Arsenic in Landfill Gas Condensates and Gas Treatment Solids: a Study of Removal by Alternative Treatment Approaches and Mobilization

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Abstract

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Landfills are commonly used to store municipal solid waste. Leachate is produced within these landfills through infiltration of water and landfill gas (LFG) is produced through anaerobic decomposition of organic material. The composition of both leachate and LFG is influenced by factors such as precipitation, temperature, refuse type and others. At Cedar Hills Regional Landfill (CHRLF) in Washington State, the leachate and LFG condensates have been shown to have elevated levels of arsenic, a highly toxic and carcinogenic compound that needs to be removed. Arsenic chemistry within the landfill, which provides a reductive environment, is complex but the presence of arsenic in LFG condensates indicate the prominent role of methylation pathways and ensuing formation of volatile arsines.
This thesis focused on two different but related aspects of arsenic contamination at CHRLF. First, it evaluated the efficacy of microelectrolysis (ME) technology to remove arsenic from landfill leachate and especially from LFG condensate, as sufficient arsenic removal through conventional treatment was deemed not possible. ME uses zero-valent iron (ZVI) combined with activated carbon in an electrolytic solution to form galvanic cells that reduce and/or immobilize arsenic. Second, this thesis focused on the quantification and mobilization of arsenic in spent LFG treatment solids used by BioEnergy Washington (BEW), an on-site gas refinery company that has historically disposed of the solids in CHRLF.

In this study, fixed bed columns were utilized to treat leachate and LFG condensate samples from CHRLF. The columns were packed with ZVI and carbon media to perform ME treatment, and numerous other media were tested to determine possible pre-treatment steps. Permanganate oxidation, zeolite and perlite adsorption pre-treatment methods did not result in improved arsenic removal. Fixed bed columns using microelectrolysis technology were often able to remove >90% of arsenic for a relatively limited number of bed volumes. However, results were inconsistent and further experimentation is required to determine if this treatment scheme can remove As from these matrices in a cost-effective manner.

Spent LFG treatment solids were exposed under conditions understood to regulate arsenic mobilization in the landfill. Analytical data indicated that arsenic and co-occurring contaminants are mobilizable, especially under reducing conditions. Environmental conditions such as redox potential, temperature, mass dose and particle size have observable implications on the re-release of toxic compounds into landfill sites. Further experiments are required to better understand this phenomenon and ultimately to improve LFG processing and landfilling operations so as to
decrease the risks of increased As mobility potentially associated with landfill gas treatment for renewable energy.
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Lastly, I thank my parents and family for their unwavering support and love.
DEDICATION

This thesis is dedicated to those who lost their lives due to Covid-19, and to those who risked their lives for others during the pandemic.
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1. INTRODUCTION

1.1 CEDAR HILLS REGIONAL LANDFILL

Storing anthropogenic waste in landfills is common practice because of its economic advantages (Wang et al. 2016). However, landfills produce leachate contaminated with hazardous substances that need to be removed. These substances include heavy metals, ammonia and toxic materials such as xenobiotic organic compounds (Ahmed & Lan, 2012). Cedar Hills Regional Landfill (CHRLF) located in Maple Valley, Washington, is no exception. It is a major landfilling operation spanning 920 acres, owned by King County, and operated by the Solid Waste Division. CHRLF, which is the only active landfill in King County, receives an average of 2550 tons of trash per day, servicing close to 2.2 million people. It is designated to collect Municipal Solid Waste (MSW) and therefore does not accept any toxic waste.

The landfill is divided into separate areas, however only Area 8 is currently active. Area 9 is a future fill area shown in Figure 1. Each area is filled in layers, compacted, and then capped with a soil layer. After an area is deemed full, it is capped with a system of soil, screening material, clay, a geomembrane, sand, and finally a soil layer with grass. Infiltration of precipitation, as well as biological degradation, continuously generate leachate contaminated with organic and inorganic substances in both closed and active areas at CHRLF.

Drainpipes at the bottom of the landfill collect leachate, which gravity drains or is pumped to Pump Stations (PS) 1, 2, 3 or 4. Leachate also gravity drains to an inlet for lined aeration lagoons, where it resides for, on the average, 12 days for BOD removal prior to discharge to the King County POTW, South Treatment Plant in Renton, WA. Leachate from the Main Hill area is pumped to PS 1. Leachate from the Southeast Pit area is collected at PS 3 and pumped to PS 4. Leachate from areas 2/3, 4, and the Central Pit, as well as condensate from the North Flare Station, are collected in PS 1 and pumped to the leachate aeration lagoon inlet station (LAPI). Runoff that is potentially contaminated, sewage and process water from BEW, and sewage from
offices and Passage Point is collected at PS 4 and pumped to LAPI. Leachate from areas 5, 6 and 7 gravity drain to LAPI. A schematic of this process is provided in Figure 2.

The leachate is sampled at seven locations throughout the landfill for laboratory testing which is performed routinely to satisfy permit requirements and to provide leachate characterization. Capped areas of the landfill generate landfill gas (containing water vapor as well) generated through the decomposition of organic material, or anaerobic digestion. CHRLF is productive in this aspect, containing 680 landfill gas wells for collection. The composition of the landfill gas, as well as the condensate, is influenced by precipitation, air temperature, and refuse type. The landfill gas is captured by a system of pipes and delivered to BioEnergy Washington (BEW), an on-site gas processing facility.

On June 23rd, 2015, a King County Industrial Waste sample detected an arsenic exceedance at CHRLF. The maximum daily load (MDL) of arsenic established for CHRLF operations is 0.27 pounds per day, and the instantaneous limit is 4.0 mg/L. Arsenic loading began to increase, initially gradually and then more dramatically, in 2009. Violations of the arsenic MDL have occurred regularly since February of 2016, shown in Figure 3. The variation in arsenic loading is due to seasonal flow variations. Peaks occur during the summer months where flow is at an annual minimum.
Figure 1. Aerial view of landfill (Photo courtesy of Belt & McArthur, 2020)

Figure 2. Cedar Hills Regional Landfill (Photo courtesy of Belt & McArthur, 2020)
Figure 3. Total As loading from leachate outflow (Figure courtesy of Belt & McArther, 2020)

Figure 4. Time profile of As concentrations in leachate (Figure courtesy of Belt & McArther, 2020)
1.2 BIOENERGY WASHINGTON (BEW)

BEW, a landfill gas refinery, began its operations in 2009. BEW collects landfill gas from CHRLF. The landfill gas consists of approximately 50% methane, 35% carbon dioxide, 6-12% nitrogen, and limited amounts of oxygen, organic chemicals, and heavy metals (Singer, 2020). BEW converts it to high-purity methane for commercial use, producing 15 million kWh every year to Puget Sound Energy (Belt & McArthur, 2020). BEW must purify the landfill gas because it contains many contaminants, including trace amounts of volatile arsenic, as well as moisture (Zhao et al. 2013).

The BEW gas purification process begins by increasing the pressure to 200 psig (Figure 5). Next, a Cabot Norit adsorbent based on activated carbon is used to strip the gas of hydrogen sulfide (H₂S). The activated carbon is non-impregnated and removes H₂S by converting it to elemental sulfur that sorbs easily to the media. The latter type of gas treatment medium has been used since 2019. Before that, a Sulfatreat gas treatment, which is composed of a combination of activated carbon and iron oxides, was used in BEW operations. Spent Sulfatreat media (about 300 tons/year) were disposed of in the currently closed areas 5, 6 and 7.

Following this process, volatile organic compounds (VOCs), siloxane, water and other condensables and heavies are removed by pressure swing adsorption beds. Membrane technology is used to remove carbon dioxide. Waste gas from these processes (off-gas) is either burned in a thermal oxidizer (TO) or recycled into the system. Another pressure swing system is used to remove nitrogen, where off-gas is sent to electric power generation and to the TO, and the product is sent to an oxygen removal unit that uses a catalyst to strip oxygen from the gas stream. Any remaining moisture is removed by a temperature swing adsorption dryer. The product is delivered to two high-pressure compressors, increasing the pressure first to 400 psig and then to 800 psig. The product is then ready for pipeline injection, delivering natural gas primarily along the west coast of the U.S. Renewable natural gas fired generators, supplemented with diesel fuel, complete the electrical power generation process, which is primarily used on-site (Singer, 2020).
The BEW process produces condensate due to the compressing and cooling of LFG. Condensate is also captured through the leachate system and at the North Flare Station. Some contaminants, such as non-volatile arsenic species and other heavy metals, may also be removed by this process and could potentially end up in the condensate stream. The BEW process water system begins at the BEW Inlet Sump, where both landfill gas and condensate are delivered to. Following the sump, the process water is pumped to an oil/water separator and then to sump T-1640, where finally the water is pumped at PS4 into the landfill leachate conveyance system, shown in Figure 5 and Figure 6 (Singer, 2020).

Figure 5. Landfill Gas Reclamation Process Schematic (Singer, 2020)
Recent data from King County Solid Waste Division has indicated that arsenic loading from BioEnergy Washington process water is a major source of total arsenic loading occurring in CHRLF. According to CHRLF Wastewater Discharge Permit 7842-03 (2019), the average arsenic loading per day was 0.56 lbs, while the average arsenic loading per day from BEW was 0.28 lbs.

The initial source of arsenic at CHRLF is municipal solid waste and cover soils. From there, arsenic contaminates the leachate from several possible pathways relating to BEW. The first and currently dominant source is the BEW process water that is discharged into the CHRLF leachate system. This is a low flow discharge system with a flowrate varying between 1 and 10 gallons per minute, but with an average arsenic concentration of up to 13.4 mg/L. Much higher concentrations of As have been periodically observed in BEW process water. Condensate arsenic speciation in BEW process water was measured in March 2020, shown in Table 1. It indicates that almost all As found in BEW process water is in a soluble form, and that practically all
arsenic in BEW process water is classified as unknown species because As(III), As(V), dimethylarsinic acid and monomethylarsonic acid concentrations are all below the applicable detection limits. Conventional methods of arsenic removal are typically designed according to the notion that arsenic present in water is typically arsenite As(III). Removal is then accomplished by the oxidation of arsenite to arsenate As(V), followed by coagulation/flocculation with ferric chloride, where metal hydroxide flocs bind and coprecipitate with arsenate. However, the unknown nature of arsenic speciation and complexation in BEW process water makes designing an effective treatment system and understanding processes exceedingly difficult.

Figure 7. Observed arsenic loading of BEW condensate. Orange line represents arsenic MDL. (Korshin, 2020)
A second pathway of arsenic release into CHRLF leachate is from BEW spent gas treatment media that have historically been disposed of at CHRLF. The spent media has been tested and exhibited high levels of arsenic. As previously mentioned, the initial source of arsenic at CHRLF is municipal solid waste and cover soils, where it is found naturally in its oxidized form, As(V). The landfill provides a reducing environment in which As(V) is reduced to As(III), and biogeochemical processes facilitate complex interactions of sequential methylation and volatilization of methylated As species within the landfill. Gas treatment solids (GTS) within BEW’s refinery process intercept and may oxidize volatile arsines during H₂S removal; spent GTS are then disposed of in the landfill, creating a feedback loop that increases arsenic levels throughout the system. The deposited media is SULFATREAT 410 CHP, an iron-oxide based technology that BEW used until 2019 to remove hydrogen sulfide from landfill gas. Spent media was tested and exhibited high levels of arsenic, up to ca. 500 mg/kg (Figure 8). Conditions within the landfill, such as low redox potential, biological activity, and long retention times favor mobilization of arsenic from metal oxide sorbents such as SULFATREAT 410 CHP (Ghosh et al. 2004). Accordingly, a decision was made in February of 2019 to no longer dispose the spent, contaminated Sulfatreat media at CHRLF.

