Evaluating Leachability of Residual Solids from Hydraulic Fracturing in the Marcellus Shale

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ABSTRACT

The process of natural gas extraction through hydraulic fracturing produces large quantities of fluid containing naturally-occurring salt, radionuclides, and heavy metals which form residual solids during storage and treatment. The purpose of this research was to characterize the residual solids from hydraulic fracturing operations in the Marcellus Shale to predict the leaching behavior of select elements in disposal environments.

Samples collected for this research were: (1) drilling mud, (2) treated sludge from the chemical treatment of process waters, (3) solids from the gravity settling of produced water, and (4) sludge solidified prior to disposal in a municipal landfill. These samples were subjected to various digestion techniques to determine the composition and leaching potential for elements of concern. Strong acid digestions were performed to determine the total environmentally available composition, whereas weak acid digestions were used to predict the leaching potential of these solids under various environmental conditions. The extraction fluids for the leaching experiments included weak acetic acid, acid rain, reagent water, and synthetic landfill leachate. Solids were agitated in a standard tumbling apparatus to simulate worst-case conditions based on ASTM and EPA recommendations. Results from EPA's Toxicity Characteristic Leaching Procedure (TCLP) were used to determine if solids were considered hazardous based on the metal leaching potential.

The results from strong and weak acid digestions were compared to better understand the types and quantity of materials that have the potential to leach from the samples. This research may be used to develop best management practices for hydraulic fracturing residual solids.

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CHAPTER 1: INTRODUCTION AND PROJECT OBJECTIVES

1.1 Introduction

The process of natural gas extraction through hydraulic fracturing produces large quantities of water containing salt, radionuclides, and naturally-occurring heavy metals. This produced water is typically stored onsite or transported to a dedicated facility to undergo treatment, resulting in the production of residual solids and treatment sludge which must undergo proper management and disposal. The purpose of this research was to characterize these solids in order to quantify the chemical composition, determine the leaching behavior for elements of concern, and predict the potential environmental impacts of residual solids in various disposal environments.

Samples for this research were collected from a dedicated treatment facility in Pennsylvania, owned and operated by Reserved Environmental Services (RES). This facility receives produced water and drilling waste from companies throughout the Marcellus Shale region. The four samples collected for the research were: (1) treated sludge from the chemical precipitation of process water, (2) raw solids from the gravity settling of produced water, (3) thickened drilling mud from well construction, and (4) solidified sludge which is disposed of in a municipal landfill. A general schematic of this process highlighting where samples were collected for this research is provided in Figure 1. Since RES manages waste from various drilling companies within the Marcellus Shale region, these solids can be considered representative samples from the hydraulic fracturing process.

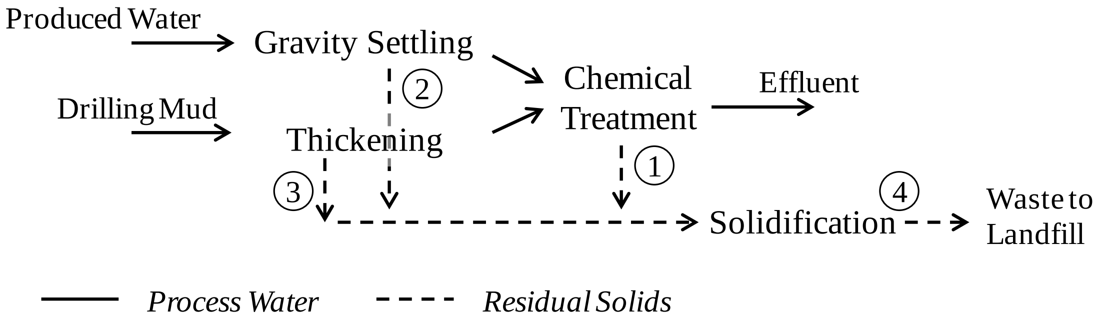

Figure 1: Reserved Environmental Services (RES) Treatment Process Schematic

1.2 Project Objectives

The purpose of this research was to chemically characterize residual solids from hydraulic fracturing operations in the Marcellus Shale to determine the environmentally available composition, hazardous waste classification, and leaching behavior in various disposal environments.

Multiple methods for strong acid digestion, including traditional and energy-coupled procedures, were evaluated to determine a suitable or preferred method for quantifying the environmentally available composition of samples. Since a large variety of elements, including heavy metals, volatiles, and radionuclides, were analyzed during this research, it was expected that results would vary based on the digestion method. After the strong acid digestion of samples, the supernatants were analyzed to determine the portion of the total composition from the liquid and solid phase. These experiments were used to chemically characterize the waste for elements of concern and compare the various types of residual solid samples.

The Toxicity Characteristic Leaching Procedure (TCLP) was used to determine the leaching potential of metal contaminants for these solids in a co-disposal municipal landfill environment. These results could be used to confirm the non-hazardous waste characterization of RES's solidified sludge and determine the classification of other solids related to hydraulic fracturing. The Synthetic Precipitation Leaching Procedure (SPLP) was used to determine the leaching potential of metal contaminants in a mono-disposal environment such as land application or burial where samples are subject to interactions with acid rain. Since the final moisture content of samples may fluctuate, another objective of this research was to evaluate the variations in leaching potential based on the solids content of the waste.

Finally, weak acid digestions were performed following an ASTM shake extraction procedure to determine the effect of extraction fluid on leaching behavior for residual solid samples. Results from these digestions were compared to the environmentally available composition identified above to determine the types and quantities of elements that will likely leach from residual solids under environmental conditions. By comparing results from these extraction fluids, it may be possible to determine which disposal environment is more aggressive and facilitates leaching from hydraulic fracturing residual solids.

Since this is one of the first efforts to characterize residual solids from hydraulic fracturing process water, the general objective of this research was to provide additional information regarding potential environmental impacts from unconventional gas production. The ultimate goal for research in this area is that it will aid industry leaders and drilling companies in their efforts to develop best management practices for residual solid waste.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction to Hydraulic Fracturing

2.1.1 Natural Gas in the United States

While coal has traditionally been the most common fuel source in the United States, natural gas production is a rapidly expanding industry. According to the Energy Information Association (EIA), natural gas currently provides 24% of the country's energy requirements, and this value is expected to remain constant, if not rise, over the coming decades (Gregory *et al.*, 2011). EIA also estimates that the United States possesses 2,552 trillion cubic feet of natural gas, or roughly enough to supply the next 110 years of the United States' natural gas requirements. Of this total volume, 827 trillion cubic feet of natural gas are stored in shale deposits (U.S. House of Representative, 2011). In 2010 natural gas in the United States reached its highest production levels in almost 40 years due to the discovery of additional gas reservoirs and the development of improved processes for natural gas extraction from shale deposits (U.S. House of Representatives, 2011). As drilling companies continue to focus on developing improved methods for extraction and processing, natural gas production will likely continue to increase in the United States.

2.1.2 Hydraulic Fracturing Practices

Shale reservoirs are categorized by low-permeability rocks with high-organic contents (Blauch, 2010). The most common practice for extracting natural gas from these deposits in the United States is through hydraulic fracturing, a process first utilized in 1947 which has since been improved and expanded to become financially viable and commercially successful (Montgomery and Smith, 2010). In modern practices, vertical deep wells are drilled and extend into horizontal wells which run through the shale formation. These wells are constructed using drilling mud (a water, oil or synthetic based slurry) to carry drill cuttings to the surface and lubricate drilling equipment (Ohio EPA, 2012). Fracturing fluid, containing sand and chemical additives, is pumped into the wells where the pressurized fluid forces cracks and fissures in the shale deposits which release natural gas, including methane and other hydrocarbons (Andrews *et al.*, 2009).

Hydraulic fracturing is typically performed once to begin natural gas production; however, this process may be repeated multiple times over the lifetime of the well (Gregory *et al.*, 2011). During typical operations in the Marcellus Shale, each of these fracturing events requires between 7,000 and 18,000 m^3 of fracturing fluid (Gregory *et al.*, 2011). Some of the injected fluid, roughly 24% of the total volume, will immediately return to the surface when the pressure is released (Haluszczak *et al.*, 2013). At the highest flow-back rate which occurs immediately after the fracturing event, water can return to the surface at a rate averaging 1000 m^3/d (Gregory *et al.*, 2011). After this initial flow-back period, small volumes of water will continue to return to the surface at a rate closer to 2-8 m^3/d, as natural gas is extracted from the well. Although the terms are often used interchangeably, fluids that return to the surface within the first two weeks after the fracturing event are categorized as 'flow-back'. Fluid returning to the surface after this initial two week period is considered 'produced' water (Haluszczak *et al.*, 2013).

Natural gas deposits in shale formations are dependent on several natural variables, including hydrocarbon content, shale maturity, porosity and shale thickness (Blauch, 2010). However, production can be improved by a number of other factors. In order to facilitate gas extraction, fracturing fluid contains a number of additives, including sand, acid, friction reducers, anti-microbial agents and scale inhibitors (Abdalla *et al.*, 2011). While some of these additives are common and relatively non-toxic, others, including benzene and lead, have potentially serious human health effects (U.S. House of Representatives, 2011). The exact list of additives varies by drilling company or well, and there is no comprehensive list of all the chemicals currently in use or approved. One organization working to provide information for onsite chemical use is FracFocus, a national registry that tracks chemicals used at specific well sites based on information provided voluntarily by drilling companies or through regulatory requirements (FracFocus, 2013).

2.1.3 Environmental Concerns

Among the concerns associated with hydraulic fracturing is contamination. Contamination occurs when hydraulic fracturing fluid, flow-back water, or residual solids enter the environment or local water systems. This is an especially major concern if contamination occurs to a drinking water supply.

Contamination can occur underground, where fracturing fluid has the potential to interact with subsurface water sources (Andrews *et al.*, 2009), or at the surface from spills, leaks, or other types of releases. One notable example of surface contamination occurred in Susquehanna County Pennsylvania, where a well released fracturing fluid which entered a local tributary (Chapman *et al.*, 2012). In other instances, high levels of total dissolved solids (TDS) suspected to be caused from hydraulic fracturing were measured in rivers and tributaries throughout Western Pennsylvania, in one case causing a significant fish kill (Chapman *et al.*, 2012).

The primary way to mitigate these risks is by practicing proper water and waste management practices during the hydraulic fracturing process.

2.1.4 Produced Water Management

When flow-back and produced water return to the surface during hydraulic fracturing, they are typically stored onsite in earth impoundments or metal tanks before being used in a subsequent well completion or transported off-site to undergo treatment, disposal, or reuse. The following treatment and disposal options are available for wastewater produced during the hydraulic fracturing process.

2.1.4.1 Underground Injection

In the United States, deep well injection is the most common disposal method for waste produced during natural gas extraction (Gregory *et al.*, 2011). During this process, fluid and brine are pumped into deep wells that discharge the waste below impermeable rock layers (Abdalla, 2011), thus minimizing the risk of contamination. These wells are permitted through the EPA and regulated under the Federal Safe Drinking Water Act of 1974 (Gaudlip *et al.*, 2008). Wells are categorized based on the type of waste they can manage, with Class I wells reserved for hazardous waste and Class II wells used solely for waste produced by the oil and gas industry (Gaudlip *et al.*, 2008). However, due to cost and geological restrictions, there are relatively few Class II wells in the Marcellus Shale region. Compared to Texas, which has approximately 7,000 Class II wells, Pennsylvania has seven, New York has six, West Virginia has 74, and Ohio has 159 (Abdalla *et al.*, 2011). Therefore, alternative treatment methods must be utilized in the Marcellus area for wastewater disposal.

2.1.4.2 Publicly Owned Treatment Works (POTW)

In some instances, flow-back and produced water can be discharged to publicly owned, municipal wastewater treatment plants (POTWs) where they will be diluted with municipal wastewater prior to treatment. However, since these facilities often have strict discharge requirements for total dissolved solids (TDS), these fluids can typically not exceed 1% of the total volume treated by the facility (Gregory *et al.*, 2011). Another consideration is how the addition of industrial wastewater may affect biosolids, the organic treatment waste produced by the facility which may undergo disposal or beneficial reuse. If the composition or leaching potential of select elements exceeds allowable limits, the waste is no longer suitable for beneficial reuse through land application or disposal in a municipal landfill (US EPA, 40 CFR 503.10, 1993; US EPA 40 CFR 261.24, 2012). This may subsequently affect the facility through loss of revenue or increased disposal costs.

Therefore, the total volume of hydraulic fracturing fluids that these facilities can treat is small in comparison to the total volume produced during gas drilling operations. While there were approximately 15 facilities in Pennsylvania that were accepting hydraulic fracturing fluids, the Department of Environmental Protection (DEP) has subsequently asked drilling companies to stop using POTW facilities due to public health concerns (Abdalla *et al.*, 2011).

2.1.4.3 Centralized Waste Treatment (CWT)

Dedicated industrial waste facilities, also known as centralized waste treatment (CWT) facilities, use methods similar to POTWs for the removal of suspended solids and organics (Hammer and VanBriesen, 2012). Additionally, they are also able to remove dissolved solids through enhanced coagulation or precipitation (Hammer and VanBriesen, 2012). Treated water can then be discharged into surface water, transported to a POTW for additional treatment, or reused for hydraulic fracturing. According to the Pennsylvania DEP, approximately half of all wastewater produced from natural gas extraction in 2011 was treated at CWT facilities (Hammer and VanBriesen, 2012).

2.1.5 Residual Solids Management

Storage and treatment of flow-back and produced water generates solid residuals which must also undergo proper disposal. Depending on the characteristics of these waste products, they can either be disposed of through land application or in landfills (Hammer and VanBriesen, 2012). Municipal waste landfills can receive certain types of waste, but toxic substances can only be deposited in permitted hazardous waste landfills, increasing the cost of disposal (Asante-Duah *et al.*, 1992).

Although it is expected that the residuals solids from produced water treatment and storage will have similar characteristics and elemental compositions as the wastewater, there has been insufficient research to determine the actual composition or predict leaching behavior of these elements in the environment.

2.2 Elemental Analysis

Produced water from hydraulic fracturing has total dissolved solids (TDS) concentrations often exceeding 200,000 mg/L (Chapman *et al.*, 2012). These solids may come from the chemical additives used by drilling companies in the fracturing process or from interactions with naturally occurring salt or brine in the shale formation (Chapman *et al.*, 2012).

Since the residual solids are expected to have a similar elemental composition as the produced water, the list of elements to be analyzed was compiled based on previous literature of hydraulic fracturing produced water and Marcellus Shale geochemistry.

2.2.1 Elements of Concern

Naturally occurring elements typically found in the Marcellus Shale include major elements like chloride, sodium, calcium, strontium, and bromide (Chapman *et al.*, 2012) and trace elements such as uranium, copper, nickel, vanadium, and molybdenum (Titler and Curry, 2011; Liermann *et al.*, 2011). Other elements commonly found in organically-rich formations like the Marcellus Shale include barium, chromium, and zinc (Bank, 2008).

Research concerning produced water from hydraulic fracturing has largely focused on the elements listed above, with the addition of others like aluminum, boron, iron, lithium, magnesium, manganese, phosphorus, potassium (Haluszczak *et al.*, 2013), arsenic, selenium (Balaba and Smart, 2012), cadmium, mercury, and lead (Hayes, 2009).

There are a number of other ways to identify the elements that may be present in produced water and residuals. For example, government agencies may implement regulations concerning produced wastewater from hydraulic fracturing. The Pennsylvania DEP requires wastewater produced from gas drilling in the Marcellus Shale to undergo chemical analysis to determine concentrations of many elements listed above, as well as beryllium, cobalt, and silver (Pennsylvania DEP, 2010). Similarly, organizations and government agencies that have identified chemical additives currently used in fracturing fluid may indicate the presence of certain elements. An example of this would be the use of crosslinkers that may contain antimony and zirconium (GoFrac, 2012).

Based on these considerations and previous findings, the elements indicated in Figure 2 were considered in this research. While chloride is expected to be a major constituent of hydraulic fracturing residual solids, it was excluded from analysis due to issues with analytical techniques which will be discussed in subsequent sections.

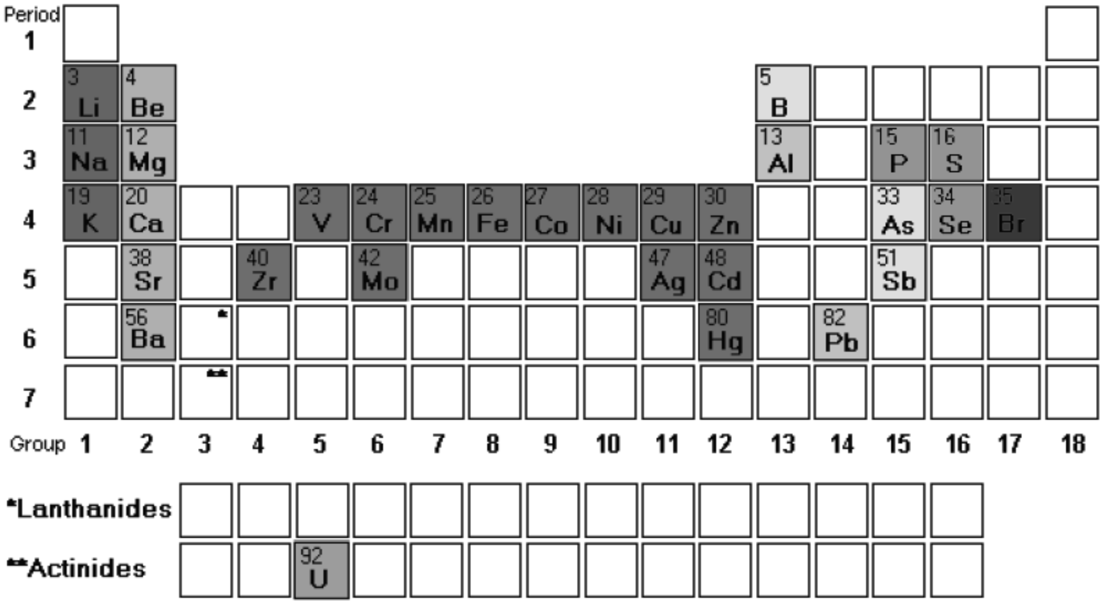

Figure 2: Chemical Elements Considered in this Research

Image adapted from (Ziemkiewicz, 2011)

2.2.2 Analytical Techniques

Inductively coupled plasma (ICP) is an analytical technique capable of measuring a wide range of metals and some non-metals simultaneously with relatively low detection limits. ICP mass spectrometry (ICP-MS) is performed by ionizing an acidified liquid sample and using a mass spectrometer to separate and precisely quantify the resulting ions based on their mass-to-charge ratio.

Due to the nature of this procedure, a common source of error with ICP-MS is due to spectroscopic interferences, which are caused by atomic and molecular ions having the same mass-to-charge ratio. While most current instrumental software can adjust for atomic ion interferences, polyatomic interferences are not corrected (May and Wiedmeyer, 1998). These interferences may be enhanced by the sample matrix or the reagents used in sample preparation. While recent equipment developments have helped reduce the frequency and effect of matrix-induced interference, it is critically important to minimize the use of reagents to ensure low detection limits and minimal interference during trace metal analysis (Gard Guide, 2012).

EPA Method 6020A – Inductively Coupled Plasma Mass Spectrometry is a method for trace metal analysis developed in 1988 which is applicable for 23 elements of concern. Common elements may have a quantitation limit below 0.1 μg/L, while less sensitive elements such as selenium and arsenic may have limits above 1.0 μg/L (US EPA 6020A, 2007). The method detection limit (MDL) and minimum reporting level (MRL) can be calculated for each element of concern to determine the applicability of this analytical technique. The MDL is the lowest concentration that can be measured which would indicate with 99% confidence that the element is present in the sample. (US EPA 40 CFR 136 Appendix B, 1997). Meanwhile, 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). Internal standards should also be utilized with all analytical techniques for quality assurance/quality control (QA/QC) during analysis.

