Evaluating Leachability of Residual Solids Generated from Unconventional Shale Gas Production Operations in Marcellus Shale

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ABSTRACT

Hydraulic fracturing operations utilized for shale gas production result in the generation of a large volume of flowback and produced water that contain suspended material, salts, hydrocarbons, metals, chemical additives, and naturally-occurring radioactive material. The water is impounded at drilling sites or treated off-site, resulting in significant generation of residual solids. These are either buried on site or are disposed in lined landfills. The objective of this study was to determine the levels of heavy metals and other elements of concern that will leach from these residual solids when placed in typical disposal environments.

For this purpose, laboratory leaching experiments were employed wherein representative samples were brought into contact with a liquid to determine the constituents that would be leached by the liquid and potentially released into the environment. The samples used included sludge resulting from the physicochemical treatment of process water (TS), sludge solidified with cement kiln dust (SS), raw solids obtained by gravity separation of process water (RS), and drilling mud (DM). The samples were subjected to both single extraction (i.e. Shake Extraction Test, SET) and multiple extraction (i.e. Immersion Test, IT) leaching tests. For the shake extraction test, samples were mixed with a specific amount of leaching solution without renewal over a short time period. In the immersion test, samples were immersed in a specific amount of leaching solution that was periodically renewed over a longer period of time. For both these tests, analyses were performed on the filtered eluate. The tests were performed as per standards with modifications. Distilled de-ionized water, synthetic acid rain (pH ~ 4.2), weak acetic acid (pH ~ 2.88), and synthetic landfill leachate were used as leaching solutions to mimic specific disposal environments.

Alkali metals (Li, K, Na), alkaline earth metals (Ba, Ca, Mg, Sr) and a halide (Br), which are typically associated with Marcellus shale and produced waters, leached at high concentrations from most of the residual solids sample. The SS sample, due to its stabilization with CKD, had a lower extraction efficiency as compared to the unconsolidated TS and RS samples. In EF 2.9 and EF SLL, the leaching took place under acidic conditions, while for EF DDI and EF 4.2, the leaching occurred in alkaline conditions. EF 2.9 and EF SLL were determined to be the most aggressive leaching solutions, causing the maximum solubility of most inorganic elements. Thus, high amounts of most EOCs may leach from these residual solids in MSW landfills disposed under co-disposal conditions. Agitation, pH and composition of the leaching solution were determined to be important variables in evaluating the leaching potential of a sample.

The results of this study should help with the design of further research experiments being undertaken to develop environmentally responsible management/disposal strategies for these residual solids and also prove useful for regulatory authorities in their efforts to develop specific guidelines for the disposal of residuals from shale gas production operations.

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ASTM	American Society for Testing and Materials
BDL	Below detection level
CKD	Cement kiln dust
CWT	Centralized waste treatment facility
DM	Drilling mud
E&P	Exploration and Production
EF 2.9	Extraction fluid of pH 2.9 prepared as defined by USEPA Method 1311- Toxicity Characteristic Leaching Procedure
EF 4.2	Extraction fluid of pH 4.2 prepared as defined by USEPA Method 1312 – Synthetic Precipitation Leaching Procedure
EF DDI	Distilled de-ionized water extraction fluid
EF SLL	Aerobic synthetic landfill leachate prepared as defined by Stanforth et. al (1979)
EOC	Elements of Concern
GWPC	Groundwater Protection Council
ICP MS	Inductively Coupled Plasma Mass Spectroscopy
L/S	Liquid to solid ratio (v/w)
MDL	Method detection limit
MRL	Minimum reporting level
MSW	Municipal solid waste
NETL	National Energy Technology Laboratory
NPDWS	National primary drinking water standards
NYS WRI	New York State Water Research Institute
PADEP	Pennsylvania Department of Environmental Protection
ppb	Parts per billion
RCRA	Resource Conservation and Recovery Act
RS	Raw solids
S/S	Solidified/Stabilized
SS	Solidified solids
TS	Treated solids
US EIA	US Energy Information Administration
US EPA	US Environmental Protection Agency
USGS	US Geological Survey
WS DOE	Washington State Department of Ecology

CHAPTER 1: INTRODUCTION

The increasing demand for energy in the world is currently being fulfilled by natural gas and is projected to be so for the next coming decades. This has been possible due to the increased exploration and extraction of unconventional natural gas resources, with shale gas being the fastest growing source of natural gas. According to the Energy Information Administration (EIA), the estimated reserves of global shale gas are about 1,013 trillion cubic meters, and is predicted to provide for the global fuel supplies for more than 100 years (GWPC and ALL 2009, EIA and ARI 2013a). This immense growth in shale gas production has been particularly attributed to the technological advances in directional well drilling and reservoir stimulation, i.e. horizontal drilling and high-volume hydraulic fracturing, which has enabled the oil and gas industry to extract shale gas at economical amounts (USEPA 2012). Thus, increased drilling activity has been observed in these shale reservoirs in the U.S. However, several environmental concerns are associated with this otherwise, economically desirable industry. Understanding and mitigating the adverse impacts are among the major challenges for the shale gas industry. In addition to water quantity and quality issues, management of residual solids due to drilling and fracturing operations is a growing concern (Hammer and VanBriesen 2012, Liroff 2011, Maloney and Yoxtheimer 2012).

This research focused on the residual solids generated during unconventional shale gas production operations in the Marcellus shale area, with an aim to improve our understanding of how these wastes should be managed.

Residual solids from unconventional shale gas production operations are generated during drilling operations and as by-products of produced water treatment. The major types of residual solids are: (1) Drill cuttings: fragments of rock and soil resulting from a drill bit grinding the rock for drilling a borehole into the earth; (2) Drilling mud: dense clay-rich slurries used for lifting and circulating the drill cuttings to the surface for removal; and, (3) Produced water treatment by-products: residual solids or sludges generated from treatment of the high volume of wastewater resulting from hydraulic fracturing operations (Hammer and VanBriesen 2012, Kargbo et al. 2010, Maloney and Yoxtheimer 2012, New York State Water Resources Institute (NYS WRI) 2012, USEPA 2002). In addition to these residuals, other potential residual solids may include tank bottoms, pit sludges, basic sediment, flowback fracturing sand, spent filter, and filter media (Maloney and Yoxtheimer 2012, USEPA 2002). In the recent years, produced water has been reported to be mixed with solidifying agents such as cement kiln dust, for solidification and stabilization purposes for direct disposal of produced water in landfills (Roche 2013). The large quantity of sludge that may be generated due to these operations can also be classified as residual solids. This work, however, was limited to studying the two major types of residual solids, the by-products of treating produced water, and drilling mud.

The increased shale gas production activities in the Marcellus shale formation will result in increased drilling and fracturing activities, ultimately resulting in higher volumes of residual solids production. With the expected increase in the magnitude of the wastes in the coming years, concerns associated with their management will only increase. The results of this study will provide a comment about current management practices and enable us to better understand if any threats are being posed that can be mitigated significantly by implementing better management practices and policies for the future.

The primary goal of this study was to evaluate the leaching behavior of heavy metals and other elements of concern (EOC) from the residual solids which are generated from unconventional shale gas production operations in Marcellus shale. The aim was to better understand the leaching behavior of the residual solids in their typical disposal environments.

To achieve this, representative samples were subjected to laboratory leaching tests wherein the samples were brought in contact with a solution and the resulting leachate was analyzed for elements of concern. The samples in this study were subjected to a single extraction leaching test and a multiple extraction leaching test. The single extraction leaching test is characterized by a large liquid to solids (L/S) ratio, short leaching period (hours to days), no replenishment of leaching solution and agitation, while the multiple extraction leaching test is characterized by a relatively smaller L/S ratio, long leaching period (days to weeks), replenishments of leaching solution and no agitation.

Leaching solutions were chosen in this study to assess the leaching behavior of the residual solids under different environmental conditions. Leaching solutions were used to specifically simulate, leaching conditions in a MSW landfill when co-disposed with other municipal refuse, mono-disposal in pits or land disposal conditions, and field conditions where the waste’s buffering capacity determines the pH of the leachate. In addition to these, a synthetic landfill leachate simulating the most aggressive characteristics of municipal landfill leachate was also considered.

The representative residual solid samples used in this study were drilling mud (DM) and three different types of produced water treatment by-products: (1) raw solids (RS) generated through liquid-solid separation by gravity of produced water prior to chemical treatment; (2) sludge generated due to physiochemical treatment (treated solids = TS) of the produced water; and (3) all the residual solids, including DM, that are solidified with cement kiln dust (solidified solids = SS) for disposal in a landfill.

In Chapter 3, results of the leaching behavior observed when all the residuals solids collected from the CWT facility were mixed in different leaching solutions using a single extraction leaching test are discussed. The procedure used for performing the experiment was a modified version of the ASTM standard method, D3987: Shake Extraction of Solid Waste with Water.

In Chapter 4, results of the leaching behavior observed when all the residual solids collected from the CWT facility (except drilling mud) were mixed in different leaching solutions using a multiple extraction flow-around leaching test are discussed. The procedure used for performing the experiment was a modified version of the Netherlands standard method, NEN 7374, developed by a national Dutch standardization organization (NEN),

In Chapter 5, the results from Chapter 3 and Chapter 4 are compared to one another to observe the impact that different parameters (such as agitation, test duration etc.,) had on the leachability of the residual solids.

This study focused on addressing one of the greatest concerns to the industry: the environmentally-responsible management of large volumes of residual solids resulting from unconventional shale gas production operations by characterizing these wastes. This is important for continued sustainable development of unconventional shale gas production necessary for United States energy independence. During an extensive literature review, a dearth in the information related to the leaching behavior of residual solids was observed. Thus, this study would be among the first to address the release of inorganics from these residuals in disposal environments. The data should prove useful for regulatory authorities in their efforts to develop specific guidelines for the disposal of residuals.

1.1 REFERENCES

Groundwater Protection Council (GWPC) and ALL Consulting (2009) *Modern Shale Gas Development in the United States: A Primer*, DE-FG26-04NT15455. http://energy.gov/sites/prod/files/2013/03/f0/ShaleGasPrimer_Online_4-2009.pdf

Hammer, R. and VanBriesen, J. (2012) *In Fracking's Wake: New Rules are Needed to Protect Our Health and Environment from Contaminated Wastewater*, D:12-05-A. http://www.nrdc.org/energy/files/fracking-wastewater-fullreport.pdf

Kargbo, D.M., Wilhelm, R.G. and Campbell, D.J., Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environmental Science & Technology* **2010,** *44*, (15), 5679-5684.

Liroff, R.A. (2011) *Extracting the facts: An investor guide to disclosing risks from hydraulic fracturing operations*, Investor Environmental Health Network. http://www.iehn.org/documents/frackguidance.pdf

Maloney, K.O. and Yoxtheimer, D.A., Production and Disposal of Waste Materials from Gas and Oil Extraction from the Marcellus Shale Play in Pennsylvania. *Environmental Practice* **2012,** *14*, 278-287.

New York State Water Resources Institute (NYS WRI), (2012), Waste Management of Cuttings, Drilling Fluids, Hydrofrack Water and Produced Water, *Gas Wells*, New York State Water Resources Institute Retrieved from http://wri.eas.cornell.edu/aboutus.html

Roche, M., "Fracking concerns: Will Ohio start accepting drilling brine at 40 landfills?". Accessed on May 20, 2014 from http://www.norwalkreflector.com/article/2074481

US Energy Information Administration (EIA) and Advanced Resources International Inc (ARI) (2013a) *EIA/ARI World Shale Gas and Shale Oil Resource Assessment*. http://www.adv-res.com/pdf/A_EIA_ARI_2013%20World%20Shale%20Gas%20and%20Shale%20Oil%20Resource%20Assessment.pdf

USEPA (2002) *Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations*, EPA530-K-01-004, US Environmental Protection Agency,. http://www.epa.gov/epawaste/nonhaz/industrial/special/oil/oil-gas.pdf

USEPA (2012) *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, EPA/601/R-12/011. http://www2.epa.gov/sites/production/files/documents/hf-report20121214.pdf

CHAPTER 2: LITERATURE REVIEW

2.1 NATURAL GAS IN UNITED STATES

The increasing demand for energy in the world is currently being fulfilled by natural gas and is projected to do so for the next coming decades. This has been possible due to the increased exploration and extraction of unconventional natural gas resources, with shale gas being the fastest growing source of natural gas. According to a study published by the United States Energy Information Administration/Advanced Resources International Inc. (EIA/ARI) in 2013, approximately 35,782 trillion cubic feet (Tcf) of assessed shale gas in-place is available globally. Of this, approximately 7,795 Tcf is technically recoverable resource (TRR) of shale gas; i.e., "the total amount of resource, discovered and undiscovered, thought to be recoverable with available technology, regardless of economics" (Groundwater Protection Council (GWPC) and ALL Consulting 2009). United States (U.S.) alone accounts for 15% of this global TRR (1,161Tcf) (EIA/ARI 2013b). The availability of these large recoverable reserves along with the development of new technologies, enabled the oil and gas industry of the U.S. to produce large quantities of natural gas from shale formations in a cost-effective way, leading to an immense boom in shale gas production over the past decade (Wang and Krupnick 2013).

Shale gas is a type of a natural gas (methane) trapped in shale formations, which are a group of fine-grained, laminated sedimentary rock; typically rich in organics and with low natural permeability and porosity. In addition to being a source of the natural gas, these shale formations also store the shale gas thereby acting as a reservoir (Groundwater Protection Council (GWPC) and ALL Consulting 2009). The U.S. currently has six active shale reservoirs: Barnett Shale, the Haynesville/Bossier Shale, the Antrim Shale, the Fayetteville Shale, the Marcellus Shale, and the New Albany Shale. Of these, Marcellus Shale is the largest shale gas play in the U.S., occurring throughout the Appalachian Basin. It encompasses large areas of Pennsylvania and West Virginia, and parts of New York, Maryland, Virginia, and Ohio. The play covers an area of more than 160,934 km^2 (Evans and Kiesecker 2014). The play is estimated to contain more than 500 Tcf of recoverable natural gas (Engelder and Lash 2008), and is the largest source of natural gas in the U.S. (Begos 2012).

2.2 OVERVIEW OF HYDRAULIC FRACTURING

The low permeability and low porosity of the shale formations resists the free flow of shale gas through these formations into a wellbore. In order to overcome the challenges presented by these formations, artificial stimulation techniques such as hydraulic fracturing combined with horizontal well drilling are employed. These techniques increase the permeability of the formation by creating pathways for easy flow of the natural gas towards the wellbore. The technological innovations in horizontal well drilling and hydraulic fracturing techniques over the past few decades has enabled the economical extraction of natural gas from unconventional shale gas reservoirs (GWPC and ALL 2009).

Horizontal well drilling is a process in which the vertically drilled well, upon reaching the target shale formation, is gradually turned to approximately 90 degrees, thereby drilling a lateral borehole through the shale formation. The horizontal section of the well is extended to 3000 – 6000 feet or more through the shale reservoir, resulting in access to a larger volume of reservoir rock through a single bore well (Maloney and Yoxtheimer 2012).

High-volume slick-water hydraulic fracturing, a formation stimulation technique, follows horizontal drilling and completion, wherein a fracturing fluid, composed mostly of water and sand with some chemical additives, is injected through the horizontal borehole under high pressure to generate cracks in the reservoir rock and keep these cracks open (Hammer and VanBriesen 2012). Approximately 3 – 8 million gallons of fracturing fluid (Rahm et al. 2013), consisting of 90%–95% water, 5%–10% sand proppant, and 0.1%–1% of chemical additives (Maloney and Yoxtheimer 2012), is required for completion of the fracturing operation. This water-based fracturing fluid is commonly referred to as “slick-water” frac, and its composition may vary from site to site (PADEP 2010). The water transmits the hydraulic pressure to the shale formation creating fractures, along with transporting the proppants and chemical additives to stimulate the formation. Proppants, such as sand and ceramic materials, are used to keep the induced fractures open, even after the hydraulic fracturing pressure is reduced (Kargbo et al. 2010). Chemical additives allow the fracturing fluid to be pumped at a higher rate and less pressure, along with preventing the growth of microorganisms and corrosion of metal pipes, inhibiting biofouling of the fracture, and removing drilling mud, thereby increasing the production of gas from the reservoir (GWPC and ALL 2009). The additives commonly used in the fracturing fluid to accomplish this include: dilute acid solution, biocide or disinfectant, scale inhibitor, iron control/stabilizing agents, friction reducing agents, corrosion inhibitors, gelling agents and cross-linking agents (PADEP 2010). However, not all of these additives are included in the fracturing fluid recipe for each fracturing operation/stage. The specific chemicals used and their proportions are controlled by the characteristics of the target formations (PADEP 2010).

Upon completion of the fracturing operation, the pressure used to inject the slick-water into the borehole is released. This results in the return of approximately 30% to 70% of water-based slick-water along with any natural formation water back to the wellhead (GWPC and ALL 2009). “Flowback fluid” or “flowback” is the water that flows back immediately after the pumping pressure is released, and this flowback phase may last until the well begins producing natural gas which may take a few days to weeks (Hammer and VanBriesen 2012). All the wastewater that flows back after the well enters the gas production phase is called “production phase water” or “brine water”. This is the fraction of the slick-water that is left behind in the fractures created in the formation. It flows back over an extended period of time and in volumes relatively smaller than the flowback fluid. For the purposes of this paper, both these wastewaters shall be collectively referred to as “produced wastewater.”

The composition of these wastewaters is defined by the chemical additives added to the fracturing fluid and their contact time with the target shale formation. While the flowback fluid is composed of both the chemicals introduced to the fracturing fluid and the chemicals leaching from the shale formation, the production phase water is mostly defined by the dissolved minerals and organic constituents from the shale formation (Hammer and VanBriesen 2012, Kargbo et al. 2010). Typically, the composition of produced wastewater includes high concentrations of naturally occurring salts (commonly referred to as total dissolved solids or TDS), organic hydrocarbons (also referred to as “oils and grease”), naturally occurring radioactive matter (NORM), and metals (Gregory et al. 2011). Due to the large volumes, high dissolved solid concentrations, and other constituents associated with these wastewaters, their proper management is essential to protect human health and prevent damage to the environment. Thus, the produced wastewaters are commonly treated either on-site or off-site, followed by dilution prior to re-use, or directly disposed of in deep injection wells (Rahm et al. 2013). On-site, the produced wastewater is temporarily stored in pits or impoundments with an embankment prior to their disposal, or treatment and reuse. With growing environmental concerns, most facilities may choose to treat the produced water and reuse the same in drilling operations. Other sources extensively discuss the production and composition of produced water along with their current management practices (Gaudlip et al. 2008, Gregory et al. 2011, Hammer and VanBriesen 2012, Hayes 2009, Kargbo et al. 2010, Rahm et al. 2013).

2.3 RESIDUAL SOLIDS GENERATION AND COMPOSITION

Residual solids from unconventional shale gas production operations are generated during drilling operations and as by-products of produced water treatment. The major types of residual solids are: (1) Drill cuttings: fragments of rock and soil resulting from a drill bit grinding the rock for drilling a borehole into the earth; (2) Drilling mud: dense clay-rich slurries used for lifting and circulating the drill cuttings to the surface for removal; and, (3) Produced water treatment by-products: residual solids or sludges generated from treatment of the high volume of wastewater resulting from hydraulic fracturing operations (Hammer and VanBriesen 2012, Kargbo et al. 2010, Maloney and Yoxtheimer 2012, New York State Water Resources Institute (NYS WRI) 2012, USEPA 2002). In addition to these residuals, other potential residual solids include tank bottoms, pit sludges, basic sediment, flowback fracturing sand, spent filter, and filter media (Maloney and Yoxtheimer 2012, USEPA 2002). In the recent years, produced water has been reported to be mixed with solidifying agents such as cement kiln dust, for solidification and stabilization purposes for direct disposal of produced water in landfills (Roche 2013). The large quantity of sludge that may be generated due to these operations can also be classified as residual solids.

Drill Cuttings

During excavation, for drilling a borehole into the earth, the drill bit grinds the rock, generating fragments of the rock and soil which are termed as drill cuttings. These drill cuttings are composed of the rock that separates the shale from the surface (generated from the vertical borehole) and the shale itself (generated from the horizontal borehole). These drill cuttings are then lifted and circulated to the surface for their removal with the aid of dense, clay-rich slurries referred to as drilling fluid or drilling mud (Rahm et al. 2013).

Due to the great depths that the wells are drilled vertically to reach the target shale formation, along with the great horizontal depths drilled through the shale formations, a large volume of drill cuttings can be expected to be generated. Drill cuttings are essentially composed of shale, sand, and clay, and they may be contaminated by the borehole and the drilling mud that they come in contact with (Kargbo et al. 2010). Low levels of radionuclide concentrations have also been reported for drill cuttings from Marcellus shale (Hammer and VanBriesen 2012, Kargbo et al. 2010, NYSDEC 2011, Ohio EPA 2014). The drill cuttings lifted to the surface are separated from the drilling mud prior to their disposal or re-utilization. It is possible that not all of the drilling mud will be removed from the drill cuttings, and thus the drill cuttings can be expected to be contaminated by the drilling mud.

Drilling Mud

Drilling mud, in addition to carrying the drill cuttings, cool and lubricate the drilling bit, keep the drilling bit clear of cuttings, control formation pressures and stabilize the wellbore, and prevent the formation fluids from entering the borehole (Ohio EPA 2014, Schlumberger 1994). Drilling mud (also known as drilling fluid), depending on the base fluid, can either be classified as water-based, oil-based (containing petroleum products or mineral oil), or synthetic-based (Schlumberger 1994). The basic ingredients of drilling mud consists of, water, heavy minerals (such as barite), clays (most commonly bentonite) or organic colloids (such as biopolymers), polymers, a stabilizing organic material (such as lignosulfonate or lignite), surfactants, inorganic chemicals (such as sodium hydroxide, potassium hydroxide, or calcium hydroxide) and certain specialized chemicals (Schlumberger 1994). The drilling mud mixes with the drill cuttings and the formation water during their circulation to the well surface and thus contaminants that are typically associated with the geological formations can be expected to dissolve or be adsorbed by the drilling muds (NYS WRI 2012, Resnikoff et al. 2010, Schlumberger 1994). Drilling muds are reused to facilitate the drilling process after separating them from the drill cuttings (NYS WRI 2012). This can result in an increase in the concentration of contaminants after each use.

Produced Water Treatment By-Products

The treatment of high volumes of wastewater from hydraulic fracturing operations, also referred to as produced water, results in the generation of residual solids. On-site treatment of produced water includes storage in open-pits or impoundments for evaporation, aeration, settling, and perhaps filtration. The waste that settles at the bottom of these pits after the treatment process can be classified as residual solids, which are commonly disposed of as solid waste

(Kargbo et al. 2010). Off-site treatment of the produced wastewaters is commonly performed in approved, industrial wastewater treatment facilities, also called centralized waste treatment facilities (CWTs). CWTs are equipped with physiochemical treatment units, such as coagulation, precipitation, flocculation, centrifugation, settling and filtration, to primarily reduce the high TDS and metal concentrations along with organic contaminants to ensure the produced wastewater is clean enough for reuse (Hammer and VanBriesen 2012). Coagulation and precipitation operations involve pH adjustment, addition of chemical precipitant, and flocculation. Through these operations the soluble salts are converted into insoluble salts that precipitate and are then separated from the treated water by physical methods (e.g., settling and/or filtration). The precipitate-containing contaminants removed from the produced wastewater, and chemical treatment residuals, are also classified as residual solids. These residual solids will contain the contaminants at concentrations higher than the original produced water, thereby making its proper management all the more important (Hammer and VanBriesen 2012).

2.4 RESIDUAL SOLIDS MANAGEMENT

Upon reaching the surface, drilling mud is separated from the drill cuttings using either solids control equipment, such as vibratory screens and hydrocyclones (Barry and Klima 2013); or separation pits, that are plastic-lined, unleveled containment pits (Resnikoff et al. 2010). The drill cuttings are then solidified and stored in separate pits on the facility. Drill cuttings are considered solid waste and are thus directly disposed of by the drilling facility into landfills (Maloney and Yoxtheimer 2012). The New York Department of Environmental Conservation (NYDEC) specifically classifies drill cuttings as construction and demolition (C&D) debris, permitting their disposal on-site, in C&D landfills, or at municipal solid waste (MSW) landfills. However, the NYDEC further clarifies that any drill cuttings generated from processes employing oil or synthetic based drilling muds can only be disposed of in MSWs.

Re-utilization of drill cuttings may also be considered for construction purposes, as a road base, or as a fill material in abandoned mines. It was noted that facilities were available in PA that stabilized these drill cuttings, both geotechnically and chemically, for their reuse as construction fill at Brownfield or PA Act II sites (Clean Earth 2012).

After separation, drilling mud is commonly reused. Upon completion of the drilling phase of production, these drilling muds are either directly disposed of in landfills or following some preliminary treatment at CWTs. Direct disposal of drilling mud in deep injection wells has also been reported(NYS WRI 2012).

Residual solids generated as a result of on-site and off-site treatment of produced water are commonly disposed of in approved MSW landfills.

2.5 REGULATIONS GOVERNING RESIDUAL SOLIDS MANAGEMENT

The Resource Conservation and Recovery Act (RCRA) explicitly excludes drill cuttings, drilling fluids, produced waters, produced water treatment by-products, and other wastes associated with oil and gas exploration and production (E&P wastes) from regulation as hazardous wastes (USEPA2002). However, management of these wastes is generally required to comply with the non-hazardous waste regulation under RCRA Subtitle D (USEPA2002). In addition, E&P wastes are to be managed in accordance with state requirements and federal laws other than RCRA, that apply to the disposal of wastes (e.g., Underground Injection Control Program (UIC) which specifies the requirements for injection of oil and gas-related wastes into Class II wells).

State regulations governing hydraulic fracturing operations are different in scope and detail among some states. For example, while the state of California does not exempt E&P waste from its hazardous waste program, the state of Ohio exempts E&P wastes, such as drill cuttings as hazardous waste (Ohio EPA 2014). While E&P wastes, such as drill cuttings and drilling muds, are not classified as hazardous by either federal or state regulations, they are classified as solid waste by state regulations and are required to be disposed of in a licensed landfill facility. Certain state regulations also require approval prior to utilizing drill cuttings off-site for beneficial purposes (Ohio EPA 2014).

The exemption of E&P wastes from RCRA Subtitle C hazardous regulations does not preclude these wastes from being a hazard to the environment and human health. This exemption, however, provides an option to the operators to employ relatively less costly waste management options. Nonetheless, it is ultimately the responsibility of the generator and the collector of these wastes to ensure the most environmentally sound management of these wastes, and are liable for future cleanup actions (USEPA2002).

2.6 ELEMENTS OF CONCERN

A gap exists in our understanding of the exact inorganic composition of various residual solids from unconventional shale gas operations. Few publications were found that extensively discussed the chemistry of various residual solids from unconventional shale gas operations in the Marcellus Shale area. The available literature focuses mostly on drill cuttings.

A study was performed to evaluate the leachability of produced water treatment by-products and drilling mud collected from a CWT in PA (U.S.), which treated only produced water from hydraulic fracturing drilling facilities located in the Marcellus shale region of PA (Countess 2014). In this study aluminum, barium, calcium, iron, magnesium, potassium, sodium, strontium, and sulfate were found to be the major constituents detected based on strong acid digestion; while arsenic, bromide, lead, lithium, molybdenum, and uranium were also detected from strong acid digestion. No other refereed articles were found that pertained specifically to the chemistry of drilling muds and produced water treatment by-products for the Marcellus shale area.

The drilling mud and produced water are expected to mimic the formation chemistry due to their long contact time with the geological formation and its contained brine water (Bank 2011, Blauch et al. 2009, Haluszczak et al. 2013, Resnikoff et al. 2010, Schlumberger 1994, Skalak et al. 2014). The by-products of treating produced water mainly consist of precipitates containing contaminants removed from the produced wastewater and treatment chemical residuals, at concentrations higher than in the original produced water (Hammer and VanBriesen 2012). Thus, the elements commonly associated with produced water will be mostly present in the by-products from its treatment.

In a study conducted by Hayes (2009), produced water samples were collected and analyzed from 19 drilling sites distributed within the Marcellus shale region at standardized times of 0, 1, 5, 14 and 90 days. The following observations were made through an analysis of the sampling results:

1) The Marcellus Shale produced waters had a pH in the range of 6 to 8.

2) Sodium, calcium, and chloride were reported as the major elements.

3) Other elements commonly detected were aluminum, barium, boron, bromide, iron, lithium, magnesium, manganese, potassium, strontium, and sulfate; of these, barium and strontium were relatively reported at higher concentrations.
4) Trace levels of toxic inorganic constituents such as antimony, arsenic, chromium, copper, nickel, zinc, cadmium, lead, molybdenum and mercury were also measured.

Several other authors have reported similar observations for produced water composition (Blauch et al. 2009, Evans and Kiesecker 2014, Pritz and Kirby 2010, ProChem Tech 2009). In addition to the above mentioned elements, selenium (Blauch et al. 2009, ProChem Tech 2009) and silicon (Evans and Kiesecker 2014) have also been reported.

Concentrations measured in the produced water have been reported to typically increase with increase in contact time of the slick-water with the target shale formation (Bank 2011, Blauch et al. 2009, Gaudlip et al. 2008, Haluszczak et al. 2013, Skalak et al. 2014). For instance, higher concentrations of calcium, magnesium, bromine, sodium, chloride, barium, strontium, iron, manganese, potassium, boron and lithium have been associated with produced water analyzed at a later stage (Haluszczak et al. 2013). The increase in the concentration of inorganic constituents in produced water has been typically attributed to the dissolution of soluble inorganic constituents from the formation into the slick-water and also to its mixing with the formation brines during its flow back to the surface after fracturing (Blauch et al. 2009, Haluszczak et al. 2013). Marcellus shale have been reported to contain metals such as barium, uranium, chromium, zinc (Bank 2011), arsenic, selenium (Balaba and Smart 2012), vanadium, molybdenum, iron, and cobalt (Liermann et al. 2011). Some of these elements can also be expected to be present in the later stage produced water.

The composition of produced water can also be influenced by the chemical additives used in slick-water (Balaba and Smart 2012, Gaudlip et al. 2008). Thus, zirconium, which has been reported to be used as metal additive in the slick-water for crosslinking purposes, can be expected to be present in produced waters. Elements such as beryllium and silver, while not typically reported in produced waters from Marcellus shale, have been considered for analysis in produced water in various studies and are typically associated with oil and gas production wastewaters.

2.7 SIGNIFICANCE OF PROPER MANAGEMENT OF RESIDUAL SOLIDS

Due to the growing quantities of residual solids resulting from unconventional shale gas operations in the U.S., the environmentally sound management of these wastes has become as critical as the management of the untreated produced water.

As per an analysis conducted by Maloney and Yoxtheimer (2012), the total quantity of drill cuttings and drilling fluids generated for the year 2011 in the state of PA was approximately 798,623 tons and 2,374,469 barrels, respectively. The authors further estimated that the complete development of the entire Marcellus shale play will generate 1.37×10^8 barrels of drilling fluid and 4.62×10^7 tons of drill cuttings (Maloney and Yoxtheimer 2012). These estimates indicate the magnitude of the wastes expected in the coming years and the concerns associated with their management will only increase.

Due to growing concerns over water quantity issues, treatment of produced water at CWTs for re-use in drilling operations has increased in recent years. In 2011, approximately half of all wastewater produced from unconventional shale gas operations was treated at CWT facilities (Hammer and VanBriesen 2012). In 2011, 20 times more gas wells were drilled in the Marcellus shale play of PA, alone, as compared to that in 2007 (Jiang et al. 2013). This rapid development of shale gas production in the Marcellus formation will result in greater volumes of produced water generated, assuming similar techniques are employed for producing shale gas. This shall ultimately result in higher volumes of residual solids production due to the treatment of produced water. These residual solids shall be concentrated with the contaminants at higher levels as compared to the un-treated produced water, thus making its proper management all the more important (Hammer and VanBriesen 2012).

The classification of residual solids as being hazardous or non-hazardous determines the type of landfill facility that can be used. Toxic materials may also leach from decomposing residual solids when they come in contact with leachates commonly found in municipal landfills. Release of these toxic leachates from landfill facilities to groundwater and surface water sources can significantly impact the environment and public health. In addition, wastewater treatment plants receiving these leachates from MSW landfills may not be designed to handle them. Due to these concerns, the residual solids may require pretreatment before their disposal, or an alternative disposal method may need to be implemented. Thus, characterization of the wastes is critical to ensure that they are handled accordingly for the sustainable development of the shale gas industry.

2.8 LEACHING

Leaching is the process by which soluble components are extracted from a solid by a fluid. Wastes deposited in a landfill environment are subjected to leaching upon their exposure to percolating rainwater, groundwater, surface water and other fluids in the landfill, causing the release of the soluble contaminants. The escape of this resulting leachate from the landfill into the permeable soil and/or groundwater can have a considerable impact on the environment and public health. To determine the suitability of the waste for disposal in landfills or for utilization without any negative impact on the environment or public health, leaching/extraction tests are employed. These tests can be performed in the laboratory and in the field.

2.8.1 Overview of Leaching Tests

Field experiments, also known as lysimeter experiments, are performed outdoors wherein the samples are exposed to natural environments, thereby closely simulating actual field conditions. The leachate is formed due to percolating natural precipitation over extended periods of time, ranging from a few months to several years (Hansen et al. 2000). They also provide an opportunity to observe the impact of natural weathering conditions on the decomposition of the sample. Field experiments are typically performed in conjunction with laboratory leaching tests to compare the results, with an intention to substantiate the results obtained from the laboratory experiments (Fällman and Aurell 1996, Hansen et al. 2000).

Laboratory leaching tests are typically performed on smaller scale as compared to the field experiments and are used to evaluate the leaching behavior of a waste in a short span of time under controlled conditions. Laboratory leaching tests are performed under the assumption that the leaching solution and other set of conditions are representative of a typical disposal environment. Various physical, chemical and biological factors that influence the release of contaminants from wastes can be controlled in laboratory leaching tests and thus specific conditions mimicking disposal environments can be simulated.

Laboratory leaching tests are performed by bringing a sample in contact with a leaching solution for a specific period of time. The leachate is collected intermittently or at the end of the testing period and analyzed for the elements of interest. Various laboratory leaching tests have been discussed in a report by Washington State Department of Ecology (2003) to help identify leaching tests appropriate for evaluating the potential impacts of fill materials.

Leaching tests are broadly categorized into three types based on practice: (1) Regulatory methods formulated and approved by regulatory agencies to characterize the material for obtaining legal compliance by comparing results with threshold values (these are typically performed for a short duration of a few hours to days), (2) Standard methods developed by certain standard organizations such as American Society for Testing and Materials (ASTM), which are typically formulated to simulate a specific disposal environment(s) and/or testing a particular type of material, and (3) Research methods which are commonly developed for achieving specific experimental objectives (Kim 2002, van der Sloot 1998).

Laboratory leaching experiments can be further classified into two types; single extraction/batch tests, collectively referred to as static tests, and multiple extraction/flow around/flow through test, collectively referred to as dynamic tests (Kim 2002, Siddique et al. 2010, van der Sloot 1998, WSDOE 2003).

2.8.2 Single Extraction Leaching Test

Static tests are performed for a shorter period of time (ranging from a few hours to days) and without renewal of leaching solution. Single extraction tests are used to predict long term leaching behavior of the samples since they are based on the assumption that the sample will reach equilibrium conditions within its short testing period (Kalbe et al. 2008). To achieve this equilibrium in a short time, the sample mixed with leaching solution is subjected to rigorous agitation throughout the testing period to ensure constant contact, which enhances mobilization of contaminants (Kalbe et al. 2008, Kim 2002, Krüger et al. 2012, Siddique et al. 2010).

According to Jackson et al. (1984) the biggest advantages of single extraction leaching tests are its greater reproducibility and their simplistic design. Their short testing period, in addition to the above mentioned advantages, makes them most suitable for compliance testing.

Some of the commonly employed single extraction tests include toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) and standard test method for shake extraction of solid waste with water (ASTM D3987). While TCLP and SPLP are regulatory methods, ASTM D3987 is a standard method (Siddique et al. 2010).

TCLP is the only leaching test defined by US Environmental Protection Agency (USEPA) to classify a waste as hazardous or non-hazardous as per the toxicity characteristics defined in federal regulations 40 CFR 261.24. It has been designed to simulate leaching behavior of waste co-disposed in MSW landfills with other municipal refuse. To achieve this, the extraction fluid consists of acetic acid/acetate, which has been found in MSW landfill leachates (Hooper et al. 1998). SPLP has been designed to simulate the leaching behavior of a waste in contact with acid rain resulting from air-borne nitric and sulfuric oxides (WSDOE 2003). The extraction fluid used for this method is primarily distilled de-ionized water (DDI), which is slightly acidified using a mixture of 60/40 H_2SO_4/HNO_3 (by weight). The extraction efficiency of TCLP and SPLP has been reported to be greatly influenced by the composition of its extraction fluid (Hooper et al. 1998). The ASTM method utilizes distilled water as the extraction fluid with an aim to simulate mono-disposal environments when the pH of the leachate is dictated by the buffering capacity of the waste. The use of water also ensures less bias in the extraction of some metals over others (Perkct and Webster 1981). In addition, ASTM method with distilled water has been reported to more closely resemble field conditions when compared to the more aggressive TCLP test (Baba and Kaya 2004).

Several publications have reported higher concentrations of metals being extracted by TCLP method as compared to other single extraction test and this higher extraction efficiency is attributed to the presence of acetic acid/acetate (Chang et al. 2001, Hooper et al. 1998, Siddique et al. 2010). The extraction power of SPLP has been reported to be poor when compared with TCLP (Hooper et al. 1998). Siddique et al. (2010) compared the leaching behavior of waste foundry sand through TCLP, SPLP and ASTM (D3984) methods and observed that the highest amounts of metals were extracted by TCLP method. As discussed above, this can be attributed to the extremely acidic leaching solution employed.

As per the TCLP standard, the pH of the leaching solution depends on the pH of the sample. If the pH of the sample is greater than 5.0, the leaching solution is of pH 2.88±0.05 and contains acetic acid; if the pH of the sample is less than 5.0, the leaching solution is of pH 4.9±0.05 and contains acetic acid and 1.0N sodium hydroxide (NaOH). In SPLP, the pH of the leaching solution is determined based on the geographic location of the disposal site. For east of the Mississippi River, a pH of 4.2 is recommended, and west of the Mississippi River a pH of 5.0 is recommended.

The drawback of single extraction leaching tests is that they do not provide information regarding the leaching behavior of the material over different time intervals. Also, TCLP and SPLP provide information only for a single environmental condition (i.e., acidic leachate, acid rain) (Kosson et al. 1996). However, the ASTM method D3987, due to the use of distilled water as leaching solution, allows the waste to define the final leachate pH, which is influenced by the buffering capacity of the waste material (WSDOE 2003).

