## REMOVAL OF OXYANIONIC SPECIES FROM COAL COMBUSTION RESIDUALS: THE CASE OF BORON AND BROMIDE

by

#### LUCAS NOVELLO FAVERO

(Under the Direction of Valentine A. Nzengung)

#### ABSTRACT

The US in 2018 generated about 102 million tons of CCRs, out of which approximately 40% were disposed of in surface impoundments and landfills. Boron is one of the elements most readily released from fly ash into the water, and as such is one of the most abundant trace elements in CCR waste streams. Beyond boron, CFPPs are also a significant source of bromide discharges to the environment. Cost-effective technologies for treating boron and bromide in coal ash leachate is an immediate need. This work provides data on low-cost sorbents and chemical precipitation alternatives for the removal of boron and bromide from coal ash leachate and FGD wastewater. Iron impregnation of bamboo biochar was identified to be the most effective in the removal of boron and bromide simultaneously. Ettringite was effective on boron removal from coal ash leachate using alternative low-cost materials such as steel slags and recycled aluminum cans.

> INDEX WORDS: Coal Combustion Residuals, CCR, Coal Ash, Flue Gas Desulfurization, Boron, Bromide, Wastewater Treatment, Reactive Media, Batch Test, Column Test, Sorption, Chemical Precipitation, Ettringite, Biochar, Steel Slag

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### DEDICATION

I dedicate this work to those who did not have the same opportunities as I have had. This work is not only the product of my effort, but the product of the sacrifice of every person that ever had to be denied something in order for me to have this opportunity.

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#### **1 INTRODUCTION AND LITERATURE REVIEW**

#### 1.1 INTRODUCTION

The electricity generation process in thermal power plants is almost identical across the globe, but the quantity and quality of Coal Combustion Residuals (CCRs) vary distinctly due to the quality of coal, temperature maintained in the boiler and process efficiency (Asokan et al., 2005). In 2005, Asokan et al. (2005) classified CCRs as the world's largest mineral resource, with its processing, handling and safe management posing significant environmental sound management and sustainable development challenges.

In the most recent industry records, it is reported that the United States generated about 102 million tons of CCRs, which include fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) byproducts (Association, 2018). From this total, approximately 60% of CCRs were beneficially used (i.e., concrete and wallboard), while the remaining 40% were disposed of in surface impoundments and landfills (Association, 2018). The EPA CCR Management Rule has documented reports of 40 confirmed and 113 potential environmental impact cases due to storage and disposal of CCRs (Register, 2010). A total of 60% of the pollution cases are groundwater or surface water contamination due to the leaking of surface impoundments. Many of these cases report concentrations of As, Se, and B, among others that exceed EPA standards for drinking water, aquatic-life exposure, and health advisory standards (Register, 2010).

Despite the efforts and the commitments for renewable power to account for a significant share of the total electricity supply, coal is still one of the most important electricity producing fuels. With growing energy demand, many industrialized and developing countries are likely to continue to rely on coal for power generation in the decades to come (Izquierdo and Querol, 2012), giving relevance to the question of how to appropriately treat and dispose of CCR.

There are many potential uses for CCR. In a literature review by Asokan et al. (2005), the compiled uses include: back fill material, bricks production, manufacture of cement, concrete, adhesives, wall board, agriculture/soil amelioration, wood substitute, paint, etc. We are a long way from full utilization of CCR; in 2011 the World-Wide Coal Combustion Products Network estimated that marginally under 50% of world production was put to use. There are large amounts of fly ash either stored temporarily in stockpiles, disposed of in ash landfills or lagooned (Izquierdo and Querol, 2012). Effective CCR and leachate treatment is a pressing environmental challenge, necessitating the need for development of cost-effective technologies for the treatment of CCR solids and leachate.

Today much attention is paid to the reuse of CCR, especially fly ash. Fly ash has been successfully used for many years in a wide range of applications. However, it is most commonly used as a high-performance substitute for Portland cement and as a clinker addition in the manufacturing of Portland cement (Izquierdo and Querol, 2012). The literature on the reuse of fly ash is abundant and the many possibilities of how to expand its use have been presented (Ahmaruzzaman, 2010; Blissett and Rowson, 2012).

The composition of CCR leachate is determined by the elements bound onto the surface of fly ash particles and more directly exposed to leaching (Izquierdo and Querol, 2012). The leachability is largely governed by the pH of the water-ash system, that is controlled by the

calcium and sulfur ratio (Querol et al., 2001). When calcium is the dominant species, it create an alkaline water-ash systems that contributes to attenuate the leachability of many heavy metals, but it also enhances the mobility of a few oxyanionic species, i.e. As, B, Cr, Mo, Sb, Se, V and W (Izquierdo and Querol, 2012).

Among the oxyanionic species listed above, boron is one of the elements most readily released from fly ash into water (Cox et al., 1978; James et al., 1982). Unlike other regulated constituents present at high concentrations in CCR, boron does not attenuate onto aquifer solids. Thus boron often produces large plumes in groundwater downgradient of CCR units (Jones, 2017). Conventional water treatment methods (e.g. coagulation, sedimentation and filtration) does not significantly remove boron. The methods likely to be effective in boron removal from solution such as ion exchange and reverse osmosis, are likely to be prohibitively expensive (WHO, 2011).

Beyond the oxyanionic species mentioned above, coal-fired power plants are also a significant source of bromide discharges to the environment. In the absence of any control mechanism, bromide would exit power plants in stack gases, but it is captured in wet flue gas desulfurization (FGD) units deployed to reduce sulfur dioxide emissions to the air (Good and VanBriesen, 2019). FGD wastewater is sometimes directed to coal ash lagoons, which introduces bromide into this environment. The concerns over bromide release from scrubbers and its accumulation in coal ash ponds is relevant because it promotes the formation of trihalomethane and bromate (BrO<sub>3</sub><sup>-</sup>) (McTigue et al., 2014). Trihalomethanes and bromate are disinfection by-products (DBPs) and have been shown to have adverse health effects after prolonged exposures (McTigue et al., 2014).

This thesis explores the forms of treatment and removal of boron and bromide from CCR leachate and Flue Gas Desulfurization (FGD) wastewater. Considering the abundance and complex nature of this type of effluent, economic viability is an imperative for the development of any treatment solutions. A wide range of chemical precipitation alternatives and low-cost sorbents were tested and will be discussed in detail in the next chapters, including sorption and coprecipitation as independent and combined solutions evaluated in batch and columns treatment systems.

#### 1.2 MANAGEMENT OF COAL COMBUSTION RESIDUES

There are two main methods of handling CCRs: storage in on-site repositories and reuse. Globally, methods of storage vary considerably from wet, slurried to dry repositories, with dry repositories applied as the preferred method of management (Heidrich et al., 2013). CCR is reused in a range of applications ranging from back fill to soil amelioration. However, any uses of CCR need to consider the long-term stability of metals of environmental concern likely to leach from the CCR.

#### 1.2.1 <u>Composition of CCR</u>

CCRs is a collective term referring to the residues produced during the combustion of coal regardless of ultimate use or disposal. It includes fly ash, bottom ash, cenospheres and other solid fine particles (Asokan et al., 2005). The description of each major component is detailed in Table 1.1.

| Table 1.1 – Coal Combustion Residues (CCRs) description. Adapted from (Associ | ation, |
|---|--------|
| 2003; Heidrich et al., 2013)  |        |

| Term           | Definition  |  |  |  |
|----------------|---|--|--|--|
| Fly Ash        | A product of burning finely ground coal in a boiler to produce electricity. It is the finer<br>ash produced in a coal-fired power station, been collected generally using electro-static<br>precipitators. This is also known as Pulverized Fuel Ash (PFA), correspond to about<br>85+% of all the ash produced.  |  |  |  |
| Bottom Ash     | The coarse ash that falls to the bottom of a furnace. Ash agglomerates formed in pulverized coal furnaces that are too large to be carried in the flue gases that end up falling to the bottom of the furnace. In many furnaces there is a water system that rapidly cools this ash, so-called 'wet bottomed' ash. Usually <15% of the ash produced is bottom ash (BA).   |  |  |  |
| Cenospheres    | Hollow ash particles that form in the furnace gas stream. Sometime these particles will contain smaller ash spheres. They float on water and are usually collected from lagoons, where ash/water disposal systems are being used. Only 1 to 2% of the ash produced are cenospheres.   |  |  |  |
| FGD byproducts | Flue gas desulfurization (FGD) is a step of removal of gaseous sulfur dioxide from boiler<br>exhaust gas. Primary types of FGD processes are wet scrubbers, dry scrubbers, and<br>sorbent injection. FGD process typically uses a high-calcium sorbent such as lime or<br>limestone. Sodium-based sorbent and high-calcium coal fly ashes are also used in some<br>systems. The physical nature of these materials varies from a wet thixotropic sludge to a<br>dry powdered material depending on the process. |  |  |  |

In terms of mineralogical analysis the predominant phase constituents of CCRs are Quartz (SiO<sub>2</sub>), alumino silicate (gehlenite, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) (Asokan, 2003). Studies have also showed that there are other mineral phases such as Albite (NaAlSi<sub>3</sub>O<sub>8</sub>), Mullite (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>), Esperite (CaPb)ZnSiO<sub>4</sub>, Nepoutite (NiMg)<sub>3</sub>Si<sub>2</sub>O<sub>15</sub>(OH)<sub>4</sub>, and Tenorite (CuO) present in CCRs (Kolay and Singh, 2001; Saxena et al., 1998).

In order to attain the mineralogical state described above the mineral fraction in coal undergoes different transformations during and after combustion, namely decomposition, volatilization, fusion, agglomeration or condensation (Jones, 1995). As the flue gas cools down after combustion, volatile elements such as As, B, Hg, Cl, Cr, Se and most prominently S, condense on the surface of the fly ash particles, forming compounds with a variable solubility and essentially combined with Ca. In addition to the latter elements, Cd, Cu, Mo, Sb, V and Zn are also preferentially enriched on the surface, whereas Ba, Co, Cr, Mn, Ni and Pb tend to be more evenly distributed between the surface and the matrix (Jones, 1995). This results not only in a strong gradient of element concentrations within fly ash particles (Kukier et al., 2003), but also in a gradient of leachability (Izquierdo and Querol, 2012). As described by Izquierdo and Querol (2012), the surface layer of fly ash particles which is microns in thickness contains a significant amount of readily leachable elements (Iyer, 2002) that, with the exception of S, stand out for being inherently more toxic at low levels than major elements.

#### 1.2.2 <u>Coal Ash Leachate</u>

Whether fly ash is landfilled, disposed in surface impoundments, lagooned or recycled into ash-based products, care should be taken to mitigate potential environmental impact of the leached constituents (Izquierdo and Querol, 2012). The leached concentrations expressed in terms of absolute value may certainly differ, but the leaching behavior appears to follow relatively common patterns (Izquierdo and Querol, 2012). CCR effluents are enriched in a large number of elements, many of which are toxic (Harkness et al., 2016). In the work of Izquierdo and Querol (2012), there is an extensive literature review of the leaching behavior of elements from coal ash identified as oxyanionic-forming species (i.e., As, B, Cr, Mo, Sb, Se, and V). The very high leachability of the latter oxyanion-forming species from coal ash is determined by pH and Ca/SO<sub>4</sub> ratios in the coal ash.

Based on Ca/S balance and the pH, Izquierdo and Querol in a 2012 review article described three main groups of fly ash:

• Group 1 - Strongly alkaline ashes: free-lime dissolution dominates leaching, with pH values typically in the pH 11-13 range (Heasman et al., 1997) and large amounts of Ca in the leachates. Ca prevails over S (Ca/S>>1).

- Group 2 Mildly alkaline ashes: anhydrite or anhydrous calcium sulfate dissolution dominates leaching, with moderately low-Ca levels and balanced Ca/S ratios that give rise to mildly alkaline conditions (pH 8–9) (Querol et al., 2001).
- Group 3 Acidic fly ash: depleted in CaO and MgO in relation to the sulphate content (Ward et al., 2009) and, therefore, retaining its original acid characteristics as the acidic components concentrated on the surface of fly ash particles are initially brought into solution as sulphuric acid (Swaine, 1990).

It should be noted that the pH of the ash-water system is not static but changes over time. As pH-controlling elements migrate with water percolation, both acid and alkaline ashes tend to progressively develop more neutral pH values, affecting the mobility of some of the elements concerned. The elements enriched in the cores of fly ash particles are not directly exposed to leaching and therefore their releases are diffusion controlled and also dependent on the dissolution rates of the surface layers (Kukier et al., 2003). Surface-associated elements are more susceptible to leaching in an aqueous environment (Izquierdo and Querol, 2012).

Izquierdo and Querol (2012) state that the alkalinity of fly ash attenuates the release of many elements of concern such as Cd, Co, Cu, Hg, Ni, Pb, Sn or Zn among others, but at the same time, it enhances the release of oxyanionic species, such as As, B, Cr, Mo, Sb, Se, V and W. It is known that oxyanionic-forming species, i.e. As, B, Cr, Mo, Sb, Se, V, and W, have maximum leachability in the pH 7-10 range. Meanwhile, non-oxyanion-forming species such as Be, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, REE, Si, Sn, Th, Tl, U, and Zn have a minimum solubility in the pH 7-10 region. These elements can be regarded as being of low concern in alkaline fly ash under environmental conditions (i.e. mildly acidic to alkaline pH).

Minerals such as ettringite  $[Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O]$ , which is among the first minerals to form in the presence of alkaline ash and water (Hassett et al., 2005) may absorb a number of trace elements (Jones, 1995). Ettringite requires Ca, Al,  $SO_4^{2-}$ , excess water, and pH >11 to form (Hassett et al., 2005). The precipitation of various Ca-bearing species is also common, given the ubiquity of Ca. Sorption on Fe oxides is another recognized process that may reduce the mobility of elements, as the Fe oxides provide sites for metal binding.

Ettringite shows a great potential for metalloid scavenging, due to its strong affinity for capturing As, B, Cr, Sb, Se, and V in the mineral lattice. However, the formation of ettringite is a slow process, as such the latter is relevant in long-term exposure scenarios (Jones, 1995). Being as unstable mineral under recarbonation conditions, ettringite cannot be viewed as an ultimate sink for oxyanions in exposed surface environments (Jones, 1995).

In a recent study, Schwartz et al. (2016) evaluated the influence of redox conditions on the mobilization of As and Se during an ash spill. The data from their study suggests that the absence of oxygen was insufficient to determine contaminant mobilization in anaerobic conditions at ash impoundments and ash spill sites. Instead, microbially-driven redox transitions, which are biostimulated in the presence of sulfate from the coal ash, are more environmentally relevant and necessary for attaining sufficiently reducing conditions for transformations of As, Se, and possibly other contaminants (e.g., mercury, chromium, etc.) (Schwartz et al., 2016).

#### 1.2.3 <u>Major Elements in CCR Leachate</u>

In order to test methodologies for the treatment of CCR leachate, it is important to establish the behavior of constituents from the coal ash in an aquatic environment. Izquierdo and Querol (2012) categorized the elements leached from coal ash into two groups; major and trace elements. This division was based on their occurrence in the coal ash solids, not leachate. The discussion below explores the major elements that play a role in the process of secondary precipitation of one of the trace elements of concern in this study, boron.

Calcium (Ca) is not regarded as an element of concern, but it does play a primary role in the environmental quality of the ash. The pH of the ash-water system is dictated by the amount of Ca (particularly in relation to that of S) and most trace elements display a pH-dependent solubility. Ca promotes the precipitation of mineral phases containing environmentally relevant elements. The presence of Ca is also essential for the precipitation of ettringite and other secondary Ca-hydrated phases that are likely to incorporate and retain environmentally relevant elements such as As, Cr or Se. Therefore, it can be stated that Ca controls the leachate composition for the most part, and also controls the leachability of trace contaminants to a large extent (Izquierdo and Querol, 2012).

Iron in fly ash is mainly present as magnetite mixed in various proportions with hematite, although a minor proportion can be assimilated in the glassy matrix (Kukier et al., 2003). Spinel structures are highly stable and resistant to weathering, therefore Fe and any isomorphous substituted elements are not easily released to the environment (Izquierdo and Querol, 2012). Iron oxyhydroxides are also present in fly ash (Dudas, 1981). These species are widely known to play a key role in the sorption of a number of elements of environmental concern, thus attenuating the concentrations in the leachates (Turner, 1981).

Sulfur is mainly associated with the surface of the fly ash, combined with the marked solubility of most sulphate-bearing compounds, making it the major soluble element in fly ash along with Ca (Izquierdo and Querol, 2012). Under most natural environmental conditions, reduced S species are generally present in negligible quantities and  $SO_4^{2-}$  is the dominant species

(Fruchter et al., 1990). The leached concentrations of S in water are correlated to its concentration in fly ash (Iwashita et al., 2005; Izquierdo et al., 2008), with typical values for alkaline ash ranging from 700 to 15,000 mg/kg  $SO_4^{2^-}$  (Izquierdo et al., 2011).

#### 1.3 BORON AS AN EMERGING CONTAMINANT

The distinction of boron as an emerging contaminant has to do mainly with coal ash sites that readily leach the element from CCR and is commonly detected at high concentrations in groundwater near coal ash basins (Jones, 2017). Boron compounds tend to be soluble, and quite mobile in the subsurface, and difficult to remediate. Boron has the highest concentration of minor and trace elements in coal ash leachate, ranging from 0.2 to more than 100 mg/L and typically occurs as a neutral boric acid species, being not readily removed by common water treatment procedures (EPRI, 2006).

One of the challenges that remain is boron association with coal combustion residuals, which when in contact with water could leach significant amounts of the element. The pronounced leachability of boron is intimately related to its dominant surface association in fly ash (Querol et al., 1995). Most of the boron is organically associated in coal (Finkelman, 1995; Swaine, 1995). Such affinity enhances the volatility during combustion and the subsequent condensation of soluble admixed borate salts onto fly ash (Dudas, 1981).

Early studies pointed out that a large fraction of boron in fly ash is in a soluble form (Cox et al., 1978; James et al., 1982). It is one of the elements most readily released from fly ash into water. A 15-min contact of fly ash with water was sufficient to leach most of the soluble boron from ash. These researchers underline boron as the most mobile trace element in coal ash. There is no substantial difference between acidic and alkaline ash, since boron leachability does not

depend significantly upon pH over pH 6 (Cox et al., 1978). Rather, the leached levels appear to be controlled by the total concentration in the fly ash (Iwashita et al., 2005).

EPA promulgated the Federal CCR Rule in 2015, which identifies boron as an Appendix III indicator constituent for detection monitoring (Register, 2015). Jones (2017) explained that a recent settlement between utilities, EPA, and NGOs indicates that boron should be added to the list of constituents in Appendix IV of the final CCR Rule. Under the proposed change, a statistical exceedance of background concentrations for boron will trigger cleanup to background with the edge of the unit as the point of compliance (Jones, 2017).

The Interstate Technology & Regulatory Council (ITRC, 2010) published guidance on mass flux and mass discharge limits for coal ash residuals, which is adopted at several CERCLA sites as interim remedial performance standards for source control measures and as metrics for the transition to less aggressive remedial operations. Jones (2017) affirms that these mass discharge metrics are now being applied at CCR sites as a management tool for large boron plumes. They provide a means to quantify the mass discharge reduction needed for source control at CCR units to achieve background or risk-based screening levels across large plume areas (Jones, 2017).

Besides the interest of the coal power industry to mitigate boron in coal ash leachate, several other segments are likely to benefit from the development of cost effective boron removal technologies, Table 1.2 summarizes congruent interests for the area.

| Type of water                    | Initial type of water boron concentration | Cause of concern   |  |  |
|----------------------------------|---|--|--|--|
| Ultrapure water                  | <0.5 mg/L                                 | Significant levels of boron pass through strong base<br>deionizers, distillation, and reverse osmosis units. Particular<br>problem in semiconductor industry where precise control of B<br>doping is required. |  |  |
| Geothermal                       | 10-100 mg/L                               | Release of boron to receiving water can exceed mg/L level in streams, limiting exploitation of geothermal resource.  |  |  |
| Nuclear                          | >3 g/L                                    | Boron concentration is varied to control rate of core reactions.<br>Boron is very effective in neutron capture, and leakage<br>represents a significant problem.   |  |  |
| Landfill leachate                | 1-10 mg/L                                 | Indicator of leachate plume and extent of potential groundwater contamination.   |  |  |
| Coal power<br>plants/fly ash     | 3-100 mg/L                                | Ash pond water and cooling pond water contain high levels of<br>boron. About 25% of the boron is carried over in this water<br>during evaporative purification, preventing reuse as potable<br>water.          |  |  |
| Irrigation water                 | >1 mg/L                                   | Removal may be necessary to prevent crop damage. May also<br>need to be leached or immobilized in soil to recover land for<br>agriculture in some cases.   |  |  |
| Seawater<br>evaporation<br>brine | g/L                                       | Boron coprecipitates with Mg(OH)2, decreasing the melting point and preventing resource recovery.  |  |  |
| Desalination                     | 5 mg/L                                    | Several countries have limit on B in drinking water in the tenths of mg/L range. Cannot be achieved by normal reverse osmosis.   |  |  |
| Sewage                           | 1-3 mg/L                                  | Boron in detergents adds to wastewater loads, and might inhibit bacterial activity and exceed mg/L levels in streams.  |  |  |
| Drinking-water<br>treatment      | <1 mg/L                                   | If boron exceeds mg/L level, could inhibit plant growth.   |  |  |

# Table 1.2 - Review of Industries and Scenarios Where Boron Removal is of Interest.Adapted from (Parks and Edwards, 2005).

The high incidence of boron in natural and wastewaters presented in so many different industries (Table 1.2) highlights the importance of research in developing and introducing an effective process for the removal of boron from aqueous medium. The most significant difficulty in developing such a method is the fact that boron occurs in water as a contaminant with many other chemical compounds and at various concentrations (Melnyk et al., 2005).

Conventional water treatment (coagulation, sedimentation, filtration) does not significantly remove boron, and special methods need to be used. EPRI (2006) reports that boron can be removed from water using boron-selective ion exchange and boron selective solvent extraction, while techniques like reverse osmosis are effective only at high pH (>9.24). Other removal mechanisms have been proposed, but none have been fully developed.

#### 1.3.1 Natural Occurrence of Boron and Uses

Boron is a ubiquitous element, it is distributed in the lithosphere as borate minerals (e.g.  $Na_2B_4O_7 \cdot 10H_2O$ , etc.) and in a range of water bodies mostly in the form of boric acid (Tang et al., 2017). The average boron content varies from 2 to 100 mg /kg in soils (Parks and Edwards, 2005). In nature, boron is always found as a compound with other elements, elemental boron has not been found yet (Guan et al., 2016). Regarding water bodies, the main boron sources are the oceans, in which the concentration ranges from 0.5 to 9.6 mg/L (Hilal et al., 2011). As a contrast, boron in uncontaminated surface and groundwater is usually lower than 0.5 mg/L. However, it has been found to increased significantly in recent years as a result of anthropogenic activities.

Boron is also an essential element for plants, animals and human beings (Guan et al., 2016). Although an essential element, the concentration range between boron deficiency and its toxicity is very narrow. The toxic effects caused by the excess boron are more common than boron deficiency in the environment (Guan et al., 2016). For plants, boron plays a role in several metabolic functions, and deficiency can cause adverse effects such as retardation of root and leaf growth, bark splitting, retardation of enzyme reactions and leaf photosynthesis, and even can lead to a death of plants (Howe, 1998). Toxic symptoms for plants include edge and tip necrosis, yellowing spots in the leaves, reduction of root cell division, dwarf, then followed by weaker photosynthesis and less yield (Hilal et al., 2011; Wei et al., 2011).

For animals and human beings, boron contributes to immune function of organisms (Hunt, 2003). It also has effects on bone metabolism and central nervous system function

(Nielsen et al., 2007). Lack of boron can cause low absorption efficiency for nutrient elements such as calcium, magnesium and phosphorus (Wang et al., 2014). For humans and animals, Wang et al. (2014) described that although the toxicity mechanism for excessive boron is not clear, the long-term effect on environment cannot be ignored. It has been reported that adverse effects of boron can lead to problems with cardiovascular, coronary, nervous and reproductive systems, change in blood composition, development retardation of children and a higher risk of birth pathology for pregnant women (Mel'nik et al., 2008; Wolska and Bryjak, 2013).

Boron is also an important raw material for numerous industries, such as the production of fiberglass, detergents, fertilizers, etc. (Parks and Edwards, 2005). The glass industry is the biggest consumer, accounting for more than half of the total production of boron compounds worldwide (Wang et al., 2014). Besides that, the isotope boron-10 plays crucial role in the nuclear industry, it can control the nuclear reaction rate, avoiding uncontrolled cascade nuclear reactions (Duderstadt and Hamilton, 1976).