2.3 Strong Acid Digestion

Because analytical techniques such as ICP-MS evaluate the liquid phase, elements in the solid mineral phase must be transferred to a suitable liquid for analysis. This is commonly achieved through wet acid digestion with the aid of common reagents like hydrochloric acid, nitric acid, hydrofluoric acid, sulfuric acid, and hydrogen peroxide (Gard Guide, 2012).

2.3.1 Digestion Techniques

Open digestion occurs under atmospheric pressure typically with the use of a reflux system or on a laboratory hot plate. Some major limitations of open digestion systems include the potential for loss of volatile compounds, long reaction times due to low digestion temperatures, and high acid demand which can lead to interferences in trace metal analysis (Berghof, 2013). Closed digestions can overcome some of these limitations by employing vessels capable of withstanding both high temperatures and pressures. These reactions can be further accelerated using direct energy coupled techniques, including laboratory microwave systems.

2.3.2 Methods for Near Total Digestion

There are a number of methods for strong acid digestion that are so aggressive they can be considered to provide nearly total digestion. The most powerful wet acid digestion technique commonly used is a four acid digestion which utilizes hydrofluoric, perchloric, nitric, and hydrochloric acids. This method is capable of dissolving most siliceous materials (Gard Guide, 2012), but has operational and safety challenges associated with hydrofluoric acid and requires a wet hood due to the use of perchloric acid.

Other methods that use hydrofluoric acid include EPA Method 3052 – Microwave Assisted Acid Digestion of Siliceous and Organically Based Matricies. This direct energy coupled method is intended to provide a total sample digestion using hydrofluoric and nitric acid with the optional addition of hydrochloric acid and hydrogen peroxide. However, it is not intended for use in typical regulatory applications (US EPA 3052, 1996) and has similar operational challenges as the four acid digestion procedures due to the use of hydrofluoric acid.

Aqua regia, which is a 3:1 by volume mixture of hydrochloric and nitric acids, is less effective for the digestion of siliceous material. However, it provides a near complete digestion of sulfates, sulfides, oxides and carbonates similar to the four acid digestion method (Gard Guide, 2012). International Organization for Standardization (ISO) Method 11466 outlines a standard procedure for the extraction of trace metals in soils with aqua regia using a reflux system (ISO 11466, 1995). This procedure requires specialized glassware for the reflux apparatus.

2.3.3 Methods for Environmentally Available Digestion

EPA offers a number of methods for the determination of ‘environmentally available’ elements, most of which utilize a combination of nitric and hydrochloric acids with the addition of hydrogen peroxide in certain applications. The traditional digestion of solids is outlined in EPA Method 3050B – Acid Digestion of Sediments, Sludges, and Soils. This digestion procedure offers alternative extraction fluids to increase stabilization of certain analytes and is performed under atmospheric conditions with a laboratory hotplate (US EPA 3050B, 1996).

Due to the often long digestion period and large volume of acid required in the traditional procedure, EPA developed an accelerated method using a direct energy technique. EPA Method 3051A – Microwave Assisted Acid Digestion of Sediments, Soils, and Oils is offered as an alternative to traditional digestion (US EPA 3051A, 2007), but uses substantially less acid and digestion periods. However, this method still only employs nitric and hydrochloric acids, meaning it cannot be considered a total digestion. Similar to EPA Method 3050B, it offers two extraction fluids for improved digestion and stabilization of select elements.

2.4 Weak Acid Digestion

In addition to the strong acid digestion procedures above, weak acid digestion methods have also been developed to predict leaching behavior of solid wastes. There are two main categories of leaching tests: static and kinetic. Static tests utilize a single volume of extraction fluid, which can either be agitated or left stagnant with the solids. Since it is assumed the system in an agitated test reaches steady-state conditions by the end of the procedure, these tests measure the overall chemical properties of a waste instead of any physical mechanisms (Harwell, 1999). In kinetic tests, the extraction fluid is replenished throughout the procedure, ensuring that conditions within the system are time-variable and dynamic. Since kinetic tests are often performed over extended periods, a static test is preferable in this application because it can provide rapid results for the quantification of leaching behavior. Time permitting, static tests can also be performed sequentially in order to determine the changes in leaching behavior over time.

Standard methods for leaching tests have been developed by various regulatory agencies within the Unites States, including the Environmental Protection Agency (EPA) and American Society for Testing and Methods (ASTM).

2.4.1 Toxicity Characteristic Leaching Procedure (TCLP)

The Toxicity Characteristic Leaching Procedure (TCLP) is a method developed by EPA to characterize waste and predict leaching behavior in a municipal landfill environment. This method was developed in response to the 1984 Hazardous and Solid Waste Amendments (HSWA) of the Resource Conservation and Recovery Act (RCRA) in order to characterize the toxicity characteristics of a solid waste (Kimmell, 1999). During this procedure, the “solid” portion of waste, which includes any liquids that cannot be removed through vacuum filtration, is agitated for 18 hours with a weak acetic acid solution with characteristics that vary depending on the sample’s alkalinity. Liquid portions separated prior to extraction are combined with the method extract prior to analysis, resulting in a final extract containing both dissolved and suspended solids (US EPA 1311, 1992). The extraction fluid characteristics for TCLP were developed to simulate leachate from predominantly municipal solid waste, and the high liquid-solid ratio (20 mL:1 g) was used to ensure that that the extract reached steady state conditions (Murarka, 1999). If an element is not present in the final extract from TCLP, it is assumed that it will not leach under typical landfill conditions. EPA has set allowable limits for select metals, volatile organics, pesticides, and other chemicals of concern, and the waste must be classified as hazardous if the extract concentration exceeds the allowable limit for any one analyte (US EPA 40 CFR 261.24, 2012).

2.4.2 Synthetic Precipitation Leaching Procedure (SPLP)

While TCLP is used to determine leaching in a municipal landfill environment, the Synthetic Precipitation Leaching Procedure (SPLP) was developed by EPA to simulate a mono-disposal environment where the in-situ waste is exposed to natural weathering (Murarka, 1999). This procedure is similar to TCLP but with an extraction fluid of weak nitric and sulfuric acid meant to simulate acid rain. Depending on the site specific conditions or waste characteristics, the aggressiveness of this synthetic acid rain varies (US EPA 1312, 1994). While EPA does not offer guidelines for allowable extract concentrations related to SPLP, other agencies including state governments may stipulate allowable mobility criteria for select regions (Connecticut DEEP, 2013) or results may be used by industries in environmental impact studies to develop best management practices for a site-specific disposal environment.

2.4.3 Shake Extraction of Solid Waste with Water

ASTM Method D3987 - The Standard Practice for Shake Extraction of Solid Waste with Water is similar to EPA’s TCLP and SPLP in terms of extraction procedure and agitation method. However, it requires less rigorous sample preparation and a neutral extraction fluid. This procedure uses reagent water as an extraction fluid to study the chemical characteristics of a solid waste and is not intended to simulate site-specific conditions or provide regulatory conclusions (ASTM D3987, 2012). The final extract is analyzed for the soluble content in order to determine leaching behavior of chemical analytes.

2.4.4 Alternative Extraction Fluids

In addition to the reagent water, inorganic acid, and organic acid extraction fluids used in ASTM and EPA leaching tests, alternative fluids can be considered to study the effect of fluid aggressiveness on leaching behavior. One alternative identified was an oxygen-sensitive synthetic landfill leachate developed by Stanforth *et al.* (1979) to simulate the maximum aggressiveness of municipal landfill leachate sampled from various landfills throughout the United States. The constituents of this leachate include acetic acid as a representative volatile acid, sodium acetate as a pH buffer and for monovalent ionic strength, glycine for organic nitrogen, pyrogallol as a complexing agent, and ferrous sulfate for divalent ionic strength (Stanforth *et al.*, 1979). Due to the possibility of iron precipitation, this oxygen sensitive leachate must be purged with an inert gas, such as nitrogen, to maintain oxygen-limited conditions.

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CHAPTER 3: MANUSCRIPT 1

Strong Acid Digestion of Residual Solids from Hydraulic Fracturing in the Marcellus Shale to Determine Total Environmentally Available Elements

ABSTRACT

Strong acid digestions of hydraulic fracturing residual solids were performed following EPA methods to determine the environmentally available composition of samples. The types of samples analyzed were raw solids, treated sludge, solidified sludge, and drilling mud. Digestion methods included a traditional digestion and an energy-coupled procedure, each with two extraction fluids. From these results, the suitability of each method could be determined for the elements under consideration. There were significant variations between procedures when analyzing for antimony, barium, bromide, mercury, and silicon; however, all methods behaved similarly for the remaining elements. Comparing results for the different sample types, it was determined that the environmentally available composition was similar between the four solids, and the major constituents included aluminum, barium, calcium, iron, magnesium, potassium, sodium, and strontium. Analyzing the supernatants of the residual solid samples, it was determined that the major elemental contribution came from the solid portion of the waste for all elements, except bromide, lithium, sodium, and strontium. It is important to note that while these digestion methods were approved by EPA, results may vary due to incomplete digestion, reagent interferences, formation of precipitates, loss of volatiles, and other factors.

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

3.1 Introduction

Hydraulic fracturing is a process for unconventional natural gas extraction which uses pressurized fluid to fracture subsurface shale formations, thereby releasing natural gas. Typical drilling configurations include a deep vertical well which extends into horizontal wells through the shale formation, which can be fractured in segments (Andrews *et al.*, 2009). These wells are constructed using drilling mud, (a water, oil or synthetic based slurry) to carry drill cuttings to the surface and lubricate drilling equipment (Ohio EPA, 2012). Once completed, each well requires between 7,000 and 18,000 m^3 of fracturing fluid, which is typically a mixture of water, sand and chemical additives (Gregory *et al.*, 2011). These additives include friction reducers, anti-microbial agents, scale inhibitors, and other chemicals to facilitate fracturing and subsequent gas extraction (Abdalla *et al.*, 2011). Some of the injected fluid, roughly 24% of the total volume, immediately returns to the surface after the fracturing event (Haluszczak *et al.*, 2013), and fluid continues to return to the surface throughout the lifetime of the well.

This produced water from hydraulic fracturing contains total dissolved solids, frequently exceeding 200,000 mg/L due to the elevated presence of naturally-occurring salts, radionuclides, and heavy metals (Chapman *et al.*, 2012). Produced water is typically stored onsite in earth impoundments or temporary containers before being reused in subsequent well completions or transported to a dedicated facility to undergo treatment (Hammer and VanBriesen, 2012). These processes generate residual solids which must be properly managed; typically being disposed of onsite or in a municipal landfill. The purpose of this research was to characterize the solids resulting from hydraulic fracturing operations and produced water treatment in the Marcellus Shale, in order to predict the total environmentally available concentration of elements present in each sample. This information may be used to understand the chemical characteristics of the waste and to help predict the leaching behavior of solids under environmental conditions.

Samples were collected from the New Stanton Plant, a 1.2 MGD dedicated treatment facility in New Stanton, PA, which is owned and operated by Reserved Environmental Services (RES). This facility receives produced water and drilling waste from companies throughout the Marcellus Shale region. Influent produced water is placed in a rock box to remove heavy solids before undergoing chemical treatment. This process uses sodium sulfate, sodium hypochlorite, and sodium hydroxide to remove dissolved elements, including barium, iron, and strontium. Influent drilling mud is thickened and the resulting supernatant is introduced into the process stream for treatment. The resulting solids, including raw residual solids from rock boxes, thickened drilling mud, and sludge from the chemical treatment of process water, are mixed and solidified with cement kiln dust (CKD) before disposal in a municipal landfill. The four samples collected for the research project were: (1) treated sludge, (2) raw solids, (3) drilling mud, and (4) solidified sludge. RES manages waste from various drilling companies within the Marcellus Shale region.

The elements of concern were identified based on previous research regarding produced water composition, Marcellus Shale geochemistry, and regulatory requirements for solid waste and wastewater. Naturally occurring elements found in the Marcellus Shale include the major components, chloride, sodium, calcium, strontium, and bromide

(Chapman *et al.*, 2012). Previous research concerning hydraulic fracturing wastewater has also focused on common elements, like aluminum, boron, iron, lithium, magnesium, manganese, phosphorus, and potassium (Haluszczak *et al.*, 2013). Overall, 32 elements were selected for final analysis. Although chloride was originally intended to be analyzed as part of this research, it was later excluded due to analytical issues which will be addressed subsequently.

Multiple methods of strong acid digestion were performed to determine the total composition of "environmentally available" elements capable of leaching under worst-case environmental conditions. Open vessel digestions were performed on a laboratory hot plate with a reflux system, using hydrogen peroxide, and either a nitric acid extraction fluid or a nitric and hydrochloric acid mixture (US EPA 3050B, 1996). Closed vessel digestions were performed in a microwave unit for direct energy coupled extraction with nitric acid or, alternatively, a nitric and hydrochloric acid mixture (US EPA 3051A, 2007). Closed vessel digestions are typically considered more aggressive due to the high temperatures and pressures achieved during digestion (Berghof, 2013). Similarly, the addition of hydrochloric acid to the extraction fluid is considered more aggressive due to the increased digestion and stabilization of select elements (US EPA 3051A, 2007). These various methods and extraction fluids were used to determine a suitable or preferred digestion method for all elements of concern.

Based on the total composition of environmentally available elements, the supernatants from centrifugation could be used to determine the contribution from the solid and soluble portions in the waste. Extracts from strong acid digestions and the centrifuged supernatants were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) to determine the total environmentally available composition of the samples and amount of the total contributed from the solid and liquid portions of the residual solid samples.

3.2 Project Objectives

The primary objective of this research was to characterize residual solids from hydraulic fracturing processes in the Marcellus Shale. Solids can be generated onsite or offsite at a dedicated treatment facility. Since samples could only be collected from an offsite location, residual solids from onsite practices were simulated using "raw solids," which were collected from the gravity settling of produced water. In addition to the solids from raw produced water and the chemical treatment process, drilling mud from well construction was also analyzed to characterize waste from various phases of the hydraulic fracturing process. Finally, solidified sludge from the dedicated treatment facility was analyzed to determine the final composition of solids being disposed of in a municipal landfill.

Four techniques for strong acid digestion were employed to determine the total environmentally available composition of samples using two unique digestion procedures and two acidic extraction fluids. These methods, one of which was a traditional open digestion and the other was a closed, energy coupled procedure, were used to identify an appropriate or preferred method of digestion for all elements of concern. Since a large variety of elements were analyzed during this research, it was expected that results for each element would vary based on the digestion method.

Finally, in order to determine the contribution of the total composition from the solid portion of the waste, the supernatants were analyzed to determine the soluble elemental composition of the waste. This was necessary to help identify the origin and phase of selected elements and to understand the effect of dewatering on the overall sample composition. This is particularly important since the typical moisture content of residual solids during disposal is unknown and could vary depending on the location, drilling company, and treatment facility.

The overall goal for characterizing these solids is to help drilling companies and other organizations within the oil and gas industry develop best management practice for residual solids. Additionally, it is important that this information be available to address the public's environmental, health, and safety concerns.

3.3 Hypothesis

It was expected that the extraction procedure with nitric and hydrochloric acid in a closed, direct energy coupled device will typically result in the most complete digestion of residual solids due to the more rigorous extraction fluid and digestion conditions. This procedure also reduces the loss of volatiles due to the closed-vessel design.

Results for the various residual solids are predicted to vary slightly based on the expected characteristics of each sample type. For example, it is likely that the raw solids from settling produced water will be high in silica due to the addition of sand in the fracturing fluid, and treated sludge will contain large concentrations of barium, iron, and strontium due to the chemical precipitation treatment process. Since the drilling mud was collected by RES from various well locations within the Marcellus Shale, it is likely a combination of water, oil, and synthetic based materials. Solidified sludge will likely have characteristics similar to the three other sample types, since it is a composite.

When determining the contribution of each element from the solid portion of the samples, it is predicted that the majority of elements will be in the solid phase of the sample. A few exceptions include barium and strontium in the raw solid samples, since these elements will likely be in the soluble form and require chemical precipitation.

3.4 Methods and Materials

3.4.1 Chemical Reagents and Glassware Preparation

Reagent grade chemicals were used in all experiments. In order to perform trace metal analysis of solid samples, trace metal grade acids were used during digestion. These included Fisher Scientific Trace Metal Grade nitric acid and hydrochloric acid. Fisher Scientific ACS Certified Grade 30% hydrogen peroxide was used when required. Nanopure reagent water was used for dilutions and solution preparation. For recovery tests and ICP-MS calibration, three standard solutions with up to 2% nitric acid were prepared by High Purity Standards in Charleston, SC, and used for all elements of concern. Specifications for these standard solutions are provided in APPENDIX A – STANDARD SOLUTIONS. Purity of chemical reagents and reagent water was monitored throughout experimentation.

Glassware, lab equipment, and polyethylene storage bottles were cleaned thoroughly with Sparkleen laboratory detergent, soaked with 10% ACS reagent grade nitric acid for at least one hour, and then rinsed thoroughly with distilled-deionized water and twice with nanopure water. Glassware, equipment, and bottles were air dried in a clean environment.

3.4.2 Sample Preparation

Solids were thickened prior to analysis by placing in a clean polyethylene bottle and centrifuging for one hour at 2,000 rpm to remove free water. After centrifugation, supernatants were removed and placed in a separate vial. Solid and supernatant samples were stored in a refrigerator to await digestion and analysis.

3.4.3 Acid Digestion of Solids

Strong acid digestion of solids was performed following EPA Method 3050B - Acid Digestion of Sediments, Sludges, and Soils to determine "environmentally available" elements. This procedure is not meant to determine the total composition of a sample, but rather the amount that is reasonably expected to leach under worst-case environmental conditions. This procedure offers two alternative methods for digestion, depending on the expected analytical technique. Analysis with ICP-MS required the use of concentrated nitric acid and hydrogen peroxide for the oxidation of organic content (US EPA 3050B, 1996). Analysis with ICP-atomic emission spectrometry (AES) would require a similar procedure with the addition of concentrated hydrochloric acid (US EPA 3050B, 1996). Although the two extracts are not interchangeable, both procedures were performed on the solid samples and the resulting fluids were analyzed for trace metals using ICP-MS to determine the most suitable digestion method for elements of concern.

3.4.3.1 Digestion Procedure

For the digestion of solids, a representative sample of centrifuged residual solids, weighing between 1-2 g (wet weight), was transferred to a 100 mL beaker and digested with nitric acid and hydrogen peroxide. The required addition of these reagents is dependent on the sample characteristics, whereas acid is added until the digestion is considered complete and brown fumes no longer form. In all cases, a total of 10 mL nitric acid was required, including the 10 mL of 1:1 HNO_3 that was added prior to digestion. In order to prevent boiling, samples were maintained at approximately 80°C during digestion. To complete the oxidation of the samples, hydrogen peroxide is added until effervescence is minimal. Treated sludge and drilling mud required a total of 6 mL hydrogen peroxide, while 9 mL was needed for raw solids and solidified sludge. For samples following the alternative digestion method, a constant 10 mL of HCl was added to the sample and refluxed based on the method guidelines. The final digestate was quantitatively transferred to a volumetric flask, diluted to 100 mL, and filtered through a 0.45 μm nylon filter. Although the EPA procedure recommends a Whatman 41 or equivalent filter, this 0.45 pore size was required to determine the soluble portion in the extract and prevent damage to ICP-MS equipment. These two procedures were performed in triplicate for each sample type. Method blanks were collected in duplicate for each extraction fluid; however, 6 mL of hydrogen peroxide was used for one blank and 9 mL was used in the other to as per the required addition in the solid samples.