The procedures for the three tests are similar in terms of agitation/equilibration period (18 h) and L/S ratio (20:1 v/w); the major difference between these tests is the type of leaching solution used (also referred to as extraction fluid).

A single extraction test was developed for this study that resembles the TCLP, SPLP and ASTM D3987 methods in terms of their agitation period, L/S ratio and leaching solution. The procedure was performed as defined by the ASTM method, D3987, with modifications mainly made in terms of sample preparation and agitation technique used.

2.8.3 Multiple Extraction Leaching Tests

In dynamic tests, or multiple extraction tests, the leaching solution is continuously or intermittently renewed over a specified period of time to eliminate the effect of ionic strength of the leachate on solubility (Kim 2002, Krüger et al. 2012, Lewin 1996). The analysis of leachates collected during different replenishment periods provides information about the kinetics that govern the mobilization of the contaminants and models the long-term exposure of the waste to leaching solution (WSDOE 2003). These tests are conducted over a longer time than single extraction leaching tests and typically are not subject to agitation.

Dynamic tests are further classified into three primary types: serial batch test, flow-through test, and flow around test (WSDOE 2003).

Serial Batch Test

The major difference between serial and single batch tests is the renewal of leaching solutions at specified intervals throughout the testing period. Some of the serial batch tests include: EPA’s Multiple Extraction Procedure (MEP) and ASTM D5284: Standard test method for sequential batch extraction of waste with acidic extraction fluid (Kim 2002).

Flow-through Column Test:

Flow-through column tests are primarily designed for porous granular material or materials through which groundwater can be expected to flow through in a disposal environment. This test is known to simulate actual field conditions more realistically than single extraction tests and most other laboratory leaching tests (Jackson et al. 1984, Kalbe et al. 2008). The method involves placing the sample material in a column and adding the leaching solution either from the top of the column and allowing it to drain down through the sample, or by forcing it up from the bottom of the column, thereby simulating the flow of percolating groundwater (Kim 2002). These tests may also include wet and dry cycles, i.e. periods of saturation with a leaching solution followed by the introduction of air, for enhancing the weathering of the waste material.

The leaching process occurs due to the downward flow of the leaching solution through the porous matrix of the sample, which carries away the readily soluble fraction of the contaminants thereby causing a concentration gradient. However, replenishment of the leaching solution re-establishes equilibrium by further releasing the soluble components of the waste (Poon and Chen 1999). The continued replenishment of the leaching solution may affect the dissolution of the rather stable components and cause their release from the sample.

Leaching impermeable wastes and fine grained solids using column tests has been reported to be difficult (Bradham and Caruccio 1990, Jackson et al. 1984). Issues commonly associated with fine grained solids in column tests are: high specific retention of leaching solution, channeling, air locks, preferential flow, compaction, and slacking.

Some of the flow-through column tests are: USEPA Method 1627: Kinetic test method for the prediction of mine drainage, ASTM D 4874: standard test method for leaching solid waste in a column apparatus, and NEN 7343: Column test, developed by a national Dutch standardization organization (NEN). A significant difference was observed among column test procedures in terms of volume of water to solid ratio, replenishment periods, column dimensions, sample preparation, wet/dry cycles, and gas composition.

Flow-around Test

Flow-around leaching test simulates a landfill environment in which the leachate, due to the low permeability of the waste, will tend to flow around the waste instead of flowing through it (Poon and Chen 1999, van der Sloot 1990). To simulate this, the sample material is immersed in the leaching solution, which is replenished at specified intervals of time. The immersed sample is not subject to any agitation and the leaching takes place due to the flow of the leaching solution around it. Diffusion is reported to be the primary mechanism responsible for leaching from the low-permeability waste (van der Sloot 1990). The contaminants would diffuse through the pores of the low-permeability waste due to the concentration gradient resulting from the flow of the leaching solution around the waste which would wash away the mobile fraction of the contaminants from the surface (Poon and Chen 1999).

Flow around tests are typically designed for monolithic materials and compacted granular materials whose surface area can be measured. The ability to determine the surface area of the waste enables modelling the long term release of contaminants from these wastes using certain complex models. Flow-around tests are also referred to as ‘Tank test’, ‘Diffusion test’ and ‘Immersion test’.

Flow-around tests have been reported to be more suitable for solidified and stabilized (S/S) wastes for determining their long term behavior, since the major mechanism for release of metals from S/S wastes is reportedly diffusion (van der Sloot 1990).

Examples of the flow-around leaching tests are: Dutch leaching characterization standard, EA NEN 7375:2004, and EPA Method 1315, also referred to as a semi-dynamic tank leaching procedure.

2.8.4 Factors Influencing Leaching

According to Kalbe et al. (2008), the leachability of wastes is influenced by physical parameters such as homogeneity, particle size, porosity, permeability of the solid phase influencing the flow rate and contact time between solution and solid, and temperature. In addition to these, other parameters such as pH value, redox conditions, total organic carbon (TOC) content, chemical reaction kinetics, chemical speciation of contaminants, complexation with other constituents and biological activity have also been reported to greatly influence the leaching behavior of wastes (Kalbe et al. 2008). Some of these parameters are typically controlled in the leaching tests by the following factors: pH of leaching solution/extraction fluid, agitation, leaching period, liquid to solid ratio (L/S), and particle size of the sample.

The pH of leaching solution has been specified by several authors to be the most critical parameter determining the solubility of metals (Fällman and Aurell 1996, Mahmoudkhani et al. 2008, Quevauviller et al. 1996, Rigol et al. 2009, van der Sloot 1990, van der Sloot 1998). pH in the acidic range has been reported to cause minimum extraction of most inorganic elements; however, certain metals, such as oxyanions (i.e. Mo, As, Sb, etc,) exhibit maximum leachability at a pH range of 7-10 (Lewin 1996, Perkct and Webster 1981, van der Sloot 1990). Thus, acidic leaching solutions in leaching tests are commonly employed to simulate a “worst case scenario”. Fällman and Aurell (1996) recommended that the pH to be employed in the leaching test should depend on the type of waste and the disposal technique the waste is subjected to.

In addition to the leaching solution chemistry, the duration of the test and frequency of renewing the leaching solution, also impacts the amount of elements extracted. According to Kylefors et al. (2003), the long duration of experiments enable chemical equilibrium to occur and also allows biological reactions to take place.

According to Fällman and Aurell (1996), the L/S ratio (i.e., the amount of water in contact with the sample), particle size and agitation impacts the rate at which chemical equilibrium is obtained. Lower water volume, smaller particle size and agitation of the sample have been associated with assisting in reaching equilibrium at a faster rate. Grinding the sample to extremely small particles has been reported to maximize leachability due to the larger surface area exposed and the shorter diffusion path (Fällman and Aurell 1996, Kylefors et al. 2003, Lewin 1996). Kylefors et al. (2003) further emphasized that sample preparation, which involves steps like grinding, crushing, drying, is a critical step since it can greatly influence the size of the particles.

The contribution of several of these parameters results in the extraction of metals from the sample upon contacting a leaching solution. Most of these parameters are typically included in the design of a leaching test to simulate various leaching mechanisms; however, not all of these parameters can be included in a single test in a practical and feasible manner. Thus, the samples in this study were subjected to more than one leaching test designed with different parameters discussed above, and several leaching solutions/extraction fluid to observe their influence on the leachability of the residual solids.

2.8.5 Comparison of Leaching Tests

The comparison of various leaching procedures for evaluating the amounts of heavy metals extracted from different environmental samples and impact of different factors influencing leachability have been studied by several investigators (Chang et al. 2001, Hooper et al. 1998, Jackson et al. 1984, Kalbe et al. 2008, Krüger et al. 2012, Kylefors et al. 2003, Mahmoudkhani et al. 2008, Rigol et al. 2009, Siddique et al. 2010).

According to van der Sloot (1998), more than one leaching test should be utilized in studying the leaching behavior of a waste, since the tests provide “insight into how factors influence release and how these in turn can be used to control release.”

According to Fällman and Aurell (1996), in comparing various leaching tests, it is important that -equilibrium-like conditions are attained during the leaching period. In single extraction tests, though characterized by a higher L/S ratio, samples are subjected to agitation to increases the rate of leaching for attaining equilibrium within the shorter test duration. In addition to this, using smaller particle sizes of the sample can further assist in reaching chemical equilibrium within a short time (Fällman and Aurell 1996). In multiple extraction tests, though no agitation is employed, the lower water volume employed, the longer test duration and multiple renewal of leaching solution is expected to assist in reaching equilibrium.

By subjecting the sample to different leaching experiments and leaching solutions, it is possible to gather information on the total amount of contaminants that can be released in leaching processes under various environmental conditions, the release of the contaminants over time and impact of pH and other parameters on the leaching process.

2.9 REFERENCES

ASTM Standard D3987, 2012, "Standard Practice for Shake Extraction of Solid Waste with Water", ASTM International, West Conshohocken, PA, 2012, 10.1520/D3987-12, http://www.astm.org/

Baba, A. and Kaya, A., Leaching characteristics of solid wastes from thermal power plants of western turkey and comparison of toxicity methodologies. *J Environ Manage* **2004,** *73*, (3), 199-207.

Balaba, R.S. and Smart, R.B., Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater. *Chemosphere* **2012,** *89*, (11), 1437-1442.

Bank, T.L., "Trace Metal Chemistry and Mobility in the Marcellus Shale". Paper Presented at the Technical Workshops for the Hydraulic Fracturing Study, February 24-25, 2011.

Barry, B. and Klima, M.S., Characterization of Marcellus Shale natural gas well drill cuttings. *Journal of Unconventional Oil and Gas Resources* **2013,** *1–2*, (0), 9-17.

Begos, K., (2012), Marcellus Shale becoming top US natural gas field, *Associated Press (AP)*, Yahoo! Finance, Retrieved from http://finance.yahoo.com/news/marcellus-shale-becoming-top-us-162527250.html

Blauch, M., Myers, R., Moore, T. and Lipinski, B., "Where is All the Salt Coming from and What are the Implications?". Paper Presented at the SPE Eastern Regional meeting, Charleston, WV, 23-25 September, 2009.

Bradham, W.S. and Caruccio, F.T., "A Comparative Study Of Tailings Analysis Using Acid/Base Accounting, Cells, Columns And Soxhlets". Paper Presented at the Mining and Reclamation Conference and Exhibition, Charleston, WV, April 23-26, 1990.

Chang, E.E., Chiang, P.C., Lu, P.H. and Ko, Y.W., Comparisons of metal leachability for various wastes by extraction and leaching methods. *Chemosphere* **2001,** *45*, (1), 91-99.

Clean Earth, "Clean Earth of Williamsport, PA". Accessed on April 15, 2014 from http://www.cleanearthinc.com/Locations/Williamsport-PA

Countess, S.J. (2014) Evaluating Leachability of Residual Solids from Hydraulic Fracturing in the Marcellus Shale, Virginia Polytechnic Institute and State University, Blacksburg, VA.

Engelder, T. and Lash, G.G., (2008), Marcellus Shale Play's Vast Resource Potential Creating Stir in Appalachia, *The American Oil & Gas Reporter*, 52, The American Oil & Gas Reporter, Retrieved from http://www.aogr.com/magazine/cover-story/marcellus-shale-plays-vast-resource-potential-creating-stir-in-appalachia

Evans, J.S. and Kiesecker, J.M., Shale Gas, Wind and Water: Assessing the Potential Cumulative Impacts of Energy Development on Ecosystem Services within the Marcellus Play. *PLoS One* **2014,** *9*, (2), e89210.

Fällman, A.M. and Aurell, B., Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. *Science of The Total Environment* **1996,** *178*, (1–3), 71-84.

Gaudlip, A.W., Paugh, L.O. and Hayes, T.D., "Marcellus Shale Water Management Challenges in Pennsylvania". Paper Presented at the SPE Shale Gas Production Conference, Fort Worth, Texas, U.S.A., 16–18 November, 2008.

Gregory, K.B., Vidic, R.D. and Dzombak, D.A., Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements* **2011,** *7*, (3), 181-186.

Groundwater Protection Council (GWPC) and ALL Consulting (2009) *Modern Shale Gas Development in the United States: A Primer*, DE-FG26-04NT15455. http://energy.gov/sites/prod/files/2013/03/f0/ShaleGasPrimer_Online_4-2009.pdf

Haluszczak, L.O., Rose, A.W. and Kump, L.R., Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* **2013,** *28*, (0), 55-61.

Hammer, R. and VanBriesen, J. (2012) *In Fracking's Wake: New Rules are Needed to Protect Our Health and Environment from Contaminated Wastewater*, D:12-05-A. http://www.nrdc.org/energy/files/fracking-wastewater-fullreport.pdf

Hansen, J.B., Holm, P.E., Hansen, E.A. and Hjelmar, O. (2000) *Nordtest Technical Report 473: Use of lysimeters for characterisation of leaching from soil and mainly inorganic waste materials*. http://www.nordtest.info/index.php/technical-reports/item/use-of-lysimeters-for-characterisation-of-leaching-from-soil-and-mainly-inorganic-waste-materials-nt-tr-473.html

Hayes, T. (2009) *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*, Marcellus Shale Coalition. http://energyindepth.org/wp-content/uploads/marcellus/2012/11/MSCommission-Report.pdf

Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., DeGuzman, M., Odion, Z., Ilejay, Z., Sy, F., Petreas, M. and Simmons, B., Toxicity Characteristic Leaching Procedure Fails To Extract Oxoanion-Forming Elements That Are Extracted by Municipal Solid Waste Leachates. *Environmental Science & Technology* **1998,** *32*, (23), 3825-3830.

Jackson, D.R., Garrett, B.C. and Bishop, T.A., Comparison of batch and column methods for assessing leachability of hazardous waste. *Environmental Science & Technology* **1984,** *18,* (9), 668-673.

Jiang, Q., Rentschler, J., Perrone, R. and Liu, K., Application of ceramic membrane and ion-exchange for the treatment of the flowback water from Marcellus shale gas production. *Journal of Membrane Science* **2013,** *431*, 55-61.

Kalbe, U., Berger, W., Eckardt, J. and Simon, F.-G., Evaluation of leaching and extraction procedures for soil and waste. *Waste Manag* **2008,** *28*, (6), 1027-1038.

Kargbo, D.M., Wilhelm, R.G. and Campbell, D.J., Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environmental Science & Technology* **2010,** *44*, (15), 5679-5684.

Kim, A.G., "CCB Leaching summary: Survey of Methods and Results". Paper Presented at the Proceedings of Coal Combustion By-Products and Western Coal Mines: A Technical Interactive Forum, Allton, IL, 2002.

Kosson, D.S., van der Sloot, H.A. and Eighmy, T.T., An approach for estimation of contaminant release during utilization and disposal of municipal waste combustion residues. *Journal of Hazardous Materials* **1996,** *47*, (1–3), 43-75.

Krüger, O., Kalbe, U., Berger, W., Simon, F.G. and Meza, S.L., Leaching experiments on the release of heavy metals and PAH from soil and waste materials. *Journal of Hazardous Materials* **2012,** *207–208*, (0), 51-55.

Kylefors, K., Andreas, L. and Lagerkvist, A., A comparison of small-scale, pilot-scale and large-scale tests for predicting leaching behaviour of landfilled wastes. *Waste Manag* **2003,** *23*, (1), 45-59.

Lewin, K., Leaching tests for waste compliance and characterisation: recent practical experiences. *Science of The Total Environment* **1996,** *178*, (1–3), 85-94.

Liermann, L.J., Mathur, R., Wasylenki, L.E., Nuester, J., Anbar, A.D. and Brantley, S.L., Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. *Chemical Geology* **2011,** *281*, (3–4), 167-180.

Mahmoudkhani, M., Wilewska-Bien, M., Steenari, B.-M. and Theliander, H., Evaluating two test methods used for characterizing leaching properties. *Waste Manag* **2008,** *28*, (1), 133-141.

Maloney, K.O. and Yoxtheimer, D.A., Production and Disposal of Waste Materials from Gas and Oil Extraction from the Marcellus Shale Play in Pennsylvania. *Environmental Practice* **2012,** *14*, 278-287.

New York State Water Resources Institute (NYS WRI), (2012), Waste Management of Cuttings, Drilling Fluids, Hydrofrack Water and Produced Water, *Gas Wells*, New York State Water Resources Institute Retrieved from http://wri.eas.cornell.edu/aboutus.html

NYSDEC (2011) *Revised Draft Supplemental Generic Environmental Impact Statement On The Oil, Gas and Solution Mining Regulatory Program*. http://www.dec.ny.gov/energy/75370.html

Ohio EPA, (2014), Fact Sheet: Drill Cuttings from Oil and Gas Exploration in the Marcellus and Utica Shale Regions of Ohio, Ohio Environmental Protection Agency (EPA), Retrieved from http://epa.ohio.gov/Portals/34/document/fact_sheets/Fact%20Sheet%20on%20Drilling%20Muds%20and%20Cuttings%20Final%2010-01-13.pdf

Pennsylvania Department of Environmental Protection (PADEP), (2010), Hydraulic Fracturing Overview, Retrieved from http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/MarcellusShale/DEP%20Fracing%20overview.pdf

Perkct, C.L. and Webster, W.C. (1981) Literature Review of Batch Laboratory Leaching and Extraction Procedures. Conway, R.A. and Malioy, B.C. (eds), pp. 7-27, American Society for Testing and Materials.

Poon, C.S. and Chen, Z.Q., Comparison of the characteristics of flow-through and flow-around leaching tests of Solidified heavy metal wastes. *Chemosphere* **1999,** *38*, (3), 663-680.

Pritz, M.E. and Kirby, C.S., "Geochemical Investigation Of Marcellus Shale Natural Gas Hydrofracturing Waters". Paper Presented at the Northeastern Section (45th Annual) and Southeastern Section (59th Annual) Joint Meeting, Baltimore, MD, 13-16 March, 2010.

ProChem Tech, (2009), Marcellus Gas Well Hydrofracture Wastewater Disposal by Recycle Treatment Process, ProChemTech International Inc., Retrieved from http://prochemtech.com/Literature/TAB/PDF_TAB_Marcellus_Hydrofracture_Disposal_by_Recycle_1009.pdf

Quevauviller, P., van der Sloot, H.A., Ure, A., Muntau, H., Gomez, A. and Rauret, G., Conclusions of the workshop: harmonization of leaching/extraction tests for environmental risk assessment. *Science of The Total Environment* **1996,** *178*, (1–3), 133-139.

Rahm, B.G., Bates, J.T., Bertoia, L.R., Galford, A.E., Yoxtheimer, D.A. and Riha, S.J., Wastewater management and Marcellus Shale gas development: trends, drivers, and planning implications. *J Environ Manage* **2013,** *120*, 105-113.

Resnikoff, M., Alexandrova, E. and Travers, J. (2010) *Radioactivity in Marcellus Shale*, Radioactive Waste Management Associates. http://energy.wilkes.edu/PDFFiles/Library/Marcellus%20Shale%20Radioactivity%20Report%205-18-2010.pdf

Rigol, A., Mateu, J., González-Núñez, R., Rauret, G. and Vidal, M., pHstat vs. single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples. *Analytica Chimica Acta* **2009,** *632*, (1), 69-79.

Roche, M., "Fracking concerns: Will Ohio start accepting drilling brine at 40 landfills?". Accessed on May 20, 2014 from http://www.norwalkreflector.com/article/2074481

Schlumberger, (1994), Designing and Managing Drilling Fluid, *Oilfield Review*, 6, Schlumberger, Retrieved from http://www.slb.com/~/media/Files/resources/oilfield_review/ors94/0494/p33_43.ashx

Siddique, R., Kaur, G. and Rajor, A., Waste foundry sand and its leachate characteristics. *Resources, Conservation and Recycling* **2010,** *54*, (12), 1027-1036.

Skalak, K.J., Engle, M.A., Rowan, E.L., Jolly, G.D., Conko, K.M., Benthem, A.J. and Kraemer, T.F., Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments. *International Journal of Coal Geology* **2014,** *126*, (0), 162-170.

US Energy Information Administration (EIA) and Advanced Resources International Inc (ARI) (2013b) *Technically Recoverable Shale Gas and Shale Oil Resources: An Assessment of 137 Shale Formations in 41 Countries Outside the United States*. http://www.adv-res.com/pdf/A_EIA_ARI_2013%20World%20Shale%20Gas%20and%20Shale%20Oil%20Resource%20Assessment.pdf

Method 1311: Toxicity Characteristic Leaching Procedure (TCLP), SW846: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, (1992), USEPA.

Method 1312: Synthetic Precipitation Leaching Procedure, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), (1994), USEPA.

Guidelines Establishing Test Procedures For The Analysis Of Pollutants, 40 CFR 136 Appendix B: Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11, (1997), US Environmental Protection Agency (USEPA).

USEPA (2002) *Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations*, EPA530-K-01-004, US Environmental Protection Agency,. http://www.epa.gov/epawaste/nonhaz/industrial/special/oil/oil-gas.pdf

van der Sloot, H.A., Leaching Behaviour of Waste and Stabilized Waste Materials; Characterization for Environmental Assessment Purposes. *Waste Management & Research* **1990,** *8*, (1), 215-228.

van der Sloot, H.A., Quick techniques for evaluating the leaching properties of waste materials: their relation to decisions on utilization and disposal. *TrAC Trends in Analytical Chemistry* **1998,** *17*, (5), 298-310.

Wang, Z. and Krupnick, A. (2013) *A Retrospective Review of Shale Gas Development in the United States: What Led to the Boom?*, RFF DP 13-12.

Washington State Department of Ecology (WSDOE) (2003) *An Assessment of Laboratory Leaching Tests for Predicting the Impacts of Fill Material on Ground Water and Surface Water Quality*, 03-09-107. https://fortress.wa.gov/ecy/publications/publications/0309107.pdf

CHAPTER 3: EVALUATING LEACHING BEHAVIOR OF RESIDUAL SOLIDS FROM UNCONVENTIONAL SHALE GAS PRODUCTION OPERATIONS USING SINGLE EXTRACTION LEACHING TEST

ABSTRACT

The objective of this study was to evaluate the leaching behavior of residual solids from unconventional shale gas production operations in Marcellus shale, when deposited in typical disposal environments. To achieve this objective, a static, single-extraction laboratory leaching test was used. The representative residual solid samples used in this study were drilling mud and three different types of produced water treatment by-products: raw solids (RS) generated through liquid-solid separation by gravity of produced water prior to chemical treatment; sludge generated due to physicochemical treatment (TS) of the produced water; and all the residual solids, including drilling mud, that was solidified (SS) with cement kiln dust (CKD) for disposal in a landfill. Distilled de-ionized water (EF DDI), synthetic acid rain (pH ~ 4.2; EF 4.2), weak acetic acid (pH ~ 2.88; EF 2.9), and synthetic landfill leachate (pH 4.55; EF SLL) were used as leaching solutions to mimic specific disposal environments.

Alkali metals (Li, K, Na), alkaline earth metals (Ba, Ca, Mg, Sr) and a halide (Br), which are typically associated with Marcellus shale and produced waters, leached at high concentrations from most of the residual solids sample. The SS sample, due to its stabilization with CKD, had a lower extraction efficiency as compared to the unconsolidated TS and RS samples. In EF 2.9 and EF SLL, the leaching took place under acidic conditions, while for EF DDI and EF 4.2, the leaching occurred in alkaline conditions. The amount of inorganic elements extracted by these leaching solutions followed the order: EF 2.9 ~ EF SLL > EF 4.2 ~ EF DDI. EF 2.9 and EF SLL were determined to be the most aggressive leaching solutions, causing the maximum solubility of most inorganic elements.

3.1 INTRODUCTION

Innovations in directional well drilling (i.e., horizontal drilling) and artificial reservoir stimulation techniques (i.e., high volume, slick-water hydraulic fracturing) over the past decade, have enabled the energy industry in the United States to recover and produce economical amounts of natural gas from unconventional shale reservoirs. This has resulted in increased drilling activity in the various shale reservoirs in the U.S. However, several environmental concerns are associated with this otherwise, economically desirable industry. Understanding and mitigating the adverse impacts are among the major challenges for the shale gas industry. In addition to water quantity and quality issues, management of residual solids due to drilling and fracturing operations is a growing concern (Hammer and VanBriesen 2012, Liroff 2011, Maloney and Yoxtheimer 2012).

This research focused on the residual solids generated during unconventional shale gas production operations in the Marcellus shale area, with an aim to improve our understanding of how these wastes should be managed.

3.1.1 Residual Solids

Residual solids from unconventional shale gas production operations are generated during drilling operations and as by-products of produced water treatment. The major types of residual solids are: (1) Drill cuttings: fragments of rock and soil resulting from a drill bit grinding the rock for drilling a borehole into the earth; (2) Drilling mud: dense clay-rich slurries used for lifting and circulating the drill cuttings to the surface for removal; and, (3) Produced water treatment by-products: residual solids or sludges generated from treatment of the high volume of wastewater resulting from hydraulic fracturing operations (Hammer and VanBriesen 2012, Kargbo et al. 2010, Maloney and Yoxtheimer 2012, New York State Water Resources Institute (NYS WRI) 2012, USEPA 2002). In addition to these residuals, other potential residual solids include tank bottoms, pit sludges, basic sediment, flowback fracturing sand, spent filter, and filter media (Maloney and Yoxtheimer 2012, USEPA 2002). In the recent years, produced water has been reported to be mixed with solidifying agents such as cement kiln dust, for solidification and stabilization purposes for direct disposal of produced water in landfills (Roche 2013). The large quantity of sludge that may be generated due to these operations can also be classified as residual solids. This work, however, was limited to studying the two major types of residual solids, the by-products of treating produced water, and drilling mud.

Drilling mud (also known as drilling fluid), depending on the base fluid, can either be classified as water-based, oil-based (containing petroleum products or mineral oil), or synthetic-based (Schlumberger 1994). The basic ingredients of drilling mud consists of, water, heavy minerals (such as barite), clays (most commonly bentonite) or organic colloids (such as biopolymers), polymers, a stabilizing organic material (such as lignosulfonate or lignite), surfactants, inorganic chemicals (such as sodium hydroxide, potassium hydroxide, or calcium hydroxide) and certain specialized chemicals (Schlumberger 1994). The drilling mud mixes with the drill cuttings and the formation water during their circulation to the well surface and thus contaminants that are typically associated with the geological formations can be expected to dissolve or be adsorbed by the drilling muds (NYS WRI 2012, Resnikoff et al. 2010, Schlumberger 1994). Drilling muds are reused to facilitate the drilling process after separating them from the drill cuttings (NYS WRI 2012). This can result in an increase in the concentration of contaminants after each use.

The treatment of high volumes of wastewater from hydraulic fracturing operations, also referred to as produced water, results in the generation of residual solids. On-site treatment of produced water includes storage in open-pits or impoundments for evaporation, aeration, settling, and perhaps filtration. The waste that settles at the bottom of these pits after the treatment process can be classified as residual solids, which are commonly disposed of as solid waste (Kargbo et al. 2010). Off-site treatment of the produced wastewaters is commonly performed in approved, industrial wastewater treatment facilities, also called centralized waste treatment facilities (CWTs). CWTs are equipped with physiochemical treatment units, such as coagulation, precipitation, flocculation, centrifugation, settling and filtration, to primarily reduce the high TDS and metal concentrations along with organic contaminants to ensure the produced wastewater is clean enough for reuse (Hammer and VanBriesen 2012). Coagulation and precipitation operations involve pH adjustment, addition of chemical precipitant, and flocculation. Through these operations the soluble salts are converted into insoluble salts that precipitate and are then separated from the treated water by physical methods (e.g., settling and/or filtration). The precipitate-containing contaminants removed from the produced wastewater, and chemical treatment residuals, are also classified as residual solids. These residual solids will contain the contaminants at concentrations higher than the original produced water, thereby making its proper management all the more important (Hammer and VanBriesen 2012).

3.1.2 Residual Solids Inorganic Composition

A gap exists in our understanding of the exact inorganic composition of various residual solids from unconventional shale gas operations. Few publications were found that extensively discussed the chemistry of various residual solids from unconventional shale gas operations in the Marcellus Shale area. The available literature focuses mostly on drill cuttings.

The drilling mud and produced water are expected to mimic the formation chemistry due to their long contact time with the geological formation and its contained brine water (Bank 2011, Blauch et al. 2009, Haluszczak et al. 2013, Resnikoff et al. 2010, Schlumberger 1994, Skalak et al. 2014). The by-products of treating produced water mainly consist of precipitates containing contaminants removed from the produced wastewater and treatment chemical residuals, at concentrations higher than in the original produced water (Hammer and VanBriesen 2012). Thus, the elements commonly associated with produced water will be mostly present in the by-products from its treatment.

The elements commonly associated with Marcellus shale formation and the produced water from Marcellus shale includes: aluminum, barium, boron, calcium, chloride, iron, lithium, magnesium, manganese, potassium, sodium, silicon, strontium, and sulfate; along with trace levels of toxic inorganic constituents such as antimony, arsenic, chromium, cobalt, copper, nickel, zinc, cadmium, lead, molybdenum, mercury, selenium, uranium, vanadium and zinc (Balaba and Smart 2012, Bank 2011, Blauch et al. 2009, Evans and Kiesecker 2014, Gaudlip et al. 2008, Hayes 2009, Liermann et al. 2011, Pritz and Kirby 2010, ProChem Tech 2009). Of these elements, the produced water from Marcellus shale are reported to be typically enriched with alkaline earth elements (Ca, Sr, Ba), alkali elements (Na, K, Li) and halides (Cl, Br) (Haluszczak et al. 2013, Hayes 2009).

The composition of produced water can also be influenced by the chemical additives used in slick-water (Balaba and Smart 2012). Thus, zirconium, which has been reported to be used as metal additive in the slick-water for crosslinking purposes, can be expected to be present in produced waters. Elements such as beryllium and silver, while not typically reported in produced waters from Marcellus shale, have been considered for analysis in produced water in various studies and are typically associated with oil and gas production wastewaters.

3.1.3 Residual Solids Waste Regulation and Management

The Resource Conservation and Recovery Act (RCRA) explicitly excludes drill cuttings, drilling fluids, produced waters, produced water treatment by-products, and other wastes associated with oil and gas exploration and production (E&P wastes) from regulation as hazardous wastes (USEPA 2002). However, management of these wastes is generally required to comply with the non-hazardous waste regulation under RCRA Subtitle D. In addition, E&P wastes are to be managed in accordance with state requirements and federal laws, other than RCRA, that apply to the disposal of wastes.

Thus, the exempt residual solids from unconventional shale gas production operations are commonly considered solid waste and are directly disposed in approved Municipal Solid Waste (MSW) landfills. Disposal of some residual solids in deep injection wells is also reported (Hammer and VanBriesen 2012, NYS WRI 2012).

The classification of residual solids as being hazardous or non-hazardous determines the type of landfill facility that can be used. Toxic materials may leach from decomposing residual solids when they come in contact with leachates commonly found in municipal landfills. Release of these toxic leachates from landfill facilities to groundwater and surface water sources can significantly impact the environment and public health. In addition, wastewater treatment plants receiving these leachates from MSW landfills may not be designed to handle them. Due to these concerns, the residual solids may require pretreatment before their disposal, or an alternative disposal method may need to be implemented. Thus, characterization of the wastes is critical to ensure that they are handled accordingly for the sustainable development of the shale gas industry.

3.1.4 Project Objective

The primary goal of this study was to evaluate the leaching behavior of heavy metals and other elements of concern (EOC) from the residual solids which are generated from unconventional shale gas production operations in Marcellus shale. The aim was to better understand the leaching behavior of the residual solids in their typical disposal environments.

3.1.5 Laboratory Leaching Test

Laboratory leaching experiments are performed for discerning the potential for dissolution and mobility of certain elements of concern from waste samples. The tests are typically performed to evaluate the leaching behavior of a waste in a short span of time under controlled conditions. Laboratory leaching tests are performed under the assumption that the leaching solution and other set of conditions are representative of a typical disposal environment. Various physical, chemical and biological factors that influence the release of contaminants from wastes can be controlled in laboratory leaching tests and thus specific conditions mimicking disposal environments can be simulated.

In this study, single extraction leaching tests were employed due to their simplistic design and greater reproducibility (Jackson et al. 1984). Their short testing period, in addition to the above mentioned advantages, makes them most suitable for compliance testing.

Single extraction tests are used to predict long term leaching behavior of the samples since they are based on the assumption that the sample will reach equilibrium conditions within its short testing period (Kalbe et al. 2008). To achieve this equilibrium in a short time, the sample mixed with leaching solution is subjected to rigorous agitation throughout the testing period to ensure constant contact, which enhances mobilization of contaminants (Kalbe et al. 2008, Kim 2002, Krüger et al. 2012, Siddique et al. 2010).

Some of the commonly employed single extraction tests include toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP) and standard test method for shake extraction of solid waste with water (ASTM D3987). While TCLP and SPLP are regulatory methods, ASTM D3987 is a standard method (Siddique et al. 2010). TCLP is the only leaching test defined by US Environmental Protection Agency (USEPA) to classify a waste as hazardous or non-hazardous as per the toxicity characteristics defined in federal regulations 40 CFR 261.24. The procedures for the three tests are similar in terms of agitation/equilibration period (18 h) and L/S ratio (20:1 v/w); the major difference between these tests is the type of leaching solution used (also referred to as extraction fluid).

The extraction fluid of TCLP has been designed to simulate leaching behavior of waste co-disposed in MSW landfills with other municipal refuse. To achieve this, the extraction fluid consists of acetic acid/acetate, which has been found in MSW landfill leachates (Hooper et al. 1998). SPLP has been designed to simulate the leaching behavior of a waste in contact with acid rain resulting from air-borne nitric and sulfuric oxides (Washington State Department of Ecology (WSDOE) 2003). The extraction fluid used for this method is primarily distilled de-ionized water (DDI), which is slightly acidified using a mixture of 60/40 H_2SO_4/HNO_3 (by weight). The extraction efficiency of TCLP and SPLP has been reported to be greatly influenced by the composition of its extraction fluid (Hooper et al. 1998). The ASTM method utilizes distilled water as the extraction fluid with an aim to simulate mono-disposal environments when the pH of the leachate is dictated by the buffering capacity of the waste. The use of water also ensures less bias in the extraction of some metals over others (Perkct and Webster 1981). In addition, ASTM method with distilled water has been reported to more closely resemble field conditions when compared to the more aggressive TCLP test (Baba and Kaya 2004).

Several publications have reported higher concentrations of metals being extracted by TCLP method as compared to other single extraction test and this higher extraction efficiency is attributed to the presence of acetic acid/acetate (Chang et al. 2001, Hooper et al. 1998, Siddique et al. 2010). The extraction power of SPLP has been reported to be poor when compared with TCLP (Hooper et al. 1998). Siddique et al. (2010) compared the leaching behavior of waste foundry sand through TCLP, SPLP and ASTM (D3984) methods and observed that the highest amounts of metals were extracted by TCLP method. As discussed above, this can be attributed to the extremely acidic leaching solution employed.

In light of the above considerations, a single extraction test was performed that resembles the TCLP, SPLP and ASTM D3987 methods in terms of their agitation period, L/S ratio and leaching solution.

Leaching solutions were chosen in this study to assess the leaching behavior of the residual solids of concern under different environmental conditions. To simulate field conditions, artificial/chemical leachates, natural landfill leachates, natural stormwater and artificially simulated stormwater have been employed by different researchers. Among the more commonly used leaching solutions are the extraction fluids used in the toxicity characteristic leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP), as well as distilled de-ionized water (DDI). They are known to simulate, leaching conditions in a MSW landfill when co-disposed with other municipal refuse (TCLP), mono-disposal in pits or land disposal conditions (SPLP), and field conditions where the waste's buffering capacity determines the pH of the leachate (DDI). In addition to these, a synthetic landfill leachate simulating the most aggressive characteristics of municipal landfill leachate was also considered.

The procedure was performed as defined by the ASTM method, D3987, with modifications mainly made in terms of sample preparation and agitation technique used. Due to these modifications employed the results of this experiment might be different from the results obtained through strict adherence to the TCLP, SPLP and ASTM D3987 methods. For instance, changes in the orientation and/or rate of agitation can have a considerable impact on the degree of mixing and the rate at which the constituents are released (ASTM D3987 2012).

Gaps exist in our understanding of the exact composition of the residual solids from unconventional shale gas production operations. The elements of concern (EOC) in this study were selected on the basis of elements commonly associated with Marcellus shale and the produced water generated from hydraulic fracturing operations in Marcellus shale. Table 3.1 provides a list of the EOCs studied.

While chloride has been reported to be a major element in produced water from Marcellus shale, it was not considered for analysis in this study due to certain molecular interference issues with the analytical instrument.

Table 3.1: Elements of Concern (EOC) Considered for Analysis

Transition Metals	Alkaline Earth Metals	Metalloids	Alkali Metals	Other Metals	Post Transition Metals	Halogen
Cadmium	Barium	Antimony	Lithium	Phosphorus	Aluminum	Bromide
Chromium	Beryllium	Arsenic	Potassium	Selenium	Lead	
Cobalt	Calcium	Boron	Sodium	Sulfate		
Copper	Magnesium	Silicon				
Iron	Strontium					
Manganese						
Mercury						
Molybdenum						
Nickel						
Silver						
Uranium						
Vanadium						
Zinc						
Zirconium						

3.1.6 Significance

As per an analysis conducted by Maloney and Yoxtheimer (2012), the total quantity of drilling fluids generated for the year 2011 in PA was approximately 2,374,469 barrels. Based on this value, it has been further estimated that complete development of the entire Marcellus shale play will generate 1.37 x 10^8 barrels of drilling fluid. With growing concerns over water quantity issues, treatment of produced water at CWTs for re-use in drilling operations has increased in recent years. In 2011, approximately half of all wastewater produced from unconventional shale gas operations was treated at CWT facilities (Hammer and VanBriesen 2012). In 2011, 20 times more gas wells were drilled in the Marcellus shale play of PA, alone, as compared to that in 2007 (Jiang et al. 2013). This rapid development of shale gas production in the Marcellus formation is expected to be accompanied with greater volumes of produced water generated and impounded at the surface for disposal, treatment or recycle, ultimately resulting in higher volumes of sludge production.

These estimates indicate the magnitude of the wastes expected in the coming years and concern associated with their management will only increase. The results of this study will provide a comment about current management practices and enable us to better understand if any threats are being posed that can be mitigated significantly by implementing better management practices and policies for the future.