Environmental conditions that occur within the municipal solid waste at CHRLF, notably the pH, redox potential as well as other physicochemical and biochemical parameters, strongly affect the chemistry of arsenic, and therefore its treatment. Thus, it is imperative to understand their effects. To illustrate this point, As(V) naturally occurring in landfill sediment tends to be reduced to As(III) due to the dominance of strongly reducing conditions within the landfill. These two

### Table 1. Arsenic Speciation in BEW Process Water (Data courtesy of WOOD PLC). Analytical data for BEW process water sampled in March 2020

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Units</th>
<th>SUMP-032120</th>
<th>SUMP-032130</th>
<th>SUMP-032320</th>
<th>SUMP-032330</th>
<th>SUMP-033420</th>
<th>SUMP-033520</th>
<th>SUMP-033530</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume discharged in 24 hours</td>
<td>gal/d</td>
<td>1.570</td>
<td>1.570</td>
<td>2.873</td>
<td>3.401</td>
<td>3.336</td>
<td>4.126</td>
<td>4.777</td>
</tr>
<tr>
<td>Biological oxygen demand</td>
<td>mg/L</td>
<td>1.930</td>
<td>D</td>
<td>1.910</td>
<td>D</td>
<td>&gt;400</td>
<td>&gt;400</td>
<td>&gt;458</td>
</tr>
<tr>
<td>Chemical oxygen demand</td>
<td>mg/L</td>
<td>4.960</td>
<td>D</td>
<td>4.950</td>
<td>D</td>
<td>&gt;400</td>
<td>&gt;458</td>
<td>&gt;402</td>
</tr>
<tr>
<td>Arsenic - Total</td>
<td>mg/L</td>
<td>10.6</td>
<td>10.8</td>
<td>11.0</td>
<td>D</td>
<td>&gt;300</td>
<td>&gt;410</td>
<td>&gt;340</td>
</tr>
<tr>
<td>Arsenic - load</td>
<td>lb/d</td>
<td>0.14</td>
<td>0.14</td>
<td>0.20</td>
<td>0.29</td>
<td>0.30</td>
<td>0.37</td>
<td>0.46</td>
</tr>
<tr>
<td>Arsenic - dissolved</td>
<td>mg/L</td>
<td>0.97</td>
<td>0.75</td>
<td>6.45</td>
<td>8.18</td>
<td>8.51</td>
<td>8.34</td>
<td>7.61</td>
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</tbody>
</table>

### Speciated Arsenic

<table>
<thead>
<tr>
<th>Speciated Arsenic</th>
<th>Units</th>
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<th>SUMP-032130</th>
<th>SUMP-032320</th>
<th>SUMP-032330</th>
<th>SUMP-033420</th>
<th>SUMP-033520</th>
<th>SUMP-033530</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (III)</td>
<td>mg/L</td>
<td>0.02</td>
<td>U</td>
<td>0.02</td>
<td>U</td>
<td>0.02</td>
<td>U</td>
<td>0.02</td>
</tr>
<tr>
<td>As (V)</td>
<td>mg/L</td>
<td>0.02</td>
<td>U</td>
<td>0.02</td>
<td>U</td>
<td>0.02</td>
<td>U</td>
<td>0.02</td>
</tr>
<tr>
<td>Dimethylarsinic acid</td>
<td>mg/L</td>
<td>0.025</td>
<td>U</td>
<td>0.025</td>
<td>U</td>
<td>0.025</td>
<td>U</td>
<td>0.025</td>
</tr>
<tr>
<td>Monomethylarsinic acid</td>
<td>mg/L</td>
<td>0.045</td>
<td>U</td>
<td>0.045</td>
<td>U</td>
<td>0.045</td>
<td>U</td>
<td>0.045</td>
</tr>
<tr>
<td>Unknown arsenic species</td>
<td>mg/L</td>
<td>0.86</td>
<td>J</td>
<td>6.64</td>
<td>J</td>
<td>6.34</td>
<td>J</td>
<td>8.07</td>
</tr>
</tbody>
</table>

Environmental conditions that occur within the municipal solid waste at CHRLF, notably the pH, redox potential as well as other physicochemical and biochemical parameters, strongly affect the chemistry of arsenic, and therefore its treatment. Thus, it is imperative to understand their effects. To illustrate this point, As(V) naturally occurring in landfill sediment tends to be reduced to As(III) due to the dominance of strongly reducing conditions within the landfill. These two
species of arsenic vary in toxicity and mobility and require different methods of treatment. For example, As(V) found in surface and groundwater is typically removed through ferric chloride coagulation. As(III) is typically treated through permanganate oxidation and the formed As(V) is then removed through adsorption. Additionally, microbial interactions with arsenic biologically transform it into species that are more difficult to treat. These processes will be discussed in the next section. By understanding the pH, redox potential, hydraulic retention time, biogeochemistry and other landfill conditions, arsenic speciation can be modelled and predicted, and treatment schemes can be designed and optimized to successfully remove arsenic.

BEW is not the only facility that treats landfill gas. According to a 2019 report conducted by the United States Environmental Protection Agency (EPA), there are currently 52 renewable landfill natural gas energy projects, and about 480 candidate landfills in the United States alone (Figure 9). There are both federal and state financial incentives for renewable natural gas (RNG) projects, and distribution companies are interested in RNG for carbon intensity reduction and the opportunity to sell renewable energy to customers. Furthermore, RNG can be used to fulfill
company sustainability goals that more and more stakeholders are requesting from large corporations. For these reasons, it is imperative to understand the story of arsenic and co-occurring elements contamination at CHRLF and BEW as it is likely to occur in many landfills that pursue landfill gas purification for vehicle fuel, electricity, and thermal applications.

![Map showing LFG energy project count](image_url)

*Figure 9. LFG energy project count from Landfill Methane Outreach Program’s Landfill and Landfill Gas Energy Database as of February 2019.*

### 1.3 Goals of the Study

This study was accordingly carried out to explore two major aspects of the treatment of LFG condensates and, on the other hand, the occurrence and mobility of As and other contaminants in the solid media employed in LFG treatment. Examination of these aspects was carried within two major tasks of the study:

1. Exploration of the removal of arsenic from BEW process water and other relevant matrices (landfill leachate) in fixed bed columns packed with Fe/C media or alternative packing materials. Evaluation of the applicability of alternative treatments for scalability and cost-effectiveness;
2. Examination of As release from spent GTS at varying contact times, presence of reducing species and other conditions pertinent to affecting contributions of spent GTS deposited in the CHRLF site to the associated As loads.
2. LITERATURE REVIEW

2.1 ARSENIC CHEMISTRY

Arsenic, a carcinogen, occurs naturally in soils and sediments primarily as the inorganic oxidized pentavalent species As(V). Landfills promote anaerobic and reducing conditions that contribute to the reductive formation of its trivalent form, As(III), which is more soluble, reactive, toxic and mobile than its oxidized form. The $LD_{50}$ of As(V) and As(III), found using Chang human hepatocytes, are 180 µM and 50 µM, respectively (Mochizuki, 2019). Sulfur is abundant within the landfill so interactions between sulfur and arsenic are likely to occur and form compounds such as the iron arsenic sulfide arsenopyrite FeAsS. Arsenopyrite is formed under high temperatures and reducing environments such as those found in landfills (Flora, 2015). In the presence of oxygen and water, FeAsS oxidizes and may precipitate in the form of scorodite ($FeAsO_4\cdot2H_2O$) or amorphous Fe(III) arsenate as it releases sulfur. The oxidation of arslenopyrite is one of the most common mechanisms for the release of As into the environment (Flora, 2015).

Anoxic conditions promote arsenic mobilization due to the abiotic reduction of iron hydroxides and the concurrent release of associated arsenic (Benner et al. 2002). Furthermore, biotransformation of inorganic arsenic in microorganisms and plants, where arsenate is reduced within cells, is important to study in order to understand the different arsenic pathways (Yin et al. 2017). As(III) is involved in numerous bio-metabolic pathways. It can be oxidized to As(V) under anoxic conditions by acting as an electron donor for microbial respiration—however, more importantly, it can be transformed into various methylated arsenic species. This process detoxifies arsenic because organic methylated arsenic species, such as monomethyl arsionic acid (MMA), dimethyl arsinic acid (DMA), and trimethyl arsine oxide (TMAO) are orders of magnitude less toxic than inorganic arsenic. However, they are difficult to control or treat (Yin et al. 2017). This microbially driven process occurs continuously in the active zone of the landfill as biovolatilization of inorganic arsenic is an important metabolic process used by organisms. (Yin et al. 2017).
Methyl derivatives of arsenic such as volatile arsines may be collected in the gas pipes under the landfill and therefore are expected to occur in the landfill gas and LFG condensate. Arsenic present in LFG may also react with carbon, sulfur or heavy metals to form soluble compounds (Wang et al. 2016). LFG reclamation has been extensively studied because it reduces pollution and generates electricity and renewable natural gas. However, as mentioned previously, LFG gas contains many impurities, such as chlorinated organic compounds, halogenated hydrocarbons, aromatics, and sulfur compounds that are produced by numerous physical, chemical, and biological waste decomposition processes (Shin et al. 2001). Thus, LFG must be extensively treated before being used as a renewable energy source. Due to the possible arsenic occurrence in CHRLF landfill gas, a brief summary of LFG properties and treatment is warranted.

### 2.2 LANDFILL GAS PROPERTIES AND TREATMENT

Trace gases present in LFG, such as hydrogen sulfide, have negative effects on human health and can create numerous operational problems if not removed. These and other impurities such as some hydrocarbons, sulfur, and chlorinated organic compounds reduce the operating life of combustion engines and boilers (El-Fadel et al. 1997). Moisture present in LFG must also be removed. This is typically done through physical processes such as compression and dehydration. Once the moisture content is reduced, activated carbon adsorption is a common and effective method to remove toxic chemicals such as chlorinated compounds and aromatics (Shin et al. 2001). Activated carbon-based gas treatment media are effective adsorbents because of their large surface area, high adsorption capacity, micropore structure and surface reactivity (Pradhan and Sandle, 1999). Arsenic removal from landfill gas using activated carbon media has not been thoroughly investigated, so the mechanisms involved are not fully understood at this time. Activated carbon characteristics, for example pore size distribution, polarity and charge, alongside arsenic characteristics such as oxidation state and form (organic vs. inorganic), will affect how arsenic is adsorbed and subsequently leached from activated carbon media.

Hydrogen sulfide can be removed by oxidizing it to elemental sulfur which then deposits onto the activated carbon. Halogenated hydrocarbons are removed through thermal swing adsorption due to the low adsorption capacity of activated carbon for halogenated hydrocarbons.
Membranes are often used for the separation of carbon dioxide, for example with solution diffusion type membranes, also known as pore-free membranes. Toxic traces can be removed by high temperature, combustion catalytic oxidation or two-stage adsorption (Rautenbach & Welsch, 1993).

2.3 LFG CONDENSATE

While inorganic arsenic removal has been extensively studied, the removal of organic arsenic, which is expected to be dominant in LFG condensate, has not. LFG condensate consists of an aqueous phase and dissolved organic hydrocarbons. Pollutants commonly found in condensate samples include benzene, toluene, phenol, naphthalene, and 2,4-dimethylphenol, with organic compounds partitioning between the aqueous and organic phase depending on the temperature and organic phase and water partition coefficients (Zhao et al. 2013). Management and treatment of LFG condensate has been only minimally studied (Zhao et al. 2013), and therefore best treatment practices have not been established. Zhao et al (2013) attempted to remove arsenic contaminated LFG with the following methods: sequencing batch reactor (SBR) biological treatment, coagulation, permanganate oxidation, Fenton’s reagent oxidation, carbon absorption, and membrane separation. Only membrane separation, in which reverse osmosis was utilized, was able to remove a sufficient amount of arsenic to meet the strict MDL for arsenic loading.

2.4 CURRENT TECHNOLOGIES TO REMOVE ARSENIC FROM LANDFILL LEACHATE AND GAS CONDENSATE

Arsenic is highly toxic and also a carcinogen that originates from both geogenic and anthropogenic sources. Because of its prevalence in the environment and consequentially its danger to human health, many technologies have been developed and successfully implemented for arsenic removal. However, these technologies have predominantly been used for drinking water and industrial wastewater treatment. Therefore, using these technologies to treat landfill leachate may prove ineffective due to the high concentrations of arsenic found in BEW process
water, as well as the relatively high concentration of dissolved organic matter that may inhibit treatment efficacy. A brief overview of known technologies will now be discussed.

Biological removal of arsenic has been shown to be effective under certain conditions. For example, Zacarias-Estrada et. al. (2020) successfully removed arsenic from water under anaerobic conditions with sulfate-reducing bacteria activated sludge. However, sulfur present in leachate and landfill gas is believed to be mostly sulfide, such that the sulfate-reducing bacteria mechanism would be inhibited. Kalaruban et. al. (2019) removed arsenic from water under aerobic conditions with iron-oxidizing bacteria that produce iron-oxide organic matter complexes that readily adsorb dissolved arsenic. However, the CHRLF leachate has high concentrations of yet to be identified organic arsenic compounds that may prove difficult to remove by this process. There are also physical-chemical treatment mechanisms for arsenic removal. Ion exchange has been shown to be effective at removing As(V) (US EPA) but is not practically implementable on CHRLF leachate due to the complex and unknown nature of its arsenic chemistry. Reverse osmosis can certainly remove arsenic but is nevertheless cost prohibitive. Other options, including oxidation with permanganate and coagulation with ferric chloride, have been tested on CHRLF leachate, but it appears that these technologies are not adequately efficient.