3.4.3.2 Recovery Test

In order to test the suitability of each method for elemental characterization, a recovery test was developed. In this recovery test, 5 mL of standard solution or nanopure water blank was added to a 100 mL beaker, and the procedure was performed as specified in EPA Method 3050B with the total reagent additions indicated above. Since the elements were in the liquid phase and not a solid matrix, this recovery test cannot be used to determine the completeness of sample digestion. However, it does indicate the amount of loss or contamination for each element of concern observed through this method. This recovery test was performed in duplicate for each extraction fluid and standard solution.

3.4.4 Microwave-Assisted Acid Digestion of Solids

Strong acid digestions of solid samples were also performed following EPA Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils, using a CEM Mars Extractor closed glass vessel system. This procedure is designed to be a rapid extraction procedure with results similar to those in conventional EPA Method 3050B digestion and should therefore not be considered a total digestion of the sample. This procedure can be performed with concentrated nitric acid or a nitric and hydrochloric acid mixture. The use of hydrochloric acid may improve recoveries of certain analytes including antimony, barium, iron, aluminum, and silver; however, it may also make quantification with certain techniques more difficult (US EPA 3051A, 2007).

3.4.4.1 Microwave Glassware Preparation

Glass digestion vessels had to be cleaned using a procedure recommended by the manufacturer due to the presence of acid-sensitive resin that could not be placed in an acid bath. All glassware used in this experiment underwent a clean cycle in the microwave unit with 10 mL of ACS reagent grade nitric acid heated to 150°C for 10 min. After the clean cycle, glass vessels and Teflon lids were rinsed thoroughly with distilled/deionized water and twice with nanopure water before being air dried in a clean environment.

3.4.4.2 Digestion Procedure

For the digestion of solid samples, a representative sample weighing less than 0.5 g (wet weight) was placed in a glass extraction vessel with either a nitric acid or nitric and hydrochloric acid extraction fluid. The vessel was capped with a Teflon lid and placed in a composite sleeve with support system. These vessels were placed in the microwave unit with a control vessel containing 0.5 g of inert solid (acid washed quartz sand), the appropriate extraction fluid, and a probe which was used to control temperature within the system. These samples were heated to 175°C for 5.5 minutes and held at that temperature for 4.5 minutes. After digestion, samples were cooled to room temperature and the pressure valve on each structure was carefully released to minimize sample loss. The sample was quantitatively transferred to a volumetric flask, diluted to 100 mL, and filtered through a 0.45 μm nylon filter. This process was performed in triplicate for samples digested with nitric acid and duplicate for those digested with a nitric and hydrochloric mixture. Only two replicates could be performed using the nitric and hydrochloric acid mixture due to issues with pressure build-up in the microwave unit.

3.4.4.3 Recovery Test

In order to test the suitability of this method for elemental characterization, a recovery test was developed. In this test, 5 mL of a standard solution was added to the digestion vessel with 0.5 g inert solid (acid washed quartz sand). The digestion was then performed as specified by EPA Method 3051A with both extraction fluids indicated above. An inert solid was used to maintain proper conditions within the vessel to regulate temperature, and separate trials were performed with nanopure water rather than the standard solution spike, in order to determine the contribution of elements from the inert solid. Since the elements were in the liquid phase and not a solid matrix, this recovery test cannot be used to determine the completeness of sample digestion. However, it does indicate the overall amount of loss or contamination from the original spike for each element of concern. This recovery test was performed in duplicate for each extraction fluid and standard solution, and it was performed in triplicate for the blank samples in order to determine the contribution from the inert solid.

3.4.5 Approved Elements for Quantification with Acid Digestion Procedures

Elements approved for quantification with EPA Methods 3050B and 3051A with the two extraction fluids are outlined in Table 1 and indicated with an “X”.

Table 1: Approved Elements for Quantification with EPA Methods 3050B and 3051A

	EPA 3050B		**EPA 3051A**	
Element	**Nitric Acid**	**Nitric/Hydrochloric Acid**	**Nitric Acid**	**Nitric/Hydrochloric Acid**
Aluminum		X		X
Antimony		X		X
Arsenic	X		X	X
Barium		X		X
Beryllium	X	X		X
Boron			X	X
Bromide				
Cadmium	X	X	X	X
Calcium		X	X	X
Chromium	X	X		X
Cobalt	X	X	X	X
Copper		X	X	X
Iron	X	X		X
Lead	X	X	X	X
Lithium				
Magnesium		X		X
Manganese		X	X	X
Mercury			X	X
Molybdenum	X	X	X	X
Nickel		X	X	X
Phosphorus				
Potassium		X	X	X
Selenium	X		X	X
Silicon				
Silver		X		X
Sodium		X	X	X
Strontium			X	X
Sulfate				
Uranium				
Vanadium		X		X
Zinc		X	X	X
Zirconium				

3.4.6 Residual Solid Supernatants Analysis

Supernatants obtained during the initial preparation of residual solids by centrifugation were filtered through a 0.45 µm filter and stored in a refrigerator to await analysis. Due to the elevated levels of elements in these samples, supernatants needed to be significantly diluted so that concentrations fell within the calibration curve. The large dilution factors may have contributed to error in calculations. Supernatant concentrations were used to estimate the portion of soluble elements in the liquid phase of the waste which were then be used to calculate the contribution from the solid portion based on the total environmentally available concentration.

3.4.7 Elemental Analysis

Extracts from the strong acid digestion of solid samples and the undigested supernatants were analyzed for metals using EPA Method 6020A – Inductively Coupled Plasma Mass Spectrometry. This was performed on a Thermo X-Series ICP-MS. Although chloride was originally intended to be analyzed, it was excluded due to the use of hydrochloric acid in certain samples which had the potential to damage the sensor and carryover between samples.

The accuracy and precision of ICP-MS was determined with two analytical limits. The minimum reporting level (MRL) is the minimum concentration that can be reported with significant confidence (99%) as the actual concentration in the sample. This was calculated following recommendations from Winslow *et al.* (2005). The method detection limit (MDL) is the minimum concentration that can be observed which indicates with significant confidence (99%) that the element is present at concentrations above zero in the sample. The MDL of each element was determined following EPA guidelines using the standard deviation from 7 trials of a low level standard (US EPA 40 CFR 136 Appendix B, 1997). For this research, the low level standard chosen for MDL determination was the MRL value calculated above. The MDL and MRL information determined for each element with ICP-MS is provided in Appendix B – Analytical Limits.

3.5 Results and Discussion

3.5.1 Recovery Test Results

During the ICP-MS analysis of recovery test samples, sample concentrations were adjusted based on the dilution factor to reflect total concentrations. If the results from ICP analysis were below the MDL, the total value was automatically set to zero. If the elements were detected during ICP-MS analysis but the values were below the MRL, they were used to calculate the approximate total concentration for the recovery test analysis. Average concentrations were calculated for the three standard solutions and blank. For each element of concern, the recovery was determined by taking the average concentration from the sample that was spiked with the appropriate standard and subtracting the average from the method blanks. These values were compared to the concentration in the original standard spike solution in order to determine the overall recovery (%) of the spike from digestion. If an approximate value for the standard solution or blank was used, the value is indicated as an approximation in the final results.

The results from EPA 3050B and 3051A recovery tests are presented in Figure 3. In this graph, "N" signifies that the procedure was performed with nitric acid extraction fluid and "NH" indicates a nitric and hydrochloric acid mixture. Note that the digestions for EPA 3050B also included 6 mL or 9 mL of hydrogen peroxide.

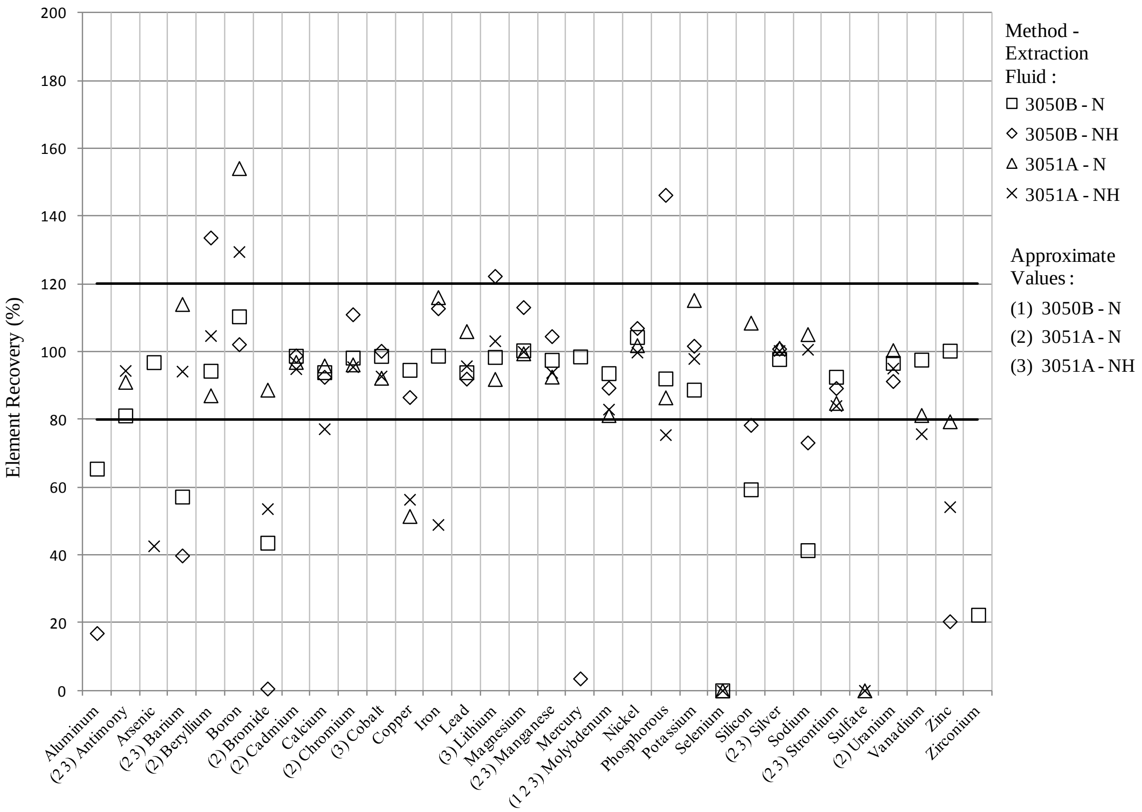


Figure 3: Recovery Test Results for Strong Acid Digestion of Residual Solid Samples following EPA Methods 3050B and 3051A

The majority of elements had reasonable recoveries that fell within the preferred range of 80-120%. Aluminum, selenium, sulfate, and zirconium presented significant issues during these recovery tests since no digestion method or extraction fluid resulted in a recovery within this range.

The recovery results represent the portion of the original standard spike that remains after digestion. Since the values were adjusted to remove the concentration in the method blanks, these results do not provide information regarding the interference from chemical reagents or any contamination from the digestion procedure. Additionally, since the standard solutions were in the aqueous phase, these results do not indicate completeness of digestion for solid samples. It's expected that the actual concentration in the sample is greater than the standard solution used during the recovery test which would help decrease error and make results more significant. Based on these considerations, it is still possible that results from the strong acid digestion of solid samples may be used to reasonably quantify elements of concern.

3.5.2 *Strong Acid Digestion Results*

Results for the strong acid digestion of samples were adjusted to remove the concentration in the blank samples. This was important for EPA Method 3050B since the chemical reagents were not all trace metal grade, meaning they would exhibit higher background concentrations, and the procedure was subject to contamination and losses in the open vessel system. The blanks for EPA Method 3051A were not digested in the microwave; however they indicate the interference from chemical reagents used during this procedure. These adjusted concentration values were averaged and used to determine the total environmentally available composition (mg/kg dry) based on the sample weight, sample moisture content, and dilution factor used during analysis. These calculations were performed following Equation 1. If the average adjusted concentration was between the detection limit and reporting limit, the composition was indicated as “Trace”. If all of the values were below the MDL, the element was indicated as not detected “ND”. Results from this analysis are provided in APPENDIX C – STRONG ACID DIGESTION RESULTS.

Equation 1

$$Total\ Composition\ (mg/kg\ dry)$$

$$= \frac{Extract\ Concentration\ x\ Extract\ Volume}{Wet\ Sample\ Weight\ x\ (1 - Moisture\ Content\ )}$$

$$= \frac{(ug/L\ extract)\ x\ (L\ extract)}{(g\ sample)(g\ dry\ /\ g\ sample)}\ x\ \frac{1\ mg}{1000\ ug}\ x\ \frac{1000\ g\ dry}{1\ kg\ dry}$$

$$where\ (g\ sample)\ is\ the\ total\ wet\ sample\ weight$$

3.5.2.1 Comparison between Digestion Methods

When analyzing the variations between the four extraction techniques, the percent relative standard deviation (%) was used to determine the effect of the extraction method quantification of the elemental composition. The relative standard deviation is the standard deviation for the results between the four methods divided by the average. The environmentally available composition determined from each procedure and the percent relative standard deviation between the four methods are presented in Figure 4. If any of the four methods resulted in a trace “T” concentration as defined above, values for the percent relative standard deviation could not be determined. The EPA standard is indicated by the method number and extraction fluid is indicated with “N” or “NH”, for a nitric acid or a nitric and hydrochloric acid mixture respectively

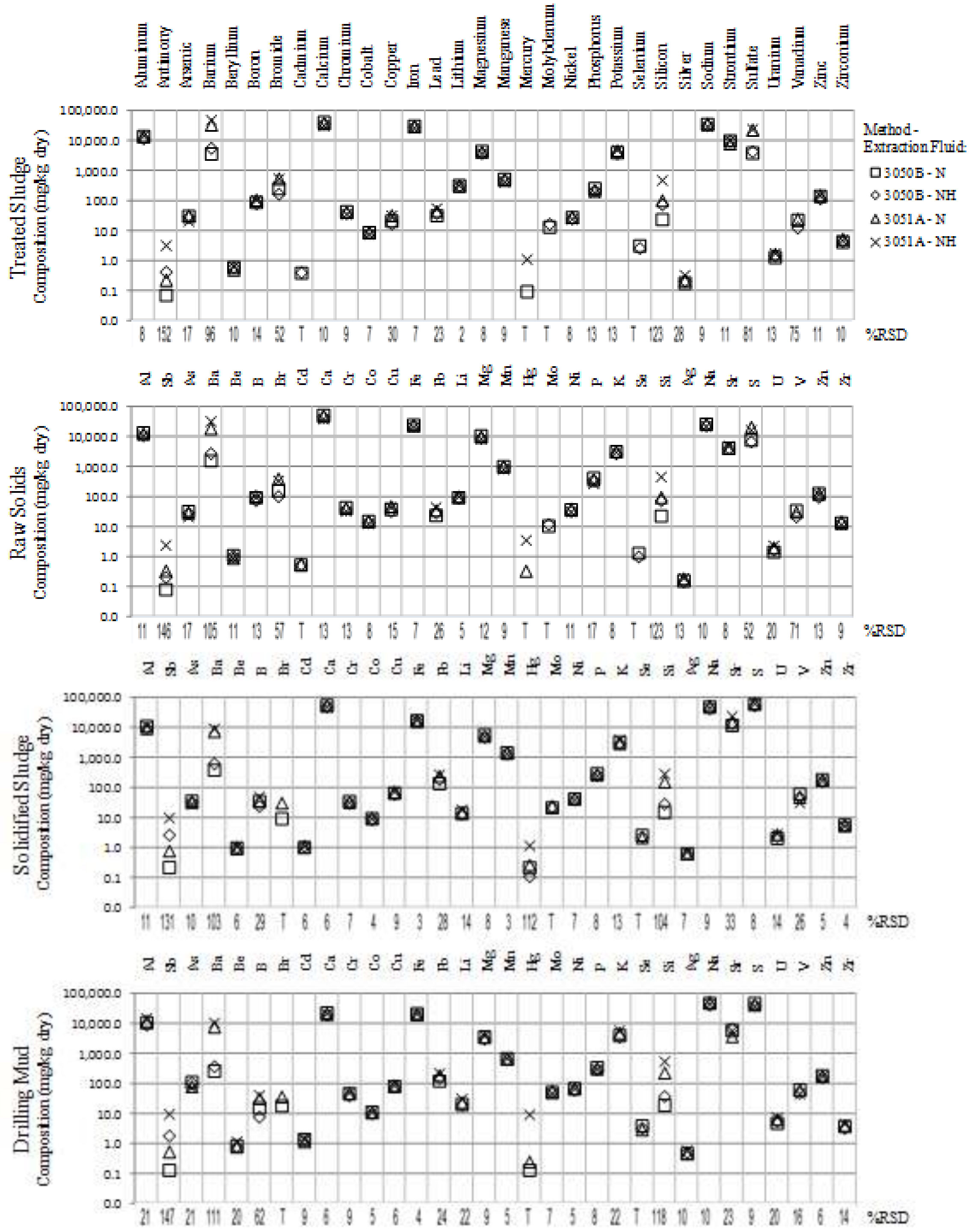


Figure 4: Environmentally Available Composition (mg/kg dry) and Percent Relative Standard Deviation (%RSD) from Acid Digestion of Residual Solid Samples

When the percent relative standard deviation is high, it indicates that there was a large variance in results between the four digestion methods. For example, a value above 100% indicates that the standard deviation was greater than the average concentration. By using a normalized technique, results from multiple elements with a broad range of values can be easily compared. From this analysis, it was determined that the digestion method plays an important role in characterizing the elements with large relative standard deviations (greater than 50%). The elements with high relative standard deviations for all solid types were antimony, barium, bromide, and silicon.

In order to study the effect of each digestion procedure when characterizing elements with high and low relative standard deviations, raw solid results from each method are presented in Table 2. The EPA standard is indicated by the method number and extraction fluid is indicated with "N" or "NH", for a nitric acid or a nitric and hydrochloric acid mixture respectively. If any of the replicates during ICP-MS analysis had a value above the detection limit but below the MRL, the average concentration was set as "Trace" since an accurate value could not be determined. If all values fell below the detection limit, the element was identified as not detected "ND".

Table 2: Raw Solids Environmentally Available Composition (mg/kg dry) and Percent Relative Standard Deviation (%RSD) of Select Elements from Strong Acid Digestions

	Digestion Procedure - Extraction Fluid				
Element	**3050B - N**	**3050B - NH**	**3051A - N**	**3051A - NH**	**%RSD**
Antimony	0.1	0.2	0.3	2.5	146
Barium	1,630	2,840	19,500	33,500	105
Bromide	163	105	407	351	57
Cobalt	15.8	14.3	15.5	13.0	8
Iron	25,800	24,200	24,000	21,800	7
Lithium	96.5	92.3	102	103	5
Potassium	3,300	2,810	3,380	3,140	8
Silicon	23.3	76.4	97.8	472	123
Strontium	4,290	4,240	4,350	5,030	8
Sulfate	8.0	7.1	21.3	17.0	52
Vanadium	35.2	22.1	31.8	ND	71
Zirconium	13.6	13.2	14.9	12.0	9

The use of the closed vessel system for direct energy coupled digestion significantly increases the results for barium and silicon. Since these elements do not significantly volatilize, it's likely that the increased digestion is due to the higher temperature and pressure of the closed system. Antimony stabilization is also improved through the use of hydrochloric acid (EPA 3051A, 2007) and further increased using the microwave extraction technique. While there are variations in bromide results between the four techniques, the trend indicates that digestion is improved by both the microwave extraction and absence of hydrochloric acid. For all residual solids, antimony, barium and silicon exhibited the highest results with the nitric and hydrochloric extraction fluid during microwave-assisted digestion. Bromide had the highest results using the microwave with a nitric acid extraction fluid.

For elements with low relative standard deviations, the various digestion methods did not exhibit a large difference when characterizing elements. This means that any of the four procedures could be used to reasonably estimate the total environmentally available concentration in solid samples.

EPA’s allowable holding time for mercury (28 days) was exceeded during this analysis, meaning the values from this research cannot be confidently reported. However, these results were included to indicate the approximate composition of mercury in the residual solids.

