse the bottles with Nanopure™ water and allowed to air dry.
2. Place dry bottles on an analytical balance, tare, and add the solid material. Record the mass of material added. Repeat with three prepared bottles.
3. Use the weight of solid added to the bottle to determine the volume of distilled water needed to achieve an L/S = 10. Assume water has a density of 1g/1mL. Note: There should be almost no headspace in the container.
4. Fill one of the HDPE bottles full of distilled water as a control.
5. Tightly cap the bottles, shake vigorously for 1 minute, and placed on the orbital shaker for 20 minutes.
6. Place the well-shaken bottles in a 35±1°C incubator for 72 hours.
7. After 72 hours, carefully removed the bottles from the incubator. Use a pipet to remove the leachate from the bottles, this must be done carefully since the solids cannot be disturbed or removed. Record the amount of leachate removed from the bottle and replenish with an equal amount of the 35±1°C distilled water.
8. The removed leachate needs to be promptly tested or preserved.
9. Repeat steps 6 – 9 until the total L/S ratio is reached.

Contact Time Batch Tests

Procedure:

1. Prepare High Density Polyethylene (HDPE) bottles for use by washing with Sparleen 1, rinsing thoroughly, and soaking in a 1% nitric acid bath for 24 hours. Upon removal, rinse the bottles with Nanopure™ water and allowed to air dry.
2. Place dry bottles on an analytical balance, tare, and add the solid material. Record the mass of material added. Repeat with three prepared bottles.
3. Use the weight of solid added to the bottle to determine the volume of distilled water needed to achieve an L/S = 10. Assume water has a density of 1g/1mL. Note: There should be almost no headspace in the container.
4. Fill one of the HDPE bottles full of distilled water as a control.
5. Tightly cap the bottles, shake vigorously for 1 minute, and placed on the orbital shaker for 20 minutes.
6. Place the well-shaken bottles in a 35±1°C incubator for the predetermined time intervals. A sample of the time intervals is presented in Table.

Table B 1: Sample Contact Time Batch Test Intervals

Sample #	# Bottles	Contact time
1	3	2 hours
2	3	7 hours
3	3	3 day
4	3	6 days
5	3	9 days
6	3	12 days
7	3	15 days
8	3	18 days
9	3	21 days

7. After the designated contact time is complete, remove the bottle removed from the incubator. Filter the contents to separate the leachate from the solid material.
8. The removed leachate needs to be promptly tested or preserved.

Appendix C: Data

Table C 1: Hillsborough Contact Time Data, Averages and Standard Deviations

Hours	2		7		72	
Date of Extraction:	7/22/04		7/22/04		7/25/04	
mL of H2O	135		135		135	
mass of Ash (g)	13.4378	0.1380	13.5698	0.1938	13.7010	0.1993
Test	H1 : Avg.	Std. Dev.	H2 : Avg.	Std. Dev.	H3 : Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1450	100	1057	12	1187	12
Aluminum (mg/L)	0.0400	0.0100	0.0900	0.0707	BDL	BDL
Bromide (mg/L)	46.7	6.8	40.3	8.0	31.2	3.6
Calcium (mg/L)	2174	300	1604	30	1806	166
Carbonate (mg/L)	870	60	634	7	712	7
Chloride (mg/L)	2615	200	2201	289	1856	169
Conductivity (mS/cm)	12.25	0.84	10.67	0.92	10.25	0.39
Copper (mg/L)	0.1190	0.0542	0.1173	0.0273	0.1183	0.0527
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	5430	745	4007	74	4510	413
Iron (mg/L)	0.2813	0.0685	0.2530	0.0922	0.2737	0.0299
Magnesium (mg/L)	0.1053	0.0806	0.0437	0.0051	0.0557	0.0058
Manganese (mg/L)	0.0633	0.0085	0.0527	0.0040	0.0637	0.0040
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)					-80	10
pH	11.87	0.12	11.64	0.06	11.90	0.06
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	200.0	20.1	172.7	36.1	156.0	16.5
Silica (mg/L as SiO_2)	0.5	0.4	0.7	0.2	0.7	0.3
Sodium (mg/L)	434.0	24.6	421.3	134.5	383.3	59.5
Solids (TDS) mg/L	6800	471	5953	637	5930	477
Sulfate (mg/L)	197.8	12.8	167.5	5.9	239.4	7.9
Temperature (°C)	21.43	0.40	23.47	0.15	21.67	1.91
TOC (mg/L as C)	7.62	0.72	4.77	0.22	BDL	
Total Nitrogen (mg/L as N)	24.5	33.2	6.0	4.2	1.7	0.6
Total Phosphorous (mg/L as PO_4)	0.5	0.4	0.7		0.3	0.2
Zinc (mg/L)	2.3850	0.3196	1.8163	0.1447	0.7073	0.0657

TDS Value	6800		5953		5930	
Σmass (dissolved)	6566.01		5250.64		5187.47	
% identified	96.56		88.20		87.48	
TDS/EC ratio	0.555		0.558		0.578	

Table C 1: Continued

Hours	144		216		288	
Date of Extraction:	7/28/04		7/31/04		8/3/04	
mL of H2O	135		135		135	
mass of Ash (g)	13.4967	0.1918	13.5647	0.2255	13.6617	0.2153
Test	H4 : Avg.	Std. Dev.	H5 : Avg.	Std. Dev.	H6 : Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1343	32	1413	60	1527	95
Aluminum (mg/L)	BDL		BDL		0.0867	0.0153
Bromide (mg/L)	44.7	0.4	42.5	13.5	35.1	9.8
Calcium (mg/L)	2140	128	2030	273	2592	421
Carbonate (mg/L)	806	19	848	36	916	57
Chloride (mg/L)	2276	118	2155	516	1940	295
Conductivity (mS/cm)	11.99	0.43	11.59	1.73	11.63	1.82
Copper (mg/L)	0.1057	0.0222	0.1193	0.0232	0.2597	0.2454
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	5343	323	5070	685	6473	1049
Iron (mg/L)	0.2707	0.0234	0.2560	0.0056	0.2387	0.0605
Magnesium (mg/L)	0.0440	0.0062	0.0390	0.0026	0.0450	0.0026
Manganese (mg/L)	0.0700	0.0061	0.0517	0.0061	0.0493	0.0042
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-101	3	-70	9	-65	5
pH	11.67	0.07	11.96	0.01	11.63	0.04
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	197.0	13.2	177.3	48.8	157.7	33.0
Silica (mg/L as SiO_2)	0.4	0.2	0.1	0.0	1.3	0.1
Sodium (mg/L)	456.0	14.7	435.7	136.0	423.3	96.7
Solids (TDS) mg/L	7150	295	6553	1133	6430	887
Sulfate (mg/L)	322.0	42.3	295.1	108.9	333.5	19.8
Temperature (°C)	21.23	0.06	20.03	0.06	22.10	1.84
TOC (mg/L as C)	6.86	0.02				
Total Nitrogen (mg/L as N)	3.5	2.1	2.0	BDL	10.7	11.0
Total Phosphorous (mg/L as PO_4)	BDL		0.8		BDL	
Zinc (mg/L)	1.1427	0.1561	0.9160	0.1733	0.6960	0.0175

TDS Value	7150		6553		6430	
Σmass (dissolved)	6246.80		5988.15		6410.54	
% identified	87.37		91.38		99.70	
TDS/EC ratio	0.596		0.566		0.553	

Appendix C (continued)

Table C 1: Continued

Hours	360		432		504	
Date of Extraction:	8/6/04		8/9/04		8/12/04	
mL of H2O	135		135		135	
mass of Ash (g)	13.4506	0.0509	13.5471	0.0774	13.5336	0.0265
Test	H7 : Avg.	Std. Dev.	H8 : Avg.	Std. Dev.	H9 : Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1590	52	1547	29	1550	44
Aluminum (mg/L)	BDL		BDL		0.0350	0.0071
Bromide (mg/L)	30.5	3.9	44.0	1.9	44.6	5.6
Calcium (mg/L)	2611	409	2085	193	1794	343
Carbonate (mg/L)	954	31	928	17	930	26
Chloride (mg/L)	2058	180	1805	215	1831	220
Conductivity (mS/cm)	12.51	0.67	12.24	0.80	10.94	0.20
Copper (mg/L)	0.2023	0.2226	0.0930	0.0035	0.2107	0.0743
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	6520	1022	5203	484	4480	854
Iron (mg/L)	0.2937	0.0420	0.2703	0.0184	0.2657	0.0258
Magnesium (mg/L)	0.0347	0.0012	0.0330	0.0017	0.0370	0.0040
Manganese (mg/L)	0.0537	0.0006	0.0560	0.0080	0.0593	0.0032
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-74	3	-79	6	-70	1
pH	11.62	0.05	11.65	0.03	11.75	0.01
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	169.3	16.6	149.7	22.1	154.3	27.1
Silica (mg/L as SiO_2)	1.7	0.3	1.2	0.1	1.4	0.2
Sodium (mg/L)	416.0	78.5	331.7	64.5	331.3	82.1
Solids (TDS) mg/L	6680	497	6333	457	6123	757
Sulfate (mg/L)	323.8	44.2	263.1	26.1	252.4	63.0
Temperature (°C)	23.23	0.29	24.00	0.26	21.67	0.06
TOC (mg/L as C)	5.64	0.02			7.11	1.39
Total Nitrogen (mg/L as N)	5.5	6.4	2.0	1.7	10.7	10.0
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	0.7047	0.0922	0.7087	0.0401	0.6433	0.1512