Due to the difficulty of treating contaminated landfill leachate, a novel approach of microelectrolysis technology has been studied (Cheng et al. 2007; Wang et al. 2016; Ying et al. 2013). This approach consists of the combined use of zero valence iron (ZVI) with granular activated carbon (GAC) to remove arsenic through reductive/adsorptive pathways. The performance of this method for LFG condensate treatment has not been examined, and some aspects of this approach are reviewed in the sections that follow.

2.5 ZERO VALENCE IRON (ZVI)

Applications of ZVI for arsenic removal have been reasonably well studied because ZVI is readily available, inexpensive, non-toxic and applications of this process require relatively limited maintenance (Fu et al. 2013). ZVI has a nominal redox potential, $E_0$, of -0.45 volts
making it an effective reductant when reacting with oxidized contaminants such as As(V). The removal mechanism involves the directional transfer of electrons from ZVI (the active reducing agent) to the contaminants, often transforming them into non-toxic or less toxic species (i.e. As(V) to As(0)). In the presence of dissolved oxygen, ZVI undergoes corrosion to form oxidation products such as Fe²⁺ and associated solids that can interact readily with organic compounds that are abundant in leachate.

ZVI has been used effectively for remediation of groundwater polluted with arsenic by being employed as the active agent in a permeable reactive barrier (Biterna et al. 2010). The efficacy of the removal of arsenite and arsenate by ZVI, which are often the most prevalent species of arsenic in the environment, has been investigated (Biterna et al. 2010). Arsenite and arsenate are typically removed through adsorption into iron-oxide particles that are formed via the oxidation of Fe(0) to Fe(II) and Fe(III) species. Arsenic species also adsorb onto iron corrosion products that form on the surfaces of ZVI particles; however, commercial ZVI products do not have a high surface area. An additional removal mechanism is the reduction of arsenic ions to elemental arsenic, which is deposited on, occluded in and/or adsorbed on the corrosion layer; alternatively, Fe/As solids can be formed. These compact structures have been shown to prevent leaching of the sorbed arsenic (Tucek et al. 2017).

There are complex variables that determine the success of ZVI to remove arsenic from leachate. For example, without a competing oxidant such as oxygen, reduction of As(V) to As(III) and As(III) to As(0) on the surface of ZVI occurs more readily (Klas et al. 2013). However, anaerobic conditions limit the formation of iron oxy-hydroxides and decrease arsenic removal rates compared to aerobic conditions (Klas et al. 2013). Yet in the presence of oxygen, while arsenic removal has been shown to be kinetically fast, As(III) may oxidize to As(V) (Klas et al. 2013). pH affects As adsorption because of the weak-acid properties of arsenic ions. Batch experiments with ZVI in aqueous solution have shown that low pH (i.e. pH 5) and high DO favor both As(V) and As(III) removal (Tanboonchuy et al. 2011). CaCO₃ co-precipitation has been shown to promote the formation of iron hydroxides that adsorb arsenic, so that increasing concentrations of Ca²⁺ or HCO₃⁻ tend to enhance arsenic removal (Fu et al. 2013). If humic acid
is present in the system, it can suppress the promoting role of calcium ions because of the formation of Fe-humate complexes that delay CaCO₃ formation (Fu et al. 2013).

2.6 MICROELECTROLYSIS TECHNOLOGY

Microelectrolysis (ME) is an attractive treatment technology because it is relatively inexpensive and the reagents it requires, iron and carbon, are abundant. ME uses a mixture of ZVI and GAC in an electrolyte solution, for example landfill leachate. Under these conditions, microscopic galvanic cells form between the ZVI particles (anode) and GAC (cathode) (Wang et al. 2016). Redox reactions occur simultaneously on the surfaces of the ZVI and GAC particles such that there is a significant electron flow between the dissimilar system components (ZVI and GAC) (Ying et al. 2013). Unlike conventional electrolysis in which an external energy source is required, ME’s electrons are supplied internally through the galvanic corrosion of ZVI (Ying et al. 2013). The nominal reaction ZVI oxidation is as follows:

\[ Fe \rightarrow Fe^{2+} + 2e^- \]
\[ E(Fe^{2+}/Fe) = -0.44V \]

Under these conditions, the ME process is believed to promote reductive reactions (Ying et al. 2013). Therefore, arsenic may be removed through reduction to its stable and less toxic elemental form due to the high potential difference between the iron and carbon electrodes. Ferrous and ferric hydroxides, generated via the oxidation and precipitation of Fe²⁺, may also reduce arsenic and other contaminants through co-precipitation, adsorption and enmeshment in the ferrous and ferric hydroxide floc (Cheng et al. 2007). The optimal initial pH was found to be 5 when using microelectrolysis on leachate, which affects the activity of the oxidant, the substrate, and the speciation of iron. A lower pH has also been shown to enhance the reduction that occurs during ME (Ying et al. 2012). Factors such as pH, Fe/C mass ratio, air flow rate and catalyst concentrations need to be studied in batch experiments in order to optimize the treatment method (Figure 10).

Landfill leachate contains DOM, COD, petroleum hydrocarbons (PHC) and other contaminants that may interfere with a microelectrolysis system’s ability to remove arsenic. For example,
DOM could overwhelm the GAC sorption capacity. Compounds comprising DOM/COD may react with ZVI making the system less efficient at accomplishing the goal of arsenic removal. Thus, pretreatment schemes, for example dissolved gas flotation to remove PHC and GAC to remove DOM, may be necessary in order to optimize ME for arsenic removal from landfill leachate.

Figure 10. Effects of different parameters on the removal efficiencies of color and COD by batch internal ME reactor in treating mature landfill leachate (Ying et al. 2012).

2.7 SUMMARY

Removing arsenic from CHRLF leachate and BEW process water (BPW) dominated by LFG condensate is a challenge. There are high concentrations of some solution components in these water matrices, notably NOM and PHCs, that interfere with the performance of some otherwise effective treatment methodologies through several phenomena, notably competitive adsorption. Arsenic speciation of BPW indicates that the majority of arsenic present is of unknown species,
such that conventional treatment technologies such as oxidation and coagulation are unlikely to be effective.

However, discovering that the majority of arsenic loading at CHRLF comes from BPW may mean that only that stream will have to be segregated and treated. With a significantly lower flowrate, novel technologies such as microelectrolysis may be able to lower arsenic loading to allowable levels. Therefore, along with limited adsorption experiments, microelectrolysis experiments were conducted in conjunction with other reagents and different pre- and post-treatment schemes with the goal to solve this difficult but fascinating problem.
3. MATERIALS AND METHODS

3.1 CHEMICALS AND REAGENTS

The complex and variable chemical nature of landfill leachate and BPW required numerous chemicals and reagents to be utilized in fixed bed column experiments performed to determine possible successful treatment schemes. Powder and granular activated carbon were used as an adsorbent for contaminants such as NOM and PHCs, and also analyzed for its potential ability to adsorb arsenic directly. Perlite and Zeolite, known to be effective PHC and ammonia adsorbents, respectively, were tested as a possible pre-treatment media. Due to the high sulfur content of LFG media, pyrite, which also has a high sulfur content and may be able to react with As(V) and As(III), was used in fixed bed columns. Table 2 presents all chemicals and media used in the fixed bed column and adsorption experiments.

Table 2. Chemicals and Media

<table>
<thead>
<tr>
<th>CHEMICALS / MEDIA</th>
<th>LOT #</th>
<th>CAS</th>
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<td>-</td>
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<td>CLINOPTILOLITE ZEOLITE</td>
<td>-</td>
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<tr>
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<td>Zentron Crystal Collection:</td>
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<td>H.B. Smith Tools®</td>
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</table>
HYDROCHLORIC ACID | 58350 | 7647-01-0 | MilliporeSigma
SODIUM HYDROXIDE | 189362 | 1310-73-2 | Fisher Chemical
POTASSIUM PERMANGANATE | 180124 | 7722-64-7 | Fisher Chemical
NITRIC ACID | 185141 | 7697-37-2 | Thermo Scientific
SODIUM SULFITE | 132468B | 7757-83-7 | Fisher Chemical
SODIUM SULFATE | 157118 | 7757-82-6 | Fisher Chemical
SODIUM HYDROSULFIDE HYDRATE | SHBL3364 | 207683-19-0 | Sigma-Aldrich
SODIUM BICARBONATE | SLBK2541 | 144-55-8 | Sigma-Aldrich
FERRIC CHLORIDE TETRAHYDRATE | | 13478-10-9 | Fisher Chemical
SODIUM CARBONATE | 138124 | 497-19-8 | Fisher Chemical
HYDROXYLAMINE HYDROCHLORIDE | MKCK7294 | 5470-11-1 | Sigma-Aldrich

*Hoganas Cleanit® LC Plus is an iron-based material consisting of 97.84% iron, 2.02% oxygen and 0.14% manganese with an apparent density of 1.42 g/cm³.

3.2 SAMPLING OF LANDFILL SAMPLES

The samples used in these experiments were collected over multiple sampling rounds (SR) from CHRLF and BEW in 2020. Analysis of the leachate and BEW process water from each SR indicated variability in As concentrations over time (Table 3). The exact reasoning for this variability has not been determined, although one possible explanation is dilution caused by excessive rainfall in December 2020.

Table 3. Concentrations of arsenic in CHRLF (data provided by KCEL)

<table>
<thead>
<tr>
<th>Sampling Round</th>
<th>Date</th>
<th>Sample Type</th>
<th>As conc (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR5</td>
<td>Jan 2020</td>
<td>LEPS</td>
<td>35</td>
</tr>
<tr>
<td>SR6</td>
<td>Mar, May 2020</td>
<td>BPW 03/26</td>
<td>10,100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BPW 05/03</td>
<td>15,890</td>
</tr>
<tr>
<td>SR7</td>
<td>Oct 2020</td>
<td>LEPS</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BPW</td>
<td>7,465</td>
</tr>
</tbody>
</table>
3.3 **SAMPLE PRE-TREATMENT**

Raw CHRLF leachate and BEW process water samples were filtered to remove particulate matter present in them. Influent was first pumped through a 5-micron membrane filter followed by a 1-micron membrane filter (Harmsco Industrial Filters were used for filtration). Effluent was then stored in a sealed plastic carboy in a cold room at 4 °C.

3.4 **FIXED BED COLUMN EXPERIMENTS**

The removal of arsenic and co-occurring contaminants from LEPS leachate (SR5 and SR7 samples), which contains mostly inorganic arsenic, was examined in fixed bed column experiments. The columns used were *Kimble Flex-Columns*, with the dimensions of 1.5 cm diameter and 30 cm height. Literature and experiments done by a fellow lab member have shown that a pH of 5 is optimal for microelectrolysis, so experiments were conducted at pH 5 and at LEPS natural pH of ca. 7.4. Various reagents, combinations of reagents and experimental conditions were used for experimentation shown in Table 4—

(i) One column was utilized to treat LEPS (SR5) leachate at its natural pH (~7.3 to 7.5) and/or at pH 5 adjusted by adding concentrated HCl. The column was completely filled with one packing medium described in Table 4 and activated with 50 mL of 0.1 M HCl. The purpose of this step is to remove any oxidized films from the surface of iron media such that a larger surface area of iron is available to react with the influent. Leachate was pumped into the top of the column using a peristaltic pump. The flow rate was adjusted to achieve an empty bed contact time of about six minutes. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(ii) Two columns were utilized to treat LEPS (SR5) leachate at its natural pH and/or at pH 5 adjusted by adding concentrated HCl. The first column was filled with
Zeolite and the second column was filled with 8-20 mesh GAC. Both columns were activated using 50 mL of 0.1 M HCl. Columns were placed next to each other and connected in a series. Leachate was pumped into Column 1 with the effluent discharging into a beaker. A tube was placed into the beaker, pumping the treated leachate into the top of Column 2, where the same sampling method took place. The flow rate was adjusted to achieve an empty bed contact time of about six minutes. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(iii) One column was utilized to treat LEPS (SR5) leachate at its natural pH (~7.3 to 7.5). The column was filled with alternating 2 cm layers of LC Plus and 8-20 mesh GAC, then activated with 50 mL of 0.1 M HCl. Leachate was pumped into the top of the column using a peristaltic pump. The flow rate was adjusted to achieve an empty bed contact time of about six minutes. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(iv) One column was utilized to treat LEPS (SR5) leachate at pH 5. The column was packed by filling two cm of one medium followed by two cm of the other medium until the column was completely packed. The reagents were activated using 0.1 M HCl. Leachate was pumped into the top of the column using a peristaltic pump. The flow rate was adjusted to achieve an empty bed contact time of about six minutes. Similarly, one column was utilized to treat LEPS (SR7) leachate at pH 5, however layers alternated every 4 cm. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