3.5.2.2 Comparison between Residual Solid Samples

In order to compare the elemental composition between the four solid samples, the maximum observed composition for each element was determined from the four digestion method averages outlined in APPENDIX C – STRONG ACID DIGESTION RESULTS. It was determined for this research that the maximum observed composition between the four procedures was likely the most indicative of the actual concentration in the residual solid sample. A comparison between the highest observed values for each sample type is presented in Figure 5.

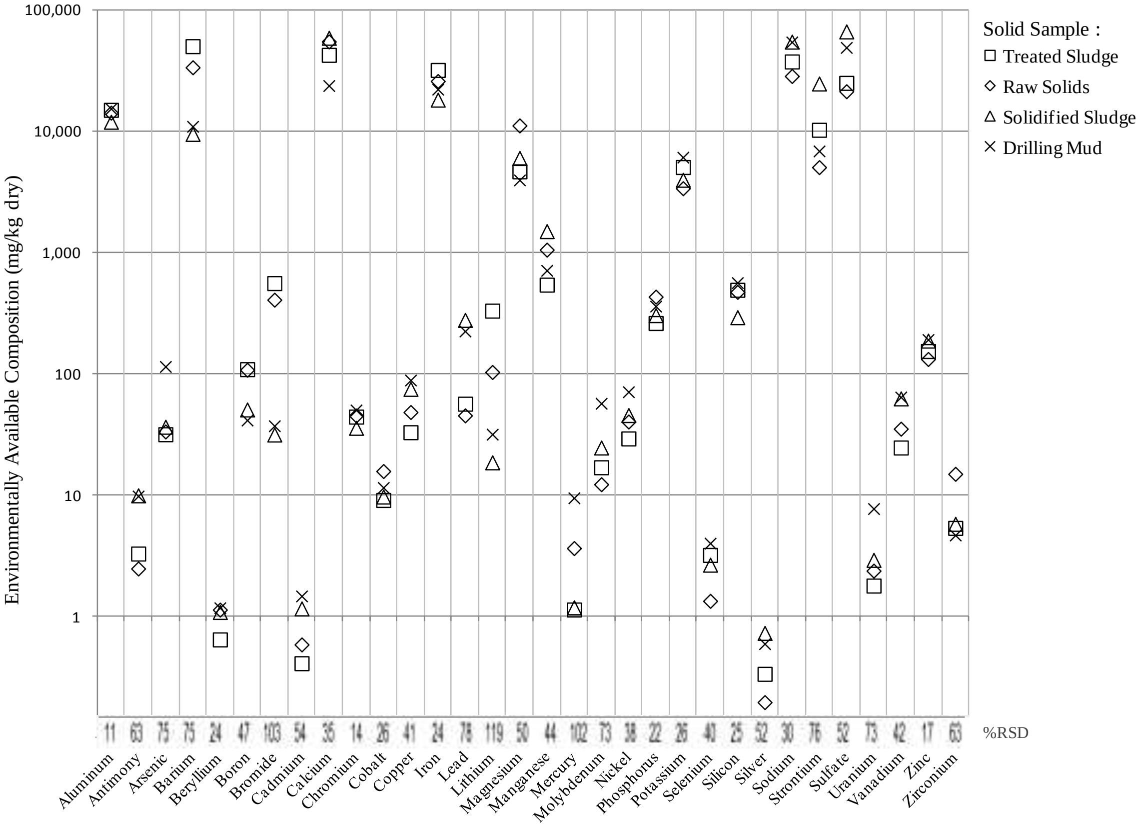


Figure 5: Maximum Observed Environmentally Available Composition (mg/kg dry) and Percent Relative Standard Deviation (%) between the Four Digestion Techniques for Residual Solid Samples

From this comparison, it was determined that the elemental composition was similar in the four solid samples. This was expected for the solidified sludge since it is a composite of the other three sample types with the addition of a solidifying agent. The major constituents identified were aluminum, barium, calcium, iron, magnesium, potassium, sodium, strontium, and sulfate. These elements were predicted to be high due to their natural occurrence in the Marcellus Shale or from previous findings in research related to produced water.

While the composition generally followed the same trend between sample types, as seen in Figure 5, there were still variations between the compositions for select elements. Elements with high variations between samples types (relative standard deviation above 66%) were arsenic, barium, bromide, lead, lithium, molybdenum, strontium, and uranium. Again, there was a high variance observed for mercury but these values cannot be confidently reported.

This variance was reasonable for barium, which was present at higher levels in the treated sludge and raw solids. Barium was expected to be a major constituent of the raw solids due to its elevated presence in produced water (Chapman *et al.*, 2012) and the treated sludge, due to RES's use of sodium sulfate to form a barium sulfate precipitate (Keister, 2010).

Arsenic, mercury, molybdenum, and uranium all had their highest concentrations in drilling mud, which may be due to the use of chemical additives which facilitate well construction. However, these elevated concentrations may also be from interactions with underground formations and natural brines during the drilling process, which are eliminated once the well is complete with cement casing barriers (Zoback *et al.*, 2010). It is difficult to make a definitive statement due to the use of proprietary chemicals and the absence of available information regarding on-site drilling practices.

3.5.3 Contribution from Liquid Portion based on Supernatant Analysis

Since residual solids were centrifuged prior to strong acid digestion, there was liquid remaining in the solids which contributed to elements in the final digestion extract. The moisture content for these centrifuged solids ranged from 30 to 54%. In order to determine the elemental composition in this liquid, supernatants from the centrifuged residual solid samples were filtered and analyzed on ICP-MS to determine the soluble composition. From these results, it was possible to determine the contribution from the liquid portion of the waste.

The maximum observed composition based on the four strong acid digestion techniques was determined for each residual solid type on a wet weight basis (mg/kg sample). Average supernatant results were used to determine the soluble elemental composition in this liquid, and the contribution from the liquid portion of the waste was determined using the average moisture content in the samples and total composition. Calculations were performed using Equation 2, and the results for the contribution (%) from the liquid portion of the waste are presented in Figure 6.

Equation 2

$$Contribution\ (\%) from\ Liquid\ Portion\ = Soluble\ Composition\ /\ Total\ Composition$$

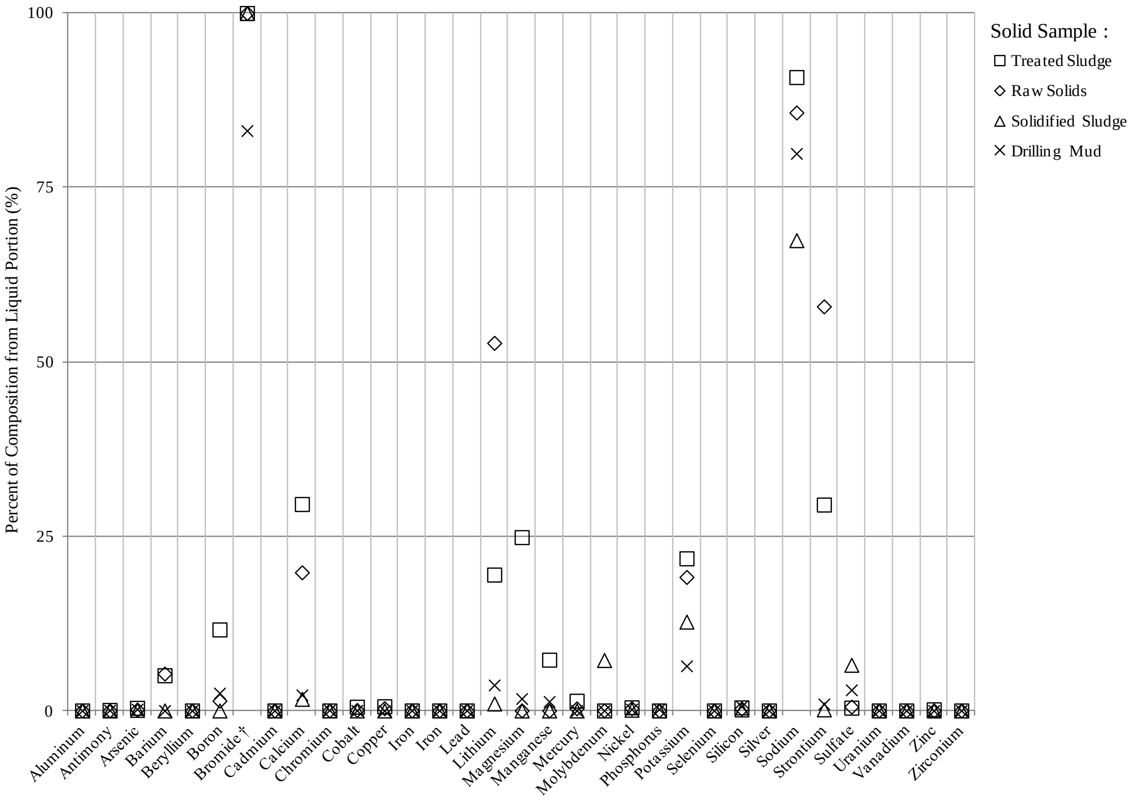
$$= \ [Supernatant\ Concentration\ x\ Moisture\ Content\ /\ Water\ Density]\ /\ Total\ Composition$$

$$= \frac{(ug/L\ supernatant)\ x\ (g\ water\ /\ g\ sample)}{(1000\ g\ water\ /\ L\ supernatant)}\ /\ (g\ total/g\ sample)$$

$$= \ (g\ in\ liquid\ portion\ of\ sample\ /\ g\ total)$$

$$where\ (g\ sample) is\ the\ total\ wet\ sample\ weight$$

If the supernatant analysis resulted in a value below the MRL, the average concentration could not be accurately quantified and the percent contributed from the liquid portion was set to zero in Figure 6 below. In three instances for bromide, calculations resulted in a value above 100% for the amount contributed from the liquid portion. These values were adjusted down to 100%, indicating that the element was entirely contributed from the liquid portion of the sample.



† Values adjusted due to results above 100%

Figure 6: Percent (%) of Environmentally Available Composition Contributed from Liquid Portion of Residual Solid Sample

It was determined from these results that the solid portion of the waste is the major source for most elements. Notable exceptions were bromide and sodium. In the case of barium, boron, calcium, lithium, magnesium, manganese, molybdenum, potassium, strontium, and sulfate, results varied based on the sample type. Large results for the liquid contribution may be caused by actual elevated levels within the supernatant or issues with the digestion process which would underestimate the total environmentally available composition in the samples.

It is important to note that these results were calculated using the average sample moisture content which ranged from 30-54% depending on the sample type. Therefore, these results are specific to the centrifuged samples used during digestion, and the percent contributed from the liquid portion could vary depending on sample preparation.

3.5.4 Comparison of Results to Regulatory Limits for Sludge Use and Disposal

The use or disposal of sewage sludge from the treatment of domestic wastewater is currently regulated by federal and local agencies. For land application and unlined surface disposal (such as burial), EPA has defined regulatory limits for the total allowable composition of select elements. If the total composition in the solids exceeds the regulatory limit for any pollutant, the sludge is not eligible for land application or unlined surface disposal (US EPA, 40 CFR 503.10, 1993).

Although sludge from industrial wastewater does not fall under these regulations, it is possible to compare results from this research and regulatory limits to estimate the suitability of land application and burial for hydraulic fracturing residual solids. The maximum observed concentration for each solid as determined above was compared to the regulatory limits for sewage sludge in Table 3.

Table 3: Maximum Observed Environmentally Available Composition of Solids Compared to Regulatory Limits for Sewage Sludge Land Application and Unlined Burial (mg/kg dry)

					Sewage Sludge Disposal Limits	
Element	**Treated Sludge**	**Raw Solids**	**Solidified Sludge**	**Drilling Mud**	**Land Application**	**Unlined Surface**
Arsenic	32	33	36	***115***	75	73
Cadmium	0	1	1	1	85	
Chromium	44	45	36	50	3000	600
Copper	33	48	75	89	4300	
Lead	57	45	277	224	840	
Mercury	1	4	1	9	57	
Molybdenum	17	12	25	57	75	
Nickel	29	40	46	71	420	420
Selenium	3	1	3	4	100	
Zinc	154	132	187	191	7500	

It was determined from this comparison that the drilling mud from RES facilities exceeded the allowable limit for arsenic, meaning it is not suitable for land application based on EPA regulations for sewage sludge. Although the other samples had pollutant concentrations below the regulatory limits, it is important to note that these values are for the environmentally available composition and solids should be tested for the total composition to determine if they meet the regulatory requirements for sewage sludge use and disposal. However, it is expected that the results from this research will be similar to total composition for the elements of concern identified in Table 3.

3.6 Conclusion

Strong acid digestion of residual solids was used to determine the total environmentally available compositions for elements of concern. During this research, recovery tests were performed to determine the most suitable of digestion procedures and extraction fluids for elemental characterization. During these recovery tests, all elements exhibited acceptable recoveries except aluminum, selenium, and zirconium. Since these tests were not designed to measure digestion efficiency, it is still possible that digestion results can be used to determine sample composition.

Based on results from the strong acid digestion of residual solid samples, it was determined that the procedure and extraction fluid play a significant role in characterizing the elements antimony, barium, bromide, and silicon. For all residual solids, results for antimony, barium and silicon were the greatest using the microwave assisted digestion (EPA 3051A) with a nitric and hydrochloric acid extraction fluid. Results for bromide were the greatest using the same method with nitric acid. While there were variations between the methods for other elements, they yielded reasonably similar results, meaning any of them could be used to determine total environmentally available composition.

This analysis revealed that the residual solids used in this research exhibited similar trends in overall environmentally available elemental composition. Major constituents included aluminum, barium, calcium, iron, magnesium, potassium, sodium, strontium, and sulfate. However, there were variations in the elemental composition between samples for arsenic, barium, bromide, lead, lithium, molybdenum, strontium, and uranium.

From analyzing the residual solid supernatants, it was determined that the majority of elements were contributed from the solid portion of the waste. Notable exceptions included bromide and sodium which were present at elevated levels in the supernatants for all residual solid samples. Depending on the sample type, barium, boron, calcium, lithium, magnesium, manganese, molybdenum, potassium, strontium, and sulfate were also found at significant levels in the liquid portion of the waste.

While these strong acid digestion methods are approved by EPA to determine the total composition of environmentally available elements, it is important to keep in mind that the results may subject to incomplete digestion, interferences, formation of precipitates, and loss of volatiles.

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CHAPTER 4: MANUSCRIPT 2

Characterizing Leaching Behavior of Residual Solids from Hydraulic Fracturing in the Marcellus Shale Based on EPA Regulatory Standards

ABSTRACT

EPA leaching procedures were performed on residual solids from hydraulic fracturing to determine the leaching potential of select elements and to characterize the waste. The solids used in this research were raw solids, treated sludge, solidified sludge, and drilling mud. The Toxicity Characteristic Leaching Procedure (TCLP) was performed to simulate leaching in a co-disposal environment, such as a municipal landfill, and results were compared to EPA allowable limits to determine if the waste was hazardous. Based on this research, it was determined that the treated sludge is hazardous based on the barium leaching potential, while all other solids passed in regards to metal leaching potential (excluding mercury).The Synthetic Precipitation Leaching Procedure (SPLP) was performed to simulate leaching in a mono-disposal environment where the solids are in contact with acid rain. Comparing results from the two procedures, it was determined that the organic extraction fluid from TCLP is typically more aggressive when characterizing leaching behavior. Also, leachate from the solidified sludge had significantly lower concentrations for select elements, indicating that the solidification process is effective.

KEYWORDS: Hydraulic Fracturing, Residual Solids, Leaching Behavior, Metal Characterization, Toxicity Characteristic Leaching Procedure, Synthetic Precipitation Leaching Procedure, Hazardous Waste

4.1 Introduction

Hydraulic fracturing is a process for unconventional natural gas extraction which uses pressurized fluid to fracture subsurface shale formations, thereby releasing natural gas. Typical drilling configurations include a deep vertical well which extends into horizontal wells through the shale formation, which can be fractured in segments (Andrews *et al.*, 2009). These wells are constructed using drilling mud, (a water, oil or synthetic based slurry) to carry drill cuttings to the surface and lubricate drilling equipment (Ohio EPA, 2012). Once completed, each well requires between 7,000 and 18,000 m^3 of fracturing fluid, which is typically a mixture of water, sand and chemical additives (Gregory *et al.*, 2011). These additives include friction reducers, anti-microbial agents, scale inhibitors, and other chemicals to facilitate fracturing and subsequent gas extraction (Abdalla *et al.*, 2011). Some of the injected fluid, roughly 24% of the total volume, immediately returns to the surface after the fracturing event (Haluszczak *et al.*, 2013), and fluid continues to return to the surface throughout the lifetime of the well.

This produced water from hydraulic fracturing contains total dissolved solids, frequently exceeding 200,000 mg/L due to the elevated presence of naturally-occurring salts, radionuclides, and heavy metals (Chapman *et al.*, 2012). Produced water is typically stored onsite in earth impoundments or temporary containers before being reused in subsequent well completions or transported to a dedicated facility to undergo treatment (Hammer and VanBriesen, 2012). These processes generate residual solids which must be properly managed; typically being disposed of onsite or in a municipal landfill. The purpose of this research was to characterize the solids resulting from hydraulic fracturing operations and produced water treatment in the Marcellus Shale, in order to predict the total environmentally available concentration of elements present in each sample. This information may be used to understand the chemical characteristics of the waste and to help predict the leaching behavior of solids under environmental conditions.

Samples were collected from the New Stanton Plant, a 1.2 MGD dedicated treatment facility in New Stanton, PA, which is owned and operated by Reserved Environmental Services (RES). This facility receives produced water and drilling waste from companies throughout the Marcellus Shale region. Influent produced water is placed in a rock box to remove heavy solids before undergoing chemical treatment. This process uses sodium sulfate, sodium hypochlorite, and sodium hydroxide to remove dissolved elements, including barium, iron, and strontium. Influent drilling mud is thickened and the resulting supernatant is introduced into the process stream for treatment. The resulting solids, including raw residual solids from rock boxes, thickened drilling mud, and sludge from the chemical treatment of process water, are mixed and solidified with cement kiln dust (CKD) before disposal in a municipal landfill. The four samples collected for the research project were: (1) treated sludge, (2) raw solids, (3) drilling mud, and (4) solidified sludge. RES manages waste from various drilling companies within the Marcellus Shale region.

Depending on the characteristics of the waste generated from hydraulic fracturing practices in the Marcellus Shale, solids can either be disposed of through land application or in landfills (Hammer and VanBriesen, 2012). Municipal waste landfills can receive certain types of waste, but toxic substances can only be deposited in permitted hazardous waste landfills, increasing the cost of disposal (Asante-Duah *et al.*, 1992). The Toxicity Characteristic Leaching Procedure (TCLP) was developed by EPA under the Resource Conservation and Recovery Act (RCRA) to predict the leaching behavior of select contaminants including metals and organics, such as pesticides, herbicides, volatiles, and semi-volatiles, in a municipal landfill environment. Co-disposal in a municipal landfill means the waste is integrated with other solids which will affect extraction fluid characteristics. If the final concentration in the TCLP extract exceeds the EPA allowable limit for any of the specified contaminants, the waste is classified as hazardous (US EPA 40 CFR 261.24, 2012). The metals of concern based on EPA's RCRA regulations include arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. In order to meet regulatory requirements, TCLP must be performed within 180 days of sample collection for general metals, and 28 days for mercury (US EPA Website, 2012). Solidified sludge from the RES facility currently undergoes TCLP testing, which is performed by an independent laboratory before disposal in a municipal landfill.

EPA's Synthetic Precipitation Leaching Procedure (SPLP) can be used to determine the leaching potential of soil contamination into the groundwater. However, it can also be used to determine the leaching of waste in a mono-disposal environment with interactions from acid rain precipitation. Mono-disposal means the waste is disposed of separately or with similar solids, and therefore the leachate characteristics are influenced only by the specified waste and natural conditions. While there are no federal allowable limits for SPLP extracts, some state agencies have established regulatory limits (Connecticut DEEP, 2013) and other industries may use SPLP results to establish best management practices for a waste.

