

Evaluating the Leachability of Elements from Residuals Generated by Hydraulic Fracturing in
Marcellus Shale

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Abstract

The purpose of this research was to characterize the residual solids produced from hydraulic fracturing operations in the Marcellus Shale region. Four field samples were evaluated: drilling mud, treated sludge from the chemical treatment of process water, solids from the gravity settling of produced water, and sludge solidified prior to disposal in a municipal landfill. Cement kiln dust (CKD), used for solidification, was also considered in this study. All samples were subjected to a variety of laboratory techniques to determine their elemental composition and the potential for the elements to leach from the landfill. Strong acid digestion using a 3:1 combination of nitric acid to hydrochloric acid in a microwave with closed vessels was used to determine overall elemental composition. Leaching experiments were performed with de-ionized water and acetic acid (0.57%, pH 2.88) in an attempt to respectively evaluate the effects of weak and strong fluids that might be encountered by the residuals in landfill environments. Elements were analyzed by means of ICP-MS revealing the increased tendency for alkali metals, alkaline earth metals and halogens to leach. Leachability was further increased for metals when exposed to acidic conditions.

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CHAPTER 1: INTRODUCTION AND PROJECT OBJECTIVES

1.1 INTRODUCTION

The increasing demand for energy is being fulfilled by exploration into alternative methods for extracting natural gas. The Energy Information Administration, or EIA, has estimated that more than 1,000 trillion cubic meters of natural gas is contained within shale formations (EIA and ARI, 2013). Recent technological advances in directional drilling allows for increased natural extraction through hydraulic fracturing. The utilization of horizontal drilling, following traditional vertical drilling, has enabled the oil and gas industries to harvest natural gas in large, cost-effective amounts (US EPA, 2012).

Hydraulic fracturing is a process of extracting natural gas from wells drilled deep into the Earth. This produces large quantities of solid containing liquid waste, referred to as produced water. Produced water contains elevated levels of salt, heavy metals, organic and inorganic compounds as well as radionuclides. Produced water is often stored on the drilling site and then transported to a dedicated treatment facility once quantities become too large to store. Upon arrival at the dedicated treatment facility, the produced water flows through a series of treatment steps that result in the production and accumulation of residual solids and treated sludge. These residual solids are also treated following strict regulations imposed by the state and EPA prior to disposal. The purpose of this research was to characterize hydraulic fracturing residual solids, quantifying the chemical compositions, investigating leaching behaviors, predicting potential environmental impacts in disposal environments and investigating how the residual solids have changed over the course of a year.

Large amounts of waste are generated from natural gas extrication and treatment of produced water. These wastes are referred to as residual solids and are further characterized into three groups: drill cuttings, drilling mud and produced water by-products. Drill cuttings consist of cuttings from the drilling process like rock pieces and soil. Drilling mud refers to the dense, clay-rich slurry that circulates within the well to lubricate the drill and lift the drill cuttings to the surface. Produced water by-products are the residual solid waste generated in chemical treatment of the produced water (Hammer and VanBriesen, 2012; Kargbo et al., 2010; Maloney and Yoxtheimer, 2012; New York State Water Resources Institute, 2012; USEPA 2002).

Samples for this study were collected from a designated hydraulic fracturing wastewater treatment facility located in Pennsylvania. The facility receives produced water from an extensive array of companies dispersed throughout the Marcellus Shale region in Pennsylvania. The five samples used for this research consist of raw solids, treated solids, solidified sludge,

drilling mud and cement kiln dust (CKD). Raw solids pertain to the solids that have been separated from the incoming produced water by gravity only. Treated solids are solids produced by chemical treatment and precipitation of produced water following gravity sedimentation. Solidified sludge is produced by aggregation of solids prior to disposal, most commonly using the solidifying agent cement kiln dust.

1.2 PROJECT OBJECTIVES

As the demand for natural gas is ever increasing, and new hydraulic fracturing sites are being established, the ability to compare environmental compositional changes from one year to another is of great value. Thus, the purpose of this research was to chemically characterize the residual solids produced by hydraulic fracturing operations throughout the Marcellus Shale region in 2014. Results obtained here will be compared to prior assessments reported in 2013. Any changes in the environmental composition and leaching behavior of the elements will be evaluated.

Strong acid digestion was performed using closed vessel microwave technology to determine and quantify the total elemental composition of hydraulic fracturing residual solids. Environmental samples contain a wide variety of elements at dramatically different levels. Although the environmental samples collected from the treatment facility contained levels of radionuclides and volatile compounds, the focus of this research was on 32 different elements distributed throughout the periodic table. Strong acid digestion was used to extract the elements from their representative samples and inductively coupled plasma mass spectrometry (ICP-MS) was used to characterize the digestate from the solid samples along with the supernatants from solid sample centrifugation. This enabled the total elemental composition of each of the samples to be compared with the various types of residual solids present.

Immersion tests were conducted using a weak acetic acid solution obtain from the Toxicity Characteristic Leaching Procedure (TCLP) and de-ionized water to determine the leaching potential of the elements of concern for each of the solids over a period of 90 days. The two extraction fluids were chosen to simulate the best and worst case scenarios which samples would potentially encounter within landfill environments. The resulting leachates were analyzed for all 32 elements of concern using ICP-MS. Results from the immersion tests were compared to the environmentally available composition determined by strong acid digestion to reveal the types and quantities of elements that are most likely to leach from hydraulic fracturing residual solids under diverse environmental conditions.

Given that this is the final division of a continuing effort to characterize the residual solids produced from hydraulic fracturing process water, the general objective was to compare current

findings to those determined in the prior year. The goal has been to develop more definitive information with regards to the potential environmental impacts from this form of natural gas collection. This combined research is intended to provide industry leaders and drilling companies guidance for the best available management practices for residual solid waste production.

CHAPTER 2: LITERATURE REVIEW

2.1 SHALE IN THE UNITED STATES

Shale is a fine-grained type of sedimentary rock that is composed of a mixture of a variety of clay and silt-sized particles of minerals including quartz and calcite. The ratio of clay to minerals and the type of minerals varies with each shale formation (Blatt, et al., 1996). According to the US Department of Energy (DOE) gas-producing shales are predominantly composed of compacted clay-sized particles with a high organic content. Over time, high subsurface pressures and temperatures convert the organic matter to oil and gas that remain within the shale and forming pockets called petroleum traps. These shale formations are referred to as shale reservoirs.

There are currently six active shale reservoirs within the United States. These reservoirs are: the Barnett Shale, the Haynesville/Bossier Shale, the Antrim Shale, the Fayetteville Shale, the Marcellus Shale, and the New Albany Shale. Of these, Marcellus Shale is the largest shale gas reservoir in the United States (Begos, 2012) and is estimated to contain more than 665 trillion cubic feet of recoverable natural gas (EIA, 2013). Marcellus Shale is a highly porous shale with low permeability bearing increased levels of natural gas (Blauch, 2010). The Marcellus Shale geologic formation spans 104,000 square miles throughout the Allegheny Plateau region of the Appalachian Basin, i.e. from southern New York across Pennsylvania into Ohio reaching south to northern West Virginia. It is of marine origin, containing naturally high levels of salt, certain metals and organic compound, radioactive materials as well as high levels of natural gas.

2.2 NATURAL GAS IN THE UNITED STATES

Natural gas plays a significant role in the nation's future when it comes to clean energy. Coal has traditionally been the go-to fuel source, however, it is rapidly being replaced by clean energy. Within the United States, there are several large natural gas reservoirs that have been made commercially available as a result of recent technological advances. These advances in hydraulic fracturing and horizontal drilling, enabling greater access to gas in deep rock formations, have encouraged expansion in the oil and natural gas industries over the last decade (US EPA, 2012). This is in part due to the long term, combined efforts of the oil and natural gas industries and the US Department of Energy to improve drilling and extraction methods while increasing exploration efforts (US EPA, 2012). According to the Energy Information Association, oil and natural gas industries provided more energy in the United States than any other energy source, fulfilling approximately 37 and 25 percent of residential and industrial usage, respectively. This number is expected to increase progressively as natural gas extractions

methods are further optimized and improved for better efficiency and lower cost (Gregory et al., 2011) to an estimated 49 percent by 2035 (Annual Energy Outlook, 2012). The number of unconventional natural gas wells in the United States rose from 18,485 in 2004 to 25,145 in 2007 and is expected to continue increasing until about 2040 (Vidas, 2008; EIA 2013). Recent studies conducted by the EIA identified more than 35,000 trillion cubic feet of shale gas that is available globally and more than 2,000 trillion cubic feet resides within in the United States. Of this total volume within the United States, 827 trillion cubic feet of natural gas is stored within shale reservoirs (U.S. House of Representatives, 2011). According to the U.S. House of Representatives, as of 2013, the highest natural gas production year was 2010. But, as a result of recent studies and vast improvements in drilling and extraction methods, dramatic increases in shale gas production are likely to continue.

2.3 HYDRAULIC FRACTURING PRACTICES

To date, the most popular method for natural gas extraction from shale reservoirs is hydraulic fracturing. The first hydraulic fracturing experiment was conducted in 1947 and was unsuccessful (Montgomery et al., 2010; Charlez, 1997). However, by 1949, the process was improved and patented with the first commercial wells being established in Texas and Oklahoma. Although these wells were successful, it was not until horizontal drilling proved to be progressively more effective at extracting shale gas that hydraulic fracturing became common practice (Bell et al., 1993).

Improvements in hydraulic fracturing, like horizontal drilling, exploit the low permeability and porosity of the shale. By drilling vertical wells into the shale, then rotating the drill 90 degrees extends the well to the optimum length of the formation, thus exposing a larger volume of shale through a single bore well (Maloney and Yoxtheimer, 2012) and increasing permeability and natural gas extraction. Technological innovations in hydraulic fracturing, such as horizontal well drilling, over the last several years has made natural gas extraction more economical (GWPC and ALL, 2009).

Hydraulic fracturing practices follow the same processes, only differing by a few variations in chemical recipes. Once the drilling site is determined, the well is established using a drill and drilling mud. Drilling mud recipes are proprietary to each company, however, they are usually either a mixture of water and oil or a synthetic based slurry used to lubricate the drill and carry cuttings produced by the drill to the surface (Ohio EPA, 2012). Fracturing fluid, a mixture of water, proppants and chemical additives, is pressurized and pumped into the wells. The pressurized fluid creates cracks and fissures along the well walls where the proppants prevent closure of the fissures allowing the natural gas out (Kargbo et al., 2010). Along with the release

of natural gas, methane and other hydrocarbons also trapped in the shale are released (Andrews et al., 2009; Hammer and VanBriesen, 2012). The chemical additives added to the fracturing fluid decrease the fluid viscosity allowing for increased fluid velocity. They also act as biocidal preservatives, preventing microbial growth and pipe corrosion. In the end, this mixture increases the production of gas from the reservoir (GWPC and ALL, 2009). The exact composition of fracturing fluid differs from one drilling company to the next, but the main constituents are water, sand proppant and chemical additives (Maloney and Yoxtheimer, 2012). The chemical additives and sand proportions are controlled by the characteristics of the target formations (PADEP, 2010). While some of these additives are common and relatively non-toxic, others including benzene and lead have potentially serious human health effects (United States House of Representatives 2011).

2.4 ELEMENTS OF CONCERN

The procedure of identifying and monitoring the vast array of elements of concern produced by hydraulic fracturing consist of government enforced methods and regulations developed by the EPA and DEP. The Pennsylvania DEP requires that all wastewater produced from drilling is chemically analyzed to determine the concentration of the elements of concern, including beryllium, cobalt, and silver (Pennsylvania DEP, 2010). New York regulations state that methods for residual solids management is dependent upon the nature of the drilling mud used in each well (see section 1.7.10 of the rdSGEIS). Due to the strict disposal and management regulations for residual solids, the elements of concern now include antimony and zirconium because of the chemical additives used in treatment (GoFrac, 2012).

Due to the increased contact time the fracturing fluid has with the geological formation, the residual solids and wastewater produced are expected to mimic the shale formation chemistry (Bank, 2011; Blauch et al., 2009; Resnikoff et al., 2010; Haluszczak et al., 2013, Skalak et al., 2014). Marcellus Shale is of marine origin so it naturally contains increased levels of sodium and chloride as well as many other elements like calcium, bromide, strontium, barium, chromium, and zinc (Chapman et al., 2012; and Bank, 2008). It is also naturally rich in trace elements such as copper, nickel, uranium, vanadium, and molybdenum (Titler and Curry, 2011; and Liermann et al., 2011). Interactions with the naturally occurring salt or brine in the shale formation result in produced water and residual solids with high total dissolved solids (Chapman et al., 2012).

There are few publications focusing on residual solid identification of hydraulic fracturing operations, and of those sources, even fewer are focused on Marcellus Shale. Most publications address drill cuttings and flow back, as well as elements of growing concern such as aluminum, boron, iron, lithium, magnesium, manganese, phosphorus, potassium, arsenic, selenium,

cadmium, mercury, and lead (Haluszczak et al., 2013; Balaba and Smart, 2012; and Hayes, 2009).

The composite list of elements of concern investigated for this study is based on the literature of hydraulic fracturing, Marcellus Shale geochemistry and the typical chemical additives used in treatment processes. They are indicated in Figure 2-1.

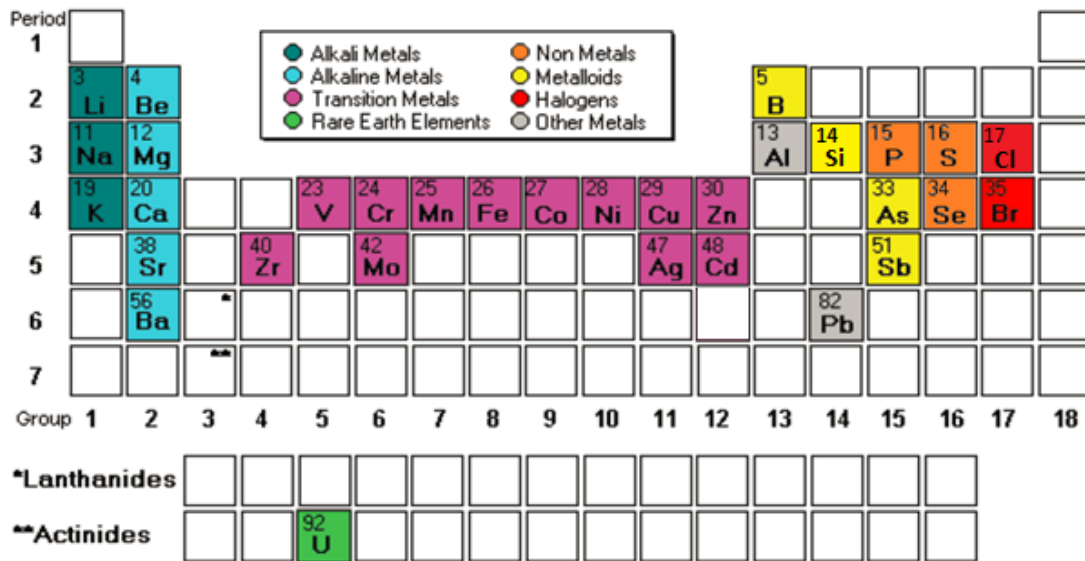


Figure 2-1: Elements Evaluated in this Study; adapted from Ziemkeiwicz, 2011

Mercury was initially intended to be analyzed; however, it was excluded from this report due to analytical complications and issues with storage time, which exceeded the maximum of 60 days.

2.5 WASTE GENERATION AND RESIDUAL SOLIDS TREATMENT

Hydraulic fracturing operations directly create large amounts of solid and liquid waste, and generate even more waste by-products in the treatment processes. These wastes are referred to as residual solids and are further characterized into three groups: drill cuttings, drilling mud and produced water by-products. Drill cuttings consist primarily of rock pieces and soil. Drilling mud refers to the dense, clay-rich slurry that circulates within the well to lubricate the drill and lift the drill cuttings to the surface. Produced water by-products are the residual solid waste generated in chemical treatment of the produced water (Hammer and VanBriesen 2012; Kargbo et al., 2010; Maloney and Yoxtheimer 2012; New York State Water Resources Institute, 2012; USEPA, 2002).

2.5.1 Drill Cuttings

Upon well construction, a drill bit is used to bore a hole by breaking up the earth. This generates a mixture of soil, rock and shale fragments called drill cuttings. These drill cuttings are then lifted to the surface by the drilling mud, a dense, clay-rich slurry, and fracturing fluid for removal and disposal (Rahm et al., 2013). Cuttings are then separated from the drilling mud for solids disposal and drilling mud reuse. Large volumes of drill cuttings are generated in this process because of the sheer depth and length of the wells.

2.5.2 Drilling Mud

Drilling mud is used to cool and lubricate the drill bit, and carry cuttings to the surface for removal. This keeps the drill bit clear of rock fragments, enhances well stabilization by controlling formation pressures, and prevents re-entry of fluids (Schlumberger, 1994; Ohio EPA, 2014). The exact composition of drilling mud is proprietary to each company; however, drilling muds are either water-based, oil-based, or a synthetic blend with the main ingredients consisting of water, minerals and stabilization agents (Schlumberger, 1994). As the drilling mud is pumped into the well, it interacts with the shale formations, altering the chemical composition. The longer the drilling mud is in contact with the shale, a greater dissolution of constituents associated with the shale is seen (Schlumberger, 1994; New York State Water Resources Institute, 2012; Resnikoff et al., 2010). Drilling mud is often separated from the cuttings for reuse. However, repeated reuse results in exponential increases in contaminant concentration as constituents associated with the geological formations dissolve and are adsorbed (New York State Water Resources Institute, 2012).

2.5.3 Produced Water Treatment By-Products

Produced water from hydraulic fracturing is stored on site in open pits and impounds for sedimentation and evaporation. When the produced water volume reaches the maximum on-site storage capacity, which varies for each company, it is then transported to a dedicated facility for chemical treatment. Chemical treatment of produced water includes coagulation, precipitation, flocculation, centrifugation, settling and filtration. Coagulation and precipitation are induced by increasing the pH and adding sodium hypochlorite, sodium hydroxide and sodium sulfate. This process reduces the total dissolved and suspended solids and removes heavy metals and organic contaminants, ultimately preparing the water for reuse (Hammer and VanBriesen 2012). The precipitate is then removed from the treatment process and classified as treated solids. These residual solids have elevated concentrations of elements of concern requiring specific management and disposal methods (Kargbo et al., 2010; Hammar and VanBriesen, 2012).

2.6 RESIDUAL SOLIDS MANAGEMENT

Storage, treatment, management and disposal of produced water and residual solids generated from the hydraulic fracturing and treatment processes depends on the characteristics of the wastes. Certain wastes can be reused following solids separation, such as drilling mud (Clean Earth, 2012) or chemically-treated produced water. Other wastes can be disposed of through land application, landfill (Hammer and VanBriesen, 2012) or deep injection wells (New York State Water Resource Institute, 2012) following treatment or stabilization. Drill cuttings, considered solid waste, are disposed of by the drilling facility into landfills (Maloney and Yoxtheimer, 2012) following separation from drilling mud (Barry and Klima, 2013; Resnikoff et al., 2010).

2.7 ANALYTICAL APPLICATIONS AND TECHNOLOGY

For trace metal analysis, EPA Method 6020A for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was deemed applicable to analyze the elemental composition in residual solids. Of the 32 chosen elements of concern, only eight were not on the analyte list found in Sect. 1.2 of EPA 6020A. For these elements, appropriate internal standards were utilized for quality assurance and quality control measures.

ICP-MS is an analytical technique that couples high-temperature Inductively Coupled Plasma (ICP) source with a mass spectrometer (MS). The ICP first converts the atoms in the acidified liquid into ions. The ions are then separated on a mass to charge ratio and quantified by the mass spectrometer. This technique measures a wide range of elements simultaneously with low detection limits.

Common sources of error regarding ICP-MS elemental detection are caused by spectroscopic interferences from atomic and molecular ions with the same mass-to-charge ratio. The interference may be enhanced by the sample matrix or the reagents used in sample preparation. For this reason, trace-metal grade reagents were employed to reduce the amount of any interference. For accurate detection and quantification, it is important to limit molecular interference during trace-metal analysis (Gard Guide, 2012).

According to EPA Method 6020A, trace metal detection and quantification limits range from below 0.1 ppb to well above 1.0 ppb. Detection varies with each element and elements such as arsenic and selenium are reported by the EPA to be detected at higher levels along with other desensitized major elements. The method detection level (MDL) and minimum reporting limits (MRL) have been calculated for each element of concern in order to establish applicability of this method. The MDL is the lowest concentration measured that indicates a 99% confidence that the particular element is present in the sample (US EPA 40 CFR 136 Appendix B, 1997), while the

MRL is the lowest concentration measured in a sample which can be reported with 99% confidence as the actual concentration (Winslow et al., 2005). In order to ascertain accurate measurements, the calibration standards ranged from 0.1 ppb to 10 ppm.

2.7.1 Strong Acid Digestion

As mentioned for ICP-MS analysis, elements in the solid mineral phase are first transferred to liquid. This is best achieved through wet acid digestion using combinations of hydrochloric acid, nitric acid, hydrofluoric acid, sulfuric acid, and hydrogen peroxide (Gard Guide 2012).

EPA Method 3051A was developed as an alternative to the previously time consuming and large acid volume procedures. This method utilizes microwave technology to accelerate and facilitate conventional acid digestion (UA EPA 3051A, 2007). Method 3051A – Microwave Assisted Acid Digestion of Sediments, Soils, and Oils is offered as an alternative to traditional digestion using a considerably lower volume of acid combined with shorter digestion periods with increased pressure. Method 3051A is a significantly faster and more efficient procedure than former methods, using a combination of nitric acid and hydrochloric acid for the strongest digestion. Other digesting agents such as hydrofluoric acid and sulfuric acid are considerably stronger and can provide total digestion. However, these are not compatible with the microwave technology as the boiling point of sulfuric acid is higher than the melting point of the Teflon microwave vessels. For the elements of concern in this study, use of hydrochloric and nitric acids in Method 3051A was found effective and will be considered a near total digestion for characterization of the environmentally available composition of the solid samples.

2.7.2 Leachability

The Hazardous and Solid Waste Amendments of the Resource Conservation and Recovery Act (RCRA) in 1984, developed a method to illustrate the toxicity characteristics of a solid waste (Kimmell, 1999). EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) was developed by the EPA to characterize waste and determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. This method ultimately forecasts the leaching behavior of the waste when disposed of in typical municipal landfill environments. Element have standardized limits established by the EPA and defined by RCRA subtitle D. A single element detected above its limit is enough to classify the waste as a hazardous material (US EPA 40 CFR 261.24, 2012) and prevent disposal in a landfill.

The TCLP extraction fluid characteristics were developed to simulate predominantly municipal solid waste leachate. The extraction fluid is a weak acetic acid solution at pH 2.88. Solid waste is exposed to the extraction fluid at a high liquid-solid ratio, 1 L:100 g ensuring

steady state is achieved (Murarka, 1999). Following experiment completion and data analysis, any analytes detected in the waste having quantities at or below analytical detection limit are considered as non-leaching elements. Wastes with analytical results below the TCLP D-list maximum contamination level (MCL) are non-hazardous and acceptable for disposal, however, if they are above D-list levels, they must be taken to a hazardous waste disposal facility.

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CHAPTER 3: CLOSED VESSEL STRONG ACID DIGESTION OF HYDRAULIC FRACTURING RESIDUAL SOLIDS IN MARCELLUS SHALE USING MICROWAVE TECHNOLOGY

ABSTRACT

Strong acid digestion was performed using closed vessel microwave technology following EPA Method 3051A - Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, to determine the total elemental composition of hydraulic fracturing residual solids. A total of five samples were analyzed in this study: raw solids, treated sludge, solidified sludge, drilling mud and cement kiln dust. The digestion method used a 3:1 mixture of nitric acid and hydrochloric acid in a Mars 5 closed vessel microwave system. Following strong acid digestion, samples were analyzed using EPA Method 6020A for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to quantify the chosen 32 elements of concern. Comparing results from the digested samples revealed similar environmentally available compositions in all samples. The major constituents included aluminum, barium, calcium, iron, magnesium, potassium, sodium, and strontium. Analysis of the supernatants revealed that most of the elemental contributions came from the solids, while bromide, lithium, sodium, and strontium were more prevalent in the liquid. It is important to note that all methods were approved by the EPA, and every effort was made to normalize all reaction vessels. Results may vary due to incomplete digestion, reagent interferences, formation of precipitates, loss of volatiles, and other factors.