#### 1.3.2 Boron Chemistry in Aqueous Environments

Being the only non-metallic element in group 13 of the periodic table, boron has an electron distribution of  $1s^22s^22p^1$ . Boron is the most electronegative element in group IIIA of the periodic table, its behavior is intermediate between metals and non-metals and for some aspects it is similar to its neighbors aluminum, carbon and silicon (Tagliabue et al., 2014).

It is electron deficient because a valence shell with eight electrons cannot be completed by three single bonds. Consequently, all boron is essentially in the trivalent oxidation state (Tang et al., 2017). The crystal ionic radius of boric acid is in the range 0.244-0.261 nm (Banasiak and Schäfer, 2009). Due to its poor hydration capacity, the boric acid molecule in aqueous solutions is expected to have a similar size to the water molecule (Tang et al., 2017).

Naturally, boron is found in three forms (1) boric acid, (2) borate, or (3) borosilicate mineral (Tang et al., 2017). Boric acid is soluble in water with a solubility of 5.5 g per 100 g solution at 25 °C. In aqueous solutions, it behaves as a Lewis acid. Its dissociation is achieved by accepting a hydroxyl ion to form the tetrahydroxyborate ion (Tang et al., 2017), equation 1.1.

$$B(OH)_3 + 2H_2O \leftrightarrow [B(OH)_4]^- + H_3O^+$$
 1.1

The intrinsic  $pK_a$  of boric acid is 9.24 under standard condition, for dilute solutions at 25 °C, on the other hand, the apparent  $pK_a$  value depends on the external conditions, such as ionic strength and temperature (Tang et al., 2017). Dickson (1990) developed an empirical equation to establish the apparent  $pK_a$  as a relation of salinity and temperature. Based on his equation, Tang et al. (2017) plotted the apparent  $pK_a$ , displayed here in Figure 1.1 (a) and (b) as a function of temperature and salinity, respectively.

The speciation of boric acid depends on its concentration (Hinz et al., 2015) as shown in Figure 1.1 (c) and (d). The monomeric  $B(OH)_3$  or  $B(OH)_4^-$  dominates at low boron concentrations (< 20 mM) while polyborate species prevail at concentrations higher than 20 mM (Tang et al., 2017). Figure 1.1 (c) and (d) shows the speciation of aqueous boron as a function of pH at concentrations of 10 and 400 mM with a salinity of 3.5% and a temperature of 25 °C (Hinz et al., 2015).



Figure 1.1 - Dissociation of boric acid as a function of (a) temperature and (b) salinity, and fraction diagram of aqueous boron species calculated for the pH range of 1-14 for (c) [B]<sub>tot</sub> = 0.01 M, and (d) [B]<sub>tot</sub> = 0.4 M. Thermodynamic data used in the calculations as reported in (Ingri, 1962; Ingri et al., 1963). Adapted from (Tang et al., 2017).

#### 1.3.3 Sorbents for Boron Removal

Adsorption is an extremely effective way to remove boron from aqueous solutions at very low concentrations (Guan et al., 2016). Many review papers have compiled a variety of boron removal techniques, among which are adsorption alternatives (Wang et al., 2014; Wolska and Bryjak, 2013; Xu and Jiang, 2008). The relevance of adsorption as a method of treatment is emphasized by Guan et al. (2016), who produced a review paper specifically exploring sorbents used in boron removal. Some of the materials utilized in the adsorption processes of boron include activated carbon, fly ash, clays, natural minerals, layered double hydroxides, biological materials, oxides, mesoporous silica, nanoparticles, complexing membranes and selective resins (Guan et al., 2016). Among these sorbents, several waste materials that are potentially cost-effective for large scale remedial process are of interest. Table 1.3 presents a summary of studies on industrial waste materials used as boron adsorbents.

Table 1.3 - Industrial waste materials potentially effective for boron removal from water.Adapted and updated from (Guan et al., 2016).

| Adsorbent                                   | Mode  | Optimal experiential conditions  | Removal<br>% | Isotherm<br>models | Adsorption<br>kinetics      | Ref.                           |
|---|-------|--|--------------|--------------------|-----------------------------|--------------------------------|
| Waste Tire<br>Rubber                        | Batch | pH: 2, 7, dosage: 0.05 g/50<br>mL, adsorption time: 48 h,<br>T: 25 °C                                  | 75.7%        | Freundlich         | Pseudo-<br>second<br>order  | (Babiker et al., 2019)         |
| Palm Oil Mill<br>Boiler Ash                 | Batch | pH: 7, dosage: 6 g/50 mL,<br>adsorption time: 12 h, T: 25<br>°C  | 65.69%       | -                  | Pseudo-<br>first-order      | (Chieng and<br>Chong,<br>2013) |
| Palm Oil Mill<br>Boiler Ash                 | Batch | pH: 8, dosage: 40/300 mL, adsorption time: 1 h   | 80%          | Freundlich         | -                           | (Chong et al., 2009)           |
| Al-based<br>water<br>treatment<br>residuals | Batch | pH: 8.2-8.5, dosage: 25 g/L  | 24.5%        | Langmuir           | Pseudo-<br>second-<br>order | (Irawan et<br>al., 2011)       |
| Concrete<br>particles                       | Batch | Calcined temperature: 175<br>°C, adsorption time: 1440<br>min, boron initial<br>concentration: 10 mg/L | 99.8%        | -                  | -                           | (Iizuka et<br>al., 2014)       |

Another line of sorbents being studied are natural materials. Guan et al. (2016) divided the natural materials into two groups; (1) natural minerals such as sepiolite, cristobalite, alunite, etc; (2) plant materials, such as seeds of plants, and natural polymers. The focus on waste based adsorbents, is due to their abundance and low. Table 1.4 lists the different natural adsorbents and their adsorption capacities.

| Adsorbent                        | Modific.                                 | Mode    | Optimal<br>experiential<br>conditions                    | Ads.<br>mg/g | Isotherm<br>models            | Kinetics &<br>break-<br>through<br>curve | Ref.                              |
|----------------------------------|--|---------|--|--------------|-------------------------------|--|-----------------------------------|
| Eggshell<br>wastes               | Calcination                              | Batch   | pH 6, adsorption time<br>48 h                            | 42.19        | Freundlich                    | -  | (Al-Ghouti<br>and Salih,<br>2018) |
| Waste calcite                    | FeCl3                                    | - Batch | pH 9, adsorption time 24 h                               | 1.6          | Langmuir<br>- &<br>Freundlich | -  | (Jalali et al.,<br>2016)          |
| Rice residues                    | -  |         | pH 8, adsorption time 48 h                               | 9.26         |                               | -  |                                   |
| Magnesite –<br>bentonite<br>clay | -  | Batch   | Adsorption time 30<br>min, ion concentration<br>20 mg/L  |              | Langmuir<br>&<br>Freundlich   | Pseudo-<br>second-order                  | (Masindi et al., 2016)            |
| Sepiolite                        | HCl                                      | Batch   | pH: 10, T: 20 °C   | 178.57       | Langmuir                      | Thomas model                             | (Öztürk and                       |
|                                  |  | Column  |  | 219.01       |                               | & Yoon and Nelson model                  | Kavak, 2004)                      |
| Vermiculite                      | Thermal<br>shock,<br>H2O2,<br>ultrasound | Batch   | pH: 9.26, dosage: 6<br>g/200 mL, adsorption<br>time: 5 h | 1.62         | Freundlich                    | -  | (Kehal et al.,<br>2010)           |
| Calcined<br>alunite              | -  | Batch   | pH: 10, dosage: 1 g/25<br>mL, T: 25 °C                   | 3.39         | Freundlich                    | -  | (Kavak,<br>2009)                  |
| Pomegranate<br>seed powder       | PVA                                      | Batch   | pH: 8.0, dosage: 2<br>g/100 mL                           | 30.0         | Langmuir                      | Pseudo-<br>second-order                  | (Oladipo and<br>Gazi, 2014)       |
|                                  |  | Column  |  | 38.5         | -                             | Modified dose response model             |                                   |
| Chitosan                         | -  | Batch   | pH: 8.0, T: 35 °C,<br>dosage: 0.15 g/25 ml               | 3.9          | Freundlich                    | Pseudo-<br>second-order                  | (Bursalı et al., 2011)            |
| Calcium<br>alginate gel          | _  | Batch   | pH: 9-10,<br>dosage: 0.2 g/100 mL                        | 94           | Langmuir                      | Pseudo-<br>second-order                  | (Ruiz et al.,                     |
|                                  | -  | Column  | pH: 6, dosage: 0.1<br>g/100 mL                           | 121          | -                             | -  | 2013a; Ruiz<br>et al., 2013b)     |

# Table 1.4 - Other natural materials for boron removal from water. Adapted and updated from (Guan et al., 2016).

In a study by Jalali et al. (2016) they evaluated several natural materials and chemically modified forms of sorbents, including bentonite, kaolinite, zeolite, waste calcite, residues of wheat, rice and green shell of walnut for the removal of boron from aqueous solutions. The study concluded that the chemical modification of natural materials with FeCl<sub>3</sub> improved boron adsorption capacity. Following modification with FeCl<sub>3</sub> the pH of zero point of charge (pH ZPC) of the sorbents fell below 9.0, resulting in the formation of surfaces with net negative charges and the subsequent preferential sorption of the predominant H<sub>3</sub>BO<sub>3</sub>. Also, the chemical

modification may help to form hydrous ferric(oxy)hydroxides, which improve boron adsorption (Guan et al., 2016).

Many oxides and hydroxides with divalent and trivalent metal ions are common sorbents in industrial and environmental applications, including aluminum oxides. Alumina is one of the most studied oxide sorbents for boron removal from aqueous solutions (Guan et al., 2016). Bouguerra et al. (2008) obtained a maximum boron adsorption efficiency of 40% with 0.8 g activated alumina in a 5 mg/L boron solution. The solution pH played a very important role in the adsorption efficacy. Bouguerra et al. (2008) found that boron adsorption increased as pH increased. Hydroxides can form complexes with  $B(OH)_4^-$  in aqueous solutions (Prodromou, 2000), resulting in the selective chemisorption of boron. Meanwhile, activated and impregnated variations of carbon have been found to be poor adsorbents of boron (Xu and Jiang, 2008).

#### 1.3.4 Boron Precipitation / Coprecipitation

Precipitation of dissolved constituents can occur for a variety of reasons, including the increase in concentration, change in pH, Eh (oxidation/reduction potential), temperature, or ionic strength (EPRI, 2006). Coprecipitation is the removal of a dissolved constituent by simultaneous precipitation with another constituent that is typically present in higher concentrations, for example, the addition of Fe(III) or Al(III) salts to achieve coagulation during water treatment. In this case, the constituent of concern is removed by trapping it within or adsorbing it to precipitates as they form (EPRI, 2006).

Both organic and inorganic compounds have been shown to be effective for boron precipitation. As described in the work from Xu and Jiang (2008), lime precipitation reduced boron from >1000 mg/L to about 400 mg/L. Meanwhile, metal salts coagulated boron in the

same test to <400 mg/L. The treatments were pH sensitive with high and low water pH reducing treatment efficiency.

In a study by Zhang and Reardon (2003), they explored the use of hydrocalumite and ettringite to remove B, Cr, Mo, and Se oxyanions from high pH waters by incorporation into the minerals. The experiments were performed by precipitating these minerals in solutions containing B, Cr, Mo, and Se oxyanions at conditions relevant for lime-leaching of fly ash and fly ash containing concrete. Zhang and Reardon (2003) evaluated the uptake of all four anions by hydrocalumite and ettringite. They observed that hydrocalumite was more effective than ettringite, reducing the anion concentrations to below drinking water standards. Ettringite showed an anion preference in the order  $B(OH)_4^{2-} > CrO^{4-} > SeO_4^{2-} > MoO_4^{2-}$ . The investigators also observed that unlike ettringite, hydrocalumite was least effective in removing borate from solution (Zhang and Reardon, 2003).

The effectiveness of borate removal from FGD by ettringite has been investigated by Hiraga and Shigemoto (2011). They synthesized ettringite in the presence of H<sub>3</sub>BO<sub>3</sub> by adding Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to FGD wastewater and alkalization by Ca(OH)<sub>2</sub>. It was observed that the precipitation of borate from the FGD increased with the concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> added. Also, the mass of boron precipitated increased with increasing pH of the FGD wastewater, reaching a peak in the range between 10 and 12. The precipitated boron concentrations were in proportion to the Al(OH)<sub>3</sub> concentrations at pH <10 and the precipitated ettringite concentration at pH >10, respectively (Hiraga and Shigemoto, 2011). Alkalization with Ca(OH)<sub>2</sub> promoted the formation of ettringite and the removal of boron.

#### 1.4 FLUE GAS DESULFURIZATION PROCESS AND BROMIDE

The Flue Gas Desulfurization (FGD) process, also known as air scrubbers, is the preferred air pollution-control technology for controlling SO<sub>2</sub> and sometimes mercury (McTigue et al., 2014). Coal-fired power plants may use SO<sub>2</sub> scrubbers to meet the requirements of Phase II of the Acid Rain SO<sub>2</sub> Reduction Program (Srivastava and Jozewicz, 2001). In the operation of scrubbers, coal-fired power plants use calcium bromide to oxidize elemental mercury (McTigue et al., 2014). Bromine, unlike chlorine, is not a usual component in coals or flue gas, and introducing too much of it into the flue gas system brings a risk of secondary pollution problems (Qu et al., 2009).

The new Mercury and Air Toxics Standards (MATS) requirements, implemented in December 2011 by the United States Environmental Protection Agency (EPA) are expected to increase bromide discharges from coal-fired power plants. That could happen in a couple of ways as described by McTigue et al. (2014). First, coal-fired power plants have already added or will be adding wet scrubbers in response to the MATS requirements for removing SO<sub>2</sub>. Even if a plant uses a coal source with a low bromide content, the increased use of wet scrubbers to remove SO<sub>2</sub> will result in more bromide releases, even in situations in which bromide is not added to improve mercury removal. Second, if the coal source has a high bromide content, these wet scrubber discharges will include even greater amounts of bromide (McTigue et al., 2014). Beyond the natural presence of bromine in coal and the bromide addition to coal to reduce air emissions of mercury, Good and VanBriesen (2019) also described a third possible source; where bromide is added to create refined coal to qualify for tax credit.

The occurrence of bromide from scrubbers in coal ash ponds is relevant because it promotes the formation of trihalomethane (THM) and bromate (BrO<sup>3-</sup>) (McTigue et al., 2014).

Trihalomethanes are among disinfection by-products (DBPs) and have been shown to have adverse health effects after prolonged exposures (McTigue et al., 2014). Bromate is generally formed by the reaction of ozone and naturally occurring bromide in drinking water, during ozonation process (Weinberg et al., 1993), but also can be formed in natural environments induced by sunlight (Iriarte et al., 2003). The World Health Organization (WHO, 2011) established a provisional guideline value of 0.01 mg/l. The provisional value arises from the fact that although there is inadequate evidence of carcinogenicity in humans, there is enough evidence for the carcinogenicity of bromate from high-dose studies in experimental animals. Thus, bromate is classified as a potential carcinogen to humans. The WHO had previously recommended that a health based guideline of 0,003 mg/L for bromate in drinking water should be implemented, however a provisional guideline value of 0.01 mg/L has been implemented due to current technical limitations with available technologies to achieve the previous target (Theiss et al., 2014).

Understanding this reality in November 2015, the EPA promulgated the Effluent Limitations Guidelines (ELGs) for the Steam Electric Power Generating Sector. These guidelines regulate permissible discharge limits for six wastewater streams produced at coal fired power plants (CFPPs), including fly ash transport water, bottom ash transport water, flue gas mercury control wastewater, gasification wastewater, CCR leachate from ash ponds or on-site landfills, and FGD wastewater (USEPA, 2015). From the six listed, only CCR leachate and FGD wastewater may be discharged to the environment following treatment, the rest would be required to be converted to dry processes (Gingerich et al., 2018). In September 2017, the EPA announced that it is reviewing the FGD wastewater and bottom ash standards for existing facilities. The current situation is that the EPA is proposing revisions to the 2015 ELGs rule,

altering compliance timelines and costly technologies requirement. Even with the proposed rule adjustments, the requirements for treatment continues, establishing a pressing need for costeffective bromide removal alternatives.

#### 1.4.1 Bromide Removal alternatives

Bromine is an element from the halogen group that is not present in nature in its free state. It may have various oxidation states (<sup>-1</sup>, 1, 3, 5, 7), with <sup>-1</sup> (bromide) being the most common oxidation state (Winid, 2015). The presence of bromide in aquatic environments has received a great deal of research interest. There are three aspects of Br- use that seem to contribute to its occurrence: (1) identification of water salination, (2) tracer to study water flows, and (3) water treatment processes (Winid, 2015).

Several studies have been conducted on bromide removal from water. Electrochemical treatment has been shown to remove bromide through a combination of two processes (1) electrolytic oxidation of bromide (Br<sup>-</sup>) to bromine (Br<sub>2</sub>), and (2) volatilization of the bromine on the surface of the electrode by the gases formed during electrolysis (Kimbrough and Suffet, 2006). Although nanofiltration has been used effectively to remove Br<sup>-</sup> from water, the high-cost imposes a limitation for its large-scale application (Chellam, 2000).

Co-precipitation of bromide with magnesium hydroxide has been investigated and reported (Chen et al., 2017; Prados-Ramirez et al., 1995). Coagulation of bromide has also been shown to be an effective alternative for removing bromide. However, Gong et al. (2013) warns that the treatment of sludge after coagulation must be considered seriously, as it contains most of the removed bromide, which is harmful to the environment. Ge et al. (2007) has reported bromide removal by aluminum coagulation. Using synthetic water the investigators succeeded in
achieving a 99.2% removal efficiency of bromide using aluminum chloride (AlCl<sub>3</sub>.6H<sub>2</sub>O) as coagulant. The effects of coexisting ions on removal of bromide by aluminum coagulation was also investigated (Ge and Zhu, 2008). Results showed that the coagulation of bromide was inhibited by the presence of organic matter and anions in natural source waters. Although the authors showed reasonable bromide reductions with small volumes of natural waters, the treatment required large coagulant doses, in order to compensate for the inhibitory effects from competing anions and Natural Organic Mater (NOM). Further investigation of the potential of this technique in more complex wastewater system and in conjunction with other techniques would be of interest.

Numerous materials, including metal impregnated sorbents, activated carbons (AC), activated carbon fibers, anion exchange resins, Ag doped activated carbon, and silver loaded porous carbon spheres have been evaluated as promising adsorbents to remove bromide from water (Chen et al., 2017; Gong et al., 2013; Hsu and Singer, 2010; Sánchez-Polo et al., 2006; Watson et al., 2012; Zhang et al., 2014). These studies revealed that Cl<sup>-</sup> and NOM were the two main competitors for sorption sites with Br<sup>-</sup>. Chen et al. (2017) observed in their experiments a decrease in Br removal with increasing Cl concentration. In addition, the Cl:Br ratio played an important role in the Br removal, the lower the Cl:Br ratio, the higher the Br removal can be achieved.

# 2 SCREENING OF ALTERNATIVES FOR BORON AND BROMIDE REMOVAL FROM COAL COMBUSTION RESIDUE WASTEWATER: BATCH AND COLUMN EXPERIMENTS <sup>1</sup>

<sup>&</sup>lt;sup>1</sup>Favero, L.N. and V.A. Nzengung. To be submitted to *Environmental Science* & *Technology*.

#### 2.1 ABSTRACT

Boron is one of the elements most readily released from fly ash into water, and as such is one of the most abundant trace elements in Coal Combustion Residue (CCR) waste streams. Beyond boron, coal-fired power plants are also a significant source of bromide discharges to the environment. Conventional water treatment does not significantly remove boron and bromide, and currently available options may be cost prohibitively. This work accesses the relative effectiveness of different steel mill slags, biochars and metal-oxyhydroxide biochar modifications for removal of boron and bromide from coal ash leachate and Flue Gas Desulfurization (FGD) wastewater. Iron impregnation of bamboo biochar was identified among the screened adsorbents to be most effective for the removal of boron and bromide simultaneously. The use of a mix of electric arc furnace (EAF) slag, ladle slag and bone biochar were identified as the most efficient for the removal of boron. This study has identified potentially effective low-cost sorbents for the removal of these two constituents from CCR waste streams.

#### 2.2 INTRODUCTION

Most countries depend on coal fired power plants (CFPPs) to meet their electricity demand, and as such have a great need for cost-effective pollution control technologies . In the United States, the Environmental Protection Agency (EPA) has implemented rules to limit air emissions at CFPPs, but has only recently set stringent effluent standards for aqueous emissions. In 2015, the EPA promulgated the Effluent Limitations Guidelines (ELGs) for the Steam Electric Power Generating Sector. These guidelines regulate permissible discharge limits for six wastewater streams produced at CFPPs, including fly ash transport water, bottom ash transport water, flue gas mercury control wastewater, gasification wastewater, leachate from ash ponds or on-site landfills, and flue gas desulfurization (FGD) wastewater (USEPA, 2015). At existing CFPPs, of the six listed streams, only CCR leachate and FGD wastewater may be discharged to the environment following treatment, the rest must be converted to dry solids prior to disposal (Gingerich et al., 2018).

In September 2017, the EPA announced that it is reviewing the FGD wastewater and bottom ash standards for existing facilities. The EPA is proposing revisions that include altering compliance timelines and costly technologies requirement. Even with the proposed rule changes, the requirements for treatment remains. As a result, there is an immediate and pressing need for cost-effective treatment technologies for these waste streams.

Boron is one of the elements most readily released from fly ash into water (Cox et al., 1978; James et al., 1982), and as such is one of the most abundant trace elements in CCR waste streams. Unlike other regulated constituents present at high concentrations in CCR, boron does not attenuate onto aquifer solids. Therefore, boron tends to produce large plumes in groundwater downgradient of CCR units (Jones, 2017).

Beyond boron, coal-fired power plants are also a significant source of bromide discharges to the environment. As described by Good and VanBriesen (2019), the discharge can occur in three ways: (1) natural presence of bromine in coal; (2) bromide addition to coal to reduce air emissions of mercury; and (3) bromide addition to create refined coal to qualify for tax credit. In the absence of any control mechanism, bromide would exit power plants in stack gases, but it is captured in wet FGD units deployed to reduce sulfur dioxide emissions to the air and concentrated in FGD wastewater (Good and VanBriesen, 2019).

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The occurrence of bromide from scrubbers is relevant because it promotes the formation of trihalomethane (THM) and bromate (BrO<sub>3</sub><sup>-</sup>) (McTigue et al., 2014). The trihalomethanes are related to disinfection by-products (DBPs) produced at water treatment plants. The THM are known to cause adverse health effects after prolonged exposures (McTigue et al., 2014). Bromate is generally formed by the reaction of bromine and ozone (WHO, 2011), but also can be formed in natural environments induced by sunlight (Iriarte et al., 2003).

Conventional water treatment (e.g. coagulation, sedimentation and filtration) does not significantly remove boron. The methods likely to work in boron rich effluents (e.g. ion exchange and reverse osmosis) are prohibitively expensive (WHO, 2011). The same situation applies for bromide removal, where conventional treatment options (sorption and co-precipitation) are shown to be poorly effective in the presence of Cl<sup>-</sup> and Natural Organic Mater (NOM); two main competitors for sorption sites with Br<sup>-</sup> (Chen et al., 2017). Electrochemical treatment has been shown to be a viable option, but has high energy demands and operational costs.

This work focuses on the development of low-cost sorbents for the removal of two anionic constituents of significant interest to CFPP in CCR waste streams. The screening performed in this study, in general terms focuses on two types of sorbents; (1) biochar as a sorbent that can be enhanced for adsorption of targeted anions and cations, and (2) steel mill slag for enhancement of precipitation reactions. The efficacy of these two treatment media is discussed in the following sections.

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#### 2.2.1 <u>Biochar</u>

Biochar is defined by the International Biochar Initiative (IBI) as "a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment" (Initiative, 2012). Biochar can be produced from many different feedstocks, such as animal waste, microbial and plant residue, sludge and tire waste. The different methods used to produce biochar are: carbonization, pyrolysis, gasification, hydrothermal treatment and other thermal methods (Li et al., 2018).

Carbonaceous materials have been used for a long time as sorbents for organic and inorganic contaminants in soil and water. Activated carbon, which is charcoal that has been treated (i.e., activated) with oxygen to increase micro porosity and surface area, is the most commonly used carbonaceous sorbent (Ahmad et al., 2014). Biochar is quite similar to activated carbon with respect to method of production via pyrolysis and its medium to high surface areas (Cao et al., 2011). However, unlike activated carbon, biochar is an effective low-cost sorbent (Li et al., 2018). Activated carbon is generally prepared at temperatures higher than 800 °C, and demands high energy input in addition to the activation requirements (e.g., steam, CO<sub>2</sub> or dehydrating chemicals) (Bhatnagar et al., 2013). In contrast, biochar is produced at temperatures lower than 800 °C from low-cost and abundant feedstocks, mainly agricultural biomass waste (Jeong et al., 2016). Biochar contains a non-carbonized fraction that may interact with contaminants (Ahmad et al., 2014). Specifically, the O-containing carboxyl, hydroxyl, and phenolic surface functional groups in biochar could effectively bind to cationic contaminants (Uchimiya et al., 2011). These multi-functional characteristics of biochar suggests that it is a

potentially effective environmental sorbent for organic and inorganic contaminants in soil and water (Ahmad et al., 2014).