3.2 METHODS AND MATERIALS

3.2.1 Sample Sources

Samples of drilling mud and by-products of produced water treatment were collected from a CWT located in Pennsylvania. This facility only treats hydraulic fracturing wastewater and spent drilling muds from unconventional shale gas production operations, which it receives from areas in the Marcellus shale region. This facility treats the produced water by chemical precipitation, settling and pressure filtration, while the drilling mud is only thickened by gravity separation. For chemical precipitation, the facility utilizes sodium sulfate, sodium hydroxide and sodium hypochlorite to precipitate dissolved elements such as, barium, iron, and strontium. The following three different types of treatment by-products, along with drilling mud (henceforth referred to as “DM”), were collected from the facility: (1) raw solids (RS) generated through liquid-solid separation by gravity of produced water prior to chemical treatment; (2) sludge generated due to physiochemical treatment (treated solids = TS) of the produced water; and (3) all the residual solids, including DM, that are solidified with cement kiln dust (solidified solids = SS) for disposal in a landfill.

3.2.2 Sample Preparation

Collected samples were stored at room temperature in high-density polyethylene (HDPE) containers for approximately two weeks prior to sample preparation, except the RS samples, which were prepared for the experiment approximately 60 days after sample collection. The samples were sticky and difficult to manipulate.

All samples were centrifuged at approximately 2,500 RPM for 40 minutes in a Beckman TJ-6R tabletop centrifuge to extract free water. The centrifuged samples were subsequently air-dried in a fume-hood for seven days. The samples were dried to preserve them from biodegradation, oxidation, sorption, precipitation and other physical and chemical processes. The air-dried samples were hand broken into smaller fractions, homogenized, and then manually grinded into fine particles using a HDPE plastic roller. The pulverized samples were again homogenized prior to use.

The samples were air-dried for this experimental procedure since only inorganic fractions (i.e., non-volatile constituents) were of interest and for reducing the particle size for achieving equilibrium during the short duration of the test.

The solids content of the sample was determined using the procedure defined by ASTM D3987-12: Standard Practice for Shake Extraction of Solid Waste with Water. The percent solids of air-dried samples was calculated using Equation 1:

$$\text{Percent Solids (\%)} = \frac{\text{DW}}{\text{WW}} \text{ X } 100 \qquad \text{Eq. (1)}$$

Where:

DW = Sample weight (g) after oven-drying at 103-105 ^{o}C

WW = Air-dried sample weight (g) before oven-drying

The solids content of the samples is given in Table 3.2.

Table 3.2: Solids Content of Different Residual Solids

Sample Type	**Residual Solids Content (%)**
Treated Solids	81.47 ± 0.04
Raw Solids	81.8 ± 0.06
Solidified Solids	96.85 ± 0.01
Drilling Mud	91.28 ± 0.08

3.2.3 Experimental Procedure for Shake Extraction

Finely ground, air- dried samples were homogenized and weighed to 5 ± 0.1 g. Refer to Table 3.2 for the solids content of each sample which were utilized in calculating the final leachate concentrations, mg EOC/kg waste-) The weighed, air-dried samples were placed in Erlenmeyer flasks (250 mL) and filled with 100 mL of leaching solution. This leaching solution to sample volume (L/S ratio) was kept constant at 20:1 v/w in this experiment for all samples in different leaching solutions.

The Erlenmeyer flasks were then placed on a gyratory shaker table and agitated continuously for a period of 18 ± 0.25 hours in a circular motion. Figure 3.1 provides a pictorial representation of the samples being mixed with leaching solutions in the flasks on the shaker table. After settling, the bulk of the aqueous phase was separated from the solid phase by decantation. The leachates were filtered through a 0.45 µm sterile syringe filter and measured for pH and conductivity. A fraction of the filtered sample was also acidified using trace metal grade nitric acid at 2% v/v for dissolved metal analysis.

All glassware and plastic material used had been soaked in 20% reagent grade nitric acid for 24 hours, followed by multiple cycles of rinsing with distilled water and high-purity water. The leaching test was performed at room temperature of 21±2 ^{o}C. All tests were performed with triplicate.

The following four different types of leaching solutions of varying pH and composition were used (henceforth, the terms ‘leaching solution’ and ‘extraction fluid (EF)’ are used interchangeably).

1) Type I grade reagent water as defined by ASTM D1193 -06 (2011), also referred to as distilled de-ionized water (EF DDI), was utilized in this test. The pH was typically observed to be approximately 5.0±0.10 after about 20 minutes of stabilization time.

2) Acetic acid extraction fluid, as defined by the TCLP procedure, USEPA Method 1311 (EF 2.9). The pH was chosen on the basis of waste alkalinity, as defined by the TCLP method. All the samples were observed to be above a pH of 5.0, and thus, as recommended, a leaching solution of pH 2.88±0.05 was used.

3) Synthetic acid rain extraction fluid; a mixture of nitric acid and sulfuric acid, as defined by the SPLP procedure, USEPA Method 1312 (EF 4.2). As recommended by the standard procedure a pH of 4.2 was used, since the study was limited to the Marcellus shale area which is located on the east of Mississippi.

4) An aerobic modified synthetic leachate, as defined by Stanforth et al. (1979), “to model the maximum leachability of industrial waste” in a MSW landfill was also used. The pH was determined to be approximately 4.55.

The sulfuric acid and acetic acid used for preparing the leaching solutions was A.C.S reagent grade, while the nitric acid used for preparing the extraction fluids was trace metal grade.

Figure 3.1: Erlenmeyer flasks with 5 g samples and 100 ml extraction fluids placed on a shaker table

3.2.4 Analysis of Leachates

Samples were analyzed for EOC using a Thermo Electron X-Series, inductively coupled plasma-mass spectrometer (ICP-MS) per Standard Method 3125-B (American Public Health Association (APHA) et al. 2012). Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume. The nitric acid used was trace metal grade.

Prior to performing analyses with the instrument, the Method Detection Limit (MDL) and Minimum Reporting Level (MRL) for the various EOC were established. EPA defines MDL as the “minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero” (USEPA 1997). This prevents reporting of an analyte detected at very low concentrations when noise and actual analyte concentration cannot be distinguished (Carolyn J. Oblinger Childress et al. 1999). MDLs for the EOCs were determined based on a guideline defined by USEPA (USEPA 40 CFR 136 Appendix B, 1997). According to this USEPA Method, seven replicate spikes of a low-level calibration standard that is close to the expected MDL were run through the ICP MS analytical method and their standard deviation was multiplied by 3.143 (the value of ‘t’ at 99% confidence for seven samples) to determine the MDL. The Method Reporting Level (MRL) value determined was the low level calibration standard used for determining the MDL. MRL has been defined as the “smallest measured concentration of a substance that can be reliably measured by using a given analytical method” (Carolyn J. Oblinger Childress et al. 1999). MRLs were determined by using a statistical procedure defined by Winslow et al. (2006).

Concentrations below the MDL are represented by the term ‘BDL’ (Below Detection Limit). The concentration detected between the MDL and MRL indicates that while the substance is present in the sample the value is estimated. Thus, this is represented by the term ‘Trace’ in the report and in tables presenting the analytical data.

All samples were analyzed at a diluted concentration since some of the EOC concentrations were expected to be above the accurate detection range of ICP-MS. The samples were diluted to a ratio of 1:10 with distilled, de-ionized water.

Details regarding the isotopes of EOCs analyzed, analytical range, method detection limit, and minimum reporting level are provided in Appendix A.

For determining the concentration of EOCs in the sample, the instrument was calibrated for elemental concentrations the samples were expected to contain. External stock standard solutions were used. Almost all concentrations of Na, Br, Ca and Sr for all samples were measured above their maximum calibrated range. Sulfate from SS and DM samples, and Br from TS and RS samples, were also measured above the calibrated range in all leaching solutions. In addition, the following were also measured beyond their analytical range: Al - TS and RS for EF SLL; Si - TS, RS and SS in EF 2.9 and/or EF SLL, and Mg – RS in EF 2.9 and EF SLL. (Refer to Appendix B for complete results of the immersion tests in which EOCs whose concentrations were measured above the ICP-MS calibration range.)

A “dry-mass correction” was applied to all of the analytical values reported in µg/L (the results are presented as mg/kg dry weight of the sample). Analyte concentrations measured in µg/L were converted to mg/kg dry weight basis by using Equation 2:

$$\text{Sample Conc. } \left(\frac{\text{mg}}{\text{kg}}\right) \text{ (dry weight basis)} = \frac{C * V}{W} \qquad \text{Eq. (2)}$$

Where:

C = Concentration in the extract (mg/L)

V = Volume of extract (L)

W = Dry weight of sample determined using solids content (kg)

3.2.5 Quality Assurance and Quality Control

Laboratory method blanks were collected by subjecting the leaching solutions to all the steps of the leaching experiment in the exact same way as the sample, including replenishment periods, to identify any air-borne contamination or contamination that could be contributed by apparatus and reagents employed in the test. This step was essential for determining the accuracy of data, particularly for those elements detected at low levels. In addition to method blank, reagent blanks were also collected to observe specific contamination that could be linked only to the reagents used in preparing the leaching solutions. Laboratory method blanks were found to be below the detection limits for most EOCs. However, Na was detected at extremely high concentrations (336,234 ppb) in EF SLL. This is due to the sodium acetate added to the extraction fluid for its preparation. This was confirmed by the reagent blank for EF SLL which contained Na at 326,000 ppb. Similarly, higher concentrations (> 1000 ppb) of SO_4 was measured for blanks in EF 4.2 which can be attributed to the sulfuric acid used for preparing EF 4.2. Al, Ca, Cu, Mg, Zn were also measured above the MRL, but at lower concentrations (< 1000 ppb).

For concentrations detected above the MDL, blank corrections were applied to the sample by deducting the blank concentrations from the sample concentrations. Since all extractions were performed in triplicate, the results reported are an average of the three values.

3.2.6 Reproducibility

The experimental procedure described above was performed on all samples in different extraction fluids in triplicates. The relative standard deviation (RSD) of certain EOCs has been tabulated and presented in Table 3.3 and 3.4. EOCs detected below MRL in all or at least one of the replicates (with concentration of other replicates measured very close to MRL value) have not been presented or censored in Table 3.3 and 3.4.

Table 3.3: Relative Standard Deviation (RSD; %) Values for Replicates of Treated Solids and Raw Solids Leached with Different Leaching Solutions in Shake Extraction Test

EOC	**Treated Solids**				**Raw Solids**			
	EF DDI	**EF 4.2**	**EF 2.9**	**EF SLL**	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**
Li	0.95	0.97	1.13	1.27	1.26	0.48	3.38	0.30
K	0.84	0.68	1.72	1.09	0.53	0.52	2.32	0.32
Na	1.25	1.33	0.70	**6.50**	0.96	0.26	3.23	**14.51**
Ba	1.28	0.95	1.30	0.68	1.63	0.55	**7.62**	0.23
Ca	0.40	0.41	1.25	1.34	1.18	0.43	1.69	2.04
Mg	0.72	0.57	1.34	1.05	0.86	0.48	4.15	0.69
Sr	0.83	0.17	1.44	0.70	1.50	0.41	0.98	0.56
Mn	1.07	1.10	1.31	0.87	NA	**19.06**	0.41	1.01
Fe	NA	NA	4.49	0.74	NA	NA	-	0.68
Cu	**-**	7.00	**6.41**	2.26	**48.76**	2.36	**8.00**	2.60
Zn	NA	NA	1.78	0.81	NA	NA	**5.22**	0.18
Al	**12.50**	0.92	4.16	1.15	**18.07**	**26.84**	**15.94**	0.66
Pb	NA	NA	NA	0.41	NA	NA	NA	1.30
B	1.40	2.01	1.21	1.09	2.45	1.63	**6.71**	1.01
Si	**8.69**	**7.41**	2.31	0.96	1.27	0.85	0.18	0.41
S	**-**	-	NA	NA	**5.31**	**8.97**	NA	NA
Br	0.74	0.25	1.42	0.79	1.23	0.52	3.32	0.17

'NA' indicates that RSD value was not available since all replicates were measured at 'Trace' and or 'BDL' values; '-' indicates at least one of the replicates was 'BDL' or 'Trace'; **Bold** indicates RSD values greater than 5%.

Table 3.4: Relative Standard Deviation (RSD; %) Values for Replicates of Solidified Solids and Drilling Mud Leached with Different Leaching Solutions in Shake Extraction Test

EOC	**Solidified Solids**				**Drilling Mud**			
	EF DDI	**EF 4.2**	**EF 2.9**	**EF SLL**	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**
Li	NA	NA	NA	1.40	NA	NA	0.47	3.09
K	0.74	2.71	1.57	2.66	1.35	2.40	2.07	2.13
Na	3.38	3.29	3.87	**6.87**	4.78	3.40	2.32	4.64
Ba	-	-	NA	-	**7.93**	**5.35**	1.12	3.59
Ca	1.73	2.91	0.16	3.90	**9.00**	1.65	1.32	1.25
Mg	**22.06**	2.55	0.71	2.70	**7.23**	2.25	0.89	2.07
Sr	0.47	0.57	2.09	1.04	4.89	1.58	0.84	0.25
Mn	-	-	1.23	1.30	**40.11**	0.56	1.08	1.43
Fe	-	NA	NA	0.85	**18.64**	**17.30**	1.76	0.80
Cu	2.47	2.86	7.79	2.69	3.81	20.15	4.91	2.75
Zn	NA	NA	3.01	1.42	NA	NA	1.86	2.81
Al	**40.30**	**26.80**	**7.63**	0.12	**17.45**	**21.73**	0.44	2.02
Pb	NA	2.02	NA	2.48	88.12	2.63	173.21	2.29
B	2.92	3.01	1.09	3.09	NA	NA	NA	NA
Si	**6.51**	2.57	1.04	0.76	**19.42**	**16.50**	2.27	2.32
S	1.34	1.75	1.07	3.76	2.97	3.16	0.36	1.33
Br	4.74	0.49	2.05	4.85	0.26	2.18	3.64	3.58

'NA' indicates that RSD value was not available since all replicates were measured at 'Trace' and or 'BDL' values; '-' indicates at least one of the replicates was 'BDL' or 'Trace'; **Bold** indicates RSD values greater than 5%.

Overall, replication was observed to be good. RSD was observed to be typically below 5 % except for EOCs that were measured at low concentrations, close to their MRL values. However, Na was observed to have a comparatively higher RSD in all samples only for EF SLL. Also, compared to other samples, EOCs measured in DM had a greater RSD in all leaching solution.

3.2.7 Statistical Analysis

Statistical analysis was performed to determine if the amount of certain EOCs extracted from a sample by the different extraction fluids was significantly different. For this, an Analysis of Variance (ANOVA) was performed to determine if at least one of the leaching solutions extracted the EOC at a significantly different concentration than concentrations extracted by other leaching solutions. A significance level (α) of 0.05 was chosen. A p-value below this significance level would indicate that the mean of at least one of the treatments (i.e., effect of leaching solutions on EOCs) was significantly different from the others. Further, to determine which leaching solution(s) extraction efficiency was significantly different, a pair-wise comparison was performed using a Tukey's HSD (Honest Significant Difference) method for multiple pairs, and a Student's t method for a single pair.

For this statistical comparison, only EOCs that were observed to leach at concentrations greater than 10 mg/kg in at least two eluates for a sample were considered.

All the above mentioned statistical functions were performed using a statistical software JMP Pro Version 10, developed by SAS Institute.

3.3 RESULTS AND DISCUSSION

3.3.1 Conductivity and pH

Table 3.3 presents the mean value and standard deviations of the final leachate pH and specific conductivity measured in all the samples at the end of the leaching period.

The final leachate pH values for distilled de-ionized water or EF DDI were a function of the buffering capacity of the solid waste (ASTM D3987, 2012). As seen in Table 3.3, the final leachate pH values for TS, RS, SS and DM in EF DDI were measured to be 7.66, 8.19, 9.38, and 7.56, respectively. This indicates that all the wastes were alkaline in nature. SS was observed to be the most alkaline waste with the highest pH (pH=9.38). Wastes solidified with cement are highly alkaline in nature due to the presence of calcium hydroxide in the cement paste (Bishop 1988, Shively et al. 1986).

Table 3.5: Final Leachate pH and Conductivity of Samples in the Shake Extraction Test (SET)

Sample	Extraction Fluid (EF)	Leachate Final pH	Specific Conductivity @ 25 ^{O}C, mS
Treated Solids	EF DDI	7.66 ± 0.09	7,980 ± 110
	EF 4.2	7.91 ± 0.05	11,900 ± 159
	EF 2.9	5.21 ± 0.00	7,920 ± 89
	EF SLL	5.23 ± 0.01	19,200 ± 75
Raw Solids	EF DDI	8.19 ± 0.15	7,070 ± 52
	EF 4.2	8.07 ± 0.58	11,500 ± 111
	EF 2.9	5.5 ± 0.03	6,970 ± 45
	EF SLL	5.32 ± 0.01	18,800 ± 82
Solidified Solids	EF DDI	9.38 ± 0.09	7,860 ± 227
	EF 4.2	9.5 ± 0.06	12,400 ± 189
	EF 2.9	5.65 ± 0.02	7,620 ± 225
	EF SLL	5.31 ± 0.04	19,500 ± 418
Drilling Mud	EF DDI	7.56 ± 0.13	13,700 ± 546
	EF 4.2	7.88 ± 0.13	15,400 ± 265
	EF 2.9	4.34 ± 0.02	13,100 ± 400
	EF SLL	4.93 ± 0.00	22,300 ± 309

As seen in Table 3.3, the final leachate pH values observed for EF 4.2 were very close to the values observed in EF DDI for all samples. For preparing EF 4.2, distilled de-ionized water was used which had a pH in the range of 5.0-5.1. Thus, an extremely low volume (< 2 µL) of HNO_3/H_2SO_4 mixture was needed to achieve the target pH of 4.2. The composition of EF DDI and EF 4.2 were therefore expected to be similar.

The results from Table 3.3 also indicate that the final pH values determined for EF 2.9 and EF SLL for all samples were close and in the range of 5.1 – 5.7, except for DM whose pH was measured at 4.34 and 4.93 for EF 2.9 and EF SLL respectively. This difference may be due to the lower buffering capacity of the drilling mud.

From the overall observations, it can be concluded that in EF 2.9 and EF SLL leaching will occur under acidic conditions, while for EF DDI and EF 4.2, the leaching will occur mostly under neutral to alkaline conditions. One would therefore expect that higher concentrations of most metals would be leached at the lower pH levels of EF 2.9 and EF SLL.

Wastes stabilized with cement additives have been typically reported to neutralize the acidic leaching solution in short-term leaching tests, such as TCLP, resulting in leaching under alkaline conditions (Bishop 1988). However, as seen in Table 3.3, SS samples in the acidic leaching solutions (EF 2.9 and EF SLL) had a final leachate pH < 6.0. This indicates that the alkalinity due to CKD in the SS samples was depleted during the test duration, resulting in leaching under somewhat acidic conditions. The high alkalinity of the SS samples can be observed in EF DDI and EF 4.2, where high pH values (~ 9.5) were noted.

As seen in Table 3.3, the conductivity values were greater in the acidic leachate (EF SLL and EF 2.9) than in EF DDI and EF 4.2. The conductivity values for all samples in different extraction fluids followed the order: EF SLL > EF 2.9 > EF DDI ≈ EF 4.2. EF SLL was considered to represent the most aggressive leachate the waste might contact in MSW landfills (Stanforth et al. 1979). While the conductivity measured for TS, RS and SS samples for EF DDI and EF 4.2 were similar, the conductivity measured for DM in these extraction fluids was much higher. Also, while the behavior was similar, the degree of difference between the conductivity measured for different extraction fluids in DM was lower when compared to other samples.

3.3.2 Elemental Analysis

The complete results for the leaching potential of the samples in different leaching solutions are provided in Appendix B. These results have been summarized and presented in Tables 3.7 and 3.8. Figure 3.2 provides a pictorial representation of the leaching behavior of TS, RS, SS and DM samples in different leaching solution.

The data are presented in the following format:

1) The release of the EOCs from the waste is presented as milligrams of EOC / kilogram of oven-dried sample.
2) For ease in reading and considering the accuracy and precision of ICP-MS, the concentrations in Tables 3.4 and 3.5 have been rounded to two significant figures for concentrations below 10 mg/kg and three significant figures for concentrations above 10 mg/kg. In Figure 3.2, the absence of a marker for a particular element indicates that it

was either detected at trace levels, below detection limit, or below a concentration of 0.001 mg/kg.

3) The release of the EOCs from the waste is presented as micrograms of EOC / liter of leaching solution in Appendix B.

4) Concentrations in the Tables, Figures and Appendix, were mathematically adjusted by the dilution factor used (factor of 10). All extractions were performed in triplicate and the data are reported as an average value.

In the discussion that follows, word descriptors are keyed to concentrations as defined in Table 3.6.

Table 3.6: Word Descriptors for Concentration Ranges

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

As can be observed in Figure 3.2, alkali metals (Li, K and Na), alkaline earth metals (Ba, Ca, Mg and Sr) and halide (Br), commonly reported at elevated levels in Marcellus shale produced waters, leached at greater concentrations in all samples in all extraction fluids (Haluszczak et al. 2013, Hayes 2009). However, Li was mostly detected at trace levels in SS and DM samples, and Ba was detected mostly at trace levels in SS and at extremely low concentrations in DM. CKD has been commonly reported to contain high amounts of sulfate (Tarun R. Naik 2003). This may explain the low amounts of Ba measured in SS which can be attributed to the formation of the extremely insoluble barium sulfate that may form when the Ba enriched hydraulic fracturing residual solids react with sulfate enriched CKD. Barite, a mineral rich in barium sulfate, has been reported to be typically used as a weighting agent in drilling mud. This might explain the low concentration of Ba leaching from DM samples.

The very high concentrations of alkali and alkaline earth metals in the leachates from all leaching solutions can be attributed to their high solubility, and thus, their leaching is commonly attributed to surface wash-off effects and dissolution (Tiruta-Barna et al. 2004).

Si was measured at greater concentrations for RS in all leaching solutions as compared to other samples. This may be due to the presence of proppant in RS, which may have been separated from the produced water during the liquid-solid separation process at the CWT.

Alkali metals (K, Na) and the halide (Br) were extracted at similar concentrations from all samples regardless of the pH of the leaching solution, while the amounts of alkaline earth metals (Ba, Ca, Mg and Sr) extracted was dependent on the pH of the leaching solution, with greater amounts being extracted under acidic conditions (EF 2.9 and EF SLL) as compared to alkaline or neutral pH conditions (EF DDI and EF 4.2). However, concentrations of Na were less for EF SLL than in the other EFs. Na was measured at extremely high concentrations, 336,234 ppb and 326,000 ppb, in the method blank and reagent blank for EF SLL. These high concentrations can be attributed to the sodium acetate used for preparing EF SLL. Thus, due to the common-ion effect, lesser amounts may have dissolved from the samples into the leachate.

Lower concentrations of certain elements (Li, Ba, Sr, B, Br) measured in SS, which is a composite of other residual solid samples as compared to the other unconsolidated samples, can be attributed to the presence of cement matrix which has been demonstrated to effectively bind the heavy metal contaminants by chemical complexation, thereby reducing their leachability (Bishop 1988, van der Sloot 1990). The SS sample was therefore more stable.

Overall, for the relatively easily soluble EOCs (Li, K, Ca, Ba, Br, Sr, Mg), the amounts extracted from the samples in different leaching solution followed the order: TS ~ RS > SS ~ DM. For Na, however, the inverse was observed, SS ~ DM > TS ~ RS.

Comparisons of amounts of most EOCs belonging to the transition, post-transition, metalloids and other metals group in different extraction fluids could not be made due to the low to extremely low concentrations measured, which may be due to the low solubility of most of the EOCs belonging to these groups.

Most transition metals (Be, U, Zr, V, Mo, Co, Ni, Ag, Cd, Hg), metalloids (Sb, As), and other metals (P, Se) from the EOCs were detected either below detection limit, at trace levels, or at extremely low concentrations (< 10 mg/kg) in the different leaching solutions in all samples. Due to the extremely high salt concentrations expected from these samples, they were diluted prior to analysis. This may have resulted in certain trace metals in the transition, post-transition and metalloids group being measured below detection limits or trace levels.

As seen in Table 3.5, SO_4 leached at extremely high concentrations in all leaching solutions (17,100 – 19,300 mg/kg) for SS sample, and high concentration in all leaching solutions for DM (4,360 – 4,930 mg/kg). Solubility of sulfate is not influenced by the ambient pH (Kalbe et al. 2008); thus, the amount of SO_4 extracted was similar for DM and SS, regardless of pH of the leachate. CKD used in SS contains high concentrations of sulfates and alkalis. The relatively lower concentrations of most EOCs from SS may be due to the formation of insoluble sulfite or sulfate compounds. For RS, SO_4 in EF DDI and EF 4.2 leached at high concentrations (442 and 480 mg/kg, respectively), while remaining not detected in EF SLL and EF 2.9. It was generally measured only at trace levels for all EFs in TS.

As seen in Figure 3.2, certain elements (Al, Cu, Fe, Pb and Zn) leached at greater concentrations for EF SLL in all samples, while measured at trace to extremely low concentrations for other leaching solutions. Certain transition metals, which were mostly not detected or measured at trace levels, leached at extremely low concentrations mostly for EF SLL. For instance, Cr, was measured at 1.4, 4.2, 2.4 and 3.3 mg/kg, respectively, for TS, RS, SS, and DM samples. The observations discussed above for Al, Zn, Fe, Cu, Pb and Cr may be indicative of the fact that EF SLL tends to be a more aggressive extraction fluid for some transition metals than EF 2.9, when pH is not the only factor influencing solubility. This observation also co-relates with highest conductivity values observed in EF SLL, as compared to the other leaching solutions.

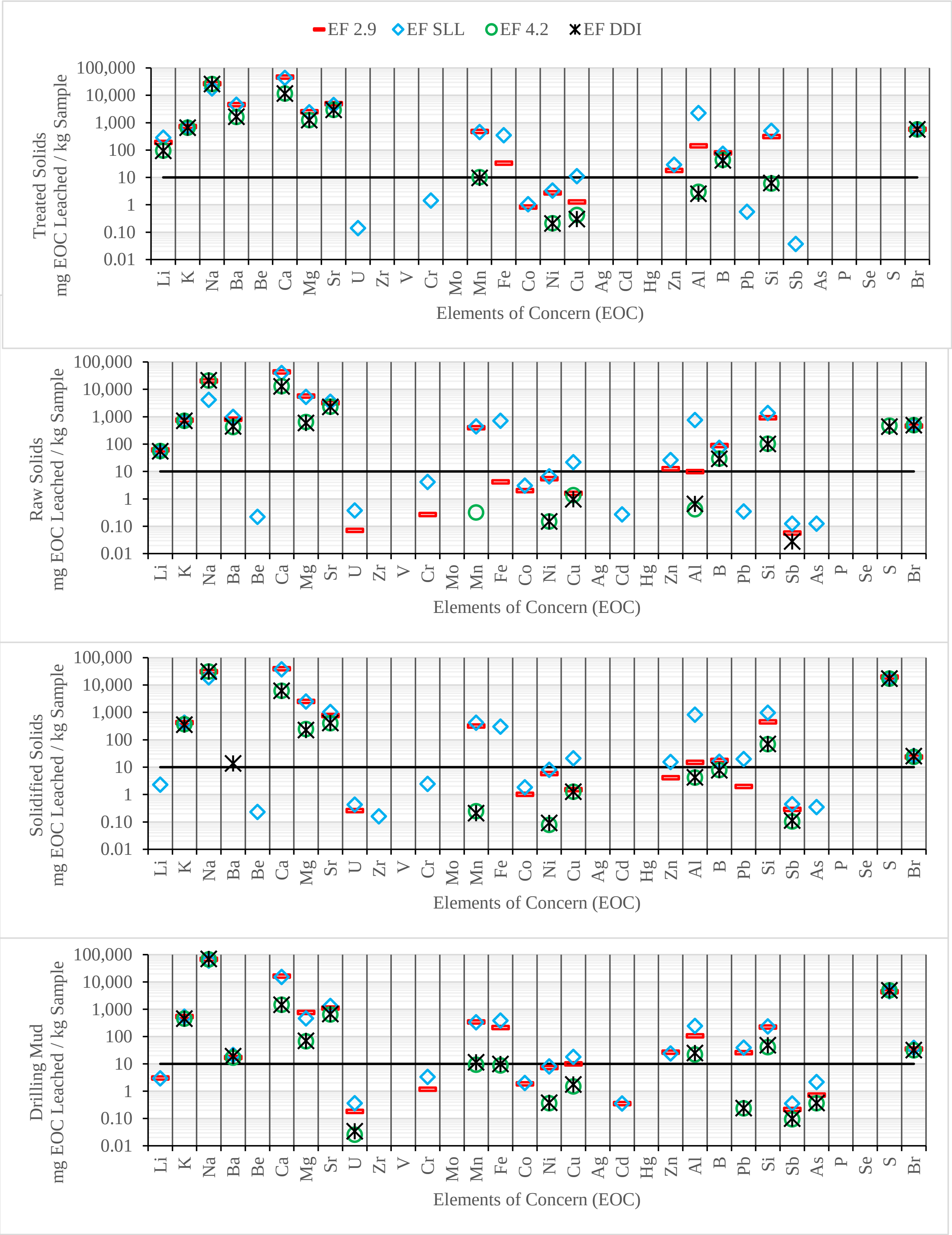


Figure 3.2: Total Amount (mg/kg) of EOC Leached from Samples for Different Leaching Solutions

By observing the leaching behavior of EOCs in different leaching solutions, Figure 3.2 and Tables 3.7 and 3.8, it can concluded that the easily soluble EOCs (alkali metals, alkaline earth metals and halides) leached at the greatest concentration mostly for EF 2.9, while the less soluble EOCs (transition and post-transition metals) leached at the greatest concentration for EF SLL.

The amount of most EOCs extracted by the leaching solutions from the air-dried residual solid samples was in the order: EF SLL ≈ EF 2.9 > EF DDI ≈ EF 4.2. Similar observations have been confirmed by other authors who employed TCLP, SPLP and ASTM methods for other waste samples (Siddique et al. 2010). Greater amounts of inorganic elements being leached by acidic leaching solutions has been commonly reported by several other authors (Perkct and Webster 1981). As mentioned above, this assessment was observed to be true for most inorganic elements, however certain elements such as K, Na, Br and SO_4 leached at similar concentrations regardless of the pH of the leaching solution.

The results associated with the acidic leaching solutions, EF 2.9 and EF SLL, can be considered as the worst case scenarios for the leaching in a MSW landfill under co-disposal conditions (Perkct and Webster 1981, Stanforth et al. 1979). Thus, co-disposal in a MSW landfill with other municipal refuse would not be an ideal disposal environment due to the expected acidic conditions, which would result in leaching of greater concentrations of several elements, as compared to mono-disposal environments.

The observations discussed above indicates that the composition of residual solids sample are greatly influenced by the produced water and the Marcellus shale formation. Though these samples were from a specific location/site, these observations may be relevant to any residual solids generated from unconventional shale gas production operations in Marcellus shale. However, this statement is mostly true for TS and RS samples. Because, SS samples may vary from site to site depending on the S/S procedure employed, and DM samples may vary depending on the base fluid used for the mud, which may vary for different operations.

Table 3.7: Results of EOCs extracted (mg EOC/kg Sample) from treated solids (TS) and raw solid (RS) in Shake Extraction Test (SET) using four different leaching solutions

	Treated Solids				**Raw Solids**			
EOC	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**
pH	7.66	7.91	5.21	5.23	8.19	8.07	5.50	5.32
Alkali Metals								
Li	94.5	94.9	187	**285**	55.2	56.1	**60.7**	54.7
K	657	659	**717**	688	723	723	**750**	702
Na	26,000	25,800	**26,400**	17,700	**21,600**	21,300	20,300	4,220
Alkaline Earth Metals								
Ba	1,650	1,620	**4,470**	**4,470**	443	424	811	**1,000**
Ca	11,500	11,500	**46,100**	43,300	13,000	13,100	**43,100**	40,200
Mg	1,230	1,240	**2,490**	2,390	600	653	**5,740**	5,360
Sr	2,960	2,940	**4,950**	4,400	2,330	2,340	3,200	**3,570**
Transition Metals								
Mn	**-**	10.2	**476**	450	Trace	**-**	392	**446**
Fe	BDL	Trace	32.8	**351**	Trace	BDL	**-**	**720**
Cu	**-**	**-**	**-**	**11.2**	**-**	**-**	**-**	**22.1**
Zn	Trace	Trace	17.8	**29.3**	Trace	Trace	12.5	**26.5**
Post Transition Metals								
Al	**-**	**-**	142	**2,260**	**-**	**-**	**-**	**756**
Pb	BDL	BDL	Trace	-	Trace	BDL	Trace	-
Metalloids								
B	42.1	43.6	**77.2**	72.7	29.2	29.9	**87.8**	74.2
Si	**-**	**-**	308	**507**	103	104	914	**1,380**
Other Metals								
S	Trace	Trace	Trace	BDL	442	**480**	BDL	BDL
Halogen								
Br	563	**566**	564	564	495	499	453	**504**

BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL); '-' indicates concentration measured below 10 mg/kg; pH represents the final leachate pH measured immediately after testing period; **Bold** indicates the highest concentration among different leaching solutions for a specific sample

Table 3.8: Results of EOCs extracted (mg EOC/kg Sample) from solidified solids (SS) and drilling mud (DM) in Shake Extraction Test (SET) using four different leaching solutions

	Solidified Solids				**Drilling Mud**			
EOC	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**
pH	9.38	9.50	5.65	5.31	7.56	7.88	4.34	4.93
Alkali Metals								
Li	Trace	Trace	Trace	-	Trace	Trace	-	-
K	354	367	**418**	414	453	449	528	**535**
Na	**30,900**	**30,900**	30,400	18,800	**70,000**	67,400	66,900	59,900
Alkaline Earth Metals								
Ba	**13.6**	Trace	Trace	Trace	19.1	16.8	16.8	**21**
Ca	6,090	6,080	**39,000**	36,800	1,460	1,450	**16,100**	15,100
Mg	226	243	2,490	**2,500**	69.3	66.4	**753**	456
Sr	404	403	762	**1,030**	666	641	1,100	**1,310**
Transition Metals								
Mn	**-**	**-**	311	**416**	11.3	**-**	**336**	331
Fe	Trace	Trace	Trace	**303**	**-**	**-**	210	**380**
Cu	**-**	**-**	**-**	**20.9**	**-**	**-**	**-**	**17.9**
Zn	Trace	Trace	**-**	**15.3**	Trace	Trace	**26.5**	23.9
Post Transition Metals								
Al	**-**	**-**	14.6	**818**	24.7	22	105	**244**
Pb	Trace	Trace	**-**	**19.6**	**-**	**-**	25.3	**39.2**
Metalloids								
B	**-**	**-**	**17.5**	15.6	BDL	BDL	Trace	Trace
Si	69.4	67.8	445	**970**	47.9	40.5	219	**234**
Other Metals								
S	17,100	17,200	**19,300**	17,300	**4,930**	4,910	4,360	4,530
Halogen								
Br	25.1	23.5	23	**25.7**	31.9	31.1	34.3	**38.4**

BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL); '-' indicates concentration measured below 10 mg/kg; pH represents the final leachate pH measured immediately after testing period; **Bold** indicates the highest concentration among different leaching solutions for a specific sample

3.3.3 Leaching Test Limitations

It has to be taken into consideration that while these leaching tests provide an estimate of release of certain elements from the wastes under specific disposal conditions, real landfill environments might be quite different from lab tests. The laboratory conditions employed for a leaching test may not accurately mimic the environmental setting. This may result in an inaccurate estimation (over- or under-estimation) of the release of EOCs.

Several physical, chemical and biological factors that may develop over a long period of time in the landfill, may cause degradation of the waste, resulting in the leaching of certain metals which are not accurately simulated in short term leaching tests (WSDOE 2003).

3.3.4 Regulatory Comparison

The concentrations leached for different extraction fluids for all samples were compared to the TCLP regulatory limit for hazardous waste classification (40 CFR Part 261) (USEPA 1984), to determine if the sample would be classified as "hazardous". The results were also compared against the US EPA national primary drinking water standards (NPDWS), which have been established to limit the level of contaminants in drinking water. The comparison was performed to determine if the leachates, when released to a surface or groundwater source, would be of concern to the public health. Refer Appendix E for the regulatory threshold values of some contaminants as defined by the above standards.

Comparison with TCLP regulatory limit for hazardous waste classification (40 CFR Part 261):

Only treated solids samples failed the TCLP regulatory limit for barium (100,000 ppb) in EF SSL (182,131 ppb) and EF 2.9 (182,056 ppb). This can be interpreted as the waste being hazardous upon disposal in MSW landfills under co-disposal conditions.

The treatment process of the CWT was designed to remove barium and strontium, commonly present at elevated levels in the produced water. Thus, the sludge from the treatment process would be expected to contain contaminants at concentrations higher than that originally present in the produced water. However, it should be noted that the treated solids were ultimately mixed with other residual solids generated at the treatment facility, followed by solidification and stabilization with cement kiln dust (CKD), before being disposed in a MSW landfill. Prior to disposal, this waste is subjected to a TCLP test at a registered laboratory.

None of the other samples, i.e., raw solids, solidified solids and drilling mud, exceeded the TCLP regulatory limits.

It should be noted that the regulatory limit for hazardous waste classification, as defined in 40 CFR Part 261, can only be applied after subjecting the sample to the TCLP procedure defined in US EPA Method 1311.

Comparison with USEPA national primary drinking water regulations

Treated Solids: Ba exceeded the regulatory limit (2,000 ppb) for all extraction fluids. Ba was measured at 67,374 ppb (EF DDI), 65,810 ppb (EF 4.2), 182,056 ppb (EF 2.9) and 182,131 ppb (EF SLL). Concentrations of Pb was measured at 22.8 ppb in EF SLL, which exceeded the regulatory limit of 15 ppb.

Raw Solids: Ba exceeded the regulatory limit (2,000 ppb) for all extraction fluids. Ba was measured at 18,114 ppb (EF DDI), 17,340 ppb (EF 4.2), 33,176 ppb (EF 2.9) and 41,018 ppb (EF SLL). Be, Cd and Cr measured at 9.1 ppb, 11.2 ppb, and 171 ppb, respectively, in EF SLL also exceeded the regulatory limits of 4 ppb, 5 ppb and 100 ppb, respectively.

Solidified Solids: Concentrations of Pb and Sb measured in EF 2.9 and EF SLL exceeded the regulatory limits of 15 ppb and 6 ppb respectively. Pb was measured at 92.92 ppb (EF 2.9) and 947.27 ppb (EF SLL), while Sb was measured at 13.52 ppb (EF 2.9) and 21.27 ppb (EF SLL). In addition to the above elements, concentrations of As (16.8 ppb), Be (11.1 ppb) and Cr (117.73 ppb) leached in EF SLL only exceeded the regulatory limits.

