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Leaching Characteristics of Selenium from Coal Fly Ash

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Leaching Characteristics of Selenium from Coal Fly Ash

Leaching Characteristics of Selenium from Coal Fly Ash

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Crop, Soil, and Environmental Science

by

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Bachelor of Science in Agricultural, Food and Life Sciences, 2004

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This thesis is approved for recommendation to the Graduate Council.

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ABSTRACT

Selenium (Se) contamination can be a potential groundwater concern near un-lined coal ash landfills. Out of all the Environmental Protection Agency (EPA) priority and non-priority pollutants, Se has the narrowest range between what is considered beneficial and detrimental for aquatic and terrestrial organisms. The effects of ash type (i.e., fresh and weathered), water-extractant type (i.e., deionized water, rainwater, and groundwater), and extraction time (i.e., 2- and 6-hours) on Se, arsenic (As), and chromium (Cr) concentrations were investigated from Class C, subbituminous coal fly ash produced at the Flint Creek Power Plant located in Benton County, AR. Water-extractable Se concentrations differed ($P = 0.03$) between ash types across water-extractants, but were unaffected by extraction times. Unexpectedly, fresh ash water-extractable Se concentrations were below minimum detection limits (i.e., $2.0 \mu\text{g L}^{-1}$) for all treatments. In contrast, averaged over extraction times, the weathered ash water-extractable Se concentration was greatest ($P < 0.05$) with groundwater and rainwater, which did not differ and averaged $60.0 \mu\text{g L}^{-1}$, compared to extraction with deionized water ($57.6 \mu\text{g L}^{-1}$). Selenite (Se^{4+}) was greater ($P < 0.001$) in the fresh (3.85 mg kg^{-1}) than in the weathered ash (0.70 mg kg^{-1}), while selenate (Se^{6+}) concentration was greater ($P < 0.001$) in the weathered (0.67 mg kg^{-1}) than in fresh ash (0.48 mg kg^{-1}). Results from this study indicate that environmental weathering of Class C, subbituminous fly ash promotes oxidation of selenite (Se^{4+}), to the less toxic, but highly mobile selenate (Se^{6+}). The formation of hydrated ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} - 26\text{H}_2\text{O}$] and calcium selenite (CaSeO_3) likely acted as a sink for weathered ash selenite (Se^{4+}). Implications of this research include a better understanding of the past, present, and future environmental and health risk potential associated with the release of water-soluble Se, As, and Cr to aid in the development of sustainable fly ash management strategies.

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DEDICATION

I dedicate this thesis to my wife, Kari Cantrell, whose support and patience throughout this entire process provided the stability that was needed to accomplish this task. I would also like to thank my grandparents, James and Pauline Cantrell. Everything that I have accomplished can be traced back to them.

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INTRODUCTION

Selenium (Se) is a naturally occurring element present in soil, water, and the air. Natural sources include weathering of the Earth's crust, wildfires, and volcanic activity (Chapman et al., 2009). Anthropogenic sources include agriculture (i.e., pesticides and feed additives), coal combustion, mining, municipal wastewater discharge, petroleum refining, photographic products, electronics, glass, ceramic, shampoo, and pigment manufacturing (Barceloux, 1999; Chapman et al., 2009). A key trait of Se is the narrow range of exposure between what is considered a deficiency ($< 40 \mu\text{g Se day}^{-1}$) and what is considered toxic ($> 400 \mu\text{g Se day}^{-1}$) for humans (WHO, 1996). Therefore, the EPA's Maximum Contaminant Level (MCL) in drinking water for humans is $50 \mu\text{g Se L}^{-1}$ (EPA, 2011). Human Se deficiency is far more widespread than human Se toxicity on a global scale (Fordyce, 2005). However, in China, human Se toxicity has been reported from the consumption of crops grown in high seleniferous soils with symptoms including garlic breath, loss of hair and nails, dental problems, gastrointestinal problems, and nervous system problems (Yang et al., 1983).

In aquatic eco-systems, water concentrations greater than $5 \mu\text{g Se L}^{-1}$ can potentially cause adverse health effects due to the bioaccumulative effects of Se within the food-chain (EPA, 2011). Aquatic Se toxicity is characterized by reproductive teratogenic deformities and embryo toxicity of both aquatic birds and fish and was first recognized within the U.S. in the early 1980s (Lemly, 1999; Spallholz and Hoffman, 2002; Chapman et al., 2009). During the 1980s, several aquatic ecosystems were severely affected by Se contamination, including agricultural drainage evaporation containments (e.g., Kesterson Reservoir, CA) and discharges from coal ash containments (e.g., Belews Lake and Hyco Reservoir, NC and Martin Lake, TX; Skorupa, 1998; Lemly, 2002). Because of the potential harm to humans and the aquatic

environment, Se removal from industrial wastestreams is necessary before discharge. One such industrial wastestream is the leachate generated from coal ash landfills.

In the US, there is approximately 43,929,517 metric tons (48,424,000 tons) of bottom ash and fly ash stored in coal ash landfills or coal ash impoundments annually (ACAA, 2011).

Leachate generated from a coal ash landfill can be laden with Se, which could cause harm to the environment. Selenium contamination can be a potential groundwater concern near un-lined coal ash landfills. A study conducted by EPRI (2006) reported that coal ash landfill leachate has a mean concentration of $19 \mu\text{g Se L}^{-1}$, with a range between 0.07 to $1,760 \mu\text{g Se L}^{-1}$ and can exist in a variety of oxidation states, such as selenide (Se^{2-}), elemental Se (Se^0), selenite (Se^{4+}), and selenate (Se^{6+}). Selenium speciation is highly affected by oxidation-reduction potential and pH and the oxidation state affects Se solubility and mobility in soils, the aquatic environment, and fly ash. During coal combustion, Se is released and transferred to fly ash through a physical (i.e., volatilization-condensation) adsorption process with selenite (Se^{4+}), and selenate (Se^{6+}) being the dominant forms present (Huang et al., 2004).

Due to Se's mobility within the environment, understanding Se's adsorption, desorption, and leaching processes are critical for assessing the amount of Se that has been, and could be, released into the environment from a fly ash landfill. Data obtained from this research should help quantify the amount of Se that has leached from a Class C, sub-bituminous, fly ash weathered at an un-lined landfill adjacent to the Flint Creek Power Plant located in Benton County, Arkansas. Implications of this research include a better understanding of the past, present, and future environmental and health risk potential associated with the release of selenium's water-soluble fraction.

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CHAPTER 1

LEACHING CHARACTERISTICS OF SELENIUM FROM COAL FLY ASH

LITERATURE REVIEW

Coal-Fired Electric Generation Plants

There are a total of 1,436 electric generators at 594 coal-fired plants in the United States (EIA, 2011). During 2009, the total US usage of electricity was 3,950 million megawatt hours, with 1,776 million megawatt hours supplied by coal-fired plants. Based on this figure, coal-fired plants provide approximately 45 % of the total net electrical generation, with 847,930 metric tons (934,683 tons) of coal consumed per day (EIA, 2011). Not since 1978 has electric generation from coal been this low (EIA, 2011). Low natural gas prices, higher coal prices, surplus of natural gas plants, and increased costs of environmental compliance has led to this decline (EIA, 2011). Coal-fired generation density by sector can be seen from the following percentages: East North Central (23.7 %), South Atlantic (19.6 %), West North Central (12.9 %), West South Central (12.6 %), Mountain (11.5 %), East South Central (11.1 %), Middle Atlantic (7.0 %), New England (0.8 %) and Pacific (0.8 %; EIA, 2011).

At a typical coal-fired plant, coal arrives by rail, barge, or may be mined near the plant and transported to the plant's coal yard by a system of conveyer belts. Once the coal has arrived at the plant, the coal is conveyed to large bunkers and then into a pulverizer, where the coal is ground into a fine talcum-powder-like consistency. From this point, the pulverized coal is injected into a boiler by forced-draft air and is combusted. The heat from this combustion turns water into high pressure steam. This high pressure steam is what turns the turbine, which in turn creates a magnetic field inside the generator and creates the electricity. This entire process is a transformation of energy, whereas the coal is a source of stored chemical energy, and the combustion of the coal to produce steam is thermal energy. Furthermore, the velocity of the moving steam is kinetic energy, and the rotation of the turbine is mechanical energy, which

produces the electrical energy (Gregory, Energy Production Supt. II, personal communication, 2010). Following the combustion of coal, a percentage of the coal is left over as a by-product known as coal ash.

Coal and Coal Ash

Coal is a heterogeneous mixture of organic and inorganic constituents formed from plants by chemical and geological processes called coalification (Kitto and Stultz, 2005). The major constituents of coal (i.e., carbon, hydrogen, oxygen, nitrogen, and sulfur) volatilize during combustion and account for 70 to 97 % of the total composition (EPRI, 1994b). The American Society for Testing and Materials (ASTM) ranks coal using volatile matter and fixed carbon as the ranking criteria. Lignite [$< 19,306 \text{ kJ kg}^{-1}$ ($< 8,300 \text{ Btu lb}^{-1}$)], sub-bituminous [$19,306$ to $26,749 \text{ kJ kg}^{-1}$ ($8,300$ to $11,500 \text{ Btu lb}^{-1}$)], bituminous [$24,423$ to $32,564 \text{ kJ kg}^{-1}$ ($10,500$ to $14,000 \text{ Btu lb}^{-1}$)], and anthracite [$> 34,890 \text{ kJ kg}^{-1}$ ($> 15,000 \text{ Btu lb}^{-1}$)] are ranks of coal ordered according to their heat values (Kitto and Stultz, 2005). Due to their wide availability, bituminous and sub-bituminous coals are the primary ranks used for the generation of electricity in the US (Kitto and Stultz, 2005).

Following combustion, 3 to 30 % of the inorganic constituents, as well as a small amount of organic matter, are left over as ash (Tripodi and Cheremisinoff, 1980; EPRI, 1994b). The composition of coal ash will vary depending on the coal origin, degree of pulverization, combustion process, and collection/disposal methods (EPRI, 1994b). The major constituents of coal ash include silicon, aluminum, iron, and calcium, which account for 95 to 99 % of the total weight (Morrison, 1970; Tripodi and Cheremisinoff, 1980). The minor constituents include magnesium, titanium, sodium, potassium, sulfur, and phosphorus, which account for less than

3.5 % of the total weight (Morrison, 1970; Tripodi and Cheremisinoff, 1980). The trace constituents can include antimony, arsenic, barium, beryllium, boron, copper, fluorine, lead, manganese, mercury, molybdenum, nickel, selenium, tellurium, thallium, tin, titanium, uranium, vanadium, and zinc (Tripodi and Cheremisinoff, 1980). In US coals, Coleman et al. (1993) reported that Se was primarily present in the organic phase within the coal and had a mean concentration of $1.7 \text{ mg Se kg}^{-1}$, with a range between 0.02 to 75 mg Se kg^{-1} . Inorganic constituents that are naturally enriched in coal are further concentrated in the coal combustion residuals (CCRs): bottom ash and fly ash.