Table 4. Fixed Bed Column Experiments, LEPS (SR5)

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>pH</th>
<th>Experimental Condition</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>natural</td>
<td>i</td>
<td>8-20 mesh GAC</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Zeolite</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>ii</td>
<td>Zeolite and 8-20 mesh GAC</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>iii</td>
<td>LCP and 8-20 mesh GAC</td>
</tr>
</tbody>
</table>
The removal of arsenic and co-occurring contaminants from BEW process water, which is thought to contain organo-arsenic compounds, was examined in fixed bed column experiments. The columns used were *Kimble Flex-Columns*, with the dimensions of 1.5 cm diameter and 30 cm height. Various reagents, combinations of reagents and experimental conditions were used for experimentation shown in

(i) One column was utilized to treat BPW (SR6, 3/26) adjusted to pH 5 with the addition of HCl. The column was packed with 12-40 mesh GAC, and then activated with 0.1 M HCl. BPW was pumped into the top of the column using a peristaltic pump. The empty bed contact time was 10 minutes. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(ii) One column was utilized to treat BPW (SR6, 3/22) adjusted to pH 5 with the addition of HCl. The column was packed with alternating 2 cm layers of LCP and 12-40 mesh GAC, with the top and bottom layers both being GAC. Next, the reagents were activated with 0.1 M HCl. BPW was pumped into the top of the column using a peristaltic pump. The EBCT was 10 minutes. This experiment was repeated with BPW (SR6, 5/3) and BPW (SR7). Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(iii) Two columns were utilized to treat BPW (SR6, 3/25) adjusted to pH 5 with the addition of HCl. The first column was packed with 12-40 mesh GAC. The second column was packed with alternating 2 cm layers of LC Plus and 12-40 mesh GAC, and then activated with 50 mL of 0.1 M HCl. BPW was pumped into the
top of the first column using a peristaltic pump and collected in a beaker. Next, the effluent from the first column was pumped into the top of the second column using a peristaltic pump. The EBCT was 10 minutes. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(iv) Experiment (iv) followed the same procedure as experiment (iii). However, following the treatment of one GAC column and one ME column, samples were oxidized with 2 g/L of permanganate KMnO₄ with a 24-hour contact time. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(v) One column was utilized to treat BPW (SR6, 3/25) pre-oxidized with 2 g/L permanganate with a 24-hour contact time, adjusted to pH 5 with the addition of HCl. The column was packed with alternating 4 cm layers of LC Plus and 12-40 mesh GAC, and then activated with 50 mL of 0.1 M HCl. BPW was pumped into the top of the column using a peristaltic pump. The EBCT was 10 minutes. Aliquots of effluent were taken at bed volume intervals and centrifuged for five minutes at 4000 rpm.

(vi) One column was utilized to treated BPW (SR7) without altering pH. The column was packed with alternating 1 cm layers 12-40 mesh GAC and LCP. The reagents were activated with 0.1 M HCl, and BPW was pumped into the top of the column using a peristaltic pump. The EBCT 10 minutes. This experiment was repeated at pH 5.

3.5 BEW SPENT GAS TREATMENT SOLIDS (GTS) EXPERIMENTS

The leaching of arsenic and co-occurring contaminants from BEW spent gas treatment solids (Norit Cabot Darco BG1 activated carbon media) sampled in April 2020 were examined under strongly reducing, acidic, basic and alkaline conditions. The media was delivered to the
University of Washington lab in glass jars and stored in a cold room at 4 °C. Weight loss measurements (air drying in a chemical hood, 24 hours) showed that the solids contained about 25% water. Aliquots of ambient solutions containing GTS suspensions were taken for a range of contact times, pH and redox potentials.

For logistical reasons, the UW research group was not able to obtain virgin GTS Norit Cabot Darco BG1 media from BEW. Therefore, no experiments were conducted to quantify baseline levels of contaminants naturally found in the gas treatment solids. However, the baseline concentration of contaminants such as arsenic within the media are expected to be minute and therefore the results presented are deemed to be an accurate representation of contaminant leaching. Exposure experiments on virgin GTS media will be conducted in the future.

3.6 BEW SPENT GTS EXPERIMENTS: COLUMN EXPOSURES

Three 53 mL Kimble Flex-Columns were packed with spent GTS. The first column was exposed to 0.04 M sodium sulfite Na₂SO₃ solution to induce reducing conditions found in the landfill. The second column was exposed to 0.01 N sodium carbonate Na₂CO₃ solution and the third column was exposed to 0.01 M sodium bicarbonate NaHCO₃ solution because bicarbonate is abundant in the leachate and in some extent in BPW. The empty bed contact time was one hour.

3.7 BEW SPENT GTS EXPERIMENTS: BATCH EXPOSURES

The first round of GTS batch exposure experiments is outlined in Table 5. The solids used in this round were non-dried and non-homogenized.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Mass Dose (g/L)</th>
<th>Solution</th>
<th>Solution Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>DI water</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1% HNO₃</td>
<td>1%</td>
</tr>
</tbody>
</table>
Round 2 of the GTS exposure experiments were concerned with determining the particle size, temperature, mass dose and hydroxylamine concentration effects on GTS As release. Hydroxylamine was used for these experiments because it is a powerful reductant that emulates the reducing conditions found in the landfill. Furthermore, unlike sulfite, hydroxylamine does not contain sulfur whose presence makes it difficult to interpret GTS sulfur release phenomena used to correlate with and better understand arsenic release and complexation. To determine GTS size effects on As release, the solids were dried in a chemical hood for 24 hours and then crushed with a ceramic mortar and pestle. The GTS were then separated and homogenized with a sieve. Four size fractions (SF) were collected: SF1 (<0.42 mm), SF2 (0.42 to 1 mm), SF3 (1 to 1.4 mm) and SF4 (1.4 to 2 mm). The pH of each sample was adjusted to about 8. If the redox potential increased to approximately -50 mV, a nominal amount of hydroxylamine was added. Round 2 of GTS exposure experiments is outlined in Table 6—

**Table 6. Gas Treatment Solids Exposure Conditions, Round 2**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Size Fraction</th>
<th>Temperature (C)</th>
<th>GTS Mass Dose (g/L)</th>
<th>Hydroxylamine Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size effect</td>
<td>SF1, SF2, SF3, SF4</td>
<td>20</td>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>Temperature effect</td>
<td>SF3</td>
<td>4, 20, 35</td>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----</td>
<td>-----------</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td>GTS mass dose effect</td>
<td>SF3</td>
<td>4, 20, 35</td>
<td>5, 10, 20, 50, 75</td>
<td>0.2</td>
</tr>
<tr>
<td>Hydroxylamine concentration effect</td>
<td>SF3</td>
<td>4, 20, 35</td>
<td>20</td>
<td>0.1, 0.2, 0.5, 1.0</td>
</tr>
</tbody>
</table>

### 3.8 SAMPLE ANALYSIS

Five methods were used to analyze samples generated in the experiments reported in this thesis. These methods included Excitation Emission Matrix (EEM), UV-Vis Absorbance Spectrophotometry, Total Organic Carbon (TOC) Analyses, elemental analyses using an Inductively Coupled Plasma Mass (ICP-MS) spectrometer or an Inductively Coupled Plasma Optical Emission (ICP-OE) spectrometer and X-ray photoelectron spectroscopy (XPS) using a Surface Science Instruments S-Probe spectrometer.

#### 3.8.1 EEM MEASUREMENTS

Fluorescence excitation emission matrices (EEM) were acquired with a Horiba AquaLog® spectrofluorometer. The EEM data were used to quantify changes of the fluorescence of initial and treated leachate samples. Prior research has shown that parameters characterizing changes of the fluorescence and absorbance of wastewater are predictive of the removal of trace-level organic contaminants (Korshin et al. 2018). This knowledge is important because organic contaminants present in the leachate may interfere with reagents used for treatment. Excitation-emission matrices of leachate have distinct characteristics with maxima found at characteristic combinations of excitation and emissions wavelengths (Korshin et al. 2018). HORIBA Scientific AquaLog® software and MATLAB® code were used to create distinct plots from EEM data, in which characteristic peaks of fulvic and humic acids could be visually seen and correlated with other parameters. A one cm cuvette was used for EEM measurements. Samples were filtered
using 0.45 µm filters and diluted 100 with DI water times prior to EEM analysis. If necessary, samples were also centrifuged at 4000 rpm for five minutes.

### 3.8.2 ABSORBANCE MEASUREMENTS

A Shimadzu UV-2700 spectrophotometer was used to measure the absorbance of treated leachate. This was a quick and reliable method to analyze how well an experiment did in the removal of light-absorbing species that may interfere with reagents used for the treatment of arsenic. The wavelength range used was from 200 to 800 nm. A 5 cm cuvette was used for UV measurements. Samples were filtered using 0.45 µm filters and diluted 100 times with DI water prior to UV analysis. If necessary, samples were also centrifuged at 4000 rpm for five minutes.

### 3.8.3 MEASUREMENTS OF CONCENTRATIONS OF INORGANIC AND ORGANIC CARBON

A Shimadzu TOC-L analyzer was used to measure the amount of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) of treated leachate. Quantifying DOC and DIC concentrations is critical in characterizing the leachate and understanding how effective different treatments schemes are. When using the Shimadzu TOC-L analyzer, calibration curves were developed from 0.5, 1, 2, 5 and 10 ppm TOC standard solutions. Samples were typically diluted 150 times with DI water when analyzed by Shimadzu TOC-L.

### 3.8.4 ICP MEASUREMENTS OF CONCENTRATIONS OF AS AND OTHER ELEMENTS

ICP analyses was used to determine arsenic and other co-contaminant concentrations of treated leachate. Other contaminants analyzed include sulfur, phosphorous, nickel, manganese, iron, calcium, antimony, and chromium. Two University of Washington ICP instruments were utilized: Perkin Elmer Optima 8300 ICP-OES in the Department of Chemistry and NexION 2000B ICP-MS in the Department of Nanoscience. Prior to ICP analyses, elemental standards were used for calibration and trace-metal grade nitric acid was used for acidification. Samples
were filtered using 0.45 μm filters and diluted according to ICP guidelines. Samples were also sent to the certified King County Environmental Lab (KCEL) for analyses of arsenic and other contaminants. Samples taken to KCEL were filtered using 0.45 μm filters, acidified 24 hours before delivery using 1% nitric acid, and kept in a cold room.

3.8.5 XPS ANALYSIS OF GTS MEDIA

XPS spectra were taken on a Surface Science Instruments S-Probe spectrometer in the Molecular Analysis Facility at the University of Washington. XPS data were used to establish the binding environment/oxidation state of elements of interest, primarily As, S, Fe and Sb. The instrument has a low energy electron flood gun for charge neutralization and a monochromatized Al x-ray source. X-ray spot size for the samples was 800 x 800 μm, and the samples were run as insulators. The pass energy for the survey spectra was 150 eV, and the analytical chamber pressure during spectral acquisition was about 1 x 10⁻⁸ Torr, while the pass energy for high resolution carbon 1s spectra was 50 eV. All binding energies for the high-resolution carbon 1s were referenced to the carbon 1s graphitic C bonds at 284.4 eV. All high-resolution spectra peak fitting used a Shirley background. The Service Physics Hawk Analysis 7 program was utilized for data analysis.
4. **RESULTS**

4.1 **RESULTS OF XPS ANALYSIS OF GAS TREATMENT SOLID MEDIA**

To examine the chemical nature of As and other components of GTS, two spent GTS samples were submitted for XPS analysis, with the only difference between the two being the size of their grains. One sample was size SF1 (<0.42 mm) and the other sample was SF2 (0.42 to 1.0 mm). No significant difference between the XPS data for the two samples was observed, indicating that the chemical environment characteristic for the two samples was generally similar. Each sample had three spots analyzed by XPS plus a high-resolution spectrum. Table 7 shows the results of the spot analysis averaged between the two samples. As expected, the spent GTS are composed mainly of carbon and have significant quantities of sulfur. Only trace amounts of As were detected by XPS (which has a relatively high threshold at which the presence of As or elements can be discerned), and no Sb was detected. Further XPS analysis is necessary to better understand this matrix.