Drilling Mud: As exceeded the regulatory limit (10 ppb) for all extraction fluids. As was measured at 16.8 ppb (EF DDI), 16.85 ppb (EF 4.2), 32 ppb (EF 2.9) and 98.26 ppb (EF SLL). Concentrations of Cd (15.77 and 16.77 ppb), Pb (1,156 and 1,790 ppb) and Sb (9.57 and 16.16 ppb) in EF 2.9 and EF SLL respectively, also exceeded the regulatory limit. Cr also leached at 151.9 ppb in EF SLL, thereby exceeding the regulatory limit of 100 ppb.

This comparison is made only to put the numbers in perspective. The concentration of elements in leachate escaping to groundwater may be attenuated by several factors, including dilution and adsorption (Kosson et al. 2002). In addition, groundwater flow, which control the rate of contaminant transport and dilution, also govern the extent to which the leachate contaminates the groundwater (O'Leary and Walsh n.a.).

3.3.5 Statistical Analysis

Table 3.9 and Table 3.10 indicate whether the amount of EOC extracted by the different leaching solutions is significantly different for a sample. In these Tables, a p-value less than 0.05 indicates that the extraction efficiency (total amount extracted) by one of the leaching solutions is significantly different from at least one other leaching solution. Only Br for TS, SO_4 for RS, and Na and Mn for DM, were observed to have a p-value greater than 0.05. This indicates that the amounts of these EOCs extracted in different leaching solution was not significantly different and maybe similar. The amounts of almost all other EOCs extracted in different leaching solutions were observed to typically have a p-value <0.0001 indicating that the amount of EOC extracted by at least one of the leaching solutions was highly significantly different from the others.

To determine which leaching solutions were statistically significantly different, a pair-wise comparison was performed. In Tables 3.9 and 3.10, leaching solutions not linked by the same letter are significantly different. For instance, if all the leaching solutions extracted significantly different amounts of EOC, they would be represented by the four letters, ‘A’, ‘B’, ‘C’ and ‘D’, with ‘A’ being assigned to the significantly highest concentration measured and ‘D’ to the significantly lowest concentration measured.

From Tables 3.9 and 3.10, it was observed that in EF 2.9 and EF SLL, significantly higher concentrations of almost all the EOCs were measured in all samples, as compared to EF DDI and EF 4.2. Also, for all samples, the amount of all the EOCs extracted by EF DDI and EF 4.2 were not significantly different; however, almost all the EOCs extracted by EF 2.9 and EF SLL were significantly different.

Tables 3.7 and 3.8 show that certain elements, such as K, Na, Br and SO_4, leached at similar concentrations, regardless of the pH of the leaching solution. However, only the concentration of Br in TS was determined to be statistically similar in all leaching solutions. While K concentrations in RS and Br in SS were statistically different, the p-value indicates that the difference was low to moderate.

Thus, statistically, it is confirmed that leaching solutions had a significant impact on the leaching potential of all samples.

Table 3.9: Results of Statistical Analysis Performed on Concentrations of Certain Elements in Different leaching Solutions for Treated Solids and Raw Solids

EOC	**Treated Solids**					**Raw Solids**				
	p-value	**EF 2.9**	**EF SLL**	**EF 4.2**	**EF DDI**	**p-value**	**EF 2.9**	**EF SLL**	**EF 4.2**	**EF DDI**
Alkali Metals										
Li	<0.0001	B	A	C	C	<0.0005	A	B	B	B
K	<0.0001	A	B	C	C	0.0016	A	B	B	B
Na	<0.0001	A	B	A	A	<0.0001	B	C	A, B	A
Alkaline Earth Metals										
Ba	<0.0001	A	A	B	B	<0.0001	B	A	C	C
Ca	<0.0001	A	B	C	C	<0.0001	A	B	C	C
Mg	<0.0001	A	B	C	C	<0.0001	A	B	C	C
Sr	<0.0001	A	B	C	C	<0.0001	B	A	C	C
Transition Metals										
Mn	0.0039	A	B	-	-	<0.0001	A	B	-	-
Fe	<0.0001	B	A	-	-	-	-	-	-	-
Zn	<0.0001	B	A	-	-	<0.0001	B	A	-	-
Post Transition Metals										
Al	<0.0001	B	A	-	-	-	-	-	-	-
Metalloids										
B	<0.0001	A	B	C	C	<0.0001	A	B	C	C
Si	<0.0001	B	A	-	-	<0.0001	B	A	C	C
Other Metals										
SO_4	-	-	-	-	-	0.1007	-	-	A	A
Halogen										
Br	0.6038	A	A	A	A	0.0002	B	A	A	A

Leaching solutions not connected by the same letter are significantly different; ‘-‘ indicates the concentration leached was below 10 mg/kg and thus no statistical analysis performed.

Table 3.10: Results of Statistical Analysis Performed on Concentrations of Certain Elements in Different leaching Solutions for Solidified Solids and Drilling Mud

EOC	**Solidified Solids**					**Drilling Mud**				
	p-value	**EF 2.9**	**EF SLL**	**EF 4.2**	**EF DDI**	**p-value**	**EF 2.9**	**EF SLL**	**EF 4.2**	**EF DDI**
Alkali Metals										
Li	-	-	-	-	-	-	-	-	-	-
K	<0.0001	A	A	B	B	<0.0001	A	A	B	B
Na	<0.0001	A	B	A	A	0.074	A	B	A	A
Alkaline Earth Metals										
Ba	-	-	-	-	-	0.0019	B	A	B	A, B
Ca	<0.0001	A	B	C	C	<0.0001	A	B	C	C
Mg	<0.0001	A	A	B	B	<0.0001	A	B	C	C
Sr	<0.0001	B	A	C	C	<0.0001	B	A	C	C
Transition Metals										
Mn	<0.0001	B	A	-	-	0.2295	A	A	-	-
Fe	-	-	-	-	-	<0.0001	B	A	-	-
Zn	-	-	-	-	-	0.0056	A	B	-	-
Post Transition Metals										
Al	<0.0001	B	A	-	-	<0.0001	B	A	C	C
Metalloids										
B	0.0031	A	B	-	-	-	-	-	-	-
Si	<0.0001	B	A	C	C	<0.0001	A	A	B	B
Other Metals										
SO_4	0.0004	A	B	B	B	0.0005	B	B	A	A
Halogen										
Br	0.0182	B	A	A, B	A, B	<0.0001	B	A	C	B, C

Leaching solutions not connected by the same letter are significantly different; ‘-‘ indicates the concentration leached was below 10 mg/kg and thus no statistical analysis performed.

3.3.6 Conclusions

In this study, residual solids generated by treating produced water and drilling mud (DM) resulting from unconventional shale gas production operations were subjected to a short-term leaching test (Shake Extraction test) to determine their leaching potential. Representative samples were collected from a CWT facility located in the Marcellus shale area, with the following treatment by-products; raw solids (RS), treated solids (TS) and solidified solids (SS). Different extraction fluids (EF) were used to simulate specific environmental conditions (EF 2.9, TCLP EF; EF DDI, distilled de-ionized water; EF 4.2, SPLP EF; EF SLL, synthetic MSW landfill leachate). The following conclusions were drawn based on the observations discussed above:

1) Alkali metals (Li, K and Na), alkaline earth metals (Ba, Ca, Mg and Sr) and a halide (Br), commonly reported at elevated levels in Marcellus shale produced waters, were observed to leach at high concentrations (> 100 mg/kg) from all samples (TS, RS, SS, DM) in different leaching solutions (EF DDI, EF 4.2, EF SLL, EF 2.9). However, Li and Ba leached at low concentrations for SS and DM (< 20 mg/kg).

2) Most of the elements commonly measured in all of the samples were characteristic of wastewaters from hydraulic fracturing operations in Marcellus shale.

3) The EOCs leaching from TS and RS in all the leaching solutions were similar except for SS due to its stabilization with cement kiln dust.

4) In EF DDI and EF 4.2, leaching occurred under neutral to alkaline conditions, with leachate pH at the end of experiment in different samples ranging from 7.5 – 9.5. In EF 2.9 and EF SLL, leaching occurred under acidic conditions, with leachate pH at the end of experiment in different samples ranging from 5.0-5.7.

5) Most transition elements (Be, U, Zr, V, Mo, Co, Ni, Ag, Cd, Hg), metalloids (Sb, As), and other metals (P, Se) were detected either below detection limits, at trace levels, or at extremely low concentrations (< 10 mg/kg) in different leaching solutions in all samples.

6) TS in EF SLL and EF 2.9 revealed that it would be classified as “hazardous waste” due to barium concentrations. This can be interpreted as TS being hazardous upon disposal in MSW landfills under co-disposal conditions.

7) Most EOCs were observed to leach in different leaching solutions in the following order: EF SLL ≈ EF ~ 2.9 > EF DDI ≈ EF ~ 4.2.

8) Almost all EOCs leached at statistically significantly higher concentrations in EF 2.9 and EF SLL than in EF DDI and EF 4.2, for all samples. The amount of all the EOCs extracted by EF DDI and EF 4.2 were not significantly different; however, almost all the EOCs extracted by EF 2.9 and EF SLL were significantly different.

9) EF 2.9 and EF SLL were the most aggressive leaching solutions for all samples.

10) Disposal of residual solids in MSW landfills under mono-disposal conditions appears to be a better management practice than disposal under co-disposal conditions.

3.4 REFERENCE

American Public Health Association (APHA), American Waterworks Association (AWWA) and Water Environment Federation (WEF) (2012) Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D. C.

ASTM Standard D1193, 2006 (2011), "Standard Specification for Reagent Water", ASTM International, West Conshohocken, PA, 2011, 10.1520/D1193-06R11, http://www.astm.org/

ASTM Standard D3987, 2012, "Standard Practice for Shake Extraction of Solid Waste with Water", ASTM International, West Conshohocken, PA, 2012, 10.1520/D3987-12, http://www.astm.org/

Baba, A. and Kaya, A., Leaching characteristics of solid wastes from thermal power plants of western turkey and comparison of toxicity methodologies. *J Environ Manage* **2004,** *73*, (3), 199-207.

Balaba, R.S. and Smart, R.B., Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater. *Chemosphere* **2012,** *89*, (11), 1437-1442.

Bank, T.L., "Trace Metal Chemistry and Mobility in the Marcellus Shale". Paper Presented at the Technical Workshops for the Hydraulic Fracturing Study, February 24-25, 2011.

Bishop, P.L., Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes. *Hazardous Waste and Hazardous Materials* **1988,** *5*, (2), 129-143.

Blauch, M., Myers, R., Moore, T. and Lipinski, B., "Where is All the Salt Coming from and What are the Implications?". Paper Presented at the SPE Eastern Regional meeting, Charleston, WV, 23-25 September, 2009.

Carolyn J. Oblinger Childress, William T. Foreman, Brooke F. Connor and Maloney, T.J. (1999) *New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory*, U.S. Geological Survey. http://water.usgs.gov/owq/OFR_99-193/ofr99_193.pdf

Chang, E.E., Chiang, P.C., Lu, P.H. and Ko, Y.W., Comparisons of metal leachability for various wastes by extraction and leaching methods. *Chemosphere* **2001,** *45*, (1), 91-99.

Evans, J.S. and Kiesecker, J.M., Shale Gas, Wind and Water: Assessing the Potential Cumulative Impacts of Energy Development on Ecosystem Services within the Marcellus Play. *PLoS One* **2014,** *9*, (2), e89210.

Gaudlip, A.W., Paugh, L.O. and Hayes, T.D., "Marcellus Shale Water Management Challenges in Pennsylvania". Paper Presented at the SPE Shale Gas Production Conference, Fort Worth, Texas, U.S.A., 16–18 November, 2008.

Haluszczak, L.O., Rose, A.W. and Kump, L.R., Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* **2013,** *28*, (0), 55-61.

Hammer, R. and VanBriesen, J. (2012) *In Fracking's Wake: New Rules are Needed to Protect Our Health and Environment from Contaminated Wastewater*, D:12-05-A. http://www.nrdc.org/energy/files/fracking-wastewater-fullreport.pdf

Hayes, T. (2009) *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*, Marcellus Shale Coalition. http://energyindepth.org/wp-content/uploads/marcellus/2012/11/MSCommission-Report.pdf

Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., DeGuzman, M., Odion, Z., Ilejay, Z., Sy, F., Petreas, M. and Simmons, B., Toxicity Characteristic Leaching Procedure Fails To Extract Oxoanion-Forming Elements That Are Extracted by Municipal Solid Waste Leachates. *Environmental Science & Technology* **1998,** *32*, (23), 3825-3830.

Jackson, D.R., Garrett, B.C. and Bishop, T.A., Comparison of batch and column methods for assessing leachability of hazardous waste. *Environmental Science & Technology* **1984,** *18*, (9), 668-673.

Jiang, Q., Rentschler, J., Perrone, R. and Liu, K., Application of ceramic membrane and ion-exchange for the treatment of the flowback water from Marcellus shale gas production. *Journal of Membrane Science* **2013,** *431*, 55-61.

Kalbe, U., Berger, W., Eckardt, J. and Simon, F.-G., Evaluation of leaching and extraction procedures for soil and waste. *Waste Manag* **2008,** *28*, (6), 1027-1038.

Kargbo, D.M., Wilhelm, R.G. and Campbell, D.J., Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environmental Science & Technology* **2010,** *44*, (15), 5679-5684.

Kim, A.G., "CCB Leaching summary: Survey of Methods and Results". Paper Presented at the Proceedings of Coal Combustion By-Products and Western Coal Mines: A Technical Interactive Forum, Allton, IL, 2002.

Kosson, D., Van der Sloot, H., Sanchez, F. and Garrabrants, A., An integrated framework for evaluating leaching in waste management and utilization of secondary materials. *Environmental Engineering Science* **2002,** *19*, (3), 159-204.

Krüger, O., Kalbe, U., Berger, W., Simon, F.G. and Meza, S.L., Leaching experiments on the release of heavy metals and PAH from soil and waste materials. *Journal of Hazardous Materials* **2012,** *207–208*, (0), 51-55.

Liermann, L.J., Mathur, R., Wasylenki, L.E., Nuester, J., Anbar, A.D. and Brantley, S.L., Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. *Chemical Geology* **2011,** *281*, (3–4), 167-180.

Liroff, R.A. (2011) *Extracting the facts: An investor guide to disclosing risks from hydraulic fracturing operations*, Investor Environmental Health Network. http://www.iehn.org/documents/frackguidance.pdf

Maloney, K.O. and Yoxtheimer, D.A., Production and Disposal of Waste Materials from Gas and Oil Extraction from the Marcellus Shale Play in Pennsylvania. *Environmental Practice* **2012,** *14*, 278-287.

New York State Water Resources Institute (NYS WRI), (2012), Waste Management of Cuttings, Drilling Fluids, Hydrofrack Water and Produced Water, *Gas Wells*, New York State Water Resources Institute Retrieved from http://wri.eas.cornell.edu/aboutus.html

O'Leary, P.R. and Walsh, P., "Landfill Course; Lesson 4: Leachate Control and Treatment ". Accessed on July 28, 2014 from http://www.bvsde.paho.org/bvsair/e/repindex/repi49-50/lesson4/lesson4.html

Perkct, C.L. and Webster, W.C. (1981) Literature Review of Batch Laboratory Leaching and Extraction Procedures. Conway, R.A. and Malioy, B.C. (eds), pp. 7-27, American Society for Testing and Materials.

Pritz, M.E. and Kirby, C.S., "Geochemical Investigation Of Marcellus Shale Natural Gas Hydrofracturing Waters". Paper Presented at the Northeastern Section (45th Annual) and Southeastern Section (59th Annual) Joint Meeting, Baltimore, MD, 13-16 March, 2010.

ProChem Tech, (2009), Marcellus Gas Well Hydrofracture Wastewater Disposal by Recycle Treatment Process, ProChemTech International Inc., Retrieved from http://prochemtech.com/Literature/TAB/PDF_TAB_Marcellus_Hydrofracture_Disposal_by_Recycle_1009.pdf

Resnikoff, M., Alexandrova, E. and Travers, J. (2010) *Radioactivity in Marcellus Shale*, Radioactive Waste Management Associates. http://energy.wilkes.edu/PDFFiles/Library/Marcellus%20Shale%20Radioactivity%20Report%205-18-2010.pdf

Roche, M., "Fracking concerns: Will Ohio start accepting drilling brine at 40 landfills?". Accessed on May 20, 2014 from http://www.norwalkreflector.com/article/2074481

Schlumberger, (1994), Designing and Managing Drilling Fluid, *Oilfield Review*, 6, Schlumberger, Retrieved from http://www.slb.com/~/media/Files/resources/oilfield_review/ors94/0494/p33_43.ashx

Shively, W., Bishop, P., Gress, D. and Brown, T., Leaching Tests of Heavy Metals Stabilized with Portland Cement. *Journal (Water Pollution Control Federation)* **1986,** *58*, (3), 234-241.

Siddique, R., Kaur, G. and Rajor, A., Waste foundry sand and its leachate characteristics. *Resources, Conservation and Recycling* **2010,** *54*, (12), 1027-1036.

Skalak, K.J., Engle, M.A., Rowan, E.L., Jolly, G.D., Conko, K.M., Benthem, A.J. and Kraemer, T.F., Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments. *International Journal of Coal Geology* **2014,** *126*, (0), 162-170.

Stanforth, R., Ham, R., Anderson, M. and Stegmann, R., Development of a Synthetic Municipal Landfill Leachate. *Journal (Water Pollution Control Federation)* **1979,** *51*, (7), 1965-1975.

Tarun R. Naik, F.C., Yoon-moon Chun (2003) *Uses of CKD Other Than for Flue Gas Desulfurization*, CBU-2003-35. https://www4.uwm.edu/cbu/Papers/2003%20CBU%20Reports/REP-529.pdf

Tiruta-Barna, L., Imyim, A. and Barna, R., Long-term prediction of the leaching behavior of pollutants from solidified wastes. *Advances in Environmental Research* **2004,** *8*, (3–4), 697-711.

Subpart C—Characteristics of Hazardous Waste, 40 CFR 261.24, Identification and Listing of Hazardous Waste, (1984), US Environmental Protection Agency (USEPA).

Method 1311: Toxicity Characteristic Leaching Procedure (TCLP), SW846: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, (1992), USEPA.

Method 1312: Synthetic Precipitation Leaching Procedure, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), (1994), USEPA.

Guidelines Establishing Test Procedures For The Analysis Of Pollutants, 40 CFR 136 Appendix B: Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11, (1997), US Environmental Protection Agency (USEPA).

USEPA (2002) *Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations*, EPA530-K-01-004, US Environmental Protection Agency,. http://www.epa.gov/epawaste/nonhaz/industrial/special/oil/oil-gas.pdf

van der Sloot, H.A., Leaching Behaviour of Waste and Stabilized Waste Materials; Characterization for Environmental Assessment Purposes. *Waste Management & Research* **1990,** *8*, (1), 215-228.

Washington State Department of Ecology (WSDOE) (2003) *An Assessment of Laboratory Leaching Tests for Predicting the Impacts of Fill Material on Ground Water and Surface Water Quality*, 03-09-107. https://fortress.wa.gov/ecy/publications/publications/0309107.pdf

Winslow, S.D., Pepich, B.V., Martin, J.J., Hallberg, G.R., Munch, D.J., Frebis, C.P., Hedrick, E.J. and Krop, R.A., Statistical procedures for determination and verification of minimum reporting levels for drinking water methods. *Environ Sci Technol* **2006,** *40*, (1), 281-288.

CHAPTER 4: EVALUATING LEACHING BEHAVIOR OF RESIDUAL SOLIDS FROM UNCONVENTIONAL SHALE GAS PRODUCTION OPERATIONS USING DYNAMIC FLOW-AROUND IMMERSION TEST

ABSTRACT

The objective of this study was to evaluate the leaching behavior of residual solids from unconventional shale gas production operations in Marcellus shale, when deposited in typical disposal environments. To achieve this objective, a multiple-extraction, flow-around laboratory leaching test (“Immersion test”) was used. The representative residual solid samples used in this study were three different types of produced water treatment by-products: raw solids (RS) generated through liquid-solid separation by gravity of produced water prior to chemical treatment; sludge generated due to physicochemical treatment (TS) of the produced water; and all the residual solids, including drilling mud, that was solidified (SS) with cement kiln dust (CKD) for disposal in a landfill. Distilled de-ionized water (EF DDI), synthetic acid rain (pH ~ 4.2; EF 4.2), and weak acetic acid (pH ~ 2.88; EF 2.9), were used as leaching solutions to mimic specific disposal environments.

Alkali metals (Li, K, Na), alkaline earth metals (Ba, Ca, Mg, Sr) and a halide (Br), which are typically associated with Marcellus shale and produced waters, leached at high concentrations from most of the residual solids sample. The SS sample, due to its stabilization with CKD, had a lower extraction efficiency as compared to the unconsolidated TS and RS samples. In EF 2.9, the leaching took place under acidic conditions, while for EF DDI and EF 4.2, the leaching occurred in neutral to alkaline conditions. The amount of inorganic elements extracted by these leaching solutions followed the order: EF 2.9 > EF DDI > EF 4.2. EF 2.9 was determined to be the most aggressive leaching solution, causing the maximum solubility of most inorganic elements.

4.1 INTRODUCTION

Innovations in directional well drilling (i.e., horizontal drilling) and artificial reservoir stimulation techniques (i.e., high volume, slick-water hydraulic fracturing) over the past decade, have enabled the energy industry in the United States to recover and produce economical amounts of natural gas from unconventional shale reservoirs. This has resulted in increased drilling activity in the various shale reservoirs in the U.S. However, several environmental concerns are associated with this otherwise, economically desirable industry. Understanding and mitigating the adverse impacts are among the major challenges for the shale gas industry. In addition to water quantity and quality issues, management of residual solids due to drilling and fracturing operations is a growing concern (Hammer and VanBriesen 2012, Liroff 2011, Maloney and Yoxtheimer 2012).

This research focused on the residual solids generated during unconventional shale gas production operations in the Marcellus shale area, with an aim to improve our understanding of how these wastes should be managed.

4.1.1 Residual Solids

Residual solids from unconventional shale gas production operations are generated during drilling operations and as by-products of produced water treatment. The major types of residual solids are: (1) Drill cuttings: fragments of rock and soil resulting from a drill bit grinding the rock for drilling a borehole into the earth; (2) Drilling mud: dense clay-rich slurries used for lifting and circulating the drill cuttings to the surface for removal; and, (3) Produced water treatment by-products: residual solids or sludges generated from treatment of the high volume of wastewater resulting from hydraulic fracturing operations (Hammer and VanBriesen 2012, Kargbo et al. 2010, Maloney and Yoxtheimer 2012, New York State Water Resources Institute (NYS WRI) 2012, USEPA 2002). In addition to these residuals, other potential residual solids include tank bottoms, pit sludges, basic sediment, flowback fracturing sand, spent filter, and filter media (Maloney and Yoxtheimer 2012, USEPA 2002). In the recent years, produced water has been reported to be mixed with solidifying agents such as cement kiln dust, for solidification and stabilization purposes for direct disposal of produced water in landfills (Roche 2013). The large quantity of sludge that may be generated due to these operations can also be classified as residual solids.

Due to growing concerns over water quantity issues, treatment of produced water at CWTs for re-use in drilling operations has increased in recent years. In 2011, approximately half of all wastewater produced from unconventional shale gas operations was treated at CWT facilities (Hammer and VanBriesen 2012). In 2011, 20 times more gas wells were drilled in the Marcellus shale play of PA, alone, as compared to that in 2007 (Jiang et al. 2013). This rapid development of shale gas production in the Marcellus formation will result in greater volumes of produced water impounded at the surface for treatment and recycle, ultimately resulting in higher volumes of sludge production. These estimates indicate the magnitude of the wastes expected in the coming years and concern associated with their management will only increase. Thus, this work is limited to only studying the by-products of treating produced water.

The treatment of high volumes of wastewater from hydraulic fracturing operations, also referred to as produced water, results in the generation of residual solids. On-site treatment of produced water includes storage in open-pits or impoundments for evaporation, aeration, settling, and perhaps filtration. The waste that settles at the bottom of these pits after the treatment process can be classified as residual solids, which are commonly disposed of as solid waste (Kargbo et al. 2010). Off-site treatment of the produced wastewaters is commonly performed in approved, industrial wastewater treatment facilities, also called centralized waste treatment facilities (CWTs). CWTs are equipped with physiochemical treatment units, such as coagulation, precipitation, flocculation, centrifugation, settling and filtration, to primarily reduce the high TDS and metal concentrations along with organic contaminants to ensure the produced wastewater is clean enough for reuse (Hammer and VanBriesen 2012). Coagulation and precipitation operations involve pH adjustment, addition of chemical precipitant, and flocculation. Through these operations the soluble salts are converted into insoluble salts that precipitate and are then separated from the treated water by physical methods (e.g., settling and/or filtration). The precipitate-containing contaminants removed from the produced wastewater, and chemical treatment residuals, are also classified as residual solids. These residual solids will contain the contaminants at concentrations higher than the original produced water, thereby making its proper management all the more important (Hammer and VanBriesen 2012).

4.1.2 Residual Solids Waste Regulation and Management

The Resource Conservation and Recovery Act (RCRA) explicitly excludes drill cuttings, drilling fluids, produced waters, produced water treatment by-products, and other wastes associated with oil and gas exploration and production (E&P wastes) from regulation as hazardous wastes (USEPA 2002). However, management of these wastes is generally required to comply with the non-hazardous waste regulation under RCRA Subtitle D. In addition, E&P wastes are to be managed in accordance with state requirements and federal laws, other than RCRA, that apply to the disposal of wastes.

Thus, the exempt residual solids from unconventional shale gas production operations are commonly considered solid waste and are directly disposed in approved Municipal Solid Waste (MSW) landfills. Disposal of some residual solids in deep injection wells is also reported (Hammer and VanBriesen 2012, NYS WRI 2012).

The classification of residual solids as being hazardous or non-hazardous determines the type of landfill facility that can be used. Toxic materials may leach from decomposing residual solids when they come in contact with leachates commonly found in municipal landfills. Release of these toxic leachates from landfill facilities to groundwater and surface water sources can significantly impact the environment and public health. In addition, wastewater treatment plants receiving these leachates from MSW landfills may not be designed to handle them. Due to these concerns, the residual solids may require pretreatment before their disposal, or an alternative disposal method may need to be implemented. Thus, characterization of the wastes is critical to ensure that they are handled accordingly for the sustainable development of the shale gas industry.

4.1.3 Project Objective

The primary goal of this study was to evaluate the leaching behavior of heavy metals and other elements of concern (EOC) from the residual solids which are generated from unconventional shale gas production operations in Marcellus shale. The aim was to better understand the leaching behavior of the residual solids in their typical disposal environments.

4.1.4 Laboratory Leaching Tests

Laboratory leaching experiments are performed for discerning the potential for dissolution and mobility of certain elements of concern from waste samples. The tests are typically performed to evaluate the leaching behavior of a waste in a short span of time under controlled conditions. Laboratory leaching tests are performed under the assumption that the leaching solution and other set of conditions are representative of a typical disposal environment. Various physical, chemical and biological factors that influence the release of contaminants from wastes can be controlled in laboratory leaching tests and thus specific conditions mimicking disposal environments can be simulated.

In this study, dynamic/multiple extraction experiments were employed, since their long testing periods and renewal of leaching solution has been reported to provide information about the kinetics that govern the mobilization of the contaminants and model the long-term exposure of the waste to leaching solution (Washington State Department of Ecology (WSDOE) 2003).

The renewal of the leaching solution eliminates the effect of ionic strength of the leachate on solubility and thus provides information that can be used to assess if the release of contaminants is equilibrium controlled or does the entire amount of the soluble contaminants dissolve easily (Kim 2002, Krüger et al. 2012, Lewin 1996, Perkct and Webster 1981). These tests are conducted over a longer time than single extraction leaching tests and typically are not subject to agitation. The two major types of multiple extraction leaching tests are flow-through column test and flow-around immersion test.

Flow-through column tests are primarily designed for porous granular material or materials through which groundwater can be expected to flow through in a disposal environment. This test is known to simulate actual field conditions more realistically than single extraction tests and most other laboratory leaching tests (Jackson et al. 1984, Kalbe et al. 2008). The method involves placing the sample material in a column and adding the leaching solution either from the top of the column and allowing it to drain down through the sample, or by forcing it up from the bottom of the column, thereby simulating the flow of percolating groundwater (Kim 2002). These tests may also include wet and dry cycles, i.e. periods of saturation with a leaching solution followed by the introduction of air, for enhancing the weathering of the waste material. Leaching impermeable wastes and fine grained solids using column tests has been reported to be difficult (Bradham and Caruccio 1990, Jackson et al. 1984). Due to the low permeability of the residual solids of concern in this study, flow-through column tests were not considered.

Flow-around leaching test simulates a landfill environment in which the leachate, due to the low permeability of the waste, will tend to flow around the waste instead of flowing through it (Poon and Chen 1999, van der Sloot 1990). To simulate this, the sample material is immersed in the leaching solution, which is replenished at specified intervals of time. The immersed sample is not subject to any agitation and the leaching takes place due to the flow of the leaching solution around it. Diffusion is reported to be the primary mechanism responsible for leaching from the low-permeability waste (van der Sloot 1990). The contaminants would diffuse through the pores of the low-permeability waste due to the concentration gradient resulting from the flow of the leaching solution around the waste which would wash away the mobile fraction of the contaminants from the surface (Poon and Chen 1999).

Flow around tests are typically designed for monolithic materials and compacted granular materials whose surface area can be measured. The ability to determine the surface area of the waste enables modelling the long term release of contaminants from these wastes using certain complex models. Flow-around tests are also referred to as ‘Tank test’, ‘Diffusion test’ and ‘Immersion test’. Examples of the flow-around leaching tests are: Dutch leaching characterization standard, EA NEN 7375:2004, and EPA Method 1315, also referred to as a semi-dynamic tank leaching procedure. Flow-around tests have been reported to be more suitable for solidified and stabilized (S/S) wastes for determining their long term behavior, since the major mechanism for release of metals from S/S wastes is reportedly diffusion (van der Sloot 1990).

A flow-around leaching test was developed for this test and shall be referred to as the ‘Immersion Test (IT)’ in this paper. The leaching intervals used for this test were adopted from NEN 7375:2004.

Leaching solutions were chosen in this study to assess the leaching behavior of the residual solids of concern under different environmental conditions. To simulate field conditions, artificial/chemical leachates, natural landfill leachates, natural stormwater and artificially simulated stormwater have been employed by different researchers. Among the more commonly used leaching solutions are the extraction fluids used in the toxicity characteristic leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP), as well as distilled de-ionized water (DDI). They are known to simulate, leaching conditions in a MSW landfill when co-disposed with other municipal refuse (TCLP), mono-disposal in pits or land disposal conditions (SPLP), and field conditions where the waste's buffering capacity determines the pH of the leachate (DDI).

The extraction fluid of TCLP has been designed to simulate leaching behavior of waste co-disposed in MSW landfills with other municipal refuse. To achieve this, the extraction fluid consists of acetic acid/acetate, which has been found in MSW landfill leachates (Hooper et al. 1998). SPLP has been designed to simulate the leaching behavior of a waste in contact with acid rain resulting from air-borne nitric and sulfuric oxides (Washington State Department of Ecology (WSDOE) 2003). The extraction fluid used for this method is primarily distilled de-ionized water (DDI), which is slightly acidified using a mixture of 60/40 H_2SO_4/HNO_3 (by weight). The extraction efficiency of TCLP and SPLP has been reported to be greatly influenced by the composition of its extraction fluid (Hooper et al. 1998). The ASTM method utilizes distilled water as the extraction fluid with an aim to simulate mono-disposal environments when the pH of the leachate is dictated by the buffering capacity of the waste. The use of water also ensures less bias in the extraction of some metals over others (Perkct and Webster 1981). In addition, ASTM method with distilled water has been reported to more closely resemble field conditions when compared to the more aggressive TCLP test (Baba and Kaya 2004).(USEPA 1992, 1994, 1997)

Gaps exist in our understanding of the exact composition of the residual solids from unconventional shale gas production operations. The elements of concern (EOC) in this study were selected on the basis of elements commonly associated with Marcellus shale and the produced water generated from hydraulic fracturing operations in Marcellus shale. Table 4.1 provides a list of the EOCs studied.

While chloride has been reported to be a major element in produced water from Marcellus shale, it was not considered for analysis in this study due to certain molecular interference issues with the analytical instrument.

Table 4.1: Elements of Concern (EOC) Considered for Analysis

Transition Metals	**Alkaline Earth Metals**	**Metalloids**	**Alkali Metals**	**Other Metals**	**Post Transition Metals**	**Halogen**
Cadmium	Barium	Antimony	Lithium	Phosphorus	Aluminum	Bromide
Chromium	Beryllium	Arsenic	Potassium	Selenium	Lead	
Cobalt	Calcium	Boron	Sodium	Sulfate		
Copper	Magnesium	Silicon				
Iron	Strontium					
Manganese						
Mercury						
Molybdenum						
Nickel						
Silver						
Uranium						
Vanadium						
Zinc						
Zirconium						

4.2 METHODS AND MATERIALS

4.2.1 Sample Sources

Samples of by-products of produced water treatment were collected from a CWT located in Pennsylvania. This facility only treats hydraulic fracturing wastewater and spent drilling muds from unconventional shale gas production operations, which it receives from areas in the Marcellus shale region. This facility treats the produced water by chemical precipitation, settling and pressure filtration, while the drilling mud is only thickened by gravity separation. For chemical precipitation, the facility utilizes sodium sulfate, sodium hydroxide and sodium hypochlorite to precipitate dissolved elements such as barium, iron, and strontium. The following three different types of treatment by-products, along with drilling mud, were collected from the facility: (1) raw solids (RS) generated through liquid-solid separation by gravity of produced water prior to chemical treatment; (2) sludge generated due to physicochemical treatment (treated solids = TS) of the produced water; and (3) all the residual solids, including drilling mud, that are solidified with cement kiln dust (solidified solids = SS) for disposal in a landfill.

4.2.2 Sample Preparation

Collected samples were stored at room temperature in high-density polyethylene (HDPE) containers for approximately two weeks prior to sample preparation, except the RS samples, which were prepared for the experiment approximately 60 days after sample collection. The samples were sticky and difficult to manipulate.

All samples were centrifuged at approximately 2,500 RPM for 40 minutes in a Beckman TJ-6R tabletop centrifuge to extract free water. The centrifuged samples were subsequently air-dried in a fume-hood for seven days. The samples were dried to preserve them from biodegradation, oxidation, sorption, precipitation and other physical and chemical processes. The air-dried samples were then pulverized, homogenized and sieved, retaining particles in the size range of 2–4 mm.

The samples were air-dried for this experimental procedure since only inorganic fractions (i.e. non-volatile constituents) were of interest and to accommodate these residual solids samples for this procedure.

The solids content of the sample was determined using the procedure defined by ASTM, D3987-12: Standard Practice for Shake Extraction of Solid Waste with Water. The percent solids in an air-dried sample was calculated using Equation 1:

$$\text{Percent Solids (\%)} = \frac{\text{DW}}{\text{WW}} \text{ X } 100 \qquad \text{Eq. (1)}$$

Where:

DW = Sample weight (g) after oven-drying at 103-105 ^{o}C

WW = Air-dried sample weight (g) before oven-drying

The solids content of the samples is given in Table 3.2.

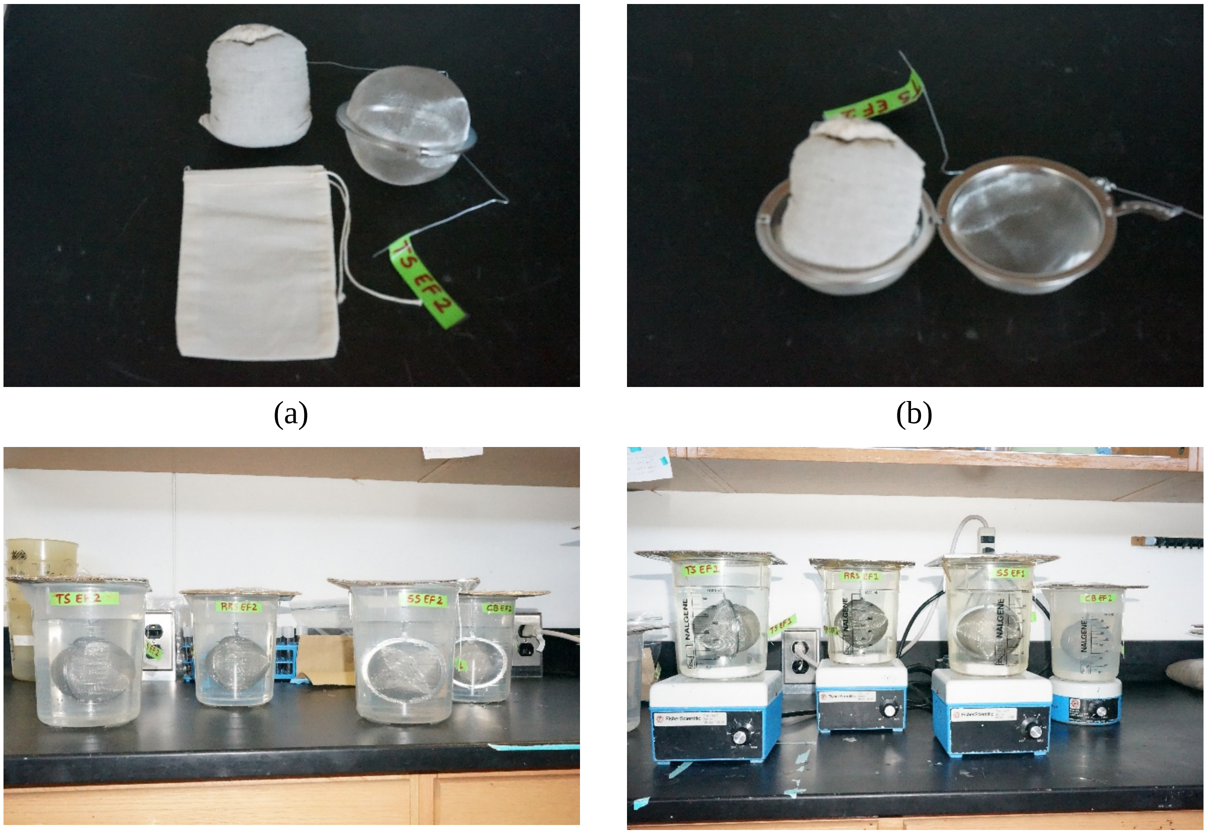
Table 4.2: Solids Content of Different Residual Solids

Sample Type	Range Solids Content (%)
Treated Solids	81.47 ± 0.04
Raw Solids	81.8 ± 0.06
Solidified Solids	96.85 ± 0.01
Drilling Mud	91.28 ± 0.08

4.2.3 Experimental Procedure for Immersion Test

Air-dried sieved samples of 100 ± 0.1 g weight were wrapped in muslin cloth and then placed in a tea-mesh ball. Refer to Table 4.2 for the solids content of each sample which were utilized in calculating the final leachate concentrations, mg EOC/kg waste-). Sieving of the sample was performed to ensure that the particle size was larger than the pore size of the muslin cloth and tea mesh ball so as to prevent the loss of sample during the experiment. A volume of 1.0 L of leaching solution was added to 1.0 L capacity high-density polyethylene (HDPE) and polypropylene beakers. The “test piece,” i.e., the tea ball with sample, was then suspended in a beaker, such that it was equidistant from the sides and approximately 2.5 cm above the bottom of the beaker. The test piece was completely immersed in the leaching solution. A liquid to solid ratio of 10:1 v/w was used throughout the duration of this experiment. The beakers were loosely covered with plastic-wrapped cardboard pieces during the test.