Bottom Ash

Bottom ash is a coarse, heavy ash that is too dense to carry over in the gas stream after combustion (Tripodi and Cheremisinoff, 1980; Fizette, 2005). Due to its density, bottom ash is collected in the bottom of the boiler. The particle size ranges from that of gravel to silt, with much of the bottom ash sized similar to that of natural sand (Fizette, 2005). Bottom ash may range in color from medium brown to a grayish black and is usually angular in shape (Fizette, 2005; Sayiri, 2005). The specific gravity of bottom ash ranges from 1.6 to 2.6 depending on the size of the ash particles (Sayiri, 2005). Approximately 44 % of the 15,059,270 metric tons (16,600,000 tons) of bottom ash produced in 2009 were re-used as a marketable product (ACAA, 2011). Some beneficial re-uses of bottom ash include construction fill material, snow and ice control, concrete/cement products, mining applications, and as road and sub-surface material (Fizette, 2005; Sayiri, 2005). The remaining unmarketable bottom ash is either landfilled or placed in impoundments for storage.

Fly Ash

In 2011, the American Coal Ash Association (ACAA) reported 57,152,640 metric tons (63,000,000 tons) of fly ash were produced from coal generation. The physical and chemical properties of fly ash are largely dependent on the mineral content, composition, source of the coal, and combustion conditions within the boiler (Lou et al., 2011). The four major constituents of fly ash are silica (SiO_2), aluminum oxide (Al_2O_3), calcium oxide (CaO), and iron oxide (Fe_2O_3 ; EPRI, 1984; Wesche, 1991). The minor minerals present are magnesium oxide (MgO), sodium oxide (Na_2O), titanium oxide (TiO_2), potassium oxide (K_2O), phosphorus oxide (P_2O_3), and sulfur trioxide (SO_3), all of which account for less than 5 % of the total weight (EPRI, 1984; Wesche, 1991). There are also trace amounts of heavy metals, such as arsenic, barium, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, strontium, vanadium, and zinc, which typically do not exceed 1 % by weight (Yeheyis, 2008). Fly ash has a mean Se concentration of $14.0 \text{ mg Se kg}^{-1}$ and a normal range between 5.5 and $46.9 \text{ mg Se kg}^{-1}$ (EPRI, 1987). Fly ash particles range in size from $0.5 \text{ }\mu\text{m}$ (clay) to $100 \text{ }\mu\text{m}$ (fine sand), with a specific gravity that ranges from 2.2 to 2.8 (Tripodi and Cheremisinoff, 1980; Yeheyis, 2008).

According to the ASTM (2006), fly ash is classified as Class C or Class F. Class C fly ash generally has more than 20 % CaO and more than 50 % SiO_2 , Al_2O_3 , and Fe_2O_3 content and is normally produced from sub-bituminous or lignite coal combustion. Class F fly ash is usually produced from bituminous and anthracite coal combustion and has less than 10 % CaO content and more than 70 % SiO_2 , Al_2O_3 , and Fe_2O_3 content (ASTM, 2006). Coal samples tested during research conducted by EPRI (1984) showed Class C fly ashes having a 14.6 to 27.2 % CaO composition and Class F having a 0.3 to 6.8 % CaO composition.

Approximately 40 % of the fly ash produced is re-used in industrial applications, with the remainder being land-filled (ACAA, 2011). Applications for re-used fly ash include concrete/cement products, structural fills, road base, soil modification, mining applications, waste stabilization, and agriculture. One concern with fly ash is the concentrated elements present, such as Se, which are transferred from the coal to the ash through a volatilization process.

Selenium

Selenium Volatization

Selenium is a volatile element that is released and transferred to fly ash during coal combustion through a physical (volatization-condensation) adsorption process (Huang et al., 2004). Of the trace elements, only mercury is more volatile than Se during the combustion of coal (Huang et al., 2004; Lopez-Anton et al., 2007). Factors affecting Se volatilization include combustion temperature, residence time, coal source, fly ash composition, and the particle size of the coal and fly ash (Senior et al., 2010). Zeng and Sarofim (2001) studied the vaporization process during coal combustion and determined that Se was present within the coal as it entered the boiler. After injection into the boiler, the coal begins to turn into a liquid “melt”, releasing gas vapors that combust. This melt, if hardened, is known as slag. The Se is transported through the liquid melt and released as a gas vapor (Zeng and Sarofim, 2001). Vaporized Se will be in the gas form as either Se(g) or hydrogen selenide (H₂Se) during coal gasification and is converted to selenium dioxide (SeO₂) as it mixes with oxygen-rich gases in the boiler during combustion (Bool and Helble, 1995; Lopez-Anton et al., 2006; Noda and Ito, 2008). Due to its recondensing temperature of 500°C (932°F), Se will begin recondensing into a solid as the gases cool while passing through the convective section of the boiler (primary super-heater and

economizer) and the electrostatic precipitator (ESP; Noda and Ito, 2008). The Se will condense on the surface of the fly ash particles forming condensed Se compounds such as $\text{SeO}_2(\text{g})$ (Bool and Helble, 1995; Lopez-Anton et al., 2006). Selenium experiences an increasing condensation ratio as the flue gas temperatures decrease (Noda and Ito, 2008). During ESP testing, Huang et al. (2004) reported that as the diameter of the fly ash particles decreased, the surface area increased, and the relative enrichment of Se upon the fly ash became greater. Huang et al. (2004) also documented the Se concentration ratio in each CCR as bottom ash (< 5 %), fly ash (~ 45 %), and flue gas (~ 50 %). Otero-Rey et al. (2003) reported similar Se concentrations in each CCR. Selenium that does not condense onto the fly ash particles passes out of the stack in a gas (vapor) form.

Selenium is not present in appreciable amounts in bottom ash due to selenium's recondensing temperature below 500 °C (932 °F; Noda and Ito, 2008). In typical coal units, bottom ash is collected at the bottom of the boiler combustion section and at the high temperatures of 635 to 1343 °C (1775 to 2450 °F) in the boiler combustion section, Se has volatilized out of the coal and is present only in the gas phase (Figure 1-1). However, Otero-Rey et al. (2003) and Huang et al. (2004) reported Se in bottom ash comprising nearly 5 % of the total Se in CCRs. Unfortunately, these studies did not differentiate between bottom and economizer ash. Economizer ash is often collectively referred to as bottom ash due to its collection point. Economizer ash is collected at the bottom of the convective section and resembles the composition and texture of bottom ash (Figure 1-1). Selenium will be present in economizer ash due to the temperature and collection point of the economizer ash within the boiler. Therefore, it is assumed that the Se being reported in the bottom ash actually condensed in the convective section and was entrained in the economizer ash. Any presence of Se in the

bottom ash may be due to the presence of ash “slag” or unburned coal in the bottom ash. After collection, fly ash that was not able to be marketed is landfilled.

Selenium’s Role in the Environment

Selenium is a naturally occurring metalloid present in soil, water, and the air. Natural sources include weathering of the Earth’s crust, wildfires, and volcanic activity (Chapman et al., 2009). While anthropogenic sources include agriculture (i.e., pesticides and feed additives), coal combustion, mining, municipal wastewater discharge, petroleum refining, photographic products, electronics, glass, ceramic, shampoo, and pigment manufacturing (Barceloux, 1999; Chapman et al., 2009). Andren and Klein (1975) reported that approximately 1.5 to 2.5 times as much Se is released into the environment from coal combustion than by natural weathering. Selenium can exist in a variety of oxidation states as selenide (2^-), elemental Se (0), selenite (4^+), and selenate (Se^{6+}). Selenium is considered essential for human and animal health, but has not been reported as being essential for plant growth (Elrashidi et al., 1987; Fordyce, 2007).

A key trait of Se is the narrow range of exposure between what is considered a deficiency (i.e., $< 40 \mu\text{g Se day}^{-1}$) and what is considered toxic (i.e., $> 400 \mu\text{g Se day}^{-1}$) for humans (WHO, 1996). Selenium is an essential element for structural proteins “selenoproteins” and for cellular defense against oxidative damage (Chapman et al., 2009). The National Academy of Sciences’ (NAS) adequate and safe intake rate for adults is 50 to $200 \mu\text{g Se day}^{-1}$, while the estimated US daily intake is 60 to $216 \mu\text{g Se day}^{-1}$ (Barceloux, 1999). The EPA’s Maximum Contaminant Level (MCL) in drinking water for humans is $50 \mu\text{g Se L}^{-1}$ (EPA, 2011). Human’s primary exposure route in descending order is diet, water, and air (Barceloux, 1999).

The consumption of meats and plants are the main sources of Se in the human diet (Fordyce, 2007).

Human Se deficiency is far more widespread than human Se toxicity on a global scale (Fordyce, 2005). Selenium deficiency has been linked to Keshan (cardiac muscle degeneration) and Kashin-Beck (bone and joint disorder) disease (Coleman et al., 1993). In China, Se toxicity has been reported from the consumption of crops grown in high seleniferous soils (Yang et al., 1983). Symptoms include garlic breath, loss of hair and nails, dental problems, gastrointestinal problems, and nervous system problems.

In the US, Se received little attention until the 1930s, when disease problems in livestock were traced to Se. Livestock exposed to selenium-rich grain and forage led to Se toxicity, often referred to as alkali disease or blind staggers (Fordyce, 2007). In the 1980s, several aquatic ecosystems were severely affected by Se contamination, including agricultural drainage evaporation containments (Kesterson Reservoir) and discharges from coal fly ash containments (Belews Lake, Hyco Reservoir, and Martin Lake; Skorupa, 1998). At the Kesterson Reservoir in California, waterfowl populations were affected by a high incidence of embryonic death and deformity within the eggs, while chronic reproductive toxicity lead to the elimination of entire communities of fish at the coal fly ash containment discharges (Skorupa, 1998; Lemly, 1999). The national aquatic water quality criterion for aquatic species is $5 \mu\text{g Se L}^{-1}$ (EPA, 2011).

In aquatic ecosystems, Se toxicity is characterized by reproductive teratogenic deformities and embryo toxicity of both aquatic birds and fish (Lemly, 1999; Spallholz and Hoffman, 2002; Chapman et al., 2009). Embryo toxicity is more pronounced in aquatic birds and teratogenic deformities are more pronounced in fish larvae (Chapman et al., 2009). Selenium bio-accumulates within the egg after being transferred from the parent's diet. Since

the egg is the primary point of impact, fish populations can decline in a matter of a few years, while adult fish appear healthy (Lemly, 1999). Therefore, Lemly (2002) suggested that chronic Se toxicity could be “invisible” due to the limited acute mortality of adult fish. Aquatic birds are exposed to Se after the ingestion of insects and fish in which organic Se bioaccumulation has occurred (Spallholz and Hoffman, 2002).