The chemical and physical properties of biochar vary widely depending on the feedstock and conditions under which it is produced (Chen et al., 2015; Lawrinenko and Laird, 2015). Surface area and porosity are one of the major physical properties that influence sorption capacity on biochars. When biomass is pyrolyzed, micropores form in biochar due to water loss in dehydration process (Bagreev et al., 2001). Studies show that elevated pyrolysis temperature generally lead to larger pore sizes, thereby creating larger surface area for adsorption (Li et al., 2017). The composition of the feedstock also plays a role in the porosity of the resulting biochar. Generally, biomass that is rich in lignin (e.g., bamboo and coconut shell) develops macroporous structured biochar, while biomass rich in cellulose (e.g., husks) yields a predominantly microporous structured biochar (Joseph et al., 2007).

In general, pristine biochars are resistant to degradation, have a high surface area and considerable negative charge (Sizmur et al., 2016). This common characteristic gives biochar the potential to be used as a sustainable sorbent to remove positively charged ions (e.g.  $Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}$ ) and polar organic molecules (e.g. phenolics, halogenated compounds, solvents) from water by ion exchange, electrostatic attraction, physical sorption and precipitation (Tan et al., 2015).

Li et al. (2018) in their review paper examined the capabilities of biochar to remove oxyanion contaminants, specifically arsenate ( $AsO_4^{3-}$ ), arsenite ( $AsO_3^{3-}$ ), chromate ( $CrO_4^{2-}$ ), nitrate ( $NO_3$ ), and phosphate ( $PO_4^{3-}$ ). They concluded that pristine biochar removal capabilities are relatively low, which is to be expected due to their predominantly negative surface charge and relatively low anion exchange capacity. However, biochar can be modified to manipulate the speciation and abundance of the functional groups that control adsorption using chemical activation or modification of the surface properties. By exploiting the high surface area of biochars as a platform to embed a metal oxide with contrasting chemical properties (and usually a positive charge), biochar-based composites are capable of removing negatively charged oxyanions from aqueous solutions (Sizmur et al., 2017).

Sizmur et al. (2017) explain that the objective of most methodologies to create metal oxide biochar-based composites is to ensure a homogenous spread of the metal over the biochar surface, where the biochar is essentially used as a porous carbon scaffold. The impregnation of biochar with metal oxides is generally performed by soaking biochars or their feedstocks in solutions of metal nitrate or chloride. The most frequently used impregnation agents in the literature are FeCl<sub>3</sub>, Fe<sup>0</sup>, Fe(NO<sub>3</sub>)<sub>3</sub> and MgCl<sub>2</sub> (Sizmur et al., 2017). After the soaking step, the biochar is heated under aerobic conditions at temperatures ranging from 50 to 300°C to allow nitrates or chlorides to be driven off as NO<sub>2</sub> and Cl<sub>2</sub> gases and convert the metal ions to metal oxides (Sizmur et al., 2017).

The anionic removal properties of biochar have been explored for the removal of anionic nutrients; phosphate and nitrate and anionic heavy metals for example hexavalent chromium and arsenic (Li et al., 2017; Li et al., 2018; Rajapaksha et al., 2016; Sizmur et al., 2017; Tan et al., 2016). A limited number of studies have evaluated the effectiveness of biochar for the removal of boron and bromide, and as such provide the basis to further screen other types of biochar.

#### 2.2.2 <u>Steel Slag</u>

Steel slag is a byproduct of the steelmaking and steel refining processes. Three different types of slags are produced by basic-oxygen-furnace (BOF) steelmaking, electric-arc-furnace

(EAF) steelmaking and ladle-furnace steel refining processes (Yildirim and Prezzi, 2011). Both BOF and EAF slags are formed during basic steelmaking operations, making their chemical and mineralogical compositions similar. Calcium oxide and iron oxide are the two major chemical constituents of both EAF and BOF slags. Ladle slag is generated during the steel refining processes in which several alloys are added to the ladle furnace to produce different grades of steel (Yildirim and Prezzi, 2011).

Because of these operational differences, the chemical constituents of ladle slag differ from those of BOF and EAF slags. Typically, the FeO content of ladle slag is much lower (<10%) than that of EAF and BOF slags. On the other hand, the Al<sub>2</sub>O<sub>3</sub> and CaO contents are typically higher for ladle slags (Yildirim and Prezzi, 2011).

Slags from steel production have long been regarded as useful materials in building and civil works. Yi et al. (2012) reports that steel slag can be utilized in many different areas such as soil conditioners, fertilizers, sinter material, production of cement and concrete, etc. As an alternative adsorbent, it has been used to remove heavy metals in environmental applications due to its unique properties and composition (Das et al., 2007). The use of slag for the removal of anionic species is more limited.

Oh et al. (2012) identified in their study the fundamental role of Ca in the leaching of steel slag, becoming the dominant substance in the leachate and used as coprecipitation catalyst for the removal of arsenic in aqueous environments. The mechanisms explored by the authors was the formation of amorphous CaCO<sub>3</sub> under alkaline conditions resulting from the high pH of the slag, which removed As from the aqueous solution by co-precipitation. Most of the amorphous CaCO<sub>3</sub> containing As would be bound to amorphous iron oxides of the slag (Oh et al., 2012).

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The mixture of coal fly ash with EAF was used to create a stabilized solid by Pereira et al. (2001). The efficacy of the process was evaluated through leaching tests on the solidified products, with the concentration of metals leached shown to be strongly pH dependent. The study only evaluated heavy metal concentrations in the leachate, leaving the boron out of the analysis, an opportunity for future studies.

In a different study by Beh et al. (2012), EAF slag was used in a fixed bed column as a form of treatment for the removal of Iron, Zinc, Manganese and Copper. The results confirmed the removal of the mentioned metals from industrial wastewater. However, boron which was not a targeted contaminant of concern was removed to undetectable levels. The study by Beh et al. (2012) showed a very promising removal of boron by EAF slag.

#### 2.3 MATERIALS AND METHODS

#### 2.3.1 <u>Wastewater</u>

Two types of CCR wastewaters were used in this study. The first and more diluted was collected from an unlined coal ash basin at a confidential power plant in the southwest of the United States, that in this study will be referred as coal ash leachate (CAL). This coal ash basin has been operational for decades and still receives the untreated coal ash stream from the power plant. FGD wastewater from the same power station was also used as a source of wastewater with high boron and bromide concentrations. The wastewater samples were collected and provided by employees of the power plants. The wastewater was delivered to our custody in 20-liter food grade clean buckets or single use 20-liter flexible sampling bags. The wastewater samples were transported from the power station to the laboratory at the University of Georgia in

coolers with ice. The wastewater samples were stored in a frozen state until the time of use when the samples were thawed in a refrigerator at 14 degrees C.

## 2.3.2 Biochar Selection and Preparation

A selection of commercially available biochars were purchased and some were produced in-house. For biochars produced in-house, the raw biomass was pyrolyzed at a desired temperature (Table 2.1) for one hour in a muffle furnace under N<sub>2</sub> atmosphere. The description of feedstock and pyrolysis conditions for biochars produced in-house and purchased commercially are presented on Table 2.1. Among the commercially available biochars, not all were accompanied by all the technical parameters of production (Table 2.1).

| Acronym | Feedstock           | Commercial Name        | Vendor                      | Pyrolysis<br>Temperature |
|---------|---------------------|------------------------|-----------------------------|--------------------------|
| PNB     | Pine Biochar        | -                      | In-house Production         | 500 °C                   |
| PWB     | Paper Waste         | -                      | In-house Production         | 500 °C                   |
| РНВ     | Peanut Hull Pellets | -                      | In-house Production         | 500 °C                   |
| HWB     | Red Oak Hardwood    | Made to order          | BioChar Central             | 600 °C                   |
| SWB     | Softwood            | Made to order          | BioChar Central             | 600 °C                   |
| BBB     | Bamboo              | Made to order          | BioChar Central             | 600 °C                   |
| BNB     | Aged Bones          | BONE CHAR 2060-BC      | Charcoal House              | NA                       |
| MBB     | Meat/Bone           | Experimental - Titan A | Titan Clean Energy Projects | 850 °C                   |

Table 2.1 – Types of biochars, sources and production temperatures.

All biochar samples used in the experiments were oven dried at 105°C for 24 hours and then crushed and sieved to 38  $\mu$ m < x < 2.00 mm.

## 2.3.3 <u>Preparation of Modified Biochar</u>

In-house produced, commercially and non-commercially available biochar listed in (Table 2.2) were screened. The methods of modification of some commercial biochars were not provided for proprietary reasons. The production of modified biochar followed an adaptation of several procedures. To produce metal modified PHB, BNB and BBB, the biochars were first rinsed 5 times with boiling distilled water, and then oven dried at 105°C for 24 hrs. The preparation of magnesium (Mg) and calcium (Ca) modified or impregnated biochars adapted the procedures in Xia et al. (2016) and Zhang et al. (2013). The aluminum (Al) modified biochars ware prepared using adapted procedures in Ganvir and Das (2011) and Chen et al. (2016). All reagent solutions in this work were prepared using distilled water. The biochar was rinsed with hot-water and mixed with 0.5 M of the metal chloride solution at a ratio of 10 mL of solution to one gram of biochar in a beaker for 12 h. A 1.0 M NaOH (or 1.5 M NaOH for the Almodification) was used to adjust the pH to around 10 (pH 7 for Al-modification) and precipitate metal oxy-hydroxides. The mixture was stirred for 12 more hours then allowed to incubate for 24 h before oven dried at 110°C for 24 h. After drying, the modified biochars were rinsed 10 times with distilled water, wet-sieved to 38  $\mu$ m < x < 2.00 mm, and oven dried at 105°C for 24 h.

Iron (Fe) modified biochar was produced using a procedure adapted from Hu et al. (2015). The biochar was rinsed with hot distilled water then mixed with 0.5 M Ferric Chloride solution at the proportion 10 mL of solution to one gram of biochar in a beaker for 12 h. The mixture was oven dried at 110°C for 24 h to precipitate Fe-oxy-hydroxide. After drying, the Fe modified biochar was rinsed 10 times with distilled water, wet-sieved to 38  $\mu$ m < x < 2.00mm, and then oven dried at 105°C for 24 h.

| Acronym | Modification /<br>Original Biochar | Commercial<br>Name | Vendor                   | Modification Procedure                                    |
|---------|------------------------------------|--------------------|--------------------------|---|
| Mg-PHB  | Mg Peanut Hull<br>Biochar          | -                  | In-house<br>Modification | MgCl <sub>2</sub> 0.5M / 105 °C Oven<br>dry / pH adjusted |
| Са-РНВ  | Ca Peanut Hull<br>Biochar          | -                  | In-house<br>Modification | CaCl <sub>2</sub> 0.5M / 105 °C Oven<br>dry / pH adjusted |
|         |                                    | 2                  | -                        |   |

 Table 2.2 - Description of different commercial and in-house modified biochars.

| Acronym     | Modification /                              | Commercial     | Vendor          | Modification Procedure               |
|-------------|---|----------------|-----------------|--------------------------------------|
|             | <b>Original Biochar</b>                     | Name           |                 |                                      |
| Al-PHB      | Al Peanut Hull                              | -              | In-house        | AlCl <sub>3</sub> 0.5M / 105 °C Oven |
|             | Biochar                                     |                | Modification    | dry / pH adjusted                    |
| Fe-PHB      | Fe Peanut Hull                              | -              | In-house        | FeCl <sub>3</sub> 0.5M / 105 °C Oven |
|             | Biochar                                     |                | Modification    | dry                                  |
| Fe-BNB      | Fe Bone Biochar                             | -              | In-house        | FeCl <sub>3</sub> 0.5M / 105 °C Oven |
|             |   |                | Modification    | dry                                  |
| Fe-BBB      | Fe Bamboo Biochar                           | -              | In-house        | FeCl <sub>3</sub> 0.5M / 105 °C Oven |
|             |   |                | Modification    | dry                                  |
| AlMg-INN    | Al-Mg Biochar                               | NA             | Innovo Biochar  | NA                                   |
| FeCaMg-PNB  | Fe-Ca-Mg Pine                               | Experimental - | Titan Clean     | NA                                   |
|             | Biochar                                     | Titan B        | Energy Projects |                                      |
| FeCaMg-PNBP | Fe-Ca-Mg Pine                               | Experimental - | Titan Clean     | NA                                   |
|             | Biochar Powder                              | Titan C        | Energy Projects |                                      |
| OXYB        | H <sub>2</sub> O <sub>2</sub> Softwood      | Experimental   | Our Laboratory  | NA                                   |
|             | Biochar                                     |                |                 |                                      |
| Ca-OXYB     | Ca-H <sub>2</sub> O <sub>2</sub> Softwood   | Experimental   | Our laboratory  | NA                                   |
|             | Biochar                                     |                |                 |                                      |
| FeNa-SWB    | FeSO <sub>4</sub> -NaBH <sub>4</sub>        | Experimental   | Our laboratory  | NA                                   |
|             | Softwood Biochar                            |                |                 |                                      |
| FeSO-SWB    | FeSO <sub>4</sub> Softwood                  | Experimental   | Our Laboratory  | NA                                   |
|             | Biochar                                     |                |                 |                                      |
| MRS-BBB     | MuniRem-FeSO <sub>4</sub>                   | Experimental   | Our Laboratory  | NA                                   |
|             | Bamboo Biochar                              |                |                 |                                      |
| CS-SWB      | CS <sub>2</sub> -FeSO <sub>4</sub> Softwood | Experimental   | Our Laboratory  | NA                                   |
|             | BC  |                |                 |                                      |

## 2.3.4 <u>Steel Mill Slag Collection and Preparation</u>

Among the three types of slags generated by steelmaking, two (EAF and Ladle slag) were selected and used in the screening and follow-on tests. Due to the similarities between BOF and EAF slag, only the more readily available EAF slag was obtained and used. The slags tested in this study were made available by Gerdau Long Steel of North America and collected from the Cartersville Steel Mill, in Georgia (Figure 2.1 and Table 2.3).

Once transported to the laboratory, both slags were air dried for two weeks. Size reduction of the ladle slag lumps was with a mortar and pestle. The manually crushed slag was screened to collect the 38  $\mu$ m < x < 2.00mm particle sizes. EAF slag is a considerably harder

solid, and as such a jaw rock crusher was used for size reduction of the aggregates. The size fraction between 38  $\mu$ m < x < 2.00mm was used in experiments.



Figure 2.1 – EAF (a) and Ladle (b) slag samples after air drying and sieving to 38  $\mu m < x < 2.00 mm.$ 

Gerdau Long Steel North America also supply the typical composition of the slags

produced by their Cartersville unit. The composition summary is presented at Table 2.3.

| (% Weight) | Al <sub>2</sub> O <sub>3</sub> | CaO   | SiO <sub>2</sub> | MgO  | Cr <sub>2</sub> O <sub>3</sub> | P2O5 | S    | FeO   | MnO  |
|------------|--------------------------------|-------|------------------|------|--------------------------------|------|------|-------|------|
| EAF Slag   | 5.71                           | 27.28 | 11.85            | 9.09 | 2.13                           | 0.33 | 0.11 | 22.99 | 6.28 |
| Ladle Slag | 2.31                           | 47.88 | 27.22            | 8.95 | 0.13                           | 0.04 | 0.64 | 1.40  | 0.68 |

Table 2.3 - Typical composition of electric arc and ladle furnace slag from GerdauCartersville, GA.

## 2.3.5 <u>Batch Sorption Tests</u>

Several rounds of batch sorption screening experiments using coal ash leachate (i.e., ash basin wastewater) were performed. For each test, the removal efficiency of boron and bromide were evaluated in replicates and compared to the corresponding leachate controls. A known mass of sorbent (0.5 g or 1.0 g) was placed in a 50 mL nominal volume centrifuge tube. The coal ash leachate of known volume (25.0 or 40 mL) was added to each tube and mixed on a rotating shaker at 3.3 rpm for 48 h (Figure 2.2). After mixing, the samples were centrifuged at 2,000 rpm for 20 min. The solution phase in each sample was decanted and filtered through 0.45  $\mu$ m filters to remove any colloids. The filtered solution was placed in two separate vials. One set of the duplicate samples was used for pH measurement while the second was immediately delivered to the analytical Lab for B and Br analysis. Each experiment was accompanied by a wastewater control sample for quality analysis and quality control determination.



Figure 2.2 - Centrifuge tubes placed on the rotating mixer.

The maximum loading tests were performed using CAL and bamboo and bone biochar. The effectiveness of iron modified bamboo, bone and peanut hull biochar was evaluated using FGD wastewater containing much higher concentrations of boron and bromide. The volume of wastewater was fixed at 40 mL while the mass on the sorbent was varied. The samples were them placed on a rotating shaker and mixed for 48 hours at a speed of 3.3 rpm.

#### 2.3.6 Fixed Bed Column Tests

Each material or combination of materials tested was packed in a column with a height of 75 cm, an internal diameter of 10 cm, and a total bed volume of approximately 5.9 L. A 2 cm fine lab grade washed sand was placed at the bottom and top of each column to hold the sorption media in place. The effective sorption media bed volume was approximately 5.5 L. CAL or FGD wastewater were fed continuously at a fixed rate by a peristaltic pump in a up flow configuration during experiment runs. The column experiments were carried out at room temperature of 21 +/- 3° Celsius.

Samples were collected form the top of the column as a predetermined volume of effluent (500 or 1000 mL) exited the column (Figure 2.3). The samples were filtered through 0.45  $\mu$ m filters to remove any colloids. The filtered solution was placed in two separate vials. One set of the duplicate samples was used for pH measurement while the second was immediately delivered to the analytical Lab for B and Br analysis. Each column run was accompanied by a wastewater control sample for quality analysis and quality control determination. The removal rate of the contaminants of concern was calculated from the difference in initial (C<sub>o</sub>) and final (C<sub>f</sub>) concentration over the elapsed pore volumes.



Figure 2.3 – Photos of packed columns.

The media in columns 1 and 2 was placed in two distinct layers, as specified in Table 2.4. Column 3 was packed homogeneously as a single treatment media. The wastewater fed to columns 1 and 2 were pre-treated in a 20-liter bucket with a hydrated aluminum sulphate salt (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O) at a concentration of 1.67 mg/L. The objective of the pre-treatment with aluminum sulphate was to stimulate the formation of ettringite in the porous spaces of the reactive media consisting of biochars and slag mixtures. The ettringite precipitation has been shown remove sulphate from mine water, coupled with the removal of metals (i.e., boron, selenium).

| Columns           | Column 01   | Column 02   | Column 03                |
|-------------------|---|---|--------------------------|
| Media Filling     | 00-02  cm = Sand  | 00-02  cm = Sand  | 00-02  cm = Sand         |
|                   | 02-35  cm = 1180 g  Ladle                                 | 02-35  cm = 1400 g  Ladle                                 | 02-73  cm = 2547.6 g Fe- |
|                   | Slag, 1180g EAF Slag, 500g                                | Slag, 1400g EAF Slag, 700                                 | BBB                      |
|                   | BBB   | BNB   |                          |
|                   | 35-70 cm = 1250g BBB                                      | 35-73 cm = 2153 g BNB                                     | -                        |
|                   | 70-72 cm = Sand   | 73-75 cm = Sand   | 73-75 cm = Sand          |
| Mass Ratios       | 40% BBB   | 50% BNB   | 100% Fe-BBB              |
|                   | 30% EAF Slag  | 25% EAF Slag  |                          |
|                   | 30% Ladle Slag  | 25% Ladle Slag  |                          |
|                   |   |   |                          |
| Wastewater        | CAL   | 1/10 Dilution FGD   | FGD                      |
| Pre-treatment     | 1.67 mg/L Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | 1.67 mg/L Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | N/A                      |
| Flow Rate         | 47 ml/min   | 62 ml/min   | 60 ml/min                |
| Pore Volumes      | 2.4   | 4.9   | 5.4                      |
| Sampling Interval | 500 ml  | 500 / 1000 ml   | 1000 ml                  |

 Table 2.4 - Experimental parameters and column treatment media tested.

After the CAL treatment, a desorption experiment was conducted on column 1. The desorption was performed at the same flow rate as the experiment run, 3 pore volumes of tap water were applied through the column, with samples collected for analysis after every liter of water discharged from the column.

## 2.3.7 <u>Analytical Methods</u>

During the first set of screening tests, the samples were only analyzed for boron using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). For subsequent experiments, the University of Georgia's research support laboratories performed the analysis because their turn around time was shorter. The analytical laboratories included the Laboratory for Environmental Analysis of the Center for Applied Isotope Studies of the University of Georgia and the University of Georgia Agricultural and Environmental Services Lab. The pH of wastewater and experiment samples was measured in-house by EPA Method 150.1 (Figure 2.4).



Figure 2.4 – pH measurement procedure.

Bromide and other baseline ions ware analyzed by ion chromatography using a DIONEX DX500 modular chromatography system with conductivity, electrochemical and absorbance detectors. Common anions separation was performed using an IonPac AS4A column and detected by suppressed conductivity. The SRS-II self-regenerating suppressor (DX500 system) enhanced the analyte sensitivity by providing superior suppression of the background carbonate eluent conductivity resulting in significant improvement in analyte detection limits. Detection limits for these constituents in the wastewaters ranged from 20 to 200 ug/l (ppb).

Working calibration standards were prepared each day from dilution of a 1,000-ppm mixed stock solution. A three-point calibration was performed, and multiple independent check QC samples of 1.0 ppm were analyzed during every run. Because of the long-term instability of nitrite in aqueous solution, this ion is not included in the results used to evaluate the success of the different treatments.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) by EPA Method 200.7 (EPA-600/4-79-020, 1984; Standard Methods for the Analysis of Water and Wastewater, 1999) was applied for boron and simultaneous multi-element determination in the treated and untreated samples. The mass-selective detector is extremely sensitive, with quantitation levels in parts per billion (ppb) to parts per trillion (ppt). The detector system is relatively immune to many of the chemical and spectroscopic interferences that plague optical emission ICP systems.

#### 2.3.8 Data Analysis

For batch experiments, the amount of boron and bromide removed was calculated by the difference between the initial and final concentration and expressed as percent (%) removal. The sorbent loading capacity was estimated using the following equilibrium adsorption equation (2.1).

$$q_e = \frac{(C_o - C_e)V}{M}$$
 2.1

Where qe is the amount of solute adsorbed after 48 hours equilibration (mg/kg), Co is the initial concentration (mg/L), Ce is the equilibrium concentration (mg/L), V is the volume solution treated in each batch vial (L), and M is the mass of biochar used (g).

Sorption screening experiments were evaluated in replicates. The difference in results from these replicates were evaluated for precision by relative percent difference (RPD) as indicated by equation 2.2 below.

$$RPD = \frac{(S-R)}{\frac{(S+R)}{2}} \times 100$$

Equation 2 describes the *RPD* as a function of concentration of analyte in the batch sample (*S*) and the concentration of analyte in the replicate sample (*R*). For quality control an RPDs of 30 percent or less was accepted.

The residence time for column experiments were evaluated by empty bed contact time (EBCT). For each column run the EBCT was calculated based on useful media volume, using equation 2.3.