Photographs of the test system are provided in Figure 4.1.



(a) (b)

(c) (d)

Figure 4.1: Photographs of (a) the muslin cloth, tea-mesh ball, and sample contained in muslin cloth, (b) muslin cloth containing sample placed in a tea-mesh ball, (c) covered beakers containing leaching solution with "test pieces" (tea ball + sample), and, (d) covered beakers containing de-ionized distilled water with test pieces.

Samples immersed in leaching solutions, EF 2.9 and EF 4.2, were not agitated, but samples immersed in EF DDI were continuously agitated on a magnetic stirrer plate. This variation in the procedure among different leaching solutions was to observe the impact of agitation on the extraction efficiency of the test. EF DDI was chosen for agitation since the initial hypothesis was that the amounts extracted by EF DDI would be lower as compared to other two acidic leaching solutions. The stirring rate was fast, but not fast enough to disrupt the sample within the test piece.

After 6.0 ± 0.5 h (0.25 days), the test pieces were removed from the leachates and allowed to drain for approximately 30 sec. The test pieces were then carefully placed in separate air-tight zip lock bags in a manner that the test piece would not be subjected to any form of disturbance. The leachate in the beaker was quickly transferred into separate 1.0 L volume sampling bottles.

The beakers were then immediately replenished with 1.0 L of fresh leaching solutions. The leachates were filtered through a 0.45 µm sterile syringe filter and measured for pH and conductivity. A fraction of the filtered sample was also acidified using trace metal grade nitric acid at 2% v/v for dissolved metal analysis. This procedure was again repeated at the specified time intervals described in Table 4.3 below.

Table 4.3: Leaching Solution Renewal Schedule in Immersion Test

Replenishment Period (n)	Cumulative Time (days)	Interval Duration (days)
1	0.25 ± 0.01	0.25
2	1 ± 0.01	0.75
3	2.25 ± 0.1	1.25
4	5 ± 0.1	2.75
5	9 ± 0.1	4
6	16 ± 0.1	7
7	36 ± 0.1	20

At the end of each leaching interval, the test piece was not dried or rinsed. All glassware and plastic material used had been soaked in 20% reagent grade nitric acid for 24 hours, followed by multiple cycles of rinsing with distilled water and high-purity water. The leaching test was performed at a room temperature of 21.0±2.0 ^{o}C.

The following three different types of leaching solutions of varying pH and composition were used (henceforth, the terms ‘leaching solution’ and ‘extraction fluid (EF)’ are used interchangeably).

1) Type I grade reagent water as defined by ASTM D1193 -06 (2011), also referred to as distilled de-ionized water (EF DDI), was utilized in this test. The pH was typically observed to be approximately 5.0±0.1 after about 20 minutes of stabilization time.

2) Acetic acid extraction fluid, as defined by the TCLP procedure, USEPA Method 1311 (EF 2.9). The pH was chosen on the basis of waste alkalinity, as defined by the TCLP method. All the samples were observed to be above a pH of 5.0, and thus, as recommended, a leaching solution of pH 2.88±0.05 was used.

3) Synthetic acid rain extraction fluid; a mixture of nitric acid and sulfuric acid, as defined by the SPLP procedure, USEPA Method 1312 (EF 4.2). As recommended by the

standard procedure a pH of 4.2 was used, since the study was limited to the Marcellus shale area which is located on the east of Mississippi.

The sulfuric acid and acetic acid used for preparing the leaching solutions was A.C.S reagent grade, while the nitric acid used for preparing the extraction fluids was trace metal grade.

The total mass of sample lost was measured by weighing the test piece on an electronic balance before the start of the experiment and at the end of the last (7th) replenishment period. For this, the test piece at the end of the test was dried in an oven at 104-105 ^{O}C, cooled to room temperature in a desiccator, and weighed at intervals of 24 h until a constant mass was recorded (i.e., two consecutive measures within 0.05 g). Sample losses observed at the end of the test are given in Appendix C.

4.2.4 Analysis of Leachates

Samples were analyzed for EOC using a Thermo Electron X-Series, inductively coupled plasma-mass spectrometer (ICP-MS) per Standard Method 3125-B (American Public Health Association (APHA) et al. 2012). Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume. The nitric acid used was trace metal grade.

Prior to performing analyses with the instrument, the Method Detection Limit (MDL) and Minimum Reporting Level (MRL) for the various EOC were established. EPA defines MDL as the “minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero” (USEPA 1997). This prevents reporting of an analyte detected at very low concentrations when noise and actual analyte concentration cannot be distinguished (Carolyn J. Oblinger Childress et al. 1999). MDLs for the EOCs were determined based on a guideline defined by USEPA (USEPA 40 CFR 136 Appendix B, 1997). According to this USEPA Method, seven replicate spikes of a low-level calibration standard that is close to the expected MDL were analyzed through the ICP MS analytical method and their standard deviation was multiplied by 3.143 (the value of ‘t’ at 99% confidence for seven samples) to determine the MDL. The Method Reporting Level (MRL) value determined was the low level calibration standard used for determining the MDL. MRL has been defined as the “smallest measured concentration of a substance that can be reliably measured by using a given analytical method" (Carolyn J. Oblinger Childress et al. 1999) . MRLs were determined by using a statistical procedure defined by Winslow et al. (2006).

Concentrations below the MDL are represented by the term 'BDL' (Below Detection Limit). The concentration detected between the MDL and MRL indicates that while the substance is present in the sample the value is estimated. Thus, this is represented by the term 'Trace' in the report and in tables presenting the analytical data.

Details regarding the isotopes of EOCs analyzed, analytical range, method detection limit, and minimum reporting limit are provided in the Appendix A.

For determining the concentration of EOCs in the sample, the instrument was calibrated for elemental concentrations the samples were expected to contain. External stock standard solutions were used. Almost all concentrations of Br, Ca and Sr for all samples were measured above their maximum calibrated range. Concentrations of SO_4 in different leaching solutions for SS samples was also detected beyond the calibration range for all samples. In addition to the above EOCs, Al, B, Br, Fe, Li, Mg, Mn, K, Si, Na, SO_4 and Zn were also measured beyond the ICP MS calibration range, but only in a few eluates for specific leaching solutions. For instance, Na was observed above the calibration range only for the first two eluate, while Li was detected beyond calibration range only for EF 2.9. (Refer to Appendix D for complete results of the immersion tests in which EOCs whose concentrations were measured above the ICP-MS calibration range.)

The total amount of an EOC leached for the entire duration of the immersion test, i.e. cumulative leached amounts were calculated using equation 3. A "dry-mass correction" was applied to all of the analytical values reported in µg/L (the results are presented as mg/kg dry weight of the sample).

$$\text{Total Amount Leached (mg/kg)} = \frac{\sum_{i=1}^{n} C_i \;\; V_i}{W} \qquad \text{for n=1 to N} \qquad (2)$$

Where:

n = replenishment periods (N=7)

i= fraction of the replenishment period

C_i = Concentration of the EOC measured in fraction 'i' (mg/L)

V_i = Volume of the leaching solution used for fraction ‘i’ (L)

W = Dry weight of sample determined using solids content (kg)

4.2.5 Quality Assurance and Quality Control

Laboratory method blanks were collected by subjecting the leaching solutions to all the steps of the leaching experiment in the exact same way as the sample, including replenishment periods, to identify any air-borne contamination or contamination that could be contributed by apparatus and reagents employed in the test. This step was essential for determining the accuracy of data, particularly for those elements detected at low levels. In addition to method blank, reagent blanks were also collected to observe specific contamination that could be linked only to the reagents used in preparing the leaching solutions. Laboratory method blanks were measured below or very close to their MRL levels for most EOCs in different leaching solutions. EOCs (Al, Ca, Cr, Mg, Si) measured above MRL were observed to be at relatively higher concentration in EF 2.9 as compared to EF 4.2 and EF DDI. Some EOCs (K, SO_4) were measured at high concentrations (<1000 ppb) in the first two eluates and then were detected below their MRL values.

For concentrations detected above the MDL, blank corrections were applied to the sample by deducting the blank concentrations from the sample concentrations.

4.3 RESULTS AND DISCUSSION

Observations

Immediately after the testing period of 36 days, the muslin cloths containing samples were opened to observe the appearance of samples. SS samples were observed to have formed a single mass in the shape of the tea-mesh ball. For TS and RS samples, the particles, while stuck together, were observed to be still distinguishable. The mass of samples in the muslin cloth was slightly broken down at the center and were observed to be completely saturated.

Sample losses at the end of the immersion test (i.e. 36 days) were determined to be between 13.51 – 39.26 g. (Refer to Appendix C for calculations related to sample mass lost during immersion tests.) The sample loss determined was least for SS in EF 4.2 and the greatest for TS in EF 2.9. Overall, the greatest amount of sample loss was recorded for TS and RS samples. Approximate losses recorded for TS and RS were in the range of 28 – 40 g, and that for SS in the range of 13 – 23 g. For all these samples, the highest amount of loss was observed in the highly acidic leaching solution, EF 2.9. The mass of sample lost for EF DDI and EF 4.2 was observed to be similar. This indicates that stirring of the sample in EF DDI did not cause any loss of the sample from the test piece.

The sample mass losses discussed above, however, are mostly exaggerated due to losses that occurred at the time of handling the test pieces at the end of the immersion test (i.e. 36 days). Hence, these numbers are only representative of the sample loss behavior that can be expected during the immersion test.

4.3.1 Conductivity and pH

Table 4.4 and Table 4.5 present the pH and specific conductivity data, respectively, for the leachates from each sample in three different leaching solutions, which were collected at the end of the seven leaching intervals.

Figure 4.2 presents a pictorial representation of the relationship between conductivity and pH of all samples in different leaching solutions.

pH

The final leachate pH values for distilled de-ionized water or EF DDI were a function of the buffering capacity of the solid waste (ASTM D3987, 2012). As seen in Table 4.4, the pH of the leachate in EF DDI for different samples was observed in the range of: TS, 7.4 - 8.16; RS, 7.92 - 9.32; and, SS, 7.59 - 8.96. This indicates that in EF DDI leaching occurred under alkaline conditions. Changes in leachate pH over time for all samples in EF DDI were observed to be similar. For example, as seen in Figure 4.2, the pH was observed to gradually increase up to 2.25 days, and then slightly decrease up to 9 days after which the leachate pH again increased (i.e., 16 and 36 days).

The pH of the leachate in EF 2.9 was observed to be highly acidic. As seen in Table 4.5, the pH of the leachate in EF 2.9 for different samples was observed to be in the range of: TS, 3.7 – 4.59; RS, 3.71 – 4.58; and, SS, 3.55 – 4.8. Acidic conditions have been reported to cause the maximum extraction of most metals (Lewin 1996, Perkct and Webster 1981). Thus, as compared to the other leaching solutions, higher concentrations of EOCs were expected in EF 2.9. As seen in Figure 4.2, the changes in pH over time were minimal for TS and RS samples (< 0.9 units);

the pH of the last three eluates were similar. However, for SS, it was observed that with the increase in contact time of the sample with the leaching solution, the pH was increasing. For example, as seen in Table 4.5, for the last three eluates of SS in EF 2.9, the pH increased from 3.96 to 4.8.

The pH of the leachate in EF 4.2 for different samples was observed to be in the range of: TS, 6.48-8.21; RS, 6.14-8.13; and, SS, 6.48-7.66. The greatest change in pH over time was observed in EF 4.2 for TS and RS (1.79 and 1.99 units), when compared against other leaching solutions. As seen in Figure 4.2, the pH gradually increased in EF 4.2 after 24 h.

According to van der Sloot (1990), the minimum release of metals is generally observed in the pH range of 7 to 10, except for oxyanions, such as As, Mo and Se, whose maximum leachability takes place at this pH range. Thus, as compared to other leaching solutions, the lowest concentrations of the inorganic EOCs can be expected in EF DDI and EF 4.2.

Table 4.4: Leachate pH of Samples in Three Different Leaching Solutions Collected at Different Leaching Intervals in Immersion Test (IT)

Replenishment Period, Cumulative (days)		**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**
Sample	**Extraction Fluid (EF)**				**pH**			
TS	EF 2.9	3.94	4.59	4.37	4.55	3.91	3.7	3.99
	EF DDI	7.74	7.75	8.02	7.86	7.4	7.94	8.16
	EF 4.2	6.48	6.66	7.08	7.28	7.43	7.49	8.21
RR	EF 2.9	3.71	4.15	4.06	4.58	4.26	4.26	4.3
	EF DDI	8.05	8.88	9.32	8.43	7.92	8.14	8.47
	EF 4.2	6.56	6.14	6.97	7.13	7.37	7.9	8.13
SS	EF 2.9	3.56	3.79	3.55	4.18	3.96	4.12	4.8
	EF DDI	8.29	8.96	8.09	7.59	7.78	7.96	8.42
	EF 4.2	7	6.48	7.19	7.02	7.25	7.35	7.66

Conductivity:

As seen in Figure 4.2, for all samples in different leaching solutions, very high conductivity values (> 10,000 mS) were measured in the first leachate collected at 6 hours, as compared to conductivity in leachates from subsequent sampling times (< 4300 mS). The extremely high, initial ionic concentrations in leachates can be attributed to the salts that may have remained on the samples after centrifugation. This is confirmed by the very small difference in conductivity measured between different extraction fluids for all samples. For example, as seen in Table 4.6, for RP #1, the conductivity of all samples in different extraction fluids was measured in the range of: TS, 15,160-16,780 mS; RS, 15,310-13,630 mS; and, SS, 10,980-13,130 mS.

In EF DDI and EF 4.2, for all samples, a greater difference was observed in the ionic concentration between RP #2 and #3. For example, from Table 4.6, the conductivity measured in EF DDI leachate for TS was 1,323 and 284.7 mS for RP #2 and #3, respectively, a difference of 1,038 mS. Similarly, the difference between the leachates in EF DDI and EF 4.2 for RP #2 and #3 was observed to be greater than 1000 mS for TS and RS. However, for subsequent leachates, the difference between the conductivity measured was observed to be much lower (<200 mS). Also, it was observed that the conductivity was in the similar range in leachates collected from 2.25 days to 36 days, indicating a much slower release of inorganic ions.

Table 4.5: Specific Conductivity of Leachate from Samples in Three Different Extraction Fluids Collected at Different Time Intervals in Immersion Test (IT)

Replenishment Period, Cumulative (days)		**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**
Sample	**Extraction Fluid (EF)**	**Specific Conductivity @ 25 ^{O}C, mS**						
TS	EF 2.9	15,770	3,706	2,866	2,760	1,714	991	936
	EF DDI	15,160	1,323	284.7	267.8	299.5	358.5	366.5
	EF 4.2	16,780	1,264	165.2	146.2	128.8	186.6	240
RR	EF 2.9	13,630	2,492	2,112	2,704	2,880	2,625	1,489
	EF DDI	13,330	1,269	266	199.4	208.7	232.5	256.9
	EF 4.2	15,310	1,241	199.8	118.5	110.6	129.9	169.7
SS	EF 2.9	11,360	4,240	1,851	1,930	2,000	2,415	3,498
	EF DDI	13,130	2,002	790	819	423.2	302.5	304.4
	EF 4.2	10,980	3,458	1,111	666	467.2	524	680

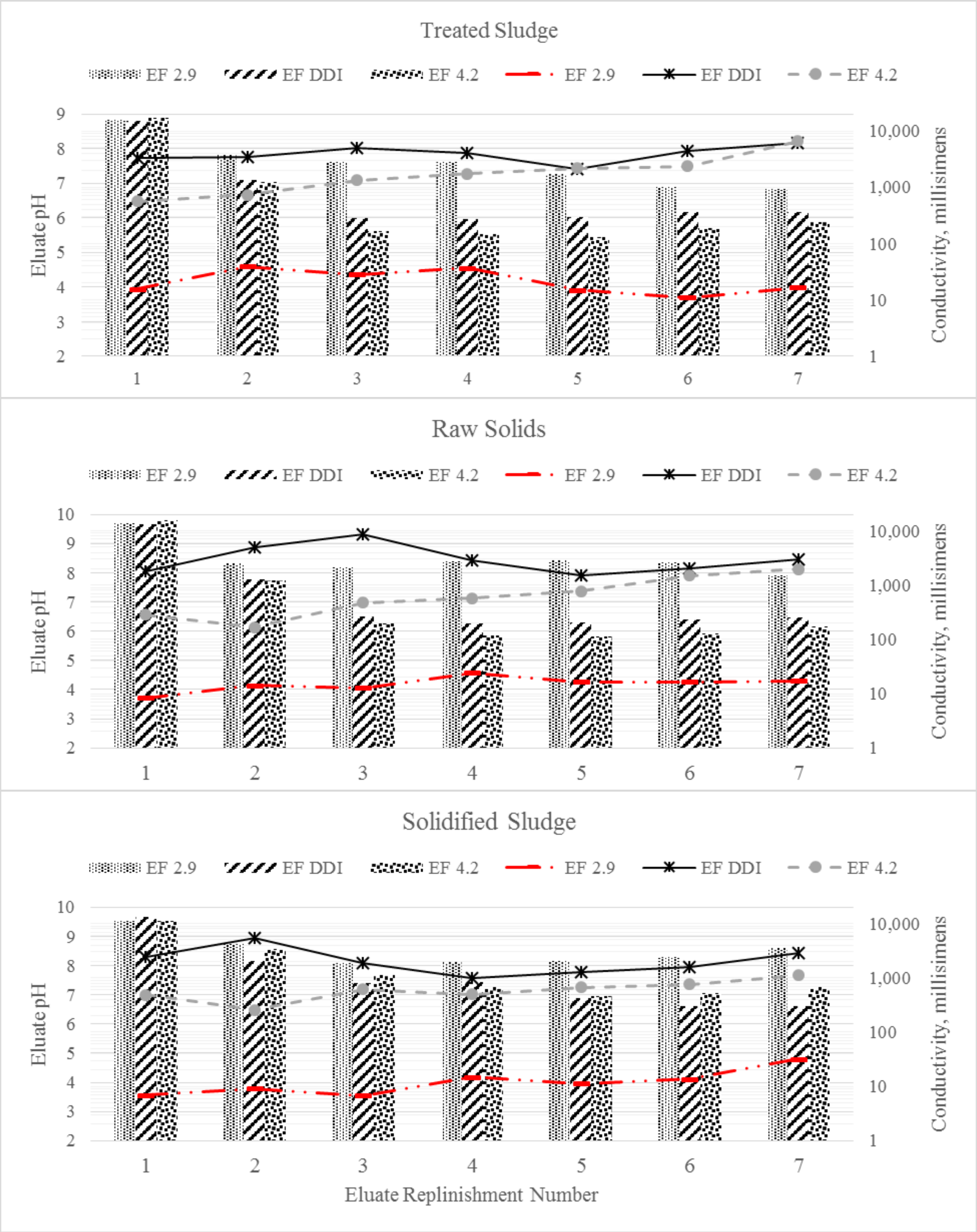


Figure 4.2: Leachate pH and Specific Conductivity (mS) of Samples in Three Different Extraction Fluids in Immersion Test (bars represent conductivity and lines with markers represent pH)

4.3.2 Elemental Analysis

The complete results of immersion tests for all the samples in different leaching solutions are presented in Appendix D. These results have been summarized and presented in Tables 4.7, 4.8, and 4.9 for TS, RS and SS, respectively. Figure 4.3 is a graphical representation, depicting a count of the number of times the leachate for each sample in different leaching solutions was detected above the MRL at each leaching interval. Figure 4.4 provides a pictorial representation of the leaching behavior of TS, RS, and SS samples in different leaching solution.

The data are presented in the following format:

1) Tables 4.7, 4.8, and 4.9 provide data regarding the highest concentration leached from the sample for a specific eluate, and the total amount of EOC released (cumulative concentration) from the sample over the test duration of 36 days. The data in these tables are presented as milligrams of EOC / kilogram of oven-dried sample (mg/kg).

2) For ease in reading and considering the accuracy and precision of ICP-MS, the concentrations in Tables 4.7, 4.8, and 4.9 have been rounded to two significant figures for concentrations below 10 mg/kg and three significant figures for concentrations above 10 mg/kg. In Figure 4.3, the absence of a marker for a particular element indicates that it was either detected at trace levels, below detection limit or below a concentration of 0.001 mg/kg.

3) The release of the EOCs from the waste is presented as micrograms of EOC / liter of leaching solution (µg/L) in Appendix D.

In the discussion that follows, word descriptors are keyed to concentrations as defined in Table 4.6.

Table 4.6: Word Descriptors for Concentration Ranges

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

As can be observed in Figure 3.2, alkali metals (Li, K and Na), alkaline earth metals (Ba, Ca, Mg and Sr) and a halide (Br), commonly reported at elevated levels in Marcellus shale produced waters, leached at greater concentrations in all samples in all extraction fluids (Haluszczak et al. 2013, Hayes 2009). For SS, however, Li, Ba and Br, were detected at relatively low concentrations. For example, as seen in Tables 4.8, 4.9 and 4.10, for TS, RS and SS, respectively, Ba was detected in a range of 3.4 – 14.2 mg/kg for SS, while for TS the range was 254-6370 mg/kg and for RS 121 – 1,840 mg/kg. Sulfate was detected at high concentrations in TS and RS samples in all leaching solutions; however, extremely high concentrations were measured in SS only in all leaching solutions. CKD used in SS has been reported to contain sulfates, which explains the high concentration of sulfates from SS (Tarun R. Naik 2003).

From the above observations, it can concluded that the low amounts of Ba leached from SS may be attributed to the formation of the extremely insoluble barium sulfate that forms when the Ba enriched solids reacted with the high concentrations of sulfate that may have be present due to the CKD.

Si, from RS, leached at high concentrations in all leaching solutions (EF DDI, 600 mg/kg; EF 2.9, 1,830 mg/kg; EF 4.2, 258 mg/kg). The raw solids sample, RS, were residuals settled from produced water during the liquid-solid separation process at the CWT. Thus, they can be expected to contain proppant (sand), which may explain the easy release of higher amounts of Si from RS samples. In TS and SS, Si was measured at high concentrations for only EF 2.9 (except SS in EF DDI; 173 mg/kg).

EOCs discussed above were extracted at different concentrations in EF DDI, EF 2.9 and EF 4.2. The amount of EOCs of alkali and alkaline earth metals extracted from all the samples was observed to follow the order: EF 2.9 > EF DDI > EF 4.2. Sulfate, whose solubility is reportedly not influenced by pH, was observed to follow the order, EF DDI > EF 2.9 ~ EF 4.2, for all samples (Kalbe et al. 2008). Similarly, alkali metals such as Li, K and Na, whose solubility is reportedly not influenced by the pH of the leaching solutions were observed to be extracted at different concentrations by the different leaching solutions. This may indicate that the leachability of EOCs from the samples may be due to mechanisms other than dissolution.

In addition to the composition and pH of the leaching solutions, the major difference in the experimental procedure was that samples in EF DDI were agitated throughout the test duration, while the samples in EF 2.9 and EF 4.2 were not. Also, the composition of EF DDI and EF 4.2 was similar since only a very small volume of acid mixture (<3 µL) was added to distilled de-ionized water to preparing EF 4.2. Thus, assuming that leachability of the samples was mostly influenced by the leaching solution, the leaching potential of samples was expected to be similar in EF DDI and EF 4.2. However, as seen in Tables 4.7, 4.8 and 4.9, for most EOCs, the extraction efficiency in all samples followed the order: EF DDI > EF 4.2. This clearly indicates that agitating the sample in the experimental procedure had a impact on the leaching potential of the sample. Stirring of the samples in the leaching solution may have accelerated the leaching process. This technique of agitation may have removed the stagnant leaching solution around the sample and in between the pore spaces of the sample. Thus, continuous dissolution of very soluble components would be enhanced, along with diffusion due to the continuous concentration gradient.

Most transition metals, post-transition metals, metalloids, and other metals were mostly measured below 10 mg/kg, at trace levels, or below detection levels in different leaching solution for all the samples.

As seen in Figure 4.3, transition metals, Zr, Va, Mo, Ag, Se and Hg, were measured mostly below detection limit or at trace levels in all leachates collected at different leaching intervals. Unlike other EOCs, the extraction of these elements was not affected by the pH of the leaching solution, type of sample, agitation or contact time with the leaching solution.

Certain EOCs (Be, U, Cd, Sb, and As), as seen in Figure 4.3, were detected above the MRL in some or all of the leachates collected at different leaching intervals for all samples in different leaching solutions. For instance, as seen Figure 4.3, while Be and Cd were only detected above the MRL for a few leachates in EF 2.9, Sb was detected above the MRL in almost all leachates in different leaching solutions for all samples. Though some of these EOCs (Sb, Be, Cd) were detected above the MRL, the concentrations leached were low to extremely low.

Al, Fe and Mn leached at high concentrations in EF 2.9, while extremely low concentrations leached in EF DDI and EF 4.2. For example, as seen in Tables 4.7, 4.8 and 4.9, Al, in EF 2.9 was measured at 3,920 mg/kg, 429 mg/kg, 231 mg/kg in TS, RS and SS, respectively. Respectively in EF DDI and EF 4.2, Al was measured at TS=10.1 and 6.5 mg/kg; RS=3.2 and 2.3 mg/kg; and, SS=12.5 mg/kg and 5.4 mg/kg. Low solubility metals (Al, Zn, Fe) typically leach at greater concentrations in lower pH as compared to neutral-alkaline pH. As discussed previously and as seen in Table 4.5, the leachate collected in EF 2.9 at different leaching intervals was determined to be acidic, while the leachate in EF DDI and EF 4.2 was determined to be neutral to alkaline in nature. Zn and Fe were also extracted at relatively much greater concentrations for EF 2.9 than in EF DDI and EF 4.2.

Several other low solubility EOCs such as Cr, Co, Ni, and Cu, were also observed to leach at relatively greater concentrations in the acidic leaching solution, EF 2.9 only. However, the total amount released was typically less than 12 mg/kg in EF 2.9, while these EOCs leached at extremely low to trace levels in EF DDI and EF 4.2.

Overall, the amounts extracted by different leaching solutions from each sample followed the order, TS ~ RS > SS, for most elements. The lower leaching potential of SS, compared to the other unconsolidated samples (TS and RS) can be attributed to the presence of cement matrix in SS, which has been demonstrated to effectively bind the heavy metal contaminants by chemical complexation, thereby reducing their leachability (Bishop 1988, van der Sloot 1990).

The concentrations measured in leachates collected at different leaching intervals in a leaching solution were compared against each other to observe the leaching behavior of EOCs over time. This comparison was performed for TS, RS and SS in the different leaching solutions. The comparisons were performed only for EOCs belonging to the alkali, alkaline earth metals, and halides groups which leached at high concentrations. Due to the mostly low concentrations measured of other EOCs, such comparisons were not considered.

Most EOCs (Na, Ca, K, Ba, Br, Mg) for TS and RS samples readily leached at high concentrations upon the samples initial contact with the leaching solution due to wash-off effects. This is mostly indicated by the highest concentrations measured in a specific leachate presented in Tables 4.7, 4.8 and 4.9 (under table heading title ‘B’) which were mostly measured in leachates collected at either 6 h or 24 h. A slower release of these EOCs from the waste matrix was noted in the leachates collected at subsequent intervals. This observation, along with the observations made above from the conductivity measured for different leachates, indicates that most of the EOCs leached primarily due to surface wash-off effects or dissolution in the first few leachates (i.e., 6 h and 24 h) followed by diffusion of the EOCs in the subsequent leachates. The extremely high concentrations of readily soluble EOCs in leachates that first contacted the solid samples, which may have also resulted in extremely high conductivity measured, can be attributed to the salts that may have remained on the samples after centrifugation. However, this observation could not be clearly made in SS for which the extraction efficiency was observed to be relatively lower compared to TS and RS for most of the EOCs.

Br, for almost all samples in different leaching solutions, was observed to leach at high concentrations in the first two leachates. The concentrations in subsequent leachates gradually decreased, and low to extremely low concentrations were measured in the last eluate (36 days). This indicated that Br in the solid was either depleted or nearing depletion towards the end of the test duration.

The results associated with the acidic leaching solution, EF 2.9, can be considered as the worst case scenario for the leaching in a MSW landfill under co-disposal conditions (Perkct and Webster 1981, Stanforth et al. 1979). Thus, co-disposal in a MSW landfill with other municipal refuse would not be an ideal disposal environment due to the expected acidic conditions, which would result in leaching of greater concentrations of several elements, as compared to mono-disposal environments.

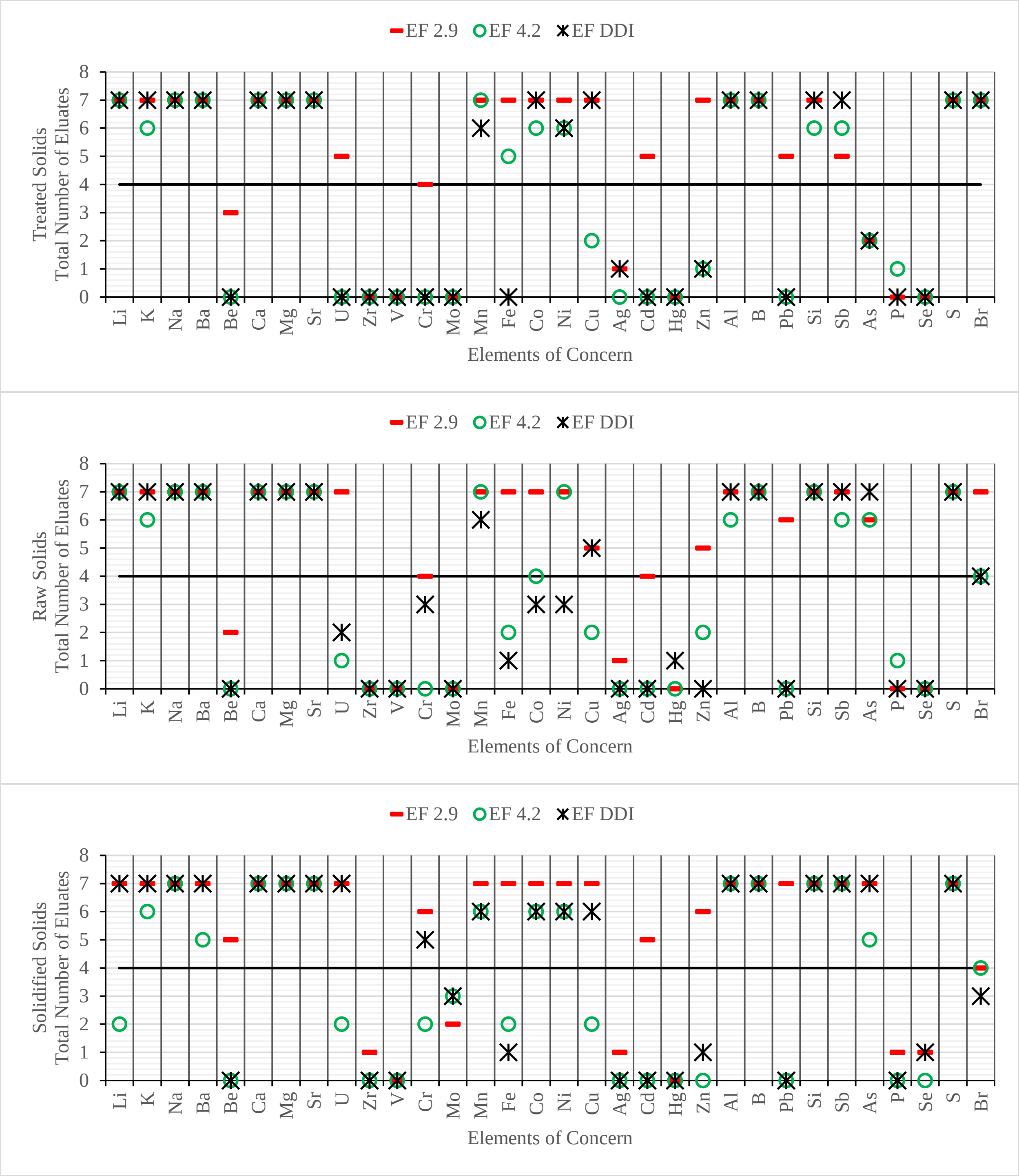


Figure 4.3: Number of times the leachate collected for each sample in different extraction fluids were detected above the minimum reporting level (MRL) for a total of seven leachates that were collected for during each RP

Table 4.7: Results of total and highest amount extracted (mg/L) of EOCs from treated solids (TS) in Immersion Test (IT) using three different leaching solutions

			TREATED SOLIDS			
	EF DDI		**EF 2.9**		**EF 4.2**	
EOC	**A**	**B**	**A**	**B**	**A**	**B**
Alkali Metals						
Li	80	147	106	411	8.6	45.7
K	588	807	735	1,230	82.9	195
Na	26,100	28,100	29,600	31,200	2,730	4,530
Alkaline Earth Metals						
Ba	1,710	2,010	2,280	6,370	68.4	254
Ca	11,800	15,200	22,600	60,400	1,180	2,940
Mg	1,230	1,750	2,150	3,410	67	272
Sr	2,460	3,410	3,000	8,030	193	674
Transition Metals						
Mn	11.5	15.1	139	601	1	4
Fe	Trace	**NA**	293	757	0.94	2.6
Cu	0.19	0.97	5.7	12.8	0.035	0.067
Zn	0.23	0.23	34.6	95	2.1	2.1
Post Transition Metals						
Al	3.4	10.1	1,560	3,920	1.7	6.5
Metalloids						
B	31	82	45.6	100	17.5	56
Si	19.7	89.3	337	1,210	16.7	53.1
Other Metals						
SO_4	374	1,420	152	646	120	621
Halogen						
Br	628	670	697	729	38.6	79

‘A’: indicates the highest concentration measured in a specific eluate of the seven eluates analyzed; ‘B’: indicates the total amount leached over a period of 36 days; BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL)

Table 4.8: Results of total and highest amount extracted (mg/L) of EOCs from raw solids (RS) in Immersion Test (IT) using three different leaching solutions

	RAW SOLIDS					
	EF DDI		**EF 2.9**		**EF 4.2**	
EOC	**A**	**B**	**A**	**B**	**A**	**B**
Alkali Metals						
Li	50.6	62.9	59.2	80.5	5.9	13.6
K	608	861	718	1,250	80.4	198
Na	20,400	22,400	24,500	26,100	1,580	2,880
Alkaline Earth Metals						
Ba	358	551	689	1,840	38.9	121
Ca	12,900	15,700	20,600	61,700	1,170	2,470
Mg	550	784	1,820	8,340	62.7	138
Sr	2,040	2,490	2,360	4,630	190	384
Transition Metals						
Mn	0.2	0.37	250	914	0.44	1.2
Fe	0.17	0.17	454	514	0.72	1
Ni	0.0088	0.016	3.2	11.4	0.15	0.23
Zn	Trace	**NA**	31	47.4	0.29	0.46
Post Transition Metals						
Al	0.94	3.2	394	469	0.59	2.3
Metalloids						
B	16.4	71.7	27.2	105	9.7	47
Si	109	600	751	1,830	79.4	258
Other Metals						
SO_4	380	1,780	199	744	168	736
Halogen						
Br	549	590	621	651	38.3	60.4

‘A’: indicates the highest concentration measured in a specific eluate of the seven eluates analyzed; ‘B’: indicates the total amount leached over a period of 36 days; BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL)

Table 4.9: Results of total and highest amount extracted (mg/L) of EOCs from solidified solids (SS) in Immersion Test (IT) using three different leaching solutions

			SOLIDIFIED SOLIDS			
	EF DDI		**EF 2.9**		**EF 4.2**	
EOC	**A**	**B**	**A**	**B**	**A**	**B**
Alkali Metals						
Li	0.3	1.3	0.69	2.9	0.16	0.27
K	267	466	222	574	53.7	204
Na	28,400	32,300	23,100	32,400	5,520	9,990
Alkaline Earth Metals						
Ba	2.1	9.2	2.5	14.2	0.78	3.4
Ca	1,970	7,600	13,100	38,600	1,330	4,860
Mg	172	419	534	3,180	31.3	119
Sr	222	861	371	1,060	113	323
Transition Metals						
Mn	0.23	0.94	246	524	0.23	0.49
Fe	0.11	0.11	18.2	46.7	0.26	0.48
Zn	0.13	0.13	3.5	9.7	BDL	**NA**
Post Transition Metals						
Al	2.4	12.5	79.4	231	1.5	5.4
Metalloids						
B	3.4	17.5	4.4	23.2	2.5	10.7
Si	34.8	173	248	711	20.9	73.8
Other Metals						
P	Trace	**NA**	10.9	10.9	BDL	**NA**
SO_4	6,960	22,600	4,510	18,500	3,310	14,000
Halogen						
Br	25.2	28.5	17.9	24.3	4.3	7.2

‘A’: indicates the highest concentration measured in a specific eluate of the seven eluates analyzed; ‘B’: indicates the total amount leached over a period of 36 days; BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL)

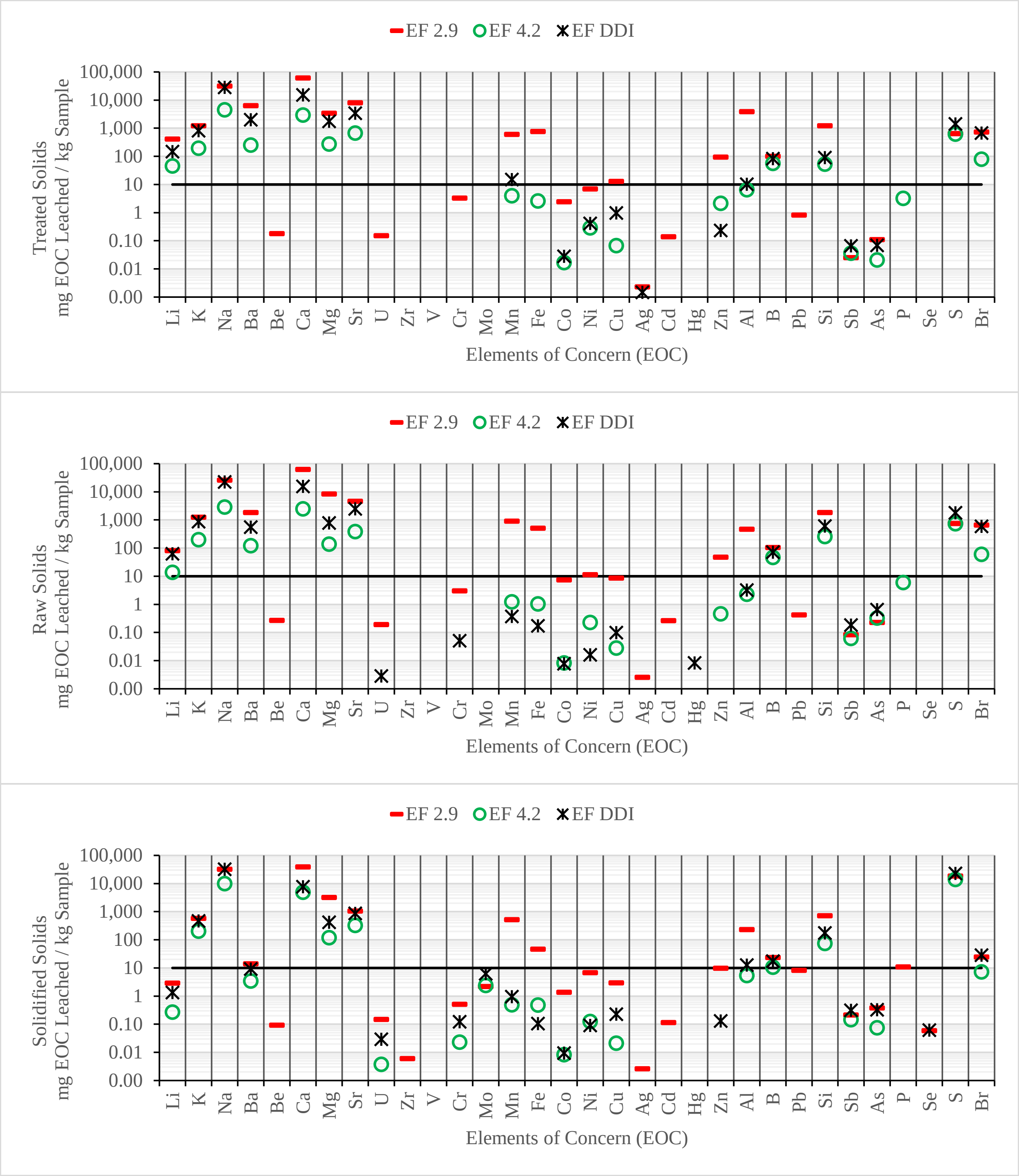


Figure 4.4: Total Amount (mg/kg) of EOCs Leached from Samples for Different Extraction Fluid

4.3.3 Leaching Test Limitations

It has to be taken into consideration that while these leaching tests provide an estimate of release of certain elements from the wastes under specific disposal conditions, real landfill environments might be quite different from lab tests. The laboratory conditions employed for a leaching test may not accurately mimic the environmental setting. This may result in an inaccurate estimation (over- or under-estimation) of the release of EOCs.