Water concentrations greater than $5 \mu\text{g Se L}^{-1}$ may potentially cause adverse effects within the food chain due to the bio-accumulative effect of Se (EPA, 2011). In the aquatic environment, Se bioaccumulation is caused by the passive uptake of Se directly from water or sediments and from the direct uptake from food sources (Barceloux, 1999; Lemly, 1999). The bioconcentration factor from passive uptake is more extensive in the lower trophic levels of the food chain (Barceloux, 1999; EPRI, 2006b). At Belews Lake in North Carolina, Lemly (2002) observed the bioaccumulation within periphyton biota (algae and microbes) and in the visceral tissue of fish to be 519 to 3975 times the background water concentrations of $10 \mu\text{g Se L}^{-1}$. Fan et al. (2002) reported primary producers absorbing inorganic Se oxyanions and biotransforming these into organic forms of Se. Following this, the organic forms of Se were transferred through the remaining trophic levels: two through four (Fan et al., 2002). The trophic levels are trophic level 1: primary producers (filamentous algae, phytoplankton, periphyton), trophic level 2: primary consumers (filter feeders and collector-gatherers), trophic level 3: secondary consumers (forage fishes and predatory/omnivorous invertebrates), and trophic level 4: tertiary consumers (predatory fish; EPRI, 2006b).

The oxidized species present also affect selenium's toxicity within the aquatic environment. Selenite (Se^{4+}) and selenate (Se^{6+}) are usually the dominate species present in the environment (EPRI, 2006b). Selenite (Se^{4+}) is readily adsorbed by aquatic species and is slightly

more toxic than selenate (Se^{6+}) in water (Barceloux, 1999). Similarly, Skorupa (1998) reported that selenite-dominated waters appeared to have a steeper environmental response curve than selenate-dominated waters.

Ash Landfill Leachate

One of the major concerns with ash landfills is the potential for groundwater contamination due to the leaching of concentrated contaminants present in the ash. Groundwater could become contaminated if allowed to come in contact with ash landfill leachate (Tripodi and Cheremisinoff, 1980). Due to their high solubility, boron, calcium, and sulfate are key indicators of leachate migration from ash landfills (EPRI, 1987). Selenium can also be a key indicator if present in the mobile selenate (Se^{6+}) form.

Under experimental laboratory conditions, Wang et al. (2007) reported leachate concentrations of less than 0.1 mg Se L^{-1} from sub-bituminous ash over the entire pH range, which suggests that the high concentration of CaO present formed hydration and precipitation products [e.g. $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ or CaSeO_3] with Se. Leaching from bituminous ash resulted in concentrations less than 0.1 mg Se L^{-1} at pH 3 to 4 with increasing Se concentrations (1.7 to 2.5 mg Se L^{-1}) as pH neared 12 (Wang et al., 2007). However, alkaline pH values for bituminous coal ash leachate are highly unlikely in the environment. Leachate from bituminous ash results in a slightly acidic pH (6 to 6.4), while leachate derived from sub-bituminous ash results in alkaline pH values (11.3 to 11.7; EPRI, 2006a). Wang et al. (2007) also reported similar natural pH values of 4.4 to 6.0 for bituminous ash and 10.6 to 12.3 for sub-bituminous ash.

As a landfill leachate plume migrates away from a landfill, the soil solution pH it comes in contact with may change chemically. The magnitude of impact will depend on the existing soil pH, buffer capacity of the soil, residence time, pH of the leachate plume, and buffer capacity of the leachate plume (EPRI, 2006a). Soils that have high concentrations of clay, extractable Fe, and extractable Al are expected to have high buffering capacities, while sandy soils generally have low buffering capacities (EPRI, 2006a).

Selenium in Soils

Selenium can be present in soils as organic Se, metal selenides (Se^{2-}), elemental Se (Se^0), selenite (Se^{4+}), and selenate (Se^{6+}). Fordyce (2005) reported the average concentration in soils ranges between 0.1 to 2.0 mg Se kg^{-1} . However, in high seleniferous soils, the average concentration was 4.5 mg Se kg^{-1} , with a maximum value of 80 mg Se kg^{-1} (Elrashidi et al., 1987). Selenium's mobility in soils is determined by the adsorption-desorption and precipitation-solubilization processes of Se (Jayaweera and Biggar, 1996; Dhillon and Dhillon, 2000). Thermodynamic equilibrium predictions of soil redox do not always hold true in the natural environment due to factors such as soil heterogeneity, kinetic barriers to equilibrium, and biological processes (Jayaweera and Biggar, 1996; Hyun et al., 2006). Adsorption onto soil particles is controlled by the redox conditions, chemistry, geologic materials, and soil pH and usually occurs rapidly within minutes or hours (Sposito, 1989; EPRI, 1994a; Barceloux, 1999; Goldberg et al., 2008).

As soil pH increases, Se oxyanions will deprotonate (e.g. $\text{HSeO}_4^- \rightarrow \text{SeO}_4^{2-}$ or $\text{HSeO}_3^- \rightarrow \text{SeO}_3^{2-}$) and the soil surface charge will become increasingly negative resulting in increased repulsion forces and decreased adsorption (Ahlrichs and Hossner, 1989; Hyun et al., 2006;

Rovira et al., 2008). With this increasing pH, there is a direct increase in leaching of Se oxyanions from soil, a characteristic of anion adsorption-desorption (EPRI, 1994a; Otero-Rey et al., 2005; Goh and Lim, 2004). Selenium adsorption can also be affected by clay and iron oxides, divalent cations, and total Se present within the soil.

Clay and iron oxide minerals have positively charged adsorption sites causing them to adsorb negatively charged Se ions more readily (White and Dubrosky, 1994; Rovira et al., 2008). Soils with high concentrations of metal oxides had the greatest ability to adsorb Se (Tan et al., 1994). Goldberg et al. (2008) researched the effect of increasing Se concentrations on adsorption and reported that selenite (Se^{4+}) adsorption increased rapidly and then plateaued (L-curve), while selenate (Se^{6+}) adsorption was nearly linear (C-curve).

Anions such as phosphate and sulfate (PO_4^{3-} , SO_4^{2-}) can also negatively affect Se adsorption by competing with Se oxyanions for adsorption sites in soils (Dhillon and Dhillon, 2000; Goh and Lim, 2004). Sulfates have been shown to strongly limit selenate (Se^{6+}) adsorption due to the competitive traits between the two (Alemi et al., 1988; EPRI, 1994a; White and Dubrovsky, 1994; Goh and Lim, 2004). Goh and Lim (2004) reported a sharp decrease in selenate (Se^{6+}) adsorption when sulfate concentrations ranged from 0 to 0.01 M (0 to 961 mg $\text{SO}_4^{2-} \text{ L}^{-1}$), while Dhillon and Dhillon (2000) reported a minimal decrease in selenite (Se^{4+}) adsorption with increasing sulfate concentrations. Both selenite (Se^{4+}) and selenate (Se^{6+}) adsorption rates decreased as phosphate concentrations increased (Goh and Lim, 2004). Dhillon and Dhillon (2000) observed soils adsorbing two to three times more phosphate than Se when competing for the same adsorption sites. Shifting from aerobic to anaerobic conditions will also affect Se speciation within soils.

Under reducing conditions, Se may exist as insoluble metal selenides (Se^{2-}) and elemental Se (Se^0 ; Elrashida et al., 1987; Flury et al., 1997). Under normal oxidizing soil conditions, soluble Se may exist in the 4^+ oxidation state as selenite (Se^{4+}) or in the 6^+ oxidation state as selenate (Se^{6+} ; Ahlrichs and Hossner, 1989). Fluctuating groundwater in the vadose zone may cause a cycling in redox conditions resulting in a cycling between both Se oxyanion species selenate (Se^{6+}) and selenite (Se^{4+} ; Jayaweera and Biggar, 1996). With fluctuating groundwater, soil pores can become filled with water instead of air with a resulting decrease in O_2 , which can lead to anaerobic conditions, while a drop in the groundwater table can lead to drying of the soil pores (increase in O_2) and a return to aerobic conditions (Sposito, 1989; Jayaweera and Biggar, 1996). Under these conditions, a rise in the groundwater table may result in the reduction of Se species and a decrease in leaching potential. On the other hand, a decreasing groundwater table may result in the oxidation of Se species and an increase in leaching potential. However, Flury et al. (1997) reported an increase in leaching with increasing rainfall during the winter months in alluvial soils. Therefore, soil parent material, water holding capacity, and water infiltration rates may have a large impact on leaching. Selenite (Se^{4+}) is typically present in acidic to neutral soils and selenate (Se^{6+}) is typically present in alkaline soils (Neal and Sposito, 1989; Goh and Lim, 2004). Changes in oxidation states affect selenium's mobility, solubility, and adsorption rates in soils (Elrashida et al., 1987; Goh and Lim, 2004; Otero-Rey et al., 2005).

Selenite (Se^{4+}) functions like the phosphate anion (inner-sphere surface complex) and has a greater adsorption than selenate (Se^{6+} ; Goldberg et al., 2008; Zhang et al., 2010). The pKa values for selenite (Se^{4+}) are 2.64 and 8.36 (Wang et al., 2007), indicating that biselenite (HSeO_3^-) is the dominate species present in neutral soils and selenite (SeO_3^{2-}) is dominate in alkaline soils. Selenite (Se^{4+}) adsorption is greatest at low pHs and decreases with increasing pHs above

6 (Frost and Griffin, 1977; EPRI, 1994a; Hyun et al., 2006). Similarly, Goh and Lim (2004) documented selenite (Se^{4+}) adsorption decreased from 83 % at pH 3 to 59 % at pH 7 using a 200 μM selenite (Se^{4+}) solution added to a tropical soil. In alluvial soils from the San Joaquin valley, Fio et al. (1991) reported greater than 50 % adsorption of selenite (Se^{4+}) after only 8 hours. In acidic and neutral soils, selenite (Se^{4+}) adsorption is also controlled by its ability to bind to ferric hydroxides and aluminum oxides (Ylaranta, 1982; Ahlrichs and Hossner, 1987; Barceloux, 1999; Goldberg et al., 2008). This adsorption characteristic is what allows selenite (Se^{4+}) removal from wastewater to be feasible with iron (III) hydroxide and alum co-precipitation (EPRI, 2006c). Once adsorbed onto the soil, selenite (Se^{4+}) is resistant to leaching (Fio et al., 1991; Dhillon and Dhillon, 2000). Ahlrichs and Hossner (1987) observed selenite (Se^{4+}) having little mobility even after 50 pore volumes of solution. Therefore, selenite (Se^{4+}) could remain in the soil matrix for extended periods, which could lead to a problematic long-term source of Se. Selenite (Se^{4+}) tends to be oxidized to selenate (Se^{6+}) in low-moisture soils, as soil temperature increases, and in alkaline soils (Ahlrichs and Hossner, 1987).