TDS Value	6680		6333		6123	
Σmass (dissolved)	6571.49		5610.83		5351.65	
% identified	98.38		88.59		87.40	
TDS/EC ratio	0.534		0.517		0.560	

Table C 2: Pasco Contact Time Data, Averages and Standard Deviations

Hours	2		7		72	
Date of Extraction:	16-Jul-04		16-Jul-04		19-Jul-04	
mL of H2O	138.9	0.7	140.0	1.1	140.6	0.5
mass of Ash (g)	13.7576	0.0292	13.6430	0.2800	13.7414	0.0992
Test	P1 : Avg.	Std. Dev.	P2 : Avg.	Std. Dev.	P3 : Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	850	218	972	276	1243	183
Aluminum (mg/L)	0.115	0.078	0.042	0.050	0.059	0.054
Bromide (mg/L)	22.0	4.1	30.9	9.0	40.1	8.3
Calcium (mg/L)	1004	142	1051	223	1509	227
Carbonate (mg/L)	510	131	583	166	746	110
Chloride (mg/L)	1232	74	1368	209	1827	319
Conductivity (mS/cm)	8.05	0.91	9.03	1.52	10.35	1.06
Copper (mg/L)	0.0403	0.0076	0.0423	0.0116	0.0540	0.0161
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	2508	354	2624	557	3768	566
Iron (mg/L)	0.1870	0.0637	0.1690	0.0696	0.2270	0.0272
Magnesium (mg/L)	0.0557	0.0187	0.0573	0.0103	0.0387	0.0284
Manganese (mg/L)	0.0530	0.0010	0.0497	0.0021	0.0537	0.0023
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-61	7	-66	26	-77	25
pH	11.71	0.07	11.79	0.11	11.74	0.07
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	109.0	2.0	124.0	20.1	157.0	19.1
Silica (mg/L as SiO_2)	0.6	0.2	0.6	0.5	0.6	0.1
Sodium (mg/L)	212.3	17.2	227.3	36.4	314.0	22.3
Solids (TDS) mg/L	3937	225	4340	742	5647	480
Sulfate (mg/L)	196.0	36.3	190.0	16.6	324.0	58.4
Temperature (°C)	23.60	0.44	25.80	0.72	23.53	0.29
TOC (mg/L as C)	8.420	0.057	8.085	0.035		
Total Nitrogen (mg/L as N)	4.7	1.5	5.0	1.0	5.3	1.2
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	2.4187	0.9705	1.7100	0.6569	1.8343	0.4087

TDS Value	3937		4340		5647	
Σmass (dissolved)	3294		3582		4925	
% identified	84		83		87	
TDS/EC ratio	0.489		0.481		0.546	

Appendix C (continued)

Table C 2: Continued

Hours	144		216		288	
Date of Extraction:	22-Jul-04		25-Jul-04		28-Jul-04	
mL of H2O	140.5	0.5	141.0	0.8	140.5	0.4
mass of Ash (g)	13.5964	0.3312	13.8089	0.1565	13.6477	0.2394
Test	P4 : Avg.	Std. Dev.	P5 : Avg.	Std. Dev.	P6 : Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1163	12	1457	71	1363	90
Aluminum (mg/L)	0.050		BDL		0.115	0.064
Bromide (mg/L)	32.4	3.9	37.4	8.4	18.8	6.1
Calcium (mg/L)	1405	138	1866	627	1634	148
Carbonate (mg/L)	698	7	874	43	818	54
Chloride (mg/L)	1856	334	1583	489	1442	288
Conductivity (mS/cm)	9.95	0.74	12.49	2.76	10.04	0.47
Copper (mg/L)	0.2190	0.2953	0.0690	0.0212	0.0687	0.0162
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	3509	345	4660	1566	4079	371
Iron (mg/L)	0.1780	0.0277	0.2307	0.0490	0.2097	0.0199
Magnesium (mg/L)	0.0580	0.0131	0.0477	0.0055	0.0530	0.0090
Manganese (mg/L)	0.0520	0.0061	0.0567	0.0076	0.0527	0.0040
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)			-103	2	-78	1
pH	11.76	0.05	11.78	0.09	11.89	0.04
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	139.0	20.8	204.0	102.6	146.7	17.0
Silica (mg/L as SiO_2)	0.2	0.0	0.5	0.1	0.5	0.6
Sodium (mg/L)	280.0	51.0	342.0	138.2	277.3	61.1
Solids (TDS) mg/L	5207	474	6503	1974	5553	215
Sulfate (mg/L)	577.7	206.2	374.3	23.3	266.0	80.9
Temperature (°C)	24.73	0.47	25.80	0.20	22.20	0.52
TOC (mg/L as C)			8.465	2.878		
Total Nitrogen (mg/L as N)	4.0	1.0	4.7	0.6	3.7	0.6
Total Phosphorous (mg/L as PO_4)	0.1	0.2	0.6	0.9	BDL	
Zinc (mg/L)	1.2020	0.1333	1.8037	0.2729	0.8677	0.1852

TDS Value	5207		6503		5553	
Σmass (dissolved)	4995		5289		4608	
% identified	96		81		83	
TDS/EC ratio	0.523		0.521		0.553	

Table C 2: Continued

Hours	360		432		504	
Date of Extraction:	31-Jul-04		3-Aug-04		6-Aug-04	
mL of H2O	141.0	0.3	141.2	0.5	140.7	1.8
mass of Ash (g)	13.6899	0.1881	13.6310	0.2777	13.6242	0.2253
Test	P7 : Avg.	Std. Dev.	P8 : Avg.	Std. Dev.	P9 : Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1450	44	1480	17	1557	23
Aluminum (mg/L)	BDL		0.153	0.100	BDL	
Bromide (mg/L)	19.2	4.0	21.5	2.6	22.7	5.4
Calcium (mg/L)	1573	67	1685	195	1562	164
Carbonate (mg/L)	870	26	888	10	934	14
Chloride (mg/L)	1462	220	1592	96	1550	73
Conductivity (mS/cm)	9.13	0.63	10.99	0.40	10.57	0.21
Copper (mg/L)	0.0817	0.0105	0.0590	0.0017	0.1033	0.0794
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	3927	167	4208	486	3900	410
Iron (mg/L)	0.2127	0.0673	0.2007	0.0471	0.1907	0.0469
Magnesium (mg/L)	0.0397	0.0035	0.0387	0.0025	0.0397	0.0064
Manganese (mg/L)	0.0557	0.0015	0.0513	0.0025	0.0520	0.0026
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-63	1	-58	2	-71	1
pH	12.03	0.03	11.71	0.04	11.74	0.02
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	123.3	20.6	143.0	11.5	137.3	7.6
Silica (mg/L as SiO_2)	0.4	0.5	0.7	0.1	0.8	0.2
Sodium (mg/L)	229.0	36.5	254.3	8.7	252.0	9.6
Solids (TDS) mg/L	5133	497	5487	214	5297	95
Sulfate (mg/L)	337.7	66.6	345.0	46.9	308.0	81.5
Temperature (°C)	19.73	0.21	23.73	0.21	23.80	0.17
TOC (mg/L as C)	61.450	0.495			14.360	11.370
Total Nitrogen (mg/L as N)	10.3	14.6	0.7	0.6	2.3	1.2
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	1.0727	0.5000	0.8833	0.1202	0.6393	0.0439

TDS Value	5133		5487		5297	
Σmass (dissolved)	4626		4931		4770	
% identified	90		90		90	
TDS/EC ratio	0.562		0.499		0.501	

Table C 3: Fly Ash Contact Time Data, Averages and Standard Deviations

Hours	2		7		72	
Date of Extraction:	28-Jun-04		28-Jun-04		1-Jul-04	
mL of H2O	135.0		135.0		135.0	
mass of Ash (g)	13.5083	0.0990	13.3782	0.0859	13.5834	0.0481
Test	FA1:Avg.	Std. Dev.	FA2:Avg.	Std. Dev.	FA3:Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1953	137	1690	115	1693	110
Aluminum (mg/L)	0.133	0.049	0.120	0.078	0.113	0.064
Bromide (mg/L)	191.3	14.2	177.4	7.4	206.0	5.3
Calcium (mg/L)	3624	196	4007	172	4304	143
Carbonate (mg/L)	1172	82	1014	69	1016	66
Chloride (mg/L)	8499	599	8523	447	8370	318
Conductivity (mS/cm)	28.33	1.66	26.97	2.37	23.67	2.32
Copper (mg/L)	0.1157	0.0119	0.1127	0.0021	0.1117	0.0050
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	9050	486	10007	431	10747	359
Iron (mg/L)	0.3283	0.0232	0.3360	0.0165	0.3483	0.0601
Magnesium (mg/L)	0.0687	0.0281	0.0480	0.0108	0.0583	0.0046
Manganese (mg/L)	0.0523	0.0049	0.0463	0.0067	0.0470	0.0036
Nitrate (mg/L)	BDL		7		BDL	
Nitrite (mg/L)	BDL		BDL		39	
ORP (mV)	-71	3	-56	25	-70	2
pH	11.66	0.05	11.53	0.06	11.60	0.02
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	988.4	51.4	829.6	301.7	1053.9	14.9
Silica (mg/L as SiO_2)	0.5	0.1	1.0	0.6	0.2	0.1
Sodium (mg/L)	1377.7	80.5	1411.7	101.0	1487.3	51.5
Solids (TDS) mg/L	16830	1079	16587	644	18077	426
Sulfate (mg/L)	623.5	164.5	569.2	83.0	605.9	93.4
Temperature (°C)	20.73	0.25	21.73	0.61	23.60	1.48
TOC (mg/L as C)	6.7	1.7	5.2	0.1	BDL	
Total Nitrogen (mg/L as N)	4.3	1.6	9.6	7.4	5.3	3.3
Total Phosphorous (mg/L as PO_4)	3.2	0.5	14.8	7.5	2.5	1.6
Zinc (mg/L)	0.558	0.237	0.919	0.065	0.643	0.268