Since the columns were dry packed, the pore volume could be calculated based on flow rate and time of first flow over the column exit port. Equation 2.4 was used in the determination.

$$Column Porosity = \frac{Flow Rate \times Time(first flow)}{Total Media Volume}$$
2.4

#### 2.4 RESULTS AND DISCUSSION

## 2.4.1 <u>Wastewater Characterization</u>

A characterization of the coal ash basin wastewater used in this study was performed and it is presented on Table 2.5. Variances in the concentration of the constituents were detected in different batches of the wastewater used in the experiments. These variances could be introduced by differences in sampling location, hydrologic variance between collection times (e.g. precipitation) and coal ash discharge regime into the basin. Diagnosing causes of these variances were not part of the goals of this study and will not be discussed.

| Ash Basin Wastewater Characterization |            |               |  |  |  |  |  |  |
|---------------------------------------|------------|---------------|--|--|--|--|--|--|
| pH                                    |            | 7.5           |  |  |  |  |  |  |
| Element                               | Unit       | Concentration |  |  |  |  |  |  |
|                                       | Major Cat  | ions          |  |  |  |  |  |  |
| Calcium                               | mg/L       | 4.11E+01      |  |  |  |  |  |  |
| Magnesium                             | mg/L       | 4.05E+01      |  |  |  |  |  |  |
| Sodium                                | mg/L       | 7.60E+00      |  |  |  |  |  |  |
| Potassium                             | mg/L       | 2.40E+00      |  |  |  |  |  |  |
| Aluminum                              | mg/L       | 9.42E-03      |  |  |  |  |  |  |
| Iron                                  | mg/L       | 2.13E-02      |  |  |  |  |  |  |
| Zinc                                  | mg/L       | 1.67E-02      |  |  |  |  |  |  |
| Major Anions                          |            |               |  |  |  |  |  |  |
| Chloride                              | mg/L       | 3.38E+02      |  |  |  |  |  |  |
| Sulfate                               | mg/L       | 5.57E+01      |  |  |  |  |  |  |
| Bromide                               | mg/L       | 3.31E+00      |  |  |  |  |  |  |
| Majo                                  | r Oxyanior | ns / Metals   |  |  |  |  |  |  |
| Boron                                 | mg/L       | 6.42E+00      |  |  |  |  |  |  |
| Vanadium                              | mg/L       | 1.40E-03      |  |  |  |  |  |  |
| Chromium                              | mg/L       | 1.90E-04      |  |  |  |  |  |  |
| Arsenic                               | mg/L       | 2.85E-03      |  |  |  |  |  |  |
| Selenium                              | mg/L       | 5.45E-03      |  |  |  |  |  |  |
| Strontium                             | mg/L       | 6.56E-01      |  |  |  |  |  |  |
| Molybdenum                            | mg/L       | 4.09E-03      |  |  |  |  |  |  |
| Antimony                              | mg/L       | 2.50E-04      |  |  |  |  |  |  |
| Tungsten                              | mg/L       | 1.00E-04      |  |  |  |  |  |  |
| Cadmium                               | mg/L       | 1.00E-04      |  |  |  |  |  |  |
| Lead                                  | mg/L       | ND            |  |  |  |  |  |  |
| Mercury                               | mg/L       | 3.00E-05      |  |  |  |  |  |  |

Table 2.5 - Coal ash basin wastewater composition.

The characterization of coal ash leachate is based on the ratio between sulphate and calcium (Izquierdo and Querol, 2012). Since the coal ash basin wastewater is not a pure leachate, but more a dynamic equilibrium between freshly deposited and old weathered coal ash, the

system presents less pronounced characteristics. The ratio between sulfur (5.57E+01mg/L) and calcium (4.11E+01 mg/L) is close to one (Table 2.5), with a circumneutral pH of 7.5. Besides the calcium content, magnesium (4.05E+01mg/L), sodium (7.60E+00 mg/L) and potassium (2.40E+00 mg/L) are the other three major cations in the coal ash leachate. The dominant anionic species was chloride (3.38E+02 mg/L) with approximately six times the concentration of sulphate (5.57E+01 mg/L). Bromide is the third most abundant anion (3.31E+00 mg/L); derived from volatiles from the coal combustion and the solubilization during cooling of the ash. Among the oxyanionic species, boron is the most abundant (6.42E+00 mg/L). Previous studies found that a large fraction of boron in fly ash is in soluble form (Cox et al., 1978; James et al., 1982), making boron one of the elements most readily released from fly ash in water.

The baseline concentrations of bromide, boron and chloride in the FGD wastewater are presented on Table 2.6. The exceedingly high concentrations of bromide and chloride in the FGD wastewater are in the range observed in brackish water.

| FGD wastewater Characterization |      |               |  |  |  |  |  |  |
|---------------------------------|------|---------------|--|--|--|--|--|--|
| pН                              |      | 7.0           |  |  |  |  |  |  |
| Element                         | Unit | Concentration |  |  |  |  |  |  |
| Boron                           | mg/L | 1.67E+02      |  |  |  |  |  |  |
| Bromine                         | mg/L | 9.09E+01      |  |  |  |  |  |  |
| Chloride                        | mg/L | 7.52E+03      |  |  |  |  |  |  |

 Table 2.6 - FGD wastewater characterization

The 30-fold increase in bromide concentration (9.09E+01 mg/L) in the FGD wastewater compared to the coal ash basin (3.31E+00 mg/L) is attributed to the concentration of bromide in the flue gas (Good and VanBriesen, 2019). The boron concentration (1.67E+02 mg/L) is relatively higher in the FGD wastewater due to the chemical process deployed to capture SO<sub>2</sub> and

other volatile gases. Chloride was included in the analysis because its high concentration (7.52E+03 mg/L) does limit the removal of bromide. Based on the chloride concentrations and per the USGS standards, the FGD wastewater is classified as moderately saline water.

#### 2.4.2 <u>Batch Sorption Screening Tests</u>

Not all sorption tests were performed using the same coal ash basin wastewater. To avoid erroneous conclusions, sorption effectiveness is based on relative comparisons between batch sorption samples and their corresponding controls. The two criteria for the relative comparisons are: (1) the amount adsorbed (qe), and (2) the relative removal efficiency. The amount absorbed is a good indication of the specific capacity of the sorbent, whereas the percent removal is an indication of the relative effectiveness of the adsorbent. Appendix A, Table 1A has the compiled laboratory results with individual analysis and control samples. A summary of results, including mass of adsorbent and volume of treated solution is presented in Table 2.7 for boron and in Table 2.8 for bromide. The materials were ranked in each table based on their observed loading capacity and color coded for simplified understanding.

| Treatment Media |                                      | W.W. | рН |      |            | Boro       | n   |              |             |
|-----------------|--------------------------------------|------|----|------|------------|------------|-----|--------------|-------------|
| Acronym         | Material /<br>Biochar<br>Composition | g    | ml | Mean | Ce<br>mg/L | Co<br>mg/L | RPD | %<br>Removal | qe<br>mg/kg |
| BNB             | Bone Biochar                         | 1.0  | 40 | 8.3  | 3.85       | 6.68       | 0%  | 42%          | 113.4       |
| AlMg-INN        | Al Peanut Hull                       | 1.0  | 40 | 8.4  | 4.10       | 6.68       | 0%  | 39%          | 103.3       |
| Mg-PHB          | Mg Peanut Hull                       | 0.5  | 25 | 9.4  | 5.42       | 7.18       | 15% | 25%          | 88.3        |
| Fe-PHB          | Fe Peanut Hull                       | 0.5  | 25 | 2.9  | 5.87       | 7.18       | -3% | 18%          | 65.5        |
| Ca-OXYB         | $Ca-H_2O_2$ Softwood                 | 1.0  | 40 | 8.8  | 5.19       | 6.78       | 2%  | 23%          | 63.6        |
| OXYB            | H2O2 Softwood                        | 1.0  | 40 | 8.8  | 5.26       | 6.78       | 2%  | 22%          | 60.8        |
| Mg-PHB          | Mg Peanut Hull                       | 1.0  | 40 | 9.9  | 5.24       | 6.68       | -3% | 22%          | 57.8        |
| BBB             | Bamboo                               | 1.0  | 40 | 9.4  | 5.34       | 6.78       | 0%  | 21%          | 57.7        |

 Table 2.7 - Screening results of low cost sorbent materials for boron removal, ranked and color coded from highest to lowest adsorption capacity (*qe*).

| Treatment Med | lia                                  |     | W.W. | рН   |            |            | Boro | n            |             |
|---------------|--------------------------------------|-----|------|------|------------|------------|------|--------------|-------------|
| Acronym       | Material /<br>Biochar<br>Composition | g   | ml   | Mean | Ce<br>mg/L | Co<br>mg/L | RPD  | %<br>Removal | qe<br>mg/kg |
| Ca-PHB        | Ca Peanut Hull                       | 0.5 | 25   | 9.5  | 6.05       | 7.18       | 5%   | 16%          | 56.5        |
| PHB           | Peanut Hull                          | 0.5 | 25   | 9.3  | 6.20       | 7.18       | -    | 14%          | 49.3        |
| EAF Slag      | EAF Slag                             | 0.5 | 25   | 11.6 | 1.56       | 2.20       | -11% | 29%          | 31.7        |
| MBB           | Meat/Bone                            | 1.0 | 40   | 7.7  | 6.29       | 6.68       | 0%   | 6%           | 15.5        |
| Ladle Slag    | Ladle Slag                           | 0.5 | 25   | 11.0 | 1.89       | 2.20       | 4%   | 14%          | 15.2        |
| Al-PHB        | Al-Mg                                | 1.0 | 40   | 4.7  | 6.48       | 6.68       | 1%   | 3%           | 8.1         |
| HWB           | Hardwood                             | 0.5 | 25   | 7.7  | 2.05       | 2.20       | 2%   | 7%           | 7.2         |
| PNB           | Pine                                 | 0.5 | 25   | 7.6  | 2.07       | 2.20       | 1%   | 6%           | 6.4         |
| Fe-PHB        | Fe Peanut Hull                       | 1.0 | 40   | 2.6  | 6.59       | 6.68       | 0%   | 1%           | 3.6         |
| FeCaMg-PNB    | Fe-Ca-Mg Pine                        | 1.0 | 40   | 3.2  | 6.59       | 6.68       | 2%   | 1%           | 3.5         |
| PWB           | Paper Waste                          | 0.5 | 25   | 7.8  | 2.15       | 2.20       | 0%   | 2%           | 2.2         |
| MRS-BBB       | MR-FeSO4 BBB                         | 1.0 | 40   | 3.1  | 6.74       | 6.68       | -1%  | -1%          | -2.4        |
| FeCaMg-PNB    | Fe-Ca-Mg Pine                        | 1.0 | 40   | 3.6  | 6.84       | 6.68       | 1%   | -2%          | -6.5        |
| Ca-PHB        | Ca Peanut Hull                       | 1.0 | 40   | 9.8  | 6.97       | 6.68       | -2%  | -4%          | -11.5       |
| FeSO-SWB      | FeSO4 Softwood                       | 1.0 | 40   | 4.5  | 7.01       | 6.68       | 1%   | -5%          | -13.0       |
| CS-SWB        | CS2-FeSO4 SWB                        | 1.0 | 40   | 2.2  | 7.45       | 6.68       | -1%  | -11%         | -30.6       |
| FeNa-SWB      | FeNa-Softwood                        | 1.0 | 40   | 2.9  | 32.48      | 6.68       | -1%  | -386%        | -1031.8     |

The results show that among the unmodified sorbents, bone (BNB), bamboo (BBB) and peanut hull (PHB) were the better performing biochars. The bone biochar had the highest loading capacity of 113.4 mg/kg and percent removal (42%). Considering the volume of the coal ash basin wastewater needing treatment, the supply of bone biochar may be limiting. The iron and magnesium impregnated peanut hull biochar (PHB) that were produced in-house showed moderate efficiency. Among the most promising commercial options was Al-Mg Innovo biochar (AlMg-INN) with percent removal of 39% and loading capacity of 103.3 mg/kg, equivalent to the BNB biochar. Oxybiochar (OXYB) and calcium oxybiochar (Ca-OXYB) also figured among the moderate performing commercial options with removal efficiency around 22% and loading around 60 mg/kg. The boron removal was higher in alkaline solutions than in acidic conditions. In basic solutions of pH >9, boron is present as Tetrahydroxyborate which is as an anion. The exception was iron modified peanut hull biochar (Fe-PHB) that showed a moderate adsorption at pH <3.0. The mechanism of boron removal by Fe-PHB is likely influenced by the Fe in the biochar. Both slags tested performed modestly among the materials. Considering that the slags are a wastes products they are worth further evaluation as low-cost treatment media. EAF had the a relatively higher loading capacity of 31.7 mg/kg.

 Table 2.8 - Screening of low cost sorbent materials for bromide removal, ranked and color coded from highest to lowest adsorption capacity (*qe*).

| Treatment Media W |                |     | W.W. | pН   |            |            | Bron  | nide         |             |
|-------------------|----------------|-----|------|------|------------|------------|-------|--------------|-------------|
| Acronym           | Composition    | g   | ml   | mean | Co<br>mg/l | Ce<br>mg/l | RPD   | %<br>Removal | qe<br>mg/Kg |
| Fe-PHB            | Fe Peanut Hull | 1.0 | 40   | 2.6  | 2.04       | 3.02       | 3.7%  | 32%          | 39.1        |
| Al-PHB            | Al Peanut Hull | 1.0 | 40   | 4.7  | 2.49       | 3.02       | 3.9%  | 17%          | 21.1        |
| CS-SWB            | CS2-FeSO4 SWB  | 1.0 | 40   | 2.2  | 2.82       | 3.02       | 2.5%  | 7%           | 8.0         |
| Fe-PHB            | Fe Peanut Hull | 0.5 | 25   | 2.9  | 0.30       | 0.45       | -0.2% | 34%          | 7.8         |
| AlMg-INN          | Al Peanut Hull | 1.0 | 40   | 8.4  | 2.86       | 3.02       | -2.2% | 5%           | 6.4         |
| Mg-PHB            | Mg Peanut Hull | 1.0 | 40   | 9.9  | 2.86       | 3.02       | 4.0%  | 5%           | 6.3         |
| Ca-PHB            | Ca Peanut Hull | 0.5 | 25   | 9.5  | 0.39       | 0.45       | 6.3%  | 13%          | 3.1         |
| PHB               | Peanut Hull    | 0.5 | 25   | 9.3  | 0.40       | 0.45       | -     | 13%          | 2.9         |
| OXYB              | H2O2 Softwood  | 1.0 | 40   | 8.8  | 3.17       | 3.22       | -0.6% | 2%           | 2.0         |
| Mg-PHB            | Mg Peanut Hull | 0.5 | 25   | 9.4  | 0.42       | 0.45       | 15.1% | 7%           | 1.7         |
| Ca-OXYB           | Ca-H2O2 SWB    | 1.0 | 40   | 8.8  | 3.18       | 3.22       | 0.5%  | 1%           | 1.3         |
| BBB               | Bamboo         | 1.0 | 40   | 9.4  | 3.20       | 3.22       | -3.6% | 1%           | 0.7         |
| BNB               | Bone           | 1.0 | 40   | 8.3  | 3.02       | 3.02       | -0.3% | 0%           | 0.0         |
| MRS-BBB           | MR-FeSO4 BBB   | 1.0 | 40   | 3.1  | 3.04       | 3.02       | 0.0%  | 0%           | -0.6        |
| Ca-PHB            | Ca Peanut Hull | 1.0 | 40   | 9.8  | 3.05       | 3.02       | 0.1%  | -1%          | -1.0        |
| FeNa-SWB          | Fe-Na SWB      | 1.0 | 40   | 2.9  | 3.16       | 3.02       | 3.3%  | -5%          | -5.5        |
| MBB               | Meat/Bone      | 1.0 | 40   | 7.7  | 3.17       | 3.02       | -1.8% | -5%          | -5.9        |
| FeCaMg-PNB        | Fe-Ca-Mg Pine  | 1.0 | 40   | 3.6  | 14.21      | 3.02       | -1.6% | -370%        | -447.4      |
| FeCaMg-PNBP       | Fe-Ca-Mg Pine  | 1.0 | 40   | 3.2  | 19.71      | 3.02       | -5.8% | -553%        | -667.6      |
| FeSO-SWB          | FeSO4 SWB      | 1.0 | 40   | 4.5  | 24.75      | 3.02       | 2.0%  | -720%        | -869.2      |

The use of sorbent materials for bromide removal was expected to be more challenging because of its high solubility in water. The size and charge density of bromide is similar to chloride, a very abundant anion in the effluent and a strong competitor for the same sorption sites. Despite the competitive effects of chloride, iron and aluminum impregnated peanut hull biochar showed a relatively high bromide loading of 39.1 and 21.1 mg/kg, respectively (Table 2.8).

Only the metal modified biochars showed significant removal of bromide from the coal ash wastewater, potentially due to the positively charged sites created on the metal impregnated biochars. Overall, iron impregnated biochar was the most promising material to remove boron and bromide simultaneously. Besides iron modified peanut hull biochar, other types of iron biochar were not prepared and evaluated during the screening tests.

#### 2.4.3 Optimum Loading Test

The maximum loading of solutes on sorbents are determined using sorption isotherm experiments in which a fixed mass of sorbent is exposed to different incremental concentrations of the desired sorbate. In this study, the latter methodology was not followed due to the importance of maintaining a constant initial ionic strength and pH of the treated wastewater. Instead, the maximum loading experiments were performed by varying the sorbent mass. Appendix A, Table 2A has the complete report of results with control samples. The graphs of the best performing biochars screened, bone and bamboo, are shown in Figure 2.5 and Figure 2.6. Negative values of adsorption indicate that the solute was leached from the sorbent.



Figure 2.5 - Evaluation of maximum adsorption and optimum pH for boron (a and b) removal by bone biochar (BNB).

Even though the loading of boron fluctuated, a maximum adsorption occurred at a pH of 7.4 with an adsorption capacity of 323 mg/kg for test with BNB (Figure 2.5 a and b). The bromide loading had an erratic behavior, not showing any removal above the 30 g/l dosage of BNB. For that reason graphs were not included and the results are only presented on Table 2A, Appendix A..



Figure 2.6 - Evaluation of maximum adsorption and optimum pH for boron (a and b) removal by bamboo biochar (BBB).

The maximum adsorption capacity of boron was 51 mg/kg at pH 9.5 for 20 g/l of bamboo biochar (Figure 2.6 a and b). The bromide loading observed in low biochar doses was only attributed to analytical errors, therefore bromide results were not included in the graphs and can be found on Table 2A, Appendix A ,. The results comparing the maximum loading of the three iron impregnated biochars used to treat the more concentrated FGD wastewater is presented in Figure 2.7.



Figure 2.7 - Evaluation of maximum adsorption and optimum pH for boron (a and b) and bromide (c and d) by Iron modified bamboo biochar (BBB), peanut hull biochar (PHB) and bone biochar (BNB).

The highest adsorption capacity of 2022 mg/kg for boron and 241 mg/kg for bromide was obtained with Fe-BBB. It is important to note that different biochar to solution ratios were used, in which the best boron removal results were achieved with 25 g/l, and the best bromide results were obtained with 100 g/l. The adsorption of boron and bromide onto Fe-PHB did not change significantly as the biochar dose was increased. Boron adsorption capacity was in the range of 281 to 366 mg/kg, while bromide was between 105 to 147 mg/kg. The pH at the end of the sorption test was in the acidic range; pH 2.0-2.5 for Fe-BBB and Fe-PHB.

The adsorption capacity of Fe-BNB for boron and bromide had opposite trends as the biochar dose was increased. The sorption of boron decreased as the biochar dosage increased (i.e., 1033 mg/kg to 327 mg/kg), while bromide removal increased from a negative value of -103 mg/kg to 45 mg/kg. The pH at the end of the sorption test was also in the acidic range, around pH 4.8 for Fe-BNB.

#### 2.4.4 Column Tests

Flow rate in the column experiments were in the range of 47 to 62 ml/min, while the duration of the sorption experiments varied between 2.4 and 5.4 pore volumes. Table 2.9 show the summary of the experimental parameters (EBTC, flow rate and pore volumes) for the column experiments, and resulting inferred media porosity.

| Columns     | Column 01      | Column 02      | Column 03   |  |  |  |
|-------------|----------------|----------------|-------------|--|--|--|
| Mass Ratios | 40% BBB        | 50% BNB        | 100% Fe-BBB |  |  |  |
|             | 30% EAF Slag   | 25% EAF Slag   |             |  |  |  |
|             | 30% Ladle Slag | 25% Ladle Slag |             |  |  |  |
| Flow Rate   | 47 ml/min      | 62 ml/min      | 60 ml/min   |  |  |  |
| Porosity    | 50%            | 62%            | 52%         |  |  |  |
| First Flow  | 65 min         | 56 min         | 49 min      |  |  |  |

 Table 2.9 - Column hydraulic experimental parameters.

| Columns                        | Column 01 | Column 02 | Column 03 |
|--------------------------------|-----------|-----------|-----------|
| EBCT                           | 120 min   | 90 min    | 94 min    |
| Flow through<br>(pore volumes) | 2.4       | 4.9       | 5.4       |

Column 1 and 2 are two-layer columns, where the lower portion is packed with a mixture of the two slags (EAFs and ladle) and biochar to serve as an initial treatment media. The top portion is designed to act as a contiguous polishing step containing only biochar. Appendix A, Table 3A has the complete data for the column runs and control samples. Figure 2.8 and Figure 2.9 contain the summary of results from column runs 1 and 2, , respectively.



## Figure 2.8 - Sorption & desorption column 1 results, ratio between inflow concentration (Co) and outflow concentration (Cf). Media composition in mass is 40% bamboo biochar (BBB), 30% EAF slag, and 30% ladle slag.

The bromide removal was poor, with complete breakthrough observed at about 0.5 pore

volumes (Figure 2.8). The column was very effective at the removing boron; with a maximum

effluent concentration of 1 mg/L after 2.4 pore volumes compared to an influent concentration (Co) of 6.11 mg/L. These results indicate that the treatment media's capacity was not yet exhausted and had a potential to sustain removal for longer. The pH stabilized after one pore volume at about pH 12.4 due to the slag buffering capacity. The desorption curve in Figure 2.8 demonstrates that boron was irreversibly removed, and unlike bromide was not susceptible to leaching by freshwater. The desorption pH stabilized at a lower value of pH 11.7. The pH sustained in the sorption and desorption phase was favorable for the formation of ettringite, higher than pH 10.5. The pre-treatment with aluminum sulphate combined with the calcium from the slag could likely contributed to the formation of ettringite which coprecipitates boron (Zhang and Reardon, 2003).



Figure 2.9 - Sorption column 2 results, ratio between inflow concentration (Co) and outflow concentration (Cf). Media composition in mass is 50% bone biochar (BNB), 25% EAF slag, and 25% Ladle Slag.

For column 2 the removal of bromide was insignificant (Figure 2.9). The higher effluent concentration suggest leaching of bromide from the treatment media. Boron, on the other hand was completely removed, and the effluent concentration remained below detection at up to 4.9 pore volumes. Thus, the boron adsorption capacity appears to be remarkably high. The pH decreased from a high of 9.8 during the first 2.4 pore volumes to a low of 8.7 by the end of the run (Figure 2.9).

Column 3, differently from 1 and 2, was designed as a single treatment step, and was filled completely with iron modified biochar. Figure 2.10 present the results from this experiment, where FGD wastewater with no pre-treatment was used as influent solution.



Figure 2.10 - Sorption column 3 results, ratio between inflow concentration (Co) and outflow concentration (Cf). Media composition in mass is 100% Iron impregnated bamboo biochar (Fe-BBB). Sustained removal of boron and bromide was observed from column 3 (Figure 2.10). Bromide was removed almost completely at the beginning of the experiment from a higher relative influent concentration of 90.8 mg/l to a effluent of 8.6 mg/l. The removal efficiency decreased rapidly after 2 pore volumes, possibly due to exhaustion of the sorption sites. The boron effluent concentrations fluctuated around 100 mg/l, representing a removal of 35%. This level of removal was sustained up to 5.4 pore volumes. The pH of the effluent water was in the acidic range, pH 1.3-2.4, which is very similar to the pH observed in batch sorption tests performed with iron impregnated biochar. The results of column 3 confirm that the removal of boron by iron biochar was inferior to the mixtures of biochar and slags and potentially influenced by the low pH in the treatment media. No test was performed with iron biochar at high pH.

#### 2.5 CONCLUSION

This work illustrates the relative effectiveness of different steel mill slags, biochars and metal-oxyhydroxide biochar for removal of boron and bromide from coal ash leachate and FGD wastewater. Overall, the screening tests showed that the most effective biochar media for removal of boron from CAL were bone biochar > bamboo biochar > peanut hull biochar. Among the promising impregnated biochars for boron removal, the relative order of effectiveness was Al-Mg > Magnesium > Iron biochar. The only media that showed significant removal of bromide from CAL were the Iron impregnated peanut hull and bamboo biochar.

The highest combined adsorption capacity in this study was observed with iron impregnated bamboo biochar during the optimum loading tests with FGD wastewater; 2022.4 mg/kg for boron, and 241.6 mg/kg for bromide. The column experiments performed with the

same biochar and wastewater confirmed the batch test results, with boron breakthrough after 2 pore volumes and sustained boron remaining consistent at 35% for up to 5.4 pore volumes.

Several potentially promising combinations of adsorption media for removal of boron alone were also identified during column experiments. The use of bamboo and bone biochar mixed with EAF and Ladle slag was proven effective in the removal of boron with the addition of an aluminum sulphate pretreatment step. Complete removal of boron for up to 4.9 pore volumes was observed in column test with the treatment media consisting of 50% bone biochar, 25% EAF slag, and 25% Ladle Slag. The removal of boron was strongly influenced by pH and attributed to the formation of ettringite which contributes to the removal of boron by coprecipitation.

More work is needed to further confirm these findings and more accurately quantify the adsorption capacities of the modified biochars for boron and bromide, as well as the influence of cations and anions in the CAL and FGD wastewater on the media performance. The influence of pH on the mechanism of boron removal is most warranted for Fe-impregnated biochars. The most effective media could be applied at the full scale as permeable treatment barriers or in pump-and-treat columns to remove boron and bromide from CCR wastewaters and stabilization of the CCR solids.