KEYWORDS: Strong Acid Digestion, Microwave Assisted Acid Digestion, Hydraulic Fracturing, Environmentally Available Composition

3.1 INTRODUCTION

Hydraulic fracturing is an unconventional process of extracting natural gas from wells drilled deep into the Earth. Throughout the hydraulic fracturing process, a variety of technologies are utilized to extract the maximum amount of natural gas from the shale. Once the drilling site is chosen, the wells are constructed using drills, drilling mud, fracturing fluid and water. Specific recipes are proprietary to each company, however, drilling mud is typically a mixture of water and oil or a synthetic based slurry that is used to lubricate the drill and carry cuttings produced by the drill to the surface (Ohio EPA, 2012). Fracturing fluid is a mixture of water, proppants and chemical additives. The chemical additives in the fluid act as scale inhibitors, biocides, and friction reducers that allow for increased fluid velocity (Abdalla et al., 2011). Fracturing fluid is pressurized and pumped into the wells to create cracks and fissures along the well walls where the proppants prevent closure of the fissures, allowing the natural gas to rise to the surface (Kargbo et al., 2010). Once the desired vertical depth is reached, the drill is rotated 90 degrees to extend the well horizontally through the shale. Improvements such as horizontal drilling extort the low permeability and porosity of the shale, ultimately exposing a larger volume through a single bore well (Maloney and Yoxtheimer, 2012) and increasing permeability and natural gas extraction.

Each completed well uses between 7,000 - 18,000 cubic meters of fracturing fluid (Gregory et al., 2011), and approximately 24% of this fluid is returned to the surface immediately (Hulszczak et al., 2013) while the rest slowly returns over the next few weeks to months. This is called produced water. It contains both solid and liquid waste and consists of elevated levels of salt, heavy metals, organic and inorganic compounds, as well as radionuclides (Chapman et al., 2012). Produced water is often stored on the drilling site in open pits and impounds and then transported to a dedicated treatment facility (Hammer and VanBriesen, 2012) once quantities become too large to be maintained on premise. Upon arrival at the dedicated treatment facility, the produced water flows through a series of treatment steps that result in the production and accumulation of residual solids and treated sludge. These residual solids are also treated following strict regulations imposed by the state and EPA prior to disposal.

Hydraulic fracturing waste treatment at a dedicated treatment facility in Pennsylvania, depicted in Figure 3-1, was initiated with the transfer of influent produced water into rock boxes to remove the heavy solids by gravity separation. The fluid was then transferred to a three step reaction tank for coagulation, flocculation and sedimentation processes using sodium sulfate, sodium hypochlorite and sodium hydroxide to increase the pH and decrease the total dissolved and suspended solids. This form of chemical treatment also removes a variety metals and organic contaminants, specifically strontium, barium and iron. This ultimately prepares the water for

reuse (Hammer and VanBriesen, 2012). The precipitate is then removed from the treatment process and classified as treated solids. These residual solids have elevated concentrations of elements of concern requiring specific management and disposal methods (Kargbo et al., 2010; Hammar and VanBriesen, 2012). Consequentially, the materials produced at the dedicated treatment facility include the residual solids from rock boxes, thickened drilling mud and treated settled sludge. These are all mixed and solidified with cement kiln dust and stored for future disposal in a municipal landfill.

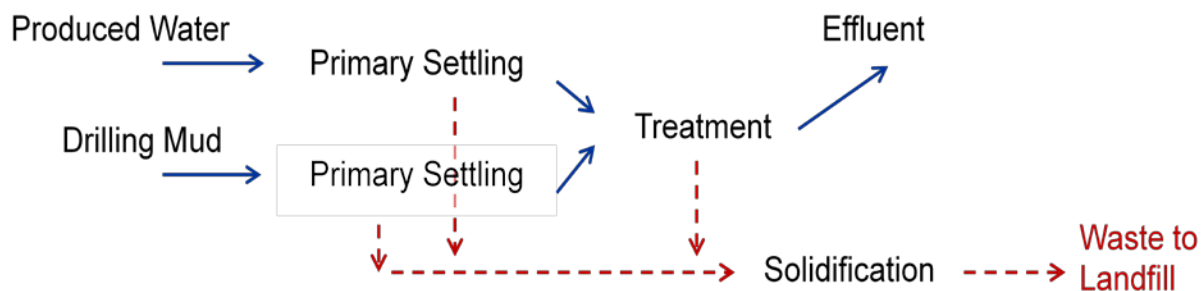


Figure 3-1: Dedicated Treatment Facility Schematic

The purpose of this research was to chemically characterize the residual solid and liquid wastes produced from hydraulic fracturing practices taking place within the Marcellus Shale region. A total of five samples were obtained from a dedicated treatment facility that treats a variety of produced water and drilling waste from drilling companies distributed throughout the region. These samples were: drilling mud, treated sludge from the chemical treatment of process waters, solids from the gravity settling of produced water, sludge solidified prior to disposal in a municipal landfill and cement kiln dust (CKD). Upon arrival, the samples were centrifuged and dried for chemical analysis and characterization.

Strong acid digestion following EPA Method 3051A using closed vessel microwave technology and a 3:1 mixture of nitric acid to hydrochloric was conducted on all samples, followed by ICP-MS analysis. The addition of hydrochloric acid to the nitric acid makes the mixture more aggressive due to increased digestion and stabilization of select elements (US EPA 3051A, 2007). While other digesting agents, such as hydrofluoric acid and sulfuric acid are considerably stronger and can provide total digestion, this was not compatible with the Teflon microwave vessels due to the high boiling point of sulfuric acid combined with the lower melting point of the Teflon. However, for the elements of concern in this study, the use of nitric and hydrochloric acids, in combination with aggressive digestion methods of high temperatures and

pressures achieved during closed vessel digestion (Berghof, 2013), was found effective and will be considered a ‘near total’ digestion. Due to the addition of hydrochloric acid in this method, a separate digestion analysis using deionized water alone was performed to determine the amount of chloride in each sample. In addition to solid waste digestion, the supernatant obtained from initial centrifugation of each sample was analyzed by ICP-MS and combined with the elemental composition from the respective solid sample. This provided the total composition of elements for each of the samples.

Elements of concern were chosen based on literature review, geological information on Marcellus shale and regulatory requirements for water and wastewater quality assurance, as supplied by the EPA and DEP. Marcellus shale is of marine origin so it naturally contains increased levels of sodium and chloride as well as many other elements such as calcium, bromide, strontium, barium, chromium and zinc (Chapman et al., 2012; and Bank, 2008). It is also naturally rich in trace elements such as copper, nickel, uranium, vanadium, and molybdenum (Titler and Curry, 2011; and Liermann et al., 2011). Previous research noted common elements in hydraulic fracturing practices and focused on elements such as aluminum, boron, iron, lithium, magnesium, manganese, phosphorus, and potassium (Haluszczak et al., 2013). In total, 32 elements were selected for final analysis. Due to analytical issues and sample storage time, mercury was not evaluated.

3.2 PROJECT OBJECTIVES

The objective of this research was to chemically characterize residual solids produced from hydraulic fracturing operations within the Marcellus Shale region. Samples were collected from a dedicated treatment facility located within the region that receives samples from multiple drilling companies. The produced water is pumped into rock boxes for gravity settling while the water is removed and treated. The samples obtained from the facility are considered composite samples and for this study considered to be representative samples from the hydraulic fracturing process.

Strong acid digestion was performed using closed vessel microwave technology to determine and quantify the total elemental composition of hydraulic fracturing residual solids. Environmental samples contain a wide variety of elements at dramatically different levels. Although the environmental samples collected from the treatment facility contained levels of radionuclides and volatile compounds, the focus of this research was on 32 different elements distributed throughout the periodic table. Strong acid digestion was used to extract the elements from their respective samples and ICP-MS was used to characterize the digestate from the solid samples along with the supernatants from solid sample centrifugation. This enabled the total

elemental composition of each of the samples to be compared with the various types of residual solids present.

The final characterization of each of the samples can be used to assist oil and gas companies in developing more definitive information with regards to the potential environmental impacts from this form of natural gas collection. This research is intended to provide industry leaders and drilling companies with information to determine the best available management practices for residual solid waste production.

3.3 MATERIALS AND METHODS

3.3.1 Glassware preparation

Glassware and other equipment was cleaned with detergent, either Sparkleen™ laboratory detergent or Dawn™ dish soap and rinsed. Following detergent wash, glassware was placed in a 10% ACS reagent grade nitric acid bath overnight and then thoroughly rinsed with deionized water and followed by nanopure water. Glassware, equipment, and bottles were air dried in a clean environment.

3.3.2 Chemical Reagents

For strong acid digestion, trace-metal grade nitric and hydrochloric acids from Fisher Scientific were used. For ICP-MS analysis and calibration, two standard solutions prepared by High Purity Standards in Charleston, SC, were used. These standards were diluted using deionized water and preserved with 2% (v/v) HPLC grade nitric acid to provide a broad calibration curve for all elements of concern. Specifications for these standard solutions are provided in Appendix A - Standard Solutions. Fresh calibration standards were made for each ICP-MS run and the standards were used as an internal check by being analyzed after every 13th sample on the ICP-MS. The purity of chemical reagents and reagent water was monitored throughout each experiment.

3.3.3 Sample Preparation

Samples were added to clean polyethylene centrifuge bottles and centrifuged at 8000 RPM for 30 minutes. The supernatant was decanted, the bottles were balanced and centrifuged again at 8000 RPM for 30 minutes. Once all the water was removed, the samples were removed from the centrifuge bottles using a spatula and placed in an oven at 40 °C for 48 hours to dry. The samples were then ground using a mortar and pestle until a uniform sandy texture. Then, 50g of each sample was placed in an oven at 105 °C overnight to remove all remaining water so that the total percent moisture in each sample could be determined. This value was used to calculate the dry

weight of each sample and factored into data analysis. The remaining percent moisture of each sample ranged from 2 - 13%, and exact values can be found in Table 3-1.

Table 3-1: Percent Moisture of Solid Samples

	Treated Solids	Raw Solids	Drilling Mud	Solidified Solids	Cement Kiln Dust
Original Weight of Sample Used (g)	100	100	100	100	100
Solids Content (%)	86.8%	97.8%	87.5%	91.8%	100.0%
Moisture Content (%)	13.2%	2.2%	12.5%	8.2%	0.0%

3.3.4 Strong Acid Digestion

Strong acid digestion of the dried solid samples was performed following EPA Method 3051A - Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils using a CEM Mars 6 Extractor and Teflon closed vessel system. Method 3051A is a significantly faster and more efficient procedure than former methods, using a 3:1 combination of nitric acid and hydrochloric acid for the strongest digestion. For the elements of concern in this study, use of hydrochloric and nitric acids in Method 3051A was found effective and will be considered a near total digestion for characterization of the environmentally available composition of the solid samples. While the use of hydrochloric acid may make quantification with certain techniques more complex, this method enhances the digestion of elements such as antimony, barium, iron, aluminum, and silver (US EPA 3051A, 2007). Elements approved for quantification with EPA Method 3051A and the 3:1 nitric and hydrochloric acid extraction fluids are listed in Table 3-2: Approved Elements for Quantification with EPA Method 3051A using 3:1 Nitric and Hydrochloric Acids and denoted with an “X”.

Table 3-2: Approved Elements for Quantification with EPA Method 3051A using 3:1 Nitric and Hydrochloric Acids

Element	Nitric/Hydrochloric
Aluminum	X
Antimony	X
Arsenic	X
Barium	X
Beryllium	X
Boron	X
Bromide	
Cadmium	X
Calcium	X
Chromium	X
Cobalt	X
Copper	X
Iron	X
Lead	X
Lithium	
Magnesium	X
Manganese	X
Mercury	X
Molybdenum	X
Nickel	X
Phosphorus	
Potassium	X
Selenium	X
Silicon	
Silver	X
Sodium	X
Strontium	X
Sulfate	
Uranium	
Vanadium	X
Zinc	X
Zirconium	

3.3.4.1 Microwave Vessel Preparation

Each of the Teflon vessels was washed with Dawn™ dish detergent, rinsed, dried and cleaned following the cleaning procedure recommended by Mars. The vessels were filled with the 3:1 mixture of nitric and hydrochloric acids and run on a cleaning cycle in the microwave unit, 150 °C for 10 minutes cycle. Following the cleaning cycle, the vessels cooled in the microwave, vented to release the pressure and rinsed completely with deionized water. The vessels and the lids were set in a clean area to air dry overnight. The cleaning cycle was completed immediately following each digestion so the vessels were ready to use the next day.

3.3.4.2 Digestion Procedure

A representative sample weighing precisely 0.5 g (+/- 0.002g) was added to each Teflon extraction vessel and placed in a chemical hood. Each vessel received 9 mL of nitric acid and 3 mL of hydrochloric acid, and was set to the side of the hood to react for 10 to 15 minutes, until there was no longer a visual reaction occurring. The vessels were capped with a Teflon lid, placed in a composite sleeve with support system and placed into the microwave unit. Before insertion into the microwave, each Teflon lid and vent was hand tightened to ensure that no volatilized acid could escape. Each sample was run in triplicate. One vessel of each triplicate housed the thermometer to monitor the temperature and the other two vessels were the reaction vessels.

The samples were heated to 175 °C and held at that temperature for 4.5 minutes. Following digestion, the samples were cooled to room temperature within the microwave. Once ambient temperature was achieved according to the control vessel, all vessels were removed from the microwave to the chemical fume hood and gently vented to depressurize and reduce sample loss. Each sample was then transferred to a 100 mL volumetric flask and filled with deionized water. The flasks were covered with para-film[®] and gently inverted to mix. Due to the unknown elemental concentrations within the samples, two sets of each sample were run on the ICP-MS, one diluted and the second undiluted. Then, 15 mL of each sample was filtered through a 0.45 µm nylon filter into a medium weigh boat. After filtration, 1 mL was removed and diluted in 9 mL of deionized water in an ICP-MS tube and stored for analysis. For the undiluted sample, 10 mL was placed in an ICP-MS tube and stored for analysis. Method blanks for the microwave assisted acid digestion of solids consisted of 0.5 g of deionized water exposed to the acid mixture and run on the microwave unit. Due to the addition of hydrochloric acid, the method blank ICP-MS results were subsequently subtracted from each sample to determine the chloride levels.

3.3.5 Supernatant Analysis

Supernatants were obtained from centrifugation the day of sample analysis avoiding the need for nitric acid addition as a preservative. Then, 10 mL of sample was filtered through a 0.45 µm nylon filter directly into an ICP-MS tube. Due to the elevated concentrations of elements such as sodium and chloride, the samples were diluted 1:10 and re-analyzed. Supernatant analysis was combined with the solid analysis on a wet weight basis to provide an estimate of concentrations present in both the solid and liquid fractions.

3.3.6 Elemental Analysis

Digestate from the strong acid digestion of the solid samples and the undigested supernatants were analyzed for the elements of concern following EPA Method 6020A – Inductively Coupled Plasma Mass Spectrometry using a Thermo X-Series ICP-MS.

According to EPA method 6020A, trace metal detection and quantification limits for ICP-MS analysis range from below 0.1 ppb to well above 1.0 ppb. The method detection level (MDL) and minimum reporting limits (MRL) were calculated for each element of concern following procedure identified by Winslow et al., in 2005 and determined by the EPA guidelines. In order to ascertain accurate measurements, the calibration standards ranged from 0.1ppb to 10 ppm. For this research, the low level standard chosen for MDL determination was one previously determined to be the MRL. Samples reported below the MRL were considered n/a or assigned a value of zero. The MDL and MRL information determined for each element with ICP-MS is provided in Appendix B – Analytical Limits.

3.4 RESULTS AND DISCUSSION

Strong acid digestion raw data was adjusted for a final volume of 100 mL and for the 1:10 dilution necessary for ICP-MS analysis. The moisture content for each sample was used to provide the elemental composition in units of mg/kg dry weight. The data were corrected by subtracting the average of the blank controls from the average of the sample triplicates to account for any elemental additions present in the deionized water and the hydrochloric and nitric acids. All reagents used were trace metal grade; however, the addition of hydrochloric acid used for digestion increased the reported chloride concentrations for each sample. Any negative values resulting from data correction were converted to zero. To quantify the total available composition for each sample, the triplicates were combined with the results of the supernatant analysis. Samples with elemental concentrations measuring below the MDL are denoted as “BDL”, samples measuring between the MDL and MRL are denoted as “trace”. The raw data from this analysis can be found in Appendix C - Microwave Assisted Strong Acid Digestion Results.

Elements with the highest concentrations following digestion were aluminum, barium, calcium, iron, sodium, strontium, and magnesium. According to EPA Method 3051A, the use of microwave technology coupled with the addition of nitric and hydrochloric acid provides improved extraction and stabilization of elements such as antimony, iron, aluminum, silicon, barium and silver. As these elements do not readily volatilize, increased extraction through digestion results from the higher temperature and pressure used in the closed vessel system.

Normalized standard deviation was calculated for all samples to evaluate digestion consistency between each triplicate and these are presented in Table 3-3. Normalized standard deviation is calculated by dividing the standard deviation by the average value of the triplicates. This was performed to alleviate high variation between samples due to the inconsistent shape of the dried, ground solids as well as the small sample size. When the normalized standard deviation value is large, it represents high variance in the digestion, values above 0.5 represent a large standard deviation, while a value above 1.0 revealed that the standard deviation was larger than the average value. Elements that showed the largest variance between triplicates for all five samples tested were bromide, antimony, selenium, silicon, vanadium and zirconium. The element with the largest normalized standard deviation for all samples was bromide, where the CKD had a normalized standard deviation of 1.73, raw solids with 0.87, and treated solids with 0.36. The element with the next highest normalized standard deviation was selenium in the raw solids, 0.67, while the remaining samples were between normalized standard deviations of 0.05 to 0.31. High variance with silicon was expected in the raw solids due to the presence of proppants and the increased melting point, which was not achieved during digestion, resulting in normalized standard deviations for CKD and raw solids of 0.47 and 0.5 respectively. The remaining elements, antimony, vanadium and zirconium had normalized standard deviations ranging from 0.03 to 0.24. These were also elements that were detected at concentrations below 5 mg/kg for the waste samples, CKD values excluded, so a higher normalized standard deviation was expected.

Table 3-3: Average Elemental Concentration (mg/kg dry weight) and Normalized Standard Deviations for all Samples

Element	Drilling Mud		Raw Solids		Treated Solids		Solidified Solids		Cement Kiln Dust	
	Average	N STDEV	Average	N STDEV	Average	N STDEV	Average	N STDEV	Average	N STDEV
Silver	0.2	0.13	0.0	0.00	0.1	0.16	0.1	0.02	0.0	0.00
Aluminum	34700	0.10	6600	0.16	34100	0.19	28100	0.12	21000	0.02
Arsenic	18.1	0.02	7.2	0.10	13.2	0.08	25.9	0.02	42.8	0.04
Boron	263	0.03	57.9	0.04	335	0.14	216	0.06	201	0.03
Barium	10000	0.05	9080	0.09	12100	0.02	2150	0.07	123	0.04
Beryllium	1.1	0.05	0.3	0.24	0.9	0.13	1.5	0.08	2.9	0.05
Bromide	849	0.21	72.5	0.87	1390	0.36	539	0.12	16.6	1.73
Calcium	58700	0.01	28300	0.02	70400	0.12	113000	0.04	306000	0.04
Cadmium	0.4	0.11	0.2	0.11	0.3	0.03	0.6	0.06	0.3	0.08
Chloride	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
Cobalt	8.9	0.00	5.4	0.05	7.5	0.13	9.1	0.03	10.4	0.03
Chromium	59.1	0.07	32.4	0.01	50.0	0.16	49.3	0.08	45.6	0.01
Copper	63.4	0.06	45.3	0.07	53.9	0.09	52.7	0.04	24.8	0.02
Iron	46200	0.00	83500	0.04	51700	0.12	33200	0.03	29300	0.03
Potassium	9790	0.13	2060	0.19	7270	0.23	7760	0.15	3060	0.07
Lithium	586	0.01	28.1	0.03	803	0.12	248	0.02	18.9	0.02
Magnesium	11600	0.03	4020	0.02	13100	0.13	14400	0.03	28600	0.06
Manganese	1170	0.00	606	0.07	1500	0.11	871	0.09	266	0.13
Molybdenum	14.6	0.13	5.6	0.09	10.0	0.09	13.0	0.03	1.8	0.15
Sodium	42600	0.04	4920	0.12	48800	0.07	37700	0.03	1210	0.19
Nickel	41.6	0.11	22.0	0.10	29.8	0.12	41.3	0.00	35.9	0.03
Phosphorus	475	0.01	192	0.12	441	0.15	488	0.02	567	0.02
Lead	98.6	0.02	25.5	0.06	80.3	0.07	86.2	0.03	8.3	0.04
Sulfate	21.5	0.02	16.4	0.02	16.2	0.18	80.1	0.02	134	0.08
Antimony	1.7	0.26	0.8	0.23	1.5	0.07	1.5	0.21	0.3	0.41
Selenium	1.4	0.18	0.4	0.67	0.7	0.30	1.9	0.11	3.5	0.05
Silicon	122	0.08	31.9	0.50	86.5	0.16	89.2	0.30	12.8	0.47
Strontium	7890	0.00	4770	0.04	9530	0.08	4200	0.02	333	0.06
Uranium	2.2	0.01	0.7	0.11	1.7	0.09	2.9	0.07	2.4	0.02
Vanadium	52.8	0.15	13.7	0.20	41.2	0.24	67.8	0.13	87.5	0.03
Zinc	157	0.04	50.1	0.18	146	0.11	130	0.05	43.7	0.03
Zirconium	3.9	0.13	1.5	0.21	3.6	0.24	7.6	0.07	19.2	0.10

Based on the strong acid microwave digestion, it was determined that the elemental composition was similar for all of the solid samples. This was expected of the solidified sludge because it is a combination of the other samples and then cement kiln dust was added to solidify the mixture. In the samples, the major constituents identified were aluminum, barium, bromide, calcium, iron, magnesium, manganese, potassium, sodium, strontium, phosphorus, and zinc. Many of these elements were predicted to be detected at elevated levels due to their natural

occurrence in Marcellus Shale and previous reporting of research findings on Marcellus Shale and produced water.

However, although the samples were very similar in elemental composition, some variations between elements were of note. Figure 3-1 provides the digested compositions of each element for all residual solid samples and cement kiln dust. Elements noted as having high variation between each sample were boron, barium, bromide, calcium, chloride, lithium and sodium. Variations in barium concentrations were expected to be highest in treated solids and raw solids due to the elevated presence of that element in produced water (Chapman et al., 2012), as well as the chemical use of sodium sulfate to form a barium sulfate precipitate (Keister, 2010) in the treatment process.

Silver, aluminum, chromium, copper, potassium, molybdenum, nickel, lead, silica, and zinc all had peak concentrations in the drilling mud. The exact composition of drilling mud is unknown due to the proprietary nature maintained by each drilling company. However, some of the elements detected can be attributed to the fracturing fluid and chemical additives used for well construction and maintenance. The elevated levels of sodium and chloride were predicted due to the high levels of salt in the recycled, treated produced water used in well construction. Other elements could be present due to dissolution and adsorption of these to the drilling mud through underground interactions with the drill and shale (Zoback et al., 2010). Considering all the unknown factors, the exact composition of fracking fluids after reuse will require more sophisticated means of analysis. Recent research by Warner and Jackson has revealed a new forensic tool in which the detection and characterization of fracking fluids is made possible by tracing the isotopic and geochemical fingerprints of enriched boron and lithium in flow back and produced water (Warner et al., 2014).