TDS Value	16830		16587		18077	
Σmass (dissolved)	16485		16560		17052	
% identified	98		100		94	
TDS/EC ratio	0.594		0.615		0.764	

Table C 3: Continued

Hours	144		216		288	
Date of Extraction:	4-Jul-04		7-Jul-04		10-Jul-04	
mL of H2O	135.0		135.0		135.0	
mass of Ash (g)	13.6186	0.0074	13.7732	0.1548	13.6717	0.1116
Test	FA4:Avg.	Std. Dev.	FA5:Avg.	Std. Dev.	FA6:Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1561	106	1403	40	1413	12
Aluminum (mg/L)	0.117	0.032	0.053	0.029	0.275	0.332
Bromide (mg/L)	232.0		231.3	7.0	285.3	20.0
Calcium (mg/L)	4398	85	4381	30	4373	102
Carbonate (mg/L)	937	63	842	24	848	7
Chloride (mg/L)	9055	197	8910	157	8297	478
Conductivity (mS/cm)	22.23	0.32	29.60	0.17	25.27	0.32
Copper (mg/L)	0.1067	0.0038	0.1240	0.0101	0.1220	0.0104
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	10983	211	10940	75	10920	252
Iron (mg/L)	0.3393	0.0127	0.3323	0.1564	0.3707	0.0273
Magnesium (mg/L)	0.0473	0.0035	0.0530	0.0070	0.0600	0.0123
Manganese (mg/L)	0.0460	0.0040	0.0410	0.0046	0.0397	0.0057
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-9	6	-69	1	-22	5
pH	11.53	0.04	11.56	0.02	11.65	0.02
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	1072.5	10.0	1098.5	14.3	1090.7	11.2
Silica (mg/L as SiO_2)	0.3	0.2	0.7	0.7	0.4	0.2
Sodium (mg/L)	1554.0	44.0	1596.3	81.8	1616.0	30.4
Solids (TDS) mg/L	17287	47	18037	255	17800	46
Sulfate (mg/L)	516.3	11.3	342.3	13.5	253.1	8.5
Temperature (°C)	25.00	0.36	24.10	0.10	25.67	0.32
TOC (mg/L as C)			5.2	0.1	4.8	0.0
Total Nitrogen (mg/L as N)	0.8	0.5	1.0	0.7	1.4	0.4
Total Phosphorous (mg/L as PO_4)	7.0	4.2	3.2	0.3	5.3	0.2
Zinc (mg/L)	0.512	0.419	0.933	0.025	0.827	0.005

TDS Value	17287		18037		17800	
Σmass (dissolved)	17774		17408		16773	
% identified	103		97		94	
TDS/EC ratio	0.778		0.609		0.704	

Table C 3: Continued

Hours	360		432		504	
Date of Extraction:	13-Jul-04		16-Jul-04		19-Jul-04	
mL of H2O	135.0		135.0		135.0	
mass of Ash (g)	13.7741	0.0574	13.6580	0.1293	13.5255	0.1077
Test	FA7:Avg.	Std. Dev.	FA8:Avg.	Std. Dev.	FA9:Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	1363	45	1323	45	1430	85
Aluminum (mg/L)	0.603	0.984	0.030		BDL	
Bromide (mg/L)	291.3	4.2	252.0	2.0	295.3	7.6
Calcium (mg/L)	4525	129	4567	11	4283	53
Carbonate (mg/L)	818	27	794	27	858	51
Chloride (mg/L)	8565	68	7435	120	8566	277
Conductivity (mS/cm)	22.83	0.47	20.55	2.00	16.67	0.16
Copper (mg/L)	0.1160	0.0070	0.1117	0.0107	0.1020	0.0010
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	11300	321	11403	25	10693	132
Iron (mg/L)	0.4403	0.0700	0.4093	0.0119	0.4100	0.1159
Magnesium (mg/L)	0.0523	0.0154	0.0433	0.0081	0.0393	0.0029
Manganese (mg/L)	0.0423	0.0055	0.0360	0.0026	0.0363	0.0025
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)			-46	9	-59	1
pH	11.50	0.05	11.44	0.01	11.55	0.01
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	1137.2	15.2	982.6	56.2	1130.8	33.4
Silica (mg/L as SiO_2)	0.8	0.5	0.2	0.1	0.3	0.1
Sodium (mg/L)	1853.0	470.8	2346.0	174.9	1598.7	33.6
Solids (TDS) mg/L	17460	201	17037	57	17323	189
Sulfate (mg/L)	198.7	13.3	111.5	54.7	71.3	13.3
Temperature (°C)	25.07	0.61	26.97	3.26	23.57	0.29
TOC (mg/L as C)	4.9	0.1	5.1			
Total Nitrogen (mg/L as N)	0.8	0.2	1.1	0.4	0.7	0.8
Total Phosphorous (mg/L as PO_4)	5.4	0.5	5.0	0.3	5.2	0.2
Zinc (mg/L)	0.583	0.293	0.568	0.070	0.416	0.181

TDS Value	17460		17037		17323	
Σmass (dissolved)	17397		16495		16810	
% identified	100		97		97	
TDS/EC ratio	0.765		0.829		1.039	

Table C 4: Bottom Ash Contact Time Data, Averages and Standard Deviations

Hours	2		7		72	
Date of Extraction:	7/1/04		7/1/04		7/4/04	
mL of H2O	132.0	0.0	132.0	0.0	134.7	1.5
mass of Ash (g)	13.6084	0.1589	13.5375	0.1376	13.5934	0.1294
Test	BA1:Avg.	Std. Dev.	BA2:Avg.	Std. Dev.	BA3:Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	470	70	580	40	650	132
Aluminum (mg/L)	18.3	4.1	46.1	10.9	126.9	91.4
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	155	13	167	17	125	27
Carbonate (mg/L)	282	42	348	24	390	79
Chloride (mg/L)	38	10	39	3	87	15
Conductivity (mS/cm)	2.13	0.12	2.21	0.18	1.73	0.39
Copper (mg/L)	0.136	0.023	0.131	0.004	0.099	0.014
Fluoride (mg/L)	0.4	0.0	0.5		0.6	0.1
Hardness (mg $CaCO_3$ / L)	387	35	417	40	313	65
Iron (mg/L)	0.193	0.044	0.161	0.064	0.186	0.010
Magnesium (mg/L)	0.038	0.009	0.048	0.013	0.025	0.004
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	0.4		BDL		0.6	0.0
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-141	4	-187	7	-155	15
pH	11.62	0.03	11.95	0.01	11.71	0.12
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	18.9	3.3	21.0	1.9	18.5	7.4
Silica (mg/L as SiO_2)	1.6	0.6	4.0	1.4	30.8	37.9
Sodium (mg/L)	42.9	10.3	49.1	7.4	43.0	8.8
Solids (TDS) mg/L	573	60	673	38	967	283
Sulfate (mg/L)	7.6	0.9	7.2	1.0	13.2	3.3
Temperature (°C)	23.80	0.26	23.37	0.25	23.80	0.36
TOC (mg/L as C)	12.05	1.91	11.55	0.35		
Total Nitrogen (mg/L as N)	4.4	4.3	2.0	0.6	1.0	0.4
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	0.062	0.014	0.070	0.004	0.059	0.011

TDS Value	573		673		967	
Σmass (dissolved)	570		684		837	
% identified	99		102		87	
TDS/EC ratio	0.269		0.305		0.559	

Table C 4: Continued

Hours	144		216		288	
Date of Extraction:	7/7/04		7/10/04		7/13/04	
mL of H2O	134.7	0.6	135.0	0.0	135.0	0.0
mass of Ash (g)	13.6185	0.0871	13.5937	0.0244	13.5941	0.1087
Test	BA4:Avg.	Std. Dev.	BA5:Avg.	Std. Dev.	BA6:Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	667	95	630	26	633	68
Aluminum (mg/L)	152.2	71.3	116.7	36.1	149.7	47.4
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	126	23	134	25	124	14
Carbonate (mg/L)	400	57	378	16	380	41
Chloride (mg/L)	84	5	36	2	104	9
Conductivity (mS/cm)	1.74	0.29	2.10	0.35	1.90	0.16
Copper (mg/L)	0.139	0.025	0.138	0.004	0.142	0.005
Fluoride (mg/L)	0.6	0.0	BDL		0.8	0.0
Hardness (mg $CaCO_3$ / L)	313	59	333	64	310	35
Iron (mg/L)	0.240	0.046	0.239	0.028	0.137	0.029
Magnesium (mg/L)	0.031	0.002	0.024	0.005	0.022	0.002
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	0.4	0.2	0.5		0.6	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-60	2	-127	28		
pH	11.56	0.13	11.67	0.05	11.43	0.23
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	22.9	1.4	23.1	1.5	23.5	1.6
Silica (mg/L as SiO_2)	25.3		9.0	3.2	13.0	4.4
Sodium (mg/L)	50.1	5.7	48.0	4.1	52.2	8.3
Solids (TDS) mg/L	1010	212	877	98	943	170
Sulfate (mg/L)	10.6	0.7	4.2	0.5	11.8	1.3
Temperature (°C)	24.17	0.06	25.50	1.21	24.93	0.25
TOC (mg/L as C)	12.40	0.57			14.05	0.35
Total Nitrogen (mg/L as N)	1.4	0.1	1.1	0.3	1.2	0.1
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	0.077	0.017	0.107	0.011	0.101	0.013