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## 3 CHEMICAL COPRECIPITATION OF BORON FROM COAL COMBUSTION WASTEWATERS AND RESIDUE LEACHATE<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>Favero, L.N. and V.A. Nzengung. To be submitted to *Environmental Science* & *Technology*.
# 3.1 ABSTRACT

Cost effective technologies for treating coal ash leachate is an immediate and growing need of coal power generating plants. CCR leachate composition is determined by the elements that are associated with the fly ash particles, and consequently, more directly exposed to leaching. boron (B) is one of the elements most readily released pollutants from fly ash into water. In this study, we evaluated the use of calcium minerals (e.g., ettringite) for coprecipitation of boron in coal ash leachate (CAL) using steel mill slags and recycled aluminum cans. The coprecipitation of ettringite and boron from CAL treated with aluminum sulphate and calcium hydroxide removed up to 99% of the initial boron. The 7.01 mg/L initial boron concentration in CAL decreased to 0.06 mg/L using 13.3 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 8.90 g of Ca(OH)<sub>2</sub> per litter solution. The use of steel mill slags as low-cost pH buffers for the coprecipitation reaction also showed promising results, with 99% removal of boron achieved with only a quarter of the doses of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Ca(OH)<sub>2</sub>. The zero-valent aluminum (ZVAL) obtained from recycled aluminum cans show promise in the precipitation of ettringite without any addition of other aluminum salts; achieving 42% removal of boron from CAL in 185 minutes of contact time. Additional testing is required to optimize and scale up the treatment process for full scale application.

### 3.2 INTRODUCTION

The electricity generation process in all thermal power plants worldwide is almost identical but, the quantity and quality of Coal Combustion Residuals (CCRs) varies distinctly due to the quality of coal, operation temperature, among other factors (Asokan et al., 2005). In the United States, about 102 million tons of CCRs, which include fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) byproducts were generated in 2018 (Association, 2018). Out of this total, approximately 60% of CCRs were applied to beneficial uses (e.g., concrete and wallboard), while the remaining 40% were disposed of in surface impoundments and landfills (Association, 2018). Much attention is paid to the reuse of CCR, especially fly ash. The literature on the reuse of fly ash is abundant and the many possibilities of how to expand the use of this waste material is presented in the literature (Ahmaruzzaman, 2010; Blissett and Rowson, 2012). On the other hand, cost effective technologies for treating the leachate generated from CCR are lacking, including a comprehensive solution for the different constituents of the leachate.

The composition of coal ash leachate is determined by the elements that are bound to the surface of the fly ash particles and tend to easily leach into water (Izquierdo and Querol, 2012). Boron is one of the elements most readily released from fly ash into water (Cox et al., 1978; James et al., 1982). The pronounced leachability of boron is intimately related to its surface association with fly ash (Querol et al., 1995). Most of the boron is organically associated in coal (Finkelman, 1995; Swaine, 1995), such affinity enhances the volatility during combustion and subsequent condensation of soluble borate salts onto fly ash (Dudas, 1981). Boron is highly soluble and it is poorly adsorbed to aquifer solids, thus it tends to produce large plumes in groundwater downgradient of CCR units (Jones, 2017). Conventional water treatment (e.g. coagulation, sedimentation and filtration) does not significantly remove boron. Therefore, customized treatment methods are needed. Existing methods for removal of boron from water (e.g. ion exchange and reverse osmosis) tend to be prohibitively expensive (WHO, 2011).

Coprecipitation is the removal of a contaminant by precipitation of another constituent that is typically present in higher concentrations. In some applications, Fe(III) or Al(III) salts are added as coagulants in water treatment systems to remove undesired constituents by coprecipitation. The constituent of concern is removed by trapping within or adsorbed to the precipitates as they form (EPRI, 2006). In this study, the use of calcium compounds, steel mill slags and recycled aluminum cans for the coprecipitation of boron in coal ash leachate (CAL) will be explored.

### 3.2.1 Formation of Calcium Minerals and their Role in Treatment of CAL

Lime precipitation is widely used for the purification of mine waters. Lime precipitation is applied to treat acidic mine waters with high metal and sulphate concentrations. However, the sulphate removal efficiency of lime precipitation is limited to the solubility of gypsum, which is approximately 1,500–2,000 mg/L, depending on solution conditions (Tolonen et al., 2016).

Sulphate precipitation as ettringite  $[Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O]$  is a modification of the high pH lime treatment method (Tolonen et al., 2015). Tolonen et al. (2016) observed that with precipitation as ettringite, sulphate concentration can be reduced to less than 200 mg/L. When ettringite precipitation is used for waters with high sulphate concentration (>3,000 mg/L), it may be economical to use traditional lime precipitation (a pH of approximately 9) as a pre-treatment. In the pre-treatment step, part of the sulphate and the metals are precipitated as gypsum and metal hydroxides, respectively. After partial sulphate removal, a smaller dosage of Aluminum is needed in the ettringite precipitation step (Tolonen et al., 2016).

The ettringite precipitation was developed as a process for sulphate removal from mine water, with the removal of metals as an additional benefit. Tolonen et al. (2016) have reviewed the many patented methods for precipitation of ettringite, and in each case the pH of the water is raised to approximately 12 with lime coupled with addition of aluminum salt (either sodium aluminate or aluminum hydroxide) to precipitate ettringite.

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The treatment of industrial wastewater containing aluminum by Álvarez-Ayuso and Nugteren (2005) demonstrates that ettringite can be applied for other treatment processes besides sulphate removal. The ettringite mineral has been shown to be an effective sorbent for arsenate removal from water (Myneni et al. (1997)).

Zhang and Reardon (2003) evaluated the preparation and use of hydrocalumite and ettringite for the removal of B, Cr, Mo, and Se oxyanions from high pH waters by incorporation in the mineral. Their approach involved precipitating the minerals in solutions containing B, Cr, Mo, and Se oxyanions. It was demonstrated that all four anions were removed by hydrocalumite better than ettringite. The anion concentrations were reduced to below drinking water standards. Ettringite showed an anion preference in the order of  $B(OH)_4^{2-} > CrO^{4-} > SeO_4^{2-} > MoO_4^{2-}$ . In contrast, hydrocalumite was least effective for the removal of borate (Zhang and Reardon, 2003).

#### 3.2.2 <u>Ettringite Formation</u>

Ettringite requires Ca, Al,  $SO_4^{2-}$ , excess water and pH >11 to form (Hassett et al., 2005). The formation of ettringite follows reaction 3.1, with an equilibrium constant of K =  $10^{-56.4}$ (Tolonen et al., 2016). The mineral formation steps are demonstrated in Figure 3.1.

$$6 \operatorname{Ca}^{2+} + 2 \operatorname{Al}^{3+} + 3 \operatorname{SO4}^{2-} + 38 \operatorname{H_2O} < - > 12 \operatorname{H^+} + \operatorname{Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O}$$
**3.1**



Figure 3.1 - Ettringite formation. Adapted from Dou et al. (2017).

In a practical application, Dou et al. (2017) applied the precipitation of ettringite in a real FGD wastewater removal of sulphate. The investigators did not investigate the co-precipitation of boron. The investigators added lime to the wastewater for 6 h, and then adjusted to pH of 11 by adding NaOH. After stirring at 250 rpm for 60 min and settling for another 60 min, the supernatant was collected for sulfate removal by the addition of AlCl<sub>3</sub>· 6H<sub>2</sub>O and NaOH to adjust pH to 11.5.

To investigate borate uptake by ettringite, Hiraga and Shigemoto (2011) synthesized ettringite in the presence of  $H_3BO_3$  by adding  $Al_2(SO_4)_3$  to FGD wastewater and alkalization with Ca(OH)<sub>2</sub>. The investigators observed that the higher the concentration of  $Al_2(SO_4)_3$  added to the wastewater the more amount of boron precipitated. Also, the precipitated mass of boron increased with increasing pH of the treated wastewater solution, with maximum removal by precipitation at pH of 10 to 12.

In the studies of Dou et al. (2017), the authors identified the inhibitory effect of  $Mg^{2+}$  on ettringite formation and precipitation. The inhibitory effects of  $Mg^{2+}$  can be attributed to the competition between  $Mg^{2+}$  and  $Ca^{2+}$  for  $Al^{3+}$  to form hydrotalcite-type compound ( $Mg_6Al_2SO_4(OH)_{16}$ ·nH2O) rather than ettringite. Hydrotalcite (HT) belongs to a supergroup of minerals with natural layered double hydroxides (LDH), also called anionic clays. Under alkaline conditions,  $Al^{3+}$  reacts with OH<sup>-</sup> to form  $Al(OH)_4^-$  which is the predominant Al species in high pH solutions that undergoes additional reaction to form octahedral  $Al(OH)_6^{3-}$  (Cho et al., 2008). In the presence of Mg<sup>2+</sup>, the Mg(OH)<sub>4</sub><sup>2-</sup> anion forms and reacts preferentially with  $Al(OH)_4^-$  and  $SO_4^{2-}$  to form hydrotalcite (HT) compound (Shi et al., 2014). The formation of ettringite dominates when the Mg<sup>2+</sup> concentration is less than 40 mmol/L, while HT is preferentially formed at higher concentrations of Mg<sup>2+</sup> (Dou et al., 2017). When Mg<sup>2+</sup> exceeded 120 mmol/L, the removed  $SO_4^{2-}$  was completely precipitated as the HT compound.

# 3.2.3 Hydrocalumite Formation

Hydrocalumite is a member of the hydrotalcite supergroup; its name is an allusion to its composition that includes water (HYDRO), Calcium (CAL), and Aluminum (ALUM). Hydrocalumite is an anionic clay mineral with a structure composed of portlandite-like principal layers in which one-third of the Ca<sup>2+</sup> sites are occupied by Al<sup>3+</sup> (Zhang and Reardon, 2003). The substitution of Al<sup>3+</sup> for Ca<sup>2+</sup> generates net positive charge to the octahedral layers, and anions are incorporated into the interlayers (Figure 3.2) to balance the charges (Zhang and Reardon, 2003). Hydrocalumite can bind with anions of various sizes. The thickness of its interlayer varies as different anions are incorporated (e.g., 7.6 Å for CO<sub>3</sub><sup>2-</sup> and 8.9 Å for SO<sub>4</sub><sup>2-</sup>) (Taylor, 1973).



Figure 3.2 - Schematic representation of the structure of Hydrocalumite. Adapted from (Zhang and Reardon, 2003).

Zhang and Reardon (2003) observed that as ettringite precipitated from fly ash leachates enriched in sulfate and the solution became depleted in sulfate, the ettringite converted to hydrocalumite with  $OH^-$  as the dominant anion. The oxyanions occupied less than 2% of the anionic sites in the interlayers of the hydrocalumite, while the rest were occupied by  $OH^-$ . The authors concluded that competition among oxyanions is not a factor in the degree of uptake. The relevant factor was their relative preference of  $OH^-$  in an interlayer site. Therefore, the trigonal planar borate appears not to show a site preference over tetrahedral coordinated oxyanions. As a result, while the removal of  $CrO4^{2-}$ ,  $MoO4^{2-}$  and  $SeO4^{2-}$  showed concentration decreases of over 2 orders of magnitude in the study, borate showed a much lower decrease (Zhang and Reardon, 2003).

# 3.3 MATERIALS AND METHODS

# 3.3.1 <u>Materials</u>

All solutions used in these experiments were prepared with deionized water and analytical grade chemicals. Acid and ultrapure water washed beakers, flasks, and disposable centrifuge tubes were used. The Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O and Ca(OH)<sub>2</sub> were obtained from Fisher Scientific and used as supplied.

#### 3.3.2 <u>Wastewater</u>

The treated wastewater was collected from an unlined coal ash basin at a confidential power plant in the southeast of the United States. This coal ash basin has been operational for decades and still receives the untreated coal ash residuals from the power plant. The coal ash basin wastewater will be referred as coal ash leachate (CAL) in this study. During the course of the experiments, multiple batches of wastewater samples were collected from the coal ash basin. The sample collection was performed by the power plant employees. The wastewater was transferred to our custody in 20-liter food grade clean buckets or single use 20-liter flexible plastic sampling bags. The CAL was transported from the power station to the laboratory in coolers containing ice. Each container was stored in frozen form and thawed in a 14 degrees C refrigerator prior to utilization in an experiment.

### 3.3.3 <u>Still Mill Slag Collection and Preparation</u>

Out of three options available for slags generated by steelmaking, two (EAF and Ladle slag) were selected and used in the screening and follow-on tests. Due to the similarities between BOF and EAF slag, only the more readily available EAF slag was obtained and used. The slags

tested in this study were made available by Gerdau Long Steel of North America and collected from the Cartersville Steel Mill, in Georgia (Figure 3.3).

Once transported to the laboratory, both slags were spread out and air dried for two weeks. Size reduction of the ladle slag lumps was with a mortar and pestle. The manually crushed slag was screened to collect the 38  $\mu$ m < x < 2.00mm particle sizes. EAF slag is considerably harder solid, and as such a jaw rock crusher was used for size reduction of the aggregates. The size fraction between 38  $\mu$ m < x < 2.00mm was used in experiments.



Figure 3.3 – EAF (a) and Ladle (b) slag samples after air drying and sieving to 38  $\mu m < x < 2.00 mm.$ 

The chemical of EAF and Ladle slag (Table 3.1) shows that EAF slag was relatively enriched in iron, manganese and aluminum oxides, while the Ladle slag was relatively enriched in calcium and silicon oxides. Both slags contained about the same proportion of magnesium oxide.

| (% Weight) | Al <sub>2</sub> O <sub>3</sub> | CaO   | SiO <sub>2</sub> | MgO  | Cr <sub>2</sub> O <sub>3</sub> | P2O5 | S    | FeO   | MnO  |
|------------|--------------------------------|-------|------------------|------|--------------------------------|------|------|-------|------|
| EAF Slag   | 5.71                           | 27.28 | 11.85            | 9.09 | 2.13                           | 0.33 | 0.11 | 22.99 | 6.28 |
| Ladle Slag | 2.31                           | 47.88 | 27.22            | 8.95 | 0.13                           | 0.04 | 0.64 | 1.4   | 0.68 |

Table 3.1 - Typical composition of electric arc and ladle furnace slag from GerdauCartersville, GA.

#### 3.3.4 <u>Preparation of Recycled Aluminum</u>

Used aluminum beverage cans were obtained from recycle trash bins at the University of Georgia, United States. These aluminum cans were cleaned with deionized (DI) water, cut into sheets, flattened and placed in a steam saturated oven for 4 hours. The paint on each sheet was removed by scrubbing with steel wool pads soaked in acetone. The external and internal plastic membranes were brushed off with stainless steel scouring pads. The aluminum can sheets were then cut into small rectangular pieces (about 2mm x 4 mm). These pieces were then washed thoroughly with DI water and then dried overnight (Figure 3.4).



Figure 3.4 – Recycled aluminum cans preparation.

# 3.3.5 Boron Coprecipitation Test

To each 250 mL Erlenmeyer flask was added 100 ml of CAL. One flask was covered with aluminum foil and kept as a control. The other four were dosed with  $Ca(OH)_2$  and  $Al_2(SO_4)_3 \cdot 18H_2O$  to obtain a theoretical (3:1) molar ratio of Ca: Al as in ettringite. The first flask was dosed with 0.445 g of powdery  $Ca(OH)_2$  and agitated until fully dissolved before adding 0.666 g of  $Al_2(SO_4)_3 \cdot 18H_2O$  (Guo et al., 2017). The other 3 flasks were prepared the same way, but with variable doses of  $Ca(OH)_2$  and  $Al_2(SO_4)_3 \cdot 18H_2O$  mass (Table 3.2).

| a ı     | CAL  | Al Source   | Alkalization            | Dose |
|---------|------|---|-------------------------|------|
| Sample  | (ml) | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (g) | Ca(OH) <sub>2</sub> (g) | (%)  |
| Control | 100  | 0.000   | 0.000                   | 0    |
| Flask 1 | 100  | 0.167   | 0.111                   | 25   |
| Flask 2 | 100  | 0.333   | 0.223                   | 50   |
| Flask 3 | 100  | 0.666   | 0.445                   | 100  |
| Flask 4 | 100  | 1.333   | 0.890                   | 200  |

 Table 3.2 – Aluminum sulphate and calcium hydroxide doses for boron coprecipitation test.

The flasks were then covered with aluminum foil, mixed using a magnetic stirrer for 10 min and the pH adjusted with  $Ca(OH)_2$  solution to 10.5 and left to settle for 48 h (Figure 3.5). After this period, liquid samples were taken and filtered through 0.45 µm membrane filter. The resulting solution was separated into two vials; one for pH measurement and the other was submitted to the analytical laboratory for boron analysis.



Figure 3.5 - Boron coprecipitation test flasks left for settling.

# 3.3.6 Boron Coprecipitation with Slag as pH Buffer

The slag buffered experiments were performed with 25% of the dose of Ca(OH)<sub>2</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O used in the unbuffered treatments. Instead of adjusting the pH with Ca(OH)<sub>2</sub>, a combination of EAF and Ladle slags were used. 40 ml of CAL were placed in eight 50 ml disposable centrifuge tubes. Four tubes were dosed with Ca(OH)<sub>2</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O to obtain the same theoretical (3:1) molar ratio of Ca: Al. In these four tubes 0.044 g of powdery Ca(OH)<sub>2</sub> was added to the 40 ml of CAL and agitated until fully dissolved, before adding 0.066 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O. One tube was kept as an unbuffered control, the other three were buffered with 0.4g of ladle slag, 0.4g of EAF slag and a mixture of 0.2g of each slag, respectively. The other four tubes were kept as controls, one as a CAL and the other three as slag controls with the same masses used to buffer the treatments (Table 3.3).

| Samula    | Experiment                 | CAL  | Al Source   | Alkalization | Buffer      |              |  |
|-----------|----------------------------|------|---|--------------|-------------|--------------|--|
| Sample    | Description                | (ml) | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (g) | Ca(OH)2 (g)  | L. Slag (g) | EAF Slag (g) |  |
| Control 1 | Effluent Control           | 40   |   |              |             |              |  |
| Flask 1   | Slag Buffered              | 40   | 0.067   | 0.045        | 0.4         |              |  |
| Flask 2   | Slag Buffered              | 40   | 0.067   | 0.045        |             | 0.4          |  |
| Flask 3   | Slag Buffered              | 40   | 0.067   | 0.045        | 0.2         | 0.2          |  |
| Flask 4   | Unbuffered                 | 40   | 0.067   | 0.045        |             |              |  |
| Control 2 | Control 2 L. Slag Control  |      |   |              | 0.4         |              |  |
| Control 3 | Control 3 EAF Slag Control |      |   |              |             | 0.4          |  |
| Control 4 | Slag Control               | 40   |   |              | 0.2         | 0.2          |  |

 Table 3.3 - Aluminum sulphate, calcium hydroxide and slag doses for buffered boron coprecipitation test.

The samples were then incubated on a rotating mixer at 3.3 rpm for 24 hours and then left to react for 6 days. At the end of the treatment, the supernatant solution was filtered through 0.45  $\mu$ m membrane filter and placed in two vials. One sample was used for pH measurement and the other submitted to the analytical laboratory for boron analysis.

# 3.3.7 <u>Recycled Aluminum Proof of Concept Test</u>

The efficacy of coprecipitating boron by ettringite synthesized using recycled aluminum can pieces was evaluated. The sulfate was supplied by the CAL, calcium by the steel slag and aluminum by the decomposition of the aluminum cans in the high pH of the slag buffered solution.

To each 500 ml nominal volume plastic flask was added 500 mL of CAL and mixed on a magnetic stir plate at the room temperature of 21.6° C. To the latter solution was added 10 g of EAF slag, 10 g of Ladle slag and 5 g of pre-processed aluminum cans pieces. The pH of the solution was continuously monitored until it reached 10.5, which is the optimum pH for ettringite precipitation (Figure 3.6). The supernatant was sampled and filtered through 0.45µm membrane

filter. The resulting solution was separated in two vials and immediately delivered to the analytical laboratory.



Figure 3.6 – Recycled aluminum proof of concept coprecipitation test.

# 3.3.8 <u>Analytical Methods</u>

The laboratories used for analytical needs included the Laboratory For Environmental Analysis of the Center for Applied Isotope Studies of the University of Georgia and the University of Georgia Agricultural and Environmental Services Lab. The pH of wastewater and experiment samples was measured in-house by EPA Method 150.1 (Figure 2.4).



Figure 3.7 – pH measurement procedure.

Baseline ions ware analyzed by ion chromatography using a DIONEX DX500 modular chromatography system with conductivity, electrochemical and absorbance detectors. Common anions separation was performed using an IonPac AS4A column and detected by suppressed conductivity. The SRS -II self-regenerating suppressor (DX500 system) enhanced the analyte sensitivity by providing superior suppression of the background carbonate eluent conductivity resulting in significant improvement in analyte detection limits. Detection limits for these constituents ranged from 20 to 200 ug/l (ppb).

Working calibration standards were prepared each day from dilution of a 1,000-ppm mixed stock solution. A three-point calibration was performed, and multiple independent check QC samples of 1.0 ppm were analyzed during every run. Because of the long-term instability of nitrite in aqueous solution this ion is not included in the results used to evaluate the success of the different treatments.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) by EPA Method 200.7

(EPA-600/4-79-020, 1984; Standard Methods for the Analysis of Water and Wastewater, 1999) was applied for boron and simultaneous multi-element determination in the treated and untreated samples. The mass-selective detector is extremely sensitive, with quantitation levels in parts per billion (ppb) to parts per trillion (ppt). The detector system is relatively immune to many of the chemical and spectroscopic interferences that plague optical emission ICP systems.

# 3.4 RESULTS AND DISCUSSION

#### 3.4.1 <u>Wastewater Characterization</u>

A characterization of the coal ash basin wastewater used in this study is presented in Table 3.4. Variances in the concentration of the constituents are expected from different batches of the wastewater used in the experiments. These variances could be introduced by differences in sampling location, hydrologic variance (e.g. precipitation) and coal ash discharge regime into the basin. The causes of these variances were not the goal of these study and will not be discussed.

| Ash Basin Wastewater Characterization |             |               |  |  |  |
|---------------------------------------|-------------|---------------|--|--|--|
|                                       | рН          | 7.5           |  |  |  |
| Element                               | Unit        | Concentration |  |  |  |
|                                       | Major Catio | ns            |  |  |  |
| Calcium                               | mg/L        | 4.11E+01      |  |  |  |
| Magnesium                             | mg/L        | 4.05E+01      |  |  |  |
| Sodium                                | mg/L        | 7.60E+00      |  |  |  |
| Potassium                             | mg/L        | 2.40E+00      |  |  |  |
| Aluminum                              | mg/L        | 9.42E-03      |  |  |  |
| Iron                                  | mg/L        | 2.13E-02      |  |  |  |
| Zinc                                  | mg/L        | 1.67E-02      |  |  |  |
|                                       | Major Anio  | ns            |  |  |  |
| Chloride                              | mg/L        | 3.38E+02      |  |  |  |
| Sulfate                               | mg/L        | 5.57E+01      |  |  |  |
|                                       |             |               |  |  |  |

Table 3.4 - Coal ash basin wastewater characterization.

| Ash Basin Wastewater Characterization |                 |          |  |  |  |  |
|---------------------------------------|-----------------|----------|--|--|--|--|
| Bromide                               | mg/L            | 3.31E+00 |  |  |  |  |
| Majo                                  | r Oxyanions / 1 | Metals   |  |  |  |  |
| Boron                                 | mg/L            | 6.42E+00 |  |  |  |  |
| Vanadium                              | mg/L            | 1.40E-03 |  |  |  |  |
| Chromium                              | mg/L            | 1.90E-04 |  |  |  |  |
| Arsenic                               | mg/L            | 2.85E-03 |  |  |  |  |
| Selenium                              | mg/L            | 5.45E-03 |  |  |  |  |
| Strontium                             | mg/L            | 6.56E-01 |  |  |  |  |
| Molybdenum                            | mg/L            | 4.09E-03 |  |  |  |  |
| Antimony                              | mg/L            | 2.50E-04 |  |  |  |  |
| Tungsten                              | mg/L            | 1.00E-04 |  |  |  |  |
| Cadmium                               | mg/L            | 1.00E-04 |  |  |  |  |
| Lead                                  | mg/L            | ND       |  |  |  |  |
| Mercury                               | mg/L            | 3.00E-05 |  |  |  |  |

The characterization of coal ash leachate is based on the ratio between sulphate and calcium (Izquierdo and Querol, 2012). Since the coal ash basin wastewater is not a pure leachate, but more a dynamic equilibrium between freshly deposited and old weathered coal ash, the system presents less pronounced characteristics. The ratio between sulfur (5.57E+01mg/L) and calcium (4.11E+01 mg/L) is close to one (Table 3.4) with a circumneutral pH of 7.5. Besides the calcium content, magnesium (4.05E+01mg/L), sodium (7.60E+00 mg/L) and potassium (2.40E+00 mg/L) are the other three major cations in the coal ash leachate. The dominant anionic species was chloride (3.38E+02 mg/L) with approximately six times the concentration of sulphate (5.57E+01 mg/L). Bromide is the third most abundant anion (3.31E+00 mg/L); derived from volatiles from the coal combustion and the solubilization during cooling of the ash. Among the oxyanionic species, boron is the most abundant (6.42E+00 mg/L). Previous studies found that a large fraction of boron in fly ash is in soluble form (Cox et al., 1978; James et al., 1982), making boron one of the elements most readily released from fly ash in water.