Due to the high salt content of the samples, ICP-MS analysis could not be performed without first removing as much of the dissolved solids content as possible. For this reason, initial steps to processing the solid portion of the samples required centrifugation. To evaluate the portion of elements located only in the solid portion of the samples, supernatant composition was not included in the total digested composition seen in Figure 3-1.

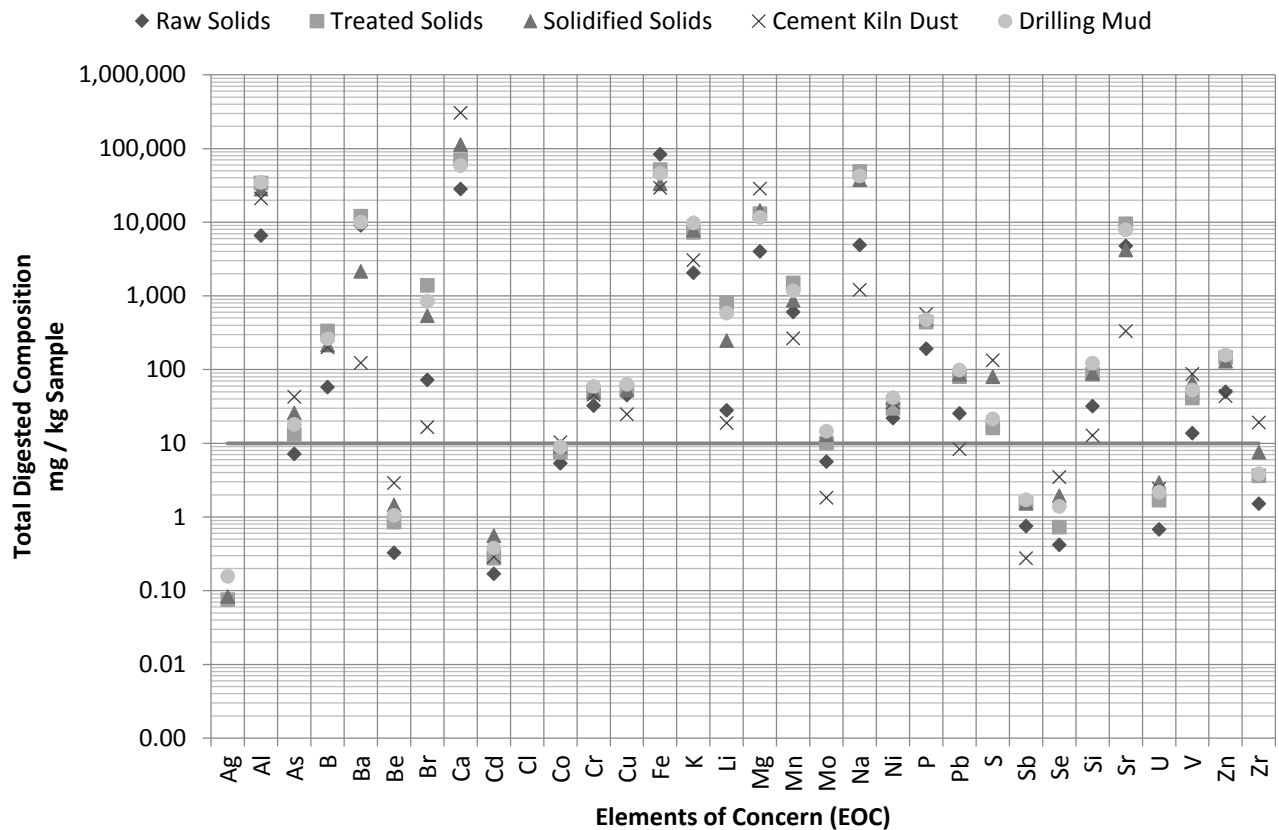


Figure 3-2: Total Digested Composition (mg/kg dry weight) of Residual Solid Samples

Liquid fraction results are presented in Table 3-4. The elements present at concentrations above 5 mg/kg were boron, barium, bromide, calcium, chloride, lithium, iron, potassium, magnesium, manganese, sodium, and strontium. All these elements had high variance between each sample indicating that the liquid portion of each of these wastes was different. The treated solids were consistently higher for all elements of concern than the other samples while the drilling mud was the lowest, with the exception of the solidified solids for select elements like magnesium, manganese, and iron, which were lower than the drilling mud.

From the percent comparison of the liquid fraction and the solid fraction, Table 3-5, the majority of the elemental composition is present in the solid fraction, i.e. 23 out of the 32 elements of concern had 100% of the composition come from the solid portion of the waste. The elements with high variance between sample types were chloride, calcium, lithium, sodium and strontium. For the treated solids and solidified solids, the chloride was 100% in the supernatant. For the raw solids and treated solids sodium was 91.8 and 92.5% in the solid portion, respectively. Due to the high content of salt in the fracturing process combined with the marine origin of Marcellus Shale, it was expected that the supernatants would contain high levels of

sodium, chloride and calcium. Treated solids and solidified solids had 178,000 and 82,200 mg/kg sodium, 85,900 and 27,100 mg/kg calcium in the supernatants.

Table 3-4: Composition of Supernatant in the Liquid Fraction (mg/kg)

Element	Supernatant Concentration (mg/kg in liquid fraction)			
	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids
Silver	0.0	0.0	0.0	0.0
Aluminum	1.0	1.1	14.5	3.4
Arsenic	0.0	0.1	0.4	0.1
Boron	6.6	19.2	72.4	0.0
Barium	27.7	12.7	1,360	1.3
Beryllium	0.0	0.0	0.0	0.0
Bromide	441	879	5,340	1,080
Calcium	7,180	15,200	85,900	27,100
Cadmium	0.0	0.0	0.0	0.0
Chloride	50.3	95.1	529	199
Cobalt	0.0	0.0	0.0	0.0
Chromium	0.2	1.0	0.0	0.0
Copper	0.2	1.4	2.8	1.5
Iron	6.5	24.8	54.3	6.0
Potassium	716	433	3,580	2,180
Lithium	17.2	70.0	218	177
Magnesium	751	1,660	9,060	2.2
Manganese	13.5	19.7	149	0.1
Molybdenum	0.0	0.0	0.0	1.3
Sodium	18,300	35,200	178,000	82,200
Nickel	0.1	0.9	0.6	0.8
Phosphorus	0.4	1.5	0.0	13.6
Lead	0.0	0.1	0.2	0.3
Sulfate	0.1	0.9	0.5	4.3
Antimony	0.0	0.0	0.0	0.0
Selenium	0.0	0.1	0.1	0.1
Silicon	0.7	6.7	8.0	8.0
Strontium	1,080	1,740	14,300	2,460
Uranium	0.0	0.0	0.0	0.0
Vanadium	0.1	0.1	0.7	0.3
Zinc	0.5	6.9	0.7	0.2
Zirconium	0.0	0.0	0.0	0.1

Table 3-5: Elemental Concentration in Solid Portion of Samples (%)

Percent Elemental Composition in Solid Portion (%)				
Element	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids
Silver	100.0	100.0	100.0	100.0
Aluminum	100.0	100.0	100.0	100.0
Arsenic	100.0	100.0	99.9	100.0
Boron	99.9	99.6	99.5	100.0
Barium	100.0	100.0	99.7	100.0
Beryllium	100.0	100.0	100.0	100.0
Bromide	99.0	92.6	92.4	97.6
Calcium	99.7	99.3	97.3	99.7
Cadmium	100.0	100.0	100.0	100.0
Chloride	99.2	98.8	0.0	0.0
Cobalt	100.0	100.0	100.0	100.0
Chromium	100.0	100.0	100.0	100.0
Copper	100.0	100.0	99.9	100.0
Iron	100.0	100.0	100.0	100.0
Potassium	99.8	99.7	98.9	99.6
Lithium	99.9	96.9	99.4	99.0
Magnesium	99.9	99.5	98.5	100.0
Manganese	100.0	100.0	99.8	100.0
Molybdenum	100.0	100.0	100.0	99.9
Sodium	99.1	91.8	92.5	97.1
Nickel	100.0	100.0	100.0	100.0
Phosphorus	100.0	100.0	100.0	100.0
Lead	100.0	100.0	100.0	100.0
Sulfate	100.0	99.9	99.9	99.9
Antimony	100.0	100.0	100.0	100.0
Selenium	100.0	99.8	99.7	99.9
Silicon	100.0	99.8	99.8	99.9
Strontium	99.7	99.5	96.7	99.2
Uranium	100.0	100.0	100.0	100.0
Vanadium	100.0	100.0	100.0	100.0
Zinc	100.0	99.9	100.0	100.0
Zirconium	100.0	100.0	100.0	100.0

3.5 REGULATORY LIMITS

Currently, the disposal of solid waste is regulated by state and federal agencies. The EPA has defined restrictions for the amount of waste that can be treated and placed limits on the quality of produced water that is recycled for new well construction. Land application and well deposition of wastes are also regulated by the EPA, where certain elements have strict guidelines that must not be exceeded (Harrison et al., 1999 and US EPA, 40 CFR 503.10, 1993).

Hydraulic fracturing residual solids are considered industrial waste; however, as a means of comparison for this research, domestic wastewater sewage EPA defined limits for land application and well deposition compared to the maximum observed concentration for each of the tested elements of concern are tabulated below in Table 3-6.

Table 3-6: Maximum Observed Elemental Composition of Residual Solids Compared to Regulatory Limits for Domestic Sludge Land Application (mg/kg dry weight) (Harrison et al., 1999)

EPA Land Application Regulated Limits		mg/kg sample dry weight				
		Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	Cement Kiln Dust
Arsenic	75	18	7	13	26	43
Cadmium	85	0	0	0	1	0
Chromium	3000	59	32	50	49	46
Copper	4300	63	45	54	53	25
Lead	840	99	25	80	86	8
Molybdenum	75	15	6	10	13	2
Nickel	420	42	22	30	41	36
Selenium	100	1	0	1	2	3
Zinc	7500	157	50	146	130	44

Following comparison of the top elements of concern regulated by the EPA for municipal sludge land application, it was determined that this waste is compatible with land application, landfill disposal and deep well deposition. Comparing the residual solids and municipal waste land application, all of the regulated elements were reported at values below regulatory limits. It is important to note that the microwave digestion values were determined by a single method, 3:1 mixture of nitric and hydrochloric acid digested at 175 °C for 4 minutes, suited to the majority of the elements of concern with the assumption that strong acid microwave digestion provided the total elemental composition and further testing, like TCLP, should be conducted to determine hazards waste characterization.

3.6 CONCLUSION

Microwave assisted strong acid digestion was conducted on a variety of residual solid samples generated throughout the hydraulic fracturing process to determine the total composition for a host of elements of concern. The digestion method followed EPA 3051A using a combination of nitric and hydrochloric acid for enhanced extraction and stabilization for select elements.

Data analysis indicated that while each residual solid sample showed different variations in characteristics, they were each very similar in composition. Following digestion, the major

elements noted following digestion were aluminum, barium, bromide, calcium, iron, magnesium, sodium, and strontium. Each element was highly represented, but large variances were seen in barium, bromide, lithium, sodium, lead, and strontium.

From supernatant analysis, it was apparent that while the solids portion of the samples contained the greater concentration for each element, a few elements were also highly represented in the liquid portion. These elements included bromide, calcium, chloride, lithium, sodium, and strontium.

Microwave assisted strong acid digestion provided a detailed elemental breakdown for each of the samples including contributions of the liquid soluble portions, and insoluble solid portions in the solid samples. However, since the exact chemical makeup of fluids used by drilling and gas companies remains proprietary, along with unknown chemical or physical changes due to interactions with elements in the shale, it is difficult to discern whether the digestion was complete or any constituents were lost in transition between the drilling site and the treatment facility prior to sample preparation and data analysis.

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CHAPTER 4: EVALUATING THE LEACHABILITY OF VARIOUS ELEMENTS IN HYDRAULIC FRACTURING RESIDUAL SOLIDS FOLLOWING IMMERSION

ABSTRACT

Leaching procedures were conducted on residual solid samples collected from a designated treatment facility that processes produced water from multiple drilling companies distributed throughout the Marcellus Shale region. Immersion tests were conducted to investigate the leaching characteristics of heavy metals and other elements of concern commonly found in hydraulic fracturing waste. The samples used for this study included raw solids, treated solids, solidified solids, drilling mud and cement kiln dust. Each representative sample was exposed to two different extraction fluids, weak acetic acid solution obtained from the toxicity characteristic leaching procedure (TCLP) and deionized water. These fluids simulate the best and worst case scenarios that solid wastes could encounter in a typical disposal environment, a municipal landfill. The leaching results were compared to EPA established and regulated limits for hazardous waste disposal. According to TCLP regulated limits, the waste should be treated as hazardous because of the amount of barium detected in the leachate.

KEYWORDS: Hydraulic Fracturing, Leaching Behavior, Toxicity Characteristic Leaching Procedure, Residual Solids, Immersion, Heavy Metals

4.1 INTRODUCTION

Hydraulic fracturing is an unconventional process of extracting natural gas from wells drilled deep into the Earth. Throughout the hydraulic fracturing process, a variety of technologies are utilized to extract the maximum amount of natural gas from the shale. Once the drilling site is chosen, the wells are constructed using drills, drilling mud, fracturing fluid and water. Specific recipes are proprietary to each company; however, drilling mud is typically a mixture of water and oil or a synthetic based slurry that is used to lubricate the drill and carry cuttings produced by the drill to the surface (Ohio EPA, 2012). Fracturing fluid is a mixture of water, proppants and chemical additives. The chemical additives in the fluid act as scale inhibitors, biocides, and friction reducers that allow for increased fluid velocity (Abdalla et al., 2011). Fracturing fluid is pressurized and pumped into the wells to create cracks and fissures along the well walls where the proppants prevent closure of the fissures, allowing the natural gas to rise to the surface (Kargbo et al., 2010). Once the desired vertical depth is reached, the drill is rotated 90 degrees to extend the well horizontally through the shale. Improvements, such as horizontal drilling, exploit the low permeability and porosity of the shale, ultimately exposing a larger volume through a single bore well (Maloney and Yoxtheimer, 2012) and increasing permeability and natural gas extraction.

Each completed well uses anywhere from 7,000 - 18,000 cubic meters of fracturing fluid (Gregory et al., 2011), approximately 24% of this fluid return to the surface immediately, flow back, (Hulszczak et al., 2013) while the rest slowly returns over the next few weeks to months, produced water. Produced water contains both solid and liquid waste and consists of elevated levels of salt, heavy metals, organic and inorganic compounds as well as radionuclides (Chapman et al., 2012). Produced water is often stored on the drilling site in open pits and impounds and then transported to a dedicated treatment facility (Hammer and VanBriesen, 2012) once quantities become too large to be maintained on premise. Upon arrival at the dedicated treatment facility, the produced water flows through a series of treatment steps that result in the production and accumulation of residual solids and treated sludge. These residual solids are also treated following strict regulations imposed by the state and EPA prior to disposal.

Hydraulic fracturing waste treatment at a facility in the Marcellus Shale region begins with produced water transferred from onsite storage pumped into rock boxes to remove the heavy solids by gravity separation. The supernatant containing suspended particles is transferred to a three step reaction tank for chemical treatment where coagulation, flocculation and sedimentation occur. Sodium sulfate, sodium hypochlorite and sodium hydroxide are used to increase the pH and decrease the total dissolved and suspended solids. Chemical treatment also removes heavy metals and organic contaminants, specifically strontium, barium and iron. This

ultimately prepares the water for reuse (Hammer and VanBriesen, 2012). The precipitate is then removed from the treatment process and classified as treated solids. These treated solids have elevated concentrations of elements of concern requiring specific management and disposal methods (Kargbo et al., 2010; Hammar and VanBriesen, 2012). Consequentially, the materials produced at the dedicated treatment facility include the residual solids from rock boxes, thickened drilling mud and treated settled sludge. These are all mixed and solidified with cement kiln dust and stored for future disposal in a municipal landfill.

Waste disposed of in a landfill environment is exposed to a host of solids and liquids, with characteristics unique to the waste and the landfill. Landfills are exposed to the environment and therefore are effected by climate and weather patterns. Solid waste disposed in a landfill comes in contact with liquid in many forms. Most commonly the liquid is supplied by precipitation, surface runoff, groundwater, decomposition fluid and liquid wastes. Solids exposed to liquid for a period of time are subject to dissolution and subsequent leaching. The characteristics of the resulting leachate are of great concern due to the environmental impacts exposure could cause. For this reason, leachability studies are conducted on an array of wastes to determine the most suitable method of disposal.

Landfill leachate consists of a number of complex factors, including solid waste composition, age of the waste, hydrogeological conditions in vicinity of the landfill site, rate of the water permeation through the waste, landfill temperature, moisture content, pH, landfill chemical and biological activities and seasonal weather variations (Westlake, 1995; McArdle et al., 1988). The production of leachate also varies widely through the successive aerobic, acetogenic, methanogenic and stabilization stages. The culmination of these factors results in leachates with pH levels that vary significantly with age, from 4.5 to 9 (Christensen et al., 2001). Leachates from younger landfills, less than 5 years, contain elevated levels of volatile fatty acids (VFA), resulting in a pH of 6.5 (Bohdziewicz et al., 2008). Intermediate landfills, between 5 and 10 years of age, have pH values ranging from 6.5 to 7.5, where humic and fulvic acids are forming and the VFAs are decreasing. Older landfills, more than 10 years, have pH levels above 7.5 where humic and fulvic acids are the dominating organic compounds (Abbas et al., 2009, Renou et al., 2008).

Solids exposed to landfill leachate have varying potentials for elemental translocation that are dependent and influenced by parameters that include homogeneity, particle size, porosity, contact time, temperature, pH, oxidation reduction potential (ORP), total organic carbon (TOC), partitioning coefficients, complexation and biological activity (Renou et al., 2008, Kalbe et al., 2008). Sample preparation is reported to be a vital step in enhancing total leachability. By drying, crushing and grinding the samples to a fine grain size, the surface area to volume ratio is

increased, thereby maximizing leachability by utilizing a shorter diffusion path (Fällman and Aurell, 1996, Kylefors et al., 2003, Lewin, 1996). For this reason, the samples were dried and ground prior to exposure to extraction fluids with different pH values and placed in a controlled environment to allow equilibrium to be attained quickly.

According to previous research, the pH of the leaching solution is a critical parameter in determining metal solubility (Fällman and Aurell, 1996, Mahmoudkhani et al., 2008, Quevauviller et al., 1996, Rigol et al., 2009, van der Sloot, 1990). The solution pH determines the surface charge on the solid along with the degree of ionization and speciation of the elements in solution, where interactions between the charged ions in solution and the sample surface contribute to the adsorption or release of elements (Kalembkiewicz et al., 2015). Leaching solutions with acidic to neutral pH values result in maximum extraction of heavy metals (Lewin, 1996). Elements such as lead, cadmium and zinc have solubilities that decrease under alkaline conditions and increase with decreasing pH (Chuan et al., 1995). However, metals can form soluble complex formations with inorganic and organic ligands, affecting metal adsorption and mobility under various pH values (McLean et al., 1992). Oxyanion forming elements such as arsenic, chromium, selenium, antimony, molybdenum, vanadium and tungsten, along with calcium and barium metalates exhibit minimum leaching potentials at alkaline pH values and pH values less than 6 (Cornelis et al., 2008; Perkct and Webster, 1981, van der Sloot, 1990). However, exceptions to this trend have been noted for constituents such as lead metalates, which are more soluble in alkaline solutions (Cornelis et al., 2008).

Due to the complex nature of metals in soils, it is often difficult to get representative results for all elements. However, acidic leaching solutions, such as the weak acetic acid solution used in the Toxicity Characterization Leaching Procedure (TCLP), are frequently used to determine the leaching potential of metals in landfill situations where microbial interactions and decomposition decrease the landfill pH (McLean et al., 1992).

The TCLP extraction method was developed by the EPA to evaluate the leaching behavior of select elements and contaminants in a landfill. The Resource Conservation and Recovery Act (RCRA), established through the EPA, has set strict disposal limits for specific contaminants including metals (specifically: arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) and organics, such as pesticides, herbicides, volatiles, and semi-volatiles. In order to meet RCRA requirements, a TCLP must be performed within 180 days of sample collection for general metals (US EPA, 2012). If the final elemental or contaminant concentration following extraction exceeds RCRA regulations, the waste is labeled hazardous and must be disposed of properly (US EPA 40 CFR 261.24, 2012). Waste that meets RCRA requirements can be disposed of by land application or in landfills (Hammer and VanBriesen, 2012); however, wastes that are

deemed hazardous must be disposed of in hazardous waste landfills or deep well injections. This ultimately increases the overall cost of disposal (Asante-Duah et al., 1992).

Elements of concern were chosen based on a literature review, geological information on Marcellus shale and regulatory requirements for water and wastewater quality assurance, and information supplied by the EPA and DEP. Marcellus shale is of marine origin so it naturally contains increased levels of sodium and chloride, as well as many other elements such as calcium, bromide, strontium, barium, chromium and zinc (Chapman et al., 2012; and Bank, 2008). It is also naturally rich in trace elements, such as copper, nickel, uranium, vanadium, and molybdenum (Titler and Curry, 2011; and Liermann et al., 2011). Previous research noted common elements in hydraulic fracturing practices and focused on aluminum, boron, iron, lithium, magnesium, manganese, phosphorus, and potassium (Haluszczak et al., 2013).

4.2 PROJECT OBJECTIVES

The objective of this research was to chemically characterize residual solid and liquid wastes produced from hydraulic fracturing operations within the Marcellus Shale region. A total of five samples were obtained from a dedicated treatment facility that treats a variety of produced water and drilling waste from drilling companies distributed throughout the region. At the designated treatment facility, produced water is pumped into rock boxes for gravity settling while the water is removed and treated. The samples obtained from the facility were composite samples and for this study are considered to be representative of the hydraulic fracturing process. These samples included: drilling mud, treated sludge from the chemical treatment of process waters, solids from the gravity settling of produced water, sludge solidified prior to disposal in a municipal landfill and cement kiln dust (CKD).

Laboratory leaching experiments were conducted to determine the presence and transport of select elements of concern found in residual solids generated from hydraulic fracturing operations. Deionized water and weak acetic acid solution, TCLP buffer, were used in immersion-extraction methods to investigate the effects of acid versus water on elements in the fracturing solids. By exposing the samples to liquid for a designated period of time, and replenishing the fluid frequently, the maximum amount of elements leached can be estimated.

The samples contained a wide variety of elements at dramatically different levels. The samples collected from the treatment facility contained volatile compounds and low levels of radionuclides, but this research only focused on 32 different elements distributed throughout the periodic table. Due to analytical issues and sample storage time, mercury was not evaluated. ICP-MS analysis was used to quantify the percentage of each element in extraction fluid over 90-

days. Final analysis revealed the elements with the highest leaching potential and the relative quantity of each element.

The final sample characterizations can be used to assist oil and gas companies in developing more definitive information about the potential environmental impacts of fracking operations. This research was also intended to provide industry leaders with information for the development of best available management practices for the residual solids.

4.3 MATERIALS AND METHODS

4.3.1 Glassware preparation

Glassware, immersion test beakers and other equipment were cleaned with detergent, either Sparkleen™ laboratory detergent or Dawn™ dish soap and rinsed. Following a detergent wash, glassware was placed in a 10% (v/v) nitric acid, ACS reagent grade, bath overnight, and then thoroughly rinsed with deionized water and nanopure water. Glassware, equipment, and bottles were air dried in a clean environment.

4.3.2 Chemical Reagents

TCLP extraction fluid was made using reagent grade glacial acetic acid from Fisher Scientific American Chemical Society (ACS) following EPA Method 1311. Deionized water was used for dilutions and solution preparation. Two standard solutions prepared by High Purity Standards in Charleston, SC were used for ICP-MS analysis and calibration. These standards were diluted using deionized water and preserved with 2% HPLC grade, nitric acid to provide a broad calibration curve for all elements of concern. Specifications for these standard solutions are provided in Appendix A – Standard Solutions. Fresh calibration standards were made for each ICP-MS trial and the standards were used as an internal check by being analyzed after every 13th sample on the ICP-MS. The purity of chemical reagents and reagent water was monitored throughout each experiment.