TDS Value	1010		877		943	
Σmass (dissolved)	874		751		861	
% identified	87		86		91	
TDS/EC ratio	0.581		0.418		0.497	

Table C 4: Continued

Hours	360		432		504	
Date of Extraction:	7/16/04		7/19/04		7/22/04	
mL of H2O	135.0	0.0	135.0	0.0	135.0	0.0
mass of Ash (g)	13.5507	0.1734	13.4526	0.0903	13.6090	0.1494
Test	BA7:Avg.	Std. Dev.	BA8:Avg.	Std. Dev.	BA9:Avg.	Std. Dev.
Alkalinity (mg $CaCO_3$ / L)	623	50	653	15	610	26
Aluminum (mg/L)	134.7	65.6	188.7	1.5	114.7	43.3
Bromide (mg/L)	BDL		2.8	0.4	BDL	
Calcium (mg/L)	139	58	101	1	122	16
Carbonate (mg/L)	374	30	392	9	366	16
Chloride (mg/L)	120	3	115	10	59	12
Conductivity (mS/cm)	2.29	0.70	1.41	0.06	1.70	0.25
Copper (mg/L)	0.128	0.002	0.131	0.009	0.141	0.007
Fluoride (mg/L)	0.8	0.0	0.7	0.0	BDL	
Hardness (mg $CaCO_3$ / L)	347	142	257	6	303	42
Iron (mg/L)	0.201	0.097	0.237	0.035	0.288	0.035
Magnesium (mg/L)	0.026	0.004	0.018	0.001	0.020	0.004
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-115	9	-93	11	-81	6
pH	11.45	0.21	11.40	0.08	11.48	0.06
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	26.3	1.4	24.7	4.1	22.6	5.3
Silica (mg/L as SiO_2)	6.8	5.6	13.8	6.4	0.4	0.4
Sodium (mg/L)	57.6	0.9	53.1	0.6	52.3	7.8
Solids (TDS) mg/L	927	95	1003	108	870	104
Sulfate (mg/L)	16.9	4.0	17.5	1.7	9.3	1.4
Temperature (°C)	30.50	0.26	22.80	0.20	23.50	0.20
TOC (mg/L as C)	16.90		14.35	3.04		
Total Nitrogen (mg/L as N)	1.1	0.1	2.0	1.4	1.3	0.4
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	0.111	0.028	0.085	0.007	0.108	0.014

TDS Value	927		1003		870	
Σmass (dissolved)	878		912		747	
% identified	95		91		86	
TDS/EC ratio	0.405		0.712		0.511	

Table C 5: Hillsborough Sequential Extraction Data, Averages and Standard Deviations

Mass of Ash = 13.4054 g						
Extraction Number	1st		2nd		3rd	
Date of Extraction:	25-Jul-04		28-Jul-04		31-Jul-04	
mL of H2O	138.5	0.9	256.2	3.1	372.8	5.1
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	1217	93	983	35	957	40
Aluminum (mg/L)	0.000	0.000	0.080	0.066	0.460	0.679
Bromide (mg/L)	59.9	10.3	11.0	3.8	2.1	0.5
Calcium (mg/L)	1457	236	585	70	462	62
Carbonate (mg/L)	730	56	590	21	574	24
Chloride (mg/L)	2152	247	373	70	103	23
Conductivity (mS/cm)	12.00	1.21	4.85	0.42	3.73	0.28
Copper (mg/L)	0.130	0.120	0.118	0.136	0.135	0.095
Fluoride (mg/L)	BDL		2.03		2.80	0.16
Hardness (mg $CaCO_3$ / L)	3639	590	1460	174	1155	154
Iron (mg/L)	0.162	0.008	0.123	0.022	0.176	0.014
Magnesium (mg/L)	0.098	0.038	0.054	0.021	0.317	0.019
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-118	13	-119	6	-90	5
pH	11.78	0.03	11.70	0.05	11.82	0.15
Phosphate (mg/L)	BDL		BDL		3.75	
Potassium (mg/L)	242.9	37.4	40.3	1.1	13.1	0.9
Silica (mg/L as SiO_2)	0.7	0.4	1.1	0.4	6.0	3.7
Sodium (mg/L)	445.7	56.5	63.0	37.0	20.4	2.2
Solids (TDS) mg/L	6400	771	2113	110	1343	188
Sulfate (mg/L)	244.3	48.6	161.1	27.9	128.7	36.9
Temperature (°C)	25.13	0.25	21.20	0.10	21.77	0.35
Total Nitrogen (mg/L as N)	11.8	4.6	6.9	3.8	3.0	2.3
Total Phosphorous (mg/L as PO_4)	0.3	0.2	0.2	0.1	0.9	0.4
Zinc (mg/L)	1.676	0.161	0.458	0.037	0.553	0.062

TDS Value	6400		2113		1343	
Σmass (dissolved)	5347		1834		1321	
% identified	84		87		98	
L/S Ratio	10		19		28	
TDS/EC ratio	0.533		0.435		0.360	

Table C 5: Continued

Mass of Ash = 13.4054 g						
Extraction Number	4th		5th		6th	
Date of Extraction:	3-Aug-04		6-Aug-04		9-Aug-04	
mL of H2O	467.2	8.1	580.8	8.4	696.8	8.4
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	780	139	543	87	400	61
Aluminum (mg/L)	0.140	0.044	0.517	0.436	1.460	0.316
Bromide (mg/L)	1.4		0.3		0.3	
Calcium (mg/L)	338	75	197	37	162	27
Carbonate (mg/L)	468	83	326	52	240	36
Chloride (mg/L)	49	14	19	2	12	2
Conductivity (mS/cm)	3.20	0.74	2.20	0.31	1.65	0.22
Copper (mg/L)	0.122	0.075	0.066	0.091	0.065	0.050
Fluoride (mg/L)	2.72	0.13	2.62	0.04	1.15	0.03
Hardness (mg $CaCO_3$ / L)	845	189	491	91	406	69
Iron (mg/L)	0.125	0.019	0.127	0.014	0.170	0.061
Magnesium (mg/L)	0.081	0.013	0.058	0.033	0.191	0.185
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-97	1	-82	6	-67	11
pH	11.34	0.11	11.15	0.11	11.35	0.14
Phosphate (mg/L)	3.66	0.13	3.55	0.02	1.81	0.11
Potassium (mg/L)	5.7	1.4	2.8	0.5	1.8	0.3
Silica (mg/L as SiO_2)	2.6	0.3	4.0	1.6	5.0	1.3
Sodium (mg/L)	11.0	1.7	6.6	0.5	5.0	1.0
Solids (TDS) mg/L	983	189	603	87	443	67
Sulfate (mg/L)	73.7	32.9	22.0	5.1	14.9	1.2
Temperature (°C)	26.27	0.31	26.37	0.12	25.87	0.78
Total Nitrogen (mg/L as N)	2.3	1.4	1.4	0.9	0.6	0.4
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	0.332	0.040	0.240	0.028	0.335	0.163

TDS Value	983		603		443	
Σmass (dissolved)	959		586		447	
% identified	98		97		101	
L/S Ratio	35		43		52	
TDS/EC ratio	0.307		0.275		0.269	

Table C 5: Continued

Mass of Ash = 13.4054 g						
Extraction Number	7th		8th		9th	
Date of Extraction:	12-Aug-04		15-Aug-04		18-Aug-04	
mL of H2O	800.5	29.0	908.7	30.5	1020.3	39.3
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	330	106	277	64	203	42
Aluminum (mg/L)	1.673	0.792	2.657	0.944	3.217	0.717
Bromide (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL
Calcium (mg/L)	133	42	117	27	86	15
Carbonate (mg/L)	198	63	166	39	122	25
Chloride (mg/L)	9	4	6	2	5	2
Conductivity (mS/cm)	1.41	0.44	1.13	0.26	0.83	0.18
Copper (mg/L)	0.059	0.045	0.068	0.042	0.034	0.035
Fluoride (mg/L)	BDL		1.07	0.01	0.56	
Hardness (mg $CaCO_3$ / L)	333	104	292	66	215	38
Iron (mg/L)	0.132	0.017	0.140	0.017	0.140	0.013
Magnesium (mg/L)	0.037	0.019	0.068	0.037	0.038	0.006
Manganese (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-34	7	-36	3	-33	5
pH	11.13	0.15	11.11	0.12	10.74	0.12
Phosphate (mg/L)	1.76	0.15	1.74	0.12	1.06	0.15
Potassium (mg/L)	1.5	0.8	1.1	0.5	3.5	3.2
Silica (mg/L as SiO_2)	4.3	0.3	5.2	0.5	5.5	0.4
Sodium (mg/L)	3.1	1.5	3.4	1.0	2.4	1.1
Solids (TDS) mg/L	363	118	330	44	287	35
Sulfate (mg/L)	14.9	3.4	20.1	6.6	22.7	3.8
Temperature (°C)	27.30	0.26	26.67	0.06	27.70	0.26
Total Nitrogen (mg/L as N)	0.8	0.4	0.6	0.2	0.4	0.1
Total Phosphorous (mg/L as PO_4)	0.9	0.2	1.1	0.6	1.2	0.2
Zinc (mg/L)	0.183	0.039	0.182	0.034	0.147	0.026