TCLP and SPLP were performed on hydraulic fracturing residual solids collected from RES in order to determine the leaching potential of select contaminants based on EPA standards. Since the focus of this research was inorganic contaminants, only metals relevant to TCLP allowable limits were analyzed using ICP-MS.

4.2 Project Objectives

The primary objective of this research was to characterize the chemical leaching behavior of residual solids from hydraulic fracturing operations in the Marcellus Shale based on EPA guidelines. Solids can be generated onsite or during offsite treatment. Since samples could only be collected from an offsite location, residual solids from onsite practices were simulated using "raw solids" which were derived from the gravity settling of produced water. In addition to the solids from raw produced water and the chemical treatment process, drilling mud from well construction was also analyzed. Finally, solidified sludge from the dedicated treatment facility was analyzed to determine the leaching potential of the solids before disposal in a municipal landfill.

TCLP was used to determine the leaching potential of metal contaminants for the solids in a co-disposal, municipal landfill. These results may be used to confirm the non-hazardous waste characterization of RES's solidified sludge and determine the classification of other solids related to hydraulic fracturing. SPLP was used to determine the leaching potential of metal contaminants in a mono-disposal environment with interactions from acid rain. The results of this study should prove useful in the development of best management practices for onsite waste disposal. By comparing the results from these two leaching procedures, it is possible to determine which disposal extraction fluid, and therefore which disposal environment, is more aggressive for hydraulic fracturing residual solids.

Samples collected from the RES facility had moisture contents ranging from 36.3-52.3% depending on the sample type. However, these samples would continue to dewater during storage prior to final disposal. Therefore, another major objective of this research was to evaluate the variations in leaching potential based on the solids content of the waste. These experiments were performed on solids collected from the facility which were gravity settled to simulate actual conditions and centrifuged to simulate the highest achievable solids content in the natural environment.

4.3 Hypothesis

Since solidified sludge from RES facilities is tested prior to disposal, it is expected that results for these samples will fall below EPA's allowable limits and be considered non-hazardous based on the metal leaching potential. However, all samples will be analyzed to determine their classification. If a hydraulic fracturing residual solid were to fail TCLP testing, it will likely be due to barium, which was present at elevated concentration in all residual solids samples collected from the RES facilities. Barium in the treated sludge was particularly concentrated, which was likely due to the use of sodium sulfate to precipitate soluble barium during the chemical treatment process. However, since all elements of concern indicated by RCRA were determined to be present based on previous strong acid digestions (outlined in Chapter 3), it is possible that the residual solids may exceed the allowable limit and be considered hazardous for in regards to any of these elements.

When evaluating differences in leaching potential between the two methods, the extraction fluid is the only variable. Typically, it is expected that pH indicates the aggressiveness of an extraction fluid. Therefore, it is predicted that the more acidic extraction fluid will result in greater leaching for residual solid samples.

4.4 Methods and Materials

4.4.1 Chemical Reagents and Glassware Preparation

Reagent grade chemicals were used in all experiments. Fisher Scientific American Chemical Society (ACS) grade glacial acetic acid and Mallinckrodt Chemicals Analytical Reagent (AR) grade 50% sodium hydroxide were used for TCLP extraction fluids. Fisher Scientific Trace Metal grade nitric acid and Sigma Aldrich ACS reagent grade sulfuric acid were used for the SPLP extraction fluid. Nanopure water was used for dilutions and solution preparation, while distilled-deionized water was used for filter washing. Purity of chemical reagents and reagent water was monitored throughout experimentation.

Glassware and polyethylene storage bottles were cleaned thoroughly with Sparkleen laboratory detergent and soaked with 10% nitric acid for at least one hour. They were then rinsed twice with distilled-deionized water and twice with nanopure water. Glassware and bottles were air dried in a clean environment.

4.4.2 Sample Preparation

In order to study the effect of moisture content on leaching behavior, two samples of each solid type were prepared. The first sample was placed in a clean polyethylene bottle and gravity settled for 3 days before the supernatant was discarded. The second sample was placed in a clean polyethylene bottle and centrifuged for one hour at 2,000 rpm before removing the supernatant. These samples were meant to simulate the actual moisture content of solids from the facility and the maximum solids content that could naturally occur. After preparation, samples were stored in a refrigerator to await analysis.

4.4.3 Toxicity Characteristic Leaching Procedure (TCLP)

The solid portion of the sample was determined by vacuum filtering a representative sample through a 0.7 μm glass fiber filter at a pressure of up to 40 psi. The filtrate is the liquid portion and the material remaining on the filter is the solid portion. Even though the dry solids percent for each sample was between 30-70%, no free water could be removed through vacuum filtration. Therefore, all samples were considered 100% solids by TCLP standards.

The required extraction fluid, which is based on sample alkalinity (US EPA 1311, 1992), was determined for each residual solid sample following method guidelines. The possible extraction fluids include: (1) acetic acid and sodium hydroxide at pH 4.93±0.05 and (2) acetic acid at pH 2.88±0.05. An overview of the required extraction fluid for each sample prepared through gravity settling or centrifugation is provided in Table 4.

Table 4: Required pH of TCLP Extraction Fluid for Residual Solids

Residual Solid	Gravity Settled	Centrifuged
Treated Sludge	4.93	2.88
Raw Solids	2.88	2.88
Solidified Sludge	2.88	2.88
Drilling Mud	4.93	4.93

For TCLP extraction, 5 g of sample were placed in a clean 125 mL polyethylene container with 100 mL of appropriate extraction fluid. This proportion was used to maintain a 20:1 (mL:g) ratio as required by TCLP guidelines. The bottle was placed in a rotary tumbler and agitated in compliance with method requirements. At the end of the procedure, the extract was passed through a 0.7 μm glass fiber filter that had been washed with 5 mL 1 N nitric acid, rinsed with distilled-deionized water, and dried in an oven at 105°C. If the sample settled slowly, it was centrifuged for 10 min at 2000 rpm before filtration. The filtrate from this process is considered the final extract and was stored for analysis. This experiment was performed in triplicate for each sample type.

4.4.4 Synthetic Precipitation Leaching Procedure (SPLP)

The solids portion of the samples was determined by vacuum filtration, similar to TCLP. Therefore, all samples were considered 100% solids by SPLP standards.

The required extraction fluid for SPLP is dependent on site specific conditions and sample characteristics. Concentrated sulfuric/nitric acid (60/40 by weight) is used to adjust reagent water to a desired pH in order to simulate acid rain. When analyzing contaminated soil, sites to the West of the Mississippi River employ an extraction fluid adjusted to pH 5.0±0.05, while those to the East have pH 4.2±0.05. However, if the samples being evaluated are solids related to waste and wastewater, the extraction fluid is required to have a pH of 4.2±0.05 (US EPA 1312, 1994). Based on the sample characteristics, an extraction fluid with pH 4.2±0.05 was used for all solids during this research.

For SPLP extraction, 5 g of sample were placed in a clean 125 mL polyethylene container with 100 mL of extraction fluid. The bottle was placed in a rotary tumbler and agitated based on SPLP requirements. At the end of this procedure, the fluid was passed through a 0.7 μm glass fiber filter that had been washed with 5 mL 1 N nitric acid, rinsed with distilled-deionized water, and dried in an oven at 105°C. Again, if the sample settled slowly, it was centrifuged for 10 min at 2000 rpm before filtration. The filtrate from this process is considered the final extract and was stored for analysis. This experiment was performed in triplicate for each sample.

4.4.5 Elemental Analysis

Extracts from TCLP and SPLP were analyzed for metals using EPA Method 6020A – Inductively Coupled Plasma Mass Spectrometry. This was performed on a Thermo X-Series ICP-MS.

The accuracy and precision of ICP-MS was determined with two analytical limits. The minimum reporting level (MRL) is the minimum concentration that can be reported with significant confidence (99%) as the actual concentration in the sample. This was calculated following recommendations from Winslow *et al.* (2005). The method detection limit (MDL) is the minimum concentration that can be observed which indicates with significant confidence (99%) that the element is present at concentrations above zero in the sample. The MDL of each element was determined following EPA guidelines using the standard deviation from 7 trials of a low level standard (US EPA 40 CFR 136 Appendix B, 1997). For this research, the low level standard chosen for MDL determination was the MRL value calculated above. The MDL and MRL information determined for each element with ICP-MS is provided in Appendix B – Analytical Limits.

4.5 Results and Discussion

Results from the two EPA leaching procedures for residual solids are outlined below. These experiments were performed within six months of sample collection, meaning that this research did not meet the regulatory requirements on holding time for mercury. Therefore, results about the mercury leaching potential cannot be confidently quantified and values have been included in this report for estimation purposes only.

4.5.1 Toxicity Characteristic Leaching Procedure (TCLP) Results

The results from TCLP outlined in Table 5 represent the total extract concentration (mg/L) for metal contaminants identified by EPA standards. The method for sample preparation is indicated as "GS" for gravity settling or "C" for centrifugation. This table also outlines the TCLP allowable limits for the appropriate elements to compare results to regulatory requirements. If results from all of trials fell below the MDL, the element is identified as not detected "ND". If the average value was above the detection limit but below the reporting limit, the value is identified as "Trace". Only if the average concentration was above the MRL could the concentration in the extract be accurately quantified.

Table 5: Final Extract Concentrations (mg/L) from Toxicity Characteristic Leaching Procedure Compared to TCLP Regulatory Limits (mg/L)

Solids Type	**Treated Sludge**		**Raw Solids**		**Solidified Sludge**		**Drilling Mud**		**TCLP Limit**
Preparation	GS	C	GS	C	GS	C	GS	C	
Dry Solids %	36.3	48.8	42.1	54.0	50.9	65.2	52.3	66.4	
Arsenic	Trace	0.0	ND	0.0	0.0	ND	0.0	0.0	**5**
Barium	**133**	**175**	68	47	Trace	Trace	2.5	2.0	**100**
Cadmium	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	**1**
Chromium	Trace	0.1	0.1	0.1	0.1	0.1	0.0	0.0	**5**
Lead	Trace	0.0	0.0	0.0	1.2	1.1	0.8	0.4	**5**
Mercury	0.0	ND	Trace	ND	ND	ND	ND	ND	**0.2**
Selenium	ND	ND	ND	Trace	ND	ND	ND	ND	**1**
Silver	Trace	ND	ND	ND	ND	ND	ND	ND	**5**

After reviewing the TCLP results, it was determined that the solidified sludge from RES's New Stanton facility passes EPA's TCLP requirements for metal contaminants. Since solidified sludge is disposed of in a municipal landfill, these results were expected. Additionally, it was determined that both the raw solids and drilling mud had extract results below the allowable limits for metals.

The only instance of an element exceeding the TCLP regulatory limits was for the barium in treated sludge samples. Since RES uses chemical precipitation to remove barium from the process water, these results are reasonable. As the solids content increases, the barium levels in the extract increase, indicating that the element is concentrated in the solid portion of the waste.

One major conclusion from these TCLP results is that the solidification process employed by RES is effective in decreasing the leaching potential of barium and other metal contaminants. The only metal contaminant that had a concentration increase in the solidified sludge extract was lead. This may be due to the nature of precipitates that form during solidification or from cement kiln dust itself. In order to test this hypothesis, the cement kiln dust should be analyzed to determine the leaching potential of the dust under similar conditions.

4.5.2 Synthetic Precipitation Leaching Procedure (SPLP) Results

The results from SPLP given in Table 6 represent the total extract concentration (mg/L) for metal contaminants, which were selected based on EPA's TCLP guidelines. The method for sample preparation is indicated as "GS" for gravity settling or "C" for centrifugation. If results from all trials fell below the MDL, the element was identified as not detected "ND". If the average value was above the detection limit but below the reporting limit, the value is identified as "Trace". Only if the average was above the MRL could the concentration in the extract be accurately quantified.

Table 6: Final Extract Concentrations (mg/L) from Synthetic Precipitation Leaching Procedure Compared to TCLP Regulatory Limits (mg/L)

Solids Type	**Treated Sludge**		**Raw Solids**		**Solidified Sludge**		**Drilling Mud**		**TCLP Limit**
Preparation	GS	C	GS	C	GS	C	GS	C	
Dry Solids %	36.3	48.8	42.1	54.0	50.9	65.2	52.3	66.4	
Arsenic	0.0	0.0	Trace	Trace	0.0	0.0	0.0	0.0	**5**
Barium	79	65	48	29	Trace	Trace	4.5	13	**100**
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	**1**
Chromium	ND	ND	Trace	Trace	Trace	Trace	Trace	0.1	**5**
Lead	ND	ND	ND	ND	Trace	Trace	0.0	0.2	**5**
Mercury	ND	ND	ND	ND	ND	ND	ND	ND	**0.2**
Selenium	ND	ND	ND	ND	ND	ND	ND	ND	**1**
Silver	ND	ND	ND	ND	ND	ND	ND	ND	**5**

Although barium still has the highest leaching potential for the selected metal contaminants, the SPLP results indicate that the leaching potential of residual solids fall below the TCLP allowable limits for all metal contaminants. While there are no defined federal limits for SPLP extracts, these results may be used to estimate the leaching potential of residual solids during mono-disposal such as onsite burial or land application.

4.5.3 Comparison between Leaching Procedures

Results from TCLP and SPLP can be compared to determine the expected leaching potential for residual solids in various disposal environments. In the case of treated sludge, the organic acid from TCLP to simulate leachate in a co-disposal environment was significantly more aggressive for barium leaching than the inorganic acid rain used in SPLP. Alternatively, barium leaching from the drilling mud increased under SPLP conditions. Since the only difference between these two methods is the extraction fluid, these variations may be due to the nature of the solids or specific interactions with the extraction fluid.

For other metal contaminants, the TCLP extraction fluid typically behaved more aggressively, resulting in higher extract concentrations. This suggests that the effect of extraction fluid should be considered when analyzing the leaching potential of elements from hydraulic fracturing residual solids.

4.6 Conclusion

The results from TCLP analysis indicate that RES's treated sludge is considered hazardous based on the barium leaching potential since the final method extract exceeded EPA's allowable limit of 100 mg/L. Since the solids failed this regulatory limit at both moisture contents, it's unlikely that dewatering techniques can be manipulated to affect the solid's classification. Additionally, since the barium leaching potential increased with higher solid contents, it is presumed that the barium is concentrated in the solid phase of the waste.

The raw solids, solidified sludge, and drilling mud are considered non-hazardous in terms of all metal contaminants except mercury. While the approximate values for mercury were below the required limit, conclusions could not be made since the holding times for mercury were exceeded

Comparing results between solids, it was determined that the solidification process employed by RES is effective at reducing the leaching potential for metal contaminants. The only instance where the solidified sludge had a higher leaching potential was for lead in the TCLP extract. This may be due to the nature of the solidified sludge samples or from the addition of a solidification agent.

When analyzing variations between the extraction fluids, the TCLP organic extraction fluid generally behaves more aggressively for metal leaching than the inorganic synthetic acid rain from SPLP. An exception to this is seen in barium leaching from drilling mud which is higher under SPLP conditions. This suggests that elemental leaching would be greater for most metal contaminants in a municipal landfill compared to a mono-disposal environment. To further explore this result, experiments should be conducted in related research to determine the effect of extraction fluid on leaching potential for all elements of concern.

It’s important to consider that these results are for RES samples specifically. Since drilling operators and alternative dedicated treatment facilities may employ different site specific practices, it is not appropriate to form definitive conclusions about other facilities based on these results. Samples from different facilities and operators should be tested independently, but these results may be useful to make approximations and inferences about residual solids throughout the Marcellus Shale.

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CHAPTER 5: MANUSCRIPT 3

Effect of Extraction Fluid on Leaching Behavior of Residual Solids from Hydraulic Fracturing in the Marcellus Shale

ABSTRACT

In order to determine the effect of extraction fluid on the leaching potentials of hydraulic fracturing residual solids, shake extraction tests were performed on samples following ASTM Method 3987. The solids used in this research include raw solids, treated sludge, solidified sludge, and drilling mud and the alternative extraction fluids were reagent water, synthetic acid rain, acetic acid, and a synthetic municipal landfill leachate. The synthetic leachate had been developed by Stanforth *et al.* (1979) to simulate worst case chemical characteristics of leachate from municipal landfills throughout the United States. By comparing the results from these digestions to the total environmentally available composition of solids determined in previous work, it was possible to determine the leaching potential (% of the composition) likely to be released from samples in various disposal environments. In general, it was determined that an organic extraction fluid behaved more aggressively than reagent water or synthetic acid rain in terms of the soluble elemental leaching. This suggests that a mono-disposal environment such as land application or burial would be preferable over disposal in a municipal landfill to mitigate leaching. However, there were also variations between elements. For example, elements like boron, bromide, calcium, lithium, magnesium, manganese, silicon, sodium, and strontium had high leaching potentials, suggesting that these elements will likely migrate from the residual solids. Elements with low leaching potentials indicate that the risk of leaching is low, even if the element is present in substantial concentrations.

KEYWORDS: Weak Acid Digestion, Leaching Potential, Extraction Fluid, Toxicity Characteristic Leaching Procedure, Synthetic Precipitation Leaching Procedure, Shake Extraction with Water, Synthetic Municipal Landfill Leachate

5.1 Introduction

Hydraulic fracturing is a process for unconventional natural gas extraction which uses pressurized fluid to fracture subsurface shale formations, thereby releasing natural gas. Typical drilling configurations include a deep vertical well which extends into horizontal wells through the shale formation, which can be fractured in segments (Andrews *et al.*, 2009). These wells are constructed using drilling mud, (a water, oil or synthetic based slurry) to carry drill cuttings to the surface and lubricate drilling equipment (Ohio EPA, 2012). Once completed, each well requires between 7,000 and 18,000 m^3 of fracturing fluid, which is typically a mixture of water, sand and chemical additives (Gregory *et al.*, 2011). These additives include friction reducers, anti-microbial agents, scale inhibitors, and other chemicals to facilitate fracturing and subsequent gas extraction (Abdalla *et al.*, 2011). Some of the injected fluid, roughly 24% of the total volume, immediately returns to the surface after the fracturing event (Haluszczak *et al.*, 2013), and fluid continues to return to the surface throughout the lifetime of the well.

This produced water from hydraulic fracturing contains total dissolved solids, frequently exceeding 200,000 mg/L due to the elevated presence of naturally-occurring salts, radionuclides, and heavy metals (Chapman *et al.*, 2012). Produced water is typically stored onsite in earth impoundments or temporary containers before being reused in subsequent well completions or transported to a dedicated facility to undergo treatment (Hammer and VanBriesen, 2012). These processes generate residual solids which must be properly managed; typically being disposed of onsite or in a municipal landfill. The purpose of this research was to characterize the solids resulting from hydraulic fracturing operations and produced water treatment in the Marcellus Shale, in order to predict the total environmentally available concentration of elements present in each sample. This information may be used to understand the chemical characteristics of the waste and to help predict the leaching behavior of solids under environmental conditions.

Samples were collected from the New Stanton Plant, a 1.2 MGD dedicated treatment facility in New Stanton, PA, which is owned and operated by Reserved Environmental Services (RES). This facility receives produced water and drilling waste from companies throughout the Marcellus Shale region. Influent produced water is placed in a rock box to remove heavy solids before undergoing chemical treatment. This process uses sodium sulfate, sodium hypochlorite, and sodium hydroxide to remove dissolved elements, including barium, iron, and strontium. Influent drilling mud is thickened and the resulting supernatant is introduced into the process stream for treatment. The resulting solids, including raw residual solids from rock boxes, thickened drilling mud, and sludge from the chemical treatment of process water, are mixed and solidified with cement kiln dust (CKD) before disposal in a municipal landfill. The four samples collected for the research project were: (1) treated sludge, (2) raw solids, (3) drilling mud, and (4) solidified sludge. RES manages waste from various drilling companies within the Marcellus Shale region.