Selenate (Se^{6+}) is known to behave like the sulfate anion (outer-sphere surface complex) with low adsorption rates, high solubility, and pronounced leachability causing selenate (Se^{6+}) to be highly mobile in soils (Elrashida et al., 1987; Neal and Sposito, 1989; Peak and Sparks, 2002). Due to selenate's (Se^{6+}) $\text{pK}_{\text{a}2}$ value of 1.91, only the completely de-protonated species (SeO_4^{2-}) exists in most soils. Selenate (Se^{6+}) adsorption is greatest at a soil pH less than 4 and quickly decreases from a pH 4 to 7 with nearly no adsorption occurring at $\text{pH} > 9$ (EPRI, 1994a; Hyun et al., 2006). Goh and Lim (2004) reported that selenate (Se^{6+}) adsorption decreased from 46 % at pH 3 to 15 % at pH 7 using a 200 μM selenate (Se^{6+}) solution added to a tropical soil. Hyun et al. (2006) noted that selenate (Se^{6+}) adsorption was greatest in clay soils and lowest in

sandy soils. However, selenate (Se^{6+}) adsorption to clay is still weak, and under alkaline conditions, selenate (Se^{6+}) could leach through relatively pure clay (Frost and Griffin, 1977; White and Dubrovsky, 1994). In sandy-loam soil, selenate (Se^{6+}) was mobile at pHs from 2 to 9 and leached with less than three pore volumes of solution (Ahlrichs and Hossner, 1987). Selenate (Se^{6+}) is also readily leached into groundwater from alluvial soils in the vadose zone, due to selenate's (Se^{6+}) low affinity for soil particles (Neal and Sposito, 1989). Under high redox conditions and with minimal microbial activity, selenate (Se^{6+}) reduction to selenite (Se^{4+}) will be limited (Elrashida et al., 1987; Alemi et al., 1988; Neal and Sposito, 1989).

Selenium Reduction in the Environment

Water-soluble Se oxyanions can be reduced to elemental Se by naturally occurring bacteria (Oremland et al., 1989; Oremland et al., 1994; Catal et al., 2009). In the environment, bio-reduction of Se is carried out naturally in soil and water (Steinberg and Oremland, 1990; Stolz and Oremland, 1999). The most effective selenium-reducing bacteria have been isolated from environments with high concentrations of Se (Maiers et al., 1988; Ike et al., 2000). Bacterial respiration reduces the soluble Se oxyanions to elemental Se through the process of anaerobic microbial respiration (Oremland et al., 2004; Lee et al., 2007; Narasingarao and Haggblom, 2007). Many different species of bacteria and archaea have been shown to be capable of reducing Se, including *Aeromonas*, *Bacillus*, *Clostridium*, *Desulfotomaculum*, *Desulfovibrio*, *Escherichia*, *Penicillium*, *Pseudomonas*, *Ralstonia*, *Salmonella*, *Shewanella*, *Sulfurospirillum*, and *Thauera* (Maiers et al., 1988; Adams et al., 1993; Oremland et al., 2004; Lee et al., 2007; Siddique et al., 2007).

During microbial respiration, the use of SeO_4^{2-} (selenate) as the electron acceptor is known as dissimilatory selenate (Se^{6+}) reduction (DSeR) written as $\text{SeO}_4^{2-} + \text{Org. C} \rightarrow \text{SeO}_3^{2-} + \text{Org. C} \rightarrow \text{Se}^0 + \text{CO}_2 + \text{H}_2\text{O}$ (Stolz and Oremland, 1999). This bio-reduction process is reversible under oxidizing conditions (Sarathchandra et al., 1981; Zhang et al., 2004). For elemental Se to re-oxidize to selenite (Se^{4+}) or selenate (Se^{6+}), a shift to aerobic and alkaline water conditions must occur (Adams et al., 1993). Electric Power Research Institute (2006c) reported that selenite (Se^{4+}) had a slow conversion rate to selenate (Se^{6+}) in natural surface waters resulting in selenite (Se^{4+}) as the dominate species normally present. Under highly anoxic conditions, the toxic gas selenide (HSe^-) can form when elemental Se is used as the terminal electron acceptor (Lovley, 1993; Siddique et al., 2006). This reaction is written as $\text{Se}^0 + \text{H}_2 \rightarrow \text{HSe}^- + \text{H}^+$. Selenide can also form as a solid which is identifiable by a black, crystalline precipitate (Herbel et al., 2003). However, selenide is unstable and is quickly oxidized back to elemental Se in the presence of oxygen (Alemi et al., 1988; Maiers et al., 1988).

Selenium speciation in natural waters is highly affected by redox and pH as seen in the Eh-pH diagram for Se (Figure 1-2; Allen et al., 1993; Iskandar et al., 2001). However, thermodynamic equilibrium models are sometimes not accurate due to many unforeseen factors affecting natural waters (EPRI, 2006b). A change in the oxidation state of Se is known to alter the solubility, toxicity, and mobility of Se (Doran and Alexander, 1977; Catal et al., 2009; Hayashi et al., 2009). Furthermore, the solubility of Se increases as the oxidation-reduction potential (ORP) and pH of the water increases (Masscheleyn et al., 1991). A study performed by Masscheleyn et al. (1991) observed that, under redox conditions from 0 to 500 mV, the solubility of Se was as much as 5 times greater at pH 7.5 compared to pH of 5. Selenate (Se^{6+}) was shown to have the greatest solubility at 500 mV under equilibrium conditions of pH 5 (Masscheleyn et

al., 1991). As redox levels decreased to 200 mV, selenite (Se^{4+}) became the pre-dominate species of Se in water and the solubility drastically decreased under equilibrium conditions (Masscheleyn et al., 1990, 1991). Further reduction of selenite (Se^{4+}) led to the formation of elemental Se under anaerobic conditions (Masscheleyn et al., 1990, 1991; Stolz and Oremland, 1999). At -200 mV, the soluble Se species selenate (Se^{6+}) and selenite (Se^{4+}) were not detected (Masscheleyn et al., 1990, 1991).

Selenium Reduction in Waste Streams

Various other oxyanions and metals present in fly ash landfill leachate may affect Se reduction. In particular, sulfates and nitrates tend to occur in greater concentrations in effluent of industrial waste streams (Kashiwa et al., 2000). Selenium and sulfur share similar chemical and biochemical properties due to their location on the periodic chart (column VIA; Doran and Alexander, 1977; Oremland et al., 1989; Higashi et al., 2005). However, Se oxyanions and sulfur oxyanions are reduced under different biogeochemical pathways (Oremland et al., 1989; Lenz et al., 2008). For example, Se reduction occurs in sediment at much shallower depths than sulfur reduction (Steinberg and Oremland, 1990; Lovley, 1993). Therefore, Se reduction is not affected by sulfate concentrations in wastewater due to the greater affinity for Se oxyanions compared to sulfate (Oremland et al., 1989; Garbisu et al., 1996).

Under reducing conditions, nitrate is used prior to selenate (Se^{6+}) as the preferred electron acceptor (Steinberg et al., 1992; Kashiwa et al., 2000). Therefore, nitrate is known as an inhibitor of Se reduction (Steinberg and Oremland, 1990; Lovley, 1993). With nitrate being the preferred electron acceptor, the reduction of selenate (Se^{6+}) will not take place until the nitrates have been reduced in the solution. The half-cell reaction for nitrate reduction to ammonium is

$\text{NO}_3^- + 10\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$ (White and Dubrovsky, 1994). When high nitrate concentrations exist in wastewater, excess carbon sources must be available to prevent a decrease in Se reduction (Adams et al., 1993; Kashiwa et al., 2000). The presence of nitrates and dissolved oxygen (DO) is a useful indicator of oxidizing conditions (White and Dubrovsky, 1994). Metals such as tungstate, molybdate, and chromate may also inhibit Se reduction (Oremland et al., 1989; Steinberg and Oremland, 1990).

ABMet™ Treatment Technology

Selenium bio-reduction can be commercially recreated using a continuous-flow-through bioreactor inoculated with naturally occurring bacteria. In these bioreactors, selenium-respiring bacteria utilize selenium oxyanions as electron acceptors and some type of carbon source, such as molasses, as the electron donor (Cantafio et al., 1996; Fujita et al., 2002). Utilizing a carbon source that is compatible with the selected strain of bacteria is critical for the bacteria's growth, sustainability, effectiveness, and redox conditions (Garbisu et al., 1996; Kashiwa et al., 2000; Astratinei et al., 2006; Zhang et al., 2008). Electron acceptors also support the growth of the selenium-respiring bacteria (Lovley, 1993).

The GE ABMet™ (Advanced Biological Metals Removal Process) system reduces dissolved selenium oxyanions selenate (Se^{6+}) and selenite (Se^{4+}) to their elemental form through a bio-reduction process (Figure 1-3). The ABMet™ system is the only commercially available, cost-effective, treatment technology that has effectively removed selenate (Se^{6+}) from industrial wastewater (EPRI, 2006c). The ABMet™ bioreactors are a fixed film, plug-flow type, proven effective at removing selenium through laboratory treatability studies, pilot trials, and several large-scale operational systems with flows up to 7.6 million liters per day (2 million gal d⁻¹; GE,

2011). These large scale operations include wastewater from mine-tailings, flue-gas desulfurization units (FGD), petroleum refineries, and agricultural drainage (GE, 2010). The first full-scale ABMet™ system went operational in 2008 (Sonstegard et al., 2010).

Selenium oxyanion removal from wastewater has proven troublesome due to its low part per billion (ppb) concentration, even lower ppb treatment target, and its bio-chemical similarity to sulfur oxyanions (Higashi et al., 2005). However, research has demonstrated that reducing bacteria are unaffected by sulfur oxyanions in wastewater (Oremland et al., 1989; Lenz et al., 2008; Smith et al., 2009). Pilot testing and full scale operation have shown a total selenium removal efficiency of greater than 98 % from various waste streams (Sonstegard and Pickett, 2005; Sonstegard et al., 2010). Similarly, a study by EPRI (2010) reported a 95.7 % removal from 214 µg Se L⁻¹ to 9.2 µg Se L⁻¹. Other advantages of the ABMet™ system include minimal sludge generation, minimal chemical addition, minimal power requirement, a compact plant footprint, speed of removal, and scalability to meet site demands (Pickett et al., 2006; Blankinship, 2009; Golder and Associates, 2009; GE, 2011).

The ABMet™ system utilizes a strain of *pseudomonas sp.*, which is a naturally occurring, non-pathogenic, gram negative, Class 1, facultative bacteria, to reduce oxidized selenium (Se⁴⁺, Se⁶⁺) to its elemental form (Se⁰; Garbisu et al., 1996; Sonstegard, GE Microbiologist, personal communication, 2011). Macy et al. (1989) were the first to describe the selenium-respiring bacteria *pseudomonas sp.* for reduction purposes. High concentrations of selenium oxyanions have not affected the growth of the *pseudomonas* species during the reduction to elemental selenium (Hunter and Manter, 2009; Hunter and Manter, 2011). Elemental selenium is highly insoluble, has low toxicity levels, is less bio-available to aquatic biota, immobile, and is stable over a wide pH range under reducing conditions (Masscheleyn et

al., 1991; Allen et al., 1993; Iskandar et al., 2001; Lenz et al., 2008; Dey and Kulkarni, 2010).

Factors such as influent water quality, temperature, pH, total suspended solids (TSS), and influent flow rates are used to determine the specific strains of *pseudomonas sp.* used in site-specific beds (Sonstegard and Pickett, 2005; Harwood, GE Water, personal communication, 2010). Following bench-scale tests, the selected bacteria strains are used to inoculate on-site pilot test bioreactors (Sonstegard and Pickett, 2005). Results from these pilot tests are then used to finalize full-scale design and operation (Sonstegard and Pickett, 2005).