Several physical, chemical and biological factors that may develop over a long period of time in the landfill, may cause degradation of the waste, resulting in the leaching of certain metals which are not accurately simulated in short term leaching tests (WSDOE 2003).

4.3.4 Regulatory Comparison

The concentrations leached for different extraction fluids for all samples were compared to the TCLP regulatory limit for hazardous waste classification (40 CFR Part 261) (USEPA 1984) to determine if the sample would be classified as “hazardous”. The results were also compared against the US EPA national primary drinking water standards (NPDWS), which have been established to limit the level of contaminants in drinking water. The comparison was performed to determine if the leachates, when released to a surface or groundwater source, would be of concern to the public health.

The cumulative concentrations leached over a period of 36 days was compared with the regulatory limits. (Refer to Appendix D for concentrations measured in each eluate and for cumulative concentrations.) Refer Appendix E for the regulatory threshold values of some contaminants as defined by the above standards.

Comparison with TCLP regulatory limit for hazardous waste classification (40 CFR Part 261):

None of the samples in different leaching solutions exceeded the TCLP regulatory limits.

Comparison with USEPA national primary drinking water regulations:

Treated Solids: Ba exceeded the regulatory limit (2,000 ppb) for all extraction fluids. Ba was measured at 23,392 ppb (EF DDI), 2,951 ppb (EF 4.2), and 74,157 ppb (EF 2.9).

Raw Solids: Ba exceeded the regulatory limit (2000 ppb) in EF DDI (6,440 ppb) and EF 2.9 (21,461 ppb).

Solidified Solids: Concentrations of Pb was measured at 114.7 ppb in EF 2.9, which exceeded the regulatory limit of 15 ppb.

This comparison is made only to put the numbers in perspective. The concentration of elements in leachate escaping to groundwater may be attenuated by several factors, including dilution and adsorption (Kosson et al. 2002). In addition, groundwater flow, which control the rate of contaminant transport and dilution, also govern the extent to which the leachate contaminates the groundwater (O'Leary and Walsh n.a.).

4.4 CONCLUSIONS

In this study, residual solids generated by treating produced water resulting from unconventional shale gas production operations were subjected to long-term leaching test (Immersion Test) to determine their leaching potential. Representative samples were collected from a CWT facility located in the Marcellus shale area, with the following treatment by-products; raw solids (RS), treated solids (TS) and solidified solids (SS). Different extraction fluids (EF) were used to simulate specific environmental conditions (EF 2.9, TCLP EF; EF DDI, distilled de-ionized water; EF 4.2, SPLP EF). The following conclusions were drawn based on the observations discussed above:

1) Alkali metals (Li, K and Na), alkaline earth metals (Ba, Ca, Mg and Sr) and a halide (Br), commonly reported at elevated levels in Marcellus shale produced waters, were observed to leach at high concentrations (> 100 mg/kg) from all samples (TS, RS and SS) in different leaching solutions (EF DDI, EF 4.2, EF 2.9). However, Li and Ba leached at low concentrations for SS (< 20 mg/kg).
2) Most of the elements commonly measured in all of the samples were characteristic of wastewaters from hydraulic fracturing operations in Marcellus shale.
3) The EOCs leaching from TS and RS in all the leaching solutions were similar except for SS due to its stabilization with cement kiln dust.
4) In EF DDI and EF 4.2, leaching occurred under neutral to alkaline conditions, while in EF 2.9 leaching occurred under acidic conditions.
5) The total amount of most transition metals (Cr, Mo, Zr, Va, Mo, Ag, U, Cd, Co, Ni, Cu and Hg), Metalloids (Sb, As), along with Be, Se, Pb and P, released from the samples in

different leaching solutions were generally less than 10 mg/kg. Some of these EOCs (Zr, Va, Mo, Ag, Se and Hg) were mostly measured below their detection limits throughout the test.

6) Al, Fe and Mn were extracted at high concentrations (>100 mg/kg) by EF 2.9 and at extremely low concentrations (<10 mg/kg) in EF DDI and EF 4.2.
7) None of the samples could be classified as "hazardous" based on the total amounts of certain EOCs released.
8) Most EOCs were observed to leach in different leaching solutions in the following order: EF 2.9 > EF DDI > EF 4.2.
9) Agitation, pH and composition of the leaching solution are important variables in evaluating the leaching potential of a sample.
10) EF 2.9 was the most aggressive leaching solution for all samples.
11) Disposal of residual solids in MSW landfills under mono-disposal conditions may be a better management practice than disposal under co-disposal conditions.

4.5 REFERENCES

American Public Health Association (APHA), American Waterworks Association (AWWA) and Water Environment Federation (WEF) (2012) Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D. C.

ASTM Standard D1193, 2006 (2011), "Standard Specification for Reagent Water", ASTM International, West Conshohocken, PA, 2011, 10.1520/D1193-06R11, http://www.astm.org/

ASTM Standard D3987, 2012, "Standard Practice for Shake Extraction of Solid Waste with Water", ASTM International, West Conshohocken, PA, 2012, 10.1520/D3987-12, http://www.astm.org/

Baba, A. and Kaya, A., Leaching characteristics of solid wastes from thermal power plants of western turkey and comparison of toxicity methodologies. *J Environ Manage* **2004,** *73*, (3), 199-207.

Balaba, R.S. and Smart, R.B., Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater. *Chemosphere* **2012,** *89*, (11), 1437-1442.

Bank, T.L., "Trace Metal Chemistry and Mobility in the Marcellus Shale". Paper Presented at the Technical Workshops for the Hydraulic Fracturing Study, February 24-25, 2011.

Bishop, P.L., Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes. *Hazardous Waste and Hazardous Materials* **1988,** *5*, (2), 129-143.

Blauch, M., Myers, R., Moore, T. and Lipinski, B., "Where is All the Salt Coming from and What are the Implications?". Paper Presented at the SPE Eastern Regional meeting, Charleston, WV, 23-25 September, 2009.

Bradham, W.S. and Caruccio, F.T., "A Comparative Study Of Tailings Analysis Using Acid/Base Accounting, Cells, Columns And Soxhlets". Paper Presented at the Mining and Reclamation Conference and Exhibition, Charleston, WV, April 23-26, 1990.

Carolyn J. Oblinger Childress, William T. Foreman, Brooke F. Connor and Maloney, T.J. (1999) *New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory*, U.S. Geological Survey. http://water.usgs.gov/owq/OFR_99-193/ofr99_193.pdf

Evans, J.S. and Kiesecker, J.M., Shale Gas, Wind and Water: Assessing the Potential Cumulative Impacts of Energy Development on Ecosystem Services within the Marcellus Play. *PLoS One* **2014,** *9*, (2), e89210.

Gaudlip, A.W., Paugh, L.O. and Hayes, T.D., "Marcellus Shale Water Management Challenges in Pennsylvania". Paper Presented at the SPE Shale Gas Production Conference, Fort Worth, Texas, U.S.A., 16–18 November, 2008.

Haluszczak, L.O., Rose, A.W. and Kump, L.R., Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* **2013,** *28*, (0), 55-61.

Hammer, R. and VanBriesen, J. (2012) *In Fracking's Wake: New Rules are Needed to Protect Our Health and Environment from Contaminated Wastewater*, D:12-05-A. http://www.nrdc.org/energy/files/fracking-wastewater-fullreport.pdf

Hayes, T. (2009) *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*, Marcellus Shale Coalition. http://energyindepth.org/wp-content/uploads/marcellus/2012/11/MSCommission-Report.pdf

Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., DeGuzman, M., Odion, Z., Ilejay, Z., Sy, F., Petreas, M. and Simmons, B., Toxicity Characteristic Leaching Procedure Fails To Extract Oxoanion-Forming Elements That Are Extracted by Municipal Solid Waste Leachates. *Environmental Science & Technology* **1998,** *32*, (23), 3825-3830.

Jackson, D.R., Garrett, B.C. and Bishop, T.A., Comparison of batch and column methods for assessing leachability of hazardous waste. *Environmental Science & Technology* **1984,** *18*, (9), 668-673.

Jiang, Q., Rentschler, J., Perrone, R. and Liu, K., Application of ceramic membrane and ion-exchange for the treatment of the flowback water from Marcellus shale gas production. *Journal of Membrane Science* **2013,** *431*, 55-61.

Kalbe, U., Berger, W., Eckardt, J. and Simon, F.-G., Evaluation of leaching and extraction procedures for soil and waste. *Waste Manag* **2008,** *28*, (6), 1027-1038.

Kargbo, D.M., Wilhelm, R.G. and Campbell, D.J., Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environmental Science & Technology* **2010,** *44*, (15), 5679-5684.

Kim, A.G., "CCB Leaching summary: Survey of Methods and Results". Paper Presented at the Proceedings of Coal Combustion By-Products and Western Coal Mines: A Technical Interactive Forum, Allton, IL, 2002.

Kosson, D., Van der Sloot, H., Sanchez, F. and Garrabrants, A., An integrated framework for evaluating leaching in waste management and utilization of secondary materials. *Environmental Engineering Science* **2002,** *19*, (3), 159-204.

Krüger, O., Kalbe, U., Berger, W., Simon, F.G. and Meza, S.L., Leaching experiments on the release of heavy metals and PAH from soil and waste materials. *Journal of Hazardous Materials* **2012,** *207–208*, (0), 51-55.

Lewin, K., Leaching tests for waste compliance and characterisation: recent practical experiences. *Science of The Total Environment* **1996,** *178*, (1–3), 85-94.

Liermann, L.J., Mathur, R., Wasylenki, L.E., Nuester, J., Anbar, A.D. and Brantley, S.L., Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. *Chemical Geology* **2011,** *281*, (3–4), 167-180.

Liroff, R.A. (2011) *Extracting the facts: An investor guide to disclosing risks from hydraulic fracturing operations*, Investor Environmental Health Network. http://www.iehn.org/documents/frackguidance.pdf

Maloney, K.O. and Yoxtheimer, D.A., Production and Disposal of Waste Materials from Gas and Oil Extraction from the Marcellus Shale Play in Pennsylvania. *Environmental Practice* **2012,** *14*, 278-287.

New York State Water Resources Institute (NYS WRI), (2012), Waste Management of Cuttings, Drilling Fluids, Hydrofrack Water and Produced Water, *Gas Wells*, New York State Water Resources Institute Retrieved from http://wri.eas.cornell.edu/aboutus.html

O'Leary, P.R. and Walsh, P., "Landfill Course; Lesson 4: Leachate Control and Treatment ". Accessed on July 28, 2014 from http://www.bvsde.paho.org/bvsair/e/repindex/repi49-50/lesson4/lesson4.html

Perkct, C.L. and Webster, W.C. (1981) Literature Review of Batch Laboratory Leaching and Extraction Procedures. Conway, R.A. and Malioy, B.C. (eds), pp. 7-27, American Society for Testing and Materials.

Poon, C.S. and Chen, Z.Q., Comparison of the characteristics of flow-through and flow-around leaching tests of Solidified heavy metal wastes. *Chemosphere* **1999,** *38*, (3), 663-680.

Pritz, M.E. and Kirby, C.S., "Geochemical Investigation Of Marcellus Shale Natural Gas Hydrofracturing Waters". Paper Presented at the Northeastern Section (45th Annual) and Southeastern Section (59th Annual) Joint Meeting, Baltimore, MD, 13-16 March, 2010.

ProChem Tech, (2009), Marcellus Gas Well Hydrofracture Wastewater Disposal by Recycle Treatment Process, ProChemTech International Inc., Retrieved from http://prochemtech.com/Literature/TAB/PDF_TAB_Marcellus_Hydrofracture_Disposal_by_Recycle_1009.pdf

Resnikoff, M., Alexandrova, E. and Travers, J. (2010) *Radioactivity in Marcellus Shale*, Radioactive Waste Management Associates. http://energy.wilkes.edu/PDFFiles/Library/Marcellus%20Shale%20Radioactivity%20Report%205-18-2010.pdf

Roche, M., "Fracking concerns: Will Ohio start accepting drilling brine at 40 landfills?". Accessed on May 20, 2014 from http://www.norwalkreflector.com/article/2074481

Schlumberger, (1994), Designing and Managing Drilling Fluid, *Oilfield Review*, 6, Schlumberger, Retrieved from http://www.slb.com/~/media/Files/resources/oilfield_review/ors94/0494/p33_43.ashx

Skalak, K.J., Engle, M.A., Rowan, E.L., Jolly, G.D., Conko, K.M., Benthem, A.J. and Kraemer, T.F., Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments. *International Journal of Coal Geology* **2014,** *126*, (0), 162-170.

Stanforth, R., Ham, R., Anderson, M. and Stegmann, R., Development of a Synthetic Municipal Landfill Leachate. *Journal (Water Pollution Control Federation)* **1979,** *51*, (7), 1965-1975.

Tarun R. Naik, F.C., Yoon-moon Chun (2003) *Uses of CKD Other Than for Flue Gas Desulfurization*, CBU-2003-35. https://www4.uwm.edu/cbu/Papers/2003%20CBU%20Reports/REP-529.pdf

Subpart C—Characteristics of Hazardous Waste, 40 CFR 261.24, Identification and Listing of Hazardous Waste, (1984), US Environmental Protection Agency (USEPA).

Method 1311: Toxicity Characteristic Leaching Procedure (TCLP), SW846: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, (1992), USEPA.

Method 1312: Synthetic Precipitation Leaching Procedure, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), (1994), USEPA.

Guidelines Establishing Test Procedures For The Analysis Of Pollutants, 40 CFR 136 Appendix B: Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11, (1997), US Environmental Protection Agency (USEPA).

USEPA (2002) *Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations*, EPA530-K-01-004, US Environmental Protection Agency,. http://www.epa.gov/epawaste/nonhaz/industrial/special/oil/oil-gas.pdf

van der Sloot, H.A., Leaching Behaviour of Waste and Stabilized Waste Materials; Characterization for Environmental Assessment Purposes. *Waste Management & Research* **1990,** *8*, (1), 215-228.

Washington State Department of Ecology (WSDOE) (2003) *An Assessment of Laboratory Leaching Tests for Predicting the Impacts of Fill Material on Ground Water and Surface Water Quality*, 03-09-107. https://fortress.wa.gov/ecy/publications/publications/0309107.pdf

Winslow, S.D., Pepich, B.V., Martin, J.J., Hallberg, G.R., Munch, D.J., Frebis, C.P., Hedrick, E.J. and Krop, R.A., Statistical procedures for determination and verification of minimum reporting levels for drinking water methods. *Environ Sci Technol* **2006,** *40*, (1), 281-288.

CHAPTER 5: COMPARISON OF SINGLE AND MULTIPLE EXTRACTION LEACHING TEST RESULTS FOR EVALUATING LEACHABILITY OF RESIDUAL SOLIDS FROM UNCONVENTIONAL SHALE GAS PRODUCTION OPERATIONS

ABSTRACT

The objective of this study was to evaluate the leaching behavior of residual solids from unconventional shale gas production operations in Marcellus shale, when deposited in typical disposal environments, using a single extraction and multiple extraction leaching tests. The shake extraction test (SET) and Immersion test (IT) were utilized for this purpose. The representative residual solid samples used in this study were three different types of produced water treatment by-products: raw solids (RS) generated through liquid-solid separation by gravity of produced water prior to chemical treatment; sludge generated due to physicochemical treatment (TS) of the produced water; and all the residual solids, including drilling mud, that was solidified (SS) with cement kiln dust (CKD) for disposal in a landfill. Distilled de-ionized water (EF DDI), synthetic acid rain (pH ~ 4.2; EF 4.2), and weak acetic acid (pH ~ 2.88; EF 2.9), were used as leaching solutions to mimic specific disposal environments.

TCLP leaching solution, composed of acetic acid of pH 2.9, resulted in the maximum extraction of the inorganic elements from the residual solids. In comparison to EF 4.2 and EF DDI, EF 2.9 is the most aggressive and simulates the "worst-case" scenario. Thus, high amounts of most EOCs may leach from these residual solids in MSW landfills disposed under co-disposal conditions. Agitation of the sample in the leaching solution along with long contact time resulted in an increased leachability from the samples. The leachability of the less soluble transition, post-transition, metalloids and other metals, in different leaching solutions (EF DDI, EF 4.2 and EF 2.9) followed the order IT > SET.

5.1 INTRODUCTION

Laboratory leaching experiments are performed for discerning the potential for dissolution and mobility of certain elements of concern from waste samples. The tests are typically performed to evaluate the leaching behavior of a waste in a short span of time under controlled conditions. Laboratory leaching tests are performed under the assumption that the leaching solution and other set of conditions are representative of a typical disposal environment. Various physical, chemical and biological factors that influence the release of contaminants from wastes can be controlled in laboratory leaching tests and thus specific conditions mimicking disposal environments can be simulated.

According to Kalbe et al. (2008), the leachability of wastes is influenced by physical parameters such as homogeneity, particle size, porosity, permeability of the solid phase influencing the flow rate and contact time between solution and solid, and temperature. In addition to these, other parameters such as pH value, redox conditions, total organic carbon (TOC) content, chemical reaction kinetics, chemical speciation of contaminants, complexation with other constituents and biological activity have also been reported to greatly influence the leaching behavior of wastes (Kalbe et al. 2008). Some of these parameters are typically controlled in the leaching tests by the following factors: pH of leaching solution/extraction fluid, agitation, leaching period, liquid to solid ratio (L/S), and particle size of the sample.

The pH of leaching solution has been specified by several authors to be the most critical parameter determining the solubility of metals (Fällman and Aurell 1996, Mahmoudkhani et al. 2008, Quevauviller et al. 1996, Rigol et al. 2009, van der Sloot 1990, van der Sloot 1998). pH in the acidic range has been reported to cause minimum extraction of most inorganic elements; however, certain metals, such as oxyanions (i.e. Mo, As, Sb, etc,) exhibit maximum leachability at a pH range of 7-10 (Lewin 1996, Perkct and Webster 1981, van der Sloot 1990). Thus, acidic leaching solutions in leaching tests are commonly employed to simulate a “worst case scenario”. Fällman and Aurell (1996) recommended that the pH to be employed in the leaching test should depend on the type of waste and the disposal technique the waste is subjected to.

In addition to the leaching solution chemistry, the duration of the test and frequency of renewing the leaching solution, also impacts the amount of elements extracted. According to

Kylefors et al. (2003), the long duration of experiments enable chemical equilibrium to occur and also allows biological reactions to take place.

According to Fällman and Aurell (1996), the L/S ratio (i.e., the amount of water in contact with the sample), particle size and agitation impacts the rate at which chemical equilibrium is obtained. Lower water volume, smaller particle size and agitation of the sample have been associated with assisting in reaching equilibrium at a faster rate. Grinding the sample to extremely small particles has been reported to maximize leachability due to the larger surface area exposed and the shorter diffusion path (Fällman and Aurell 1996, Kylefors et al. 2003, Lewin 1996). Kylefors et al. (2003) further emphasized that sample preparation, which involves steps like grinding, crushing, drying, is a critical step since it can greatly influence the size of the particles.

The contribution of several of these parameters results in the extraction of metals from the sample upon contacting a leaching solution. Most of these parameters are typically included in the design of a leaching test to simulate various leaching mechanisms; however, not all of these parameters can be included in a single test in a practical and feasible manner. Thus, the samples in this study were subjected to more than one leaching test designed with different parameters discussed above, and several leaching solutions/extraction fluid to observe their influence on the leachability of the residual solids.

Leaching tests can be broadly classified into two types: static/single extraction test and dynamic/multiple extraction test. While static leaching test are for a shorter duration of a few hours to days and do not comprise of renewal of leaching solution, dynamic leaching tests are characterized by periodic renewal of fresh leaching solution and are performed for a longer period of time of a few days to months (Kim 2002). By subjecting the sample to different leaching experiments and leaching solutions, it is possible to gather information on the total amount of contaminants that can be released in leaching processes under various environmental conditions, the release of the contaminants over time and impact of pH and other parameters on the leaching process.

The objective of this research was to evaluate the ability of two different types of leaching tests, a single extraction test and a multiple extraction test, to extract metals from residuals solids generated from treatment of produced water from hydraulic fracturing operations in Marcellus shale.

Different types of single and multiple extraction tests exist with variations in testing period, leaching solution, sample size, etc. to simulate specific environmental conditions. These were discussed in Chapter 3 and Chapter 4.

For this study, the single extraction leaching procedure and multiple extraction flow-around leaching procedure were developed on the basis of standard procedures. The single extraction procedure was designed on the basis of ASTM D3987: Standard Test Method for Shake Extraction of Solid Waste with Water. The modified ASTM D3987 method is hereafter referred to as the “Shake Extraction Test (SET)”. Due to the low permeability of the residual solids sample, a flow-around immersion test was developed. The procedure for this method was designed on the basis of a Netherlands leaching standard, EA NEN 7375:2004 (developed by a national Dutch standardization organization, NEN). This modified version of EA NEN 7375:2004 method is hereafter referred to as the “Immersion Test (IT)”.

Leaching solutions were chosen in this study to assess the leaching behavior of the residual solids of concern under specific environmental conditions. To simulate these field conditions, artificial/chemical leachates, natural landfill leachates, natural stormwater and artificially simulated stormwater have been employed. Some of the most commonly used leaching solutions include extraction fluids used in toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP), along with distilled de-ionized water (DDI). They are known to simulate, leaching conditions in a MSW landfill when co-disposed with other municipal refuse (TCLP), mono-disposal in pits or land disposal conditions (SPLP), and field conditions where the waste’s buffering capacity determines the pH of the leachate (DDI).

The difference and similarities between the variables of these two leaching tests are presented in Table 5.1. A more thorough description of these tests and the experimental procedures are provided in Chapters 3 and 4.

Table 5.1: Differences and Similarities between Design Parameters of Shake Extraction and Immersion Test

Test Variable	**Shake Extraction Test (SET)**	**Immersion Test (IT)**
Sample Preparation	Centrifuged, air-dried, pulverized, homogenized,	Centrifuged, air-dried, pulverized, homogenized
Particle Size	Extremely fine, < 1 mm	2 – 4 mm
Amount of Sample	5 g	100 g
Leaching Solution	TCLP (EF 2.9 SPLP (EF 4.2) Water	TCLP (EF 2.9 SPLP (EF 4.2) Water
Liquid-Solid Ratio	20:1 v/w, constantly 100 mL (volume)	10:1 v/w, constantly 1.0 L (volume)
Replenishment of Leaching Solution	No	Yes 7 times; 0.25, 1, 2.25, 5, 9, 16, 36 days
Temperature	21.0± 2.0 ^{0}C	21.0 ± 2.0 ^{0}C
Agitation Techniques	Shaker Table; circular in motion	Magnetic stirrer plate; stirring Only samples in EF DDI No agitation of samples in EF 2.9 and EF 4.2
Analysis	ICP-MS	ICP-MS

5.2 METHODS AND MATERIALS

Sample sources, sample preparation, experimental procedure, analysis of leachate and quality assurance and quality control were discussed in extensive detail in Chapters 3 and 4.

5.3 RESULTS AND DISCUSSION

The total amounts of elements of concern (EOCs) extracted by different leaching solutions in SET and IT for treated solid (TS), raw solids (RS) and solidified solids (SS) samples were compared and are presented in Tables 5.4, 5.5, and 5.6, respectively.

The discussion for the observations made on the leachability of the samples has been divided into two sections based on the periodic table groups of the EOCs. The highly soluble alkali metals (Li, K, Na), alkaline earth metals (Ca, Mg, Sr) and a halide (Br), which leached at great concentrations in both leaching procedures, IT and SET, in all leaching solutions are discussed separately from the slightly soluble, transition, post-transition, metalloids and other metals that were considered for this study. (Refer to Table 5.2 for a list of all EOCs considered in this study.)

Table 5.2: Elements of Concern (EOC) Considered for Analysis

Transition Metals	**Alkaline Earth Metals**	**Metalloids**	**Alkali Metals**	**Other Metals**	**Post Transition Metals**	**Halogen**
Cadmium	Barium	Antimony	Lithium	Phosphorus	Aluminum	Bromide
Chromium	Beryllium	Arsenic	Potassium	Selenium	Lead	
Cobalt	Calcium	Boron	Sodium	Sulfate		
Copper	Magnesium	Silicon				
Iron	Strontium					
Manganese						
Mercury						
Molybdenum						
Nickel						
Silver						
Uranium						
Vanadium						
Zinc						
Zirconium						

In the discussion that follows, word descriptors are keyed to concentrations as defined in Table 5.3.

Table 5.3: Word Descriptors for Concentration Ranges

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

Alkali metals, Alkaline earth metals and halogen

The term EOCs will be limited to only alkali metals (Li, K, Na), alkaline earth metals (Ca, Mg, Sr) and a halide (Br), in this section of the discussion.

Produced waters from Marcellus shale are reported to be enriched with alkali metals (Li, K, Na), alkaline earth metals (Ca, Mg, Sr) and a halide (Br) (Hayes 2009). These elements leached at high to extremely high concentrations in all the samples in all the leaching solutions in both SET and IT. However, Ba, Li and Br were observed at low to extremely low concentrations from SS sample in all extraction fluids in both SET and IT.

Considering the amount of EOCs extracted by the leaching solutions for each test: samples subjected to SET followed the order: EF 2.9 > EF DDI ~ EF 4.2; however, for IT the same samples followed the order: EF 2.9 > EF DDI > EF 4.2. This indicates that regardless of any parameters employed in the tests, the TCLP leaching solution, EF 2.9, extracted the greatest amount of the EOCs. Thus, it can be concluded that pH of the leachate had the greatest influence on the leachability of the waste and that acidic leachate resulted in the maximum extraction of the inorganic elements. Several authors have reported the same behavior (Fällman and Aurell 1996, Mahmoudkhani et al. 2008, Quevauviller et al. 1996, Rigol et al. 2009, van der Sloot 1990, van der Sloot 1998). Thus, it can be concluded that residual solids disposed in MSW landfills with other municipal refuse can be expected to leach the inorganic elements at high concentrations. This is based on the assumption that EF 2.9 mimics all MSW landfill leachates with co-disposal and does not consider several other factors (such as aerobic/anaerobic conditions, biological factors, temperature etc.) that can contribute to the leachability of a waste in a landfill.

Comparing the amount of the aforementioned EOCs extracted in EF 2.9 by the two tests, SET and IT, it was observed that IT extracted greater amounts than SET. However, the percentage difference between the amounts extracted was generally less than 50%. The lower percentage difference between the amounts extracted by IT and SET in EF 2.9 may be attributed to the longer testing duration of IT, even though in SET the samples were continuously agitated at a larger L/S ratio to ensure more contact with the leaching solution.

In terms of the amount of EOCs extracted, SET followed the order, EF DDI ~ EF 4.2, and for IT the order was, EF DDI > EF 4.2. Further, it can be observed from Tables 5.3, 5.4 and 5.5 that the extraction efficiency of EF DDI followed the order, IT > SET, whereas for EF 4.2, the order was SET > IT. The major difference between these two tests was that while the samples in EF DDI and EF 4.2 in SET were agitated continuously, in IT, only samples in EF DDI were agitated. This indicates that agitation of the sample in leaching solution may have a substantial impact on leachability of the sample, in addition to the pH and composition of the leaching solution.

The percentage difference between the amounts extracted by IT and SET in EF 4.2 was mostly greater than 100%; while in EF DDI, the percentage difference was mostly less than 25%. This observation strengthens the hypothesis that agitation also played a major role in influencing the solubility of EOCs from the samples. Stirring the samples in the leaching solution accelerated the leaching process. Agitation may have removed stagnant leaching solution around the sample and in the pore spaces of the sample.

However, the observation that EF 4.2 extracted greater amounts of EOCs in SET than IT (% difference > 100) is true mostly for TS and RS samples, in which the EOCs leached at greater concentrations. For SS, though greater amounts leached for SET than IT in EF 4.2, the percentage differences between concentrations in IT and SET were relatively less (% difference < 100). This is a clear indication that leachability of the samples is greatly influenced by the association of the EOCs with the waste material. The mixing of the waste with cement based products, such as cement kiln dust, has been reported to results in formation of cement paste, resulting in a highly alkaline environment and the conversion of heavy metals to insoluble metal hydroxides and silicates (Bishop 1988). Thus, the EOCs in SS waste are made less soluble, such that even agitation did not yield a substantial difference in leachability.

While certain alkali metals (Na, Ba, K, Br) were measured to leach at similar concentrations in all leaching solutions for SET, the same was not observed in IT. This may be due to the different mechanisms that influenced the leaching behavior of the samples in these two tests. While for SET, the primary mechanism responsible for leaching of most of the EOCs is dissolution and surface-wash off effects. For IT, the primary mechanism is diffusion in addition to other leaching mechanisms that cause the release of the EOCs over a longer test period. The longer contact time of the sample with the leaching solution may also be responsible for differing concentrations in leaching solutions. For instance, the longer contact time with the acidic leachates may cause more disintegration of the sample.

Transition Metals, Post-transition Metal, Metalloids and Other Metals

The term EOCs will be limited to only transition (U, Zr, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Cd, Hg, Zn), post-transition metals (Al, Pb), Metalloids (B, Si, Sb, As) and other metals (P, Se, SO_4) in this section.

Most of the EOCs belonging to transition, post-transition, metalloids and other metals were measured below detection limits, trace levels, or at extremely low concentrations (<10 mg/kg). Transition metals, if detected above the minimum reporting level (MRL), were typically measured at the greatest concentrations for the highly acidic leaching solution, EF 2.9. This observation was true in both IT and SET. Also, these EOCs, which are mostly slightly soluble, when measured above MRL, followed the order IT > SET. This observation was also true for observations made in EF 4.2. Certain elements (Al, Fe), in EF 2.9, leached at high concentrations for IT, but at relatively lower concentrations in SET. For example, as pointed in Table 5.3, Al and Fe in IT were measured at 3,920 and 757 mg/kg, respectively, while for SET they were measured at 142 and 32.8 mg/kg, respectively. Similar observations were made for RS and SS samples, as pointed out in Tables 5.4 and 5.5.

Not all EOCs of transition, post-transition and metalloids group that were detected above the MRL for IT were found in SET. Certain EOCs (As, Cr, U, Mo, Cd and Pb), while measured below detection limits or at trace levels in the SET, were measured above the MRL values in IT. However, the concentrations leached were low. For example, Cr for TS, RS and SS samples in EF 2.9 for SET was detected at trace, 0.27 mg/kg, and trace concentrations, respectively, while for IT, 3.3 mg/kg, 3.03 mg/kg, and 0.52 mg/kg were extracted for TS, RS and SS samples, respectively, over a period of 36 days.

Table 5.4: Comparison of Concentrations (mg/kg) Leached by Treated Solids in Different Extraction Fluids in Shake Extraction Test (SET) and Immersion Test (IT)

EOC	**TREATED SOLIDS**					
	EF 2.9		**EF DDI**		**EF 4.2**	
	IT	**SET**	**IT**	**SET**	**IT**	**SET**
Alkali Metals						
Li	**411**	187	**147**	94.5	45.7	**94.9**
K	**1,230**	717	**807**	657	195	**659**
Na	**31,200**	26,400	**28,100**	26,000	4,530	**25,800**
Alkaline Earth Metals						
Ba	**6,370**	4,470	**2,010**	1,650	254	**1,620**
Ca	**60,400**	46,100	**15,200**	11,500	2,940	**11,500**
Mg	**3,410**	2,490	**1,750**	1,230	272	**1,240**
Sr	**8,030**	4,950	**3,410**	2,960	674	**2,940**
Transition Metals						
Mn	**601**	476	**15.1**	*9.6*	*4*	**10.2**
Fe	**757**	32.8	-	-	-	-
Cu	**12.8**	*1.3*	-	-	-	-
Zn	**95**	17.8	-	-	-	-
Post-transition Metals						
Al	**3,920**	142	**10.1**	*2.6*	-	-
Metalloids						
B	**100**	77.2	**82**	42.1	**56**	43.6
Si	**1,210**	308	**89.3**	*6.3*	**53.1**	*6*
Other Metals						
SO_4	**646**	*Trace*	**1,420**	*Trace*	**621**	*Trace*
Halides						
Br	**729**	564	**670**	563	79	**566**

BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL); '-' indicates concentration measured below 10 mg/kg; pH represents the final leachate pH measured immediately after testing period; **Bold** indicates highest concentration measured between the two tests for a specific leaching solution; *Italics* represent concentrations measured below 10 mg/kg in a test which have been still represented for comparison with the other test concentration of measured above 10 mg/kg

Table 5.5: Comparison of Concentrations (mg/kg) Leached by Raw Solids in Different Extraction Fluids in Shake Extraction Test (SET) and Immersion Test (IT)

EOC	**RAW SOLIDS**					
	EF 2.9		**EF DDI**		**EF 4.2**	
	IT	**SET**	**IT**	**SET**	**IT**	**SET**
Alkali Metals						
Li	**80.5**	60.7	**62.9**	55.2	13.6	**56.1**
K	**1,250**	750	**861**	723	198	**723**
Na	**26,100**	20,300	**22,400**	21,600	2,880	**21,300**
Alkaline Earth Metals						
Ba	**1,840**	811	**551**	443	121	**424**
Ca	**61,700**	43,100	**15,700**	13,000	2,470	**13,100**
Mg	**8,340**	5,740	**784**	600	138	**653**
Sr	**4,630**	3,200	**2,490**	2,330	384	**2,340**
Transition Metals						
Mn	**914**	392	-	-	-	-
Fe	**514**	*4.1*	-	-	-	-
Cu	**11.4**	*5.5*	-	-	-	-
Zn	**47.4**	12.5	-	-	-	-
Post-transition Metals						
Al	**469**	*9.9*	-	-	-	-
Metalloids						
B	**105**	87.8	**71.7**	29.2	**47**	29.9
Si	**1,830**	914	**600**	103	**258**	104
Other Metals						
SO_4	**744**	BDL	**1,780**	442	**736**	480
Halides						
Br	**651**	453	**590**	495	60.4	**499**

BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL); '-' indicates concentration measured below 10 mg/kg; pH represents the final leachate pH measured immediately after testing period; **Bold** indicates highest concentration measured between the two tests for a specific leaching solution; *Italics* represent concentrations measured below 10 mg/kg in a test which have been still represented for comparison with the other test concentration of measured above 10 mg/kg

Table 5.6: Comparison of Concentrations (mg/kg) Leached by Solidified Solids in Different Extraction Fluids in Shake Extraction Test (SET) and Immersion Test (IT)

EOC	**SOLIDIFIED SOLIDS**					
	EF 2.9		**EF DDI**		**EF 4.2**	
	IT	**SET**	**IT**	**SET**	**IT**	**SET**
Alkali Metals						
K	**574**	418	**466**	354	204	**367**
Na	**32,400**	30,400	**32,300**	30,900	9,990	**30,900**
Alkaline Earth Metals						
Ba	**14.2**	*Trace*	*9.2*	**13.6**	-	-
Ca	38,600	**39,000**	**7,600**	6,090	4,860	**6,080**
Mg	**3,180**	2,490	**419**	226	119	**243**
Sr	**1,060**	762	**861**	404	323	**403**
Transition Metals						
Mn	**524**	311	-	-	-	-
Fe	**46.7**	*Trace*	-	-	-	-
Post-transition Metals						
Al	**231**	14.6	**12.5**	*4.2*	-	-
Metalloids						
B	**23.2**	17.5	**17.5**	*7.6*	**10.7**	*7.8*
Si	**711**	445	**173**	69.4	**73.8**	67.8
Other Metals						
P	**10.9**	*BDL*	-	-	-	-
SO_4	18,500	**19,300**	**22,600**	17,100	14,000	**17,200**
Halides						
Br	**24.3**	23	**28.5**	25.1	*7.2*	**23.5**

BDL: measured below the Method Detection Limit (MDL); Trace: measured between the MDL and Minimum Reporting Level (MRL); '-' indicates concentration measured below 10 mg/kg; pH represents the final leachate pH measured immediately after testing period; **Bold** indicates highest concentration measured between the two tests for a specific leaching solution; *Italics* represent concentrations measured below 10 mg/kg in a test which have been still represented for comparison with the other test concentration of measured above 10 mg/kg

For analysis, the samples from SET were diluted (dilution ratio=1:10), while samples from IT were not diluted. This might explain why certain EOCs were below the MRL for SET while somewhat above the MRL for IT.