EPA has developed methods to predict the leaching potential of solid waste in various disposal environments. The Toxicity Characteristic Leaching Procedure (TCLP) utilizes a simple acetic acid to simulate co-disposal in a municipal landfill (US EPA 1311, 1992) and the Synthetic Precipitation Leaching Procedure (SPLP) employs a synthetic acid rain of nitric and sulfuric acid to simulate a mono-disposal environment in contact with natural precipitation (US EPA 1312, 1994).

ASTM Method 3987 is a shake extraction procedure which can be used to rapidly determine the soluble leaching potential of solid waste in a laboratory environment. This method is not intended to simulate site-specific conditions and typically uses a reagent water extraction fluid to monitor the soluble leaching potential when a solid waste is the dominant contributing factor to leaching (ASTM D3987, 2012). This method was selected due to its ease of use to serve as a model leaching experiment with modifications for an acidic extraction fluid.

In order to study the effect of extraction fluids on the leaching behavior of a solid waste, this procedure was performed with four extraction fluids: (1) reagent water, (2) synthetic acid rain, (3) weak acetic acid, and (4) oxygen sensitive synthetic municipal landfill leachate. The reagent water was selected based on the ASTM method recommendations, while the synthetic acid rain and weak acetic acid were prepared following EPA Methods 1312 and 1311 respectively. The oxygen sensitive synthetic municipal landfill leachate was developed by Stanforth *et al.* (1979) to simulate the worst-case aggressive nature of a municipal landfill leachate. This synthetic leachate models volatile acids in landfills with acetic acid, organic nitrogen with glycine, and pH with a sodium acetate buffer. Complexation, ionic strength and redox potential are also controlled to simulate actual conditions. Due to the possibility of iron precipitation in the oxygen sensitive leachate, low dissolved oxygen levels must be maintained to minimize interference from precipitation (Stanforth *et al.,* 1979).

By using these four extraction fluids, it was possible to predict leaching from residual solids in two disposal environments. Extractions with reagent water and synthetic acid rain were used to predict leaching in mono-disposal environments such as land application and burial where major interactions are from natural precipitation. Extractions with acetic acid and the synthetic municipal landfill leachate were used to predict leaching in a co-disposal environment where there are other types of waste which affect leachate characteristics and conditions.

Strong acid digestions of these residual solid samples had been performed previously to determine the environmentally available composition of samples (see Chapter 3). Results from strong acid digestions and the leaching procedures outlined in this manuscript were compared to better understand the types and quantity of materials that will likely leach from the residual solids under various conditions.

5.2 Project Objectives

The primary objectives of this research were to characterize the soluble leaching potential of residual solids from hydraulic fracturing processes in the Marcellus Shale and determine the effect of extraction fluid in various disposal environments. Solids can be generated onsite or during offsite treatment at a dedicated treatment facility. Since samples could only be collected from an offsite treatment plant, the “raw solids” generated through settling at the treatment plant were used to represent the solids that would settle at onsite drilling operations. In addition to the solids from raw produced water and the chemical treatment process, drilling mud from well construction was also analyzed to characterize waste from the various phases of hydraulic fracturing. Finally, solidified sludge from the dedicated treatment facility was analyzed to determine the leaching potential of the solids in a municipal landfill.

Four extraction fluids were employed to determine the effect of extraction fluid on leaching potential: (1) reagent water, (2) synthetic acid rain, (3) acetic acid, and (4) a complex synthetic municipal landfill leachate. Results from the extraction with reagent water can be used to determine the chemical characteristics of the waste since there are no interference in the extraction fluid. Synthetic acid rain and acetic acid were used to simulate leaching potential from disposal through land application or in a municipal landfill, based on EPA's SPLP and TCLP recommendations for extraction fluid. Finally, the complex oxygen-sensitive landfill leachate was used to more accurately simulate interactions in a typical municipal landfill.

Based on the results from these leaching procedures, the extract concentration could be used to predict the leaching of elements in a disposal environment, and results could be compared to regulatory standards to determine the potential health and environmental impacts. Finally, these extracts could be used to calculate the leaching potential of the solids in terms of their total composition to better characterize the residual solids and predict how they will behave in the environment.

5.3 Hypothesis

It was expected that the leaching potential of solids would vary based on the aggressiveness of the extraction fluid. For example, it was determined during TCLP and SPLP testing in previous research (see Chapter 4) that the acetic acid extraction fluid behaved more aggressively for select elements. Similar results were expected during this analysis; however, it was not possible to predict which of the extraction fluids would result in the highest leaching potential. Since the oxygen-sensitive, municipal landfill leachate was developed to simulate worst case environmental conditions in typical landfills, it is expected that this fluid would behave the most aggressively.

When comparing these results to regulatory standards for water, it was expected that the extracts from leaching experiments would have concentrations for select elements that exceed regulatory limits. However, by calculating the percent at which the extracts exceed the regulatory standards, it is possible to determine how much these fluids need to be treated or diluted to reduce the potential risk in the environment.

5.4 Methods and Materials

5.4.1 Chemical Reagents and Glassware Preparation

Reagent grade chemicals were used in all experiments. The reagents included Fisher Scientific trace metal grade nitric acid, American Chemical Society (ACS) glacial acetic acid, certified ACS sodium acetate trihydrate, United States Pharmacopeia (USP) grade glycine, certified ACS ferrous sulfate, Sigma Aldrich ACS grade sulfuric acid, and Alfa Aesar ACS pyrogallol. Nanopure reagent water was used for dilutions and solution preparation. Purity of chemical reagents and reagent water was monitored during experimentation through the analysis of method blanks.

Glassware and polyethylene storage bottles were cleaned thoroughly with Sparkleen laboratory detergent and soaked with 10% nitric acid for at least one hour.

They were then rinsed twice with distilled-deionized water and twice with nanopure water. Glassware and bottles were air dried in a clean environment.

5.4.2 Sample Preparation

Solids were thickened prior to analysis by centrifuging for one hour at 2,000 rpm to remove free water. After centrifugation, the supernatant was discarded and the solid sample was stored in a refrigerator to await digestion and analysis.

5.4.3 Extraction Fluid Preparation

The following extraction fluids were used for the shake extraction procedure as outlined in ASTM D3987.

- Reagent water – distilled-deionized water
- Acid Rain – sulfuric and nitric acid (60/40 by weight) at pH 4.20 ± 0.05 following EPA Method 1312
- Acetic Acid – Acetic acid at pH 2.88 ± 0.05 following EPA Method 1311
- Oxygen-Sensitive Synthetic Municipal Landfill Leachate – Synthetic municipal landfill leachate containing acetic acid, sodium acetate, glycine, pyrogallol, and ferrous sulfate prepared following recommendations from Stanforth *et al.* (1979)

Due to the possibility of iron precipitation, the oxygen sensitive leachate was purged with nitrogen gas during preparation to maintain oxygen-limited conditions and the vessel headspace was purged prior to extraction or storage.

5.4.4 ASTM Method 3987 – Shake Extraction of Solid Waste

For the shake extraction procedure, 5 g of sample were placed in a clean 125 mL polyethylene container with 100 mL of appropriate extraction fluid. This proportion was used to maintain a 20:1 (mL:g) ratio as required by ASTM D3987. The bottle was placed in a rotary tumbler and agitated in compliance with method requirements. At the end of the procedure, the extract was passed through a 0.45 µm nylon filter to determine the soluble portion based on EPA definitions. A pore size of 0.45 µm is used to operationally define soluble, however there may be colloidal materials present in the sample that were are not removed through filtration. If the sample was slow to settle, it was initially centrifuged for 10 min at 2000 rpm or filtered through an 1.0 µm filter. The filtrate from this process was considered the final extract and stored for analysis. This experiment was performed in triplicate for each sample type and extraction fluid.

5.4.5 Elemental Analysis

Extracts from the shake extraction of waste with various extraction fluids were analyzed for metals using EPA Method 6020A – Inductively Coupled Plasma Mass Spectrometry. This was performed on a Thermo X-Series ICP-MS.

The accuracy and precision of ICP-MS was determined with two analytical limits. The minimum reporting level (MRL) is the minimum concentration that can be reported with significant confidence (99%) as the actual concentration in the sample. This was calculated following recommendations from Winslow *et al.* (2005). The method detection limit (MDL) is the minimum concentration that can be observed which indicates with significant confidence (99%) that the element is present at concentrations above zero in the sample. The MDL of each element was determined following EPA guidelines using the standard deviation from 7 trials of a low level standard (US EPA 40 CFR 136 Appendix B, 1997). For this research, the low level standard chosen for MDL determination was the MRL value calculated above. The MDL and MRL information determined for each element with ICP-MS is provided in Appendix B – Analytical Limits.

5.5 Results and Discussion

Since trace metal grade reagents were not used during digestion, it was expected that the method blanks would have significant background concentrations for certain elements. Therefore, the final extract concentration was adjusted to remove the average background concentration from the method blanks. If the average adjusted extract concentration was between the detection limit and reporting level, the value could not be quantified and was reported as “Trace”. If the average adjusted concentration was above the minimum reporting level, it was used to quantify the final extract concentration from the sample. In instances where the extract concentration was below the MDL or the method blank concentration was greater than the sample extract concentration for all method trials, it was assumed there was no leaching during the extraction procedure and the element was indicated as not detected “ND”. A complete list of results from the leaching experiments is provided in APPENDIX D – WEAK ACID DIGESTION RESULTS.

5.5.1 Extract Concentration from Leaching Experiments with Residual Solids

The average adjusted soluble extract concentrations from these leaching experiments are presented graphically in Figure 7. If a point is not provided, it is because the value was either a trace concentration which could not be quantified or not detected.

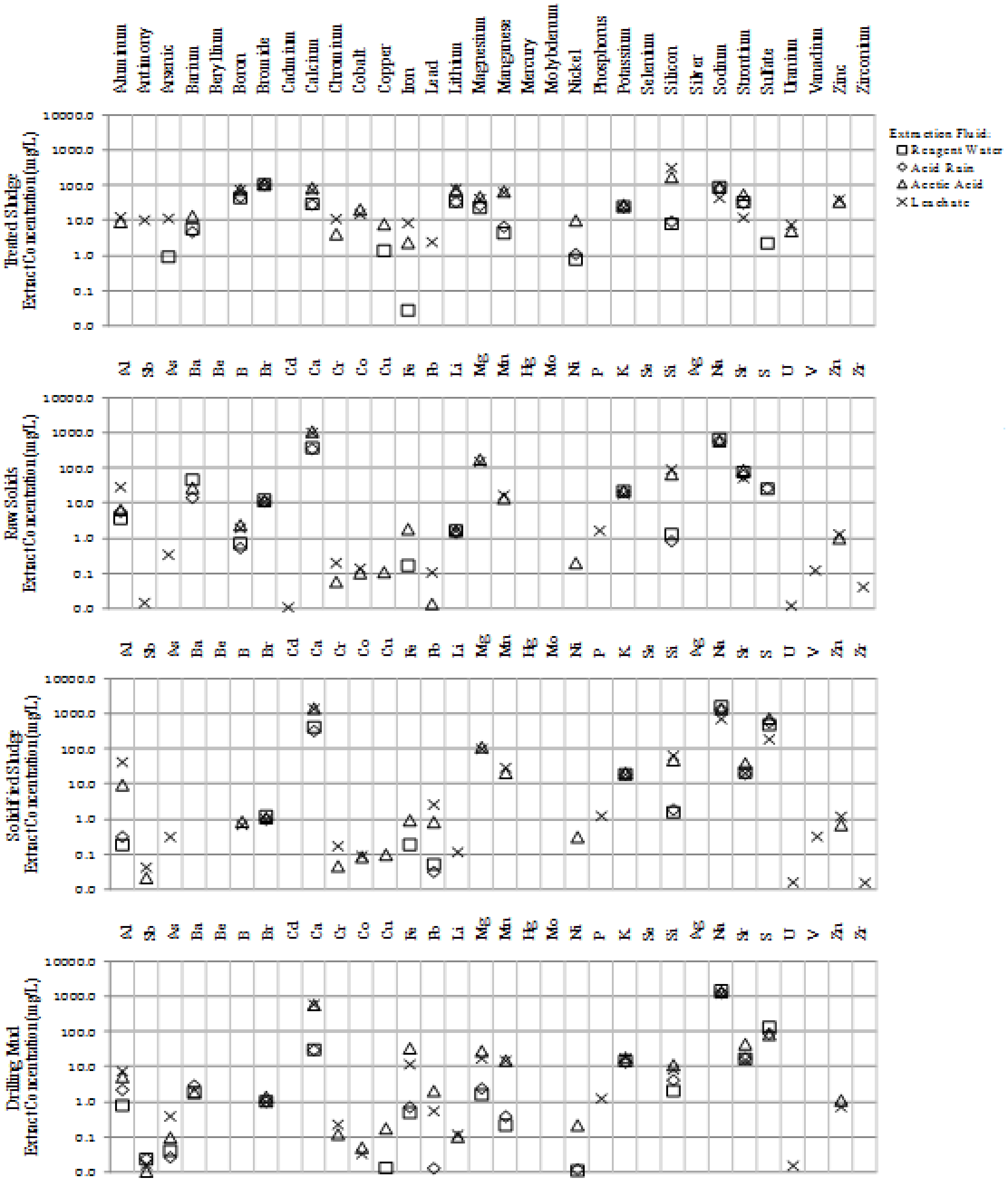

Figure 7: Adjusted Soluble Extract Concentrations (mg/L) from Leaching Experiments with Residual Solids

Based on the design of the ASTM D3987 procedure, the extract was assumed to reach steady state conditions during the extraction process. Therefore, these concentrations represent results under worst-case or well-mixed conditions.

Considering the general trends between the solids, it was observed that the adjusted extract concentrations for all elements in the treated sludge were fairly consistent, with quantifiable values typically falling between 1 - 100 mg/L. Alternatively, the other solids exhibited a broader range of extract concentrations with many values below 1 mg/L and several exceeding 1,000 mg/L. These variations were probably caused by differences in sample characteristics and the complexity of the solids. Since the treated sludge was formed during the chemical treatment of hydraulic fracturing wastewater, it is likely composed of relatively simple precipitates.

EPA's allowable holding time for mercury (28 days) was exceeded during this analysis. Therefore, results for mercury cannot be confidently quantified and these results were included to indicate approximate leaching of mercury from residual solids.

5.5.2 Comparison of Leaching Experiment Results to Regulatory Standards

Extracts from these leaching experiments were compared to various regulatory limits to better understand the potential impacts of elemental leaching from residual solids. To simplify this analysis, only the synthetic acid rain and acetic acid extraction fluids were used for comparison. These were selected since these were recommended by EPA to simulate leaching in mono-disposal and co-disposal environments respectively.

These results were compared to EPA's primary drinking water standards to determine the potential health effects from human exposure and secondary drinking water standards to identify potential cosmetic and aesthetic issues (US EPA "Drinking Water Contaminants", 2013). This comparison to regulatory limits is presented in Table 7.

In this table, the extraction fluid is indicated as "AR" and "AA" for acid rain and acetic acid respectively, and the regulatory standards are for EPA's national primary and secondary drinking water standards. The values in this section should be considered approximate since the required level of precision could not be achieved for all elements to compare results to regulatory standards. If results from all of the replicates fell below the MDL, the element was identified as not detected "ND".

Table 7: Approximate Adjusted Soluble Extract Concentration (mg/L) of Residual Solids from Leaching Experiments Compared to Regulatory Standards (mg/L)

	Treated Sludge		Raw Solids		Solidified Sludge		Drilling Mud		National Drinking Water Standards	
Element	AR	AA	AR	AA	AR	AA	AR	AA	Primary	Secondary
Aluminum	0.0	34.7	5.9	6.6	0.3	9.7	2.3	5.2		0.2
Antimony	Trace	Trace	Trace	0.002	Trace	0.022	0.024	0.011	0.006	
Arsenic	Trace	0.00	0.00	0.00	Trace	Trace	0.03	0.10	0.01	
Barium	59.7	170.3	14.6	28.3	Trace	Trace	3.0	1.9	2	
Beryllium	ND	ND	ND	Trace	ND	ND	ND	ND	0.004	
Cadmium	ND	Trace	ND	Trace	ND	Trace	ND	Trace	0.005	
Chromium	ND	0.05	Trace	0.06	Trace	0.05	Trace	0.12	0.1	
Copper	Trace	0.1	Trace	0.1	ND	0.1	0.0	0.2	1.3	1
Iron	ND	19.1	ND	1.9	ND	1.0	0.7	34.5		0.3
Lead	ND	Trace	ND	0.014	0.032	0.850	0.013	2.085	0.015	
Manganese	0.9	9.3	ND	14.0	ND	21.2	0.4	15.4		0.05
Mercury	ND	ND	ND	ND	ND	ND	ND	ND	0.002	
Selenium	ND	ND	ND	ND	Trace	ND	ND	ND	0.05	
Silver	ND	ND	ND	ND	ND	ND	ND	ND		0.1
Sulfate	Trace	Trace	27.4	Trace	593.6	760.2	89.7	85.2		250
Zinc	Trace	1.4	ND	1.0	ND	0.7	Trace	1.1		5

Primary drinking water standards are the most stringent because they are regulated to reduce the risk of health issues caused by human exposure to and ingestion of pollutants. Therefore, it is reasonable that all solids in this experiment exceeded the allowable limit for at least one regulated element. By comparing results from these leaching experiments to the regulatory limit, it was possible to determine the required level of treatment for each of these extracts. In the worst instance, the drilling mud digested with acetic acid had a lead concentration 139 times the allowable limit. Alternately, the solidified sludge digested with acid rain is only about twice as large as the allowable lead limit and passes the regulatory requirements for all other primary drinking water contaminants. It is important to note that these values are for the concentrated extract and these concentrations would likely decrease in the natural environment due to dilution from other water sources and filtration through natural barriers or disposal liners.

For additional perspective about the effect of leaching from residual solids, it would be possible to compare these extract concentrations to discharge limits and surface water standards. Since effluent standards for wastewater related to oil and gas extraction are dependent on available treatment technologies and incorporated into the NPDES permit (US EPA 40 CFR 435, 1979), specific regulatory discharge limits were not available for comparison. Similarly, national recommended surface water quality standards for metals (cadmium, chromium, lead, nickel, silver, and zinc) are site-specific based on water hardness. (US EPA "National Recommended Water Quality Criteria", 2013). If the disposal location for these residual solids is known, it would be possible to compare the leaching results and water quality standards to determine the potential impact of extracts migrating in the environment and entering natural waterways.

5.5.3 *Leaching Potential of Residual Solids*

While the extract concentrations can be used to identify the major contaminants that will leach from residual solids, it is also possible to determine the percent of the total solid that will leach under environmental conditions. These results indicate the elements which leach freely and those that are bound in the solid phase.

The total environmentally available composition of the residual solid samples had been previously determined through this research (see Chapter 3). Solids were digested following two EPA methods (3050B and 3051A), each with two strong acid digestion fluids. Results from these four procedures were compared and the maximum observed composition for each element was assumed to be the actual composition in the solids.

The average adjusted soluble extract concentrations from these leaching experiments were adjusted based on the sample weight and moisture content to determine the amount that had leached (mg/kg dry). These results were compared to the maximum observed environmentally available composition mentioned above to determine the leaching potential (% of composition) for elements of concern. These calculations were performed following Equation 3.