# 3.4.2 <u>Thermodynamics of Ettringite Precipitation</u>

Magnesium (Mg <sup>2+</sup>) inhibits the formation of ettringite. When Mg<sup>2+</sup> and Ca<sup>2+</sup> coexist, Mg<sup>2+</sup> competes with Ca<sup>2+</sup> for Al(OH)<sup>-</sup><sub>4</sub> to block the formation of Al(OH)<sub>6</sub><sup>3-</sup> octahedra, and instead reacts with sulfate to form Hydrotalcite type compounds rather than ettringite. This formation is expected to occur at the Mg<sup>2+</sup> concentrations measured in the CAL but the thermodynamic data for the different Hydrotalcite type compounds would require analysis and modeling of constituents not yet fully understood. Table 3.5 presents the concentrations and conversion calculations performed on the relevant constituents in the coal ash leachate.

| Unit               | Al <sup>3+</sup> | Ca <sup>+2</sup> | <b>SO4</b> <sup>2-</sup> |
|--------------------|------------------|------------------|--------------------------|
| Molar Mass (g/mol) | 26.98            | 40.08            | 96.05                    |
| CAL (g/L)          | 1.0E-05          | 4.1E-02          | 5.6E-02                  |
| CAL (mol/L)        | 3.7E-07          | 1.0E-03          | 5.8E-04                  |

 Table 3.5 – CAL concentration conversion.

A thermodynamic analysis based on the equilibrium reactions of formation of aluminum hydroxide and ettringite (Table 3.6) was used to prepare the solubility/stability diagram of amorphous aluminum and ettringite plotted in Figure 3.8.

Table 3.6 – Thermodynamic equilibrium reactions for Aluminum Hydroxide andEttringite.

| Amorphous Aluminum Hydroxide - Al(OH)3  | Ettringite - Ca6Al2(SO4)3(OH)12.26H2O  |
|---|--|
| $Al^{3+} + 3H_2O < - > Al(OH)_3 + 3H^+$ | $6\ Ca^{2+} + 2\ Al^{3+} + 3\ SO_4{}^{2-} + 38\ H_2O\ < \text{-} >\ 12\ H^+ +$                         |
|   | Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> .26H <sub>2</sub> O |
| $K = 10^{-9.66}$ (Willard, 1979)        | $K = 10^{-56.4}$ (Tolonen et al., 2016)  |
| Log K = -9.66                           | Log K = -56.4  |
| $Log (Al^{3+}) = 9.66 - 3pH$            | $Log (Al^{3+}) = 28.2 - 3Log(Ca^{2+}) - 3/2Log(SO_4^{2-}) - 6pH$                                       |



Figure 3.8 - Solubility diagram of Amorphous Aluminum Hydroxide and Ettringite compared to the Al<sup>3+</sup> concentration in the wastewater.

Based on the results in Figure 3.8, it would appear that the concentration of  $Al^{3+}$ measured in the CAL is only stable in the solution below the pH 5.5. Between a pH of 5.5 to 10.5 the more stable form is amorphous aluminum hydroxide and the mineral ettringite will tend to be stable above pH 10.5. Ostwald ripening rule states that smaller, less stable crystals tend to form first and then dissolve to form larger, more energetically favored particles (Sparks, 2003). As a result, Al(OH)<sub>3</sub> should precipitate first at pH > 10.5 followed by its transformation to ettringite. If the reaction is performed at pH 10.5, then ettringite is likely to form directly without Al(OH)<sub>3</sub>. However, if the precipitated ettringite came into contract with lower pH water (i.e., pH < 10) later, it should dissolve unless aluminum concentrations are high enough as determined by a thermodynamic analysis for that given pH.

# 3.4.3 Boron Coprecipitation Test

The coprecipitation experiment was performed by increasing the dose of aluminum sulfate and the alkalization by calcium hydroxide to determine the limits of efficacy of the coprecipitation technique (Table 3.7).

| Sample ID | CAL           | Al Source  | Alkalization               | Dose | Initial | Sampling | Boron  |         |                 |
|-----------|---------------|--|----------------------------|------|---------|----------|--------|---------|-----------------|
|           | ( <b>ml</b> ) | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub><br>(g) | Ca(OH) <sub>2</sub><br>(g) | (%)  | рН      | pH       | (mg/L) | Removal | Avg.<br>Control |
| Control 1 | 100           | 0.000  | 0.000                      | 0    | 7.3     | 7.3      | 4.39   | -       | -               |
| Control 2 | 100           | 0.000  | 0.000                      | 0    | 7.3     | 7.3      | 4.82   | -       | -               |
| Flask 1   | 100           | 0.167  | 0.111                      | 25   | 10.5    | 9.6      | 2.10   | 54%     | 4.60            |
| Flask 2   | 100           | 0.333  | 0.223                      | 50   | 10.4    | 9.9      | 1.22   | 74%     | 4.60            |
| Flask 3   | 100           | 0.666  | 0.445                      | 100  | 10.4    | 10.2     | 0.14   | 97%     | 4.60            |
| Flask 4   | 100           | 1.333  | 0.890                      | 200  | 10.5    | 10.2     | 0.06   | 99%     | 4.60            |

Table 3.7 – Ettringite Coprecipitation Experiment Results

Using the dose of aluminum sulfate and calcium hydroxide by Guo et al. (2017), adopted in this study as reference (100%), a 97% removal of boron from solution was achieved. The lower dose of calcium hydroxide and aluminum sulphate tested (25%) removed 54% of boron out of solution. The removal efficiency increased from 54% to 99% as the dosage of aluminum sulphate and calcium hydroxide was increased (Figure 3.9)., which is in agreement with Hiraga and Shigemoto (2011). The higher the concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> added to the CAL, the larger the mass of boron removed by coprecipitation



Figure 3.9 – Removal of boron as a function of Calcium Hydroxide and Aluminum Sulphate.

As suggested in the thermodynamic equilibrium analysis, a pH between 10.0 and 10.5 would be the ideal for the outright formation of ettringite. Therefore, the initial pH in all treated samples was adjusted to 10.5 with a saturated solution of calcium hydroxide (Column initial pH from Table 3.7). After the settling period and mineral(s) precipitation the pH changed to what is presented as sampling pH (Table 3.7). This pH decrease is consistent with the formation of ettringite; for each molecule of ettringite formed there was a release of 12 H<sup>+</sup>. This decrease in pH highlights the necessity to buffer the solution and ensure the stability of the precipitated ettringite.

# 3.4.4 <u>Slag Buffered Boron Coprecipitation Test</u>

In subsequent experiments, steel slag was evaluated as low-cost a buffer that should potentially reduce the cost of Ca(OH)<sub>2</sub>. Since the steel slags are manufacturing wastes, they provide a low-cost buffer for large scale treatment systems. Table 3.8 show the results of screening the different combinations of slags.

| Somulo    | Decomintion         | CAL  | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | Ca(OH) <sub>2</sub> | L. Slag | EAF Slag     | TI   | Boron  |         |
|-----------|---------------------|------|---|---------------------|---------|--------------|------|--------|---------|
| Sample    | Description         | (ml) | ( <b>g</b> )                                    | (g)                 | (g)     | ( <b>g</b> ) | рн   | (mg/L) | Removal |
| Control 1 | Effluent<br>Control | 40   | -   | -                   | -       | -            | 8.2  | 7.01   | -       |
| Flask 1   | Unbuffered          | 40   | 0.067   | 0.045               | -       | -            | 11.4 | 1.72   | 75%     |
| Flask 2   | Slag<br>Buffered    | 40   | 0.067   | 0.045               | 0.40    | -            | 11.5 | 0.18   | 97%     |
| Flask 3   | Slag<br>Buffered    | 40   | 0.067   | 0.045               | -       | 0.40         | 11.5 | 0.16   | 98%     |
| Flask 4   | Slag<br>Buffered    | 40   | 0.067   | 0.045               | 0.20    | 0.20         | 11.3 | 0.08   | 99%     |
| Control 2 | L. Slag<br>Control  | 40   | -   | -                   | 0.40    | -            | 11.3 | 6.11   | 13%     |
| Control 3 | EAF Slag<br>Control | 40   | -   | -                   | -       | 0.40         | 11.6 | 5.53   | 21%     |
| Control 4 | Slag Mix<br>Control | 40   | -   | -                   | 0.20    | 0.20         | 10.5 | 5.58   | 20%     |

**Table 3.8 - Slag Buffered Boron Coprecipitation Results** 

The removal of boron using coprecipitation by aluminum sulphate and calcium hydroxide was replicated in the experiments in Table 3.8, using an equivalent dose of 25%. The higher removal of boron observed in the unbuffered flask appears to be the result of an initial high pH of the CAL, which should lead to the coprecipitation of some amount of boron. Note that the pH of the CAL used in this test was 8.21 which is more alkaline than in the previous experiments (Table 3.7).

The slag alone removed boron from the CAL. The EAF slag removed 21% of boron from solution, 50/50 EAF and ladle slag mixture removed 20%, while the ladle slag removed 13%. The aluminum sulphate and calcium hydroxide buffered with slag increased the removal of boron from 75% to > 97% (Table 3.8). The pH remained above 10.5 confirming that the slag performed well as a buffer and ensured the theoretical ettringite stability.

### 3.4.5 <u>Recycled Aluminum Coprecipitation Test</u>

To further develop a low-cost treatment method, the commercial aluminum salt was replaced with pieces of aluminum from recycled cans (zero-valent AL or ZVAL). It was hypothesized that in the slag buffered treatments ZVAL would be corroded at the high pH of >11. The Aluminum corrosion and dissolution in alkaline mediums is represented by the reaction 3.2.

$$Al + 3H_2O + HO^- = \frac{3}{2}H_2 + Al(OH)_4^-$$
 3.2

The corrosion of pure Aluminum in alkaline solution proceeds mainly by water reduction accompanied by the hydrogen formation (Zhang et al., 2009). During the experiment, the formation of gas bubbles believed to be hydrogen gas was observed after 40 minutes of agitation. The agitation was performed until the solution pH stabilized after 185 minutes. Figure 3.10 demonstrate the pH evolution of the mixture after the initial addition of ZVAL and slags as pH buffers to the CAL.



Figure 3.10 – pH change in experiment solution over the 185 minutes recycled aluminum coprecipitation test.

The CAL pH increased from 11.0 to 11.8 following addition of EAF slag, ladle slag and the ZVAL. Table 3.9 presents the analytical results for solution samples taken after the solution pH stabilized at about pH 10.5 (i.e., 185 minutes), with the ZVAL can pieces visibly corroded.

| Sample ID | CAL           | Al Source   | Alkalization |              |        | Boron  |         |
|-----------|---------------|-------------|--------------|--------------|--------|--------|---------|
|           | ( <b>ml</b> ) | Al Cans (g) | L. Slag (g)  | EAF Slag (g) | рп     | (mg/L) | Removal |
| Dup-01    | 500           | 5           | 10           | 10           | 10 5   | 4.02   | 42%     |
| Dup-02    | 500           | 5           | 10           | 10           | - 10.3 | 4.02   | 42%     |
| Control   | 500           | -           | -            | -            | 7.4    | 6.97   | -       |

**Table 3.9 - Recycled Aluminum Proof of Concept Results** 

The boron concentration decreased by 42% in just 3 h of treat, meaning higher removal is likely for a longer duration test at pH .10.5. It is assumed that the removal of boron was associated with the formation of ettringite because the optimum conditions for the formation ettringite were realized in the treatments. Other investigators have attributed the boron removal in similar treatments to the formation of aluminum-boron complexes and/or boron adsorption onto the corroded surfaces of the Aluminum can pieces (Zhang et al., 2009). Most likely all the removal mechanisms described above played a role in the boron removal. The results of this experiment suggested that a mixture of two wastes consisting of recycled aluminum can pieces and steel slag is a potentially viable solution for removal of boron from CAL. Future tests are need to optimize the removal of boron from the CAL using recycled Aluminum cans as an alternative and low-cost source of Aluminum.

#### 3.5 CONCLUSION

There are large amounts of fly ash either stored temporarily in stockpiles, disposed of in ash landfills and/or in basins. There is a growing and immediate need for cost-effective solutions to

treat and dispose of Coal Combustion Residuals. Coprecipitation is the removal of a contaminant by precipitation of another constituent that is typically present in higher concentrations. This study evaluated the use of zero-valent aluminum or aluminum salts and calcium salts to coprecipitate boron at alkaline pH. Ettringite coprecipitation treatments consisting of aluminum sulphate and calcium hydroxide addition removed up to 99% of the initial boron concentration from CAL. The 7.01 mg/L initial boron concentration in CAL decreased to 0.06 mg/L using 13.3 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 8.90 g of Ca(OH)<sub>2</sub> per litter solution.

The use of steel mill slags as low-cost pH buffers for the coprecipitation reaction also showed significant results, with 99% removal of boron achieved with only a quarter of the doses of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Ca(OH)<sub>2</sub>. The use of recycled Aluminum cans was also evaluated under the alkaline conditions generated by the steel slags. In the latter test, sulfate was supplied by the CAL, calcium by the steel slag and aluminum by the decomposition of the aluminum cans in the high pH of the slag buffered solution. The proof-of-concept tests suggest that ZVAL from recycled aluminum cans shows good promise in the precipitation of ettringite and removal of boron without any addition of other aluminum salts. As a result, a mixture of aluminum can pieces and slag removed 42% of boron from solution in only 185 minutes of contact time.

The mineral phases associated with coprecipitation of boron from the CAL is still to be confirmed in future tests. But as observed in the studies by Hiraga and Shigemoto (2011), the removal of boron from the solution increased with the concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> added. Removal of boron from CAL in the presence of aluminum hydroxides, aluminum borate and most especially recycled aluminum can pieces is promising and will be further developed for full scale application.

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# 4 SUMMARY AND CONCLUSION

This thesis explores the different forms of treatment and removal of boron and bromide from CCR leachate and FGD. Considering the abundance and complex nature of this type of effluent, economic viability is an imperative for the development of any treatment solutions. different low-cost sorbents and chemical precipitation alternatives were evaluated, including sorption and coprecipitation as independent and combined solutions evaluated in batch and columns treatment systems.

The results of the batch sorption experiments indicate that among all the materials analyzed, biochar impregnated with iron was the most efficient media for simultaneous removal of boron and bromide under acidic pH conditions. The highest adsorption capacity in this study was observed with iron impregnated bamboo biochar; 2,022mg/kg for boron and 241mg/kg for bromide. In column treatment, a sustained boron removal of 35% for 5.4 pore volumes was observed using FGD wastewater with an exceedingly high boron concentration of 160 mg/L and an empty bed contact time (EBCT) of 94 minutes. The removal of equally very high bromide concentration (90.8 mg/L) was sustained over 2 pore volumes before attaining breakthrough (95% of influent concentration).

For removal of boron alone, bone biochar demonstrated the highest efficacy among unmodified biochars, with an adsorption capacity of 113 mg/kg. The use of bamboo and bone biochar mixed with EAF and Ladle slag was quite effective for removal of boron from CAL pretreated with aluminum sulphate. Complete removal of boron for up to 4.9 pore volumes was observed in columns with two treatment layers consisting of 50% bone biochar, 25% EAF slag, and 25% Ladle Slag.

The combination of sorption and precipitation media identified in this study create an opportunity for developing a cost-effective remedy for the removal of boron and bromide. Figure 4.1 summarizes all of the promising products and methods evaluated.



Figure 4.1 - Summary of the main findings of this work for the use in a treatment train for boron and bromide from CCRs.

The mineral involved in the removal of boron from the CAL by coprecipitation is ettringite. Ettringite coprecipitation induced by the addition of aluminum sulphate and calcium hydroxide remove up to 99% of boron, from CAL with an initial concentration of 7.01 mg/L. The use of steel mill slags as buffers for the coprecipitation reaction showed significant promise with a 99% boron removal using only one fourth of aluminum sulphate and calcium hydroxide doses used to achieve the same level of removal in other tests. The use of recycled aluminum cans pieces was also evaluated under the alkaline conditions sustained using steel slags. The preliminary tests suggest that zero-valent Aluminum (ZVAL) from recycled aluminum cans showed good promise in the precipitation of ettringite without any addition of other aluminum salt.

More work is needed to further confirm these findings and more accurately quantify the adsorption capacities of the modified biochars for boron and bromide from the CAL and FGD wastewater. The influence of EBCT and pH on treatment efficiency of the most effective treatment media needs further study before scale-up to pilot testing. Characterization of these mineral phases by X-ray powder diffraction (XRD) would give good insights on mineral phases formed and bonds being established. Finally, the evaluation of chloride effect on treatment options are of imperative importance, especially in FGD wastewater. The characterization of the virgin and spent treatment media by Fourier Transform Infrared Spectroscopy (FTIR) Analysis should improve general understanding of the boron removal mechanisms.

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# APPENDIX A

## ANALYTICAL RESULTS

#### Table 1A - Sorption Screanning Results

| Treatment Media                      |     | w.w.          | Treatment Media  | Contact  |            |           |         | pH    |              |              |        |                | Boron         |              |              |       |             | Bromide       |
|--------------------------------------|-----|---------------|------------------|----------|------------|-----------|---------|-------|--------------|--------------|--------|----------------|---------------|--------------|--------------|-------|-------------|---------------|
| Туре                                 | (g) | ( <b>ml</b> ) | Fraction         | Time (h) | Sample ID  | Replicate | Mean    | RPD   | Ce<br>(mg/L) | Co<br>(mg/L) | RPD    | Removal<br>(%) | qe<br>(mg/kg) | Ce<br>(mg/L) | Co<br>(mg/L) | RPD   | Removal (%) | qe<br>(mg/kg) |
|                                      |     |               |                  |          |            | ]         | Round 1 |       |              |              |        |                |               |              |              |       |             |               |
| Ladle F. Slag (Gerdau)               | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-01      | 1 of 2    | 11.08   |       | 1.93         | 2.20         |        | 12%            | 13.43         | N/A          |              |       |             |               |
| Ladle F. Slag (Gerdau)               | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-02      | 2 of 2    | 10.84   |       | 1.86         | 2.20         |        | 15%            | 16.95         | N/A          |              |       |             |               |
| Ladle F. Slag (Gerdau)               | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-02LS-01 | Avg       | 10.96   | 2.2%  | 1.89         | 2.20         | 3.7%   | 14%            | 15.19         | N/A          |              |       |             |               |
| EAF. Slag (Gerdau)                   | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-04      | 1 of 2    | 11.67   |       | 1.48         | 2.20         |        | 33%            | 36.08         | N/A          |              |       |             |               |
| EAF. Slag (Gerdau)                   | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-05      | 2 of 2    | 11.46   |       | 1.65         | 2.20         |        | 25%            | 27.28         | N/A          |              |       |             |               |
| EAF. Slag (Gerdau)                   | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-05LS-04 | Avg       | 11.57   | 1.8%  | 1.56         | 2.20         | -11.3% | 29%            | 31.68         | N/A          |              |       |             |               |
| Pine Biochar                         | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-07      | 1 of 2    | 7.72    |       | 2.08         | 2.20         |        | 6%             | 6.08          | N/A          |              |       |             |               |
| Pine Biochar                         | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-08      | 2 of 2    | 7.48    |       | 2.06         | 2.20         |        | 6%             | 6.78          | N/A          |              |       |             |               |
| Pine Biochar                         | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-08LS-07 | Avg       | 7.60    | 3.2%  | 2.07         | 2.20         | 0.7%   | 6%             | 6.42          | N/A          |              |       |             |               |
| Hardwood Biochar                     | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-10      | 1 of 2    | 7.69    |       | 2.07         | 2.20         |        | 6%             | 6.38          | N/A          |              |       |             |               |
| Hardwood Biochar                     | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-11      | 2 of 2    | 7.73    |       | 2.04         | 2.20         |        | 7%             | 7.93          | N/A          |              |       |             |               |
| Hardwood Biochar                     | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-11LS-10 | Avg       | 7.71    | -0.5% | 2.05         | 2.20         | 1.5%   | 7%             | 7.15          | N/A          |              |       |             |               |
| Paper Waste Biochar                  | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-13      | 1 of 2    | 7.78    |       | 2.15         | 2.20         |        | 2%             | 2.33          | N/A          |              |       |             |               |
| Paper Waste Biochar                  | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-14      | 2 of 2    | 7.83    |       | 2.16         | 2.20         |        | 2%             | 2.03          | N/A          |              |       |             |               |
| Paper Waste Biochar                  | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-14LS-13 | Avg       | 7.81    | -0.6% | 2.15         | 2.20         | -0.3%  | 2%             | 2.17          | N/A          |              |       |             |               |
| Peanut Hull Biochar                  | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-16      | 1 of 2    | 9.45    |       | 2.08         | 2.20         |        | 6%             | 6.10          | N/A          |              |       |             |               |
| Peanut Hull Biochar                  | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-17      | 2 of 2    | 9.44    |       | 2.24         | 2.20         |        | -2%            | -2.15         | N/A          |              |       |             |               |
| Peanut Hull Biochar                  | 0.5 | 25            | 0.038 - 2.0 mm   | 48       | LS-17LS-16 | Avg       | 9.45    | 0.1%  | 2.16         | 2.20         | -7.6%  | 2%             | 1.97          | N/A          |              |       |             |               |
| Leachete Control                     | 0.5 | 25            | -                | 48       | LS-19      | REF       | 7.51    |       | 2.20         |              |        |                |               | N/A          |              |       |             |               |
| Ladle F. Slag Control (DI H2O)       | 0.5 | 0             | 0.038 - 2.0 mm   | 48       | LS-03      | Cont.     | 11.14   |       | 0.19         |              |        |                |               | N/A          |              |       |             |               |
| EAF. Slag Control (DI H2O)           | 0.5 | 0             | 0.038 - 2.0 mm   | 48       | LS-06      | Cont.     | 11.64   |       | 0.17         |              |        |                |               | N/A          |              |       |             |               |
| Pine Biochar Control (DI H2O)        | 0.5 | 0             | 0.038 - 2.0 mm   | 48       | LS-09      | Cont.     | 7.46    |       | 0.23         |              |        |                |               | N/A          |              |       |             |               |
| Hardwood Biochar Control (DI H2O)    | 0.5 | 0             | 0.038 - 2.0 mm   | 48       | LS-12      | Cont.     | 7.77    |       | 0.29         |              |        |                |               | N/A          |              |       |             |               |
| Paper Waste Biochar Control (DI H2O) | 0.5 | 0             | 0.038 - 2.0 mm   | 48       | LS-15      | Cont.     | 8.15    |       | 0.35         |              |        |                |               | N/A          |              |       |             |               |
| Peanut Hull Biochar Control (DI H2O) | 0.5 | 0             | 0.038 - 2.0 mm   | 48       | LS-18      | Cont.     | 9.67    |       | 0.34         |              |        |                |               | N/A          |              |       |             |               |
| Blank Control (DI H2O)               | 0.0 | 0             | 0                | 48       | LS-19      | Cont.     | 7.56    |       | 0.24         |              |        |                |               | N/A          |              |       |             |               |
|                                      |     |               |                  |          |            | 1         | Round 2 |       |              |              |        |                |               |              |              |       |             |               |
| Mg Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-01      | 1 of 2    | 9.36    |       | 5.82         | 7.18         |        | 19%            | 68.30         | 0.45         | 0.45         |       | 0%          | 0.07          |
| Mg Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-02      | 2 of 2    | 9.45    |       | 5.02         | 7.18         |        | 30%            | 108.35        | 0.39         | 0.45         |       | 14%         | 3.25          |
| Mg Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-02ES-01 | Avg       | 9.41    | -1.0% | 5.42         | 7.18         | 14.8%  | 25%            | 88.33         | 0.42         | 0.45         | 15.1% | 7%          | 1.66          |
| Fe Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-03      | 1 of 2    | 2.86    |       | 5.79         | 7.18         |        | 19%            | 69.50         | 0.30         | 0.45         |       | 34%         | 7.78          |
| Fe Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-04      | 2 of 2    | 2.88    |       | 5.95         | 7.18         |        | 17%            | 61.40         | 0.30         | 0.45         |       | 34%         | 7.75          |
| Fe Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-04ES-03 | Avg       | 2.87    | -0.7% | 5.87         | 7.18         | -2.8%  | 18%            | 65.45         | 0.30         | 0.45         | -0.2% | 34%         | 7.76          |
| Ca Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-05      | 1 of 2    | 9.48    |       | 6.21         | 7.18         |        | 13%            | 48.45         | 0.41         | 0.45         |       | 11%         | 2.43          |
| Ca Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-06      | 2 of 2    | 9.53    |       | 5.89         | 7.18         |        | 18%            | 64.45         | 0.38         | 0.45         |       | 16%         | 3.67          |
| Ca Peanut Hull Biochar               | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-06ES-05 | Avg       | 9.51    | -0.5% | 6.05         | 7.18         | 5.3%   | 16%            | 56.45         | 0.39         | 0.45         | 6.3%  | 13%         | 3.05          |
| Peanut Hull Biochar                  | 0.5 | 25            | 0.038 to 2.00 mm | 48       | ES-07      | 1 of 1    | 9.27    |       | 6.20         | 7.18         |        | 14%            | 49.30         | 0.40         | 0.45         |       | 13%         | 2.86          |
| Leachate Control                     | 0   | 25            | 0.038 to 2.00 mm | 48       | ES-08      | REF       | 7.94    |       | 7.18         |              |        |                |               | 0.45         |              |       |             |               |
| DI water Blank                       | 0   | 0             | 0.038 to 2.00 mm | 48       | ES-09      | Cont.     | 6.25    |       | 0.26         |              |        |                |               | BD           |              |       |             |               |
| Mg Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-01      | 1 of 2    | 9.87    |       | 5.16         | 6.68         |        | 23%            | 60.72         | 2.92         | 3.02         |       | 3%          | 4.00          |
| Mg Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-02      | 2 of 2    | 9.87    |       | 5.31         | 6.68         |        | 21%            | 54.92         | 2.81         | 3.02         |       | 7%          | 8.60          |
| Mg Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-02ES-01 | Avg       | 9.87    | 0.0%  | 5.24         | 6.68         | -2.8%  | 22%            | 57.82         | 2.86         | 3.02         | 4.0%  | 5%          | 6.30          |
| Fe Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-03      | 1 of 2    | 2.66    |       | 6.59         | 6.68         |        | 1%             | 3.64          | 2.08         | 3.02         |       | 31%         | 37.60         |
| Fe Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-04      | 2 of 2    | 2.61    |       | 6.59         | 6.68         |        | 1%             | 3.64          | 2.01         | 3.02         |       | 34%         | 40.60         |
| Fe Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-04ES-03 | Avg       | 2.63    | 2.1%  | 6.59         | 6.68         | 0.0%   | 1%             | 3.64          | 2.04         | 3.02         | 3.7%  | 32%         | 39.10         |
| Ca Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-05      | 1 of 2    | 9.73    |       | 6.90         | 6.68         |        | -3%            | -8.64         | 3.05         | 3.02         |       | -1%         | -1.12         |
| Ca Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-06      | 2 of 2    | 9.79    |       | 7.04         | 6.68         |        | -5%            | -14.28        | 3.04         | 3.02         |       | -1%         | -0.96         |
| Ca Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-06ES-05 | Avg       | 9.76    | -0.6% | 6.97         | 6.68         | -2.0%  | -4%            | -11.46        | 3.05         | 3.02         | 0.1%  | -1%         | -1.04         |
| Al Peanut Hull Biochar               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-07      | 1 of 2    | 4.80    |       | 6.51         | 6.68         |        | 3%             | 6.72          | 2.54         | 3.02         |       | 16%         | 19.20         |