TDS Value	363		330		287	
Σmass (dissolved)	370		327		254	
% identified	102		99		89	
L/S Ratio	60		68		76	
TDS/EC ratio	0.258		0.291		0.344	

Table C 5: Continued

Mass of Ash = 13.4054 g						
Extraction Number	10th		11th		12th	
Date of Extraction:	21-Aug-04		24-Aug-04		27-Aug-04	
mL of H2O	1132.8	43.2	1247.8	51.8	1362.3	52.1
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	167	31	157	21	127	12
Aluminum (mg/L)	3.673	0.556	4.593	0.597	4.487	0.571
Bromide (mg/L)	BDL		0.2	0.0	0.6	
Calcium (mg/L)	75	8	78	8	69	8
Carbonate (mg/L)	100	18	94	12	76	7
Chloride (mg/L)	5	2	4	3	3	2
Conductivity (mS/cm)	0.71	0.13	0.65	0.09	0.60	0.07
Copper (mg/L)	0.035	0.028	0.085	0.005	0.046	0.001
Fluoride (mg/L)	BDL		BDL		BDL	
Hardness (mg $CaCO_3$ / L)	187	21	196	21	172	21
Iron (mg/L)	0.123	0.014	0.145	0.050	0.145	0.024
Magnesium (mg/L)	0.053	0.002	0.227	0.108	0.143	0.120
Manganese (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL
Nitrate (mg/L)	BDL		1.04		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-26	4	1	2	31	2
pH	11.10	0.10	11.04	0.10	10.69	0.07
Phosphate (mg/L)	0.99	0.12	0.93	0.03	0.85	0.02
Potassium (mg/L)	3.8	5.3	4.3	6.3	3.2	5.0
Silica (mg/L as SiO_2)	4.6	0.2	7.5	1.6	4.5	0.4
Sodium (mg/L)	2.3	0.7	1.9	0.7	1.6	0.6
Solids (TDS) mg/L	230	0	240	10	253	12
Sulfate (mg/L)	30.8	8.9	34.4	4.0	38.7	3.0
Temperature (°C)	27.50	0.46	25.83	0.06	31.13	0.49
Total Nitrogen (mg/L as N)	0.3	0.1	0.2	0.2	0.2	0.1
Total Phosphorous (mg/L as PO_4)	1.3	0.4	0.6	0.1	1.0	0.5
Zinc (mg/L)	0.133	0.013	0.256	0.092	0.182	0.073

TDS Value	230		240		253	
Σmass (dissolved)	228		232		204	
% identified	99		97		80	
L/S Ratio	85		93		102	
TDS/EC ratio	0.324		0.369		0.425	

Appendix C (continued)

Table C 6: Pasco Sequential Extraction Data, Averages and Standard Deviations

Mass of Ash = 13.5983g						
Extraction Number	1st		2nd		3rd	
Date of Extraction:	19-Jul-04		22-Jul-04		25-Jul-04	
mL of H2O	140	0	262	5	369	5
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	1167	47	907	57	587	58
Aluminum (mg/L)	0.333	0.197	0.190	0.105	0.130	0.070
Bromide (mg/L)	30.1	3.6	5.6	1.3	BDL	
Calcium (mg/L)	1167	87	505	48	283	35
Carbonate (mg/L)	700	28	544	34	352	35
Chloride (mg/L)	1463	146	203	38	60	9
Conductivity (mS/cm)	10.39	0.62	4.82	0.38	2.55	0.16
Copper (mg/L)	0.081	0.032	BDL		BDL	
Fluoride (mg/L)	BDL		1.39	0.03	1.26	0.13
Hardness (mg $CaCO_3$ / L)	2915	218	1260	119	707	87
Iron (mg/L)	0.103	0.079	0.081	0.016	0.086	0.018
Magnesium (mg/L)	0.081	0.027	0.063	0.012	0.157	0.143
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	BDL		4.59	0.93	5.14	2.24
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-151	18			-84	10
pH	11.71	0.03	11.55	0.08	11.73	0.12
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	149.8	14.9	27.6	4.1	7.5	1.7
Silica (mg/L as SiO_2)	0.3	0.2	0.5	0.4	2.3	0.1
Sodium (mg/L)	255.5	39.7	40.9	8.5	11.8	2.0
Solids (TDS) mg/L	5060	422	1967	216	990	199
Sulfate (mg/L)	320.3	34.4	166.9	19.9	113.6	19.6
Temperature (°C)	26.77	0.32	27.70	0.10	25.03	0.55
Total Nitrogen (mg/L as N)	26.7	20.3	10.0	1.0	6.7	1.5
Total Phosphorous (mg/L as PO_4)	0.0	0.0	0.0	0.0	0.0	0.0
Zinc (mg/L)	2.786	0.364	0.858	0.214	0.292	0.045

TDS Value	5060		1967		990	
Σmass (dissolved)	4117		1510		843	
% identified	81		77		85	
L/S Ratio	10		19		27	
TDS/EC ratio	0.487		0.408		0.389	

Appendix C (continued)

Table C 6: Continued

Mass of Ash = 13.5983g						
Extraction Number	4th		5th		6th	
Date of Extraction:	28-Jul-04		31-Jul-04		3-Aug-04	
mL of H2O	460	19	552	33	657	37
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	407	71	280	56	213	29
Aluminum (mg/L)	0.340	0.125	0.923	0.379	1.467	0.415
Bromide (mg/L)	0.9	0.5	0.8		BDL	
Calcium (mg/L)	188	39	123	29	71	13
Carbonate (mg/L)	244	43	168	33	128	17
Chloride (mg/L)	42	27	23	6	8	3
Conductivity (mS/cm)	1.79	0.33	1.18	0.24	0.88	0.16
Copper (mg/L)	BDL		BDL		BDL	
Fluoride (mg/L)	1.13	0.02	1.09	0.03	1.06	0.02
Hardness (mg $CaCO_3$ / L)	470	97	308	71	178	33
Iron (mg/L)	0.088	0.037	0.169	0.040	0.187	0.059
Magnesium (mg/L)	0.107	0.048	0.160	0.117	0.086	0.034
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	2.63	1.76	2.65	1.95	1.62	0.89
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-64	7	-50	12	-38	6
pH	11.43	0.11	11.58	0.12	10.84	0.12
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	4.0	2.0	3.1	2.0	1.5	0.8
Silica (mg/L as SiO_2)	2.9	1.1	4.5	0.4	5.6	0.7
Sodium (mg/L)	7.6	2.6	5.5	2.1	3.7	2.0
Solids (TDS) mg/L	570	125	393	90	287	70
Sulfate (mg/L)	68.3	15.3	46.1	9.4	35.6	4.8
Temperature (°C)	23.83	0.64	23.13	1.17	25.43	1.27
Total Nitrogen (mg/L as N)	8.3	2.1	0.7	0.3	0.9	0.2
Total Phosphorous (mg/L as PO_4)	0.0	0.0	0.0	0.0	0.0	0.0
Zinc (mg/L)	0.222	0.032	0.205	0.045	0.134	0.029

TDS Value	570		393		287	
Σmass (dissolved)	571		380		258	
% identified	100		97		90	
L/S Ratio	34		41		48	
TDS/EC ratio	0.318		0.333		0.327	

Appendix C (continued)

Table C 6: Continued

Mass of Ash = 13.5983g						
Extraction Number	7th		8th		9th	
Date of Extraction:	6-Aug-04		9-Aug-04		12-Aug-04	
mL of H2O	772	37	889	39	1003	41
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	167	25	133	12	120	10
Aluminum (mg/L)	2.383	0.227	2.687	0.506	3.040	0.140
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	65	11	59	5	53	7
Carbonate (mg/L)	100	15	80	7	72	6
Chloride (mg/L)	6	4	2	0	2	0
Conductivity (mS/cm)	0.67	0.09	0.63	0.05	0.47	0.06
Copper (mg/L)	BDL		BDL		BDL	
Fluoride (mg/L)	0.57	0.02	0.57	0.00	0.56	0.01
Hardness (mg $CaCO_3$ / L)	163	26	149	13	134	16
Iron (mg/L)	0.228	0.005	0.239	0.018	0.313	0.105
Magnesium (mg/L)	0.269	0.073	0.171	0.070	0.151	0.091
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	1.14	0.46	0.90	0.36	0.63	0.26
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-44	5	-28	4	-4	5
pH	10.58	0.08	10.93	0.04	10.80	0.08
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	0.7	0.3	0.4	0.2	0.3	0.1
Silica (mg/L as SiO_2)	6.3	0.6	6.6	0.4	5.9	1.0
Sodium (mg/L)	1.7	1.1	1.5	0.2	1.0	0.3
Solids (TDS) mg/L	250	20	210	20	190	20
Sulfate (mg/L)	37.2	2.7	39.5	3.0	37.8	5.0
Temperature (°C)	26.10	0.20	28.00	0.10	24.87	0.31
Total Nitrogen (mg/L as N)	1.0	0.5	0.7	0.3	0.1	0.0
Total Phosphorous (mg/L as PO_4)	0.0	0.0	0.0	0.0	0.0	0.0
Zinc (mg/L)	0.222	0.044	0.164	0.045	0.156	0.038