Equation 3

$$Leaching\ Potential\ (\%) = Leached\ Composition\ /\ Total\ Composition$$

$$= \frac{Extract\ Concentration\ x\ Extract\ Volume}{Wet\ Sample\ Weight\ x\ (1 - Moisture\ Content\ )}\ /\ Total\ Composition$$

$$= \frac{(ug/L\ extract)\ x\ (L\ extract)}{(\ g\ sample\ )(g\ dry\ /\ g\ sample\ )} x\ \frac{1\ mg}{1000\ ug}\ x\ \frac{1000\ g\ dry}{1\ kg\ dry}\ /\ (mg/kg\ dry)$$

$where\ (g\ sample)\ is\ the\ total\ wet\ sample\ weight$

Leaching potential results for residual solids are presented in Figure 8. For reference, the total composition in the sample as determined through strong acid digestions is also provided. If a point is not presented, it is because the value was either a trace concentration which could not be quantified or the element was not detected.

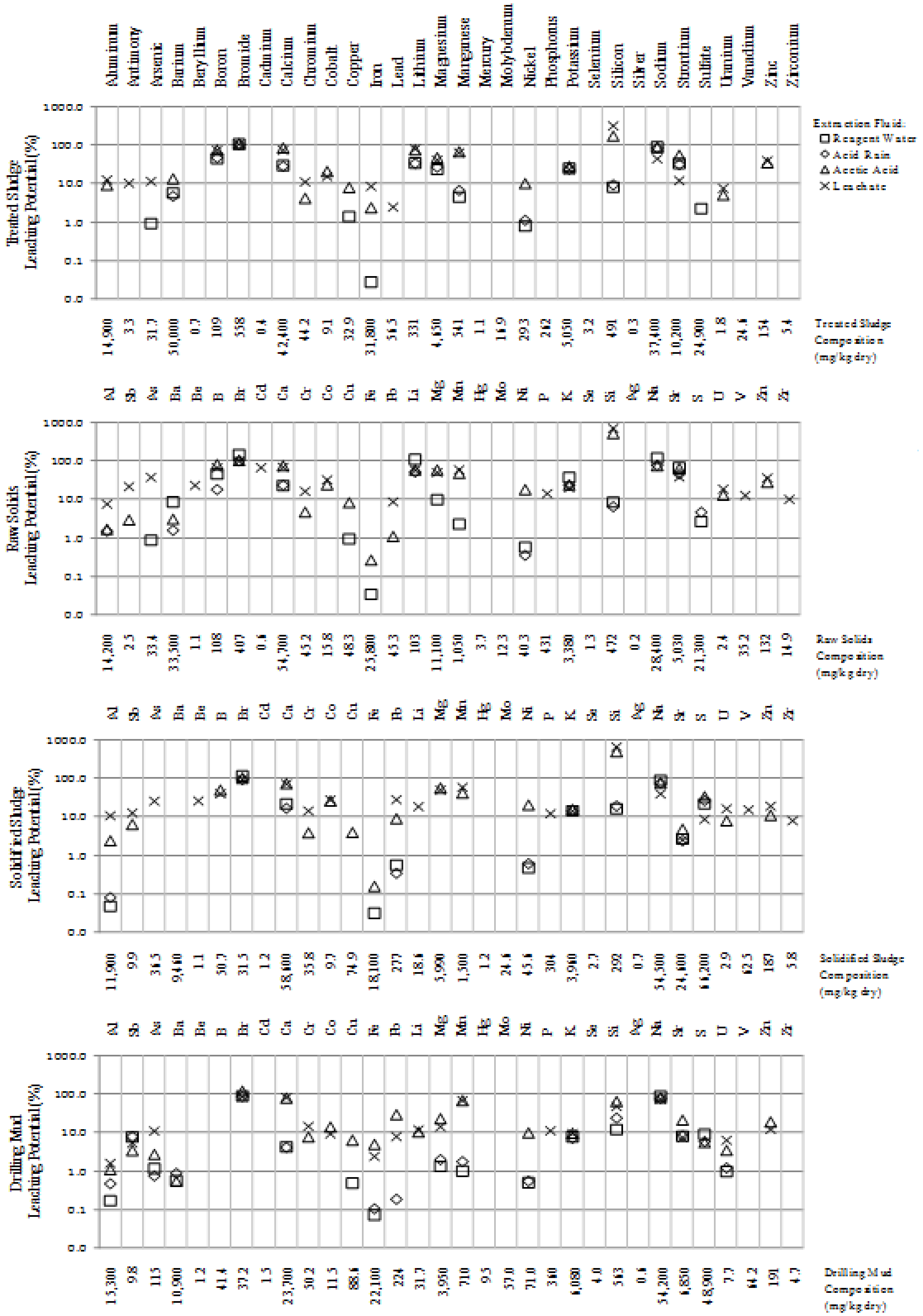

Figure 8: Maximum Observed Environmentally Available Composition (mg/kg dry) and Leaching Potential (% of Composition) for Residual Solid Samples

5.5.4 Comparison between Extraction Fluids

Although the leaching potential (%) results vary based on the element, there were some general trends between the extraction fluids. The acetic acid and synthetic landfill leachate tended to behave similarly while the reagent water and acid rain also produced similar results. The leaching potentials for chromium, cobalt, manganese and zinc were all positively impacted by the presence of the organic extraction fluids for all residual solids, meaning that disposal in a municipal landfill could result in more aggressive elemental leaching for these elements. Depending on the sample type, this was also observed for aluminum, antimony, boron, iron, lead, magnesium, silicon, and uranium. For example, the leaching potential of zinc reached as much as 40.1% in the presence of an organic extraction fluid while no leaching was observed with the reagent water or acid rain. Similarly, the magnesium leaching potential reached 59.7% with the acetic acid extraction fluid compared to the highest value from an inorganic fluid being 10%. There were no clear instances where extraction with reagent water or synthetic acid rain resulted in a significantly higher leaching potential than the organic extraction fluids. This suggests that mono-disposal would be a more suitable disposal environment for hydraulic fracturing residual solids in regards to limiting the mobility of elements.

The extract concentrations from the synthetic landfill leachate are quantifiably higher than results from the acetic acid for 34– 44% of the analyzed elements depending on the sample type. Alternatively, the acetic acid results are quantifiably higher than those from the synthetic leachate for 44 – 50% of the elements. This suggests that the acetic acid extraction fluid employed by EPA is less aggressive than actual landfill conditions for certain elements (aluminum, chromium, and uranium) and more aggressive for others (bromide, magnesium, nickel, potassium, sodium, strontium, and sulfate). In the case of nickel, the acetic acid extraction fluid behaved significantly more aggressively than the synthetic leachate developed by Stanforth *et al.* (1979) to simulate worst case conditions in a typical municipal landfill. The leaching potential of nickel with acetic acid ranged from 10.1 - 20.7% depending on the solid sample while no leaching was observed with the synthetic landfill leachate from any samples. It is important to consider that the synthetic leachate used in the research was developed by Stanforth *et al.* in 1979 and current conditions in municipal landfills may vary.

5.5.5 Comparison between Residual Solids

From the results in Figure 8, it was possible to compare differences in leaching behavior between residual solids for select elements. For example, barium leaching could not be quantified from solidified sludge but had a maximum of 13.7% and 8.8% from the treated sludge and raw solids respectively. This indicated that the solidification process was effective for reducing barium leaching. This is particularly important since barium is an element regulated by EPA to determine if a waste is hazardous (US EPA 40 CFR 261.24, 2012).

Magnesium in the treated sludge had relatively high leaching potentials for all extraction fluids (23.8 – 48.3%) while results for other solids with an inorganic extraction fluid typically fell below 10%. Similarly, antimony and uranium leached from the drilling mud with all extraction fluids while none was detected from the extraction of other solids with the inorganic extraction fluids. This indicates that the magnesium in the treated sludge and the antimony and uranium in the drilling mud were loosely bound or present in the liquid portion of the sample considering they could be easily leached regardless of extraction fluid.

5.5.6 Comparison between Elements of Concern

From Figure 8, it was determined that bromide and sodium have consistently high leaching potentials for all residual solids. In order to better compare the results for more variable elements of concern, the maximum observed leaching potential between the four extraction fluids was determined for each residual solid type. These results are presented in Figure 9 to highlight differences in leaching behavior for elements of concern. From these maximum observed values, and average was determined from the four residual solid samples and is presented below.

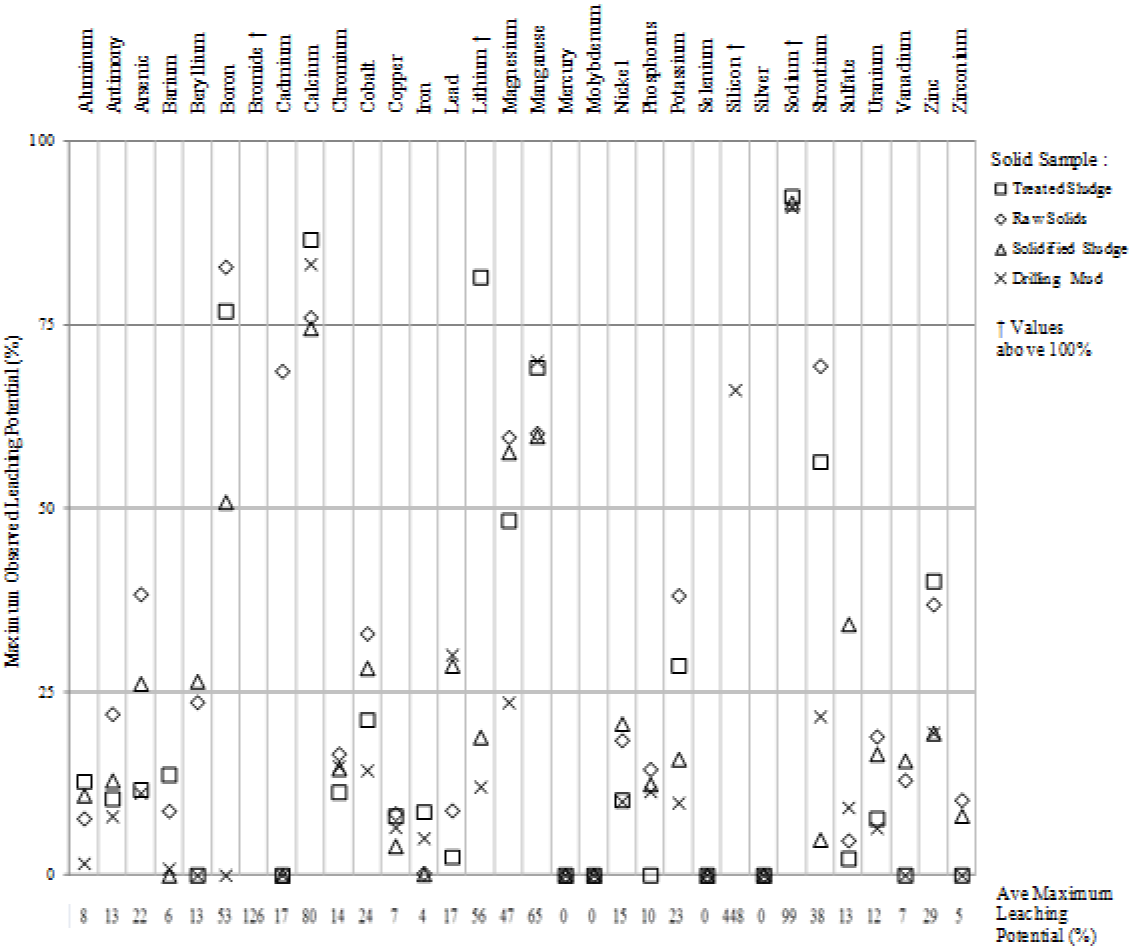

Figure 9: Maximum Observed Leaching Potential (%) and Average Maximum Value (%) for Residual Solid Samples

The following elements had large average maximum leaching potentials (>50%) between all residual solid samples: boron (53%), bromide (126%), calcium (80%), lithium (56%), manganese (65%), silicon (448%) and sodium (99%). For major constituents like calcium and sodium which are present in large concentrations, these high leaching potentials also indicated that the elements will be present at high concentrations in the leached extract.

For elements with small average maximum leaching potentials (<10%), there is a reduced risk that these elements will leach and migrate under environmental conditions. These elements are aluminum (8%), barium (6%), copper (7%), iron (4%), molybdenum (0%), phosphorus (10%), selenium (0%), silver (0%), vanadium (7%), and zirconium (5%). These results are notable in the case of aluminum which has a relatively large composition in the samples (11,912 – 14,314 mg/kg dry) but a small risk of leaching due to the low leaching potential. It is also important to note that elements with an average maximum leaching potential of 0% indicates that the element was not detected or the average value was below the MRL and could not be quantified for all residual samples.

The observed leaching potential of silicon typically exceeded 100%, which indicates that the leaching from weak acid digestions was greater than the maximum observed environmentally available composition determined through EPA strong acid digestions. In actuality, this suggests that the strong acid digestions did not sufficiently digest the treated sludge, raw solids, or solidified sludge which had maximum leaching potentials of 325.6%, 725.8% and 674.6% respectively for silicon. Recognizing that large qualities of sand are used during hydraulic fracturing, it is likely that silicon is present as quartz (SiO_2), an oxide which can be difficult for strong acids to completely digest (Gard Guide, 2012).

5.5.7 Limitations of Leaching Experiments

While these results may help to predict leaching of residual solids in the natural environment, the biggest limitations of this research were that it was a static leaching experiment which employed a rigorous agitation technique. The use of a static leaching procedure, where extraction fluid is not replenished or varied during the experiment, means that variations in leaching potential over time cannot be evaluated. The rigorous agitation method, which ensures that leachate reached steady-state conditions during extraction, means that results reflect the highest possible leaching potential in a static disposal environment. Although this is useful to determine the worst-case leaching behavior of solids, additional experiments may be required to simulate actual leaching in the natural environment.

5.6 Conclusion

Since the extraction fluids used for leaching experiments contained significant background concentrations, the soluble extracts results were adjusted to remove interferences in the method blanks. When evaluating the soluble extract concentrations between the various samples, it was determined that the treated sludge exhibited similar concentrations for most elements. The treated sludge results typically fell within the range of 1.0 – 100 mg/L compared to the more variable values from other residual solids which ranged between 0.01 – 1,000 mg/L. This was likely due the simple nature of treated sludge which is formed from the chemical treatment of hydraulic fracturing wastewater.

Results from acetic acid and acid rain extractions were compared to drinking water primary and secondary standards to determine the level of treatment required to meet stringent regulatory requirements. In the best and worst cases, solidified sludge digested with acid rain was 2.1 times the primary standard for lead and drilling mud digested with acetic acid was 139 times greater than the same standard. However, these results are for the concentrated extract from residual solids and contaminants may be removed through natural processes before entering a water system. Results from this analysis also confirmed previous findings that acetic acid is typically more aggressive than acid rain in terms of chemical leaching for select elements.

Adjusted extract concentrations were used to determine the leaching potential of each element compared to the environmentally available composition of the sample. This analysis again confirmed that the organic extraction fluids, acetic acid and synthetic municipal landfill leachate, generally resulted in higher leaching potentials from solids than the reagent water and acid rain. This was most notably observed for chromium, cobalt, manganese, and zinc. Results suggest that mono-disposal of hydraulic fracturing residual solids, including onsite burial or land application, would be preferable to reduce the leaching from hydraulic fracturing residual solids in the natural environment.

When comparing results for the two organic extraction fluids, the synthetic municipal landfill was quantifiably more aggressive than the acetic acid for 34.4 – 43.8% of elements and the opposite for 43.8 – 50.0 % of elements depending on the solid type. This means that an acetic acid extraction fluid, which is used by EPA to determine if a waste is hazardous, can be more aggressive than a synthetic leachate designed to simulate worst-case conditions in a typical municipal landfill.

By looking at variations between the residual solids, it was determine that barium is tightly bound in the solidified sludge compared to the other solids, meaning it is less likely to leach. Alternatively, magnesium in the treated sludge and antimony and uranium in the drilling mud are more loosely bound than in other solids, which means leaching occurs more easily in these samples.

On average, bromide and sodium have the highest leaching potential across all solid samples. Because the leaching potential for silicon regularly exceeded 100% it is speculated that the digestion procedures previously performed to determine the environmentally available composition of samples underestimates values for silicon.

Although there are trends in this data, the results vary depending on the sample type, extraction fluid, and element. Therefore, recommendations about proper disposal practices and potential environmental impacts may vary based on which variables are considered. Therefore, while these results serve as a good indication about the potential leaching behavior of residual solids, it is important that site-specific waste be tested and analyzed to determine best management practices.

5.7 References

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CHAPTER 6: ENGINEERING SIGNIFICANCE

This research is significant as it is one of the first efforts to focus on characterizing the residual solids generated during hydraulic fracturing operations in the Marcellus Shale. This includes quantifying the composition and predicting the leaching potential of these solids in natural environments. By comparing results from this research to regulatory standards, it is possible to determine the suitability of various disposal methods, characterize waste based on its hazardous nature, and identify the potential environmental impacts from the leaching of contaminants into natural waterways, While other investigators have worked to characterize produced water or drill cuttings, this research provides additional information concerning hydraulic fracturing residual solids.

As the United States works to secure energy independence, hydraulic fracturing will likely play a vital role in domestic gas production. Therefore, it is important that information concerning current industry practices, technical knowledge, and potential impacts are publicly known to promote public perception and confidence in this practice.

Finally, this research is useful for industry leaders to serve as an initial analysis of residual solid waste. Although some samples collected for this research are specific to the dedicated treatment facility in Pennsylvania, the raw solids from produced water and drilling mud from well construction can be used to represent samples from facilities throughout the Marcellus Shale region. While all waste generated from hydraulic fracturing operations should be analyzed to determine site-specific characteristics, the results from this research can serve as a guide for characterizing residual solid samples to predict leaching behavior in disposal environments. This in turn may be used by drilling companies and industry leaders to develop best management practices for residual solids.

CHAPTER 7: DISCLAIMER

As part of the National Energy Technology Laboratory’s Regional University Alliance (NETL-RUA), this technical effort was performed under the RES contract DE-FE0004000. 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.

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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 8: Elemental Composition and Matrix for Standard Solutions

Standard A (Matrix: 2% HNO3)

Element	[C] mg/L
Calcium	100
Iron	100
Magnesium	100
Potassium	100
Sodium	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 B (Matrix: 2% HNO3)

Element	[C] ppb
Mercury	100

Standard C (Matrix: H2O)

Element	[C] mg/L
Bromide	10
Chloride	100
Sulfate	100

APPENDIX B – ANALYTICAL LIMITS

The analytical limits are defined as follows:

- Method Detection Limit (MDL) – minimum value that indicates with 99% confidence that the element is present in the sample
- Minimum Reporting Level (MRL) – minimum value that can be claimed with 99% confidence as the actual concentration in the sample

The MDL and MRL values determined for ICP-MS analysis are provided in Table 9

Table 9: Method Detection Limits (MDLs) and Minimum Reporting Levels (MRLs) for Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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	12.2	50
Chloride	35Cl	29.8	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	0.10	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	10.9	100
Strontium	88Sr	0.24	10
Sulfate	34S	392	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 RESULTS

The results from the strong acid digestion of solid samples are provided in this appendix. The EPA method is indicated by the method number and extraction fluid is indicated with “N” or “NH”, for a nitric acid or a nitric and hydrochloric acid mixture respectively. If the average adjusted concentration from ICP-MS analysis had a value above the detection limit but below the minimum reporting level, the composition was set as “Trace”. If all of the replicates had values below the detection limit, the element was identified as not detected “ND”.