#### Table 1A - Sorption Screanning Results

| Treatment Media                                 |     | w.w.          | Treatment Media  | Contact  |                         |                  |         | pH    |        |        |       |         | Boron    |        |        |       |             | Bromide |
|---|-----|---------------|------------------|----------|-------------------------|------------------|---------|-------|--------|--------|-------|---------|----------|--------|--------|-------|-------------|---------|
| Туре  | (g) | ( <b>ml</b> ) | Fraction         | Time (h) | Sample ID               | Replicate        | Mean    | RPD   | Ce     | Co     | RPD   | Removal | qe       | Ce     | Co     | RPD   | Removal (%) | qe      |
|   |     |               |                  |          |                         |                  | Round 3 |       | (mg/L) | (mg/L) |       | (%)     | (mg/kg)  | (mg/L) | (mg/L) |       |             | (mg/kg) |
| Al Peanut Hull Biochar                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-08                   | 2 of 2           | 4.67    |       | 6.45   | 6.68   |       | 4%      | 9.44     | 2.44   | 3.02   |       | 19%         | 23.04   |
| Al Peanut Hull Biochar                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-08ES-07              | Ave              | 4.73    | 2.7%  | 6.48   | 6.68   | 1.0%  | 3%      | 8.08     | 2.49   | 3.02   | 3.9%  | 17%         | 21.12   |
| Al-Mg Biochar (Innovo)                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-09                   | 1 of 2           | 8.40    |       | 4.09   | 6.68   |       | 39%     | 103.64   | 2.83   | 3.02   | ,,,   | 6%          | 7.68    |
| Al-Mg Biochar (Innovo)                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-10                   | 2 of 2           | 8.48    |       | 4.11   | 6.68   |       | 39%     | 102.92   | 2.89   | 3.02   |       | 4%          | 5.12    |
| Al-Mg Biochar (Innovo)                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-10ES-09              | Avg              | 8.44    | -1.0% | 4.10   | 6.68   | -0.4% | 39%     | 103.28   | 2.86   | 3.02   | -2.2% | 5%          | 6.40    |
| Bone Biochar (Charcoal House LLC)               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-11                   | 1 of 2           | 8.30    |       | 3.85   | 6.68   |       | 42%     | 113.44   | 3.02   | 3.02   |       | 0%          | 0.16    |
| Bone Biochar (Charcoal House LLC)               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-12                   | 2 of 2           | 8.30    |       | 3.85   | 6.68   |       | 42%     | 113.44   | 3.02   | 3.02   |       | 0%          | -0.16   |
| Bone Biochar (Charcoal House LLC)               | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-12ES-11              | Avg              | 8.30    | 0.0%  | 3.85   | 6.68   | 0.0%  | 42%     | 113.44   | 3.02   | 3.02   | -0.3% | 0%          | 0.00    |
| Meat/Bone Biochar (Titan A - 850 °C)            | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-16                   | 1 of 2           | 7.71    |       | 6.28   | 6.68   |       | 6%      | 15.92    | 3.14   | 3.02   |       | -4%         | -4.80   |
| Meat/Bone Biochar (Titan A - 850 °C)            | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-17                   | 2 of 2           | 7.75    |       | 6.30   | 6.68   |       | 6%      | 15.12    | 3.20   | 3.02   |       | -6%         | -7.04   |
| Meat/Bone Biochar (Titan A - 850 °C)            | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-17ES-16              | Avg              | 7.73    | -0.5% | 6.29   | 6.68   | -0.3% | 6%      | 15.52    | 3.17   | 3.02   | -1.8% | -5%         | -5.92   |
| Pine Fe-Ca-Mg Biochar (Titan B - 600 °C)        | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-18                   | 1 of 2           | 3.74    |       | 6.87   | 6.68   |       | -3%     | -7.48    | 14.09  | 3.02   |       | -367%       | -442.80 |
| Pine Fe-Ca-Mg Biochar (Titan B - 600 °C)        | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-19                   | 2 of 2           | 3.45    |       | 6.82   | 6.68   |       | -2%     | -5.44    | 14.32  | 3.02   |       | -374%       | -452.00 |
| Pine Fe-Ca-Mg Biochar (Titan B - 600 °C)        | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-19ES-18              | Avg              | 3.59    | 7.9%  | 6.84   | 6.68   | 0.7%  | -2%     | -6.46    | 14.21  | 3.02   | -1.6% | -370%       | -447.40 |
| Pine Fe-Ca-Mg Biochar Powder (Titan C - 600 °C) | 1.0 | 40            | < 0.42 mm        | 48       | ES-20                   | 1 of 2           | 3.20    |       | 6.67   | 6.68   |       | 0%      | 0.44     | 19.14  | 3.02   |       | -534%       | -644.80 |
| Pine Fe-Ca-Mg Biochar Powder (Titan C - 600 °C) | 1.0 | 40            | < 0.42 mm        | 48       | ES-21                   | 2 of 2           | 3.17    |       | 6.52   | 6.68   |       | 2%      | 6.56     | 20.28  | 3.02   |       | -572%       | -690.40 |
| Pine Fe-Ca-Mg Biochar Powder (Titan C - 600 °C) | 1.0 | 40            | < 0.42 mm        | 48       | ES-21ES-20              | Avg              | 3.18    | 1.2%  | 6.59   | 6.68   | 2.3%  | 1%      | 3.50     | 19.71  | 3.02   | -5.8% | -553%       | -667.60 |
| FeSO4-NaBH4 Softwood Biochar                    | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-09                   | 1 of 2           | 2.95    |       | 32.28  | 6.68   |       | -383%   | -1023.80 | 3.21   | 3.02   |       | -6%         | -7.60   |
| FeSO4-NaBH4 Softwood Biochar                    | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-10                   | 2 of 2           | 2.93    |       | 32.67  | 6.68   |       | -389%   | -1039.72 | 3.11   | 3.02   |       | -3%         | -3.40   |
| FeSO4-NaBH4 Softwood Biochar                    | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-10ES-09              | Avg              | 2.94    | 0.7%  | 32.48  | 6.68   | -1.2% | -386%   | -1031.76 | 3.16   | 3.02   | 3.3%  | -5%         | -5.50   |
| CS2-FeSO4 Softwood BC                           | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-13                   | 1 of 2           | 3.03    |       | 7.51   | 6.68   |       | -12%    | -32.96   | 3.22   | 3.02   |       | -7%         | -8.00   |
| CS2-FeSO4 Softwood BC                           | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-14                   | 2 of 2           | 3.02    |       | 7.53   | 6.68   |       | -13%    | -33.80   | 3.01   | 3.02   |       | 0%          | 0.40    |
| CS2-FeSO4 Softwood BC                           | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-14ES-13              | Avg              | 3.02    | 0.2%  | 7.52   | 6.68   | -0.3% | -12%    | -33.38   | 3.12   | 3.02   | 6.7%  | -3%         | -3.80   |
| MuniRem-FeSO4 Bamboo Biochar                    | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-15                   | 1 of 2           | 3.05    |       | 6.72   | 6.68   |       | -1%     | -1.64    | 3.04   | 3.02   |       | 0%          | -0.60   |
| MuniRem-FeSO4 Bamboo Biochar                    | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-16                   | 2 of 2           | 3.13    |       | 6.76   | 6.68   |       | -1%     | -3.16    | 3.04   | 3.02   |       | 0%          | -0.60   |
| MuniRem-FeSO4 Bamboo Biochar                    | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-16ES-15              | Avg              | 3.09    | -2.7% | 6.74   | 6.68   | -0.6% | -1%     | -2.40    | 3.04   | 3.02   | 0.0%  | 0%          | -0.60   |
| FeSO4 Softwood Biochar                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-17                   | 1 of 2           | 2.24    |       | 7.42   | 6.68   |       | -11%    | -29.44   | 2.86   | 3.02   |       | 5%          | 6.60    |
| FeSO4 Softwood Biochar                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-18                   | 2 of 2           | 2.24    |       | 7.47   | 6.68   |       | -12%    | -31.72   | 2.79   | 3.02   |       | 8%          | 9.40    |
| FeSO4 Softwood Biochar                          | 1.0 | 40            | 0.038 to 2.00 mm | 48       | ES-18ES-17              | Avg              | 2.24    | 0.0%  | 7.45   | 6.68   | -0.8% | -11%    | -30.58   | 2.82   | 3.02   | 2.5%  | 7%          | 8.00    |
| Leachate Control                                | 0.0 | 40            | -                | 48       | ES-13                   | REF              | 7.72    |       | 6.68   |        |       |         |          | 3.02   |        |       |             |         |
| Co H2O2 Softward Dischart                       | 1.0 | 40            | 0.028 to 2.00 mm | 44       | ES 01                   | 1 of 2           | 0 77    |       | 5.24   | 6 70   |       | 220/    | 61.90    | 2.10   | 2.22   |       | 10/         | 1.00    |
| Ca-H2O2 Softwood Biochar                        | 1.0 | 40            | 0.038 to 2.00 mm | 44       | ES-01                   | 1 01 2<br>2 of 2 | 8.77    |       | 5.14   | 6.78   |       | 2370    | 65.48    | 2.19   | 3.22   |       | 1 70        | 1.00    |
| Ca-H2O2 Softwood Biochar                        | 1.0 | 40            | 0.038 to 2.00 mm | 44       | ES-02<br>ES-02<br>ES-01 | 2 01 2           | 8.70    | 0.2%  | 5.14   | 6.78   | 1.8%  | 24%     | 63.64    | 3.18   | 3.22   | 0.5%  | 1%          | 1.00    |
| H2O2 Softwood Biochar                           | 1.0 | 40            | 0.038 to 2.00 mm | 44       | FS_03                   | 1 of 2           | 8 77    | 0.270 | 5 32   | 6.78   | 1.070 | 2370    | 58.48    | 3.16   | 3.22   | 0.570 | 204         | 2 40    |
| H2O2 Softwood Biochar                           | 1.0 | 40            | 0.038 to 2.00 mm | 44       | ES-04                   | 2 of 2           | 8.74    |       | 5.32   | 6.78   |       | 22%     | 63.04    | 3.18   | 3.22   |       | 1%          | 1.60    |
| H2O2 Softwood Biochar                           | 1.0 | 40            | 0.038 to 2.00 mm | 44       | ES-04ES-03              | 2 01 2<br>Avo    | 8.75    | 0.3%  | 5.26   | 6.78   | 2.2%  | 23%     | 60.76    | 3.17   | 3.22   | -0.6% | 2%          | 2.00    |
| Bamboo Biochar (BioChar Central)                | 1.0 | 40            | 0.038 to 2.00 mm | 44       | ES-05                   | 1 of 2           | 9.34    | 0.070 | 5.35   | 6.78   | 2.270 | 21%     | 57.20    | 3.14   | 3.22   | 0.070 | 2%          | 3.00    |
| Bamboo Biochar (BioChar Central)                | 1.0 | 40            | 0.038 to 2.00 mm | 44       | ES-06                   | 2 of 2           | 9.41    |       | 5.33   | 6.78   |       | 21%     | 58.16    | 3.26   | 3.22   |       | -1%         | -1.60   |
| Bamboo Biochar (BioChar Central)                | 1.0 | 40            | 0.038 to 2.00 mm | 44       | ES-06ES-05              | Avg              | 9.38    | -0.7% | 5.34   | 6.78   | 0.4%  | 21%     | 57.68    | 3.20   | 3.22   | -3.6% | 1%          | 0.70    |
| Leachate Control                                | 0.0 | 40            | -                | 44       | ES-07                   | REF              | 7.43    | -     | 6.78   |        |       |         |          | 3.22   |        |       |             |         |

## Table 2A - Maximum Loading Results

| Bone Biochar Ma | ximum  | Loading  |            |         |                 |      |              |                |                            |                          |               |              |                |                            |                          |               |
|-----------------|--------|----------|------------|---------|-----------------|------|--------------|----------------|----------------------------|--------------------------|---------------|--------------|----------------|----------------------------|--------------------------|---------------|
|                 | Wastev | vater    | Bone l     | Biochar |                 |      | Boron        |                |                            |                          |               | Bromide      |                |                            |                          |               |
| Sample ID       | (ml)   | Туре     | Dose (g/l) | (g)     | Contact<br>Time | рН   | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/kg) | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/Kg) |
| BS-01 (Control) | 40     | FGD      | 0.0        | 0.00    | 48 hours        | 6.96 | 146.57       |                |                            |                          |               | 82.20        |                |                            |                          |               |
| BS-03           | 40     | FGD      | 2.5        | 0.10    | 48 hours        | 7.08 | 162.05       | -10.6%         | -15.48                     | -619.32                  | -6137.96      | 87.00        | -5.8%          | -4.80                      | -192.00                  | -1902.87      |
| BS-04           | 40     | FGD      | 5.0        | 0.20    | 48 hours        | 7.27 | 155.79       | -6.3%          | -9.22                      | -368.76                  | -1842.88      | 76.80        | 6.6%           | 5.40                       | 216.00                   | 1079.46       |
| BS-05           | 40     | FGD      | 10.0       | 0.40    | 48 hours        | 7.25 | 145.46       | 0.8%           | 1.11                       | 44.60                    | 111.31        | 78.80        | 4.1%           | 3.40                       | 136.00                   | 339.41        |
| BS-07           | 40     | FGD      | 25.0       | 1.00    | 48 hours        | 7.29 | 144.30       | 1.6%           | 2.27                       | 90.96                    | 90.90         | 71.80        | 12.7%          | 10.40                      | 416.00                   | 415.71        |
| BS-08           | 40     | FGD      | 37.5       | 1.50    | 48 hours        | 7.26 | 142.51       | 2.8%           | 4.06                       | 162.48                   | 108.24        | 78.40        | 4.6%           | 3.80                       | 152.00                   | 101.26        |
| BS-09           | 40     | FGD      | 62.5       | 2.50    | 48 hours        | 7.32 | 141.27       | 3.6%           | 5.30                       | 211.96                   | 84.76         | 86.40        | -5.1%          | -4.20                      | -168.00                  | -67.18        |
| BS-10           | 40     | FGD      | 100.0      | 4.00    | 48 hours        | 7.34 | 115.25       | 21.4%          | 31.32                      | 1252.80                  | 313.16        | 83.60        | -1.7%          | -1.40                      | -56.00                   | -14.00        |
| BS-11           | 40     | FGD      | 175.0      | 7.00    | 48 hours        | 7.41 | 90.01        | 38.6%          | 56.56                      | 2262.32                  | 323.11        | 83.00        | -1.0%          | -0.80                      | -32.00                   | -4.57         |
| BS-12           | 40     | FGD      | 250.0      | 10.00   | 48 hours        | 7.49 | 74.42        | 49.2%          | 72.15                      | 2886.04                  | 288.58        | 86.40        | -5.1%          | -4.20                      | -168.00                  | -16.80        |
| Domboo Dioshou  | Movim  | um Loodi |            |         |                 |      |              |                |                            |                          |               |              |                |                            |                          |               |

|                 | Wastew | vater | Bamboo     | Biochar |                 |       | Boron        |                |                            |                          |               | Bromide      |                |                            |                          |              |
|-----------------|--------|-------|------------|---------|-----------------|-------|--------------|----------------|----------------------------|--------------------------|---------------|--------------|----------------|----------------------------|--------------------------|--------------|
| Sample ID       | (ml)   | Туре  | Dose (g/l) | (g)     | Contact<br>Time | рН    | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/kg) | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/Kg |
| BS-10 (Control) | 40     | CAL   | 0.0        | 0.00    | 48 hours        | 7.36  | 6.21         |                |                            |                          |               | 4.12         |                |                            |                          |              |
| BS-09           | 40     | CAL   | 1.3        | 0.05    | 48 hours        | 8.33  | 6.21         | 0.1%           | 0.00                       | 0.16                     | 3.16          | 4.19         | -1.7%          | -0.07                      | -2.80                    | -55.23       |
| BS-01           | 40     | CAL   | 2.5        | 0.10    | 48 hours        | 8.78  | 6.13         | 1.4%           | 0.08                       | 3.36                     | 33.50         | 4.08         | 1.0%           | 0.04                       | 1.60                     | 15.95        |
| BS-02           | 40     | CAL   | 5.0        | 0.20    | 48 hours        | 9.23  | 5.99         | 3.6%           | 0.22                       | 8.92                     | 44.42         | 4.23         | -2.7%          | -0.11                      | -4.40                    | -21.91       |
| BS-03           | 40     | CAL   | 10.0       | 0.40    | 48 hours        | 9.39  | 5.69         | 8.4%           | 0.52                       | 20.92                    | 52.18         | 4.18         | -1.5%          | -0.06                      | -2.40                    | -5.99        |
| BS-04           | 40     | CAL   | 20.0       | 0.80    | 48 hours        | 9.50  | 5.14         | 17.2%          | 1.07                       | 42.84                    | 53.53         | 4.14         | -0.5%          | -0.02                      | -0.80                    | -1.00        |
| BS-05           | 40     | CAL   | 25.0       | 1.00    | 48 hours        | 9.52  | 4.92         | 20.8%          | 1.29                       | 51.76                    | 51.71         | 4.04         | 1.9%           | 0.08                       | 3.20                     | 3.20         |
| BS-06           | 40     | CAL   | 37.5       | 1.50    | 48 hours        | 9.78  | 4.53         | 27.0%          | 1.68                       | 67.16                    | 44.79         | 4.17         | -1.2%          | -0.05                      | -2.00                    | -1.33        |
| BS-07           | 40     | CAL   | 50.0       | 2.00    | 48 hours        | 9.92  | 4.17         | 32.8%          | 2.04                       | 81.52                    | 40.75         | 4.09         | 0.7%           | 0.03                       | 1.20                     | 0.60         |
| BS-08           | 40     | CAL   | 125.0      | 5.00    | 48 hours        | 10.23 | 2.40         | 61.4%          | 3.81                       | 152.56                   | 30.51         | 4.12         | 0.0%           | 0.00                       | 0.00                     | 0.00         |

## Table 2A - Maximum Loading Results

| Fe-Modified Bio        | char Ma | ximum Lo | oading     |            |                 |      |              |                |                            |                          |               |              |                |                            |                          |               |
|------------------------|---------|----------|------------|------------|-----------------|------|--------------|----------------|----------------------------|--------------------------|---------------|--------------|----------------|----------------------------|--------------------------|---------------|
|                        | Waster  | water    | Fe-Bamb    | oo Biochar |                 |      | Boron        |                |                            |                          |               | Bromide      |                |                            |                          |               |
| Sample ID              | (ml)    | Туре     | Dose (g/l) | (g)        | Contact<br>Time | рН   | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/kg) | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/Kg) |
| BS-06                  | 40      | FGD      | 0.0        | 0.00       | 48 hours        | 6.97 | 176.68       |                |                            |                          |               | 91.20        |                |                            |                          |               |
| BS-10                  | 40      | FGD      | 25.0       | 1.00       | 48 hours        | 2.37 | 126.07       | 28.6%          | 50.62                      | 2024.68                  | 2022.46       | 88.80        | 2.6%           | 2.40                       | 96.00                    | 95.89         |
| BS-11                  | 40      | FGD      | 50.0       | 2.00       | 48 hours        | 2.08 | 117.87       | 33.3%          | 58.81                      | 2352.48                  | 1175.77       | 81.40        | 10.7%          | 9.80                       | 392.00                   | 195.92        |
| BS-12                  | 40      | FGD      | 100.1      | 4.01       | 48 hours        | 1.84 | 113.17       | 35.9%          | 63.51                      | 2540.56                  | 634.20        | 67.00        | 26.5%          | 24.20                      | 968.00                   | 241.64        |
|                        | Waster  | water    | Fe-Bone    | e Biochar  |                 |      | Boron        |                |                            |                          |               | Bromide      |                |                            |                          |               |
| Sample ID              | (ml)    | Туре     | Dose (g/l) | (g)        | Contact<br>Time | рН   | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/kg) | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/Kg) |
| BS-13                  | 40      | FGD      | 50.1       | 2.00       | 48 hours        | 4.78 | 124.89       | 29.3%          | 51.79                      | 2071.72                  | 1033.64       | 96.40        | -5.7%          | -5.20                      | -208.00                  | -103.78       |
| BS-14                  | 40      | FGD      | 100.0      | 4.00       | 48 hours        | 4.76 | 115.70       | 34.5%          | 60.99                      | 2439.44                  | 609.72        | 91.80        | -0.7%          | -0.60                      | -24.00                   | -6.00         |
| BS-15                  | 40      | FGD      | 200.1      | 8.00       | 48 hours        | 4.74 | 111.20       | 37.1%          | 65.49                      | 2619.44                  | 327.26        | 82.20        | 9.9%           | 9.00                       | 360.00                   | 44.98         |
|                        | Waster  | water    | Fe-Peanut  | H. Biochar |                 |      | Boron        |                |                            |                          |               | Bromide      |                |                            |                          |               |
| Sample ID              | (ml)    | Туре     | Dose (g/l) | (g)        | Contact<br>Time | pН   | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/kg) | Ce<br>(mg/L) | Removal<br>(%) | [C]<br>reduction<br>(mg/L) | Mass<br>Adsorbed<br>(mg) | qe<br>(mg/Kg) |
| BS-16                  | 40      | FGD      | 50.3       | 2.01       | 48 hours        | 2.30 | 158.26       | 10.4%          | 18.42                      | 736.88                   | 366.52        | 84.00        | 7.9%           | 7.20                       | 288.00                   | 143.25        |
| BS-17                  | 40      | FGD      | 100.1      | 4.00       | 48 hours        | 2.11 | 148.52       | 15.9%          | 28.16                      | 1126.56                  | 281.46        | 76.40        | 16.2%          | 14.80                      | 592.00                   | 147.90        |
| BS-20                  | 40      | FGD      | 200.1      | 8.00       | 48 hours        | 1.98 | 109.69       | 37.9%          | 66.99                      | 2679.72                  | 334.84        | 70.00        | 23.2%          | 21.20                      | 848.00                   | 105.96        |
| <b>Control Samples</b> |         |          |            |            |                 |      |              |                |                            |                          |               |              |                |                            |                          |               |
|                        | Waster  | water    | Fe-Bamb    | oo Biochar | Contact         |      | Boron        |                |                            |                          |               | Bromide      |                |                            |                          |               |
| Sample ID              | (ml)    | Туре     | Dose (g/l) | (g)        | Time            | рН   | Ce<br>(mg/L) | R              | PE                         | Replicate                | Sample        | Ce<br>(mg/L) | R              | PE                         | Replicate                | Sample        |
| BS-22 (BS-17)          | 40      | FGD      | 100.1      | 4.00       | 48 hours        | 2.09 | 126.14       | 8.             | 1%                         |                          |               | 80.40        | -2.            | 6%                         |                          |               |
| BS-18                  | 40      | Br- STD  | 79.9       | mg/L       | 48 hours        | 5.61 |              |                |                            |                          |               | 83.80        | -2.            | 4%                         | STD Sa                   | ample         |