Following selection, these microbes are inoculated in a packed bed bioreactor filled with granular activated carbon (GAC; Dey and Kulkarni, 2010). Inoculation “seeding” consists of spreading the bacteria over the top of the bioreactor bed and allowing them to grow and colonize within. Due to carbon’s large, irregular surface area, the carbon provides an ideal growth medium and protects the microbes from sheer and abrasive force, which prevents the bacteria from being washed out of the bioreactor (Pickett et al., 2006). This protective environment allows the bacteria to colonize and form a fixed biological film on the GAC called a “biomatrix” (Pickett et al., 2006; Sonstegard et al., 2010). The biomatrix provides a more stable selenium effluent concentration when upset conditions are encountered (Pickett et al., 2006; Sonstegard et al., 2010). Upset conditions may include fluctuations in temperature, pH, influent flow, and/or influent selenium concentrations.

Depending on the influent pH of the wastestream, sulfuric acid or caustic soda may need to be mixed with the influent to obtain a pH between 7.5 to 8.0. A neutral influent pH ensures proper functioning of the microbes and prevents scaling within the bioreactors. A molasses-based nutrient source is mixed with the influent after pH neutralization and prior to entering the bioreactor. The molasses acts as the carbon and energy source for the microbes (Harwood, GE

Water, personal communication, 2010). The molasses also acts as an electron donor and is oxidized during the reduction of oxyanions, and has proven to be an inexpensive and effective energy source for several species of selenium-reducing bacteria (Zhang and Frankenberger, 2006; Zhang et al., 2008). Molasses from sugar cane consists of sucrose (~ 36 %), dextrose (~ 12 %), fructose (~ 6 %), and glucose (~ 3 %) in solution (USSC, 2011). The molasses dosage concentration is dependent upon the influent wastewater quality (Sonstegard et al., 2008). As selenium and nitrate influent concentrations increase, or as influent temperatures decrease, the influent molasses concentration will also need to increase (Pickett et al., 2006; Sonstegard et al., 2008). Since nitrates are reduced prior to selenium reduction, the amount of molasses is dependent on the nitrate concentration in the wastewater stream (EPRI, 2006c). A study conducted by Zhang et al. (2008) reported most effective bio-reduction with 0.1 to 0.2 % molasses influent concentrations. Other carbon sources used for bio-reduction include acetate, ethanol, glucose, lactate, methanol, rice straw, and fermented whey (Doran and Alexander, 1977; Cantafio et al., 1996; Bledsoe et al., 1999; Fujita et al., 2002; Zhang and Frankenberger, 2003).

Once reduced in anaerobic conditions, the insoluble elemental selenium will precipitate onto the biomass (Figure 1-4) within the bioreactor (Sonstegard and Pickett, 2005). This precipitation of elemental selenium is a key feature of the ABMet™ system. Without removal, elemental selenium could re-oxidize once it re-enters an aquatic environment (Zhang et al., 2004). Precipitated elemental selenium (Se^0) can be identified on the GAC by its amorphous nanospheres, which are reddish in color and 200 to 400 nanometers in diameter (Fujita et al., 2002; Oremland et al., 2004; Lenz et al., 2008). The precipitated Se^0 remains in the bed, collecting in the biomatrix, until the bed is backwashed (Sonstegard et al., 2008). Some current

full-scale backwash ponds have been designed to hold 20 years of backwash solids (Sonstegard et al., 2008).

The ABMet™ bioreactors are not pressure filters. The waste stream flows naturally, from top to bottom via distribution headers, to ensure correct contact retention time between the wastewater and the biomatrix (Harwood, GE Water, personal communication, 2010). Retention time varies from 2 to 12 hours depending on certain parameters such as water chemistry, TSS, temperature, and effluent standards (Pickett et al., 2006; Sonstegard and Pickett, 2006; Dey and Kulkarni, 2010). Constraints imposed on the influent wastewater include nitrate-N ($< 250 \text{ mg L}^{-1}$), chloride ($< 25,000 \text{ mg L}^{-1}$), TSS ($< 250 \text{ mg L}^{-1}$), temperature (1 to 40 °C), pH (6 to 9), and total dissolved solids ($< 150,000 \text{ mg L}^{-1}$; GE, 2011). The ABMet™ system has also been shown to reduce the levels of arsenic, copper, hexavalent chromium, nickel, nitrate, zinc, and mercury from the waste stream during the bio-reduction process (Sonstegard and Pickett, 2005; Harwood, GE Water, personal communication, 2010). However, a case study performed by EPRI (2006c) reported that ammonia and organic nitrogen were not effectively removed from the waste stream by the ABMet™ bioreactors.

The ABMet™ system utilizes facultative bacteria that are capable of both aerobic and anaerobic respiration (Sonstegard et al., 2010). Wastewater entering the bioreactor will have a positive ORP ranging from +200 to +300mV (Sonstegard et al., 2008). As the wastewater travels downward, oxygen is respired and the ORP decreases to near 0 mV (Sonstegard et al., 2010). The loss of oxygen forces the bacteria to begin respiring oxyanion electron acceptors such as NO_3^- , SeO_4^{2-} , SeO_3^{2-} , and SO_4^{2-} (Sonstegard et al., 2008). The reduction of electron acceptors is essential for the growth of the bacteria and creates a multi-layered, gradually

reducing environment within the bioreactor bed (Figure 1-5; Lenz et al., 2008; Sonstegard et al., 2010).

Since dissolved oxygen is the most preferred electron acceptor, this element is the first one to be reduced (White and Dubrovsky, 1994). The half-cell reaction for DO is written as $\frac{1}{2} \text{O}_2 (\text{aq}) + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ (White and Dubrovsky, 1994). Next, nitrates are reduced and released as nitrogen gas through the process of denitrification (Sonstegard et al., 2008; Smith et al., 2009). This de-nitrification occurs in the ORP range of +50 to -50 mV and is written as $\text{NO}_3^- + \text{Org. C} \rightarrow \text{NO}_2^- + \text{Org. C} \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}$ (Sonstegard et al., 2008). As the wastewater continues downward through the bed, the ORP steadily declines and becomes more negative as selenate (Se^{6+}) and selenite (Se^{4+}) are reduced to elemental selenium (Sonstegard et al., 2008; Smith et al., 2009; Sonstegard et al., 2010). This reaction is written as $\text{SeO}_4^{2-} + \text{Org. C} \rightarrow \text{SeO}_3^{2-} + \text{Org. C} \rightarrow \text{Se}^0 + \text{CO}_2 + \text{H}_2\text{O}$ (Sonstegard et al., 2008). If ORP levels are allowed to continually decline, sulfates will be reduced to hydrogen sulfide and methane gas will develop within the bed (Sonstegard et al., 2008; Smith et al., 2009). The formation of hydrogen sulfide may inhibit selenium reduction within the bed (EPRI, 2006c). If the ORP inside the bed is allowed to decrease beyond desired levels, reduction of sulfate to toxic hydrogen sulfide gas will occur (White et al., 1991; Harwood, GE Water, personal communication, 2010). The half reaction for hydrogen sulfide at pH 7 and -200 mV is $\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{HS}^- + 4\text{H}_2\text{O}$ (Masscheleyn et al., 1990; White et al., 1991). The gradually reducing condition in the bioreactor provides a healthy, life-sustaining environment for the bacteria to grow and colonize.

JUSTIFICATION

This study will evaluate the effects of water-extractant type (i.e., rainwater, groundwater, and deionized water) on fly ash Se concentrations collected from the Flint Creek Power Plant located in Benton County, Arkansas. Compared to previous studies, which utilized only deionized (DI) water as the extractant type, this study will analyze and characterize the differences between DI water, groundwater, and rainwater to better understand the leaching behavior of Se from a Class C, sub-bituminous fly ash (Narukawa et al., 2005; Otero-Rey et al., 2005; Wang et al., 2007; EPRI, 2008; Seshadri et al., 2011). While DI water offers a convenient base-line approach, using groundwater and locally collected rainwater should provide data that are more environmentally representative of in-situ conditions present near the ash landfill.

Site-specific information is essential at the Flint Creek site to better understand the complex relationship of selenium-laden leachate and the leachates' interaction with the vadose zone and underlying groundwater. Results from this study should provide Flint Creek and ADEQ personnel with a better understanding of the nature and mobility of the Se plume that currently extends approximately 200 meters (656 feet) to the west of the Flint Creek ash landfill. In addition, comparison of the three different extractant types may provide the scientific community with enough data to help make an informed decision on a preferred extractant type. Even if this study finds that Se concentrations are similar for each water-extractant type, this information will be useful for future studies because collection of ground- and rainwater can be cumbersome and time consuming compared to the collection of DI water.

Previous Se speciation analysis of the ash landfill seep has indicated that the Se is predominately in the selenate (Se^{6+}) form (i.e., > 95 %). However, these samples were collected from in-situ-derived leachate, which has presumably undergone extensive oxidation and a possible change in speciation from selenite (Se^{4+}) to selenate (Se^{6+}). EPRI (2006a) reported

similar results indicating in-situ leaching of sub-bituminous coal fly ash (i.e., weathered fly ash) usually resulted in selenate (Se^{6+}) as the dominate species present. On the other hand, sub-bituminous coal fly ash samples collected directly from ash handling systems (i.e., fresh fly ash) have resulted in selenite (Se^{4+}) as the dominate species present (Narukawa et al., 2005; Huggins et al., 2007; Wang et al., 2007). Speciation is important because selenate (Se^{6+}) is less toxic, but more mobile in an aqueous environment than selenite (Se^{4+}).

The focus of this research was on the leaching characteristics of Se from coal fly ash; however, many similarities exist between fly ash Se, As, and Cr concentrations, speciation, and mobility within the environment. The volatility and re-condensation characteristics are also similar, with Se being the most volatile followed by As and then Cr (Xu, 2003). In the environment, Se and As behave similarly due to their oxy-anionic species that can exist. Selenium can exist as selenate (Se^{6+}) and selenite (Se^{4+}), while As can exist as arsenate (As^{5+}) and arsenite (As^{3+}). Chromium differs slightly because Cr can exist as cationic and anionic species, forming both trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) Cr (EPRI, 2011). In the aquatic environment, Se and As toxicity are similar with the more oxidized species selenate (Se^{6+}) and arsenate (As^{5+}) being less toxic than selenite (Se^{4+}) and arsenite (As^{3+}); in contrast, the more oxidized hexavalent (Cr^{6+}) Cr is more toxic than trivalent (Cr^{3+}) Cr (EPRI, 2005). Furthermore, the more oxidized species of Se, As, and Cr are dominate under alkaline and mildly to strongly oxidizing conditions, while the less oxidized species tend to be dominate under acidic conditions. Previous research on subbituminous Powder River Basin (PRB) fly ash landfill leachates determined that the most oxidized species (i.e., Se^{6+} , As^{5+} , and Cr^{6+}) were the dominate species present and exhibited greater mobility, except for arsenate (As^{5+} ; EPRI, 2006a). Once released into the environment, reactions with Fe and Ca are similar for Se and As, while Se, As, and Cr

can all be incorporated into ettringite $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} - 26\text{H}_2\text{O}]$ by substitution with the sulfate ion (Hassett and Pflughoeft-Hassett, 2002). Therefore, due to these similarities, it is relevant to simultaneously study As and Cr along with Se.

OBJECTIVES

The primary objective of this study is to evaluate Se leaching characteristics from a Class C, sub-bituminous fly ash using three different water-extractants (i.e., rainwater, groundwater, and DI water).