4.3.3 Sample Preparation

Samples were added to clean, polyethylene centrifuge bottles and centrifuged at 8000 RPM for 30 minutes. The supernatant was decanted, and the bottles were balanced and centrifuged again at 8000 RPM for 30 minutes. After the water was removed, the samples were removed from the centrifuge bottles using a spatula and placed in an oven at 40 °C for 48 hours to dry. The samples were then ground using a mortar and pestle until reaching a uniform sandy texture. Then, 50g of each sample was placed in an oven at 105 °C overnight to remove all remaining water so that the total percent moisture in each sample could be determined.

4.3.4 Water Chemistry Tests

pH and conductivity were measured on each sample on the day of fluid replenishment using Oakton portable meters. Conductivity measurements were converted from mS/cm to $\mu\text{S}/\text{cm}$ and multiplied by 0.67 to calculate the TDS for each sample. This was a ballpark adjustment, conductivity to TDS conversion factors range from 0.54 - 0.96. A value of 0.67 is commonly used as an approximation if the actual factor is unknown. Due to the saline nature of the produced water, this value could be higher.

Alkalinity was measured using Hach low range alkalinity kits, TNT 870.

4.3.5 Immersion Test

Dried, ground samples (100 ± 0.1 g) were poured into cotton, reusable tea bags, that were sealed and placed inside a 3 inch, metal-mesh tea diffuser, Figures 4-1 and 4-2. The tea diffusers were centered in a 1000 mL beaker using a paperclip and 1 mL glass pipette, so that the bottom of the tea ball was elevated slightly above the bottom of the beaker.



Figure 4-1: Dried, pre-ground samples in the following order: raw solids, solidified solids, drilling mud and treated solids

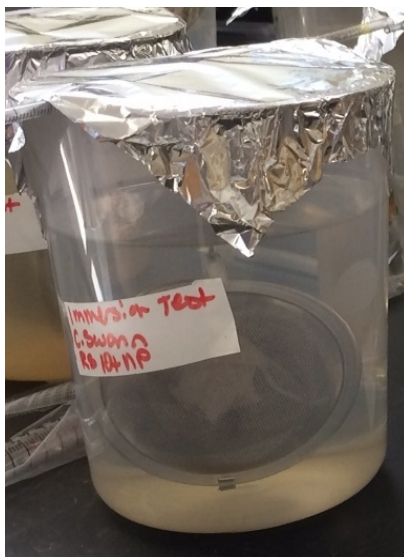


Figure 4-2: Immersion test set up where tea diffuser is immersed in extraction fluid, covered during longer immersion times

Once the tea diffusers were placed, 1000 mL of the extraction fluids was added to their respective beakers. This provided a 10:1 ratio of liquid to solid that was maintained throughout the duration of the experiment. Each sample was tested in triplicate, beginning with duplicates. The third replicates were tested a week later for maximum comparability.

The samples were immersed for a total period of 90 days. Extraction fluids were intermittently refreshed by removing the tea ball from solution, pouring out the used extraction fluid, replacing and re-centering the tea ball, and adding fresh fluid. The intervals for replenishing the extraction fluid can be found in Table 4-1. Following extraction fluid replacement, pH, conductivity and alkalinity were measured on the spent fluid. A total of 20 mL spent fluid was syringe filtered through a nylon, 0.45 μm filter. The samples were diluted in the ICP-MS tubes using 1 mL filtered fluid, 8.8 mL deionized water, and 0.2 mL nitric acid. The remaining 19 mL filtered sample was used for pH, conductivity, alkalinity and TOC tests.

Table 4-1: Extraction Fluid Replenishment Schedule

Replenishment Period	Cumulative Time (days)	Interval Duration (days)
1	0.25	0.25
2	1	0.75
3	2.25	1.25
4	5	2.75
5	9	4
6	16	7
7	36	20
8	65	29
9	90	25

The leachability study was conducted at room temperature, 21.0±2.0 °C, in a clean, dry space where the samples remained undisturbed. For the longer interval duration times, the beakers were covered with aluminum foil to minimize evaporation.

Following test completion, the tea diffusers were oven dried at 105 °C for 24 - 48 hours, and the final weight was recorded. Monitoring the change in total mass of the sample enabled evaluation of sample lost during the experiment (Table: 4-2 and Table: 4-3). Sample loss raw data are represented in Appendix D - Leachability Losses. The samples that had the largest decrease in mass following 90 days of immersion were the treated solids, with a 28% and 20% loss in weak acetic acid solution and de-ionized water extraction fluids, respectively. The samples that had the least loss of mass were the raw solids, which lost 9% and 4% for the extraction fluids, respectively, and CKD which lost 10% and 1% for TCLP and de-ionized water, respectively.

Table: 4-2 - Percent Total Mass lost during immersion in TCLP extraction fluid

Weak Acid Extraction Fluid				
Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	CKD
24%	9%	28%	27%	10%

Table: 4-3 - Percent Total Mass lost during immersion in De-ionized water extraction fluid

Deionized Water Extraction Fluid				
Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	CKD
16%	4%	20%	15%	1%

4.3.6 Elemental Analysis

Extraction fluid samples were analyzed for all nine time intervals for each of the elements of concern following EPA Method 6020A – Inductively Coupled Plasma Mass Spectrometry using

a Thermo X-Series ICP-MS. According to EPA method 6020A, trace metal detection and quantification limits for ICP-MS analysis range from below 0.1 ppb to well above 1.0 ppb. The method detection level (MDL) and minimum reporting limits (MRL) were calculated for each element of concern following the procedure identified by Winslow et al., (2005) and determined by EPA guidelines. In order to ascertain accurate measurements, the calibration standards ranged from 0.1ppb to 10 ppm. For this research, the low level standard chosen for MDL determination was the MRL. Samples reported below the MRL were considered n/a or assigned a value of zero. The MDL and MRL information determined for each element with ICP-MS is provided in Appendix B – Analytical Limits for ICP-MS Analysis.

4.3.7 Total Organic Carbon

One sample of each triplicate of each solid sample was chosen for total organic carbon (TOC) evaluation for replenishment intervals 0.25, 5, 16 and 90 days. Samples were measured on a Shimadzu TOC-V CSN following combustion catalytic oxidation with NDIR (Non-dispersive infrared detector) detection method; referencing Standard Methods 5310 B. MDLs for the samples containing less than 25 mg/L TOC was 0.05 mg/L, and the MDL for samples with 1000 mg/L or more TOC, was 0.25 mg/L.

4.4 RESULTS AND DISCUSSION

4.4.1 pH

The average pH values over the 90 day period are provided in Figure 4-1 and Figure 4-2. Raw data are presented in Appendix E - pH, Conductivity, Alkalinity, and TOC Raw Data.

In the weak acid extraction fluid, Figure 4-1, all the samples maintained a pH of 3-5 throughout the duration of the experiment, the only exception being the CKD. The CKD, used as a stabilization and binding agent to solidify the solids, followed the same trend until 16 days, when the pH increased to nearly 11, where it remained for 56 days before decreasing to a final pH of 6.5. This trend reveals a delayed dissolution and wash out of a constituent within the CKD.

All samples in the de-ionized water extraction fluid maintained the same pH for the duration of the experiment, ranging from 6-8, Figure 4-2. Initially, some fluctuations in pH were noted and can be attributed to the low amount of ions present in the shorter immersion times. Again, the CKD was the outlier with a steady pH of 11.5.

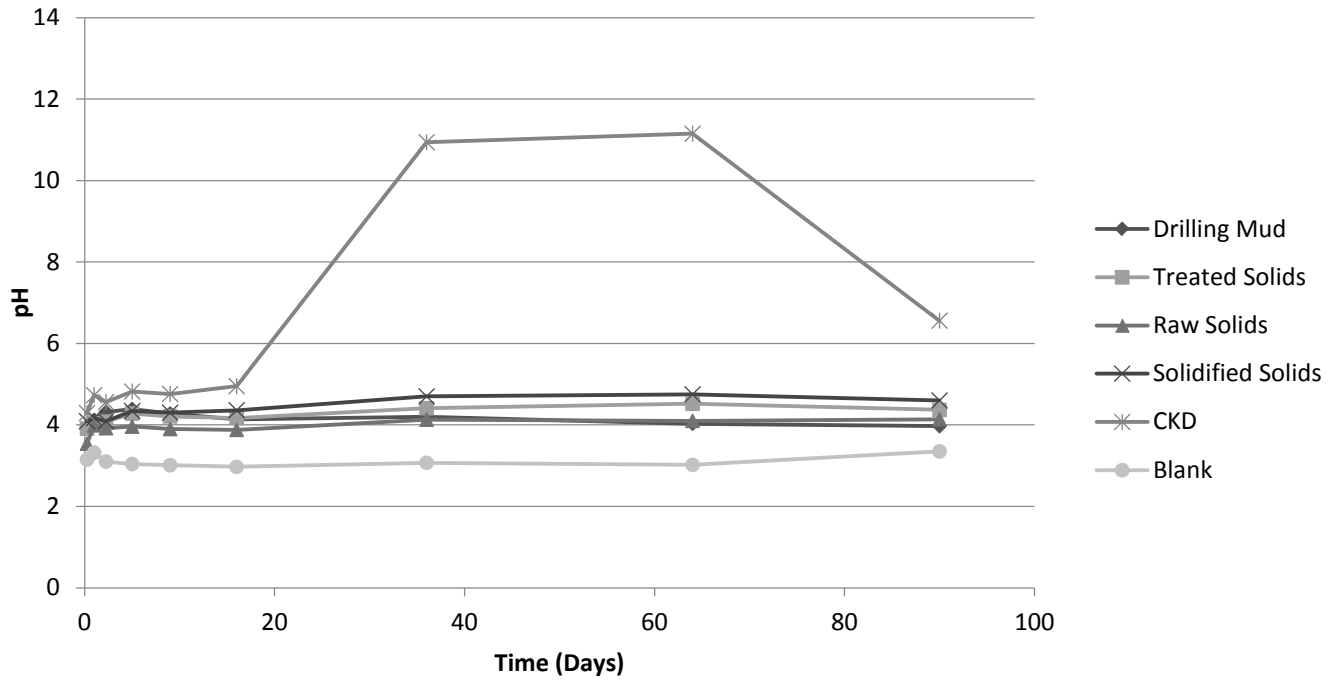


Figure 4-3: pH for Samples Immersed in Weak Acid Extraction Fluid. Blank reference to Weak Acid fluid alone.

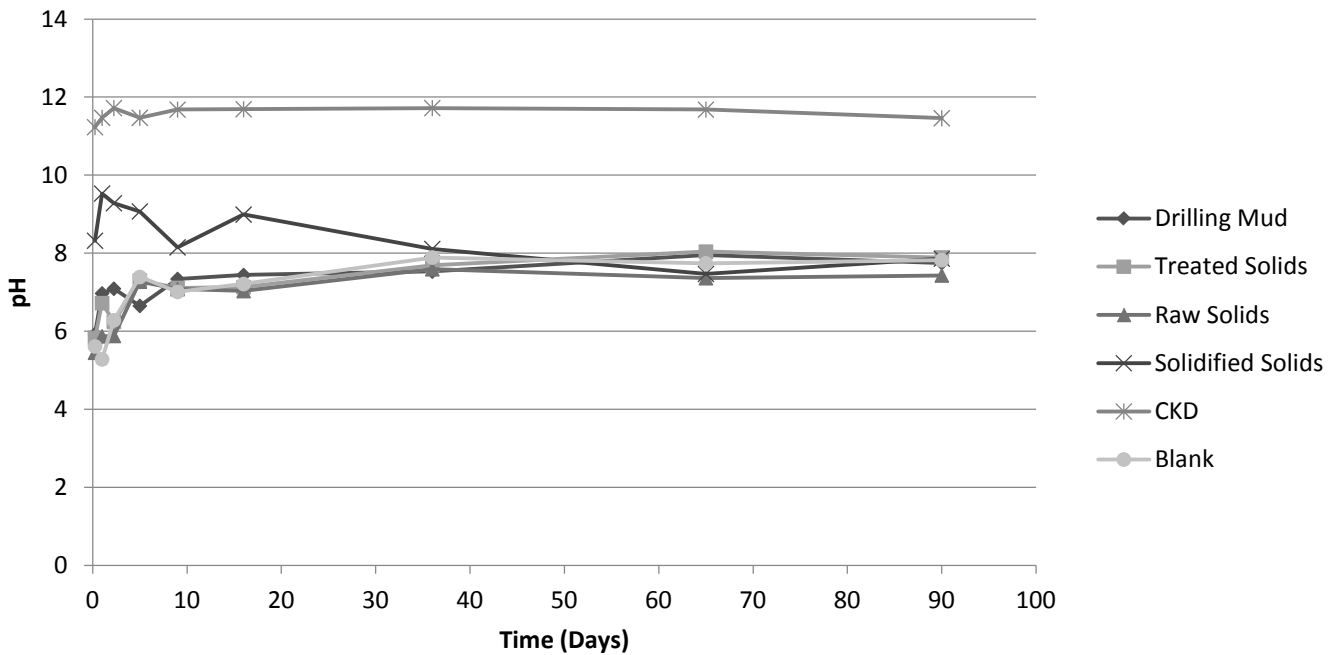


Figure 4-4: pH for Samples Immersed in Deionized Water. Blank refers to deionized water alone.

4.4.2 Conductivity

The conductivity data recorded for the triplicate samples were averaged and are shown in Figures 4-3 and 4-4. Raw data can be found in Appendix E - pH, Conductivity, Alkalinity, and TOC Raw Data.

Samples immersed in weak acid extraction fluid had their highest conductivities on day 0.25 and 1 day. Drilling mud and treated solids had conductivities of 14.81 mS/cm and 15.40 mS/cm on day 0.25 and on day 1, 8.88 and 10.62 mS/cm respectively; solidified solids peaked at 8.77 mS/cm. Following the initial peak activity, the sample conductivities dropped dramatically to a range of 2-4 mS/cm. As immersion and sample exposure time increased, a slight increase in conductivity was noted with elevated conductivities at 65 days that gradually declined for the final reading at 90 days. Overall, the sample with the lowest conductivity, aside from the control, was the raw solids. The raw solids maintained a conductivity range of 1.30 to 3.72 mS/cm. The CKD did not follow the trend set by the other samples. The CKD conductivity started off low, at 1.02 mS/cm, and steadily increased to peak at day 90 with a conductivity of 7.69 mS/cm.

A similar trend was noted in the samples immersed in de-ionized water. The samples with the highest initial conductivity were drilling mud and treated solids, 5.38 and 4.98 mS/cm for time 0.25 days and 9.92 and 7.37 mS/cm for time 1 day, where the solidified solids peaked at 6.68 mS/cm. Similar to the weak acid extraction fluid, the CKD was the outlier with conductivity increasing from 1.34 on day 0.25 to 6 mS/cm at day 36. Conductivity slowly decreased to 3.9 mS/cm at day 90. All other samples, except solidified solids which had a final conductivity of 1.15 mS/cm, decreased to conductivities below 1 mS/cm.

The high initial conductivity values can be attributed to residual salts that were not removed during centrifugation and sample prep, that once in contact with liquid, quickly dissolved. The presence of un-removed salts also explains why, with the exception of the CKD, the ionic strength of the samples increased with extended immersion time, as the easily accessible ions were dissolved and removed. Then, the ionic strength gradually decreased as the ions were removed from the system.

Typical conductivity for municipal landfill leachates is between 2 mS/cm and 8 mS/cm, with an upper limit of 9 mS/cm (Canter et al., 1988; McGinley and Kmet, 1984; and Lee and Jones, 1991). According to the Lenntech's report on water conductivity in 2013, high quality deionized water has a conductivity of about 5.5 μ S/m, while typical drinking water is in the range of 5-50 mS/m with sea water being one million times greater, with a conductivity of 5 S/m. For all samples evaluated, with the exception of CKD, the conductivity was within the typical range for municipal landfill leachates. The CKD alkalinity fell within the upper level of the typical range

for both weak acid extraction fluid only. All values greatly exceeded the drinking water conductivity range but were well below that of sea water.

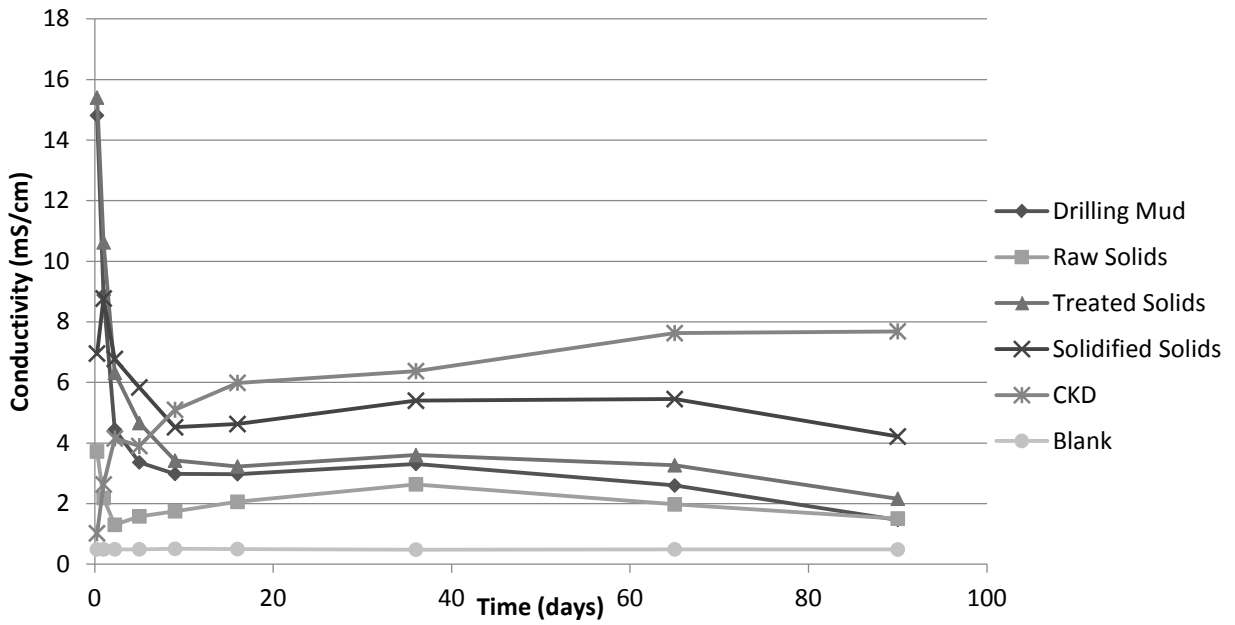


Figure 4-5: Average Conductivity for Samples Immersed in Weak Acid Extraction Fluid. Blank refers to weak acid fluid alone.

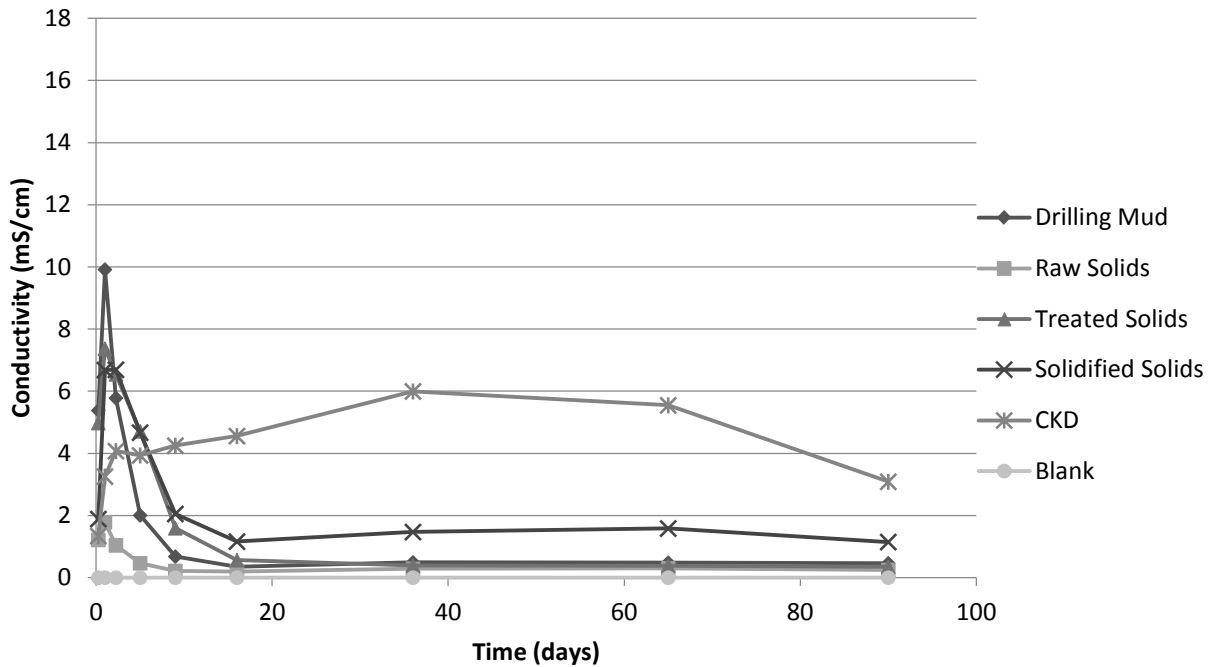


Figure 4-6: Average Conductivity for Samples Immersed in De-Ionized Water Extraction Fluid. Blank refers to deionized water alone.

Following conductivity analysis, TDS was calculated, as mentioned above (Figures 4-5 and 4-6). The samples follow the same trend noted for both extraction fluids, where initial sample intervals had the highest concentration of dissolved salts and the later time interval samples had the lowest TDS.

Typical TDS for municipal landfill leachates is between 1,000 mg/L and 2,000 mg/L, with an upper limit of 55,000 mg/L (Canter et al., 1988; McGinley and Kmet, 1984; and Lee and Jones, 1991). All samples evaluated in the weak acid extraction fluid were above the typical range for TDS, but below the upper limit. Both the treated solids and drilling mud had peak TDS values at 0.25 days with values of 10,320 mg/L and 9,925 mg/L, respectively. CKD had its peak TDS value, 5,150 mg/L, at day 90.

TDS in the deionized water extraction fluid were above the established typical range for the first few time intervals, but below the upper limit for all samples, with the exception of CKD which remained above the typical range. Raw solids was the sample with the lowest TDS throughout the duration of the experiment. Drilling mud, treated solids, raw solids, and solidified solids peaked on day one with values of 6,644 mg/L, 4,938 mg/L, 1,196 mg/L, and 4,478 mg/L respectively. Control blanks in weak acid extraction fluid had TDS values corresponding to the weak acetic acid solution. Control blanks in the deionized water extraction fluid had very little to no TDS due to the fluid being water only.