The concentrations of Cr were also observed to gradually increase in the eluates collected at the 5th, 9th, 16th and 36th days of IT, but were below detection limits in the 0.25 and 1 day eluates. This further strengthens the argument that for certain EOCs contact time with the leaching solution may have a great influence on their leachability. However, these concentrations of Cr, though measured above MRL, were extremely low.

Sulfate was also measured at very high concentrations in IT for TS samples in all leaching solutions, but was detected only at trace levels for SET. For examples, as shown in Table 5.3, SO4 was measured at 1,416 mg/kg in EF DDI, 646 mg/kg in EF 2.9, and 621 mg/kg in EF 4.2. For the RS sample, SO_4 leached at 744 mg/kg in EF 2.9. However, SO_4 was measured only at trace or below detection levels in SET. One possible explanation for this could be the re-adsorption or precipitation of SO_4 in SET.

5.4 CONCLUSIONS

A single extraction leaching test (SET) and a multiple extraction leaching test (IT) were used to determine the leaching potential of residual solids resulting from the treatment of produced water. The total amount of the elements of concern (EOCs) released from the samples were compared to determine the impact of varying parameters on the leaching behavior of the samples. Three leaching solutions of varying pH and composition were utilized to observe their impact on the leaching process. The following conclusions were drawn based on the observations discussed above:

1) The amount of EOCs extracted by the leaching solutions from all samples subjected to SET followed the order: EF 2.9 > EF DDI ~ EF 4.2. For IT the same samples followed the order: EF 2.9 > EF DDI > EF 4.2.

2) Regardless of any parameters employed in the tests, the TCLP leaching solution, composed of acetic acid of pH 2.9, resulted in the maximum extraction of inorganic elements from the residual solids. In comparison to EF 4.2 and EF DDI, EF 2.9 was the most aggressive and simulated the “worst-case” scenario.

3) Agitation of the sample in the leaching solution and longer contact time resulted in increased leachability of elements from the samples.

4) Transition, post-transition, metalloids and other metals, which are mostly slightly soluble, tended to leach more in IT than SET.

5) Some transition, post-transition and metalloids, such as Cr, Pb, and As, while measured at low concentrations in IT, were mostly observed below detection limits or at trace levels only in SET, for the different leaching solutions.

5.5 REFERENCES

Bishop, P.L., Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes. *Hazardous Waste and Hazardous Materials* **1988,** *5*, (2), 129-143.

Fällman, A.M. and Aurell, B., Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. *Science of The Total Environment* **1996,** *178*, (1–3), 71-84.

Hayes, T. (2009) *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*, Marcellus Shale Coalition. http://energyindepth.org/wp-content/uploads/marcellus/2012/11/MSCommission-Report.pdf

Kalbe, U., Berger, W., Eckardt, J. and Simon, F.-G., Evaluation of leaching and extraction procedures for soil and waste. *Waste Manag* **2008,** *28*, (6), 1027-1038.

Kim, A.G., "CCB Leaching summary: Survey of Methods and Results". Paper Presented at the Proceedings of Coal Combustion By-Products and Western Coal Mines: A Technical Interactive Forum, Allton, IL, 2002.

Kylefors, K., Andreas, L. and Lagerkvist, A., A comparison of small-scale, pilot-scale and large-scale tests for predicting leaching behaviour of landfilled wastes. *Waste Manag* **2003,** *23*, (1), 45-59.

Lewin, K., Leaching tests for waste compliance and characterisation: recent practical experiences. *Science of The Total Environment* **1996,** *178*, (1–3), 85-94.

Mahmoudkhani, M., Wilewska-Bien, M., Steenari, B.-M. and Theliander, H., Evaluating two test methods used for characterizing leaching properties. *Waste Manag* **2008,** *28*, (1), 133-141.

Perkct, C.L. and Webster, W.C. (1981) Literature Review of Batch Laboratory Leaching and Extraction Procedures. Conway, R.A. and Malioy, B.C. (eds), pp. 7-27, American Society for Testing and Materials.

Quevauviller, P., van der Sloot, H.A., Ure, A., Muntau, H., Gomez, A. and Rauret, G., Conclusions of the workshop: harmonization of leaching/extraction tests for environmental risk assessment. *Science of The Total Environment* **1996,** *178*, (1–3), 133-139.

Rigol, A., Mateu, J., González-Núñez, R., Rauret, G. and Vidal, M., pHstat vs. single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples. *Analytica Chimica Acta* **2009,** *632*, (1), 69-79.

van der Sloot, H.A., Leaching Behaviour of Waste and Stabilized Waste Materials; Characterization for Environmental Assessment Purposes. *Waste Management & Research* **1990,** *8*, (1), 215-228.

van der Sloot, H.A., Quick techniques for evaluating the leaching properties of waste materials: their relation to decisions on utilization and disposal. *TrAC Trends in Analytical Chemistry* **1998,** *17*, (5), 298-310.

CHAPTER 6: ENGINEERING SIGNIFICANCE

Due to the growing quantities of residual solids resulting from increased unconventional shale gas production operations in the U.S., the environmentally sound management of these wastes has become as critical as the management of production wastewaters. This research aimed at understanding the leaching behavior of heavy metals and other elements of concern (EOC) from the residual solids in their typical disposal environments. The residual solids of particular concern in this study were produced water treatment by-products which are expected to be concentrated with the contaminants at higher levels as compared to the un-treated produced water, thus making its proper management all the more important.

This study is among the first to address the release of inorganics from residual solids in disposal environments. The data should prove useful for regulatory authorities in their efforts to develop specific guidelines for the disposal of residual solids.

The data from the laboratory scale tests can be utilized to determine the suitability of the current management practices and provide a comment on whether the wastes require some form of treatment prior to their disposal. The data can also be utilized for conducting risk assessment studies to determine the suitability of these wastes for utilization purposes instead of disposal, which can result in savings related to disposal costs.

This study focused on addressing one of the greatest concerns to the industry: the environmentally-responsible management of large volumes of residual solids resulting from hydraulic fracturing operations by characterizing these wastes. This is important for continued sustainable development of unconventional shale gas production necessary for United States energy independence.

CHAPTER 7: OVERALL REFERENCES

American Public Health Association (APHA), American Waterworks Association (AWWA) and Water Environment Federation (WEF) (2012) Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D. C.

ASTM Standard D1193, 2006 (2011), "Standard Specification for Reagent Water", ASTM International, West Conshohocken, PA, 2011, 10.1520/D1193-06R11, http://www.astm.org/

ASTM Standard D3987, 2012, "Standard Practice for Shake Extraction of Solid Waste with Water", ASTM International, West Conshohocken, PA, 2012, 10.1520/D3987-12, http://www.astm.org/

Baba, A. and Kaya, A., Leaching characteristics of solid wastes from thermal power plants of western turkey and comparison of toxicity methodologies. *J Environ Manage* **2004,** *73*, (3), 199-207.

Balaba, R.S. and Smart, R.B., Total arsenic and selenium analysis in Marcellus shale, high-salinity water, and hydrofracture flowback wastewater. *Chemosphere* **2012,** *89*, (11), 1437-1442.

Bank, T.L., "Trace Metal Chemistry and Mobility in the Marcellus Shale". Paper Presented at the Technical Workshops for the Hydraulic Fracturing Study, February 24-25, 2011.

Barry, B. and Klima, M.S., Characterization of Marcellus Shale natural gas well drill cuttings. *Journal of Unconventional Oil and Gas Resources* **2013,** *1–2*, (0), 9-17.

Begos, K., (2012), Marcellus Shale becoming top US natural gas field, *Associated Press (AP)*, Yahoo! Finance, Retrieved from http://finance.yahoo.com/news/marcellus-shale-becoming-top-us-162527250.html

Bishop, P.L., Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes. *Hazardous Waste and Hazardous Materials* **1988,** *5*, (2), 129-143.

Blauch, M., Myers, R., Moore, T. and Lipinski, B., "Where is All the Salt Coming from and What are the Implications?". Paper Presented at the SPE Eastern Regional meeting, Charleston, WV, 23-25 September, 2009.

Bradham, W.S. and Caruccio, F.T., "A Comparative Study Of Tailings Analysis Using Acid/Base Accounting, Cells, Columns And Soxhlets". Paper Presented at the Mining and Reclamation Conference and Exhibition, Charleston, WV, April 23-26, 1990.

Carolyn J. Oblinger Childress, William T. Foreman, Brooke F. Connor and Maloney, T.J. (1999) *New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory*, U.S. Geological Survey. http://water.usgs.gov/owq/OFR_99-193/ofr99_193.pdf

Chang, E.E., Chiang, P.C., Lu, P.H. and Ko, Y.W., Comparisons of metal leachability for various wastes by extraction and leaching methods. *Chemosphere* **2001,** *45*, (1), 91-99.

Clean Earth, "Clean Earth of Williamsport, PA". Accessed on April 15, 2014 from http://www.cleanearthinc.com/Locations/Williamsport-PA

Countess, S.J. (2014) Evaluating Leachability of Residual Solids from Hydraulic Fracturing in the Marcellus Shale, Virginia Polytechnic Institute and State University, Blacksburg, VA.

Engelder, T. and Lash, G.G., (2008), Marcellus Shale Play's Vast Resource Potential Creating Stir in Appalachia, *The American Oil & Gas Reporter*, 52, The American Oil & Gas Reporter, Retrieved from http://www.aogr.com/magazine/cover-story/marcellus-shale-plays-vast-resource-potential-creating-stir-in-appalachia

Evans, J.S. and Kiesecker, J.M., Shale Gas, Wind and Water: Assessing the Potential Cumulative Impacts of Energy Development on Ecosystem Services within the Marcellus Play. *PLoS One* **2014,** *9*, (2), e89210.

Fällman, A.M. and Aurell, B., Leaching tests for environmental assessment of inorganic substances in wastes, Sweden. *Science of The Total Environment* **1996,** *178*, (1–3), 71-84.

Gaudlip, A.W., Paugh, L.O. and Hayes, T.D., "Marcellus Shale Water Management Challenges in Pennsylvania". Paper Presented at the SPE Shale Gas Production Conference, Fort Worth, Texas, U.S.A., 16–18 November, 2008.

Gregory, K.B., Vidic, R.D. and Dzombak, D.A., Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements* **2011,** *7*, (3), 181-186.

Groundwater Protection Council (GWPC) and ALL Consulting (2009) *Modern Shale Gas Development in the United States: A Primer*, DE-FG26-04NT15455. http://energy.gov/sites/prod/files/2013/03/f0/ShaleGasPrimer_Online_4-2009.pdf

Haluszczak, L.O., Rose, A.W. and Kump, L.R., Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* **2013,** *28*, (0), 55-61.

Hammer, R. and VanBriesen, J. (2012) *In Fracking's Wake: New Rules are Needed to Protect Our Health and Environment from Contaminated Wastewater*, D:12-05-A. http://www.nrdc.org/energy/files/fracking-wastewater-fullreport.pdf

Hansen, J.B., Holm, P.E., Hansen, E.A. and Hjelmar, O. (2000) *Nordtest Technical Report 473: Use of lysimeters for characterisation of leaching from soil and mainly inorganic waste materials*. http://www.nordtest.info/index.php/technical-reports/item/use-of-lysimeters-for-characterisation-of-leaching-from-soil-and-mainly-inorganic-waste-materials-nt-tr-473.html

Hayes, T. (2009) *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas*, Marcellus Shale Coalition. http://energyindepth.org/wp-content/uploads/marcellus/2012/11/MSCommission-Report.pdf

Hooper, K., Iskander, M., Sivia, G., Hussein, F., Hsu, J., DeGuzman, M., Odion, Z., Ilejay, Z., Sy, F., Petreas, M. and Simmons, B., Toxicity Characteristic Leaching Procedure Fails To Extract Oxoanion-Forming Elements That Are Extracted by Municipal Solid Waste Leachates. *Environmental Science & Technology* **1998,** *32*, (23), 3825-3830.

Jackson, D.R., Garrett, B.C. and Bishop, T.A., Comparison of batch and column methods for assessing leachability of hazardous waste. *Environmental Science & Technology* **1984,** *18*, (9), 668-673.

Jiang, Q., Rentschler, J., Perrone, R. and Liu, K., Application of ceramic membrane and ion-exchange for the treatment of the flowback water from Marcellus shale gas production. *Journal of Membrane Science* **2013,** *431*, 55-61.

Kalbe, U., Berger, W., Eckardt, J. and Simon, F.-G., Evaluation of leaching and extraction procedures for soil and waste. *Waste Manag* **2008,** *28*, (6), 1027-1038.

Kargbo, D.M., Wilhelm, R.G. and Campbell, D.J., Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environmental Science & Technology* **2010,** *44*, (15), 5679-5684.

Kim, A.G., "CCB Leaching summary: Survey of Methods and Results". Paper Presented at the Proceedings of Coal Combustion By-Products and Western Coal Mines: A Technical Interactive Forum, Allton, IL, 2002.

Kosson, D., Van der Sloot, H., Sanchez, F. and Garrabrants, A., An integrated framework for evaluating leaching in waste management and utilization of secondary materials. *Environmental Engineering Science* **2002,** *19*, (3), 159-204.

Kosson, D.S., van der Sloot, H.A. and Eighmy, T.T., An approach for estimation of contaminant release during utilization and disposal of municipal waste combustion residues. *Journal of Hazardous Materials* **1996,** *47*, (1–3), 43-75.

Krüger, O., Kalbe, U., Berger, W., Simon, F.G. and Meza, S.L., Leaching experiments on the release of heavy metals and PAH from soil and waste materials. *Journal of Hazardous Materials* **2012,** *207–208*, (0), 51-55.

Kylefors, K., Andreas, L. and Lagerkvist, A., A comparison of small-scale, pilot-scale and large-scale tests for predicting leaching behaviour of landfilled wastes. *Waste Manag* **2003,** *23*, (1), 45-59.

Lewin, K., Leaching tests for waste compliance and characterisation: recent practical experiences. *Science of The Total Environment* **1996,** *178*, (1–3), 85-94.

Liermann, L.J., Mathur, R., Wasylenki, L.E., Nuester, J., Anbar, A.D. and Brantley, S.L., Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. *Chemical Geology* **2011,** *281*, (3–4), 167-180.

Liroff, R.A. (2011) *Extracting the facts: An investor guide to disclosing risks from hydraulic fracturing operations*, Investor Environmental Health Network. http://www.iehn.org/documents/frackguidance.pdf

Mahmoudkhani, M., Wilewska-Bien, M., Steenari, B.-M. and Theliander, H., Evaluating two test methods used for characterizing leaching properties. *Waste Manag* **2008,** *28*, (1), 133-141.

Maloney, K.O. and Yoxtheimer, D.A., Production and Disposal of Waste Materials from Gas and Oil Extraction from the Marcellus Shale Play in Pennsylvania. *Environmental Practice* **2012,** *14*, 278-287.

New York State Water Resources Institute (NYS WRI), (2012), Waste Management of Cuttings, Drilling Fluids, Hydrofrack Water and Produced Water, *Gas Wells*, New York State Water Resources Institute Retrieved from http://wri.eas.cornell.edu/aboutus.html

NYSDEC (2011) *Revised Draft Supplemental Generic Environmental Impact Statement On The Oil, Gas and Solution Mining Regulatory Program*. http://www.dec.ny.gov/energy/75370.html

O'Leary, P.R. and Walsh, P., "Landfill Course; Lesson 4: Leachate Control and Treatment ". Accessed on July 28, 2014 from http://www.bvsde.paho.org/bvsair/e/repindex/repi49-50/lesson4/lesson4.html

Ohio EPA, (2014), Fact Sheet: Drill Cuttings from Oil and Gas Exploration in the Marcellus and Utica Shale Regions of Ohio, Ohio Environmental Protection Agency (EPA), Retrieved from http://epa.ohio.gov/Portals/34/document/fact_sheets/Fact%20Sheet%20on%20Drilling%20Muds%20and%20Cuttings%20Final%2010-01-13.pdf

Pennsylvania Department of Environmental Protection (PADEP), (2010), Hydraulic Fracturing Overview, Retrieved from http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/MarcellusShale/DEP%20Fracing%20overview.pdf

Perkct, C.L. and Webster, W.C. (1981) Literature Review of Batch Laboratory Leaching and Extraction Procedures. Conway, R.A. and Malioy, B.C. (eds), pp. 7-27, American Society for Testing and Materials.

Poon, C.S. and Chen, Z.Q., Comparison of the characteristics of flow-through and flow-around leaching tests of Solidified heavy metal wastes. *Chemosphere* **1999,** *38*, (3), 663-680.

Pritz, M.E. and Kirby, C.S., "Geochemical Investigation Of Marcellus Shale Natural Gas Hydrofracturing Waters". Paper Presented at the Northeastern Section (45th Annual) and Southeastern Section (59th Annual) Joint Meeting, Baltimore, MD, 13-16 March, 2010.

ProChem Tech, (2009), Marcellus Gas Well Hydrofracture Wastewater Disposal by Recycle Treatment Process, ProChemTech International Inc., Retrieved from http://prochemtech.com/Literature/TAB/PDF_TAB_Marcellus_Hydrofracture_Disposal_by_Recycle_1009.pdf

Quevauviller, P., van der Sloot, H.A., Ure, A., Muntau, H., Gomez, A. and Rauret, G., Conclusions of the workshop: harmonization of leaching/extraction tests for environmental risk assessment. *Science of The Total Environment* **1996,** *178*, (1–3), 133-139.

Rahm, B.G., Bates, J.T., Bertoia, L.R., Galford, A.E., Yoxtheimer, D.A. and Riha, S.J., Wastewater management and Marcellus Shale gas development: trends, drivers, and planning implications. *J Environ Manage* **2013,** *120*, 105-113.

Resnikoff, M., Alexandrova, E. and Travers, J. (2010) *Radioactivity in Marcellus Shale*, Radioactive Waste Management Associates. http://energy.wilkes.edu/PDFFiles/Library/Marcellus%20Shale%20Radioactivity%20Report%205-18-2010.pdf

Rigol, A., Mateu, J., González-Núñez, R., Rauret, G. and Vidal, M., pHstat vs. single extraction tests to evaluate heavy metals and arsenic leachability in environmental samples. *Analytica Chimica Acta* **2009,** *632*, (1), 69-79.

Roche, M., "Fracking concerns: Will Ohio start accepting drilling brine at 40 landfills?". Accessed on May 20, 2014 from http://www.norwalkreflector.com/article/2074481

Schlumberger, (1994), Designing and Managing Drilling Fluid, *Oilfield Review*, 6, Schlumberger, Retrieved from http://www.slb.com/~/media/Files/resources/oilfield_review/ors94/0494/p33_43.ashx

Shively, W., Bishop, P., Gress, D. and Brown, T., Leaching Tests of Heavy Metals Stabilized with Portland Cement. *Journal (Water Pollution Control Federation)* **1986,** *58*, (3), 234-241.

Siddique, R., Kaur, G. and Rajor, A., Waste foundry sand and its leachate characteristics. *Resources, Conservation and Recycling* **2010,** *54*, (12), 1027-1036.

Skalak, K.J., Engle, M.A., Rowan, E.L., Jolly, G.D., Conko, K.M., Benthem, A.J. and Kraemer, T.F., Surface disposal of produced waters in western and southwestern Pennsylvania: Potential for accumulation of alkali-earth elements in sediments. *International Journal of Coal Geology* **2014,** *126*, (0), 162-170.

Stanforth, R., Ham, R., Anderson, M. and Stegmann, R., Development of a Synthetic Municipal Landfill Leachate. *Journal (Water Pollution Control Federation)* **1979,** *51*, (7), 1965-1975.

Tarun R. Naik, F.C., Yoon-moon Chun (2003) *Uses of CKD Other Than for Flue Gas Desulfurization*, CBU-2003-35. https://www4.uwm.edu/cbu/Papers/2003%20CBU%20Reports/REP-529.pdf

Tiruta-Barna, L., Imyim, A. and Barna, R., Long-term prediction of the leaching behavior of pollutants from solidified wastes. *Advances in Environmental Research* **2004,** *8*, (3–4), 697-711.

US Energy Information Administration (EIA) and Advanced Resources International Inc (ARI) (2013a) *EIA/ARI World Shale Gas and Shale Oil Resource Assessment*. http://www.adv-res.com/pdf/A_EIA_ARI_2013%20World%20Shale%20Gas%20and%20Shale%20Oil%20Resource%20Assessment.pdf

US Energy Information Administration (EIA) and Advanced Resources International Inc (ARI) (2013b) *Technically Recoverable Shale Gas and Shale Oil Resources: An Assessment of 137 Shale Formations in 41 Countries Outside the United States.* http://www.adv-res.com/pdf/A_EIA_ARI_2013%20World%20Shale%20Gas%20and%20Shale%20Oil%20Resource%20Assessment.pdf

Subpart C—Characteristics of Hazardous Waste, 40 CFR 261.24, Identification and Listing of Hazardous Waste, (1984), US Environmental Protection Agency (USEPA).

Method 1311: Toxicity Characteristic Leaching Procedure (TCLP), SW846: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, (1992), USEPA.

Method 1312: Synthetic Precipitation Leaching Procedure, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), (1994), USEPA.

Guidelines Establishing Test Procedures For The Analysis Of Pollutants, 40 CFR 136 Appendix B: Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11, (1997), US Environmental Protection Agency (USEPA).

USEPA (2002) *Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations*, EPA530-K-01-004, US Environmental Protection Agency,. http://www.epa.gov/epawaste/nonhaz/industrial/special/oil/oil-gas.pdf

USEPA (2012) *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, EPA/601/R-12/011. http://www2.epa.gov/sites/production/files/documents/hf-report20121214.pdf

van der Sloot, H.A., Leaching Behaviour of Waste and Stabilized Waste Materials; Characterization for Environmental Assessment Purposes. *Waste Management & Research* **1990,** *8*, (1), 215-228.

van der Sloot, H.A., Quick techniques for evaluating the leaching properties of waste materials: their relation to decisions on utilization and disposal. *TrAC Trends in Analytical Chemistry* **1998,** *17*, (5), 298-310.

Wang, Z. and Krupnick, A. (2013) *A Retrospective Review of Shale Gas Development in the United States: What Led to the Boom?*, RFF DP 13-12.

Washington State Department of Ecology (WSDOE) (2003) *An Assessment of Laboratory Leaching Tests for Predicting the Impacts of Fill Material on Ground Water and Surface Water Quality*, 03-09-107. https://fortress.wa.gov/ecy/publications/publications/0309107.pdf

Winslow, S.D., Pepich, B.V., Martin, J.J., Hallberg, G.R., Munch, D.J., Frebis, C.P., Hedrick, E.J. and Krop, R.A., Statistical procedures for determination and verification of minimum reporting levels for drinking water methods. *Environ Sci Technol* **2006,** *40*, (1), 281-288.

APPENDIX A: TABLE REPRESENTING ELEMENTS OF POTENTIAL CONCERN, ANALYTICAL MASS MONITORED, METHOD DETECTION LIMIT, MINIMUM REPORTING LEVEL AND ANALYTICAL INSTRUMENT CALIBRATION RANGE

Note:

(1) Concentrations detected below Method Detection Limit (MDL) are assumed to be 'zero' and represented in 'Tables' by the term 'BDL'; (2) Concentrations detected between MDL and Method Reporting Level (MRL) is considered estimated and represented in 'Tables' by the term 'Trace'; (3) Concentrations detected beyond the analytical range considered estimated since it exceeds the linear range of the instrument and is represented in 'Tables' by an 'Underscore' below the represented concentration.

Sl No.	Elements Of Potential Concern	Symbol	Isotope	Method Detection Limit (ppb)	Minimum Reporting Level (ppb)	Analytical Range (ppb)
1	Aluminum	Al	27	0.07	1	0.05 - 2000
2	Antimony	Sb	121	0.02	0.1	0.1 - 20
3	Arsenic	As	75	0.07	0.5	0.1 - 20
4	Barium	Ba	137	0.92	50	0.05 - 2000
5	Beryllium	Be	9	0.10	0.5	0.1 - 20
6	Boron	B	11	0.60	10	0.05 - 2000
7	Bromide	Br	79	2.11	20	0.5 - 100
8	Cadmium	Cd	111	0.09	1	0.05 - 2000
9	Calcium	Ca	43	12.19	50	0.5 - 20000
10	Chromium	Cr	52	0.10	1	0.05 - 2000
11	Cobalt	Co	59	0.02	0.1	0.05 - 2000
12	Copper	Cu	65	0.19	1	0.05 - 2000
13	Iron	Fe	54	0.79	10	0.5 - 20000
14	Lead	Pb	208	0.03	1	0.05 - 2000
15	Lithium	Li	7	0.13	10	0.05 - 2000
16	Magnesium	Mg	25	0.81	10	0.5 - 20000
17	Manganese	Mn	55	0.05	1	0.05 - 2000
18	Mercury	Hg	202	0.10	0.5	0.5 - 20
19	Molybdenum	Mo	98	1.85	50	0.05 - 2000
20	Nickel	Ni	60	0.03	0.1	0.05 - 2000
21	Phosphorus	P	31	3.02	50	0.05 - 2000
22	Potassium	K	39	4.54	100	0.5 - 20000

APPENDIX A: TABLE REPRESENTING ELEMENTS OF POTENTIAL CONCERN, ANALYTICAL MASS MONITORED, METHOD DETECTION LIMIT, MINIMUM REPORTING LEVEL AND ANALYTICAL INSTRUMENT CALIBRATION RANGE

Sl No.	Elements Of Potential Concern	Symbol	Isotope	Method Detection Limit (ppb)	Minimum Reporting Level (ppb)	Analytical Range (ppb)
23	Selenium	Se	78	0.67	5	0.1 - 20
24	Silicon	Si	28	0.75	10	0.05 - 2000
25	Silver	Ag	107	0.02	0.1	0.05 - 2000
26	Sodium	Na	23	10.91	100	0.5 - 20000
27	Strontium	Sr	88	0.24	10	0.05 - 2000
28	Sulfate	SO_4	34	392.27	1000	5 - 10000
29	Uranium	U	238	0.01	0.05	0.05 - 2000
30	Vanadium	V	51	0.32	10	0.05 - 2000
31	Zinc	Zn	66	0.38	10	0.05 - 2000
32	Zirconium	Zr	90	0.04	0.5	0.1 - 20

APPENDIX B: RESULTS OF SHAKE EXTRACTION TEST USING FOUR DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLE

Note:

(1) All concentrations of Elements of Concern (EOC) are in ppb (parts per billion); (2) Concentration indicated are an average of the replicates and have been corrected for the dilution factor; (3) 'BDL' indicates the concentration was below Method Detection Limit (MDL); (4) Concentrations in grey with italics indicates the concentration was detected below Minimum Reporting Level (MRL) but above MDL; (5) Underline indicates the concentration was detected beyond the calibrated concentration range of the analytical instrument; (6) The MDL and MRL values have also been multiplied by the dilution factor.

a) **Treated Solids**

			TREATED SOLIDS			
EOC	**MDL**	**MRL**	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**
Alkali Metals						
Li	1.30	100	3,850	3,866	7,630	11,590
K	45.38	1000	26,774	26,828	29,214	28,043
Na	109.15	1000	1,057,883	1,051,886	1,075,221	720,667
Alkaline Earth Metals						
Ba	9.16	500	67,374	65,810	182,056	182,131
Be	1.01	5	BDL	BDL	BDL	BDL
Ca	121.88	500	467,304	470,199	1,878,163	1,765,570
Mg	8.15	100	50,216	50,374	101,541	97,196
Sr	2.36	100	120,465	119,865	201,463	179,193
Transition Metals						
U	0.05	0.5	BDL	BDL	*0.38*	5.76
Zr	0.39	5	BDL	BDL	BDL	*0.92*
V	3.21	100	*6.79*	*5.09*	*4.94*	*4.80*
Cr	1.05	10	BDL	BDL	*8.10*	58.75
Mo	18.49	500	BDL	BDL	BDL	BDL
Mn	0.50	10	389.15	416.48	19,386	18,347
Fe	7.92	100	BDL	*9.91*	1,336	14,283
Co	0.21	1	*0.75*	*0.83*	33.64	43.12
Ni	0.34	1	8.53	8.65	109.88	134.33

			TREATED SOLIDS			
EOC	**MDL**	**MRL**	**EF DDI**	**EF 4.2**	**EF 2.9**	**EF SLL**
Cu	1.94	10	12.28	17.21	51.81	455.70
Ag	0.15	1	BDL	BDL	BDL	BDL
Cd	0.92	10	BDL	BDL	*3.81*	*4.59*
Hg	0.99	5	BDL	BDL	BDL	BDL
Zn	3.80	100	*7.29*	*7.53*	726.74	1,192
Post Transition Metals						
Al	0.69	10	104.34	121.34	5,769	92,202
Pb	0.31	10	BDL	BDL	*2.91*	22.77
Metalloids						
B	6.04	100	1,716	1,776	3,146	2,960
Si	7.46	100	257.07	242.80	12,548	20,664
Sb	0.22	1	BDL	BDL	*0.37*	1.51
As	0.72	5	BDL	BDL	BDL	BDL
Other Metals						
P	30.23	500	BDL	BDL	BDL	BDL
Se	6.71	50	BDL	BDL	BDL	BDL
S	3,922.66	10000	*7,951*	*9,064*	*5,373*	BDL
Halogen						
Br	21.13	200	22,952	23,054	22,995	22,967

b) Raw Solids

			RAW SOLIDS			
EOC	**MDL**	**MRL**	**EF DDI**	**EF ~ 4.2**	**EF ~ 2.9**	**EF SLL**
Alkali Metals						
Li	1.30	100	2,257	2,294	2,483	2,237
K	45.38	1000	29,574	29,578	30,677	28,713
Na	109.15	1000	881,617	871,686	828,688	172,667
Alkaline Earth Metals						
Ba	9.16	500	18,114	17,340	33,176	41,018
Be	1.01	5	BDL	BDL	BDL	9.13

APPENDIX B: RESULTS OF SHAKE EXTRACTION TEST USING FOUR DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLE

			RAW SOLIDS			
EOC	**MDL**	**MRL**	**EF DDI**	**EF ~ 4.2**	**EF ~ 2.9**	**EF SLL**
Ca	121.88	500	532,604	534,233	1,764,163	1,645,570
Mg	8.15	100	24,560	26,711	234,575	219,286
Sr	2.36	100	95,128	95,765	131,063	145,893
Transition Metals						
U	0.05	0.5	*0.06*	BDL	2.91	15.45
Zr	0.39	5	BDL	BDL	BDL	*1.94*
V	3.21	100	*5.48*	*6.15*	*5.13*	*5.19*
Cr	1.05	10	*1.36*	*1.26*	10.89	171.03
Mo	18.49	500	BDL	BDL	BDL	BDL
Mn	0.50	10	*7.50*	13.03	16,016	18,261
Fe	7.92	100	*31.68*	BDL	169.26	29,429
Co	0.21	1	*0.58*	*0.56*	82.42	125.67
Ni	0.34	1	6.19	6.13	223.02	275.53
Cu	1.94	10	40.15	56.87	65.40	903.33
Ag	0.15	1	BDL	BDL	BDL	BDL
Cd	0.92	10	BDL	BDL	*8.73*	11.21
Hg	0.99	5	BDL	BDL	BDL	BDL
Zn	3.80	100	*40.11*	*38.28*	512.91	1,084
Post Transition Metals						
Al	0.69	10	27.16	17.25	404.66	30,936
Pb	0.31	10	*0.59*	BDL	*0.57*	14.26
Metalloids						
B	6.04	100	1,194	1,223	3,592	3,035
Si	7.46	100	4,205	4,270	37,381	56,307
Sb	0.22	1	1.15	*0.99*	2.30	5.11
As	0.72	5	BDL	BDL	BDL	5.13
Other Metals						
P	30.23	500	BDL	BDL	BDL	BDL
Se	6.71	50	BDL	BDL	BDL	BDL
S	3,922.66	10000	18,075	19,627	BDL	BDL
Halogen						

			RAW SOLIDS			
EOC	**MDL**	**MRL**	**EF DDI**	**EF ~ 4.2**	**EF ~ 2.9**	**EF SLL**
Br	21.13	200	20,265	20,411	18,548	20,597

c) Solidified Solids

			SOLIDIFIED SOLIDS			
EOC	**MDL**	**MRL**	**EF DDI**	**EF ~ 4.2**	**EF ~ 2.9**	**EF SLL**
Alkali Metals						
Li	1.30	100	*27.55*	*28.57*	*81.25*	110.53
K	45.38	1000	17,158	17,778	20,224	20,057
Na	109.15	1000	1,494,883	1,495,552	1,470,555	909,667
Alkaline Earth Metals						
Ba	9.16	500	660.63	*483.45*	*278.15*	*390.24*
Be	1.01	5	BDL	BDL	BDL	11.10
Ca	121.88	500	295,037	294,266	1,888,163	1,782,570
Mg	8.15	100	10,931	11,784	120,475	120,986
Sr	2.36	100	19,565	19,538	36,897	49,869
Transition Metals						
U	0.05	0.5	*0.10*	BDL	12.21	20.66
Zr	0.39	5	BDL	BDL	*0.64*	7.68
V	3.21	100	*25.02*	*23.91*	*10.33*	*15.48*
Cr	1.05	10	*6.52*	*6.19*	*6.49*	117.73
Mo	18.49	500	*202.40*	*202.33*	*75.08*	*53.64*
Mn	0.50	10	10.07	11.90	15,070	20,157
Fe	7.92	100	*55.79*	*61.41*	*24.62*	14,659
Co	0.21	1	*0.25*	BDL	48.71	88.55
Ni	0.34	1	4.45	3.78	275.38	387.47
Cu	1.94	10	61.33	61.10	71.31	1,011
Ag	0.15	1	BDL	BDL	BDL	BDL
Cd	0.92	10	BDL	BDL	*7.95*	*9.90*
Hg	0.99	5	BDL	BDL	BDL	BDL
Zn	3.80	100	*48.52*	*37.78*	194.77	738.63

			SOLIDIFIED SOLIDS			
EOC	**MDL**	**MRL**	**EF DDI**	**EF ~ 4.2**	**EF ~ 2.9**	**EF SLL**
Post Transition Metals						
Al	0.69	10	205.00	200.54	706.29	39,609
Pb	0.31	10	*1.83*	*1.30*	92.92	947.27
Metalloids						
B	6.04	100	366.87	376.97	847.87	755.83
Si	7.46	100	3,360	3,285	21,528	46,974
Sb	0.22	1	5.38	5.01	13.52	21.27
As	0.72	5	BDL	BDL	BDL	16.80
Other Metals						
P	30.23	500	BDL	BDL	BDL	BDL
Se	6.71	50	BDL	BDL	BDL	*12.61*
S	3,922.66	10000	828,585	830,844	934,897	839,727
Halogen						
Br	21.13	200	1,217	1,138	1,114	1,246

d) Drilling Mud

			DRILLING MUD			
EOC	**MDL**	**MRL**	**EF DDI**	**EF ~ 4.2**	**EF ~ 2.9**	**EF SLL**
Alkali Metals						
Li	1.30	100	*66.81*	*66.08*	137.47	133.47
K	45.38	1000	20,698	20,495	24,120	24,400
Na	109.15	1000	3,194,550	3,075,219	3,054,221	2,734,000
Alkaline Earth Metals						
Ba	9.16	500	869.67	765.45	768.31	958.27
Be	1.01	5	BDL	BDL	BDL	*1.94*
Ca	121.88	500	66,830	66,049	732,896	687,403
Mg	8.15	100	3,161	3,031	34,351	20,819
Sr	2.36	100	30,395	29,262	49,977	59,759
Transition Metals						

Appendix B: Results Of Shake Extraction Test Using Four Different Leaching Solutions On Residual Solids Sample

			DRILLING MUD			
EOC	**MDL**	**MRL**	**EF DDI**	**EF ~ 4.2**	**EF ~ 2.9**	**EF SLL**
U	0.05	0.5	1.52	1.15	8.20	16.32
Zr	0.39	5	*0.76*	*0.71*	*1.23*	*2.72*
V	3.21	100	*23.02*	*19.87*	*15.44*	*24.28*
Cr	1.05	10	*5.21*	*4.44*	52.57	151.89
Mo	18.49	500	*70.09*	*67.57*	BDL	BDL
Mn	0.50	10	517.25	422.58	15,343	15,121
Fe	7.92	100	448.90	399.88	9,571	17,339
Co	0.21	1	*0.74*	*0.53*	83.85	89.89
Ni	0.34	1	16.90	16.24	330.65	363.43
Cu	1.94	10	80.60	67.30	449.19	815.50
Ag	0.15	1	*0.57*	*0.52*	*0.72*	*0.54*
Cd	0.92	10	BDL	BDL	15.77	16.17
Hg	0.99	5	*1.55*	BDL	BDL	BDL
Zn	3.80	100	*60.24*	*40.06*	1,207	1,089
Post Transition Metals						
Al	0.69	10	1,127	1,003	4,779	11,159
Pb	0.31	10	10.88	10.55	1,156	1,790
Metalloids						
B	6.04	100	BDL	BDL	*51.33*	*18.47*
Si	7.46	100	2,185	1,847	9,993	10,694
Sb	0.22	1	4.52	4.23	9.57	16.16
As	0.72	5	16.85	16.31	32.04	98.26
Other Metals						
P	30.23	500	*81.59*	*74.22*	*63.83*	*338.76*
Se	6.71	50	*11.84*	*14.31*	*9.01*	*10.06*
S	3,922.66	10000	225,085	224,077	199,197	206,560
Halogen						
Br	21.13	200	1,456	1,420	1,567	1,751

APPENDIX C: SUMMARY OF SAMPLE MASS LOST DURING IMMERSION TEST

Note:

(1) All weight measurements are approximated to ± 0.01 g; (2) Test Piece comprises of the tea mesh ball, muslin cloth and the sample contained within them; (3) Weight of the test piece measured at the end of the seventh replenishment period or leaching experiment; (4) Weight of the test piece after drying the wet test piece in an oven at 103-105 °C till constant mass was achieved; (5) Most of these sample losses determined are mostly exaggerated due to losses that occurred at the time of handling. Hence, these numbers are only representative of the sample loss behavior that can be expected during the immersion test.