The second objective of this study is to compare the leaching characteristics of fly ash collected directly from the hot-side precipitators (i.e., fresh fly ash) to samples collected from within the Flint Creek ash landfill (i.e., weathered fly ash), which have already undergone an unknown amount of leaching. The goal of this comparison is to determine if differences exist between fresh and weathered samples. Evaluating this data may help quantify the amount of Se that has already leached from the weathered fly ash compared to fresh samples.

The third objective is to compare extraction times of 2 and 6 hours.

TESTABLE HYPOTHESES

The first hypothesis is the water-extractable Se concentration should be greatest with DI water as the extractant type compared to rain- and groundwater. Water-extractable Se concentrations between rain- and groundwater should not differ significantly. Hypothesis 2 is that fly ash collected directly from the precipitator will have a lower water-extractable Se concentration when compared to fly ash that has been weathered at the ash landfill. Hypothesis 3 is that no significant differences will exist between extraction times of 2 and 6 hours.

Hypothesis 1 is expected to hold true because pH and buffering capacity of the extractant type should be a controlling factor for Se extraction. The Flint Creek fly ash is alkaline in nature (pH = 11.5); and extractable Se concentrations have been observed to be the greatest at a pH of near 12. Due to DI water's low buffering capacity, the DI water should result in a more alkaline pH extraction solution compared to rain- and groundwater. Furthermore, DI water will have the lowest solute concentration compared to that of rain- and groundwater. Solutes, such as Ca, have been shown to inhibit Se leaching from sub-bituminous coal fly ash (EPRI, 2005; Wang et al., 2007; EPRI, 2008; Wang et al., 2009). Pre- and post-fly-ash Se concentrations will be used to determine the percent Se extracted from the fly ash, which will be the readily soluble fraction.

With Hypothesis 2, three factors must be taken into consideration when determining Se water-extraction: initial Se concentration, initial Ca concentration, and Se speciation. Fresh samples collected directly from the precipitator are expected to have greater initial Se concentrations present, when compared to that of fly ash stored in the landfill. Fly ash that has been stored in the landfill is expected to have already undergone a certain amount of Se water-extraction. Therefore, greater initial Se concentrations should be positively correlated with increased extraction (Iwashita et al., 2005). However, fresh samples should have a greater concentration of Ca present compared to the weathered samples, which have undergone weathering, cementation, and some leaching of Ca (Wang et al., 2009). Therefore, a decreased Ca concentration in the weathered samples should result in greater Se leaching. Another factor to consider is the speciation of the Se present in the fresh and weathered fly ash. Greater leaching from the weathered samples may occur if selenate (Se^{6+}) is the dominate species present in the weathered samples and selenite (Se^{4+}) in the fresh samples.

Hypothesis 3 is expected to be true because research by Mattigod and Quinn (2003) reported no significant change in Se extractability from 1.5 to 24 hours. Therefore, no significant differences should be noted from 2 to 6 hours extraction time.

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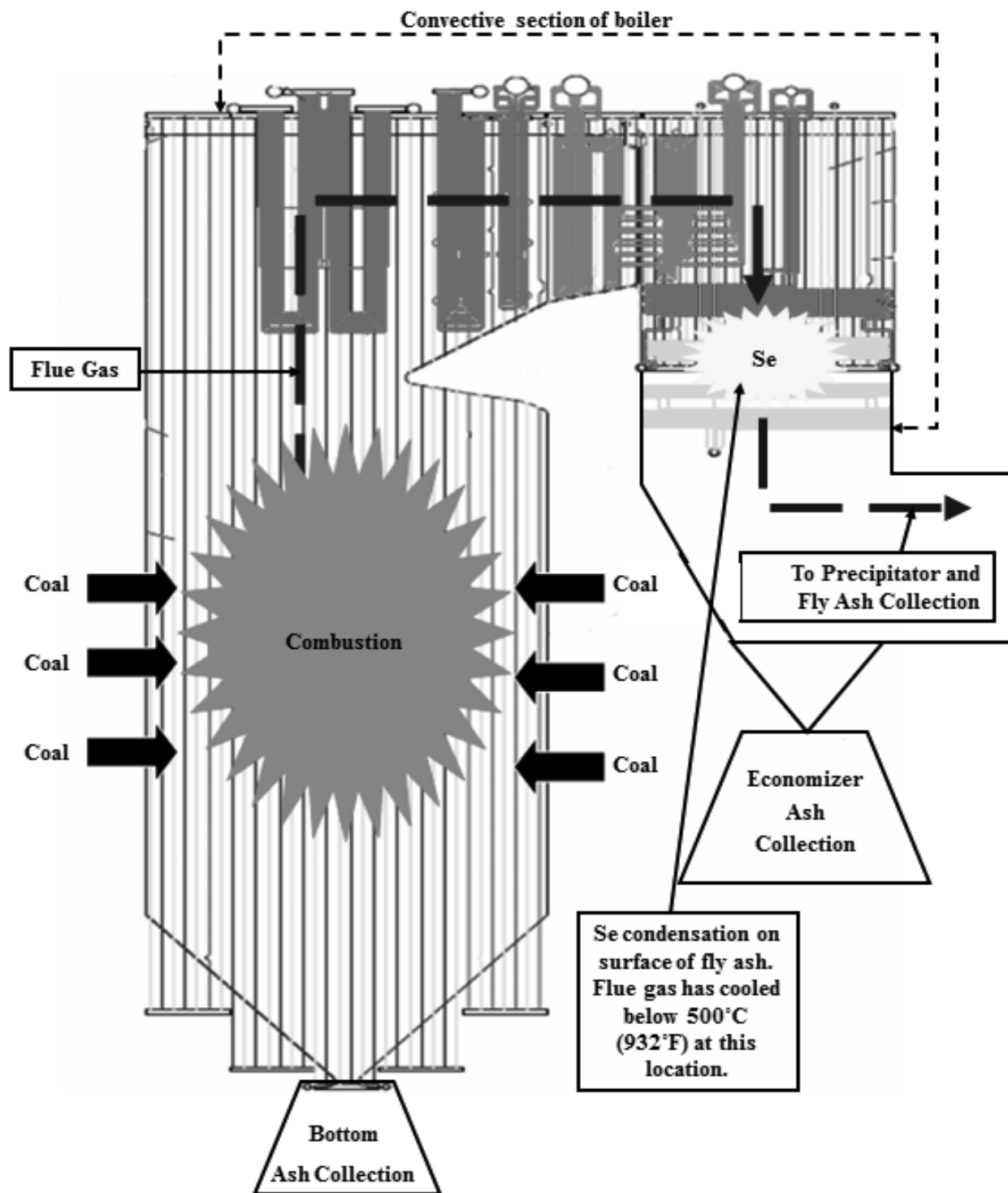


Figure 1-1. Basic diagram of the boiler at the Flint Creek Power Plant. Selenium that is naturally enriched in the coal volatilizes upon combustion and is carried with the flue gas stream through the convective section of the boiler. The flue gas enters the convective section around 1371 °C (2500 °F) and cools to a temperature of 399 °C (750 °F) before exiting the convective section. Selenium will condense on the surface of the fly ash at temperatures below 500 °C (932 °F; Sargent and Lundy Engineers, 1974).

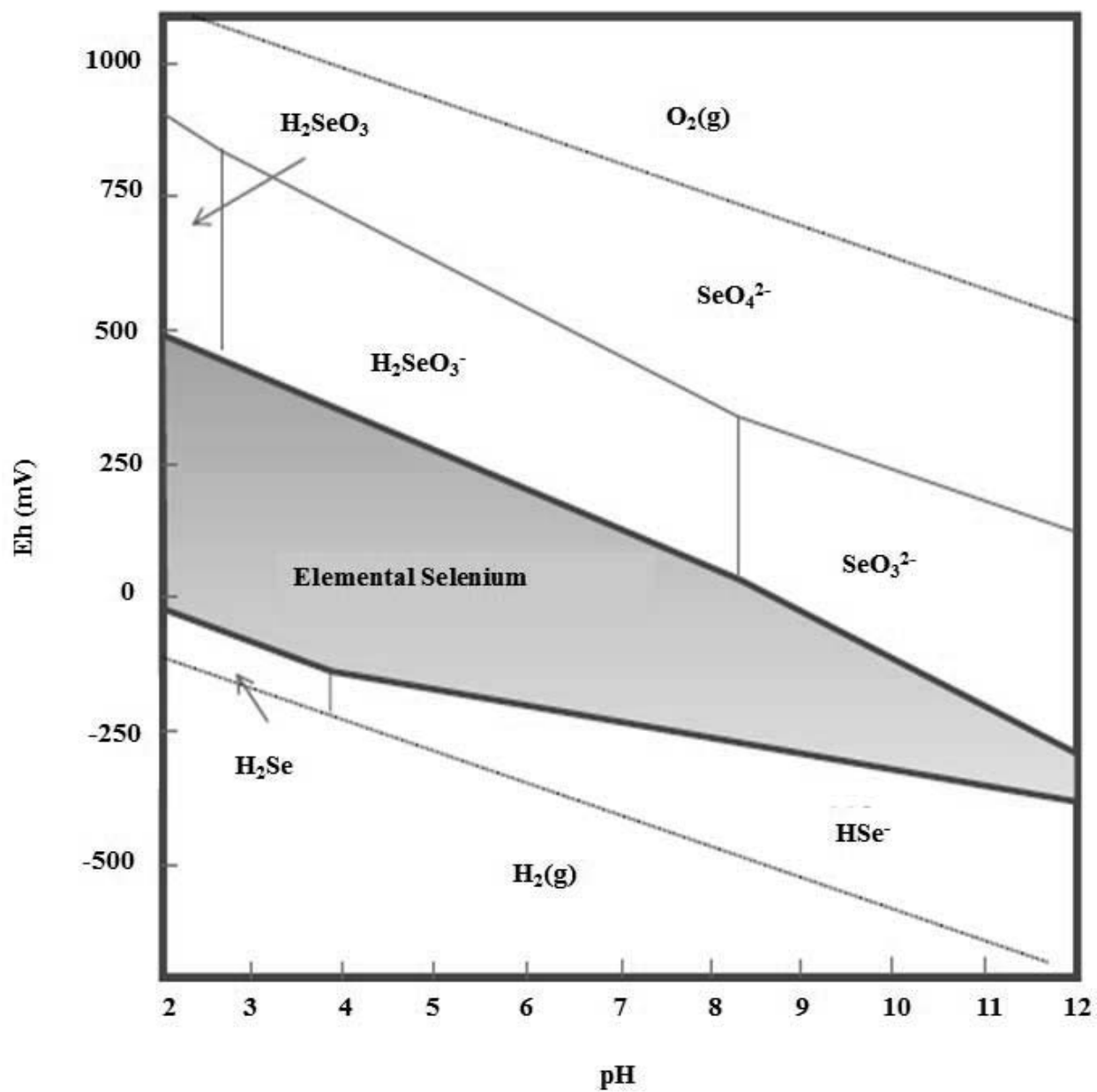


Figure 1-2. Oxidation-reduction potential (Eh)-pH diagram for selenium (EPRI, 2013).