#### Table 3A - Column Test Results

| Column 1 (Sorption) - 40%   | 6 Bamboo Biochar   | + 30% EAF Slag   | g + 30% Lad  | lle Slag  |   |   |   |   | Boron                          |                                  |   | Bromide                          |                          |
|---|--|--|--|---|---|---|---|---|--------------------------------|----------------------------------|---|----------------------------------|--------------------------|
| Sample ID   | Elepsed<br>Time  | Elepsed Time<br>(min)  | Sample<br>Interval<br>(ml)   | Sample<br>(ml)  | Flow (ml)   | Pore<br>Volumes   | pН  | mg/L  | % remov                        | [B] e/o                          | mg/L  | % remov                          | [Br] e/o                 |
| EB-01 (CAL)   | 0 min  | 0  | 0  | 50  | 0   | 0.00  | 3.76  | 6.11  | -                              |                                  | 3.15  | -                                |                          |
| CS-01   | 1h5min   | 65   | 100  | 50  | 150   | 0.05  | 9.51  | 0.13  | 98%                            | 0.02                             | 0.25  | 92%                              | 0.08                     |
| CS-02   | 1h18min  | 78   | 500  | 50  | 700   | 0.25  | 9.72  | 0.07  | 99%                            | 0.01                             | 1.62  | 49%                              | 0.51                     |
| CS-03   | 1h29min  | 89   | 500  | 50  | 1250  | 0.44  | 10.06   | 0.06  | 99%                            | 0.01                             | 2.58  | 18%                              | 0.82                     |
| CS-04   | 1h41min  | 101  | 500  | 50  | 1800  | 0.64  | 11.88   | 0.06  | 99%                            | 0.01                             | 3.05  | 3%                               | 0.97                     |
| CS-05   | 1h53min  | 113  | 500  | 50  | 2350  | 0.83  | 12.29   | 0.07  | 99%                            | 0.01                             | 2.84  | 10%                              | 0.90                     |
| CS-06   | 2h5min   | 125  | 500  | 50  | 2900  | 1.03  | 12.39   | 0.07  | 99%                            | 0.01                             | 2.77  | 12%                              | 0.88                     |
| CS-07   | 2h18min  | 138  | 500  | 50  | 3450  | 1.22  | 12.46   | 0.07  | 99%                            | 0.01                             | 2.83  | 10%                              | 0.90                     |
| CS-08   | 2h29min  | 149  | 500  | 50  | 4000  | 1.42  | 12.48   | 0.13  | 98%                            | 0.02                             | 2.56  | 19%                              | 0.81                     |
| CS-09   | 2h42min  | 162  | 500  | 50  | 4550  | 1.61  | 12.48   | 0.25  | 96%                            | 0.04                             | 2.86  | 9%                               | 0.91                     |
| CS-10   | 2h54min  | 174  | 500  | 50  | 5100  | 1.81  | 12.49   | 0.43  | 93%                            | 0.07                             | 2.86  | 9%                               | 0.91                     |
| CS-11   | 3h08min  | 188  | 500  | 50  | 5650  | 2.00  | 12.50   | 0.63  | 90%                            | 0.10                             | 3.02  | 4%                               | 0.96                     |
|   |  |  |  |   |   |   |   |   |                                |                                  |   |                                  | 0.00                     |
| CS-12   | 3h20min  | 200  | 500  | 50  | 6200  | 2.20  | 12.52   | 0.80  | 87%                            | 0.13                             | 2.85  | 10%                              | 0.90                     |
| CS-12<br>CS-13  | 3h20min<br>3h33min   | 200<br>213   | 500<br>500   | 50<br>50  | 6200<br>6750  | 2.20<br>2.39  | 12.52<br>12.51  | 0.80<br>0.96  | 87%<br>84%                     | 0.13                             | 2.85<br>2.79  | 10%<br>11%                       | 0.90<br>0.89             |
| CS-12<br>CS-13  | 3h20min<br>3h33min   | 200<br>213   | 500<br>500   | 50<br>50  | 6200<br>6750  | 2.20<br>2.39  | 12.52<br>12.51  | 0.80<br>0.96  | 87%<br>84%                     | 0.13 0.16                        | 2.85<br>2.79  | 10%<br>11%                       | 0.90                     |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 44  | 3h20min<br>3h33min<br>0% Bamboo Bioch  | 200<br>213<br>ar + <b>30% EAF S</b>  | 500<br>500<br>Slag + <b>30% I</b>                                  | 50<br>50<br>Ladle Slag  | 6200<br>6750  | 2.20<br>2.39  | 12.52<br>12.51  | 0.80<br>0.96  | 87%<br>84%<br>Boron            | 0.13 0.16                        | 2.85<br>2.79  | 10%<br>11%<br>Bromide            | 0.90                     |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID  | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time   | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)  | 500<br>500<br>Slag + 30% I<br>Sample<br>Interval<br>(ml)           | 50<br>50<br>Ladle Slag<br>Sample<br>(ml)  | 6200<br>6750<br>Flow (ml)   | 2.20<br>2.39<br>Pore<br>Volumes   | 12.52<br>12.51<br><b>pH</b>   | 0.80<br>0.96<br>mg/L  | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16                     | 2.85<br>2.79<br>mg/L  | 10%<br>11%<br>Bromide<br>% remov | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID<br>EB-01 (Tap Water)   | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min  | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0   | 500<br>500<br>Slag + 30% I<br>Sample<br>Interval<br>(ml)<br>0      | 50<br>50<br>2adle Slag<br>Sample<br>(ml)<br>50  | 6200<br>6750<br>Flow (ml)<br>0  | 2.20<br>2.39<br>Pore<br>Volumes<br>0  | 12.52<br>12.51<br><b>pH</b><br>8.06   | 0.80<br>0.96<br>mg/L<br><0.01   | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16<br>[ <b>B</b> ] e/o | 2.85<br>2.79<br>mg/L<br><0.25   | 10%<br>11%<br>Bromide<br>% remov | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01  | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min<br>28min   | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28   | 500<br>500<br>500<br>500<br>500<br>500<br>500<br>500               | 50<br>50<br>.adle Slag<br>Sample<br>(ml)<br>50<br>50  | 6200<br>6750<br>Flow (ml)<br>0<br>100   | 2.20<br>2.39<br>Pore<br>Volumes<br>0<br>2.430   | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19  | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04   | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16<br>[ <b>B</b> ] e/o | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80   | 10%<br>11%<br>Bromide<br>% remov | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01<br>DS-02   | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min<br>28min<br>49min  | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28<br>49   | 500<br>500<br>500<br>500<br>500<br>500<br>500<br>1000              | 50<br>50<br>.adle Slag<br>Sample<br>(ml)<br>50<br>50  | 6200<br>6750<br>Flow (ml)<br>0<br>100<br>1150   | 2.20<br>2.39<br>Pore<br>Volumes<br>0<br>2.430<br>2.802  | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19<br>11.34   | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04<br>0.02   | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16<br>[ <b>B</b> ] e/o | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80<br>1.33   | 10% 11% Bromide % remov          | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 44<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01<br>DS-02<br>DS-03   | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min<br>28min<br>49min<br>1h12min   | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28<br>49<br>72   | 500<br>500<br>500<br>500<br>500<br>500<br>500<br>1000<br>1000      | 50<br>50<br>2adle Slag<br>Sample<br>(ml)<br>50<br>50<br>50  | 6200<br>6750<br>Flow (ml)<br>0<br>100<br>1150<br>2200   | 2.20<br>2.39<br>Pore<br>Volumes<br>0<br>2.430<br>2.802<br>3.174   | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19<br>11.34<br>11.63  | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04<br>0.02<br>0.03   | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16<br>[ <b>B</b> ] e/o | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80<br>1.33<br>0.87   | 10% 11% Bromide % remov          | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01<br>DS-02<br>DS-03<br>DS-04   | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min<br>28min<br>49min<br>1h12min<br>1h34min  | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28<br>49<br>72<br>94   | 500<br>500<br>500<br>500<br>500<br>500<br>1000<br>1000<br>1000     | 50<br>50<br>2adle Slag<br>Sample<br>(ml)<br>50<br>50<br>50<br>50<br>50                              | 6200<br>6750<br>Flow (ml)<br>0<br>100<br>1150<br>2200<br>3250                                 | 2.20<br>2.39<br><b>Pore</b><br>Volumes<br>0<br>2.430<br>2.802<br>3.174<br>3.547                                     | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19<br>11.34<br>11.63<br>11.69                                     | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04<br>0.02<br>0.03<br>0.03                                 | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16<br>[B] e/o          | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80<br>1.33<br>0.87<br>0.72                                 | 10% 11% Bromide % remov          | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01<br>DS-02<br>DS-03<br>DS-04<br>DS-05                                      | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min<br>28min<br>49min<br>1h12min<br>1h34min<br>1h57min   | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28<br>49<br>72<br>94<br>117                                  | 500<br>500<br>500<br>500<br>500<br>500<br>1000<br>1000<br>1000     | 50<br>50<br>2adle Slag<br>(ml)<br>50<br>50<br>50<br>50<br>50<br>50                                  | 6200<br>6750<br>Flow (ml)<br>0<br>100<br>1150<br>2200<br>3250<br>4300                         | 2.20<br>2.39<br>Pore<br>Volumes<br>0<br>2.430<br>2.802<br>3.174<br>3.547<br>3.919                                   | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19<br>11.34<br>11.63<br>11.69<br>11.79                            | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04<br>0.02<br>0.03<br>0.03<br>0.04                         | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16<br>[B] e/o          | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80<br>1.33<br>0.87<br>0.72<br>0.56                         | 10% 11% Bromide % remov          | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01<br>DS-02<br>DS-03<br>DS-04<br>DS-05<br>DS-06                             | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min<br>28min<br>49min<br>1h12min<br>1h34min<br>1h57min<br>2h22min  | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28<br>49<br>72<br>94<br>117<br>142                           | 500<br>500<br>500<br>500<br>500<br>500<br>500<br>1000<br>1000<br>1 | 50<br>50<br>2adle Slag<br>Sample<br>(ml)<br>50<br>50<br>50<br>50<br>50<br>50<br>50<br>50            | 6200<br>6750<br>Flow (ml)<br>0<br>100<br>1150<br>2200<br>3250<br>4300<br>5350                 | 2.20<br>2.39<br>Pore<br>Volumes<br>0<br>2.430<br>2.802<br>3.174<br>3.547<br>3.919<br>4.292                          | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19<br>11.34<br>11.63<br>11.69<br>11.79<br>11.81                   | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04<br>0.02<br>0.03<br>0.03<br>0.04<br>0.04                 | 87%<br>84%<br>Boron<br>% remov | 0.13<br>0.16<br>[B] e/o          | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80<br>1.33<br>0.87<br>0.72<br>0.56<br>0.51                 | 10% 11% Bromide % remov          | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 4<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01<br>DS-02<br>DS-03<br>DS-04<br>DS-05<br>DS-06<br>DS-07                    | 3h20min<br>3h33min<br>0% Bamboo Bioch<br>Elepsed<br>Time<br>0 min<br>28min<br>49min<br>1h12min<br>1h34min<br>1h57min<br>2h22min<br>2h47min   | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28<br>49<br>72<br>94<br>117<br>142<br>167                    | 500<br>500<br>500<br>500<br>500<br>50<br>50<br>1000<br>1000<br>100 | 50<br>50<br>50<br><b>Sample</b><br>(ml)<br>50<br>50<br>50<br>50<br>50<br>50<br>50                   | 6200<br>6750<br>Flow (ml)<br>0<br>100<br>1150<br>2200<br>3250<br>4300<br>5350<br>6400         | 2.20<br>2.39<br><b>Pore</b><br>Volumes<br>0<br>2.430<br>2.802<br>3.174<br>3.547<br>3.919<br>4.292<br>4.664          | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19<br>11.34<br>11.63<br>11.69<br>11.79<br>11.81<br>11.82          | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04<br>0.02<br>0.03<br>0.03<br>0.04<br>0.04<br>0.04         | 87% 84% Boron % remov          | 0.13<br>0.16<br>[ <b>B</b> ] e/o | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80<br>1.33<br>0.87<br>0.72<br>0.56<br>0.51<br>0.40         | 10% 11% Bromide % remov          | 0.90<br>0.89<br>[Br] e/o |
| CS-12<br>CS-13<br>Column 1 (Desorption) - 44<br>Sample ID<br>EB-01 (Tap Water)<br>DS-01<br>DS-02<br>DS-03<br>DS-04<br>DS-05<br>DS-06<br>DS-06<br>DS-07<br>DS-08 | 3h20min           3h33min           0% Bamboo Bioch           Elepsed           Time           0 min           28min           49min           1h12min           1h34min           1h57min           2h47min           3h11min | 200<br>213<br>ar + 30% EAF S<br>Elepsed Time<br>(min)<br>0<br>28<br>49<br>72<br>94<br>72<br>94<br>117<br>142<br>167<br>191 | 500<br>500<br>500<br>500<br>500<br>500<br>500<br>1000<br>1000<br>1 | 50<br>50<br>50<br><b>Sample</b><br>(ml)<br>50<br>50<br>50<br>50<br>50<br>50<br>50<br>50<br>50<br>50 | 6200<br>6750<br>Flow (ml)<br>0<br>100<br>1150<br>2200<br>3250<br>4300<br>5350<br>6400<br>7450 | 2.20<br>2.39<br><b>Pore</b><br>Volumes<br>0<br>2.430<br>2.802<br>3.174<br>3.547<br>3.919<br>4.292<br>4.664<br>5.037 | 12.52<br>12.51<br><b>pH</b><br>8.06<br>10.19<br>11.34<br>11.63<br>11.69<br>11.79<br>11.81<br>11.82<br>11.79 | 0.80<br>0.96<br>mg/L<br><0.01<br>0.04<br>0.02<br>0.03<br>0.03<br>0.04<br>0.04<br>0.04<br>0.04 | 87% 84% Boron % remov          | 0.13<br>0.16<br>[ <b>B</b> ] e/o | 2.85<br>2.79<br>mg/L<br><0.25<br>1.80<br>1.33<br>0.87<br>0.72<br>0.56<br>0.51<br>0.40<br>0.36 | 10% 11% Bromide % remov          | 0.90<br>0.89<br>[Br] e/o |

#### Table 3A - Column Test Results

| Column 2 (Sorption) - 50% Bor | ne Biochar + 2  | 5% EAF Slag +         | 25% Ladle Slag             |                |           |                 |          |       | Boron   |         | Bromide |         |          |  |
|-------------------------------|-----------------|-----------------------|----------------------------|----------------|-----------|-----------------|----------|-------|---------|---------|---------|---------|----------|--|
| Sample ID                     | Elepsed<br>Time | Elepsed Time<br>(min) | Sample<br>Interval<br>(ml) | Sample<br>(ml) | Flow (ml) | Pore<br>Volumes | pH       | mg/L  | % remov | [B] e/o | mg/L    | % remov | [Br] e/o |  |
| EB-01 Pre-Treated Control     | 0 min           | 0                     | 0                          | 75             | 0         | -               | 3.92     | 16.57 | -       |         | 8.88    | -       |          |  |
| EB-03 D.I. Water              | 0 min           | 0                     | 0                          | 75             | 0         | -               | 8.09     | 0.11  | -       |         | 0.73    |         |          |  |
| EB-02 Effluent Control        | 0 min           | 0                     | 0                          | 50             | 0         | 0               | 7.37     | 16.95 | -       |         | 9.00    | -       |          |  |
| CS-01                         | 57min           | 57                    | 100                        | 75             | 175       | 0.05            | 9.27     | 0.05  | 99.7%   | 0.00    | 20.10   | -123%   | 2.23     |  |
| CS-02                         | 1h07min         | 67                    | 500                        | 75             | 750       | 0.22            | 9.73     | 0.02  | 99.9%   | 0.00    | 11.46   | -27%    | 1.27     |  |
| CS-03                         | 1h17min         | 77                    | 500                        | 75             | 1325      | 0.38            | 9.86     | 0.01  | 99.9%   | 0.00    | 8.28    | 8%      | 0.92     |  |
| CS-04                         | 1h26min         | 86                    | 500                        | 75             | 1900      | 0.55            | 9.85     | 0.00  | 100.0%  | 0.00    | 8.34    | 7%      | 0.93     |  |
| CS-05                         | 1h35min         | 95                    | 500                        | 75             | 2475      | 0.71            | 9.95     | 0.00  | 100.0%  | 0.00    | 0.41    | 95%     | 0.05     |  |
| CS-06                         | 1h44min         | 104                   | 500                        | 75             | 3050      | 0.88            | 9.97     | 0.00  | 100.0%  | 0.00    | 8.10    | 10%     | 0.90     |  |
| CS-07                         | 2h02min         | 122                   | 1000                       | 75             | 4125      | 1.19            | 9.98     | 0.00  | 100.0%  | 0.00    | 8.04    | 11%     | 0.89     |  |
| CS-08                         | 2h19min         | 139                   | 1000                       | 75             | 5200      | 1.50            | 9.91     | 0.00  | 100.0%  | 0.00    | 8.26    | 8%      | 0.92     |  |
| CS-09                         | 2h36min         | 156                   | 1000                       | 75             | 6275      | 1.81            | 9.86     | 0.00  | 100.0%  | 0.00    | 9.70    | -8%     | 1.08     |  |
| CS-10                         | 2h53min         | 173                   | 1000                       | 75             | 7350      | 2.12            | 9.92     | 0.00  | 100.0%  | 0.00    | 8.10    | 10%     | 0.90     |  |
| CS-11                         | 3h10min         | 190                   | 1000                       | 75             | 8425      | 2.43            | 9.70     | 0.00  | 100.0%  | 0.00    | 10.54   | -17%    | 1.17     |  |
| CS-12                         | 3h27min         | 207                   | 1000                       | 75             | 9500      | 2.74            | 9.42     | 0.00  | 100.0%  | 0.00    | 11.40   | -27%    | 1.27     |  |
| CS-13                         | 3h45min         | 225                   | 1000                       | 75             | 10575     | 3.05            | 9.05     | 0.00  | 100.0%  | 0.00    | 12.18   | -35%    | 1.35     |  |
| CS-14                         | 4h02min         | 242                   | 1000                       | 75             | 11650     | 3.36            | 9.04     | 0.00  | 100.0%  | 0.00    | 15.06   | -67%    | 1.67     |  |
| CS-15                         | 4h20min         | 260                   | 1000                       | 75             | 12725     | 3.67            | 9.00     | 0.00  | 100.0%  | 0.00    | 16.23   | -80%    | 1.80     |  |
| CS-16                         | 4h37min         | 277                   | 1000                       | 75             | 13800     | 3.97            | 8.93     | 0.00  | 100.0%  | 0.00    | 14.07   | -56%    | 1.56     |  |
| CS-17                         | 4h55min         | 295                   | 1000                       | 75             | 14875     | 4.28            | 8.84     | 0.00  | 100.0%  | 0.00    | 13.62   | -51%    | 1.51     |  |
| CS-18                         | 5h14min         | 314                   | 1000                       | 75             | 15950     | 4.59            | 8.85     | 0.00  | 100.0%  | 0.00    | 13.89   | -54%    | 1.54     |  |
| CS-19                         | 5h33min         | 333                   | 1000                       | 75             | 17025     | 4.90            | 8.73     | 0.00  | 100.0%  | 0.00    | 14.61   | -62%    | 1.62     |  |
| DUP-01 (CS-17)                |                 |                       |                            |                |           | Relativ         | ve Error | 0.07  |         | N/A     | 15.64   |         | -6.9%    |  |

#### Table 3A - Column Test Results

| Column 3 (Sorption) - 100% Fe | Imn 3 (Sorption) - 100% Fe-Bamboo Biochar |                       |                            |                |           |                 |          |        | Boron   |         |       | Bromide |          |
|-------------------------------|---|-----------------------|----------------------------|----------------|-----------|-----------------|----------|--------|---------|---------|-------|---------|----------|
| Sample ID                     | Elepsed<br>Time                           | Elepsed Time<br>(min) | Sample<br>Interval<br>(ml) | Sample<br>(ml) | Flow (ml) | Pore<br>Volumes | pН       | mg/L   | % remov | [B] e/o | mg/L  | % remov | [Br] e/o |
| EB-02 Br- std 79.9 ppm        | 0 min                                     | 0                     | 0                          | 50             | 0         |                 | -        | 0.58   | -       |         | 82.6  | -       |          |
| EB-01 Effluent Control        | 0 min                                     | 0                     | 0                          | 50             | 0         |                 | 6.95     | 160.13 | -       |         | 90.8  | -       |          |
| CS-01                         | 50min                                     | 50                    | 100                        | 50             | 150       | 0.05            | 1.33     | 24.22  | 85%     | 0.15    | 8.58  | 91%     | 0.09     |
| CS-02                         | 1h09min                                   | 69                    | 1000                       | 50             | 1200      | 0.41            | 1.57     | 70.64  | 56%     | 0.44    | 30.60 | 66%     | 0.34     |
| CS-03                         | 1h27min                                   | 87                    | 1000                       | 50             | 2250      | 0.77            | 1.89     | 107.98 | 33%     | 0.67    | 54.40 | 40%     | 0.60     |
| CS-04                         | 1h44min                                   | 104                   | 1000                       | 50             | 3300      | 1.12            | 2.06     | 93.03  | 42%     | 0.58    | 60.40 | 33%     | 0.67     |
| CS-05                         | 2h01min                                   | 121                   | 1000                       | 50             | 4350      | 1.48            | 2.18     | 96.17  | 40%     | 0.60    | 68.20 | 25%     | 0.75     |
| CS-06                         | 2h19min                                   | 139                   | 1000                       | 75             | 5425      | 1.85            | 2.28     | 104.25 | 35%     | 0.65    | 73.20 | 19%     | 0.81     |
| CS-07                         | 2h37min                                   | 157                   | 1000                       | 50             | 6475      | 2.20            | 2.37     | 111.26 | 31%     | 0.69    | 75.60 | 17%     | 0.83     |
| CS-08                         | 2h54min                                   | 174                   | 1000                       | 50             | 7525      | 2.56            | 2.50     | 108.47 | 32%     | 0.68    | 78.20 | 14%     | 0.86     |
| CS-09                         | 3h12min                                   | 192                   | 1000                       | 50             | 8575      | 2.92            | 2.51     | 82.14  | 49%     | 0.51    | 79.20 | 13%     | 0.87     |
| CS-10                         | 3h29min                                   | 209                   | 1000                       | 50             | 9625      | 3.27            | 2.56     | 85.41  | 47%     | 0.53    | 82.20 | 9%      | 0.91     |
| CS-11                         | 3h47min                                   | 227                   | 1000                       | 50             | 10675     | 3.63            | 2.62     | 66.70  | 58%     | 0.42    | 82.00 | 10%     | 0.90     |
| CS-12                         | 4h04min                                   | 244                   | 1000                       | 50             | 11725     | 3.99            | 2.67     | 115.17 | 28%     | 0.72    | 82.80 | 9%      | 0.91     |
| CS-13                         | 4h22min                                   | 262                   | 1000                       | 50             | 12775     | 4.35            | 2.70     | 106.78 | 33%     | 0.67    | 83.40 | 8%      | 0.92     |
| CS-14                         | 4h40min                                   | 280                   | 1000                       | 75             | 13850     | 4.71            | 2.73     | 97.20  | 39%     | 0.61    | 85.40 | 6%      | 0.94     |
| CS-15                         | 4h57min                                   | 297                   | 1000                       | 50             | 14900     | 5.07            | 2.73     | 112.37 | 30%     | 0.70    | 85.40 | 6%      | 0.94     |
| CS-16                         | 5h16min                                   | 316                   | 1000                       | 50             | 15950     | 5.43            | 2.77     | 106.15 | 34%     | 0.66    | 85.40 | 6%      | 0.94     |
| DUP-01 (CS-06)                |   |                       |                            |                |           | Relativ         | ve Error | 90.06  |         | 7.3%    | 73.00 |         | 0.1%     |
| DUP-02 (CS-14)                |   |                       |                            |                |           | Relativ         | ve Error | 81.16  |         | 9.0%    | 84.80 |         | 0.4%     |