Sample	**Leaching Solution**	**Sample Weight, g**	**Initial Test Piece (2) Weight, g**	**Test Piece Weight (Wet) (3), g**	**Final Test Piece Weight (Dry) (4), g**	**Sample Weight Loss, g**
Treated Solids	EF DDI	100	130.82	169.59	101.26	29.56
	EF 2.9	100	133.78	156.5	94.52	39.26
	EF 4.2	100	131.91	164.1	102.9	29.01
Raw Solids	EF DDI	100	131.15	181.89	103.08	28.07
	EF 2.9	100	131.26	169.24	93.93	37.33
	EF 4.2	100	130.93	178.8	102.9	28.03
Solidified Solids	EF DDI	100	131.62	178.45	117.44	14.18
	EF 2.9	100	133.25	173.66	111.16	22.09
	EF 4.2	100	132.61	183.65	119.1	13.51

Appendix D: Results of Immersion Test Using Three Different Leaching Solutions On Residual Solids Samples

Note:

(1) All concentrations of Elements of Concern (EOC) are in ppb (parts per billion); (2) ‘BDL’ indicates the concentration was below Method Detection Limit (MDL); (3) Concentrations in grey with italics indicates the concentration was detected below Minimum Reporting Level (MRL) but above MDL; (4) Underline indicates the concentration was detected beyond the calibrated concentration range of the analytical instrument; (5) ‘NA’ indicates that concentrations in all the eluates were measured below MRL value.

a.1) Treated solids; EF DDI

TREATED SOLIDS

			EF DDI							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**7.74**	**7.75**	**8.02**	**7.86**	**7.4**	**7.94**	**8.16**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10	6,515	1,800	900.60	768.80	736.10	684.50	564.40	1,710
K	4.54	100	47,890	7,156	2,675	1,902	2,045	1,886	2,196	9,393
Na	10.91	100	2,126,614	139,697	14,524	3,914	2,161	2,292	3,829	327,576
Alkaline Earth Metals										
Ba	0.92	50	139,496	12,987	3,832	3,246	2,251	1,401	529.41	23,392
Be	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Ca	12.19	50	957,499	82,790	32,266	36,107	41,488	45,892	44,980	177,289
Mg	0.81	10	99,916	7,894	3,037	5,132	6,894	9,664	10,357	20,413

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

TREATED SOLIDS

			EF DDI							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**7.74**	**7.75**	**8.02**	**7.86**	**7.4**	**7.94**	**8.16**	
EOC	**MDL**	**MRL**								
Sr	0.24	10	200,297	20,153	7,272	8,685	10,647	15,039	15,869	39,709
Transition Metals										
U	0.01	0.05	BDL	BDL	BDL	BDL	BDL	*0.03*	*0.02*	NA
Zr	0.04	0.5	*0.06*	*0.08*	*0.04*	*0.07*	BDL	*0.05*	*0.06*	NA
V	0.32	10	*5.77*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Cr	0.10	1	BDL	BDL	BDL	BDL	BDL	BDL	*0.92*	NA
Mo	1.85	50	*16.54*	*17.52*	*24.99*	*19.38*	*16.43*	*19.84*	*25.08*	NA
Mn	0.05	1	939.20	56.64	31.18	46.69	72.94	82.89	*0.65*	175.74
Fe	0.79	10	BDL	*4.43*	*3.10*	*1.39*	*2.60*	*2.72*	BDL	NA
Co	0.02	0.1	0.38	0.32	0.27	0.27	0.30	0.40	0.36	0.33
Ni	0.03	0.1	BDL	5.69	5.36	4.86	3.95	5.69	7.81	4.76
Cu	0.19	1	15.59	9.28	8.55	7.44	8.32	13.87	15.64	11.24
Ag	0.02	0.1	0.12	BDL	BDL	BDL	BDL	BDL	BDL	NA
Cd	0.09	1	*0.36*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Hg	0.10	0.5	BDL	*0.13*	BDL	BDL	BDL	BDL	BDL	NA
Zn	0.38	10	18.77	*8.19*	BDL	*2.78*	BDL	BDL	*6.63*	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

TREATED SOLIDS

			EF DDI							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**7.74**	**7.75**	**8.02**	**7.86**	**7.4**	**7.94**	**8.16**	
EOC	**MDL**	**MRL**								
Post Transition Metals										
Al	0.07	1	108.57	273.10	148.00	108.15	78.36	60.23	49.66	118.01
Pb	0.03	1	*0.24*	BDL	*0.17*	*0.14*	*0.22*	*0.19*	*0.11*	NA
Metalloids										
B	0.60	10	2,523	1,435	921.10	640.80	454.00	373.60	336.80	954.90
Si	0.75	10	563.57	517.35	712.60	1,022	1,320	1,607	1,533	1,039
Sb	0.02	0.1	0.35	0.58	0.83	0.56	0.98	1.14	0.90	0.76
As	0.07	0.5	5.07	*0.28*	BDL	BDL	*0.08*	0.54	*0.48*	0.92
Other Metals										
P	3.02	50	BDL	BDL	*11.15*	*13.86*	*12.25*	*13.22*	*15.48*	NA
Se	0.67	5	*3.13*	*1.75*	BDL	BDL	BDL	BDL	*3.14*	NA
S	392.27	1000	7,331	11,092	17,010	15,880	15,630	17,960	30,480	16,483
Halogen										
Br	2.11	20	51,134	3,047	230.51	55.04	30.77	34.65	49.08	7,797

a. 2) Treated Solids; EF 2.9

			TREATED SOLIDS							
			EF 2.9							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.94**	**4.59**	**4.37**	**4.55**	**3.91**	**3.7**	**3.99**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10	6,295	3,809	3,895	5,433	8,674	4,721	652.00	4,783
K	4.54	100	59,851	7,840	5,556	5,288	5,099	7,389	8,894	14,274
Na	10.91	100	2,414,727	86,737	12,838	7,288	6,483	8,169	9,151	363,627
Alkaline Earth Metals										
Ba	0.92	50	185,949	78,783	66,376	65,413	53,881	17,217	51,478	74,157
Be	0.10	0.5	BDL	BDL	BDL	BDL	3.24	6.56	4.72	2.07
Ca	12.19	50	1,837,526	748,889	1,013,651	952,790	281,624	52,795	35,625	703,271
Mg	0.81	10	174,773	31,330	19,804	23,214	16,337	6,753	5,420	39,662
Sr	0.24	10	244,188	62,524	56,766	69,708	58,268	72,058	90,338	93,407
Transition Metals										
U	0.01	0.05	0.07	*0.01*	*0.03*	0.09	1.52	5.06	5.55	1.76
Zr	0.04	0.5	*0.12*	BDL	BDL	*0.12*	*0.33*	*0.37*	*0.09*	NA
V	0.32	10	*6.70*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Cr	0.10	1	BDL	BDL	BDL	4.57	64.80	98.58	100.87	38.40
Mo	1.85	50	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			TREATED SOLIDS							
			EF 2.9							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.94**	**4.59**	**4.37**	**4.55**	**3.91**	**3.7**	**3.99**	
EOC	**MDL**	**MRL**								
Mn	0.05	1	9,915	8,760	11,069	11,329	4,572	1,803	1,520	6,995
Fe	0.79	10	202.85	115.00	406.68	2,322	13,383	21,351	23,904	8,812
Co	0.02	0.1	9.26	6.49	11.09	31.92	53.59	42.43	43.91	28.38
Ni	0.03	0.1	23.29	42.42	57.36	80.65	103.92	118.53	134.87	80.15
Cu	0.19	1	26.01	17.27	28.21	7.50	50.45	447.18	468.23	149.26
Ag	0.02	0.1	0.19	*0.02*	*0.02*	*0.02*	*0.04*	*0.03*	*0.06*	NA
Cd	0.09	1	5.03	*0.46*	*0.48*	1.00	2.24	1.84	1.19	1.75
Hg	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Zn	0.38	10	175.60	2,821	234.81	336.30	1,940	1,496	733.58	1,105
Post Transition Metals										
Al	0.07	1	517.66	242.47	1,521	6,905	127,161	112,790	69,847	45,569
Pb	0.03	1	16.00	1.08	*0.52*	BDL	5.27	10.00	33.77	9.52
Metalloids										
B	0.60	10	3,712	1,665	851.60	658.40	441.40	418.10	428.50	1,168
Si	0.75	10	4,108	6,639	7,809	8,489	20,877	23,198	27,468	14,084
Sb	0.02	0.1	0.75	0.48	0.22	0.42	0.20	*0.04*	*0.07*	0.31
As	0.07	0.5	8.45	*0.20*	0.57	*0.36*	*0.26*	*0.23*	*0.35*	1.49

			TREATED SOLIDS							
			EF 2.9							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.94**	**4.59**	**4.37**	**4.55**	**3.91**	**3.7**	**3.99**	
EOC	**MDL**	**MRL**								
Other Metals										
P	3.02	50	BDL	BDL	BDL	*21.72*	*23.69*	*26.44*	*8.97*	NA
Se	0.67	5	*3.20*	*1.15*	BDL	BDL	BDL	BDL	BDL	NA
S	392.27	1000	6,730	3,022	9,229	8,775	2,615	12,350	9,891	7,516
Halogen										
Br	2.11	20	56,745	2,066	236.93	69.07	57.38	78.14	106.54	8,480

a.3) Treated Solids; EF 4.2

						TREATED SOLIDS				
						EF 4.2				
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**6.48**	**6.66**	**7.08**	**7.28**	**7.43**	**7.49**	**8.21**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10	303.05	489.30	689.50	700.30	448.10	530.80	561.40	531.78
K	4.54	100	BDL	6,754	1,690	1,850	1,397	2,018	2,200	2,273
Na	10.91	100	222,348	129,198	9,728	2,923	1,334	1,615	2,289	52,776
Alkaline Earth Metals										
Ba	0.92	50	5,574	3,301	2,668	2,534	2,211	2,146	2,220	2,951
Be	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Ca	12.19	50	38,499	96,172	16,827	20,630	16,782	21,416	29,155	34,211
Mg	0.81	10	3,836	5,136	1,400	1,990	1,593	2,738	5,456	3,164
Sr	0.24	10	9,281	15,696	3,621	4,378	3,992	6,178	11,769	7,845
Transition Metals										
U	0.01	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Zr	0.04	0.5	BDL	BDL	BDL	BDL	BDL	BDL	*0.08*	NA
V	0.32	10	*2.05*	*0.43*	BDL	BDL	BDL	BDL	BDL	NA
Cr	0.10	1	*0.47*	BDL	BDL	BDL	BDL	BDL	BDL	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

							TREATED SOLIDS			
							EF 4.2			
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**6.48**	**6.66**	**7.08**	**7.28**	**7.43**	**7.49**	**8.21**	
EOC	**MDL**	**MRL**								
Mo	1.85	50	BDL	*1.89*	*14.62*	*23.12*	*13.10*	*16.67*	*17.27*	NA
Mn	0.05	1	52.59	9.27	35.27	54.73	40.19	49.15	82.41	46.23
Fe	0.79	10	57.93	BDL	*9.76*	76.64	35.42	23.25	19.39	31.77
Co	0.02	0.1	BDL	0.13	0.29	0.33	0.18	0.21	0.25	0.20
Ni	0.03	0.1	BDL	0.63	5.99	6.20	2.80	3.91	3.94	3.35
Cu	0.19	1	BDL	*0.55*	2.83	2.65	*0.85*	BDL	*0.47*	1.05
Ag	0.02	0.1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Cd	0.09	1	*0.23*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Hg	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Zn	0.38	10	*2.59*	174.38	BDL	*4.96*	BDL	BDL	BDL	25.99
Post Transition Metals										
Al	0.07	1	1.93	18.23	86.87	81.13	142.40	124.66	70.66	75.13
Pb	0.03	1	*0.86*	BDL	*0.28*	*0.71*	*0.17*	*0.30*	BDL	NA
Metalloids										
B	0.60	10	132.70	548.10	1,424	966.20	432.10	505.70	551.40	651.46
Si	0.75	10	BDL	1,359	257.80	506.10	432.80	671.20	1,101	618.34

			TREATED SOLIDS							
			EF 4.2							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**6.48**	**6.66**	**7.08**	**7.28**	**7.43**	**7.49**	**8.21**	
EOC	**MDL**	**MRL**								
Sb	0.02	0.1	0.11	0.42	0.25	0.72	0.55	0.92	*0.07*	0.43
As	0.07	0.5	0.55	1.14	BDL	BDL	BDL	BDL	*0.23*	NA
Other Metals										
P	3.02	50	260.10	*14.45*	*17.03*	*14.29*	BDL	*5.83*	*3.05*	NA
Se	0.67	5	*0.76*	BDL	*2.14*	*3.02*	*1.89*	BDL	BDL	NA
S	392.27	1000	1,945	7,701	7,445	9,538	5,260	9,760	8,946	7,228
Halogen										
Br	2.11	20	2,916	3,143	187.68	56.53	24.77	41.85	67.27	919.56

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

b.1) Raw Solids; EF DDI

			RAW SOLIDS							
			EF DDI							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**8.05**	**8.88**	**9.32**	**8.43**	**7.92**	**8.14**	**8.47**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10.00	4,140	466.20	161.90	123.00	104.30	78.12	69.74	734.70
K	4.54	100	49,740	8,701	3,561	2,416	2,426	1,865	1,762	10,067
Na	10.91	100	1,671,614	128,697	20,724	6,728	2,866	1,178	871.80	261,811
Alkaline Earth Metals										
Ba	0.92	50	29,286	4,673	1,564	1,843	2,299	2,733	2,679	6,440
Be	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Ca	12.19	50	1,051,599	83,970	25,766	27,117	31,528	30,722	33,370	183,439
Mg	0.81	10	45,006	4,011	1,299	1,989	2,956	3,596	5,263	9,160
Sr	0.24	10	166,797	14,793	3,889	3,962	4,346	4,785	4,934	29,072
Transition Metals										
U	0.01	0.05	*0.02*	*0.01*	*0.02*	*0.04*	*0.04*	0.08	0.16	0.05
Zr	0.04	0.5	BDL	*0.05*	BDL	BDL	BDL	BDL	BDL	NA
V	0.32	10	*5.56*	*1.25*	*2.29*	*1.43*	*1.02*	*0.71*	*0.57*	NA
Cr	0.10	1	BDL	*0.35*	1.71	1.39	1.10	*0.55*	*0.22*	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			RAW SOLIDS						
			EF DDI						
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**8.05**	**8.88**	**9.32**	**8.43**	**7.92**	**8.14**	**8.47**	
EOC	**MDL**	**MRL**								
Mo	1.85	50	*12.62*	*10.71*	*12.02*	*8.00*	*6.88*	*7.62*	*11.39*	NA
Mn	0.05	1	15.98	BDL	1.83	1.17	3.61	3.39	4.27	4.32
Fe	0.79	10	BDL	BDL	*2.63*	*1.00*	14.17	*5.05*	*2.88*	NA
Co	0.02	0.1	0.39	0.11	*0.04*	*0.06*	*0.08*	*0.06*	0.13	0.12
Ni	0.03	0.1	BDL	0.72	0.17	BDL	BDL	*0.05*	0.43	0.20
Cu	0.19	1	1.19	2.74	1.84	1.16	1.09	*0.40*	BDL	1.20
Ag	0.02	0.1	*0.07*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Cd	0.09	1	*0.34*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Hg	0.10	0.5	BDL	*0.24*	BDL	0.67	*0.48*	*0.24*	BDL	NA
Zn	0.38	10	*5.64*	BDL	*2.79*	BDL	BDL	*1.37*	BDL	NA
Post Transition Metals										
Al	0.07	1	7.91	27.25	46.27	33.69	76.87	44.46	28.52	37.85
Pb	0.03	1	BDL	BDL	BDL	BDL	BDL	*0.11*	BDL	NA
Metalloids										NA
B	0.60	10	1,341	1,290	1,123	773.50	572.70	405.00	358.20	837.63
Si	0.75	10	3,213	5,709	6,851	7,587	8,531	8,299	8,892	7,012

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			RAW SOLIDS							
			EF DDI							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**8.05**	**8.88**	**9.32**	**8.43**	**7.92**	**8.14**	**8.47**	
EOC	**MDL**	**MRL**								
Sb	0.02	0.1	0.95	2.11	2.66	2.32	2.33	2.19	2.60	2.17
As	0.07	0.5	7.36	4.59	10.40	9.13	7.89	6.76	6.97	7.59
Other Metals										
P	3.02	50	BDL	BDL	*41.85*	*33.93*	*30.17*	*18.18*	*13.11*	NA
Se	0.67	5	*1.18*	BDL	BDL	BDL	BDL	BDL	BDL	NA
S	392.27	1000	18,301	20,492	31,100	27,830	21,910	13,760	12,430	20,832
Halogen										
Br	2.11	20	44,914	3,008	275.61	33.74	*5.54*	*8.20*	*6.96*	6,893

b.2) Raw solids; EF 2.9

			RAW SOLIDS							
			EF 2.9							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.71**	**4.15**	**4.06**	**4.58**	**4.26**	**4.26**	**4.3**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10.00	4,846	576.20	335.30	258.70	214.20	198.10	155.50	940.57
K	4.54	100	58,751	9,155	8,758	8,060	5,977	5,142	6,313	14,594
Na	10.91	100	2,005,727	100,727	14,488	4,643	3,998	3,125	3,655	305,194
Alkaline Earth Metals										
Ba	0.92	50	28,759	6,827	5,958	10,173	17,671	24,467	56,368	21,461
Be	0.10	0.5	BDL	BDL	BDL	BDL	*0.29*	2.43	19.80	3.22
Ca	12.19	50	1,688,526	308,089	435,951	740,590	876,524	766,465	234,135	721,469
Mg	0.81	10	148,573	90,310	128,254	120,774	84,717	62,033	47,841	97,500
Sr	0.24	10	192,888	28,734	24,486	30,658	33,738	33,068	35,158	54,104
Transition Metals										
U	0.01	0.05	1.18	0.31	0.40	0.65	0.96	2.00	10.18	2.24
Zr	0.04	0.5	*0.41*	*0.10*	*0.23*	*0.29*	*0.21*	*0.15*	*0.30*	NA
V	0.32	10	*6.34*	BDL	BDL	*0.36*	BDL	BDL	BDL	NA
Cr	0.10	1	BDL	BDL	BDL	1.12	4.80	16.24	225.87	35.43
Mo	1.85	50	*2.65*	*2.20*	*5.02*	*3.28*	BDL	BDL	BDL	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			RAW SOLIDS							
			EF 2.9							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.71**	**4.15**	**4.06**	**4.58**	**4.26**	**4.26**	**4.3**	
EOC	**MDL**	**MRL**								
Mn	0.05	1	1,578	1,584	3,651	13,459	19,119	20,450	14,929	10,681
Fe	0.79	10	269.15	124.90	227.08	298.12	1,028	2,937	37,154	6,005
Co	0.02	0.1	8.23	5.85	9.74	21.38	72.99	216.30	271.66	86.59
Ni	0.03	0.1	37.40	24.15	36.77	109.31	214.32	248.03	264.87	133.55
Cu	0.19	1	BDL	4.50	12.88	BDL	27.18	59.20	592.33	99.44
Ag	0.02	0.1	0.21	BDL	BDL	BDL	BDL	BDL	*0.02*	NA
Cd	0.09	1	4.36	*0.33*	*0.35*	*0.65*	1.60	5.48	10.24	3.29
Hg	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Zn	0.38	10	BDL	55.57	340.91	BDL	114.07	829.61	2,534	553.43
Post Transition Metals										
Al	0.07	1	277.56	246.17	419.64	517.22	1,196	3,455	32,237	5,478
Pb	0.03	1	6.52	4.24	2.04	BDL	3.38	4.08	14.43	4.95
Metalloids										NA
B	0.60	10	2,075	2,134	2,228	1,077	490.00	303.10	256.00	1,223
Si	0.75	10	5,324	7,484	12,805	17,673	19,617	25,338	61,418	21,380
Sb	0.02	0.1	0.94	0.84	1.18	1.64	1.23	0.73	0.26	0.97
As	0.07	0.5	8.43	BDL	0.74	0.88	1.32	2.47	4.56	2.63

Appendix D: Results of Immersion Test Using Three Different Leaching Solutions On Residual Solids Samples

						RAW SOLIDS				
						EF 2.9				
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.71**	**4.15**	**4.06**	**4.58**	**4.26**	**4.26**	**4.3**	
EOC	**MDL**	**MRL**								
Other Metals										
P	3.02	50	BDL	BDL	*38.22*	*17.62*	*17.00*	*11.72*	*17.26*	NA
Se	0.67	5	*1.13*	BDL	BDL	BDL	BDL	BDL	BDL	NA
S	392.27	1000	16,300	5,428	11,150	10,450	7,902	6,634	2,965	8,690
Halogen										
Br	2.11	20	50,835	2,095	158.43	41.12	30.45	26.02	42.31	7,604

b.3) Raw Solids; EF 4.2

			RAW SOLIDS							
			EF 4.2							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**6.56**	**6.14**	**6.97**	**7.13**	**7.37**	**7.9**	**8.13**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10.00	139.35	486.10	110.60	87.23	81.57	92.91	116.80	159.22
K	4.54	100	BDL	6,579	1,995	1,966	1,850	1,818	1,979	2,312
Na	10.91	100	74,468	129,398	15,165	7,305	4,222	2,817	1,920	33,614
Alkaline Earth Metals										
Ba	0.92	50	669.73	3,184	1,004	934.37	994.95	1,351	1,753	1,413
Be	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Ca	12.19	50	26,959	95,432	15,407	12,970	13,422	15,376	22,775	28,906
Mg	0.81	10	1,077	5,132	660.30	777.00	781.30	1,071	1,818	1,617
Sr	0.24	10	4,658	15,546	2,403	1,682	1,756	2,130	3,203	4,483
Transition Metals										
U	0.01	0.05	BDL	BDL	BDL	BDL	BDL	*0.02*	0.08	NA
Zr	0.04	0.5	BDL	BDL	BDL	BDL	BDL	BDL	*0.05*	NA
V	0.32	10	*1.46*	*0.64*	*0.51*	*0.66*	*0.51*	*0.42*	BDL	NA
Cr	0.10	1	*0.36*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Mo	1.85	50	BDL	*2.13*	*3.06*	*7.67*	*6.38*	*5.39*	*6.81*	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

						RAW SOLIDS				
						EF 4.2				
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**6.56**	**6.14**	**6.97**	**7.13**	**7.37**	**7.9**	**8.13**	
EOC	**MDL**	**MRL**								
Mn	0.05	1	4.85	4.55	3.64	15.03	13.90	23.34	35.63	14.42
Fe	0.79	10	58.66	BDL	BDL	BDL	BDL	*4.12*	26.03	12.69
Co	0.02	0.1	0.23	0.15	*0.09*	*0.09*	*0.06*	0.13	0.17	0.13
Ni	0.03	0.1	12.00	1.07	0.93	0.97	0.83	1.98	0.73	2.64
Cu	0.19	1	BDL	*0.34*	BDL	1.08	*0.57*	1.21	BDL	NA
Ag	0.02	0.1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Cd	0.09	1	*0.11*	BDL	BDL	BDL	BDL	BDL	BDL	NA
Hg	0.10	0.5	BDL	BDL	BDL	*0.33*	*0.20*	BDL	BDL	NA
Zn	0.38	10	BDL	BDL	23.71	*0.63*	BDL	*9.21*	13.70	NA
Post Transition Metals										
Al	0.07	1	*0.29*	14.65	9.91	25.05	47.91	44.36	44.58	26.68
Pb	0.03	1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Metalloids										NA
B	0.60	10	57.20	537.80	524.60	793.30	695.40	567.20	665.20	548.67
Si	0.75	10	81.38	1,278	1,692	3,186	3,846	4,546	6,494	3,018
Sb	0.02	0.1	BDL	0.36	0.71	1.38	1.69	0.30	0.61	0.72
As	0.07	0.5	*0.26*	0.89	1.48	3.56	4.49	6.36	9.84	3.84

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			RAW SOLIDS							
			EF 4.2							
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**6.56**	**6.14**	**6.97**	**7.13**	**7.37**	**7.9**	**8.13**	
EOC	**MDL**	**MRL**								
Other Metals										
P	3.02	50	493.50	*6.73*	*4.07*	*16.62*	*4.24*	*11.02*	*9.08*	77.89
Se	0.67	5	BDL	*0.93*	*0.78*	BDL	*0.97*	BDL	BDL	NA
S	392.27	1000	1,874	6,152	5,753	13,748	11,375	10,790	10,480	8,596
Halogen										
Br	2.11	20	1,405	3,131	348.28	60.70	*8.32*	*14.02*	*13.26*	711.48

c.1) Solidified Solids; EF DDI

			SOLIDIFIED SOLIDS							
			EF DDI							
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**8.29**	**8.96**	**8.09**	**7.59**	**7.78**	**7.96**	**8.42**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10.00	29.36	14.35	12.40	18.99	19.87	17.48	17.86	18.62
K	4.54	100	25,820	6,022	3,598	3,513	2,385	1,929	1,854	6,446
Na	10.91	100	2,753,614	328,797	35,524	8,001	2,706	1,731	1,737	447,444
Alkaline Earth Metals										
Ba	0.92	50	103.40	85.28	96.79	92.57	136.83	175.92	200.61	127.34
Be	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Ca	12.19	50	190,399	105,660	121,146	170,087	67,928	42,092	39,060	105,196
Mg	0.81	10	16,706	4,517	2,493	4,027	3,004	3,953	5,850	5,793
Sr	0.24	10	7,023	5,574	7,570	11,409	13,417	16,889	21,489	11,910
Transition Metals										
U	0.01	0.05	0.13	0.08	0.16	0.33	0.28	0.69	1.19	0.41
Zr	0.04	0.5	*0.08*	BDL	*0.04*	BDL	BDL	BDL	BDL	NA
V	0.32	10	*9.13*	*6.86*	*5.88*	*7.90*	*8.37*	*6.43*	*5.32*	NA
Cr	0.10	1	BDL	2.39	2.89	3.69	1.71	1.06	*0.76*	1.79
Mo	1.85	50	379.40	164.00	*48.52*	*40.04*	*30.77*	*35.81*	57.44	108.00

			SOLIDIFIED SOLIDS							
			EF DDI							
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**8.29**	**8.96**	**8.09**	**7.59**	**7.78**	**7.96**	**8.42**	
EOC	**MDL**	**MRL**								
Mn	0.05	1	14.23	*0.84*	6.98	20.25	22.01	14.08	13.91	13.18
Fe	0.79	10	BDL	BDL	BDL	*4.55*	*7.94*	10.25	*9.80*	NA
Co	0.02	0.1	BDL	0.13	0.13	0.21	0.17	0.16	0.12	0.13
Ni	0.03	0.1	BDL	2.82	2.34	1.87	0.96	0.54	0.24	1.25
Cu	0.19	1	6.13	4.48	2.85	4.02	2.08	2.68	BDL	3.18
Ag	0.02	0.1	*0.03*	BDL	BDL	BDL	BDL	*0.10*	BDL	NA
Cd	0.09	1	*0.36*	*0.11*	BDL	BDL	BDL	BDL	BDL	NA
Hg	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Zn	0.38	10	*1.43*	12.74	BDL	*4.50*	*8.27*	BDL	BDL	NA
Post Transition Metals										
Al	0.07	1	46.73	174.80	161.00	151.75	227.30	231.60	219.20	173.20
Pb	0.03	1	BDL	BDL	*0.05*	BDL	*0.04*	*0.18*	BDL	NA
Metalloids										
B	0.60	10	285.20	328.30	312.60	330.30	182.60	138.10	119.40	242.36
Si	0.75	10	814.37	1,780	2,265	3,375	2,903	2,854	2,784	2,397
Sb	0.02	0.1	2.63	2.81	3.77	4.87	5.28	5.29	5.86	4.36
As	0.07	0.5	5.62	2.82	2.65	3.11	4.27	6.31	6.73	4.50

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			SOLIDIFIED SOLIDS							
			EF DDI							
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**8.29**	**8.96**	**8.09**	**7.59**	**7.78**	**7.96**	**8.42**	
EOC	**MDL**	**MRL**								
Other Metals										
P	3.02	50	BDL	*12.09*	*35.05*	*38.62*	*17.17*	*21.60*	*13.44*	NA
Se	0.67	5	5.93	*1.79*	BDL	BDL	BDL	BDL	BDL	NA
S	392.27	1000	673,911	452,932	322,500	419,300	164,300	89,130	68,270	312,906
Halogen										
Br	2.11	20	2,444	289.54	31.72	*10.57*	*4.74*	*6.28*	*2.91*	398.48

c.2) Solidified Solids; EF 2.9

			SOLIDIFIED SOLIDS							
			EF 2.9							
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.56**	**3.79**	**3.55**	**4.18**	**3.96**	**4.12**	**4.8**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10.00	28.13	24.79	29.23	38.61	43.76	49.70	66.73	40.14
K	4.54	100	21,521	8,894	4,863	4,673	4,290	4,726	6,618	7,941
Na	10.91	100	2,234,727	684,327	137,268	49,795	12,452	6,875	8,556	447,714
Alkaline Earth Metals										
Ba	0.92	50	197.57	139.63	205.10	226.89	240.17	187.88	173.97	195.89
Be	0.10	0.5	BDL	BDL	0.77	1.10	1.44	2.13	3.45	1.27
Ca	12.19	50	230,026	229,589	326,551	453,490	527,824	704,865	1,265,635	533,997
Mg	0.81	10	41,943	34,110	36,024	51,684	50,477	45,603	48,541	44,055
Sr	0.24	10	4,858	5,065	8,520	11,848	15,638	20,788	35,958	14,668
Transition Metals										
U	0.01	0.05	1.34	0.96	1.26	1.34	2.20	3.03	4.26	2.05
Zr	0.04	0.5	*0.36*	*0.19*	*0.25*	*0.24*	*0.31*	*0.35*	0.58	NA
V	0.32	10	*8.12*	*3.07*	*1.73*	*0.87*	*0.75*	*0.62*	*0.73*	NA
Cr	0.10	1	*0.76*	1.42	2.57	4.12	7.55	12.41	21.98	7.26
Mo	1.85	50	116.80	95.88	*25.49*	*20.66*	*12.29*	*11.24*	*12.30*	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

						SOLIDIFIED SOLIDS				
						EF 2.9				
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.56**	**3.79**	**3.55**	**4.18**	**3.96**	**4.12**	**4.8**	
EOC	**MDL**	**MRL**								
Mn	0.05	1	987.38	1,506	3,045	4,617	6,492	10,240	23,829	7,245
Fe	0.79	10	239.65	167.80	341.58	378.92	650.49	985.87	1,761	646.41
Co	0.02	0.1	6.02	4.66	9.28	12.99	18.26	26.73	54.99	18.99
Ni	0.03	0.1	140.58	29.96	44.40	60.49	76.79	104.63	204.47	94.47
Cu	0.19	1	22.12	11.99	20.95	8.98	45.70	61.73	114.63	40.87
Ag	0.02	0.1	0.25	*0.06*	BDL	BDL	BDL	BDL	BDL	NA
Cd	0.09	1	2.57	*0.68*	*0.72*	1.03	1.50	2.07	4.05	1.80
Hg	0.10	0.5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	NA
Zn	0.38	10	BDL	150.28	69.81	62.50	116.17	200.91	343.68	134.76
Post Transition Metals										
Al	0.07	1	426.16	654.67	2,023	2,448	3,968	5,187	7,692	3,200
Pb	0.03	1	36.67	29.34	46.24	64.14	114.04	177.68	334.75	114.69
Metalloids										
B	0.60	10	358.30	332.60	321.50	424.40	342.20	246.10	224.10	321.31
Si	0.75	10	1,783	3,437	6,142	8,543	10,967	13,978	24,048	9,843
Sb	0.02	0.1	2.65	2.40	2.17	2.85	2.81	3.26	4.43	2.94
As	0.07	0.5	5.91	1.56	2.08	2.80	4.42	6.86	12.80	5.20

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			SOLIDIFIED SOLIDS							
			EF 2.9							
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**3.56**	**3.79**	**3.55**	**4.18**	**3.96**	**4.12**	**4.8**	
EOC	**MDL**	**MRL**								
Other Metals										
P	3.02	50	1,061	*47.50*	*39.93*	*43.30*	*36.90*	*36.16*	*33.72*	185.43
Se	0.67	5	5.75	*1.48*	BDL	BDL	BDL	BDL	BDL	NA
S	392.27	1000	288,340	227,490	161,100	218,800	209,900	252,200	436,800	256,376
Halogen										
Br	2.11	20	1,737	494.57	95.43	30.69	*12.78*	*13.81*	*17.04*	342.99

c.3) Solidified Solids; EF 4.2

			SOLIDIFIED SOLIDS							
			EF 4.2							
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**7**	**6.48**	**7.19**	**7.02**	**7.25**	**7.35**	**7.66**	
EOC	**MDL**	**MRL**								
Alkali Metals										
Li	0.13	10.00	*1.71*	*6.14*	*6.10*	*7.04*	*8.20*	10.27	15.76	NA
K	4.54	100	BDL	5,201	3,072	2,762	2,384	2,761	3,605	2,826
Na	10.91	100	176,348	534,398	168,625	61,251	16,243	6,312	4,201	138,197
Alkaline Earth Metals										
Ba	0.92	50	*43.63*	75.33	*43.17*	66.71	66.27	64.57	60.37	60.01
Be	0.10	0.5	BDL	BDL	BDL	BDL	0.00	0.00	0.00	NA
Ca	12.19	50	7,208	47,022	51,447	68,980	72,752	94,596	128,825	67,261
Mg	0.81	10	329.10	2,859	1,116	1,160	1,271	1,740	3,029	1,644
Sr	0.24	10	256.92	1,712	2,332	3,907	5,004	7,172	10,909	4,470
Transition Metals										
U	0.01	0.05	BDL	BDL	BDL	*0.03*	*0.03*	0.09	0.27	0.06
Zr	0.04	0.5	BDL	BDL	BDL	BDL	0.00	0.00	*0.04*	NA
V	0.32	10	*2.39*	*3.19*	*3.77*	*3.80*	*2.94*	*3.04*	*4.23*	NA
Cr	0.10	1	BDL	*0.19*	1.14	1.12	0.00	0.00	*0.16*	NA
Mo	1.85	50	*11.68*	97.91	77.13	55.39	*28.89*	*26.35*	*39.40*	NA

APPENDIX D: RESULTS OF IMMERSION TEST USING THREE DIFFERENT LEACHING SOLUTIONS ON RESIDUAL SOLIDS SAMPLES

			SOLIDIFIED SOLIDS							
			EF 4.2							
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**7**	**6.48**	**7.19**	**7.02**	**7.25**	**7.35**	**7.66**	
EOC	**MDL**	**MRL**								
Mn	0.05	1	BDL	1.77	3.72	5.89	9.33	22.13	4.47	6.76
Fe	0.79	10	25.51	20.84	BDL	BDL	0.00	*4.65*	*1.79*	NA
Co	0.02	0.1	BDL	0.11	0.11	0.12	0.10	0.18	0.19	0.12
Ni	0.03	0.1	BDL	2.40	1.53	2.05	2.03	2.17	1.98	1.74
Cu	0.19	1	BDL	BDL	*0.86*	*0.44*	1.02	0.00	1.05	NA
Ag	0.02	0.1	BDL	BDL	BDL	BDL	0.00	0.00	0.00	NA
Cd	0.09	1	BDL	BDL	BDL	BDL	0.00	0.00	0.00	NA
Hg	0.10	0.5	BDL	BDL	BDL	BDL	0.00	0.00	0.00	NA
Zn	0.38	10	BDL	BDL	BDL	BDL	0.00	0.00	0.00	NA
Post Transition Metals										
Al	0.07	1	2.50	17.75	61.31	93.49	101.30	145.86	96.91	74.16
Pb	0.03	1	*0.05*	*0.12*	BDL	*0.09*	0.00	*0.07*	0.00	NA
Metalloids										
B	0.60	10	15.98	94.65	136.00	186.40	166.90	198.70	240.70	148.48
Si	0.75	10	55.89	332.15	723.10	1,157	1,248	1,604	2,027	1,021
Sb	0.02	0.1	0.49	0.87	1.34	2.12	2.22	2.62	4.34	2.00
As	0.07	0.5	*0.27*	0.62	*0.35*	0.89	1.19	1.68	2.84	1.12

							SOLIDIFIED SOLIDS			
							EF 4.2			
EOC	**MDL**	**MRL**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Cumulative**
Cumulative Test Period, Days			**0.25**	**1**	**2.25**	**5**	**9**	**16**	**36**	**36**
pH			**7**	**6.48**	**7.19**	**7.02**	**7.25**	**7.35**	**7.66**	
EOC	**MDL**	**MRL**								
Other Metals										
P	3.02	50	BDL	BDL	BDL	BDL	0.00	0.00	0.00	NA
Se	0.67	5	BDL	*2.01*	*1.44*	*1.02*	*1.47*	0.00	0.00	NA
S	392.27	1000	20,635	173,041	191,268	227,818	192,625	229,500	320,100	193,570
Halogen										
Br	2.11	20	122.96	416.52	120.38	34.43	0.00	*8.42*	*9.12*	101.69

APPENDIX E: REGULATORY LEVELS OF CONTAMINANTS AS DEFINED BY VARIOUS STANDARDS USED FOR COMPARISON

Note:

(1) All concentrations below are in ppb; (2) National Primary Drinking Water Regulations (NPDWRs or primary standards), are regulatory levels that apply to public water systems and are defined by United States Environmental Protection Agency (USEPA). They are legally enforceable standards and have been developed to protect public health by controlling the contaminant levels in drinking water; (3) These limits have been defined in 40 CFR §261.24, for characterizing waste as 'hazardous' or 'non-hazardous' based on the results of Toxicity Characteristic Leaching Procedure (TCLP) defined by USEPA in Method 1311.

Contaminant	National Primary Drinking Water Regulations (2)	TCLP Regulated Level (D List) (3)
Antimony	6	-
Arsenic	10	5000
Barium	2000	100000
Beryllium	4	-
Cadmium	5	1000
Chromium	100	5000
Copper	1300	-
Lead	15	5000
Mercury	2	200
Selenium	50	1000
Silver	-	5000
Uranium	30	-