Flow Through Bioreactor	Final Electron Acceptor	Approximate ORP
	Oxygen	> 0 mV
	Nitrate	< 0 mV
	Nitrite	< -50 mV
	Selenate	< -100 mV
	Selenite	< -150 mV
	Sulfate	< -200mV

Figure 1-3. Gradually reducing conditions created within the bioreactors as landfill leachate gravity flows downward through the bioreactor and different electron acceptors are used for bacterial respiration.

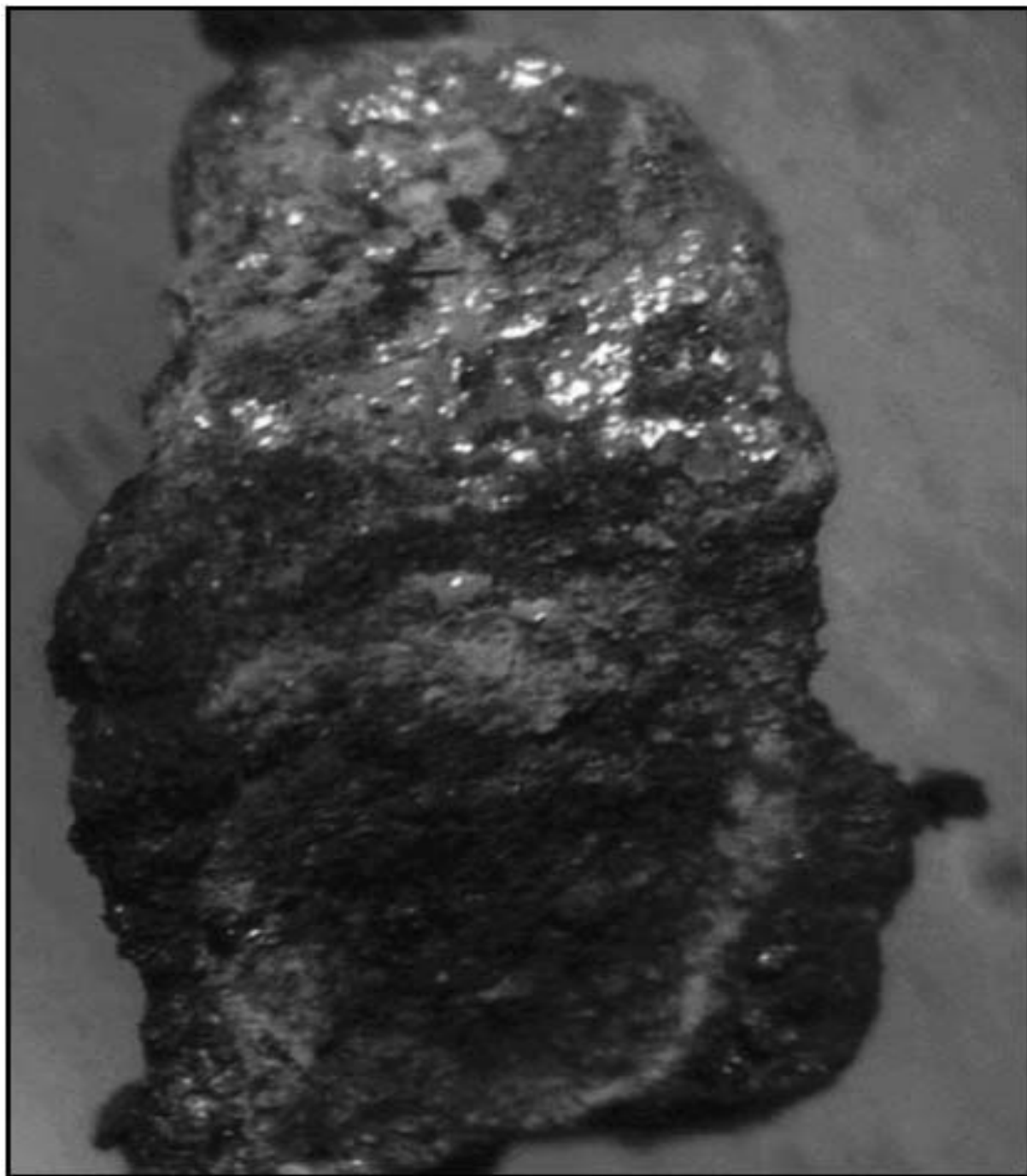


Figure 1-4. Precipitated elemental selenium (Se^0) on the granular activated carbon. The Se^0 is indicated by the reddish orange precipitant on the black carbon. This is a key feature of the ABMet™ system because it allows for easy removal and collection of the Se^0 by backwashing the bioreactors.

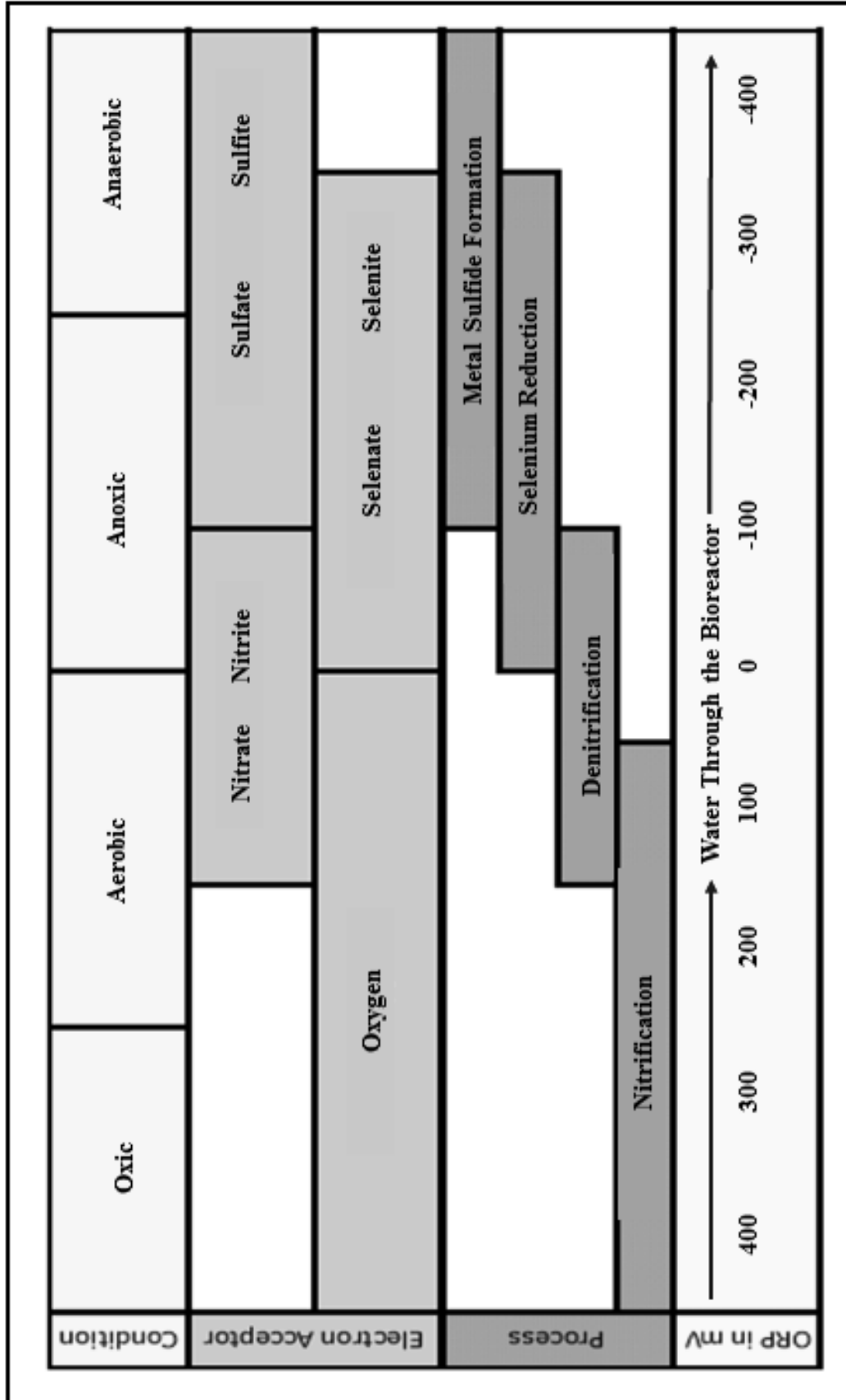


Figure 1-5. Fixed biofilm oxidation-reduction potential (ORP) gradient created as wastewater passes through a GE ABMet™ bioreactor; modified from (GE, 2010).

CHAPTER 2

LEACHING CHARACTERISTICS OF SELENIUM AS AFFECTED BY COAL FLY ASH TYPE, WATER EXTRACTANT, AND EXTRACTION TIME

ABSTRACT

Selenium (Se) contamination can be a potential groundwater concern near un-lined coal ash landfills. Out of all the Environmental Protection Agency (EPA) priority and non-priority pollutants, Se has the narrowest range between what is considered beneficial and detrimental for aquatic and terrestrial organisms. The effects of ash type (i.e., fresh and weathered), water-extractant type (i.e., deionized water, rainwater, and groundwater), and extraction time (i.e., 2- and 6-hours) on Se, arsenic (As), and chromium (Cr) concentrations were investigated from Class C, subbituminous coal fly ash produced at the Flint Creek Power Plant located in Benton County, AR. Water-extractable Se concentrations differed ($P = 0.03$) between ash types across water-extractants, but were unaffected by extraction times. Unexpectedly, fresh ash water-extractable Se concentrations were below minimum detection limits (i.e., $2.0 \mu\text{g L}^{-1}$) for all treatments. In contrast, averaged over extraction times, the weathered ash water-extractable Se concentration was greatest ($P < 0.05$) with groundwater and rainwater, which did not differ and averaged $60.0 \mu\text{g L}^{-1}$, compared to extraction with deionized water ($57.6 \mu\text{g L}^{-1}$). Selenite (Se^{4+}) was greater ($P < 0.001$) in the fresh (3.85 mg kg^{-1}) than in the weathered ash (0.70 mg kg^{-1}), while selenate (Se^{6+}) concentration was greater ($P < 0.001$) in the weathered (0.67 mg kg^{-1}) than in fresh ash (0.48 mg kg^{-1}). Results from this study indicate that environmental weathering of Class C, subbituminous fly ash promotes oxidation of selenite (Se^{4+}), to the less toxic, but highly mobile selenate (Se^{6+}). The formation of hydrated ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} - 26\text{H}_2\text{O}$] and calcium selenite (CaSeO_3) likely acted as a sink for weathered ash selenite (Se^{4+}). Implications of this research include a better understanding of the past, present, and future environmental and health risk potential associated with the release of water-soluble Se, As, and Cr to aid in the development of sustainable fly ash management strategies.