TDS Value	250		210		190	
Σmass (dissolved)	222		195		177	
% identified	89		93		93	
L/S Ratio	57		65		74	
TDS/EC ratio	0.375		0.335		0.402	

Appendix C (continued)

Table C 6: Continued

Mass of Ash = 13.5983g						
Extraction Number	10th		11th		12th	
Date of Extraction:	15-Aug-04		18-Aug-04		21-Aug-04	
mL of H2O	1107	29	1221	30	1340	30
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	117	6	107	6	107	6
Aluminum (mg/L)	2.993	0.341	3.047	0.742	3.867	0.729
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	55	5	48	6	50	6
Carbonate (mg/L)	70	3	64	3	64	3
Chloride (mg/L)	6	6	2	0	2	0
Conductivity (mS/cm)	0.49	0.03	0.46	0.04	0.45	0.04
Copper (mg/L)	BDL		BDL		BDL	
Fluoride (mg/L)	0.55	0.01	0.56	0.01	0.56	0.00
Hardness (mg $CaCO_3$ / L)	138	12	120	14	127	14
Iron (mg/L)	0.381	0.060	0.044		BDL	
Magnesium (mg/L)	0.129	0.037	0.112	0.052	0.498	0.195
Manganese (mg/L)	BDL		BDL		BDL	
Nitrate (mg/L)	0.53	0.04	0.49	0.07	0.48	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-16	3	-1	1	2	1
pH	10.78	0.08	10.64	0.06	11.02	0.07
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	0.2	0.1	0.2	0.1	0.1	0.0
Silica (mg/L as SiO_2)	5.6	1.5	5.9	1.6	6.3	1.7
Sodium (mg/L)	0.6	0.2	0.7	0.1	0.7	0.2
Solids (TDS) mg/L	177	23	200	10	170	17
Sulfate (mg/L)	37.8	4.0	33.9	4.5	34.5	4.0
Temperature (°C)	25.23	0.40	27.90	0.17	28.40	0.10
Total Nitrogen (mg/L as N)	0.0	0.0	0.2	0.1	0.1	0.1
Total Phosphorous (mg/L as PO_4)	0.0	0.0	0.0	0.0	0.0	0.0
Zinc (mg/L)	0.138	0.026	0.132	0.021	0.349	0.116

TDS Value	177		200		170	
Σmass (dissolved)	180		159		163	
% identified	102		79		96	
L/S Ratio	81		90		99	
TDS/EC ratio	0.364		0.438		0.377	

Table C 7: Fly Ash Sequential Extraction Data, Averages and Standard Deviations

Mass of Ash = 13.7065g						
Extraction Number	1st		2nd		3rd	
Date of Extraction:	4-Jun-04		7-Jun-04		10-Jun-04	
mL of H2O	135	0	233	7	333	7
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	1303	25	1343	78	1233	311
Aluminum (mg/L)	0.020	0.035	0.057	0.055	0.190	0.104
Bromide (mg/L)	177.2	9.6	76.5	13.5	17.3	3.1
Calcium (mg/L)	5638	231	2179	226	892	119
Carbonate (mg/L)	782	15	806	47	740	186
Chloride (mg/L)	7652	257	3051	519	666	102
Conductivity (mS/cm)	33.10	0.17	16.02	1.38	7.85	1.16
Copper (mg/L)	0.175	0.017	0.101	0.010	0.080	0.014
Fluoride (mg/L)	BDL		BDL		4.29	0.12
Hardness (mg $CaCO_3$ / L)	14078	577	5441	564	2228	298
Iron (mg/L)	0.313	0.070	0.201	0.167	0.159	0.085
Magnesium (mg/L)	0.291	0.075	0.104	0.034	0.073	0.034
Manganese (mg/L)	0.099	0.007	0.070	0.007	0.057	0.001
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-73	2	-85	5	-68	8
pH	11.16	0.04	11.59	0.09	11.98	0.12
Phosphate (mg/L)	BDL		BDL		5.83	0.52
Potassium (mg/L)	1163.8	44.4	300.9	69.6	68.0	15.6
Silica (mg/L as SiO_2)	10.8	6.8	11.6	4.7	2.9	2.4
Sodium (mg/L)	1834.0	107.0	553.3	99.4	159.1	18.8
Solids (TDS) mg/L	18677	42	7300	849	2780	278
Sulfate (mg/L)	512.3	18.4	209.7	26.2	29.9	4.9
Temperature (°C)	24.43	0.42	26.30	0.10	25.07	0.68
Total Nitrogen (mg/L as N)	0.2	0.1	0.3	0.0	0.2	0.1
Total Phosphorous (mg/L as PO_4)	17.3	8.6	0.3		1.3	1.2
Zinc (mg/L)	2.338	0.221	1.450	0.053	0.800	0.110

TDS Value	18677		7300		2780	
Σmass (dissolved)	15957		6637		2429	
% identified	85		91		87	
L/S Ratio	10		17		24	
TDS/EC ratio	0.564		0.456		0.354	

Table C 7: Continued

Mass of Ash = 13.7065g						
Extraction Number	4th		5th		6th	
Date of Extraction:	13-Jun-04		16-Jun-04		19-Jun-04	
mL of H2O	433	7	525	26	625	26
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	1047	193	1557	117	1067	81
Aluminum (mg/L)	0.047	0.045	0.233	0.108	0.380	0.080
Bromide (mg/L)	5.7	1.0	4.3	1.7	2.6	
Calcium (mg/L)	562	52	539	66	545	49
Carbonate (mg/L)	628	116	934	70	640	48
Chloride (mg/L)	207	30	145	67	50	20
Conductivity (mS/cm)	5.15	0.61	6.94	0.60	4.89	0.34
Copper (mg/L)	0.066	0.006	0.072	0.005	0.062	0.000
Fluoride (mg/L)	3.11	0.60	4.44	0.20	2.87	0.71
Hardness (mg $CaCO_3$ / L)	1404	130	1345	165	1360	123
Iron (mg/L)	0.164	0.060	0.054	0.031	0.221	0.085
Magnesium (mg/L)	0.041	0.027	0.063	0.019	0.053	0.046
Manganese (mg/L)	0.044	0.005	0.045	0.000	0.038	0.004
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-77	2	-100	0	-129	4
pH	12.26	0.14	12.32	0.05	12.05	0.07
Phosphate (mg/L)	5.37	0.49	4.53	0.47	3.83	0.44
Potassium (mg/L)	28.1	1.3	20.2	7.4	11.6	1.6
Silica (mg/L as SiO_2)	1.1	0.4	4.1	2.1	1.1	0.3
Sodium (mg/L)	58.7	8.7	35.6	10.3	20.7	5.6
Solids (TDS) mg/L	1670	139	1827	224	1250	166
Sulfate (mg/L)	16.0	0.6	7.7	0.5	6.8	0.3
Temperature (°C)	23.63	0.59	24.00	0.36	24.37	0.06
Total Nitrogen (mg/L as N)	0.1	0.1	0.2	0.1	0.3	0.2
Total Phosphorous (mg/L as PO_4)	2.0	1.1	1.0	1.2	8.9	
Zinc (mg/L)	0.471	0.014	0.744	0.078	0.448	0.083

TDS Value	1670		1827		1250	
Σmass (dissolved)	1460		1665		1273	
% identified	87		91		102	
L/S Ratio	32		38		46	
TDS/EC ratio	0.324		0.263		0.256	

Table C 7: Continued

Mass of Ash = 13.7065g						
Extraction Number	7th		8th		9th	
Date of Extraction:	22-Jun-04		25-Jun-04		28-Jun-04	
mL of H2O	716	40	805	43	905	43
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	1073	114	850	101	767	90
Aluminum (mg/L)	0.640	0.100	0.607	0.031	0.937	0.225
Bromide (mg/L)	1.9		1.1	0.1	1.2	0.2
Calcium (mg/L)	517	74	429	30	347	41
Carbonate (mg/L)	644	68	510	61	460	54
Chloride (mg/L)	43	14	33	6	30	5
Conductivity (mS/cm)	4.88	0.48	4.02	0.32	3.36	0.44
Copper (mg/L)	0.071	0.016	0.058	0.009	0.076	0.019
Fluoride (mg/L)	5.81	0.57	7.20	1.08	4.61	0.73
Hardness (mg $CaCO_3$ / L)	1292	185	1071	75	868	101
Iron (mg/L)	0.174	0.143	0.061	0.009	0.243	0.080
Magnesium (mg/L)	0.146	0.164	0.036	0.028	0.197	0.195
Manganese (mg/L)	0.047	0.009	0.038	0.001	0.035	0.008
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-100	9	-82	2	-68	1
pH	12.04	0.14	11.91	0.02	12.18	0.02
Phosphate (mg/L)	3.96	0.11	2.84	0.27	2.95	0.28
Potassium (mg/L)	10.4	2.1	10.9	1.9	6.0	4.3
Silica (mg/L as SiO_2)	0.5	0.3	1.1	0.7	1.3	0.9
Sodium (mg/L)	17.7	4.4	16.7	1.1	8.1	4.1
Solids (TDS) mg/L	1237	131	973	71	790	131
Sulfate (mg/L)	9.6	1.3	9.6	1.4	16.9	5.5
Temperature (°C)	24.90	0.72	23.70	0.17	25.43	0.38
Total Nitrogen (mg/L as N)	0.2	0.1	0.3	0.1	0.2	0.0
Total Phosphorous (mg/L as PO_4)	7.6		BDL		BDL	
Zinc (mg/L)	0.511	0.212	0.326	0.038	0.493	0.227