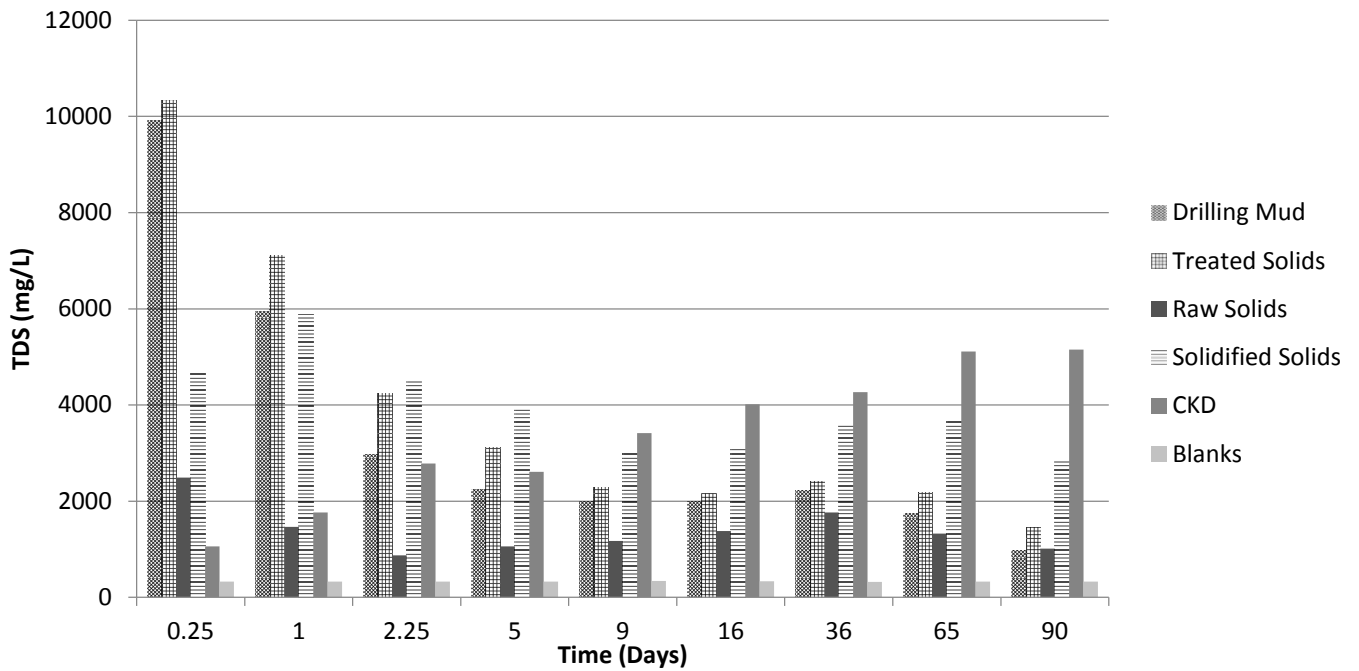


Figure 4-7: Average TDS for Samples Immersed in Weak Acid Extraction Fluid. Blank refers to weak acid alone.

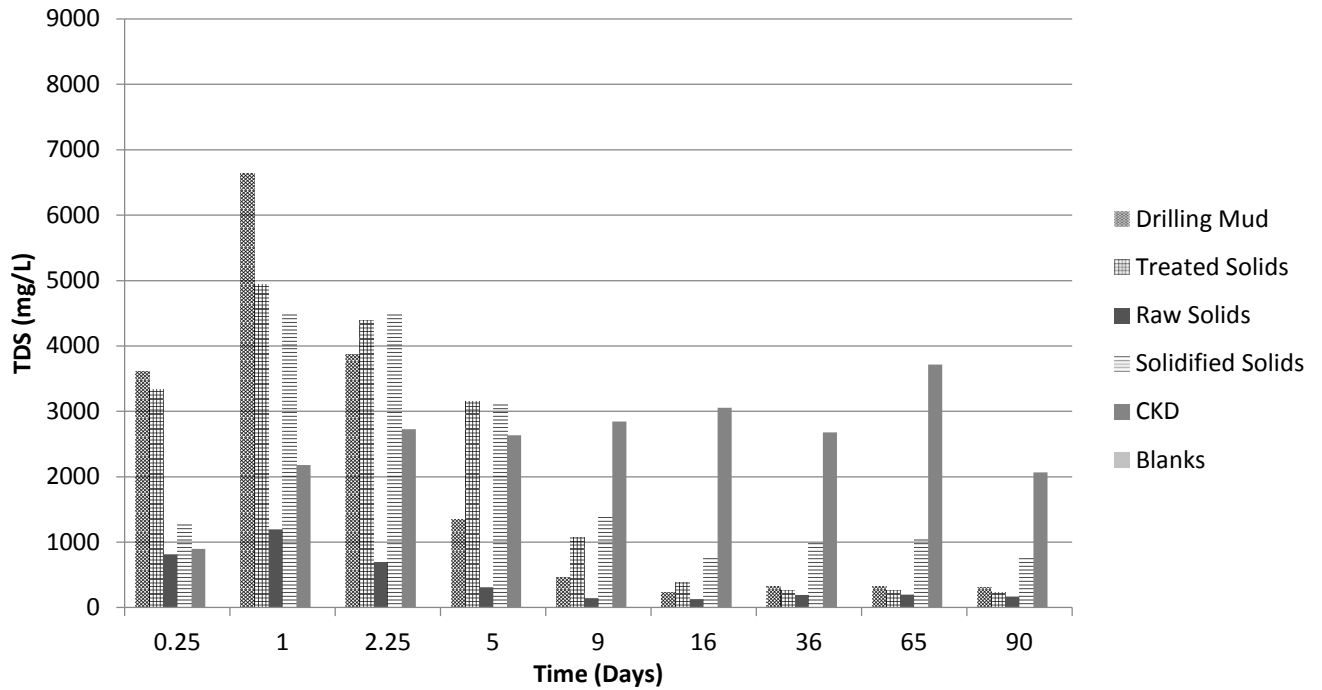


Figure 4-8: Average TDS for Samples Immersed in Deionized Water Extraction Fluid. Blank refers to deionized water alone.

4.4.3 Alkalinity

One sample from each triplicate was chosen for alkalinity analysis on days spread throughout the experiment; days 1, 5, 9, 36, and 90. Data are graphed in Figures 4-5 and 4-6. Raw data can be found in Appendix E - pH, Conductivity, Alkalinity, and TOC Raw Data.

The sample with the highest alkalinity for both extraction fluids was the CKD. In the weak acid extraction fluid, the CKD alkalinity ranged from 260 to 651 mg/L as CaCO₃, on day 1 and day 36, respectively. The other samples peaked in alkalinity at day 36 and then decreased greatly. The samples with the highest alkalinity, aside from the CKD, was the solidified solids. This was predictable because CKD is the solidifying agent mixed with treated solids to create the solidified solids. The samples with the lowest alkalinity were the raw solids and the drilling mud.

In the de-ionized water extraction fluid, the CKD alkalinity ranged from 645 to 830 mg/L as CaCO₃, on day one and day five. Subsequent samples had an alkalinity of approximately 750 mg/L as CaCO₃. The samples with the second highest alkalinity were drilling mud and the treated solids. The sample with the lowest alkalinity was the solidified solids. This was unexpected due to the inclusion of CKD in the solidified solids, but the deionized water was apparently not able to dissolve or release alkalinity from the complexed solids.

In both extraction fluids, the steady increase in alkalinity to day 36 can be attributed to the buffering capacity of the samples. With increased exposure time, the constituents providing buffering capacity were dissolved in the extraction fluid, increasing the pH to a more neutral level and increasing the alkalinity. Once all the constituents providing the buffering capacity were removed, the alkalinity declined, as seen in the weak acid extraction fluid, or was maintained as seen in the de-ionized water.

Typical alkalinity for municipal landfill leachates is between 730 mg/L as CaCO₃ and 15,050 mg/L as CaCO₃, with an upper observed value of 20,850 mg/L as CaCO₃ (Canter et al., 1988; McGinley and Kmet, 1984; and Lee and Jones, 1991). For all samples evaluated, with the exception of CKD, the alkalinity was below the typical range for municipal landfill leachates. The CKD alkalinity fell within the lower level of the typical range for both extraction fluids.

Comparing Figures 4-1: pH for Samples Immersed in Weak Acid Extraction Fluid and 4-7: Alkalinity Data for samples Immersed in Weak Acid Extraction Fluid, it can be noted that alkalinity rises at pH values of 4.5 and lower, primarily for the weak acid extraction fluid up to a maximum of 388 mg/L as CaCO₃ for raw solids and 232 mg/L as CaCO₃ for solidified solids. This indicates that the samples are releasing ions into solution that can contribute to alkalinity. The weak acetic acid solution that comprises the weak acid extraction fluid consumed any buffering capacity naturally found in water. Typical buffering materials are bicarbonate, carbonate and occasionally hydroxide ions, but at a pH below 4.5, those ions are no longer present. The measured alkalinity ranges increased with increasing exposure time until day 36, where there was a gradual decline in alkalinity for all samples. This is indicative of the release of buffering materials from the actual samples, which if not one if the more typical materials can be attributed to the presence of borates, silicates, phosphates, ammonium, sulfides and organic ligands (Hem, 1985). The HACH alkalinity method is designed for the carbonate system, however, other buffers can be detected, so in these samples, the exact contributions to alkalinity are unknown and the results could be due to interference of the samples with the kit reagents.

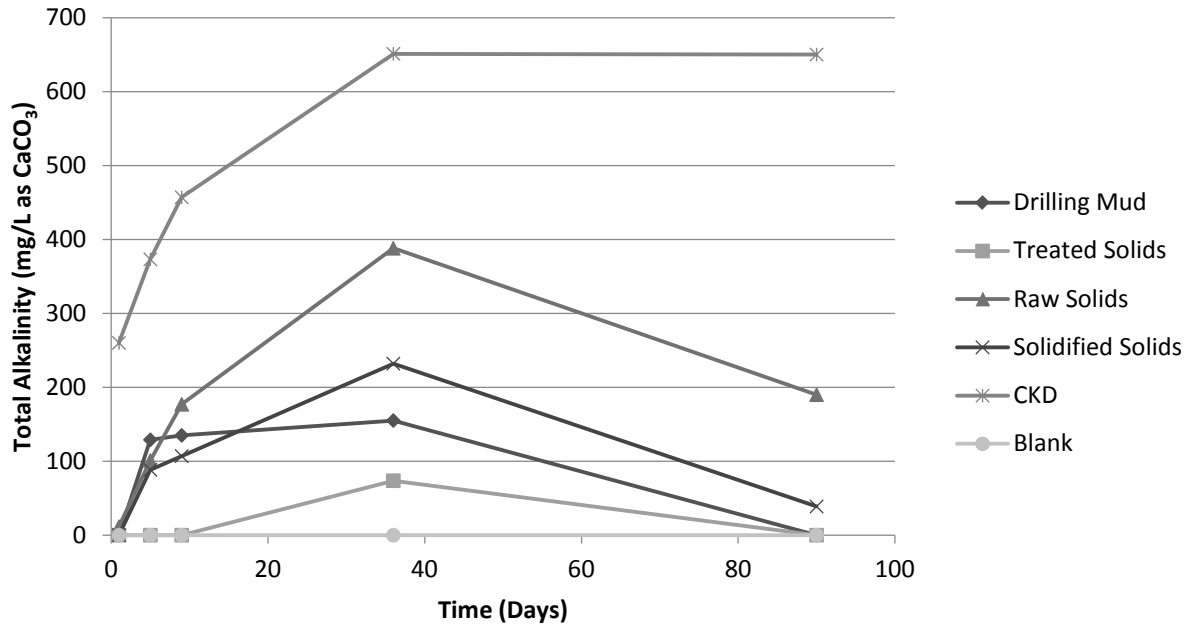


Figure 4-9: Alkalinity Data for samples Immersed in Weak Acid Extraction Fluid. Blank refers to weak acid fluid alone.

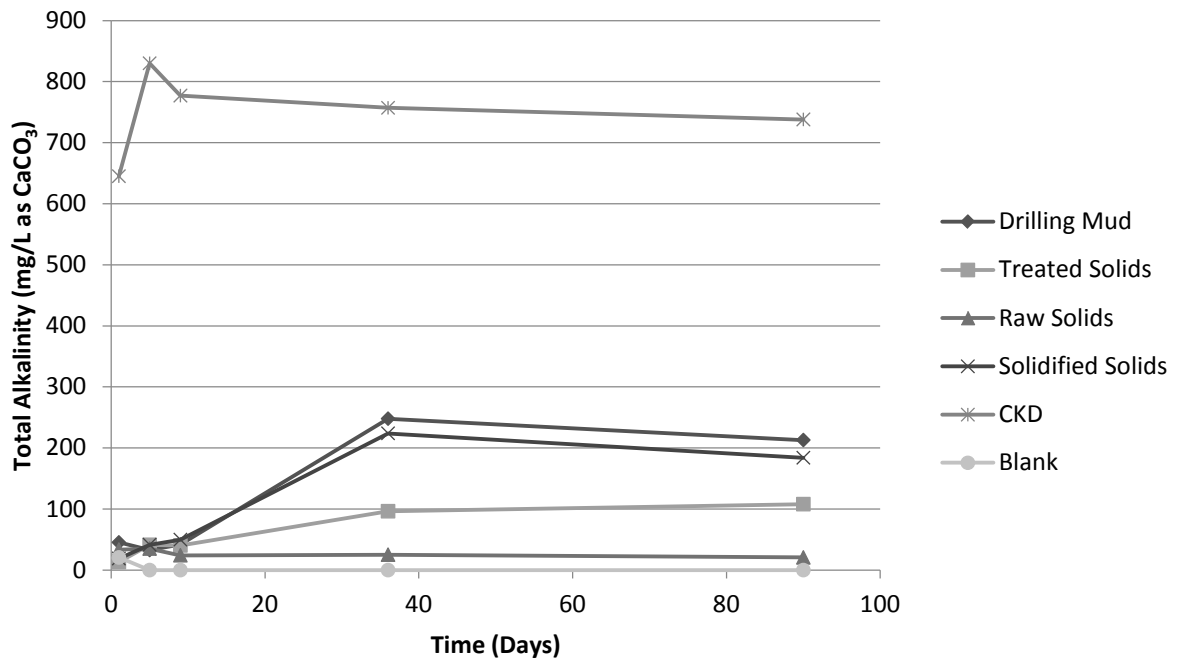


Figure 4-10: Alkalinity Data for samples Immersed in De-Ionized Water Extraction Fluid. Blank refers to deionized water alone.

4.4.4 TOC

One sample from each triplicate was chosen for TOC analysis on days spread throughout the experiment; days 0.25, 5, 16, and 90, listed in Tables 4-2 and 4-3. Raw data can be found in Appendix E - pH, Conductivity, Alkalinity, and TOC Raw Data.

Sample TOC values have been corrected by subtracting the control blank value from the sample values. This was to account for the additional carbon added to the system from the acetic acid and any carbon the samples may have absorbed through the air during equilibration. TOC contributed to the system from the weak acid extraction fluid was 1205 mg/L C, which is far greater than any contribution from the atmosphere from carbon dioxide. Following this normalization, negative values were converted to 0, and any samples in the deionized water extraction fluid measuring below 1 mg/L as C were labeled as 'Trace', and samples with TOC values below 0.05 mg/L as C were labeled 'BDL'. Weak acid extraction fluid samples with TOC values below 0.25 mg/L as C were labeled 'BDL'.

The samples with the highest TOC in the weak acid extraction fluid were collected on day five. The TOC of the leachates from the solidified solids, treated solids and CKD were 64, 117 and 206 mg/L as C, respectively. The lowest TOC values were seen in the drilling mud and the raw solids. For the most part, those samples had a TOC of 0 mg/L as C, with the only exception being from drilling mud on day 16 (102 mg/L as C), and raw solids on day one (20 mg/L as C). The CKD consistently had the highest TOC of all samples. Blank samples were not included in the graphs due to the normalization of the values.

All of the samples immersed in the deionized water had TOC values of 0 mg/L as C on day 0.25. This can be attributed to the low contact time that the samples had with water. Samples with the highest TOC values were taken from raw solids, solidified solids and treated solids on day 16. These samples contained 11.15, 12.32, and 8.24 mg/L as C, respectively. The samples with the lowest TOC were associated with CKD.

TOC on samples in the weak acetic acid extraction fluid were measured, but due to the error resulting from adjustment for the acetic acid, results were variable and therefore are not included,

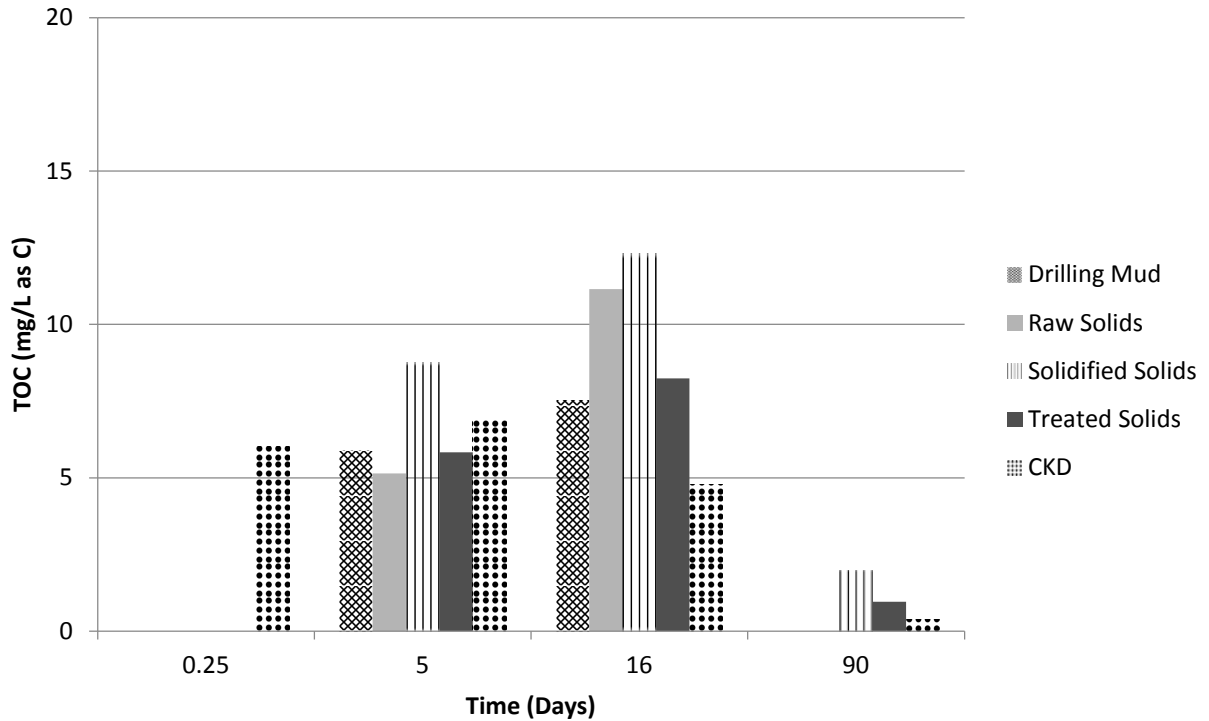


Figure 4-11: Normalized Total Organic Carbon Results for Deionized Water Extraction Fluid

4.4.5 Elemental Analysis

A compilation of all the elemental analysis data generated from the immersion has been tabulated and can be found in Appendix F - Elemental Analysis Data from Immersion Test. In addition to the tabulated results, a graphical representation of each sample and extraction fluid can be found in Figures 4-11, 4-12, 4-13, 4-14, and 4-15. In discussing the relative concentrations of each of the elements of concern, the descriptive terms located in Table 4-4 will be used.

Table 4-4: Descriptive Words Applied to Leachability Element Comparison

Description	Concentration, mg/kg
extremely high concentrations	> 10,000
High concentration	100 - 10,000
Low concentration	10 - 99
extremely low concentrations	< 10

Data analysis revealed that the elements commonly reported at the extremely high concentrations were lithium, potassium, sodium, barium, calcium, chloride, magnesium, strontium, sulfate, and bromide. All these elements are alkali metals and alkaline earth metals, with the exception of bromide, which is a halide. It is important to note that in the treated solids

and raw solids, iron and silicon were present at high concentrations, while the treated solids also had high concentrations of aluminum and manganese. All of the elements of concern leached at increased levels when exposed to the weak acid extraction fluid with the exceptions of chloride, sodium, and sulfate. These elements were extracted roughly the same in both fluids.

These observations are consistent with what was expected due to the nature of Marcellus Shale through research conducted on produced water in the play, and the chemicals used to treat the produced water. Elevated levels of barium and sulfate present in the treated solids result from the use of sodium sulfate to form a barium sulfate precipitate (Keister, 2010). Drilling mud and raw solids both contained extremely high concentrations of calcium, chloride and sodium can be attributed to the reuse of chemically treated, highly saline water for well construction and maintenance.