_Table 7. XPS data on average composition analysis of sample SF1 and SF2_

<table>
<thead>
<tr>
<th>XPS Line</th>
<th>Average atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>18.9</td>
</tr>
<tr>
<td>C 1s</td>
<td>68.6</td>
</tr>
<tr>
<td>S 2p</td>
<td>10.7</td>
</tr>
<tr>
<td>As 3d</td>
<td>trace</td>
</tr>
<tr>
<td>Fe 2p</td>
<td>trace</td>
</tr>
<tr>
<td>F 1s</td>
<td>1.2</td>
</tr>
<tr>
<td>Mg</td>
<td>trace</td>
</tr>
<tr>
<td>Ca 2s</td>
<td>trace</td>
</tr>
</tbody>
</table>

*Trace: detected, but signal too low to accurately quantify*
High resolution XPS spectra of GTS sample SF1 are shown in Figure 11. For sulfur, peaks at binding energies of 163.8 (S 2p3/2) and 165.0 eV (S2p1/2) suggest several possible identities such as carbon sulfides, metal sulfides, and elemental sulfur, while peaks at 169.0 and 170.2 eV indicate the presence of oxidized sulfur species. Figure 12 shows the hi-res spectra for arsenic. These spectra exhibit significant noise which makes it challenging to assess accurately the binding environment, therefore only qualitative identifications can be made. As such, possible peaks at 44.7 and 45.4 eV may correspond to a combination of reduced and oxidized arsenic species. Further measurements for a wider set of GTS materials and model compounds are necessary to obtain more specific information concerning the chemical nature of As in GTS. Such information may be critical for determining the speciation of As in GTS and BEW process water.

Figure 11. Sulfur 2p XPS hi-resolution spectra for sample SF1

Figure 12. Arsenic 3d XPS hi-resolution spectra for sample SF1
4.2 REMOVAL OF AS AND CO-OCcurring CONTAMINANTS IN FIXED BED COLUMN EXPERIMENTS. DATA FOR LEPS LEACHATE (SR5, SR6 AND SR7 SAMPLE)

The removal of As and co-occurring contaminants from LEPS (SR5 and SR7) leachate was investigated in fixed bed column experiments with alternating layers of 12-40 mesh GAC and LC Plus ZVI material. The pH of LEPS was adjusted to 5 before treatment. This design of column packing was selected to represent modified microelectrolysis conditions.

Measurements of As concentration in the column effluent are shown in Figure 13. 100% of the dissolved As was removed after the first bed volume. After eight bed volumes, As removal plateaued at about 75%. The removal of other heavy metals in these conditions was also examined. Figure 14 shows that this treatment removed all chromium present in the influent, however nickel and manganese (Figure 15) concentrations in effluent slightly increased over those in the influent. This is likely to be the result of leaching of Ni and Mn from LC Plus ZVI material. Iron concentrations in the column effluent also increased by several orders of magnitude (Figure 16).

![As removal from LEPS, packed Fe/C column, pH5](image)

*Figure 13. As removal versus bed volume. LEPS (SR5) influent, pH 5. Treatment in fixed bed column with alternating 2 cm layers of 12-40 mesh GAC and LC Plus. 6-minute EBCT. (KCEL ICP/MS data).*
Figure 14. Cr and Ni concentrations versus bed volume. LEPS (SR5) influent, pH 5. Treatment in fixed bed column with alternating 2 cm layers of 12-40 mesh GAC and LC Plus. 6-minute EBCT. (KCEL ICP/MS data).

Figure 15. Mn concentrations versus bed volume. LEPS (SR5) influent, pH 5. Treatment in fixed bed column with alternating 2 cm layers of 12-40 mesh GAC and LC Plus. 6-minute EBCT. (KCEL ICP/MS data).
The removal of As and co-occurring contaminants from LEPS (SR5) leachate was investigated in fixed bed column experiments packed with GAC. Results of these measurements are shown in Figure 17. The maximum removal efficiency of the dissolved As was 32% after the first bed volume. It decreased to an even more modest 20% after the 15\textsuperscript{th} bed volume. This indicates the limited potential of relying on adsorption for As removal in fixed bed columns, and the positive effect of adding LCP to the treatment matrix in order to induce a modified microelectrolysis scheme.
Further experiments were carried out utilizing fixed bed columns packed with zeolite. In the practice of water treatment, zeolite is primarily used for ammonia and heavy metal cation removal. The rationale of examining the performance of zeolite in the context of leachate treatment was primarily related to the possibility of leachate pretreatment by zeolite to remove excessive levels of ammonia that would interfere with biological leachate treatment which was suggested by King County. Another possibility is that a fraction of As in the leachate may have positive or neutral charges, such as arsenobetaine or trimethylarsine oxide. Charged species may be amenable to removal via ion exchange processes.

Two experiments were designed to determine if zeolite provides an effective means for As removal from leachate. First, one fixed bed column packed with only zeolite was used to treat LEPS (SR5) leachate at pH 5. Subsequently, a two-column series was utilized, in which the first column was packed with only zeolite, and the second column was packed with only 8-20 mesh GAC. Figure 18 shows that zeolite per se did not remove any arsenic. Furthermore, combining a zeolite column with a GAC column in a series was found to result in lower arsenic removal compared with GAC on its own as seen in Figure 17.
Figure 18. Comparison of As removal from LEPS leachate (SR5 sample) treated by either a single zeolite fixed bed column or a two-column series with the first and second columns packed with zeolite and 8-20 mesh GAC, respectively. Experiments were conducted at pH 5 and 6-minute EBCT. LEPS leachate (KCEL ICP/MS data).

Figure 21 shows complete removal of Cr was achieved after the 15th bed volume by the two column GAC and zeolite experiment, while Figure 20 shows no meaningful removal of Ni occurred. Figure 21 displays no meaningful Mn removal by zeolite only. With the addition of the adsorptive GAC in the two-column experiment, about 25% of Mn is initially removed after the first bed volume, but after the fifth bed volume Mn removal is insignificant. Interestingly, more significant Mn removal begins after the 15th bed volume, and by the 17th bed volume Mn removal reaches about 20%. These data demonstrate that zeolite is not a viable option for As removal from LEPS, and therefore zeolite experiments were terminated. Along with zeolite, experiments with pyrite and steel wool both proved unsuccessful. While steel wool unsurprisingly removed essentially no arsenic, arsenic levels in the effluent from pyrite-packed column were higher than in the influent. This was indicative of the leaching of As from the naturally occurring pyrite which is known to contain arsenopyrite FeAsS as an impurity.
Figure 19. Comparison of Cr removal from LEPS leachate (SR5 sample) treated by either a single zeolite fixed bed column or a two-column series with the first and second columns packed with zeolite and 8-20 mesh GAC, respectively. Experiments were conducted at pH 5 and 6-minute EBCT. (KCEL ICP/MS data).

Figure 20. Comparison of Ni removal from LEPS leachate (SR5 sample) treated by either a single zeolite fixed bed column or a two-column series with the first and second columns packed with zeolite and 8-20 mesh GAC, respectively. Experiments were conducted at pH 5 and 6-minute EBCT. (KCEL ICP/MS data).
Figure 21. Comparison of Mn removal from LEPS leachate (SR5 sample) treated by either a single zeolite fixed bed column or a two-column series with the first and second columns packed with zeolite and 8-20 mesh GAC, respectively. Experiments were conducted at pH 5 and 6-minute EBCT. (KCEL ICP/MS data).
Figure 22. As, Ni, and Cr removal versus bed volume. LEPS (SR7) influent, pH 5. Treatment in fixed bed column with alternating 4 cm layers of 12-40 mesh GAC and LC Plus. 10-minute EBCT. (KCEL IC/MSP data).

Figure 22 represents the first packed column experiment conducted on LEPS (SR7) leachate sample. The bed was packed with alternating 4 cm layers of 12-40 mesh GAC and LCP. Influent LEPS was altered to pH 5 and had a 10-minute residence time. During this experiment, 40 BV of influent were treated. During this experiment, >80% of As and Cr was consistently removed. 80% of Ni was removed after the eighth bed volume, however removal decreased over time and only 31% of Ni was removed after the 40th bed volume. The consistency of ME effectiveness in this experiment was noted and examined further to determine efficacy.

4.3 FIXED BED COLUMN EXPERIMENTS FOR AS REMOVAL FROM BEW PROCESS WATER

The removal of As and co-occurring contaminants from BEW process water was investigated in fixed bed column experiments packed with GAC and altering the pH of the influent to 5. Results of these measurements are shown in Figure 23. No As removal occurred over the first four bed volumes. Subsequently modest As removal of between 10 and 25% occurred over the next 16 bed volumes. This result is consistent with previous experiments with LEPS leachate, namely that adsorption through GAC cannot be relied upon for As removal.
Next, a fixed bed column was packed with alternating 2 cm layers of 12-40 mesh GAC and LC Plus ZVI, and the BPW influent was adjusted to pH 5. Results of this experiment are shown in Figure 24. 100% of As was removed after the first bed volume, however after the second bed volume removal was negligible, and after the third bed volume iron-carbon matrix was leaching As. While this experiment was not successful, further ME column experiments were performed to determine how to optimize the process. Permanganate oxidation was utilized for this purpose.

Three experiments were conducted to determine the effectiveness of fixed bed columns for As removal from BPW. One experiment pre-oxidized the BPW with a 2 g/L does of permanganate. Permanganate oxidation for As removal works by oxidizing As(III) to As(V) which adsorbs to MnO$_2$. The oxidation state and chemical nature of As in these matrixes is unknown. Thus, this pre-oxidation step was attempted because it is a conventional As treatment choice, and it is important to see if it could improve As removal when combined with a microelectrolysis column. Alternatively, the effluent from a 2 cm alternating ME stacked column was oxidized using the same dosage to determine if this would increase As removal. The results of these two experiments were compared to the results of the experiment that only utilized the Fe/GAC medium. Their results presented are in Figure 25. Arsenic removal among all three experiments was modest. Both the ME column and the ME column followed by permanganate oxidation averaged about 40% over the 20 bed volumes treated. Permanganate post-oxidation of the effluent did not improve removal efficiency over the course of the treatment. Meanwhile, pre-oxidation interfered with the ability of the Fe/GAC column to remove arsenic, demonstrating that oxidizing the As species before microelectrolysis treatment inhibits the reductive reactions that take place.

Figure 26 through Figure 28 show results of a subsequent iteration of the Fe/GAC stacked column experiment treating 40 bed volumes of BPW. About 60% and 98% arsenic and antimony removal occurred, respectively, after 40 bed volumes (Figure 26). While no iron was present in the influent sample, high levels of iron were found in the effluent, indicating iron mobility and release occurred. After the fourth bed volume, 300 mg/L of Fe was released, but this value decreased to 13.8 mg/L after the 40th bed volume (Figure 28).
The same experimental set up was utilized to treat BPW (SR7) sample, with the results shown in Figure 29. Under these conditions, 72% of As was removed after the fourth bed volume, with removal increasing over time resulting in >90% removal after the 40th bed volume. This experiment also yielded successful Ni and Sb removal, achieving 100% and 98%, respectively, after the 40th bed volume. Both S (Figure 30) and Mn (Figure 31) release occurred.

A similar experimental set up was utilized to treated 90 bed volumes of BPW (SR7) sample, however the influent pH was not altered. Under these conditions, As removal once again increased over time, with 98% removal achieved at bed volumes 70 through 90 (Figure 32). The column removed 100% of Ni and Sb by the 30th bed volume and continued to exhibit this efficiency until the experiment was terminated at 90 bed volumes. Mn removal was about 80% by the 90th bed volume (Error! Reference source not found.), and sulfur removal was insignificant (Figure 33).

![Graph](image-url)

**Figure 23. As removal versus bed volume for BPW (SR6, 03/26 sample), pH 5. Influent As concentration of 10.1 mg/L. Data for a fixed bed column packed with 12-40 mesh GAC. 10-minute EBCT. (UW Chem. ICP/OE data).**
Figure 24. As concentration versus bed volume for BPW (SR6, 03/26 sample), pH 5. Influent As concentration of 10.1 mg/L. Data for a fixed bed column packed with alternating 4 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (UW Chem. ICP/OE data).

Figure 25. Comparison of As removal from BPW (SR6, 03/26 sample) by (i) one 12-40 mesh GAC column followed by an ME column (series) versus (ii) one 12-40 mesh GAC column followed by an ME column (series) followed by KMnO₄ oxidation versus (iii) permanganate pre-oxidized BPW followed by ME column. Influent As concentration of 10.1 mg/L. 6-minute EBCT, altered (UW Chem. ICP/OE data)
Figure 26: A, Sb and S removal versus bed volume for BPW (SR6, 05/03 sample), pH 5. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP, 10-minute EBCT. (KCEL ICP/MS data).

Figure 27: Ni concentration versus bed volume for BPW (SR6, 05/03 sample), pH 5. Initial Ni concentration was 15 ug/L. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP, 10-minute EBCT. (KCEL ICP/MS data).
Figure 28: Fe concentration versus bed volume for BPW (SR6, 05/03 sample), pH 5. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).