Table 10: Environmentally Available Composition of Residual Solid Samples (mg/kg dry) from Four Strong Acid Digestion Techniques

Element	Treated Sludge Composition (mg/kg dry)			
	3050B - N	3050B - NH	3051A - N	3051A - NH
Aluminum	14,400	12,300	14,500	14,900
Antimony	0.1	0.4	0.2	3.3
Arsenic	31.4	30.1	31.7	21.4
Barium	3,760	5,800	34,600	50,000
Beryllium	0.6	0.6	0.5	0.7
Boron	90.3	82.0	109	107
Bromide	259	171	558	550
Cadmium	0.4	0.4	Trace	Trace
Calcium	42,400	38,100	38,600	33,200
Chromium	44.2	38.2	42.4	36.5
Cobalt	9.1	8.5	8.8	7.7
Copper	21.4	17.5	32.9	32.3
Iron	31,800	29,900	30,400	27,200
Lead	32.7	38.9	45.0	56.5
Lithium	329	321	316	331
Magnesium	4,650	3,900	4,350	3,950
Manganese	541	508	500	434
Mercury	0.1	Trace	Trace	1.1
Molybdenum	13.5	16.9	Trace	Trace
Nickel	28.6	25.8	29.3	24.8
Phosphorus	262	223	220	189
Potassium	4,130	3,810	4,820	5,050
Selenium	3.2	2.7	Trace	Trace
Silicon	24.1	76.4	104	491
Silver	0.2	0.2	0.2	0.3
Sodium	37,000	33,300	37,400	30,800
Strontium	10,200	10,000	8,130	10,200
Sulfate	3,980	4,430	23,700	24,900
Uranium	1.3	1.5	1.7	1.8
Vanadium	23.2	12.8	24.6	ND
Zinc	145	119	154	148
Zirconium	4.3	4.5	5.4	4.9

Table 10 Continued

Element	**Raw Solids Composition (mg/kg dry)**			
	3050B - N	**3050B - NH**	**3051A - N**	**3051A - NH**
Aluminum	14,200	11,200	12,900	11,400
Antimony	0.1	0.2	0.4	2.5
Arsenic	33.4	29.6	29.5	21.9
Barium	1,630	2,840	19,500	33,500
Beryllium	1.1	1.1	0.9	0.9
Boron	95.8	77.1	108	95.0
Bromide	163	105	407	351
Cadmium	0.6	0.6	0.6	Trace
Calcium	54,700	47,400	50,500	40,300
Chromium	45.2	38.2	42.3	33.4
Cobalt	15.8	14.3	15.5	13.0
Copper	39.2	33.5	48.3	44.1
Iron	25,800	24,200	24,000	21,800
Lead	24.4	29.9	35.8	45.3
Lithium	96.5	92.3	102	103
Magnesium	11,100	9,150	10,400	8,590
Manganese	1,050	966	1,030	856
Mercury	Trace	ND	0.3	3.7
Molybdenum	10.9	12.3	Trace	Trace
Nickel	38.0	33.2	40.3	32.1
Phosphorus	431	364	379	282
Potassium	3,300	2,810	3,380	3,140
Selenium	1.34	1.02	Trace	Trace
Silicon	23.3	76.4	97.8	472
Silver	0.2	0.2	0.2	0.2
Sodium	27,400	23,800	28,400	22,900
Strontium	4,290	4,240	4,350	5,030
Sulfate	7,970	7,050	21,300	17,000
Uranium	1.5	1.7	2.0	2.4
Vanadium	35.2	22.1	31.8	ND
Zinc	132	98	131	120
Zirconium	13.6	13.2	14.9	12.0

Table 10 Continued

Element	**Solidified Sludge Composition (mg/kg dry)**			
	3050B - N	**3050B - NH**	**3051A - N**	**3051A - NH**
Aluminum	11,600	9,630	9,740	11,900
Antimony	0.2	2.7	0.8	9.9
Arsenic	36.5	34.0	33.4	28.8
Barium	395	647	7,690	9,460
Beryllium	1.0	1.0	1.0	1.1
Boron	36.1	24.7	36.6	50.7
Bromide	9.4	Trace	31.5	ND
Cadmium	1.0	1.2	1.1	1.2
Calcium	58,600	52,200	55,000	51,100
Chromium	35.8	30.6	33.3	32.0
Cobalt	9.6	9.0	9.7	9.2
Copper	66.7	61.5	73.4	74.9
Iron	17,500	17,500	17,000	18,100
Lead	141	193	250	277
Lithium	14.1	13.8	15.0	18.6
Magnesium	5,990	4,950	5,360	5,350
Manganese	1,500	1,410	1,450	1,390
Mercury	0.2	0.1	0.3	1.2
Molybdenum	22.0	23.6	24.6	Trace
Nickel	43.2	39.4	45.6	40.2
Phosphorus	304	264	276	253
Potassium	3,400	3,040	3,030	3,960
Selenium	2.7	2.3	2.2	Trace
Silicon	15.4	29.1	159	292
Silver	0.6	0.6	0.7	0.7
Sodium	50,200	44,700	54,500	46,800
Strontium	12,300	14,600	15,100	24,600
Sulfate	62,700	55,100	66,200	64,000
Uranium	2.1	2.4	2.8	2.9
Vanadium	62.5	48.8	48.8	31.9
Zinc	187	165	184	178
Zirconium	5.8	5.6	5.6	5.3

Table 10 Continued

Element	**Drilling Mud Composition (mg/kg dry)**			
	3050B - N	**3050B - NH**	**3051A - N**	**3051A - NH**
Aluminum	11,100	9,320	12,500	15,300
Antimony	0.1	1.9	0.5	9.8
Arsenic	115	110	81.4	74.5
Barium	272	380	7,980	10,900
Beryllium	0.9	0.8	0.8	1.2
Boron	16.2	7.92	33.1	41.4
Bromide	18.7	Trace	37.2	ND
Cadmium	1.4	1.5	1.2	1.4
Calcium	23,700	20,700	21,000	22,000
Chromium	47.9	40.8	49.3	50.2
Cobalt	11.5	10.4	11.1	11.5
Copper	83.1	78.1	87.1	88.6
Iron	22,100	20,500	20,700	22,000
Lead	125	160	192	224
Lithium	21.0	20.3	23.7	31.7
Magnesium	3,760	3,160	3,620	3,950
Manganese	706	642	674	710
Mercury	0.1	Trace	0.3	9.5
Molybdenum	52.5	55.4	57.0	48.0
Nickel	71.0	63.1	70.7	68.8
Phosphorus	360	306	319	311
Potassium	4,130	3,720	4,960	6,080
Selenium	4.0	3.4	3.0	Trace
Silicon	19.6	38.5	234	563
Silver	0.5	0.5	0.5	0.6
Sodium	49,200	43,000	54,200	47,000
Strontium	6,140	6,850	3,800	5,920
Sulfate	48,900	42,000	43,900	39,500
Uranium	4.9	5.7	6.6	7.7
Vanadium	63.9	49.7	64.2	47.4
Zinc	191	165	182	179
Zirconium	3.9	3.4	4.2	4.7

APPENDIX D – WEAK ACID DIGESTION RESULTS

The results from the weak acid digestion of solid samples are provided in this appendix. All digestions were performed following ASTM Method D3987, however various extraction fluid were used and are indicated below. If the average adjusted concentration from ICP-MS analysis was above the detection limit but below the minimum reporting level, the extract concentration and leaching potential are indicated as “Trace”. If all of the replicates had values below the detection limit, the element was identified as not detected “ND”.

Table 11: Extract Concentration (mg/L) and Leaching Potential (% of Composition) compared to Maximum Observed Environmentally Available Composition (mg/kg dry) for Residual Solid Samples

Treated Sludge Results

Element	Extract Concentration (mg/L)				Composition	Leaching Potential (% of Composition)			
	Reagent Water	Acid Rain	Acetic Acid	Leachate	(mg/kg dry)	Reagent Water	Acid Rain	Acetic Acid	Leachate
Aluminum	0.0	0.0	34.7	47.5	14,900	0.0	0.0	9.37	12.8
Antimony	ND	Trace	Trace	0.0	3.3	ND	Trace	Trace	10.4
Arsenic	0.0	Trace	ND	0.1	31.7	0.9	Trace	ND	11.6
Barium	72.8	59.7	170	Trace	50,000	5.9	4.8	13.7	Trace
Beryllium	ND	ND	ND	Trace	0.6	ND	ND	ND	Trace
Boron	1.2	1.3	2.1	2.1	109	45.9	48.3	76.9	75.6
Bromide	15.2	14.8	15.4	14.9	558	110	107	111	107
Cadmium	ND	ND	Trace	Trace	0.4	ND	ND	Trace	Trace
Calcium	318	304	913	799	42,400	30.3	29.0	86.7	75.9
Chromium	ND	ND	0.1	0.1	44.2	ND	ND	4.2	11.3
Cobalt	Trace	ND	0.1	0.0	9.1	Trace	ND	21.2	15.7
Copper	0.0	Trace	0.1	ND	32.9	1.4	Trace	8.1	ND
Iron	0.2	ND	19.1	68.3	31,800	0.0	ND	2.4	8.6
Lead	Trace	ND	Trace	0.0	56.5	Trace	ND	Trace	2.5
Lithium	2.9	2.8	6.4	6.7	331	35.1	34.3	77.3	81.5
Magnesium	27.5	31.6	55.9	48.5	4,650	23.8	27.4	48.3	42
Manganese	0.6	0.9	9.3	8.7	541	4.5	6.8	69.2	64.7
Mercury	ND	ND	ND	ND	1.1	ND	ND	ND	ND
Molybdenum	ND	ND	ND	ND	16.9	ND	ND	ND	ND
Nickel	0.0	0.0	0.1	ND	29.3	0.8	1.1	10.3	ND
Phosphorus	ND	ND	ND	Trace	262	ND	ND	ND	Trace
Potassium	31.9	30.4	35.8	30.0	5,050	25.5	24.3	28.6	23.9
Selenium	ND	ND	ND	ND	3.2	ND	ND	ND	ND
Silicon	1.0	1.2	21.6	39.7	491	8.3	9.5	177	326
Silver	ND	ND	ND	ND	0.3	ND	ND	ND	ND
Sodium	858	799	834	419	37,400	92.5	86.3	89.8	45.1
Strontium	86.7	81.0	143	31.2	10,200	34.2	32.0	56.3	12.3
Sulfate	14.1	Trace	Trace	ND	24,900	2.3	Trace	Trace	ND
Uranium	ND	ND	0	0	1.8	ND	ND	5.1	7.7
Vanadium	ND	ND	ND	Trace	24.6	ND	ND	ND	Trace
Zinc	ND	Trace	1.4	1.5	154	ND	Trace	35.8	40.1
Zirconium	ND	Trace	ND	Trace	5.4	ND	Trace	ND	Trace

Table 11 Continued

Raw Solids Results

Element	Extract Concentration (mg/L)				Composition	Leaching Potential (% of Composition)			
	Reagent Water	**Acid Rain**	**Acetic Acid**	**Leachate**	**(mg/kg dry)**	**Reagent Water**	**Acid Rain**	**Acetic Acid**	**Leachate**
Aluminum	3.7	5.9	6.6	29.7	14,200	0.0	1.5	1.7	7.7
Antimony	Trace	Trace	0.0	0.0	2.5	ND	Trace	3.0	22.0
Arsenic	ND	ND	ND	0.4	33.4	0.9	ND	ND	38.3
Barium	47.4	14.6	28.3	Trace	33,500	8.8	1.6	3.1	Trace
Beryllium	ND	ND	Trace	0.0	1.1	ND	ND	Trace	23.6
Boron	0.7	0.5	2.4	2.0	108	46.4	18.4	82.9	68.1
Bromide	12.7	11.5	11.8	11.3	407	151	103	107	102
Cadmium	ND	ND	Trace	0.0	0.6	ND	ND	Trace	68.7
Calcium	389	359	1130	1040	54,700	23.5	24.0	76.0	70.2
Chromium	Trace	Trace	0.1	0.2	45.2	ND	Trace	4.8	16.5
Cobalt	ND	ND	0.1	0.1	15.8	Trace	ND	24.6	32.9
Copper	Trace	Trace	0.1	ND	48.3	1.0	Trace	8.4	ND
Iron	0.2	ND	1.9	ND	25,800	0.0	ND	0.3	ND
Lead	Trace	ND	0.0	0.1	45.3	Trace	ND	1.1	8.8
Lithium	1.7	1.5	1.7	1.6	103	113	52.9	60.2	58.6
Magnesium	Trace	Trace	181	155	11,100	10.0	Trace	59.7	51.2
Manganese	ND	ND	14	17.2	1,050	2.3	ND	48.9	60.2
Mercury	ND	ND	ND	ND	3.7	ND	ND	ND	ND
Molybdenum	ND	ND	ND	ND	12.3	ND	ND	ND	ND
Nickel	0	0	0.2	ND	40.3	0.6	0.4	18.4	ND
Phosphorus	ND	ND	ND	1.69	431	ND	ND	ND	14.4
Potassium	22.7	21.9	22.5	18.7	3,380	38.1	23.8	24.5	20.4
Selenium	ND	ND	ND	ND	1.3	ND	ND	ND	ND
Silicon	1.3	0.9	69.1	93.0	472	8.61	6.6	538	726
Silver	ND	ND	ND	ND	0.2	ND	ND	ND	ND
Sodium	698	614	599	ND	28,400	122	79.3	77.5	ND
Strontium	78.5	64.3	89.7	53.7	5,030	69.4	46.9	65.4	39.3
Sulfate	26.3	27.4	Trace	ND	21,300	2.7	4.7	Trace	ND
Uranium	ND	ND	0.0	0.0	2.4	ND	ND	13.3	18.9
Vanadium	ND	ND	ND	0.1	35.2	ND	ND	ND	12.9
Zinc	ND	ND	1.0	1.3	132	ND	ND	28.4	36.9
Zirconium	ND	ND	Trace	0.0	14.9	ND	ND	Trace	10.3

Table 11 Continued

Solidified Sludge Results

Element	Extract Concentration (mg/L)				Composition	Leaching Potential (% of Composition)			
	Reagent Water	Acid Rain	Acetic Acid	Leachate	(mg/kg dry)	Reagent Water	Acid Rain	Acetic Acid	Leachate
Aluminum	0.2	0.3	9.7	43.4	11,900	0.1	0.1	2.4	10.9
Antimony	Trace	Trace	0.0	0.0	9.9	Trace	Trace	6.5	12.9
Arsenic	Trace	Trace	Trace	0.3	36.5	Trace	Trace	Trace	26.1
Barium	Trace	Trace	Trace	Trace	9,460	Trace	Trace	Trace	Trace
Beryllium	ND	ND	ND	0.0	1.1	ND	ND	ND	26.4
Boron	ND	ND	0.9	0.7	50.7	ND	ND	50.9	40.8
Bromide	1.3	1.0	1.1	1.0	31.5	118	95.2	105	97.2
Cadmium	ND	ND	Trace	Trace	1.2	ND	ND	Trace	Trace
Calcium	433	334	1470	1430	58,600	22.0	17.0	74.6	72.8
Chromium	Trace	Trace	0.1	0.2	35.8	Trace	Trace	3.9	14.6
Cobalt	ND	ND	0.1	0.1	9.7	ND	ND	26.4	28.3
Copper	ND	ND	0.1	Trace	74.9	ND	ND	4.0	Trace
Iron	0.2	ND	1.0	ND	18,100	0.0	ND	0.2	ND
Lead	0.1	0.0	0.9	2.7	277	0.6	0.3	9.1	28.6
Lithium	Trace	Trace	Trace	0.1	18.6	Trace	Trace	Trace	18.8
Magnesium	Trace	ND	116	102	5,990	Trace	ND	57.6	51.0
Manganese	ND	ND	21.2	30.0	1,500	ND	ND	42.3	59.8
Mercury	ND	ND	ND	ND	1.2	ND	ND	ND	ND
Molybdenum	Trace	Trace	ND	Trace	24.6	Trace	Trace	ND	Trace
Nickel	0.0	0.0	0.3	ND	45.6	0.5	0.6	20.7	ND
Phosphorus	ND	ND	ND	1.3	304	ND	ND	ND	12.4
Potassium	19.5	19.4	21.0	19.0	3,960	14.7	14.7	15.8	14.3
Selenium	Trace	Trace	ND	Trace	2.7	Trace	Trace	ND	Trace
Silicon	1.6	1.9	50.1	66.0	292	16.5	19.5	510	675
Silver	ND	ND	ND	ND	0.7	ND	ND	ND	ND
Sodium	1670	1400	1410	735	54,500	91.7	77	77.3	40.3
Strontium	22.3	20.1	40.1	20.9	24,600	2.7	2.4	4.9	2.5
Sulfate	496	594	760	195	66,200	22.4	26.8	34.2	8.8
Uranium	ND	ND	0.0	0.0	2.9	ND	ND	8.03	16.5
Vanadium	Trace	Trace	Trace	0.3	62.5	Trace	Trace	Trace	15.6
Zinc	ND	ND	0.7	1.2	187	ND	ND	11.3	19.4
Zirconium	ND	ND	Trace	0.0	5.8	ND	ND	Trace	8.1

Table 11 Continued

Drilling Mud Results

Element	Extract Concentration (mg/L)				Composition	Leaching Potential (% of Composition)			
	Reagent Water	Acid Rain	Acetic Acid	Leachate	(mg/kg dry)	Reagent Water	Acid Rain	Acetic Acid	Leachate
Aluminum	0.8	2.3	5.3	7.6	15,300	0.2	0.5	1.1	1.6
Antimony	0.0	0.0	0.0	0.0	9.8	7.9	8.0	3.5	5.4
Arsenic	0.0	0.0	0.1	0.4	115	1.2	0.8	2.8	11.2
Barium	1.9	3.0	1.9	Trace	10,900	0.6	0.9	0.6	Trace
Beryllium	ND	ND	ND	Trace	1.2	ND	ND	ND	Trace
Boron	Trace	ND	Trace	Trace	41.4	Trace	ND	Trace	Trace
Bromide	1.1	1.0	1.4	1.0	37.2	91.5	88.9	123	86.8
Cadmium	ND	ND	Trace	ND	1.5	ND	ND	Trace	ND
Calcium	31.8	30.8	596	610	23,700	4.3	4.2	81.3	83.3
Chromium	Trace	Trace	0.1	0.2	50.2	Trace	Trace	7.9	14.8
Cobalt	ND	ND	0.1	0.0	11.5	ND	ND	14.3	9.5
Copper	0.0	ND	0.2	ND	88.6	0.5	ND	6.5	ND
Iron	0.5	0.7	34.5	12.0	22,100	0.1	0.1	5.1	2.4
Lead	Trace	0.0	2.1	0.6	225	Trace	0.2	30	8.1
Lithium	Trace	Trace	0.1	0.1	31.7	Trace	Trace	10.5	12.0
Magnesium	1.7	2.5	28.8	17.7	3,950	1.4	2.0	23.5	14.5
Manganese	0.2	0.4	15.4	15.3	710	1.0	1.8	70.1	69.9
Mercury	ND	ND	ND	ND	9.5	ND	ND	ND	ND
Molybdenum	Trace	Trace	ND	Trace	57.0	Trace	Trace	ND	Trace
Nickel	0.0	0.0	0.2	ND	71.0	0.5	0.6	10.1	ND
Phosphorus	Trace	Trace	Trace	1.3	360	Trace	Trace	Trace	11.4
Potassium	15.0	13.7	18.5	18.2	6,080	8.0	7.3	9.9	9.7
Selenium	Trace	ND	ND	Trace	4.0	Trace	ND	ND	Trace
Silicon	2.1	4.3	11.5	8.5	563	12.2	24.5	66.2	48.7
Silver	ND	ND	ND	ND	0.6	ND	ND	ND	ND
Sodium	1530	1320	1380	1260	54,200	91.1	79.1	82.1	75.4
Strontium	17.3	17.8	45.8	15.9	6,850	8.2	8.4	21.6	7.5
Sulfate	139	89.7	85.2	ND	48,900	9.2	6.0	5.6	ND
Uranium	0	0	0.0	0.0	7.7	1.0	1.2	3.5	6.4
Vanadium	Trace	Trace	Trace	Trace	64.2	Trace	Trace	Trace	Trace
Zinc	ND	Trace	1.2	0.7	191	ND	Trace	19.4	12.4
Zirconium	Trace	Trace	Trace	Trace	4.7	Trace	Trace	Trace	Trace