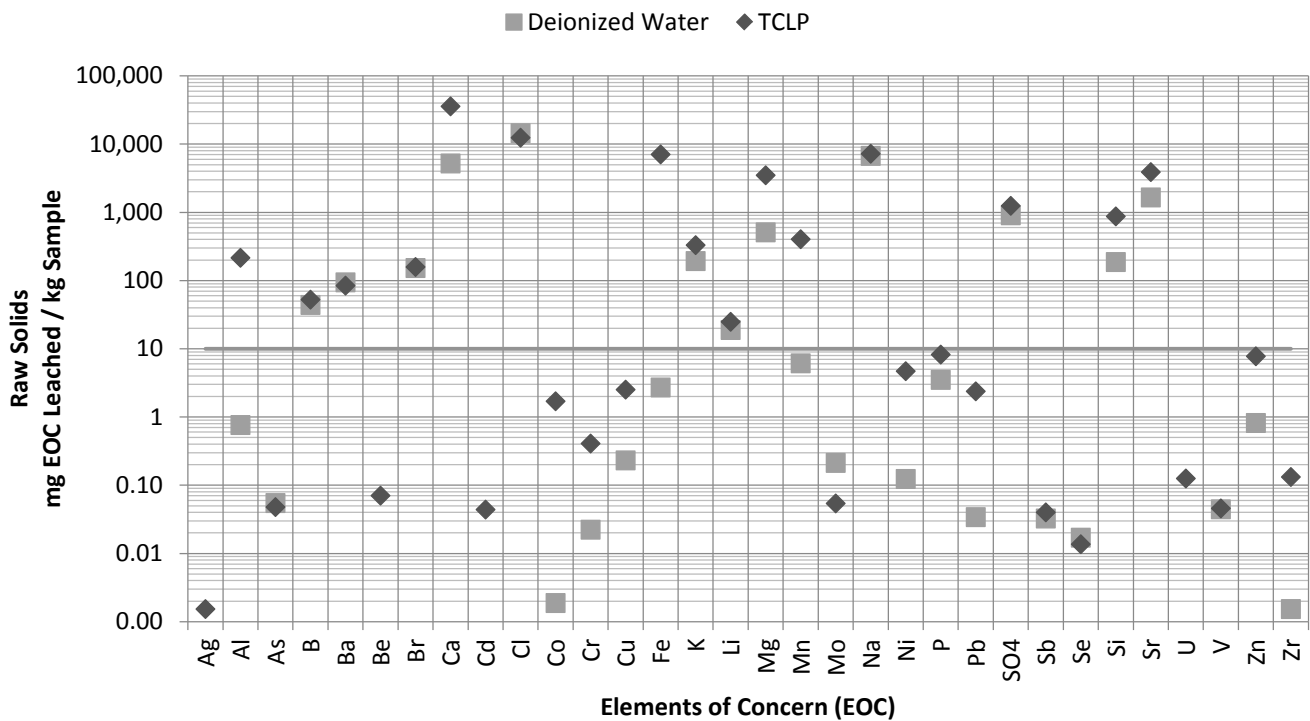


Figure 4-12: Raw Solids Leachability Results for Elements of Concern

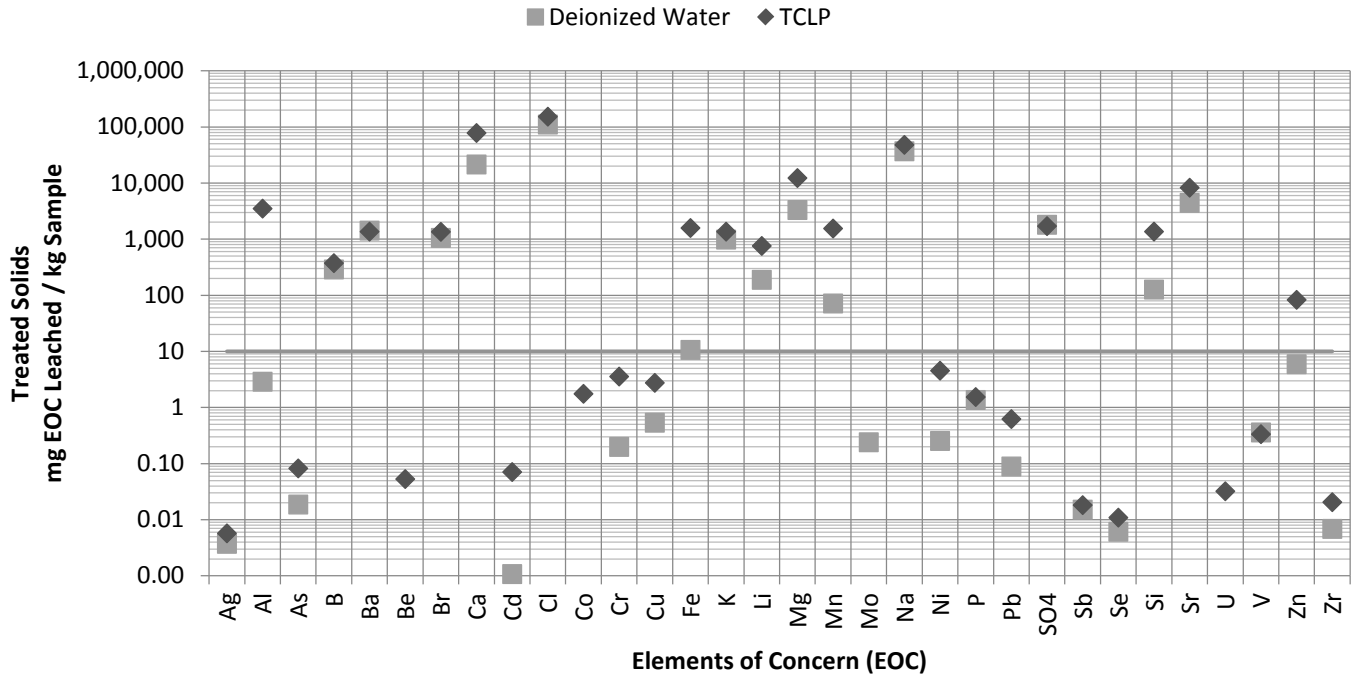


Figure 4-13: Treated Solids Leachability Results for Elements of Concern

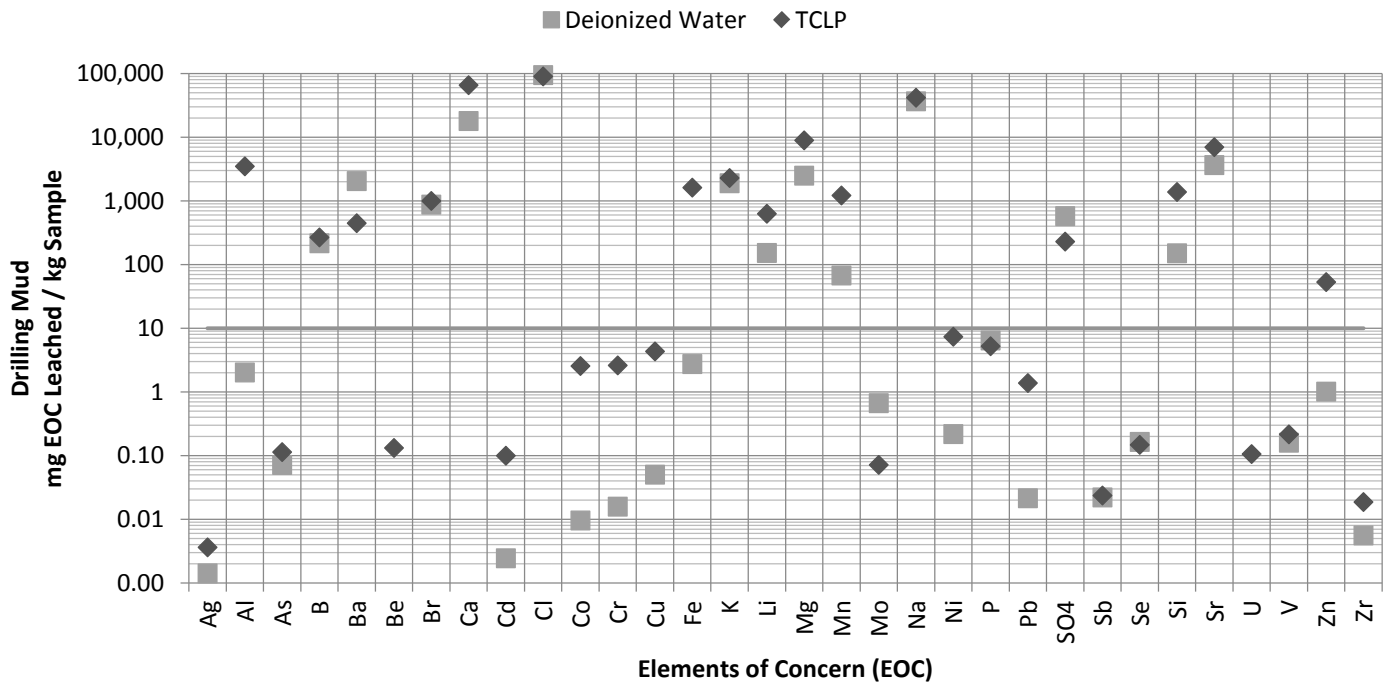


Figure 4-14: Drilling Mud Leachability Results for Elements of Concern

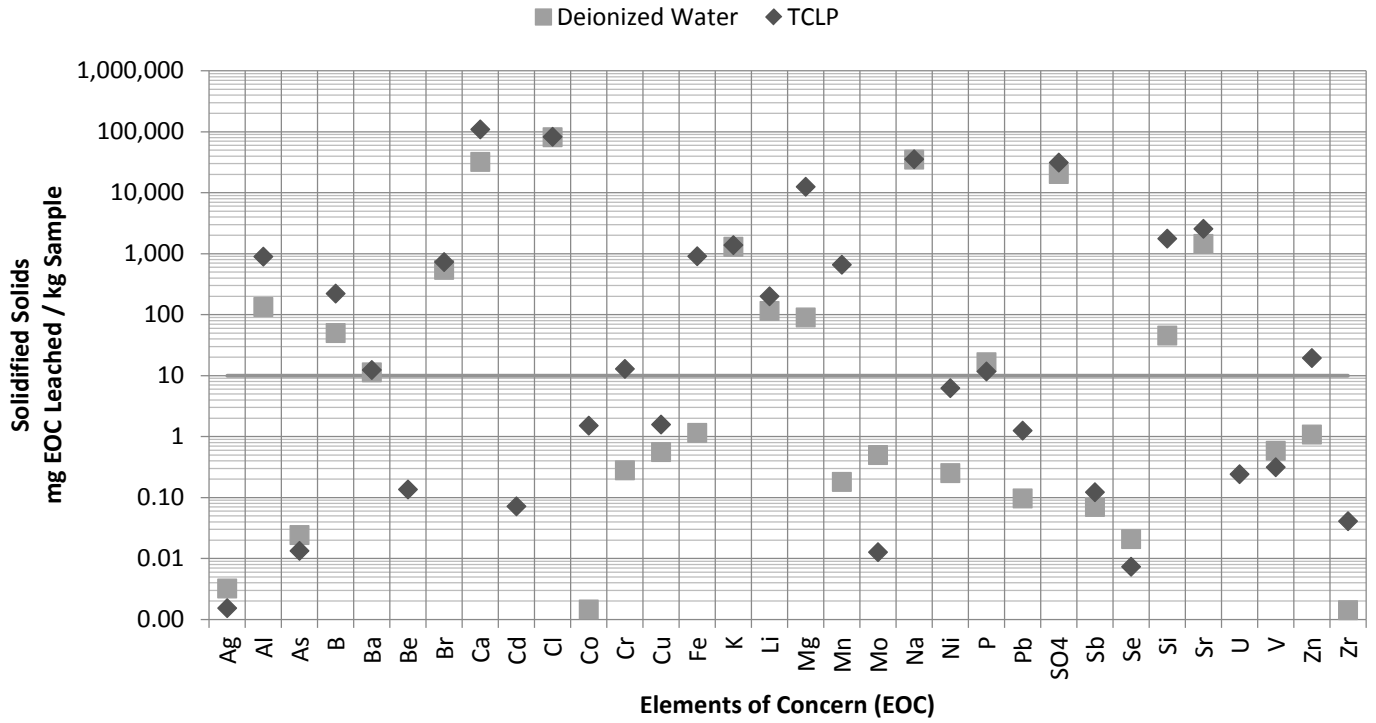


Figure 4-15: Solidified Solids Results for Elements of Concern

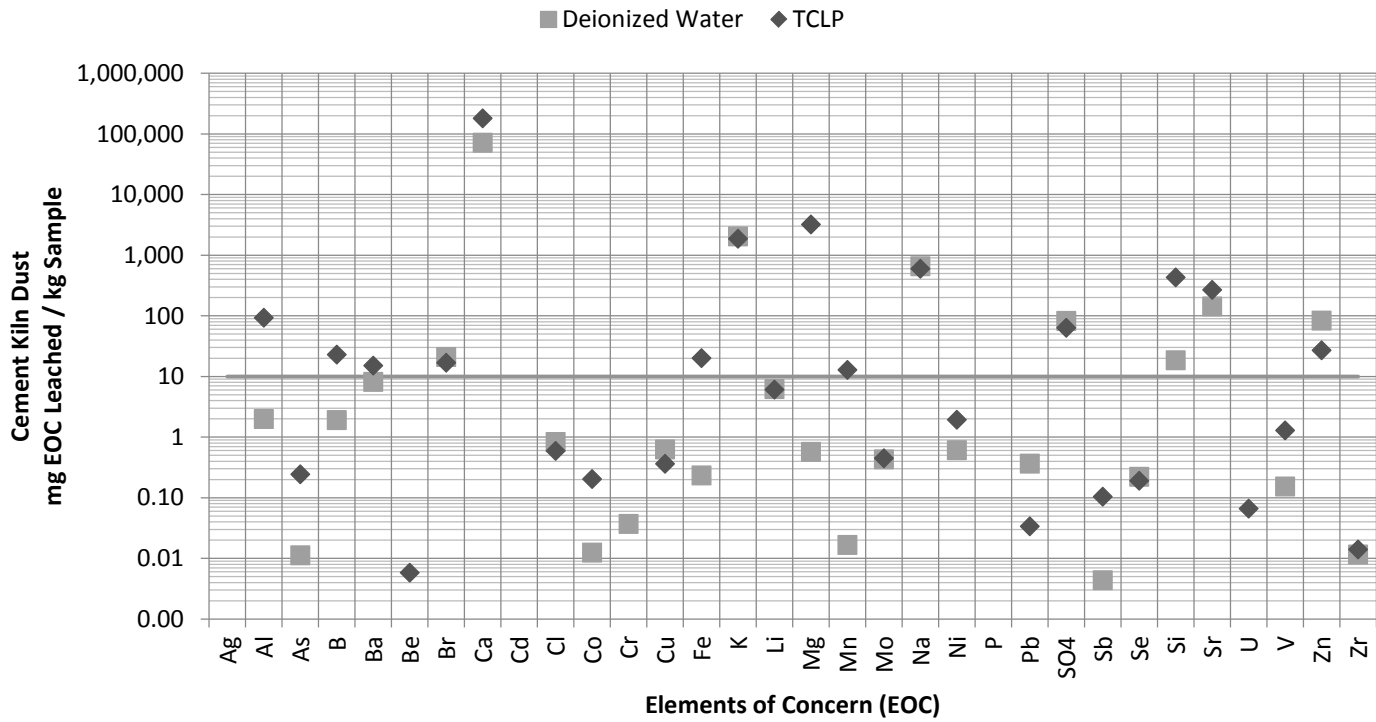


Figure 4-16: Cement Kiln Dust Results for Elements of Concern

In Tables 4-5 and 4-8, the total accumulations of elements that leached at higher concentrations throughout the 90 time period are given. The tabulated data provide a final summary of the total leachability of the elements that contributed most to the total composition of the solids.

Elements not included in the tables are: silver, arsenic, beryllium, cadmium, cobalt, chromium, copper, molybdenum, nickel, phosphorus, lead, uranium, vanadium and zirconium. These elements leached at less than 5 mg/kg in the 90 day time period.

For sodium, it was expected that the highest concentration would be found in the raw solids due to the nature of the recycled produced water, with increased salinity, for well construction and the marine nature of the shale with naturally high sodium levels. According to Haluszczak in 2013, the average sodium concentration injected into a well was 80 mg/L, while the 14 day range in flow back and produced water was 1,100 - 44,100 mg/L sodium.

Table 4-5: Total Amount of Elements of Concern Leached at High Concentrations and above in Weak Acid Extraction Fluid

Element	Concentration, (mg/kg) dry weight				
	Treated Solids	Raw Solids	Drilling Mud	Solidified Solids	CKD
Aluminum	3,510.0	216.0	3,510.0	895.0	93.4
Boron	3,74.0	52.7	269.0	222.0	23.0
Barium	1,360.0	84.7	450.0	12.4	15.2
Bromide	1,350.0	159.0	1,010.0	730.0	16.9
Calcium	78,000.0	35,900.0	66,100.0	109,000.0	181,000.0
Chloride	152,000.0	12,500.0	90,700.0	82,800.0	0.6
Iron	1,580.0	7,100.0	1,630.0	909.0	20.2
Potassium	1,360.0	332.0	2,300.0	1,380.0	1,880.0
Lithium	757.0	24.9	632.0	200.0	6.1
Magnesium	123,00.0	3,510.0	9,000.0	12,500.0	3,220.0
Manganese	1,550.0	405.0	1,230.0	659.0	12.9
Sodium	47,900.0	7,250.0	42,000.0	35,500.0	601.0
Sulfate	1,710.0	1,250.0	231.0	31,200.0	63.7
Silicon	1,360.0	876.0	1,390.0	1,770.0	432.0
Strontium	8,260.0	3,910.0	7,030.0	2,560.0	269.0
Zinc	82.9	7.8	53.5	19.4	27.1

Table 4-6: Total Amount of Elements of Concern Leached at High Concentrations and above in De-Ionized Water Extraction Fluid

Element	Concentration, (mg/kg) dry weight				
	Treated Solids	Raw Solids	Drilling Mud	Solidified Solids	CKD
Aluminum	2.9	0.8	2.0	134.0	2.0
Boron	288.0	44.1	218.0	50.0	1.9
Barium	1,420.0	94.5	2,060.0	11.3	8.2
Bromide	1,050.0	153.0	881.0	544.0	21.0
Calcium	21,400.0	5,230.0	18,100.0	32,100.0	72,000.0
Chloride	110,000.0	14,500.0	95,200.0	81,400.0	0.8
Iron	10.6	2.7	2.8	1.2	0.2
Potassium	982.0	194.0	1,910.0	1,300.0	2,050.0
Lithium	189.0	18.9	153.0	115.0	6.2
Magnesium	3,310.0	511.0	2,510.0	90.0	0.6
Manganese	71.4	6.1	67.9	0.2	0.0
Sodium	36,800.0	6,760.0	36,900.0	35,000.0	660.0
Sulfate	1,810.0	909.0	581.0	20,300.0	82.9
Silicon	126.0	188.0	151.0	45.4	18.6
Strontium	4,440.0	1,660.0	3,680.0	1,450.0	143.0
Zinc	5.9	0.8	1.0	1.1	83.8

4.5 COMPARISON OF THE EFFECT OF pH ON LEACHABILITY

To evaluate the effect of pH on elemental leachability, the 16 elements that leached the most over the 90 day time period were plotted on a scatter plot (Figure 4-17). These elements are aluminum, boron, barium, bromide, calcium chloride, iron, potassium, lithium, magnesium, manganese, sodium, sulfate, silicon, strontium and zinc. This plot enabled the visualization of the increased extraction potential provided by the weak acid.

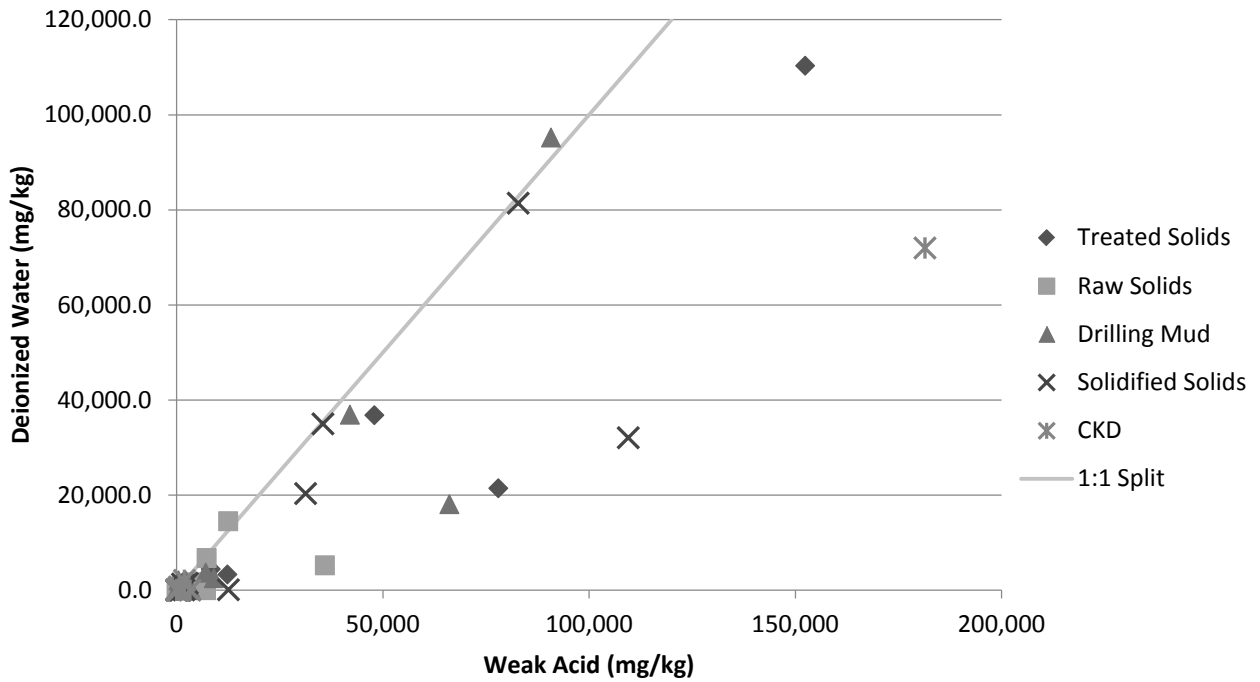


Figure 4-17: Comparison of Deionized Water Extraction Fluid to Weak Acid Extraction Fluid

Tabulated results using greater than (<), less than (>), equal to (=) signs expressing increased, decreased or equal leachability in extraction fluids can be found in Table 4-7.

Elements below 1:1 designation leached at higher concentrations in the weak acid, while elements above leached better in the deionized water. While the majority of the 16 elements plotted here are leached at higher concentrations in the weak acid, there are a few elements that leached higher in deionized water.

Important elements to note that had increased extraction in the deionized water were barium for raw solids and drilling mud; bromide for CKD; chloride for raw solids and CKD; potassium for CKD; sodium for CKD; sulfate for treated solids, drilling mud, and CKD; and zinc for CKD. Elements that leached at equal portion for both extraction fluids were: barium for treated solids; bromide for raw solids; chloride for drilling mud and solidified solids; lithium for CKD; and sodium for solidified solids.

Table 4-7: Comparison of Deionized Water Extraction Fluid to Weak Acid Extraction Fluid, > denotes that elements leached higher in weak acid, = denotes that both fluids leached the same, and < denotes that elements leached higher in deionized water

Deionized Water vs. Weak Acid Extraction (mg/kg)					
Element	Treated Solids	Raw Solids	Drilling Mud	Solidified Solids	CKD
Aluminum	>	>	>	>	>
Boron	>	>	>	>	>
Barium	=	<	<	>	>
Bromide	>	=	>	>	<
Calcium	>	>	>	>	>
Chloride	>	<	=	=	<
Iron	>	>	>	>	>
Potassium	>	>	>	>	<
Lithium	>	>	>	>	=
Magnesium	>	>	>	>	>
Manganese	>	>	>	>	>
Sodium	>	>	>	=	<
Sulfate	<	>	<	>	<
Silicon	>	>	>	>	>
Strontium	>	>	>	>	>
Zinc	>	>	>	>	<

4.6 COMPARISON OF STRONG ACID DIGESTION AND IMMERSION TEST RESULTS

Final comparative analysis of the microwave digestion experiments (from Chapter 3) and immersion test experiments (from Chapter 4) conducted on the representative hydraulic fracturing residual solid samples revealed that the majority of all elements of concern did not leach out of the samples. Strong acid microwave digestion was used to provide the total elemental composition of the tested solids and immersion tests provided the amount of each element that leached over a 90 day test period. The percent of each element removed from the solids, or leached, was calculated dividing the immersion test results by the digestion results (Equation 1). Due to the use of hydrochloric acid for strong acid digestion, chloride concentration was normalized to zero when the blanks were subtracted from the samples, therefore, this comparison for chloride is unavailable. The results are shown in Figure 4-16 and 4-17 and supporting data can be found in Appendix G: Comparison of Strong Acid Digestion and Immersion Test Results.

$$\frac{90 \text{ Day Immersion}}{\text{Strong Acid Digestion}} * 100 = \text{Percent Element Leached}$$

In the weak acid extraction fluid, elements such as boron, bromide, calcium, lithium, magnesium, manganese, sodium, sulfate, silicon and strontium leached the most over 90 days, with leached percentage levels above 80% of the total environmentally available composition. Silicon and sulfate leached at levels above 1000%, this can be related to poor representation from microwave digestion. According to EPA Method 3051A, the use of nitric and hydrochloric acid provides a near total digestion. For silicon, the digestion temperature exceeds the experimentally attained temperature correlating to inaccurate digestion results.

Elements that leached less than 10% in the weak acid extraction fluid were aluminum, barium, chromium, copper, iron, phosphorus, lead, antimony, selenium, uranium, and vanadium. Elements that leached less than 1% were arsenic, barium, molybdenum, and zirconium. For all 32 elements of concern, with the exception of barium, potassium, antimony, silicon, and zinc, cement kiln dust leached the least. Elements with the largest variance between sample types were aluminum, beryllium, potassium, lithium and magnesium.

In the deionized water extraction fluid, only three elements leached at or above 100%. These elements were bromide, sulfate and silicon. Elements that leached at or above 50% were boron and sodium. The majority of the elements leached below 10%. For all 32 elements of concern, with the exception of copper, potassium, lithium, molybdenum and zinc, cement kiln dust leached the least. Notable exceptions with the highest sample variation were boron, barium, lithium, magnesium and strontium.