Figure 29. As, Sb and Ni removal versus bed volume for BPW (SR7 sample), pH 5. Influent As concentration of 7.5 mg/L. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).
Figure 30. S concentration versus bed volume for BPW (SR7 sample), pH 5. Initial S concentration was 433 mg/L. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).

Figure 31. Mn concentration versus bed volume for BPW (SR7 sample), pH 5. Initial Mn concentration was 1.6 mg/L. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).
Figure 32: Contaminant removal versus bed volume for BPW (SR7 sample), natural pH. Influent As concentration of 7.5 mg/L. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).

Figure 33: Sulfur concentration versus bed volume for BPW (SR7 sample), natural pH. Initial S concentration was 427 mg/L. Data for a fixed bed column packed with alternating 2 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).
Results of another Fe/C packed column, where the alternating Fe/C layers were 1 cm as opposed to 2 cm to stimulate increased ME reactions between the iron and carbon media, are shown in Figure 34 through Figure 41. In this iteration, 900 bed volumes of BPW influent were treated. For microelectrolysis column treatment to be cost effective, it must be able to treat high volumes of BPW due to the high quantity of iron and carbon used compared to batch treatment methods. Figure 34 demonstrates that the removal of As from BPW was successful (>90% removal) for bed volumes up to 100. However, what appears to be a chromatographic release occurred after the 200th bed volume, in which all of the arsenic that was removed and adsorbed on the GAC was released into the effluent. Figure 35 shows As concentration vs bed volume for the same experiment.

The concentration of arsenic associated with the chromatographic release was so high, the estimate of the overall As mass retained by the column was negative (Figure 36). However, this is an artifact caused by insufficiently detailed data on As concentration in the column effluent immediately before and after the chromatographic As release event. Further measurements are necessary to address this issue. That is, column effluent samples must be taken at smaller bed volume increments to generate a detailed As concentration vs. bed volume profile which is necessary to understand As accumulation and release in Fe/C columns in sufficient detail.

This result may be viewed in both a positive and negative light. It raises the concern of the ability of the GAC to adsorb significant quantities of arsenic present in BPW and therefore its overall efficacy must be studied in more detail. One possible solution would be to simply add more GAC or include a GAC post-treatment column. This also raises the potential of reagent regeneration, where the Fe/C column could be “washed” after a certain amount of bed volumes have been treated and then re-used. This would significantly lengthen the lifetime of the Fe/C media and reduce the cost of treatment.

Figure 37 and Figure 38 describe antimony removal and accumulation. Similarly to As, Sb removal was successful for the first 100 bed volumes (>98% removal). Some breakthrough occurred after the 200th bed volume, however treatment was still relatively successful (>60%) up
to 500 bed volumes. After that, treatment plateaued at about 35%. Unlike As, there was no leaching of Sb.

Figure 39 demonstrates iron mobility within the Fe/C column. Nominal concentrations of iron are found in BPW, so the source of the release of 450 mg/L after the 600th bed volume is LCP media. This could be due to the corrosion processes that occur and form oxidation products such as Fe$^{2+}$ that may leach and be present in effluent. Iron release continued to be significant until the end of the run, which coincides with a decrease in contaminant removal. This phenomenon needs to be studied further.

Manganese removal is shown in Figure 40. Mn removal efficiency fluctuates over the first 500 bed volumes. Breakthrough occurs after the 600th bed volume, where manganese concentrations of ca. 4 mg/L were found in the effluent samples. The initial concentration of Mn in the BPW influent was about 2.2 mg/L, so Mn leaching was taking place from the Fe/C matrix. Sulfur concentrations are shown in Figure 41. Minimal removal of sulfur other than an outlier at 200 bed volumes occurred.

![Figure 34. Arsenic removal versus bed volume for BPW (SR7 sample), natural pH. Influent As concentration of 7.5 mg/L. Data for a fixed bed column packed with alternating 1 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).](image)
Figure 35. Arsenic concentration versus bed volume for BPW (SR7 sample), natural pH. Data for a fixed bed column packed with alternating 1 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).

Figure 36. Apparent arsenic accumulation versus bed volume for BPW (SR7 sample), natural pH. Data for a fixed bed column packed with alternating 1 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).
Figure 37. Antimony removal versus bed volume for BPW (SR7 sample), natural pH. Data for a fixed bed column packed with alternating 1 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).

Figure 38. Antimony accumulation versus bed volume for BPW (SR7 sample), natural pH. Data for a fixed bed column packed with alternating 1 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).
Figure 39. Iron concentration versus bed volume for BPW (SR7 sample), natural pH. Data for a fixed bed column packed with alternating 1 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).

Figure 40. Manganese concentration versus bed volume for BPW (SR7 sample), natural pH. Data for a fixed bed column packed with alternating 1 cm layers of 12-40 mesh GAC and LCP. 10-minute EBCT. (KCEL ICP/MS data).
4.4 SUMMARY ON PERFORMANCE OF FIXED BED COLUMNS IN AS REMOVAL FROM LANDFILL LEACHATE AND BEW PROCESS WATER

The use of fixed bed columns using microelectrolysis technology for arsenic removal from landfill leachate and landfill gas treatment condensate resulted in mixed but promising results. Over the course of experimentation, it has become clear that the removal of As and co-occurring contaminants from the aforementioned matrices is exceedingly difficult due to the complex nature of the wastewater and the still unknown speciation of As. While some experiments proved unsuccessful, it has also been proven over the course of multiple trials that this reductive/adsorptive technology has the ability to remove >90% of dissolved BPW arsenic for a relatively limited number of bed volumes (Figure 32). This is accomplished by reducing the dissolved arsenic and co-precipitating it with oxidized ferrous and ferric hydroxides, following which the As becomes enmeshed and adsorbed by the activated carbon media. The observation of As adsorbing by the Fe/C media and then undergoing a chromatographic release event (Figure 36) indicates that regeneration of media is possible. Regeneration steps include first backwashing the media with sodium hydroxide to facilitate ion exchange followed by rinsing the media with...
hydrochloric acid to remove oxides from the zero-valence iron media. Further experimentation is required to determine if this treatment scheme can remove As from BPW in a cost-effective manner.

4.5 AS LEACHING FROM SPENT LANDFILL GTS

Gas treatment solids from BioEnergy Washington that have historically been deposited at CHRLF are almost certainly a major source of arsenic in both BPW and landfill leachate waste streams. While SulfaTreat media that were used for LFG treatment and deposited in the CHRLF site until 2019 were unavailable for this study, we examined As release from spent Norit Cabot Darco BG1 media that have been used for LFG treatment since then.

Due to the decision of KC SWD to stop depositing spent LFG media in the CHRLF site, Norit Cabot Darco BG1 are not present in the landfill. However, assuming that the accumulation and release of As and co-occurring species from Norit Cabot Darco BG1, which comprises activated carbon only, is largely similar to that from SulfaTreat which combines iron oxides and activated carbon, experiments described in this section provide information needed to quantify As release from these solids under conditions understood to regulate this occurrence in the landfill.

Thus, another goal of this research project was to investigate the mobility of As in spent LFG treatment solids exemplified, as mentioned above, by activated carbon-based Norit Cabot Darco BG1 media. Spent GTS were obtained in April 2020 and stored in a cold room in sealed glass jars, as shown in Figure 42.
4.6 EXAMINATION OF AS LEACHING FORM SPENT GTS, PACKED COLUMNS

Columns were packed with spent GTS and exposed to synthetic influents that had varying concentrations of sulfite and carbonate added as sodium carbonate or bicarbonate salts. Sulfite was used to induce the highly reducing conditions found in the landfill. Carbonate and bicarbonate were used because bicarbonate is abundant in the leachate and in some extent in BPW. Figure 43 shows the results of these experiments. Effluents from the packed columns that received the sulfite or carbonate-containing influents had very similar arsenic leaching trends, with arsenic levels decreasing exponentially with bed volume. High levels of arsenic were observed to leach from the GTS in the early stage of each run. For example, 1330 ug/L of arsenic was found in the second bed volume of GTS treated with sulfite. The level of arsenic leaching approaches about 160 ug/L after 20 bed volumes for GTS treated with sulfite or carbonate.

Figure 44 compares TOC and As concentrations for columns packed with GTS solids. TOC present in the effluent primarily comes from dissolved organic carbon. The correlation between
TOC and As levels in the column effluents is generally ambiguous. The data for the bicarbonate influent have the highest As leached vs. TOC correlation with an $R^2$ of 0.75. Carbonate treatment has a $R^2$ of 0.42, while sulfite treatment has the least significant correlation with an $R^2$ of 0.22. However, the low $R^2$ value obtained for the sulfite data is strongly affected by one datapoint which appear to be an outlier. These results indicate no unambiguously strong correlation between arsenic and TOC release from GTS packed columns exposed to either sulfite or carbonate-containing effluents. On the other hand, batch GTS exposures discussed in the section that follows show the presence of such correlations.

Figure 45 correlates UV absorbance at 254 nm to As release for columns packed with GTS solids. Sulfite treatment has the highest correlation with an $R^2$ of 0.44. Carbonate treatment has a $R^2$ of 0.22, while bicarbonate treatment has the least significant correlation with an $R^2$ of 0.11. Given these results, there is no correlation between UV absorbance and arsenic release from GTS packed columns treated with either sulfite, carbonate or bicarbonate.

In all, results of exposures of spent GTS exposed to synthetic solutions in fixed bed columns are ambiguous. For instance, the solids were not homogenized in terms of their size and thus the pattern of flow of the influent through the column was likely far from optimal, with a high likelihood of channeling due to the presence of both large and small GTS particles. It can also be assumed that significantly longer contact times are necessary to mimic the exposure conditions that actually take place in the landfill where the disposed GTS interact with the humidity, condensates and leachates in the time frame of months to many years. Thus, these experiments need to be continued in the future.
Figure 43. As leaching from spent GTS in packed column, treated with 0.04 M \( \text{Na}_2\text{SO}_3 \), 0.01 N \( \text{Na}_2\text{CO}_3 \) or 0.01 M \( \text{NaHCO}_3 \). 60-minute EBCT. (KCEL ICP/MS data).

Figure 44. Correlation between As leaching and TOC release from GTS in packed column, treated with 0.04 M \( \text{Na}_2\text{SO}_3 \), 0.01 N \( \text{Na}_2\text{CO}_3 \) or 0.01 M \( \text{NaHCO}_3 \). 60-minute EBCT. (KCEL ICP/MS data).
4.7 EXAMINATION OF AS LEACHING FROM SPENT GTS, BATCH EXPOSURES

Initial batch exposures of spent GTS utilized a dose of 10 grams of non-dried, non-homogenized (meaning different particle sizes) GTS media per 100 mL of solution (100 g solid/L). These exposures were conducted to further understand and quantify As mobility under conditions deemed to be relevant for As release in the conditions typical for active zones of the CHRLF sites, and also in analytical determinations of As concentrations in GTS. The batch exposures were accordingly done for acidic, basic, high alkaline and strongly reducing conditions. Such conditions were imposed by additions of requisite amounts of HNO₃, NaHCO₃, Na₂CO₃, Na₂CO₃, NaHS and hydroxylamine (NH₂OH). Carbonate and bicarbonate were chosen because they are present in excess in landfill leachate. Batch experiments were utilized in order to observe As release from GTS undergoing long contact times.

Figure 45. Correlation between As leaching and UV absorbance at 254 nm from GTS in packed column, treated with 0.04 M Na₂SO₃, 0.01 N Na₂CO₃ or 0.01 M NaHCO₃. 60-minute EBCT. (KCEL ICP/MS data).
Figure 46 shows As leaching from GTS under the initially selected exposure conditions: two carbonate solutions (0.04 and 0.08 M); two sulfite solutions (0.04 and 0.08 M); and two conditions with equal concentration of carbonate and sulfite (0.02 M each and 0.04 M each).

As release observed for all six exposure conditions display the same trend of gradually increasing As concentrations over time. GTS exposed to 0.04 M sulfite exhibited about the same release as GTS exposed to 0.08 M sulfite. The same can be said for GTS exposed to bicarbonate, where the release of As is about the same for the 0.04 M and 0.08 M bicarbonate exposures. However, GTS exposed to 0.04 M sulfite and bicarbonate induced notably more As release than GTS exposed to 0.02 M sulfite and bicarbonate. After one week of exposure, GTS exposed to 0.04 M sulfite and bicarbonate released 30,000 ug/L of As, while GTS exposed to 0.02 M sulfite and bicarbonate released 25,700 ug/L of As. This difference may be attributed to the more negative average redox potential observed for the 0.04 M sulfite and bicarbonate solution which induces more As release over time.