TDS Value	1237		973		790	
Σmass (dissolved)	1246		1006		873	
% identified	101		103		110	
L/S Ratio	52		59		66	
TDS/EC ratio	0.253		0.242		0.235	

Table C 7: Continued

Mass of Ash = 13.7065g						
Extraction Number	10th		11th		12th	
Date of Extraction:	1-Jul-04		4-Jul-04		10-Jul-04	
mL of H2O	995	40	1095	40	1184	45
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	587	45	503	40	493	31
Aluminum (mg/L)	1.423	0.140	1.497	0.068	1.787	0.266
Bromide (mg/L)	1.2	0.2	1.3	0.1	1.5	0.1
Calcium (mg/L)	294	69	244	20	225	11
Carbonate (mg/L)	352	27	302	24	296	18
Chloride (mg/L)	23	4	26	2	22	1
Conductivity (mS/cm)	2.67	0.17	2.40	0.19	2.32	0.10
Copper (mg/L)	0.072	0.006	0.064	0.004	0.067	0.005
Fluoride (mg/L)	4.10	0.47	6.05	0.88	4.48	0.95
Hardness (mg $CaCO_3$ / L)	735	172	609	51	563	28
Iron (mg/L)	0.127	0.019	0.166	0.032	0.134	0.023
Magnesium (mg/L)	0.096	0.105	0.034	0.016	0.067	0.046
Manganese (mg/L)	0.036	0.006	0.037	0.002	0.035	0.006
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-120	21	-69	6	-58	5
pH	12.06	0.04	11.93	0.05	11.61	0.13
Phosphate (mg/L)	3.05	0.04	2.10	0.22	2.22	0.12
Potassium (mg/L)	8.0	0.6	6.6	0.6	8.7	0.5
Silica (mg/L as SiO_2)	1.9	0.3	2.3	0.4	3.2	0.4
Sodium (mg/L)	0.8	0.3	2.5	2.0	3.7	2.2
Solids (TDS) mg/L	667	143	597	40	587	40
Sulfate (mg/L)	18.2	3.1	18.7	3.8	24.9	4.8
Temperature (°C)	26.37	0.25	25.33	0.47	25.20	0.10
Total Nitrogen (mg/L as N)	BDL		BDL		BDL	
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	0.344	0.135	0.240	0.022	0.282	0.058

TDS Value	667		597		587	
Σmass (dissolved)	708		611		591	
% identified	106		102		101	
L/S Ratio	73		80		86	
TDS/EC ratio	0.250		0.248		0.253	

Table C 7: Continued

Mass of Ash = 13.7065g				
Extraction Number	13th		14th	
Date of Extraction:	13-Jul-04		16-Jul-04	
mL of H2O	1284	45	1381	57
Test	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	390	20	390	36
Aluminum (mg/L)	2.307	0.146	2.080	0.132
Bromide (mg/L)	1.0	0.0	1.1	0.1
Calcium (mg/L)	178	14	185	13
Carbonate (mg/L)	234	12	234	22
Chloride (mg/L)	14	1	15	1
Conductivity (mS/cm)	1.76	0.08	1.78	0.11
Copper (mg/L)	0.066	0.002	0.066	0.010
Fluoride (mg/L)	5.83	0.56	7.30	0.55
Hardness (mg $CaCO_3$ / L)	446	34	462	34
Iron (mg/L)	0.150	0.082	0.098	0.042
Magnesium (mg/L)	0.062	0.054	0.033	0.003
Manganese (mg/L)	0.042	0.003	0.043	0.002
Nitrate (mg/L)	BDL		BDL	
Nitrite (mg/L)	BDL		BDL	
ORP (mV)	-56	4	-57	3
pH	11.66	0.05	11.53	0.03
Phosphate (mg/L)	1.90	0.10	2.13	0.12
Potassium (mg/L)	5.9	0.8	7.0	5.3
Silica (mg/L as SiO_2)	4.2	0.5	1.6	0.6
Sodium (mg/L)	1.3	1.1	0.3	0.1
Solids (TDS) mg/L	483	21	447	31
Sulfate (mg/L)	25.2	3.1	19.7	1.2
Temperature (°C)	25.30	0.46	25.23	0.31
Total Nitrogen (mg/L as N)	BDL		BDL	
Total Phosphorous (mg/L as PO_4)	BDL		BDL	
Zinc (mg/L)	0.258	0.058	0.211	0.009

TDS Value	483		447	
Σmass (dissolved)	474		475	
% identified	98		106	
L/S Ratio	94		101	
TDS/EC ratio	0.274		0.251	

Table C 8: Bottom Ash Sequential Extraction Data, Averages and Standard Deviations

Mass of Ash = 13.6278g						
Extraction Number	1st		2nd		3rd	
Date of Extraction:	4-Jun-04		7-Jun-04		10-Jun-04	
mL of H2O	135	0	252	3	352	3
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	637	160	490	53	583	93
Aluminum (mg/L)	11.86	13.68	7.23	8.88	8.67	12.29
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	411	82	308	39	267	73
Carbonate (mg/L)	382	96	294	32	350	56
Chloride (mg/L)	34.7	5.5	16.8	2.2	10.5	2.1
Conductivity (mS/cm)	4.18	0.69	3.22	0.44	2.70	0.57
Copper (mg/L)	0.442	0.102	0.180	0.049	0.191	0.051
Fluoride (mg/L)	BDL		BDL		0.41	0.15
Hardness (mg $CaCO_3$ / L)	1029	206	770	96	667	182
Iron (mg/L)	0.666	0.478	0.156	0.065	0.208	0.078
Magnesium (mg/L)	0.764	0.334	0.054	0.026	0.118	0.045
Manganese (mg/L)	0.143	0.136	0.034	0.002	0.034	0.003
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-180	55	-159	43	-150	48
pH	12.08	0.06	12.22	0.05	11.99	0.10
Phosphate (mg/L)	BDL		BDL		0.82	
Potassium (mg/L)	51.4	62.2	14.8	19.2	5.8	7.2
Silica (mg/L as SiO_2)	5.3	3.7	0.7	0.4	1.5	1.2
Sodium (mg/L)	60.6	19.0	12.3	3.7	6.2	2.6
Solids (TDS) mg/L	1023	240	707	95	640	131
Sulfate (mg/L)	15.7	19.4	24.9	33.0	33.9	50.2
Temperature (°C)	25.23	0.21	26.27	0.12	25.27	0.29
Total Nitrogen (mg/L as N)	2.3	0.4	0.8	0.1	0.6	0.3
Total Phosphorous (mg/L as PO_4)	BDL		11.4		0.3	0.2
Zinc (mg/L)	1.021	1.123	0.266	0.072	0.254	0.096

TDS Value	1023		707		640	
Σmass (dissolved)	978		692		686	
% identified	96		98		107	
L/S Ratio	10		18		26	
TDS/EC ratio	0.245		0.220		0.237	

Table C 8: Continued

Mass of Ash = 13.6278g						
Extraction Number	4th		5th		6th	
Date of Extraction:	13-Jun-04		16-Jun-04		19-Jun-04	
mL of H2O	452	3	552	3	652	3
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	460	120	363	85	233	23
Aluminum (mg/L)	10.27	13.84	16.98	22.74	16.55	16.82
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	210	66	151	35	97	20
Carbonate (mg/L)	276	72	218	51	140	14
Chloride (mg/L)	13.4	9.2	5.5	2.6	3.4	1.9
Conductivity (mS/cm)	1.89	0.49	1.47	0.37	0.97	0.17
Copper (mg/L)	0.164	0.049	0.145	0.037	0.108	0.023
Fluoride (mg/L)	0.30	0.15	0.28	0.12	0.42	0.39
Hardness (mg $CaCO_3$ / L)	525	165	377	86	244	51
Iron (mg/L)	0.240	0.006	0.318	0.097	0.272	0.035
Magnesium (mg/L)	0.101	0.042	0.087	0.038	0.032	0.009
Manganese (mg/L)	0.037	0.002	0.034	0.002	0.034	0.003
Nitrate (mg/L)	0.10		BDL		0.02	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-108	21	-114	26	-154	15
pH	11.85	0.34	12.04	0.14	10.98	0.29
Phosphate (mg/L)	0.82		0.40		0.43	0.01
Potassium (mg/L)	2.6	2.7	1.9	1.8	1.2	1.2
Silica (mg/L as SiO_2)	1.6	0.6	2.2	0.9	2.2	0.9
Sodium (mg/L)	2.9	1.5	2.9	1.7	3.1	1.6
Solids (TDS) mg/L	530	130	433	76	320	61
Sulfate (mg/L)	28.1	36.1	29.8	32.4	26.0	24.3
Temperature (°C)	22.63	0.15	23.43	0.47	23.67	0.40
Total Nitrogen (mg/L as N)	0.4	0.2	0.4	0.2	0.2	0.2
Total Phosphorous (mg/L as PO_4)	1.6	0.2	1.7	1.5	1.4	0.1
Zinc (mg/L)	0.213	0.039	0.230	0.101	0.130	0.022