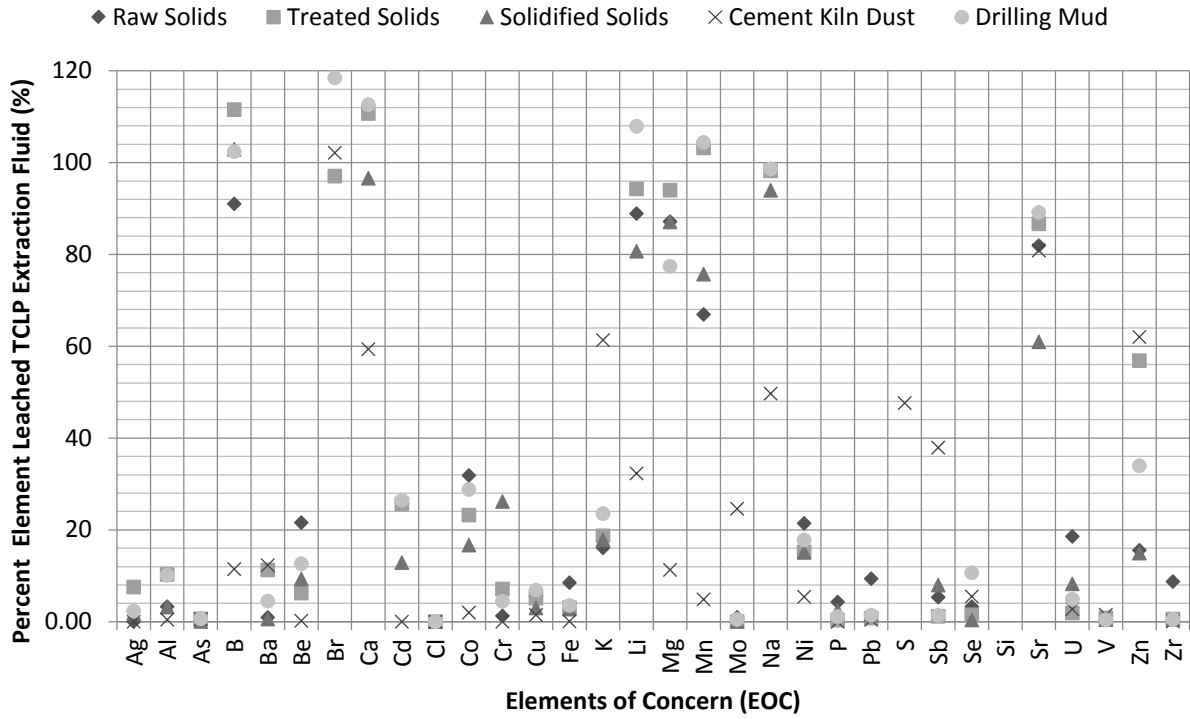


Figure 4-18: Direct Comparison of Microwave Digestion to Weak Acid Immersion Results

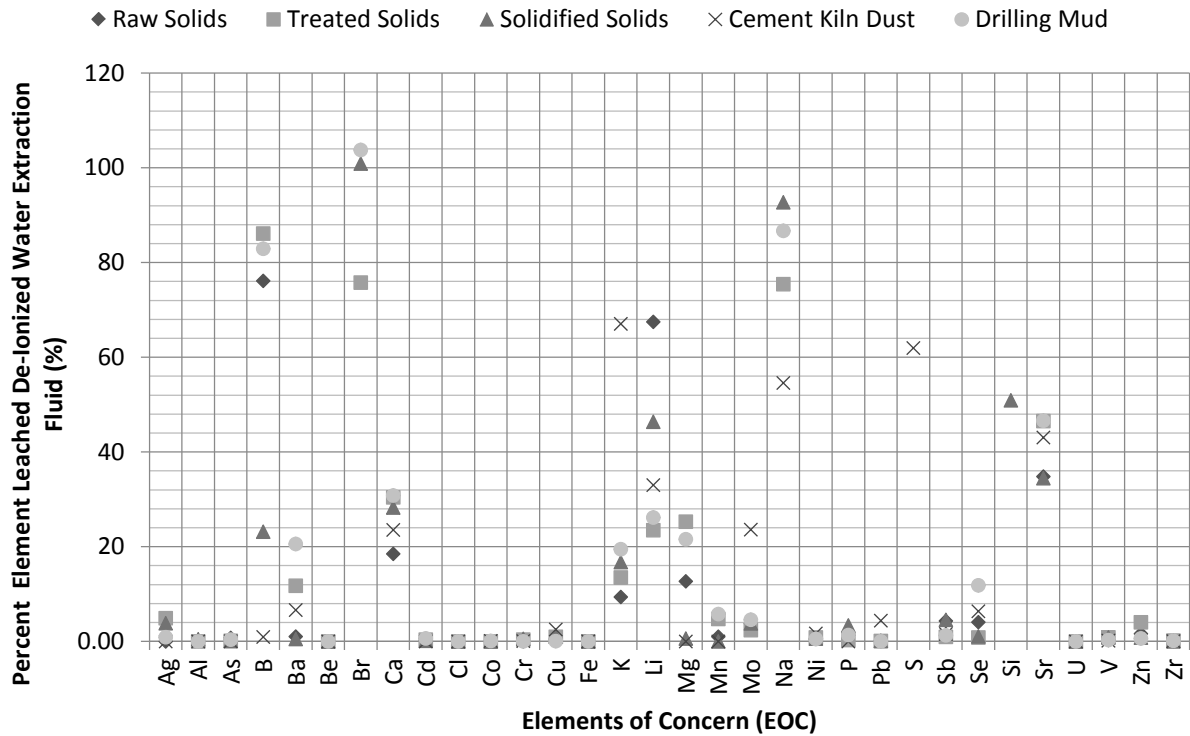


Figure 4-19: Direct Comparison of Microwave Digestion to DI-Water Immersion Results

4.7 REGULATORY LIMITS

The elemental concentrations quantified for each sample in each extraction fluid were compared to the TCLP regulatory limit for hazardous waste classification established by the EPA in 1984 along with national drinking water standards. While the TCLP method uses a tumbler apparatus for increased extraction, and this study did not, values were compared for reference purposes only.

Treated solids in both extraction fluids exceeded the TCLP regulatory limit of 100,000 ppb for barium, along with drilling mud exposed to de-ionized water. The treated solid samples, extracted with weak acid buffer, contained 118,100 ppb Ba and deionized water contained 123,300 ppb Ba; while drilling mud in deionized water contained 178,900 ppb Ba.

Comparing the residual solids to the National Drinking Water Standards, Tables 4-7 and 4-8, treated solids, raw solids and drilling mud in both deionized water and weak acid solution exceeded the regulated limit of 2,000 ppb for barium. All residual solids samples, with the exception of CKD, exceeded the drinking water limit of 4 ppb for beryllium and 15 ppb for lead when exposed to weak acid solution. Chromium levels of 100 ppb were exceeded for treated solids, drilling mud and solidified solids when exposed to weak acid solution. In deionized water, the drinking water for lead was exceeded by CKD only.

Further tests, like TCLP, should be conducted on the solids to confirm the solids are compliant with regulatory limits.

Table 4-8: Maximum Observed Elemental Composition of Residual Solids in Weak Acid Solution Compared to National Drinking Water Standards (NDWS) and TCLP Hazardous Waste Characterization (ppb); samples above NDWS are italicized, samples above TCLP Limit are bolded

National Drinking Water Standards and TCLP Hazardous Waste Characterization, ppb							
EOC	NDWS	TCLP LIMIT	Treated Solids	Raw Solids	Drilling Mud	Solidified Solids	CKD
Barium	2,000	100,000	<i>118,175</i>	<i>7,348</i>	<i>39,036</i>	1,074	1,316
Beryllium	4	-	<i>4.61</i>	<i>6.13</i>	<i>11.52</i>	<i>11.79</i>	0.51
Uranium	30	-	<i>2.79</i>	10.94	9.24	20.98	5.77
Chromium	100	5,000	<i>309</i>	35.58	228	<i>1,120</i>	0.00
Silver	100	5,000	0.50	0.13	0.32	0.13	0.00
Copper	1,300	-	239	219	378	137	31.64
Cadmium	5	1,000	<i>6.15</i>	3.83	<i>8.71</i>	<i>6.23</i>	0.00
Lead	15	5,000	<i>54.03</i>	<i>207</i>	<i>120</i>	<i>109</i>	2.95
Arsenic	10	5,000	7.13	4.17	9.92	1.16	<i>21.25</i>
Antimony	6	-	1.58	3.49	2.06	<i>10.63</i>	<i>9.08</i>
Selenium	50	1,000	0.95	1.19	12.89	0.64	16.62

Table 4-9: Maximum Observed Elemental Composition of Residual Solids in Deionized Water Compared to National Drinking Water Standards (NDWS) and TCLP Hazardous Waste Characterization (ppb) samples above NDWS are italicized, samples above TCLP Limit are bolded

National Drinking Water Standards and TCLP Hazardous Waste Characterization, ppb							
EOC	NDWS	TCLP LIMIT	Treated Solids	Raw Solids	Drilling Mud	Solidified Solids	CKD
Barium	2,000	100,000	<i>123,347</i>	<i>8,205</i>	<i>178,907</i>	983	711
Beryllium	4	-	0.00	0.01	0.01	0.00	0.00
Uranium	30	-	0.00	0.02	0.00	0.00	0.00
Chromium	100	5,000	17.24	1.94	1.38	24.29	3.23
Silver	100	5,000	0.32	0.01	0.12	0.28	0.00
Copper	1,300	-	46.53	20.15	4.39	48.43	54.69
Cadmium	5	1,000	0.09	0.03	0.21	0.07	0.00
Lead	15	5,000	<i>7.71</i>	<i>2.97</i>	<i>1.87</i>	<i>8.40</i>	<i>31.86</i>
Arsenic	10	5,000	1.62	4.77	6.23	2.11	0.98
Antimony	6	-	1.31	2.83	1.93	6.10	0.38
Selenium	50	1,000	0.53	1.48	14.35	1.81	19.31

4.8 CONCLUSIONS

The weak acid extraction fluid is a weak acetic acid solution, with an initial pH of 2.88. Within a matter of hours, the samples equilibrated to a less acidic pH, ranging from 4-5, with the exception of CKD. For CKD immersed in the weak acid fluid, the pH normalized to 5 for the first 16 days, then increased to 11 for 48 days before dropping to 7 at day 90. Because the extraction fluids were periodically replaced, the fluctuations in pH values over the duration of the experiment for the CKD could be attributed to a removal of the buffering capacity of the solid, or a chemical change in the solid creating a proton sink.

Conductivity readings were the highest initially and then decreased rapidly as the first few samples were replenished, stabilizing between 1 and 4.5 mS/cm, with the exception of CKD which stabilized at 7.5 mS/cm.

Alkalinity on day 36 was the highest for all samples, and decreased throughout the duration of the test. The alkalinity of the CKD increased steadily, peaked at day 36 and maintained an alkalinity of 650 mg/L CaCO₃ for the duration of the experiment.

According to Standard Methods D3987, Extraction of Solid Waste with Water, the use of deionized water as a leaching solution allows the waste to define the final pH. All the samples fluctuated in pH over the initial time periods. The buffering capacity supplied by the samples took approximately 9 days to equilibrate to a neutral pH range of 7-8. CKD liquids maintained a pH of 11.5 after 6 hours.

Conductivity data for all samples followed a similar trend to that seen with the weak acid extraction fluid, where the highest conductivity was observed in the initial replenishment samples, which then decreased and maintained conductivity levels below 2 mS/cm from day 5 to replenishment on day 90. CKD extracts had the highest conductivity at day 36 and slowly decreased to 3.5 mS/cm on the final day.

Alkalinity data correlated to trends noted in pH for deionized water extraction fluid. CKD had the highest amount of alkalinity ranging from 830 mg/L CaCO₃ at its peak on day 5, followed by a gradual decrease to an alkalinity of 738 mg/L CaCO₃ at 90 days. All other samples had peak alkalinities on day 36 and maintained alkalinities from 21 mg/L CaCO₃ in solidified solids to 213 mg/L CaCO₃ in drilling mud.

Of the 32 elements of concern tested, the elements in the alkali and alkaline earth metal families were present in leachates for both extraction fluids at the highest amounts, along with sulfate and barium. This was expected because these are the elements that are commonly found in Marcellus Shale and would therefore be expected to be in produced water from that region.

The elements of concern found in the leachates from both extraction fluids was similar for the treated solids, raw solids and drilling mud. The difference between each of the samples tested was minimal for the majority of the elements in both extraction fluids. However, the exceptions were aluminum and iron, where concentrations were much greater in the weak acid extraction fluid than the deionized water extraction fluid.

Comparatively, based on the initial assumption that strong acid digestion provided the total available composition of each of the samples, following immersion for 90 days, neither extraction fluid had significant amounts of elements leach completely. This assumption has been proven inaccurate for some elements by their extraction of over 1000%. These elements are bromide, sulfate and silicon. According to EPA Method 3051A, the use of nitric and hydrochloric acid provides a near total digestion, but the digestion temperature of 175 °C was too low for silicon and sulfate digestion correlating to inaccurate digestion results, while bromide is not on the extraction/dissolution list for EPA Method 3051A, refer to Table 3-2: Approved Elements for Quantification with EPA Method 3051A using 3:1 Nitric and Hydrochloric Acids. However, that being said, for both extraction fluids, boron, lithium, sodium and strontium leached at the highest percentages.

For the weak acid extraction fluid for boron, extraction percentages from highest to lowest are: treated solids, solidified solids, drilling mud, raw solids and CKD with corresponding values of 112, 103, 102, 91 and 11.5%. Lithium from highest to lowest are: drilling mud, treated solids, raw solids, solidified solids and CKD with corresponding values of 108, 94, 89, 81, and 32%. Sodium from highest to lowest are: raw solids, drilling mud, treated solids, solidified solids and CKD with corresponding values of 147, 99, 98, 94 and 50%. Strontium from highest to lowest are: drilling mud, treated solids, raw solids, CKD and solidified solids with corresponding values of 89, 87, 82, 81 and 61%.

For the deionized water extraction fluid for boron, extraction percentages from highest to lowest are: treated solids, drilling mud, raw solids, solidified solids, and CKD with corresponding values of 86, 83, 76, 23, and 1%. Lithium from highest to lowest are: raw solids, solidified solids, CKD, drilling mud, and treated solids with corresponding values of 67.5, 46, 33, 26, and 24%. Sodium from highest to lowest are: raw solids, solidified solids, drilling mud, treated solids, and CKD with corresponding values of 137, 93, 87, 75, and 55%. Strontium from highest to lowest are: drilling mud, treated solids, CKD, raw solids, and solidified solids with corresponding values of 47, 47, 43, 35, and 35%.

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CHAPTER 5: SUMMARY AND ENGINEERING SIGNIFICANCE

The strong acid digestion results of this study are similar to those results obtained previously in our lab by Stephanie Countess. Results are tabulated in Table 5-1. While both assays were performed using EPA Method 3015A, with a 3:1 mixture of nitric and hydrochloric acids and a Mars6 microwave unit, previous digestions were conducted in glass vessels, whereas Teflon vessels were used in this study.

The following elements were quantified at higher levels using glass vessels: aluminum, boron, bromide, calcium, iron, potassium, lithium, magnesium, manganese, molybdenum, lead, selenium, silicon and vanadium.

The following elements were quantified at lower levels using glass vessels: arsenic, barium, chromium, copper, phosphorus, sulfate, antimony and strontium. The elements that were similar and quantification were: silver, beryllium, cadmium, sodium, nickel, uranium, zinc and zirconium.

Normalized standard deviation was calculated to evaluate digestion consistency between vessel types for the same digestion method, see Table 5-2. Normalized standard deviation is calculated by dividing the standard deviation by the average value of the results for each vessel. When the normalized standard deviation value is large, it represents a high variance, values above 0.5 represent a large standard deviation, while a value above 1.0 reveals, of course, that the standard deviation was larger than the average value. Values determined as “Trace” were converted to zero for this comparison. Samples with the highest variation were the raw solids and the treated solids. The reason for this variance could be attributed to the development of new wells, resulting in elevated levels of silicon, aluminum, and boron, along with variances in digestion efficacy, with the Teflon vessels providing enhanced digestion.

Table 5-1: Comparison Between 2013 and 2014 using EPA Method 3051A Microwave Strong Acid Digestion (mg/kg dry weight)

Mg/kg dry weight								
Element	Glass Vessels				Teflon Vessels			
	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids
Silver	0.6	0.2	0.3	0.7	0.2	0.0	0.1	0.1
Aluminum	15,314.00	11,436.00	14,935.00	11,912.00	34,719.00	6,598.00	34,068.00	28,137.00
Arsenic	74.5	21.9	21.4	28.8	18.1	7.2	13.2	25.9
Boron	41.4	95	107.5	50.7	262.6	57.9	334.9	215.5
Barium	10,924.00	33,495.00	50,041.00	9,461.00	10,011.00	9,077.00	12,076.00	2,156.00
Beryllium	1.2	0.9	0.6	1.1	1.1	0.3	0.9	1.5
Bromide	0	351.4	550.3	0	848.7	72.5	1,391.0	538.8
Calcium	22,030.00	40,303.00	33,179.00	51,081.00	58,695.00	28,250.00	70,432.00	113,340.00
Cadmium	1.4	Trace	Trace	1.2	0.4	0.2	0.3	0.6
Chromium	50.2	33.4	36.5	32	8.9	5.4	7.5	9.1
Cobalt	11.5	13	7.7	9.2	59.1	32.4	50.0	49.3
Copper	88.6	44.1	32.3	74.9	63.4	45.3	53.9	52.7
Iron	21,962.00	21,832.00	27,196.00	18,120.00	46,181.00	83,518.00	51,716.00	33,179.00
Potassium	6,085.00	3,136.00	5,046.00	3,960.00	9,789.00	2,062.00	7,271.00	7,761.00
Lithium	31.7	103.2	330.5	18.6	585.8	28.1	803.1	248.0
Magnesium	3,953.00	8,586.00	3,949.00	5,348.00	11,620.00	4,024.00	13,071.00	14,395.00
Manganese	710.4	856.1	433.6	1,392.00	1,174.00	605.7	1,500.00	871.0
Molybdenum	48	Trace	Trace	Trace	14.6	5.6	10.0	13.0
Sodium	47,029.00	22,895.00	30,821.00	46,843.00	42,574.00	4,916.00	48,792.00	37,727.00
Nickel	68.8	32.1	24.8	40.2	41.6	22.0	29.8	41.3
Lead	224.5	45.3	56.5	277.3	475.4	192.2	440.6	487.6
Phosphorus	311.2	281.9	189.1	253.2	98.6	25.5	80.3	86.2
Sulfate	39,495.00	16,965.00	24,918.00	64,047.00	21.5	16.4	16.2	80.1
Antimony	9.8	2.5	3.3	9.9	1.7	0.8	1.5	1.5
Strontium	5,920.00	5,034.00	10,201.00	24,621.00	1.4	0.4	0.7	1.9
Selenium	Trace	Trace	Trace	Trace	122.4	31.9	86.5	89.2
Silicon	562.7	471.7	491	292.1	7,885.00	4,767.00	9,532.00	4,202.00
Uranium	7.7	2.4	1.8	2.9	2.2	0.7	1.7	2.9
Vanadium	47.4	0	0	31.9	52.8	13.7	41.2	67.8
Zinc	178.9	120.1	148.3	177.8	157.4	50.1	145.8	130.1
Zirconium	4.7	12	4.9	5.3	3.9	1.5	3.6	7.6

Table 5-2: Normalized Standard Deviation between Glass and Teflon Vessels for Microwave Strong Acid Digestion

Element	Glass vs. Teflon Vessels Normalized Standard Deviation			
	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids
Silver	0.71	1.41	0.71	1.06
Aluminum	0.55	0.38	0.55	0.57
Arsenic	0.86	0.71	0.34	0.07
Boron	1.03	0.34	0.73	0.88
Barium	0.06	0.81	0.86	0.89
Beryllium	0.06	0.71	0.28	0.22
Bromide	1.41	0.93	0.61	1.41
Calcium	0.64	0.25	0.51	0.54
Cadmium	0.79	1.41	1.41	0.47
Chromium	0.99	1.02	0.93	0.79
Cobalt	0.95	0.60	1.04	0.97
Copper	0.23	0.02	0.35	0.25
Iron	0.50	0.83	0.44	0.42
Potassium	0.33	0.29	0.26	0.46
Lithium	1.27	0.81	0.59	1.22
Magnesium	0.70	0.51	0.76	0.65
Manganese	0.35	0.24	0.78	0.33
Molybdenum	0.75	1.41	1.41	1.41
Sodium	0.07	0.91	0.32	0.15
Nickel	0.35	0.26	0.13	0.02
Lead	0.51	0.87	1.09	0.39
Phosphorus	0.73	1.18	0.57	0.70
Sulfate	1.41	1.41	1.41	1.41
Antimony	1.00	0.73	0.53	1.04
Strontium	1.41	1.41	1.41	1.41
Selenium	1.41	1.41	1.41	1.41
Silicon	1.23	1.16	1.28	1.23
Uranium	0.79	0.78	0.04	0.00
Vanadium	0.08	1.41	1.41	0.51
Zinc	0.09	0.58	0.01	0.22
Zirconium	0.13	1.10	0.22	0.25

As the United States continues to search for more economical methods for energy independence, hydraulic fracturing will play a vital role by providing adequate natural gas to meet the national need. It is crucial that information regarding industry’s knowledge and practices, technological advances, and environmental impacts are publically available to maintain the support of the public.

This research is relevant and useful to leaders in the energy industry because it relays important information about the chemical compositions of each of the types of residual solids

generated by hydraulic fracturing. The information presented in this research will hopefully assist in the development of better management practices for residual solid wastes, which will minimize environmental impacts. The comparative results indicate that leaching behaviors under best and worst case scenarios are similar. As hydraulic fracturing continues to increase in the United States, proper management and disposal of generated wastes are vital.

CHAPTER 6: DISCLAIMER

As part of the National Energy Technology Laboratory's Regional University Alliance (NETL-RUA), this technical effort was performed under the RES contract DEFE0004000. Neither the United States Government nor any agency thereof, nor any of their employees, nor URS Energy & Construction, Inc., nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

APPENDICIES

APPENDIX A - STANDARD SOLUTIONS

The elemental compositions for standard solutions used in this experiment are provided below. These solutions were prepared by High Purity Standards in Charleston, SC.

Table A-1: Calibration Solution Limits for Standard A and C

Standard A:

Element	Concentration mg/L
Calcium	100
Iron	100
Magnesium	100
Potassium	100
Sodium	100
Chloride	100
Aluminum	10
Barium	10
Boron	10
Cadmium	10
Chromium	10
Cobalt	10
Copper	10
Lead	10
Lithium	10
Manganese	10
Molybdenum	10
Nickel	10
Phosphorus	10
Silicon	10
Silver	10
Strontium	10
Uranium	10
Vanadium	10
Zinc	10
Antimony	0.1
Arsenic	0.1
Beryllium	0.1
Selenium	0.1
Zirconium	0.1

Standard C:

Element	Concentration mg/L
Bromide	10
Chloride	100
Sulfate	100

APPENDIX B – ANALYTICAL LIMITS FOR ICP-MS ANALYSIS

MDL - Method Detection Limit – the minimum value reported that indicates with 99% confidence the element is present in the sample

MRL - Method Reporting Level – the minimum value that can be claimed with 99% confidence as the actual concentration in the sample

Table B-1: EPA Guidelines for ICP-MS MRL and MDL

Element	Isotope	MDL(ppb)	MRL (ppb)
Aluminum	27Al	0.07	1
Antimony	121Sb	0.02	0.1
Arsenic	75As	0.07	0.5
Barium	137Ba	0.92	50
Beryllium	9Be	0.10	0.5
Boron	11B	0.60	10
Bromide	79Br	2.11	20
Cadmium	111Cd	0.09	1
Calcium	43Ca	12.19	50
Chloride	35Cl	29.75	200
Chromium	52Cr	0.11	1
Cobalt	59Co	0.02	0.1
Copper	65Cu	0.19	1
Iron	54Fe	0.79	10
Lead	208Pb	0.03	1
Lithium	7Li	0.13	10
Magnesium	25Mg	0.82	10
Manganese	55Mn	0.05	1
Mercury	202Hg	0.1	0.5
Molybdenum	98Mo	1.85	50
Nickel	60Ni	0.03	0.1
Phosphorus	31P	3.02	50
Potassium	39K	4.54	100
Selenium	78Se	0.67	5
Silicon	28Si	0.75	10
Silver	107Ag	0.02	0.1
Sodium	23Na	10.92	100
Strontium	88Sr	0.24	10
Sulfate	34S	392.27	1000
Uranium	238U	0.01	0.05
Vanadium	51V	0.32	10
Zinc	66Zn	0.38	10
Zirconium	90Zr	0.04	0.5

APPENDIX C - STRONG ACID DIGESTION ANALYSIS

The results from the strong acid digestion of solid samples are provided in this appendix following EPA Method 3051A. If the average adjusted concentration from ICP-MS analysis had a value above the detection limit but below the method reporting level, the composition was set as “Trace”.