Figure 47 shows changes of the redox potential (mV) over time for seven GTS exposure experiments. The values of the redox potential observed over the initial eight hours of exposures were relatively stable. After eight hours, exposures with a negative redox potential (sulfite and sulfite bicarbonate combinations) began to rise and after a week they were all between a redox potential of -25 mV and +20 mV. This suggests the adsorption or complexation of sulfite by the GTS and the resultant decrease of the concentration of the reductants.

Exposure experiments which did not have the sulfite reductant (0.02, 0.04 and 0.08 M bicarbonate) had a positive redox potential. The measured redox potential values were more stable than those with a negative redox potential. After a week, they approach a redox potential of between +50 and +80 mV. Figure 48 depicts change in pH over time. Initial pH ranged from between 8.0 and 8.5. The pH of GTS exposed to bicarbonate solutions varied over time more than those exposed to sulfite solutions. Overall, pH values observed in these experiments were relatively more stable than the redox potentials.
Figure 46. As leaching from 100 g/L GTS in the presence of carbonate and sulfite, batch exposures. (KCEL ICP/MS data).

Figure 47. Change of redox potential (mV) over time for 100 g/L GTS batch exposure.
Exposures of the GTS in solutions containing sulfite released consistently more As than the exposures to solutions containing only bicarbonate. This is most evident for exposure times exceeding 24 hours. This leads to the tentative conclusion that GTS contain at least two fractions of mobile As. The first fraction is not significantly affected by the ambient water chemistry, and is rapidly released after exposure, which is similar to the results of the fixed bed columns packed with GTS (Figure 43). Unlike the first phase, the second phase of arsenic release is affected by the redox potential. The attributes of components governing the mobilization of these fractions must be studied in more detail.

Figure 49 correlates As release to TOC for GTS exposed to varying concentrations of sulfite and carbonate in batch conditions. Data generated in the presence of sulfite exhibit the highest As vs. TOC correlation with an $R^2$ of 0.97. As and TOC data for the exposures to solutions containing both sulfite and carbonate have a $R^2$ of 0.72, while carbonate exposures have the least significant correlation with an $R^2$ of 0.44. These results show correlations between arsenic and TOC release from GTS exposed to either sulfite or carbonate. The lower $R^2$ values obtained for the carbonate with sulfite, as well as just carbonate, are each affected by one datapoint which may be an outlier.
The presence of correlations between As and organic compounds’ release is supported by UV absorbance spectra measurements. Figure 50 correlates absorbance at 254 nm to As release for the same GTS exposure conditions. Carbonate and sulfite exposure has the highest correlation with an $R^2$ of 0.82. Sulfite has an $R^2$ of 0.65, and carbonate has an $R^2$ of 0.57. As opposed to the As vs. TOC correlations, the As release data when correlated with absorbance at 254 nm form a single dataset. This may indicate an interreference from residual sulfite in the TOC measurements of GTS sulfite exposures, whose presence may have decreased the efficiency of oxidation of organic matter. This matter must be addressed in the future by conducting TOC measurements on sulfite solutions with no GTS and subtracting the signal from samples containing GTS.

Figure 51 through Figure 57 shows changes of the absorbance spectra recorded for the experiments described above. These spectra are different, as expected for the carbonate and sulfite exposures because sulfite per se absorbs light while carbonate does not have any appreciable absorbance. Despite their differences, the spectra consistently show that absorbance increases with time, and that GTS exposed to sulfite exhibits higher absorbance than GTS exposed to carbonate.

Arsenic release from spent GTS exposed to only DI water is shown in Figure 58. As mobilization was relatively modest in the absence of a reductant, with ca. 240 ug/L leaching after 2 hours, increasing to 800 ug/L after nine days of exposure. Figure 59 describes As release from spent GTS under varying sulfite concentrations. Mobilization of As clearly depends on the concentration of sulfite and is not instantaneous but rather increases with time. Figure 60, which shows As release over time from GTS exposed to 5 g/L sulfide, further enhances the point. These results confirm that reducing conditions enhance the mobility of As released from spent GTS; this effect becomes increasingly notable for sufficiently long exposure times. Figure 61 shows As leaching from spent GTS exposed to ca. 1% nitric acid. While there was more As release over the first two hours as compared to those observed in the case of the exposures to sulfite, levels were similar after 24 hours (ca. 30 mg/L).
Figure 49. Correlation between TOC and As release from GTS (KCEL ICP/MS data).

Figure 50. Correlation between UV absorbance at 254 nm and As release from GTS (KCEL ICP/MS data).
Figure 51. Changes in UV spectra for 100 g/L GTS exposure in 0.04 M sulfite solution.

Figure 52. Changes in UV spectra for 100 g/L GTS exposure in 0.08 M sulfite solution.
Figure 53. Changes in UV spectra for 100 g/L GTS exposure in 0.02 M bicarbonate solution.

Figure 54. Changes in UV spectra for 100 g/L GTS exposure in 0.04 M bicarbonate solution.
Figure 55. Changes in UV spectra for 100 g/L GTS exposure in 0.08 M bicarbonate solution.

Figure 56. Changes in UV spectra for 100 g/L GTS exposure in 0.02 M sulfite and bicarbonate solution.
Figure 57. Changes in UV spectra for 100 g/L GTS exposure in 0.04 M sulfite and bicarbonate solution.

Figure 58. As leaching from 100 g/L GTS exposed to DI water. (UW Chem. ICP/OE data).
Figure 59. As leaching from 100 g/L GTS at varying sulfite concentrations. (UW Chem. ICP/OE data).

Figure 60. As leaching from GTS exposed to 5 g/L sulfide solution. (KCEL ICP/MS data).
Further experiments concerned with the release of As from GTS were carried out with the reductant hydroxylamine NH$_2$OH. This change was done because hydroxylamine is a stronger reductant than sulfite and it does not contain sulfur, whose presence in sulfite makes it difficult to interpret data on the release of S from GTS.

Hydroxylamine induced a strongly reducing environment similar to those found in a landfill. Changes of the redox potential of solutions containing varying concentrations of NH$_2$OH and pH in the absence of GTS are shown in Figure 63 and Figure 64. In absence of GTS, the redox potential was relatively stable. For a 0.04 M initial NH$_2$OH concentration, the redox potential in the absence of GTS was ca. -175 mV for 21 days at which it started to gradually decrease to ca. -80 mV at the end of a 49-day observation period (Figure 65). Over time, the exposed GTS consumed hydroxylamine, as demonstrated by the consistent increase in the redox potentials over the first three weeks (Figure 65). The hydroxylamine solution that contained no GTS maintained a negative redox potential, further proving this point. Redox potential was between about +50 and +75 mV for solutions containing GTS after three weeks, which may have inhibited a further increase in As release. Figure 66 shows that pH consistently increased over
the first three weeks, after initially being adjusted to pH 8, and then plateaued in a similar manner to redox potential.

Figure 67 demonstrates that As was released logarithmically over time. As concentrations largely plateaued after ca. 28 days of exposure, which is when the redox potential changed from negative to positive values. While higher doses of hydroxylamine resulted in increased As release, the differences between the observed As concentrations were small.

Release of sulfur (Figure 68) and antimony (Figure 69) follow a similar trend. However, S and Sb concentrations showed a more pronounced increment after the initial exposure phase of ca. 28 days during which As release largely stabilized. Variation of hydroxylamine concentrations affected sulfur release only marginally. In contrast, antimony release noticeably increased when the hydroxylamine concentration was increased from 0.02 to 0.04 M. However, further increments of hydroxylamine concentration did not significantly affect Sb release.

Vanadium release (Figure 70), in contrast to the consistent and logarithmic release of As, Sb and S, had two decidedly different phases. Vanadium release increased expeditiously during the first seven days of exposure, following which they decreased exponentially. This phenomenon was caused by the readsorption of V by the GTS. Higher hydroxylamine concentrations, most significantly 0.08 M NH₂OH, were associated with higher V release. The change in behavior of vanadium concentration transpired when the observed redox potentials began to decrease. This is emblematic of the significance of redox conditions to the mobility of GTS retained contaminants. It may be important to monitor V concentrations in leachate because vanadium’s mobility is affected by its oxidation state which looks to be more sensitive to redox conditions than that of arsenic.

Like vanadium, there is limited environmental concern for the release of sulfur from spent GTS, however it is relevant for attaining a better comprehension of As mobility and mechanisms of its transfer throughout the landfill system, that is from LFG to GTS, and from spent GTS to landfill gas condensates. For example, high correlations between sulfur and arsenic release may indicate the presence of As-S compounds, which would give insight into the oxidation state and chemical
nature of arsenic and therefore its mobility and/or stability between the systems within the landfill. Due to knowledge of the formation of multiple sulfur containing arsenic compounds in the environment, and the understanding that As in BPW is chemically associated with sulfur, it is reasonable to compare release of sulfur and arsenic, as well as that of antimony which is an important co-occurring contaminant.

Figure 71 shows the linear correlation between arsenic and sulfur release from spent GTS for all three of the initial concentrations of hydroxylamine. Antimony and sulfur release followed the same trend (Figure 72). The \( R^2 \) coefficients for the As vs. S and Sb vs. S correlations are 0.92, while \( R^2 \) coefficient for As vs. Sb is 0.94. Further analysis of these data show that 0.065 grams of arsenic and 0.029 grams of antimony are released per each gram of released sulfur. The data indicate that, in terms of molar yields, each mole of sulfur released from spent GTS is correlated with the release of 0.028 and 0.008 moles of As and Sb, respectively.

The strong linear correlations and high values of molar yields of arsenic and antimony indicate a substantial extent of arsenic volatilization processes that exist during the generation of landfill gas at CHRLF. These results show that the retention of arsenic and its release from GTS is fundamentally related to that of sulfur, which is significantly more abundant in spent GTS. These results indicate the arsenic removal from BPW may be regulated by the generation and reactivity of sulfur containing arsenic species developed in GTS and discharged to BPW.
Figure 62. Redox potential (mV) at varying pH and sulfite concentrations.

Figure 63. Redox potential (mV) at varying pH and hydroxylamine concentrations.
Hydroxylamine effects on redox potential, pH 5

Hydroxylamine effects on redox potential, pH 7
Figure 64. Hydroxylamine effects on redox potential on DI, BPW (SR7) and LEPS (SR7) solutions at pH 5, 7, 9 and 11.
Figure 65. Changes of redox over time for GTS exposed to solutions containing varying hydroxylamine (NH$_2$OH) concentrations. GTS concentration 100 g/L. Decrease in redox potential indicative of addition of nominal amount of hydroxylamine.

Figure 66: Changes of pH over time for GTS exposed to solutions containing varying hydroxylamine concentrations. GTS concentration 100 g/L. Addition of nominal amount of hydroxylamine after 49 days.
Figure 67: Arsenic release from 100 g/L GTS in the presence of varying hydroxylamine concentrations. (KCEL ICP/MS data).

Figure 68: Sulfur release from 100 g/L GTS in the presence of varying hydroxylamine concentrations. (KCEL ICP/MS data).
Figure 69: Antimony release from 100 g/L GTS in the presence of varying hydroxylamine concentrations. (KCEL ICP/MS data).

Figure 70: Vanadium release from 100 g/L GTS in the presence of varying hydroxylamine concentrations. (KCEL ICP/MS data).
Figure 71 Correlation between arsenic and sulfur concentrations released from 100 g/L GTS in the presence of varying hydroxylamine concentrations.

Figure 72 Correlation between antimony and sulfur concentrations released from 100 g/L GTS in the presence of varying hydroxylamine concentrations.
Figure 73 shows the change in redox potential that occurred over time for the four experiments conducted during “Round 2” of the spent GTS exposure experiments. These experiments utilized air-dried and sieved GTS solids. As explained elsewhere in this thesis, the four size fractions (SF) used in these experiments were denoted as SF1 (<0.42 mm), SF2 (0.42 to 1 mm), SF3 (1 to 1.4 mm) and SF4 (1.4 to 2 mm).

GTS particle size did not significantly affect change in redox potential, as all experiments gradually increased the solution redox potential at a similar same rate. Temperature did have an effect on the behavior of redox potential. GTS solids exposed to 4°C temperature initially had the least negative redox potential at ca. -100 mV, with this value decreasing somewhat linearly over the next 42 days. GTS exposed to 20 and 35°C temperature, respectively, initially had more negative redox potentials of about -250 mV after the third day of exposure. The 35°C exposure then increased the redox potential rapidly, reaching < -50 mV after 28 days, at which point hydroxylamine was added to decrease the redox potential back down to -250 mV. The 20°C exposure followed the same pattern but less rapidly, reaching a < -50 mV redox potential after 35 days. Meanwhile, both mass dose and hydroxylamine concentration had considerable effects on redox potential.