TDS Value	530		433		320	
Σmass (dissolved)	549		431		293	
% identified	104		100		92	
L/S Ratio	33		40		48	
TDS/EC ratio	0.281		0.296		0.330	

Appendix C (continued)

Table C 8: Continued

Mass of Ash = 13.6278g						
Extraction Number	7th		8th		9th	
Date of Extraction:	22-Jun-04		25-Jul-04		28-Jun-04	
mL of H2O	752	3	852	3	952	3
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	217	15	193	35	177	35
Aluminum (mg/L)	20.97	20.86	22.92	20.20	23.20	20.81
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	85	20	77	15	68	15
Carbonate (mg/L)	130	9	116	21	106	21
Chloride (mg/L)	2.8	1.9	5.4	3.9	1.6	1.0
Conductivity (mS/cm)	0.86	0.14	0.66	0.08	0.55	0.22
Copper (mg/L)	0.084	0.064	0.112	0.014	0.109	0.012
Fluoride (mg/L)	0.19	0.06	0.33	0.20	0.33	0.23
Hardness (mg $CaCO_3$ / L)	212	49	192	37	171	38
Iron (mg/L)	0.353	0.037	0.368	0.063	0.454	0.093
Magnesium (mg/L)	0.063	0.007	0.095	0.021	0.066	0.021
Manganese (mg/L)	0.042	0.005	0.041	0.007	0.041	0.003
Nitrate (mg/L)	BDL		BDL		0.28	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-100	40	-64	30	-85	38
pH	10.81	0.19	11.36	0.07	11.74	0.07
Phosphate (mg/L)	BDL		BDL		BDL	
Potassium (mg/L)	3.6	5.2	1.0	1.0	1.1	0.3
Silica (mg/L as SiO_2)	3.2	1.0	2.2	0.6	7.2	4.2
Sodium (mg/L)	2.2	0.5	1.7	0.8	1.4	0.6
Solids (TDS) mg/L	270	26	280	36	220	36
Sulfate (mg/L)	38.0	28.4	33.7	25.5	39.5	30.8
Temperature (°C)	24.90	0.40	22.77	0.15	24.80	0.26
Total Nitrogen (mg/L as N)	0.7	0.6	0.3	0.1	0.3	0.2
Total Phosphorous (mg/L as PO_4)	0.6	0.3	BDL		BDL	
Zinc (mg/L)	0.159	0.036	0.169	0.063	0.142	0.030

TDS Value	270		280		220	
Σmass (dissolved)	288		261		250	
% identified	107		93		114	
L/S Ratio	55		62		70	
TDS/EC ratio	0.315		0.425		0.402	

Appendix C (continued)

Table C 8: Continued

Mass of Ash = 13.6278g						
Extraction Number	10th		11th		12th	
Date of Extraction:	1-Jul-04		4-Jul-04		10-Jul-04	
mL of H2O	1052	3	1159	3	1275	5
Test	Average	Std.Dev.	Average	Std.Dev.	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	160	46	153	42	147	31
Aluminum (mg/L)	22.07	17.12	22.13	19.46	19.87	11.63
Bromide (mg/L)	BDL		BDL		BDL	
Calcium (mg/L)	73	10	57	12	59	20
Carbonate (mg/L)	96	27	92	25	88	18
Chloride (mg/L)	1.2	0.9	1.1	0.6	0.5	0.5
Conductivity (mS/cm)	0.60	0.01	0.54	0.05	0.53	0.08
Copper (mg/L)	0.116	0.015	0.093	0.007	0.097	0.020
Fluoride (mg/L)	0.21	0.18	BDL		0.19	
Hardness (mg $CaCO_3$ / L)	182	26	141	30	147	51
Iron (mg/L)	0.539	0.063	0.468	0.023	0.557	0.037
Magnesium (mg/L)	0.095	0.042	0.057	0.012	0.086	0.046
Manganese (mg/L)	0.043	0.000	0.044	0.005	0.041	0.002
Nitrate (mg/L)	BDL		BDL		BDL	
Nitrite (mg/L)	BDL		BDL		BDL	
ORP (mV)	-81	46	-81	36	-48	35
pH	11.44	0.11	11.47	0.06	11.25	0.07
Phosphate (mg/L)	0.40		0.73		BDL	
Potassium (mg/L)	0.2		BDL		BDL	
Silica (mg/L as SiO_2)	3.7	2.1	1.9	0.5	3.3	1.3
Sodium (mg/L)	0.9	0.3	0.6	0.3	0.7	0.2
Solids (TDS) mg/L	227	25	240	56	223	25
Sulfate (mg/L)	29.7	17.6	33.4	20.3	38.7	28.0
Temperature (°C)	26.20	0.10	24.93	0.45	25.33	0.25
Total Nitrogen (mg/L as N)	1.1		3.5	2.8	BDL	
Total Phosphorous (mg/L as PO_4)	BDL		BDL		BDL	
Zinc (mg/L)	0.184	0.110	0.140	0.036	0.151	0.049

TDS Value	227		240		223	
Σmass (dissolved)	229		213		211	
% identified	101		89		94	
L/S Ratio	77		85		94	
TDS/EC ratio	0.380		0.447		0.420	

Table C 8: Continued

Mass of Ash = 13.6278g		
Extraction Number	13th	
Date of Extraction:	13-Jul-04	
mL of H2O	1390	5
Test	Average	Std.Dev.
Alkalinity (mg $CaCO_3$ / L)	113	23
Aluminum (mg/L)	18.20	9.57
Bromide (mg/L)	BDL	
Calcium (mg/L)	48	14
Carbonate (mg/L)	68	14
Chloride (mg/L)	0.4	0.3
Conductivity (mS/cm)	0.43	0.05
Copper (mg/L)	0.087	0.015
Fluoride (mg/L)	BDL	
Hardness (mg $CaCO_3$ / L)	120	34
Iron (mg/L)	0.508	0.102
Magnesium (mg/L)	0.042	0.006
Manganese (mg/L)	0.036	0.005
Nitrate (mg/L)	BDL	
Nitrite (mg/L)	BDL	
ORP (mV)	-60	25
pH	11.17	0.12
Phosphate (mg/L)	BDL	
Potassium (mg/L)	BDL	
Silica (mg/L as SiO_2)	2.9	0.3
Sodium (mg/L)	0.5	0.2
Solids (TDS) mg/L	227	61
Sulfate (mg/L)	30.0	20.1
Temperature (°C)	24.63	0.12
Total Nitrogen (mg/L as N)	BDL	
Total Phosphorous (mg/L as PO_4)	BDL	
Zinc (mg/L)	0.118	0.017

TDS Value	227	
Σmass (dissolved)	169	
% identified	74	
L/S Ratio	102	
TDS/EC ratio	0.529	

Table C 9: Pasco County Ash Monofill Data, Averages and Standard Deviations

Date: Oct. 22, 2004					
Number	1	2	3	Avg.	Std. Dev.
Test					
Alkalinity (mg $CaCO_3$ / L)	140	140	140	140	0
Aluminum (mg/L)	0.200	0.240	0.400	0.280	0.106
Bromide (mg/L)	BDL	249	BDL	249	
Calcium (mg/L)	5341	5371	5440	5384	50
Carbonate (mg/L)	84	84	84	84	0
Chloride (mg/L)	9400	8163	9987	9183	931
Conductivity (mS/cm)	44.00	44.10	44.00	44.03	0.06
Copper (mg/L)	0.390	0.430	0.420	0.413	0.021
Fluoride (mg/L)	BDL	BDL	BDL	BDL	
Hardness (mg $CaCO_3$ / L)	13356	13430	13602	13462	126
Iron (mg/L)	6.130	7.750	7.190	7.023	0.823
Magnesium (mg/L)	4.580	4.710	4.660	4.650	0.066
Manganese (mg/L)	0.680	0.710	0.630	0.673	0.040
Nitrate (mg/L)	BDL	BDL	BDL	BDL	
Nitrite (mg/L)	BDL	BDL	BDL	BDL	
ORP (mV)	32	28	21	27	6
pH	5.86	5.64	5.92	5.81	0.15
Phosphate (mg/L)	BDL	BDL	BDL	BDL	
Potassium (mg/L)	1771.9	1787.8	1774.0	1777.9	8.6
Silica (mg/L as SiO_2)	1.2	1.3	0.9	1.1	0.2
Sodium (mg/L)	2464.2	2422.0	3225.5	2703.9	452.2
Solids (TDS) mg/L	25000	24965		24983	25
Sulfate (mg/L)	522	502	528	517	14
Temperature (°C)	28.60	28.50	28.50	28.53	0.06
TOC (mg/L as C)	7.29	7.35	7.32	7.32	0.03
Total Nitrogen (mg/L as N)	27.5	26.5	15.4	23.1	6.7
Total Phosphorous (mg/L as PO_4)	12.8	9.2		11.0	2.5
Zinc (mg/L)	0.190	0.180	0.180	0.183	0.006

TDS Value	25000.00	24965.00		24982.50	
Σmass (dissolved)	19636.97	18629.42		19947.72	
% identified	78.55	74.62		79.85	
TDS/EC ratio	0.568182	0.5660998		0.5673543	