Table C-1: Total Elemental Composition of Residual Solid Samples following Strong Acid Digestion (mg/kg)

Element	Solid Samples mg/kg dry weight				
	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	Cement Kiln Dust
Silver	0.16	Trace	0.08	0.08	Trace
Aluminum	34,718.79	6,598.17	34,067.96	28,137.35	21,041.94
Arsenic	18.07	7.18	13.22	25.88	42.78
Boron	262.60	57.93	334.92	215.51	201.06
Barium	10,010.90	9,077.10	12,076.40	2,154.57	123.38
Beryllium	1.05	0.33	0.85	1.46	2.89
Bromide	848.66	72.54	1,391.00	538.79	16.57
Calcium	58,695.20	28,250.12	70,431.71	113,340.41	305,568.73
Cadmium	0.38	0.17	0.28	0.56	0.29
Chloride	Trace	Trace	Trace	Trace	Trace
Cobalt	8.92	5.36	7.55	9.07	10.35
Chromium	59.11	32.45	50.00	49.26	45.65
Copper	63.37	45.26	53.92	52.74	24.81
Iron	46,180.80	83,517.59	51,715.64	33,179.12	29,305.07
Potassium	9,789.46	2,061.64	7,271.30	7,761.24	3,057.96
Lithium	585.75	28.06	803.09	248.02	18.87
Magnesium	11,620.44	4,023.80	13,071.16	14,395.43	28,571.32
Manganese	1,173.91	605.68	1,499.77	871.00	265.75
Molybdenum	14.60	5.65	10.04	13.03	1.83
Sodium	42,574.22	4,915.80	48,791.78	37,726.53	1,208.73
Nickel	41.60	21.99	29.84	41.28	35.90
Phosphorus	475.38	192.21	440.65	487.56	567.23
Lead	98.56	25.49	80.28	86.16	8.34
Sulfate	21.45	16.38	16.19	80.10	133.78
Antimony	1.71	0.75	1.55	1.54	0.28
Selenium	1.39	0.42	0.73	1.95	3.49
Silicon	122.40	31.91	86.45	89.23	12.78
Strontium	7,885.41	4,767.81	9,532.10	4,202.33	332.93
Uranium	2.17	0.68	1.69	2.93	2.43
Vanadium	52.83	13.73	41.22	67.81	87.49
Zinc	157.40	50.09	145.82	130.10	43.74
Zirconium	3.86	1.52	3.62	7.56	19.19

APPENDIX D - LEACHABILITY LOSSES

The results of total mass lost following sample immersion for 90 days. Includes 100g dried solid sample, muslin cloth and tea mesh ball. Where DM = drilling mud, TS = treated solids, RS = raw solids, SS = solidified solids, CKD = Cement kiln dust and numbers 1, 2, 3 denote replicates and 4, 5 and 6 are de-ionized water replicated for the cement kiln dust.

Table D-1: Initial and Final weights for Weak Acid Extraction Fluid, Replicates 1 and 2; Deionized water CKD replicate 1 and 2

Sample Name	Starting Weight (g)	Final Weight (g)	Percent Mass Lost (%)
CKD1	133.2	119.1	11%
CKD2	132.5	118.7	10%
CKD3	132.2	130.2	2%
CKD4	132.0	130.5	1%
DM1	132.9	101.2	24%
DM2	133.2	101.7	24%
TS1	132.6	95.2	28%
TS2	131.6	93.3	29%
RS1	130.9	119.4	9%
RS2	131.9	119.1	10%
SS1	131.0	95.4	27%
SS2	130.7	96.8	26%

Table D-2: Initial and Final weights for Weak Acid Extraction Fluid, Replicate 3

Sample Name	Starting Weight (g)	Final Weight (g)	Percent Mass Lost (%)
CKD2.5	131.0	118.8	9%
CKD5	131.7	129.8	1%
DM3	132.7	101.6	23%
TS3	131.5	95.6	27%
RS3	132.0	120.1	9%
SS3	131.8	95.3	28%
Blank 1	32.2	31.9	1%
Blank 2	32.3	32.1	1%
Blank 3	32.4	32.2	1%

Table D-3: Initial and Final weights for De-Ionized water extraction fluid, all replicates

Sample Name	Starting Weight (g)	Final Weight (g)	Percent Mass Lost (%)
DM10	128.0	107.0	16%
DM11	129.1	108.1	16%
DM12	128.2	106.9	17%
TS10	129.5	103.6	20%
TS11	129.1	104.1	19%
TS12	128.9	103.5	20%
RS10	131.8	126.9	4%
RS11	132.0	127.4	3%
RS12	131.6	127.1	3%
SS10	131.4	111.4	15%
SS11	131.5	111.6	15%
SS12	131.5	111.3	15%
Blank10	32.3	32.0	1%
Blank11	32.4	32.1	1%
Blank12	32.3	31.9	1%

APPENDIX E - pH, CONDUCTIVITY, ALKALINITY, AND TOC RAW DATA

Table E-1: Averaged pH Data for Weak Acid Extraction Fluid

Sample Name	0.25	1	2.25	5	9	16	36	64	90
CKD	4.29	4.73	4.56	4.82	4.76	4.95	10.94	11.15	6.56
Drilling Mud	3.97	4.12	4.32	4.39	4.28	4.14	4.2	4.03	3.97
Treated Solids	3.91	4.04	4.08	4.28	4.21	4.17	4.41	4.52	4.37
Raw Solids	3.54	3.99	3.92	3.96	3.90	3.88	4.13	4.1	4.14
Solidified Solids	4.09	4.17	4.09	4.34	4.3	4.36	4.7	4.75	4.6
Blank	3.15	3.32	3.10	3.04	3.01	2.97	3.07	3.02	3.35

Table E-2: Averaged pH Data for Deionized Water Extraction Fluid

Sample Name	0.25	1	2.25	5	9	16	36	65	90
CKD	11.23	11.47	11.72	11.47	11.68	11.69	11.72	11.68	11.46
Drilling Mud	5.93	6.97	7.09	6.65	7.34	7.44	7.53	7.95	7.75
Treated Solids	5.83	6.72	6.24	7.30	7.11	7.13	7.69	8.04	7.89
Raw Solids	5.45	5.87	5.88	7.27	7.08	7.03	7.59	7.36	7.43
Solidified Solids	8.32	9.53	9.28	9.07	8.15	8.99	8.11	7.47	7.86
Blank	5.61	5.28	6.28	7.39	7.01	7.21	7.89	7.74	7.82

Table E-3: Conductivity Raw Data for Weak Acid Extraction Fluid (mS/cm)

Time	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	CKD	Blank
0.25	14.81	3.72	15.40	6.95	1.02	0.49
1	8.88	2.18	10.62	8.77	2.63	0.49
2.25	4.45	1.30	6.32	6.77	4.15	0.49
5	3.36	1.58	4.66	5.83	3.90	0.49
9	2.98	1.75	3.42	4.52	5.10	0.51
16	2.97	2.06	3.23	4.63	5.99	0.50
36	3.31	2.64	3.60	5.40	6.37	0.48
65	2.60	1.98	3.27	5.45	7.63	0.49
90	1.46	1.51	2.16	4.21	7.69	0.49

Table E-4: Conductivity Raw Data for De-Ionized Water Extraction Fluid (mS/cm)

Time	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	CKD
0.25	5.38	1.22	4.98	1.89	1.34
1	9.92	1.78	7.37	6.68	3.25
2.25	5.78	1.04	6.54	6.69	4.07
5	2.01	0.46	4.71	4.67	3.93
9	0.68	0.22	1.59	2.05	4.25
16	0.35	0.20	0.56	1.16	4.56
36	0.49	0.29	0.39	1.47	6.00
65	0.48	0.30	0.38	1.58	5.55
90	0.46	0.25	0.35	1.15	3.09

Table E-5: Alkalinity Raw Data for Weak Acid Extraction Fluid (mg/L as CaCO₃)

Sample Name	Day				
	1	5	9	36	90
Raw Solids	0	0	0	73.7	0
Drilling Mud	0	129	135	155	0
Solidified Solids	11.6	101	177	388	190
Treated Solids	0	88.4	107	232	38.8
CKD	260	373	457	651	650
Blank	0	0	0	0	0

Table E-6: Alkalinity Raw Data for De-Ionized Water Extraction Fluid (mg/L as CaCO₃)

Sample Name	Day				
	1	5	9	36	90
Raw Solids	13	41.4	40.4	96.4	108
Drilling Mud	45.4	32.8	41.9	248	213
Solidified Solids	33.7	35.3	24.3	25.3	20.8
Treated Solids	19	41.6	49.9	224	184
CKD	645	830	777	757	738
Blank	20.7	0	0	0	0

Table E-7: TOC Raw Data for Weak Acid Extraction Fluid (mg/L as C)

Sample Name	Time Interval	TOC Unit(mg/L as C)
Blank	nanopure	BDL
Check	100 ppm	94.3
Blank	T:0.25	1205.0
Drilling Mud	T:0.25	1176.0
Raw Solids	T:0.25	1225.0
Solidified Solids	T:0.25	1172.0
Treated Solids	T:0.25	1136.0
CKD	T:0.25	1225.0
Blank	T:5	1329.0
Drilling Mud	T:5	1318.0
Raw Solids	T:5	1323.0
Solidified Solids	T:5	1393.0
Treated Solids	T:5	1446.0
CKD	T:5	1535.0
Blank	T:16	1426.0
Drilling Mud	T:16	1528.0
Raw Solids	T:16	1385.0
Solidified Solids	T:16	1445.0
Treated Solids	T:16	1407.0
CKD	T:16	1595.0
Blank	T:90	1452.0
Drilling Mud	T:90	1453.0
Raw Solids	T:90	1339.0
Solidified Solids	T:90	1356.0
Treated Solids	T:90	1427.0
CKD	T:90	1442.0
Check	100 ppm	95.9
Blank	nanopure	BDL

Table E-8: TOC Raw Data for De-Ionized Water Extraction Fluid (mg/L as C)

Sample Name	Time Interval	TOC Unit(mg/L as C)
Blank	nanopure	BDL
Check	5 ppm	4.60
Blank	T:0.25	11.82
Drilling Mud	T:0.25	8.07
Raw Solids	T:0.25	9.11
Solidified Solids	T:0.25	8.15
Treated Solids	T:0.25	11.38
CKD	T:0.25	17.84
Blank	T:5	5.46
Drilling Mud	T:5	11.35
Raw Solids	T:5	10.60
Solidified Solids	T:5	14.21
Treated Solids	T:5	11.29
CKD	T:5	12.40
Blank	T:16	7.53
Drilling Mud	T:16	15.06
Raw Solids	T:16	18.68
Solidified Solids	T:16	19.85
Treated Solids	T:16	15.77
CKD	T:16	12.31
Blank	T:90	9.82
Drilling Mud	T:90	4.66
Raw Solids	T:90	6.40
Solidified Solids	T:90	11.79
Treated Solids	T:90	10.78
CKD	T:90	10.19
Check	5 ppm	5.17
Blank	nanopure	BDL

Table E-9: Normalized Total Organic Carbon Results for Weak Acid Extraction Fluid

Sample Name	Time Interval	TOC (mg/L as C)
Drilling Mud	T:0.25	BDL
Raw Solids	T:0.25	20.00
Solidified Solids	T:0.25	BDL
Treated Solids	T:0.25	BDL
CKD	T:0.25	20.00
Drilling Mud	T:5	BDL
Raw Solids	T:5	BDL
Solidified Solids	T:5	64.00
Treated Solids	T:5	117.00
CKD	T:5	206.00
Drilling Mud	T:16	102.00
Raw Solids	T:16	BDL
Solidified Solids	T:16	19.00
Treated Solids	T:16	BDL
CKD	T:16	169.00
Drilling Mud	T:90	Trace
Raw Solids	T:90	BDL
Solidified Solids	T:90	BDL
Treated Solids	T:90	BDL
CKD	T:90	BDL

Table E-10: Normalized Total Organic Carbon Results for Deionized Water Extraction Fluid

Sample Name	Time Interval	TOC (mg/L as C)
Drilling Mud	T:0.25	BDL
Raw Solids	T:0.25	BDL
Solidified Solids	T:0.25	BDL
Treated Solids	T:0.25	BDL
CKD	T:0.25	6.02
Drilling Mud	T:5	5.89
Raw Solids	T:5	5.14
Solidified Solids	T:5	8.75
Treated Solids	T:5	5.83
CKD	T:5	6.94
Drilling Mud	T:16	7.53
Raw Solids	T:16	11.15
Solidified Solids	T:16	12.32
Treated Solids	T:16	8.24
CKD	T:16	4.78
Drilling Mud	T:90	BDL
Raw Solids	T:90	BDL
Solidified Solids	T:90	Trace
Treated Solids	T:90	BDL
CKD	T:90	BDL

Table E-11: TDS Raw Data for Weak Acid Extraction Fluid (mg/L)

Time	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	CKD	Blank
0.25	7406.7	1860.0	7701.7	3476.7	791.7	243.3
1	4441.7	1091.3	5311.7	4385.0	1315.0	244.2
2.25	2223.3	650.0	3158.3	3386.7	2076.7	246.2
5	1680.0	789.8	2330.0	2916.7	1950.0	246.2
9	1490.0	873.7	1710.0	2260.0	2548.3	253.5
16	1485.0	1029.5	1613.3	2313.3	2993.3	249.7
36	1655.0	1318.3	1800.0	2698.3	3186.7	241.0
65	1298.3	987.7	1633.3	2725.0	3813.3	245.3
90	731.7	754.0	1080.8	2106.7	3843.3	242.7

Table E-12: TDS Raw Data for Deionized Water Extraction Fluid (mg/L)

Time	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	CKD	Blank
0.25	2690.0	607.7	2488.3	943.2	669.7	0.25
1	4958.3	892.2	3685.0	3341.7	1627.3	0.28
2.25	2890.0	520.5	3271.7	3345.0	2036.7	0.35
5	1003.3	231.7	2355.0	2333.3	1967.2	0.40
9	340.2	108.5	795.5	1025.3	2123.8	0.36
16	174.3	97.8	281.8	580.2	2278.3	0.33
36	245.3	143.5	196.2	734.5	1998.3	0.29
65	240.8	148.5	190.5	790.8	2773.3	0.29
90	231.3	124.7	173.7	573.5	1543.5	0.25

APPENDIX F - FINAL ELEMENTAL ANALYSIS DATA FROM IMMERSION TEST

Table F-1: Drilling mud raw data (mg/kg)

Element of Concern	DRILLING MUD	
	Deionized Water	Weak Acid
Silver	0.0	0.0
Aluminum	2.0	3,513.1
Arsenic	0.1	0.1
Boron	217.8	268.9
Barium	2,061.1	449.7
Beryllium	0.0	0.1
Bromide	880.7	1,005.3
Calcium	18,092.7	66,108.4
Cadmium	0.0	0.1
Chloride	95,228.6	90,744.9
Cobalt	0.0	2.6
Chromium	0.0	2.6
Copper	0.1	4.4
Iron	2.8	1,627.6
Potassium	1,907.7	2,304.1
Lithium	153.3	632.2
Magnesium	2,509.2	8,995.6
Manganese	67.9	1,225.6
Molybdenum	0.7	0.1
Sodium	36,916.1	41,990.3
Nickel	0.2	7.4
Phosphorus	6.5	5.3
Lead	0.0	1.4
Sulfate	580.7	231.0
Antimony	0.0	0.0
Selenium	0.2	0.1
Silicon	151.5	1,389.5
Strontium	3,676.6	7,029.6
Uranium	0.0	0.1
Vanadium	0.2	0.2
Zinc	1.0	53.5
Zirconium	0.0	0.0

Table F-2: Raw solids raw data (mg/kg)

Element of Concern	RAW SOLIDS	
	Deionized Water	Weak Acid
Silver	0.0	0.0
Aluminum	0.8	216.3
Arsenic	0.1	0.0
Boron	44.1	52.7
Barium	94.5	84.7
Beryllium	0.0	0.1
Bromide	153.2	158.8
Calcium	5,226.4	35,920.7
Cadmium	0.0	0.0
Chloride	14,502.5	12,476.3
Cobalt	0.0	1.7
Chromium	0.0	0.4
Copper	0.2	2.5
Iron	2.7	7,095.4
Potassium	193.7	331.7
Lithium	18.9	24.9
Magnesium	511.2	3,507.4
Manganese	6.1	405.4
Molybdenum	0.2	0.1
Sodium	6,755.3	7,248.8
Nickel	0.1	4.7
Phosphorus	3.5	8.3
Lead	0.0	2.4
Sulfate	908.8	1,250.2
Antimony	0.0	0.0
Selenium	0.0	0.0
Silicon	187.5	876.1
Strontium	1,660.5	3,906.3
Uranium	0.0	0.1
Vanadium	0.0	0.0
Zinc	0.8	7.8
Zirconium	0.0	0.1

Table F-3: Treated solids raw data (mg/kg)

Element of Concern	TREATED SOLIDS	
	Deionized Water	Weak Acid
Silver	0.0	0.0
Aluminum	2.9	3,505.2
Arsenic	0.0	0.1
Boron	288.5	373.6
Barium	1,421.1	1,361.5
Beryllium	0.0	0.1
Bromide	1,054.1	1,350.2
Calcium	21,436.9	77,967.6
Cadmium	0.0	0.1
Chloride	110,325.6	152,366.6
Cobalt	0.0	1.8
Chromium	0.2	3.6
Copper	0.5	2.7
Iron	10.6	1,581.5
Potassium	982.3	1,360.3
Lithium	188.7	757.1
Magnesium	3,306.4	12,287.2
Manganese	71.4	1,547.9
Molybdenum	0.2	0.0
Sodium	36,810.8	47,914.4
Nickel	0.3	4.5
Phosphorus	1.4	1.5
Lead	0.1	0.6
Sulfate	1,806.2	1,707.4
Antimony	0.0	0.0
Selenium	0.0	0.0
Silicon	126.4	1,363.3
Strontium	4,436.7	8,262.0
Uranium	0.0	0.0
Vanadium	0.4	0.3
Zinc	5.9	82.9
Zirconium	0.0	0.0

Table F-4: Solidified solids raw data (mg/kg)

Element of Concern	SOLIDIFIED SOLIDS	
	Deionized Water	Weak Acid
Silver	0.0	0.0
Aluminum	133.8	895.4
Arsenic	0.0	0.0
Boron	50.0	221.8
Barium	11.3	12.4
Beryllium	0.0	0.1
Bromide	543.7	729.7
Calcium	32,064.5	109,482.5
Cadmium	0.0	0.1
Chloride	81,410.6	82,790.9
Cobalt	0.0	1.5
Chromium	0.3	12.9
Copper	0.6	1.6
Iron	1.2	909.0
Potassium	1,301.5	1,383.6
Lithium	115.1	200.1
Magnesium	90.0	12,535.7
Manganese	0.2	659.3
Molybdenum	0.5	0.0
Sodium	34,985.9	35,451.9
Nickel	0.3	6.2
Phosphorus	16.6	11.7
Lead	0.1	1.3
Sulfate	20,323.3	31,245.3
Antimony	0.1	0.1
Selenium	0.0	0.0
Silicon	45.4	1,767.2
Strontium	1,448.9	2,561.8
Uranium	0.0	0.2
Vanadium	0.6	0.3
Zinc	1.1	19.4
Zirconium	0.0	0.0

Table F-5: Cement kiln dust raw data (mg/kg)

Element of Concern	CEMENT KILN DUST	
	Deionized Water	Weak Acid
Silver	0.0	0.0
Aluminum	2.0	93.4
Arsenic	0.0	0.2
Boron	1.9	23.0
Barium	8.2	15.2
Beryllium	0.0	0.0
Bromide	21.0	16.9
Calcium	71,983.9	181,420.7
Cadmium	0.0	0.0
Chloride	0.8	0.6
Cobalt	0.0	0.2
Chromium	0.0	0.0
Copper	0.6	0.4
Iron	0.2	20.2
Potassium	2,050.9	1,875.8
Lithium	6.2	6.1
Magnesium	0.6	3,223.4
Manganese	0.0	12.9
Molybdenum	0.4	0.4
Sodium	659.8	600.5
Nickel	0.6	1.9
Phosphorus	0.0	0.0
Lead	0.4	0.0
Sulfate	82.9	63.7
Antimony	0.0	0.1
Selenium	0.2	0.2
Silicon	18.6	432.5
Strontium	143.4	269.2
Uranium	0.0	0.1
Vanadium	0.2	1.3
Zinc	83.8	27.1
Zirconium	0.0	0.0

APPENDIX G: COMPARISON OF STRONG ACID DIGESTION AND IMMERSION TEST RESULTS

Table G-1: Percent (%) Element Extracted in Weak Acid Extraction Fluid

Element	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	Cement Kiln Dust
Silver	2.3	-	7.6	1.8	-
Aluminum	10.1	3.3	10.3	3.2	0.4
Arsenic	0.6	0.7	0.6	0.1	0.6
Boron	102.4	91.0	111.6	102.9	11.5
Barium	4.5	0.9	11.3	0.6	12.3
Beryllium	12.6	21.6	6.2	9.3	0.2
Bromide	118.5	218.9	97.1	135.4	102.1
Calcium	112.6	127.2	110.7	96.6	59.4
Cadmium	26.5	26.0	25.6	12.9	0.0
Chloride	-	-	-	-	-
Cobalt	28.8	31.9	23.2	16.7	2.0
Chromium	4.4	1.3	7.1	26.2	0.0
Copper	6.9	5.6	5.1	3.0	1.5
Iron	3.5	8.5	3.1	2.7	0.1
Potassium	23.5	16.1	18.7	17.8	61.3
Lithium	107.9	88.9	94.3	80.7	32.3
Magnesium	77.4	87.2	94.0	87.1	11.3
Manganese	104.4	66.9	103.2	75.7	4.9
Molybdenum	0.5	1.0	0.0	0.1	24.6
Sodium	98.6	147.5	98.2	94.0	49.7
Nickel	17.8	21.4	15.2	15.1	5.4
Phosphorus	1.1	4.3	0.3	2.4	0.0
Lead	1.4	9.4	0.8	1.5	0.4
Sulfate	1076.9	7632.3	10542.9	39008.0	47.6
Antimony	1.4	5.3	1.2	8.0	37.9
Selenium	10.7	3.3	1.5	0.4	5.5
Silicon	1135.2	2745.6	1576.9	1980.5	3383.3
Strontium	89.1	81.9	86.7	61.0	80.9
Uranium	4.9	18.6	1.9	8.2	2.7
Vanadium	0.4	0.3	0.8	0.5	1.5
Zinc	34.0	15.6	56.9	14.9	62.0
Zirconium	0.5	8.7	0.6	0.5	0.1

Table G-2: Percent (%) Element Extracted in Deionized Water Extraction Fluid

Element	Drilling Mud	Raw Solids	Treated Solids	Solidified Solids	Cement Kiln Dust
Silver	0.9	-	4.9	3.9	-
Aluminum	0.0	0.0	0.0	0.5	0.0
Arsenic	0.4	0.8	0.1	0.1	0.0
Boron	82.9	76.1	86.1	23.2	1.0
Barium	20.6	1.0	11.8	0.5	6.6
Beryllium	0.0	0.0	0.0	0.0	0.0
Bromide	103.8	211.2	75.8	100.9	127.0
Calcium	30.8	18.5	30.4	28.3	23.6
Cadmium	0.6	0.2	0.4	0.2	0.0
Chloride	-	-	-	-	-
Cobalt	0.1	0.0	0.0	0.0	0.1
Chromium	0.0	0.1	0.4	0.6	0.1
Copper	0.1	0.5	1.0	1.1	2.5
Iron	0.0	0.0	0.0	0.0	0.0
Potassium	19.5	9.4	13.5	16.8	67.1
Lithium	26.2	67.5	23.5	46.4	33.0
Magnesium	21.6	12.7	25.3	0.6	0.0
Manganese	5.8	1.0	4.8	0.0	0.0
Molybdenum	4.6	3.8	2.4	3.8	23.6
Sodium	86.7	137.4	75.4	92.7	54.6
Nickel	0.5	0.6	0.9	0.6	1.7
Phosphorus	1.4	1.8	0.3	3.4	0.0
Lead	0.0	0.1	0.1	0.1	4.4
Sulfate	2706.9	5548.0	11153.0	25372.5	62.0
Antimony	1.3	4.3	1.0	4.6	1.6
Selenium	11.9	4.1	0.8	1.1	6.4
Silicon	123.7	587.6	146.3	50.9	145.4
Strontium	46.6	34.8	46.5	34.5	43.1
Uranium	0.0	0.0	0.0	0.0	0.0
Vanadium	0.3	0.3	0.9	0.9	0.2
Zinc	0.6	1.6	4.1	0.8	191.6
Zirconium	0.1	0.1	0.2	0.0	0.1