Figure 73 shows that 50 and 75 g/L dried GTS doses rapidly consumed hydroxylamine. The redox potential was ca. 0 mV after only two weeks. In contrast, the 20 g/L dried dose exposure had a redox potential of below -150 mV after four weeks, and the 5 and 10 g/L dried doses maintained a redox potential of ca. -200 mV for the duration of the six-week experiment. Lastly, the data show that, as expected, a higher hydroxylamine concentration maintains a lower redox potential. The 0.1 and 0.2 M exposures both maintained a redox potential between -300 and -250 mV throughout the duration of the experiment, while more hydroxylamine had to be administered to the 0.1 and 0.2 M exposures after four and five weeks, respectively, because their observed redox potentials were increased to above the -50 mV limit.

pH was also measured for this experiment. All exposures began with a pH of ca. 8.5 to 9, increasing slowly to ca. 10 over the course of the experiment.
Redox potentials, size effects

Redox potentials, temperature effects

Redox potentials, mass effects
Figure 73. Change of redox potential (mV) over time for Round 2 GTS batch exposure experiments. Decrease in redox potential indicative of addition of nominal amount of hydroxylamine.

Figure 74 through Figure 77 present the effect of particle size, temperature, mass dose and hydroxylamine concentration on the release of arsenic from spent GTS. Overall, particle size, temperature and mass dose display relatively clear and expected effects on As release. GTS particle size results show that there is an inverse relationship between size and As release. This is due to the increased surface area of the smaller media (SF1) resulting in more contact with the outside environment and a subsequent higher release of arsenic compared to the largest media, SF4 (Figure 74). With an R^2 linear correlation coefficient of 0.98, the results indicate that a 1.0 mm decrease in GTS diameter will result in a ca. 9000 ug/L increase in As release (this correlation utilized the results from 28 days of exposure).

Meanwhile, temperature results indicate that at a low temperature such as 4°C, As release from GTS is inhibited. However, there is no appreciable difference between As release at 20°C and 35°C. These trends may have to do with the effect temperature had on redox potential (Figure 73). For example, the inhibited release of As from the 4°C sample correspond to a higher redox potential (-100 mV) over the first three weeks of the experiment. These findings need to be studied further.

GTS mass dose effects on arsenic release are shown in Figure 76. A clear trend is observed, that a higher mass dose results in increased As release over time. With an R^2 linear correlation
coefficient of 0.99, the results indicate that a 10 g/L increase in GTS mass dose results in a 1 mg/L increase in arsenic release (this correlation utilized the results from 28 days of exposure). Lastly, hydroxylamine concentration effects on As release are shown in Figure 77. These results are inconclusive and contradict earlier findings that a higher concentration of hydroxylamine results in an increase in As release over time (see Figure 67). In this experiment, GTS exposed to 0.2 M hydroxylamine exhibited the highest As release followed by 0.1 M and then 0.5 and 1.0 M displayed no meaningful difference. It is however likely that at sufficiently high concentrations, hydroxylamine can form binary or ternary complexes or other yet to be identified compounds with As, S and other components of GTS and thus affect the mobility of these elements. Further experiments should be conducted to verify these findings.

![Figure 74. Effect of GTS particle size on arsenic release, batch conditions. 20 g/L GTS mass dose, 20°C, 0.2 M hydroxylamine. (KCEL ICP/MS data).](image-url)

Figure 74. Effect of GTS particle size on arsenic release, batch conditions. 20 g/L GTS mass dose, 20°C, 0.2 M hydroxylamine. (KCEL ICP/MS data).
Figure 75. Effect of temperature on arsenic release from GTS, batch conditions. 20 g/L GTS mass dose, 0.2 M hydroxylamine, SF3 solids. (KCEL ICP/MS data).

Figure 76. Effect of GTS mass dose on arsenic release, batch conditions. 20°C, 0.2 M hydroxylamine, SF3 solids. (KCEL ICP/MS data).
Figure 77. Effect of hydroxylamine concentration on arsenic release from GTS, batch conditions. 20 g/L GTS mass dose, 20°C, SF3 solids. (KCEL ICP/MS data).

Figure 78 shows how particle size, temperature, mass dose and hydroxylamine concentration effect antimony release from spent GTS. All four variables have the exact same effects on Sb release as they do on As release. Figure 79 shows how these same four variables effect vanadium release from spent GTS. Apart from mass dose experiment, these results correspond to earlier findings, namely that V release increases rabidly over the first week, following which they decreased rabidly, caused by readsorption by GTS associated with observed redox potentials becoming less negative. The last co-occurring contaminant release shown is sulfur (Figure 80), whose release is important to study due to the formation of S containing As compounds in the environment. S release from spent GTS follow the same patterns as As release, with the exception of the hydroxylamine concentration effect experiment. 0.1, 0.2 and 0.5 M hydroxylamine exhibit no meaningful difference in S release, whereas 1.0 M hydroxylamine releases significantly more S, increasing linearly overtime such that after 42, 900 mg/L of S was released, compared to between ca. 200 and 300 mg/L for the other three experiments.
Figure 78. Effect of GTS particle size, temperature, mass dose and hydroxylamine concentration on antimony release, batch conditions. SF3, 20°C, 20 g/L GTS, and 0.2 M hydroxylamine unless otherwise noted by figure title. (KCEL ICP/MS data).
Figure 79. Effect of GTS particle size, temperature, mass dose and hydroxylamine concentration on vanadium release, batch conditions. SF3, 20°C, 20 g/L GTS, and 0.2 M hydroxylamine unless otherwise noted by figure title. (KCEL ICP/MS data).
Figure 80. Effect of GTS particle size, temperature, mass dose and hydroxylamine concentration on sulfur release, batch conditions. SF3, 20°C, 20 g/L GTS, and 0.2 M hydroxylamine unless otherwise noted by figure title. (KCEL ICP/MS data).
Figure 81 shows the correlation between arsenic and sulfur release for the four GTS exposure experiments. These correlations are important because of the probable domination of sulfur-containing arsenic species present in BPW formed by the sulfidation of arsines within Cedar Hills Regional landfill. The four correlations do not tell a clear story, as the $R^2$ coefficients range from 0.051 for the hydroxylamine concentration effects experiment to 0.971 for the mass dose effects experiment. Further experiments are required to ascertain the correlation between As and S release from GTS.
Figure 81. Arsenic vs. sulfur release correlations on GTS particle size, temperature, mass dose and hydroxylamine concentration effects experiments, batch conditions. (KCEL ICP/MS data).

4.8 SUMMARY OF SPENT GTS EXPOSURE EXPERIMENTS

Experiments concerned with exposing spent BEW gas treatment solids show that they contain high levels of arsenic originating from CHRLF landfill gas. The analytical data indicate As and other co-occurring contaminants are mobilizable under reducing conditions which are the norm for landfill sites. Environmental conditions such as temperature and redox potential, as well as GTS factors such as mass dose and particle size have noticeable implications on the re-release of toxic compounds into landfill sites, and therefore the concentrations of these compounds in leachate that must be treated. Further experiments are necessary to better understand this phenomenon and decrease the risk associated with landfill gas treatment for renewable energy, and to find solutions regarding spent GTS storage.
5. CONCLUSIONS

5.1 AS REMOVAL FROM LEACHATE AND LFG CONDENSATES

The results of this study demonstrate the complexity involved with the removal of arsenic from landfill leachate and LFG condensates. Furthermore, the variability in contaminant concentration between different samples from different samplings rounds makes it difficult to establish a baseline. However, this thesis has shown that microelectrolysis technology has the ability to remove arsenic from these matrices unlike conventional treatment such as coagulation with ferric chloride or oxidation.

Leachate contains high levels of organic matter along with other contaminants which may compete with arsenic during ME treatment. Therefore, several mediums were tested on leachate to determine if they could be effective for pre-treatment. This includes GAC, zeolite, perlite, pyrite and steel wool. Aside from GAC, these methods did not improve arsenic removal efficiency. A column packed with only GAC was able to remove ca. 30% of arsenic present in the leachate. This indicates that carbon adsorption for pre-treatment may be beneficial both to remove organic matter and a modest but not insignificant amount of As. Stacked Fe/C columns were able to remove >90% arsenic, as well as co-occurring contaminants such as chromium and nickel, for a limited number of bed volumes. While these findings are important, the concentration of As found in leachate at CHRLF are comparatively minor compared to that found in BEW process water, so assessing the ability of ME to treat BPW is paramount.

Arsenic removal from BPW using only a GAC packed column was between 10 and 20% for a limited number of bed volumes, and thus could be considered as a potential pre-treatment step. Permanganate oxidation was also tested as a possible pre- or post-treatment step; however, it provided no meaningful improvement in arsenic removal. As with the experiments with leachate, Fe/C stacked columns were able to remove >90% of arsenic for a limited number of bed volumes. It was also successful in removing antimony, nickel and manganese. Further experiments were conducted at higher bed volumes to determine if this process was scalable. As removal was effective (>90%) over the first 100 bed volumes, however what appeared to be a
chromatographic release occurred after the 200th bed volume, in which the arsenic that was adsorbed into the GAC/Fe packing was quantitatively released back into the effluent. This result raises a concern of the ability of GAC to remove significant quantities of arsenic. But it also indicates the potential of regenerating GAC media over time. Overall, experimentation has shown that microelectrolysis technology can successfully remove high levels of arsenic. This is an important finding given that conventional treatment has not proven to be effective. Further investigation is required in order to optimize this process, determine its cost, and scale it to a pilot level demonstration.

5.2 AS QUANTIFICATION AND MOBILIZATION FROM SPENT LFG TREATMENT SOLIDS

The second part of this thesis focused on the quantification and mobilization of arsenic from spent LFG treatment solids used by BEW. The results are relevant due to the prevalence of landfill gas treatment for renewable energy in both the United States and globally. Experiments exposing spent GTS show that they contain high levels of arsenic that originate from landfill gas at CHRLF.

Results indicate that spent GTS may contain at least two fractions of mobile As, which can be seen when comparing GTS exposed to either sulfite or carbonate. The first fraction appears to not be significantly affected by ambient water chemistry and is rapidly released after exposure. Conversely, the second fraction is affected by the redox potential, resulting in a second phase of As release in which a lower redox potential (provided by sulfite) results in increased levels of As release. Overall, the release of As follows a logarithmic trend.

Vanadium release from GTS had two decidedly different phases. V release rapidly increased over the first week of exposure, following which it decreased rapidly. This change occurred when redox potentials began to become more positive and is emblematic of the importance of redox conditions to the mobility of contaminants within spent GTS. While there is limited environmental concern for the release of V from GTS, it is important to monitor V
concentrations in leachate because its oxidation state affects its mobility and appears to be more sensitive to redox conditions than As.

Meanwhile, sulfur release from spent GTS is relevant because of the formation of S containing As compounds in the environment, while Sb is also an important co-occurring contaminant. Therefore, it is possible to gain a better understanding of As mobility within the landfill system by observing and correlating S and Sb release with As release. This study found strong linear correlations between As and S release, as well as between As and Sb release from spent GTS. In terms of molar yields, each mole of S release from spent GTS was correlated with the release of 0.028 moles of As and 0.008 moles of Sb. These correlations indicate that a considerable degree of arsenic volatilization occurs during the generation of LFG at CHRLF, and that As retention and release from GTS is fundamentally related to that of sulfur. The results suggest that As removal from BPW may be governed by the generation and reactivity of sulfur containing As species found in GTS and discharged to BPW.

Further experiments were conducted on dried and homogenized spent GTS to determine the effect of temperature, mass dose and particle size on As release. Analytical data indicate that higher temperatures and mass dosage and lower particle sizes will result in increased As and co-occurring contaminant release. Furthermore, lower redox potentials also resulted in increased As release over time.

5.3 RECOMMENDATIONS FOR FUTURE WORK

Future work needs to address the following major aspects of BEW process water treatment and As mobilization from spent landfill gas treatment solids:

(i) Determination of As speciation in CHRLF leachate and LFG condensates, as well as in effluent from microelectrolysis stacked columns;

(ii) Optimization and scale of microelectrolysis stacked column technology for As removal from landfill leachate and landfill gas condensates. Assess the ability of an up-flow pumping regime to reduce clogging and preferential flow paths within the columns;
(iii) Experiments on virgin GTS media to establish As and co-occurring contaminant baseline;
(iv) Determination of best practices regarding spent GTS detoxification and/or disposal.
6. REFERENCES