INTRODUCTION

Within the US, coal-fired plants provide approximately 45 % of the total net electrical generation, with 847,930 metric tons (934,683 tons) of coal consumed per day (EIA, 2011). During the combustion of coal, inorganic constituents that are naturally enriched in the coal are further concentrated in the coal combustion residuals (CCRs): fly ash and bottom ash. One of these inorganic constituents of concern is selenium (Se). Out of all of the EPA priority and non-priority pollutants, Se has the narrowest range between what is considered beneficial and detrimental to aquatic species and terrestrial organisms. In aquatic eco-systems, water concentrations greater than $5 \mu\text{g Se L}^{-1}$ can potentially cause teratogenic deformities within fish populations and embryo toxicity of waterfowl through the bioaccumulative effects of Se in the aquatic food chain (Lemly, 1999; Spallholz and Hoffman, 2002; Chapman et al., 2009). Humans have a narrow exposure range between what is considered a deficiency ($< 40 \mu\text{g Se day}^{-1}$) and what is considered toxic ($> 400 \mu\text{g Se day}^{-1}$; WHO, 1996). Therefore, the EPA's Maximum Contaminant Level (MCL) in drinking water for humans is $50 \mu\text{g Se L}^{-1}$ (EPA, 2011).

Approximately 43,929,517 metric tons (48,424,000 tons) of bottom ash and fly ash is stored in coal ash landfills or impoundments within the US annually (ACAA, 2011). Leachate generated from a coal ash landfill can be laden with Se, which could cause harm if released into the environment. Through environmental weathering, Se can be released from stored fly ash and become mobilized in the groundwater if the landfill does not have a properly engineered liner (EPRI, 2001, 2002, 2006c). The Se-laden leachate can be transported with the groundwater and become a human and ecological threat. One such potential threat would be the un-lined ash landfill located adjacent to the Flint Creek Power Plant located in Benton County, AR. The Flint Creek landfill is an above-grade landfill, which has received ash since the plant went operational

in 1978. Measurable Se concentrations were first detected in one of the monitoring wells located along the landfill boundary in 1994, but were not considered a statistically significant increase (SSI) until 2002, and, in 2009, the well experienced an exceedence for Se under the groundwater protection standard (GWPS; ADEQ, 2014). Therefore, there was a considerable amount of time (i.e., 24 years) before Se became mobilized and transported with the groundwater past the boundaries of the landfill. The slow mobilization may have been due to the pozzolanic properties of the fly ash restricting the percolating rainwater, slow oxidation to the mobile selenate (Se^{6+}) form, the formation of secondary products that act as a sink for Se, or a combination of all three factors (Wesche, 1991; EPRI, 2005, 2006a). Site-specific information is essential to better understand the complex relationship among Se-laden leachate and the leachates' interaction with the vadose zone and underlying groundwater.

The Se plume currently extends approximately 200 m (656 feet) to the west of the plant's 16 ha (40 acre) landfill. The Se has not yet posed a threat to local drinking water sources or the aquatic environment because the contamination is currently perched in the regolith. However, this Se plume needs to be remediated to prevent any further spread. Remediation will consist of installing an intermediate liner, a leachate collection system, and three GE ABMet™ (Advanced Biological Metals Removal Process) bioreactors that will reduce the Se oxyanions selenate (Se^{6+}) and selenite (Se^{4+}) to their elemental form (Se^0). The biological reduction to elemental Se (Se^0) will cause the Se to precipitate out within the bioreactors, which will allow the Se to be easily removed from the waste stream (Sonstegard and Pickett, 2005).

To be able to effectively operate the ABMet™ bioreactors a better understanding of selenium's water-soluble fraction is needed. The water-soluble fraction is the readily available fraction that can be easily released into the environment through contact with rainwater and

groundwater, and therefore is the most environmentally representative fraction (Narukawa et al., 2005 and Yuan, 2009). Once released into the environment, Se usually exists as the highly mobile selenate (Se^{6+}) or the more toxic, but far less mobile selenite (Se^{4+} ; EPRI, 2006a; EPA, 2004). Changes in oxidation states affect selenium's mobility, solubility, and adsorption rates in soils (Elrashida et al., 1987; Goh and Lim, 2004; Otero-Rey et al., 2005). Selenite (Se^{4+}) functions like the phosphate anion (i.e., inner-sphere surface complex), has a greater adsorption rate than selenate (Se^{6+}), and is controlled by its ability to bind to ferric hydroxides and aluminum oxides in acidic and neutral soil (Ylaranta, 1982; Ahlrichs and Hossner, 1987; Barceloux, 1999; Goldberg et al., 2008). In contrast, selenate (Se^{6+}) is known to behave like the sulfate anion (i.e., outer-sphere surface complex) with low adsorption rates, high solubility, and pronounced leachability causing selenate (Se^{6+}) to be highly mobile in soils (Elrashida et al., 1987; Neal and Sposito, 1989; Peak and Sparks, 2002). Recognizing and understanding the differences between species is critical for assessing the amount of Se that has been, and could be, released into the environment from an ash landfill and to better predict selenium's natural mitigation, such as biotic or abiotic reduction of selenate (Se^{6+}) to selenite (Se^{4+}) followed by precipitation and adsorption of selenite (Se^{4+}) to Fe in soil.

The main objective of this study was to evaluate the effects of ash type (i.e., fresh and weathered), water-extractant type (i.e., deionized water, rainwater, and groundwater), and extraction time (i.e., 2- and 6-hours) on water-extractable Se, arsenic (As), and chromium (Cr) concentrations from a Class C, sub-bituminous fly ash produced at the Flint Creek Power Plant. It was hypothesized that water-extractable Se concentrations would be greatest from weathered ash extracted with deionized water, with no difference between extraction times. Comparison of

the three different water-extractants may provide the scientific community with useful data to help make an informed decision on a preferred water-extractant.

MATERIALS AND METHODS

Site Description - Flint Creek Power Plant

Flint Creek Power Plant is a base-load, coal-fired, electric generation plant located in Benton County, Arkansas. Construction of the plant began in 1974. By 1978, the plant was operational. The plant is located approximately 1.6 km (1 mile) west of Gentry, Arkansas (population 3,129), in the extreme northwest portion of the state (N 36°, 15', 45" latitude and W 94°, 31', 15" longitude), with a grade elevation of 354 meters (1160 ft; Wolniak et al., 1978; US Census, 2010). The land surrounding the plant is largely rural. The plant is jointly owned by American Electric Power-Southwestern Electric Power Company (AEP-SWEPCO) and the Arkansas Electric Cooperative Corporation (AECC). The AEP-SWEPCO company staffs the plant, handles daily operations, and provides the AECC with half of the electric generation (Gregory, Energy Production Supt. II, personal communication, 2010).

Flint Creek Power Plant was the first commercial power plant in Arkansas to use coal as its fuel source (Gregory, Energy Production Supt. II, personal communication, 2010). The plant has the electrical capacity to produce 528 net megawatts per hour, which is enough electricity to supply approximately 365,000 households at an average Arkansas household usage of 1,076 Kw per month (EIA, 2010). At full capacity, the plant will burn approximately 6,350 metric tons (7,000 tons) of coal per day (Wolniak et al., 1978). The coal arrives by railroad and can be transported directly into the plant's coal bunkers or stored in the coal yard until needed. Before being injected into the boiler, the coal is pulverized into a fine talcum-powder-like consistency. The pulverized coal is then injected into the boiler with pre-heated, forced-draft air (Figure 2-1). The combustion of the coal produces temperatures over 1,370°C (2,500°F) inside the boiler,

eventually producing high-pressure steam delivered to the turbine at 169 kg cm^{-2} (2,400 lbs in⁻²) and 538°C (1,000° F; Wolniak et al., 1978).

Sub-bituminous Coal

Flint Creek Power Plant uses Powder River Basin (PRB) coal mined from the Wyodak Beds in Wyoming. This PRB coal is a Class C, sub-bituminous coal with a heat value of 19,306 to 26,749 kJ kg⁻¹ (8,300 to 11,500 Btu lb⁻¹), and is one of the cleanest burning coals available in the US with respect to sulfur dioxide emissions (Sargent and Lundy Engineers, 1974; Kitto and Stultz, 2005). A typical analysis of sub-bituminous coal (Table 2-1) yields the following mineral content: carbon (69.7 %), hydrogen (4.8 %), oxygen (17.9 %), nitrogen (0.9 %), and sulfur (0.3 %). The ash produced from burning sub-bituminous coal produces an alkaline, calcium-based ash different from the acidic ash produced from burning eastern US bituminous coals. The coal being used at Flint Creek has a total ash content ranging from 3 to 5 %.

Bottom Ash

Bottom ash represents approximately 30 % (4.0 metric tons hr⁻¹ or 4.4 tons hr⁻¹) of the total ash produced at Flint Creek. The color of the bottom ash produced varies from a dark brown to a dark grayish black. This bottom ash is collected at the bottom of the boiler as it falls out of the gas stream. The plant utilizes a dry-bottom furnace, in which the bottom ash will fall into a water-filled hopper. The bottom ash is sluiced (i.e., the act of using water to transport the bottom ash through piping) from the hoppers every 12 hours using a hydro-ejector “wet-sluicing” system and then conveyed to the primary ash settling pond (Gregory, Energy Production Supt. II, personal communication, 2010). The bottom ash then settles out in the primary ash pond where

it can be collected. The settling pond is sized to handle approximately 90,718 metric tons (100,000 tons) of bottom ash before needing to be dredged (Burns and McDonnell, 1993). Flint Creek's primary ash pond has been dredged approximately once every 15 years since 1978 (Carney, Plant Environmental Coordinator, personal communications, 2010). The dredged bottom ash is then marketed as a road-base material.

Fly Ash

The second type of coal ash produced at Flint Creek is fly ash. Fly ash represents approximately 70 % (9.3 metric tons hr⁻¹ or 10.2 tons hr⁻¹) of the total ash produced at this site. Flint Creek uses PRB sub-bituminous coal, which produces a Class C fly ash during combustion. The color of the fly ash produced varies from a yellowish to light tan. Fly ash is transported out of the boiler in the gas stream, and is then collected by the electrostatic precipitator (ESP) and silo baghouse.

Flint Creek uses "hot side" ESPs that receive the flue gas at a maximum temperature of 399°C (750°F) with a dust loading of 2.0 to 2.5 grains m⁻³ (0.057 to 0.070 grains ft⁻³; Wolniak et al., 1978). Flint Creek ESPs use anodic plates and cathodic wires to remove fly ash from the flue gas with greater than 99.5 % removal efficiency (EPRI, 1982; Terracon, 2006). Electrostatic precipitation, in this case, is the process in which fly ash suspended in the flue gas is given a negative charge from negatively charged electrodes (cathodic wires) hanging in the ESP. The negatively charged fly ash is then collected onto the positively charged (anodic) plates (EPRI, 1982). The plates are periodically rapped (vibrated) causing the fly ash to fall and be collected in hoppers located below the ESP. The fly ash is then transported to a silo via a hydro-vactor exhaust system, which utilizes water to create an air vacuum. With this type of design, there is

a small amount of fly ash that becomes entrained into the hydro-vactor water (Terracon, 2006). Historically, this entrained fly ash would then travel with the hydro-vactor water into the plant's primary ash settling pond. Engineers at AEP calculated that at least 72 % of the Se loading into the primary ash pond was from this fly ash carryover. To remediate this problem, in April 2011 the plant placed a new high-efficiency baghouse in service on top of the existing ash silo. This baghouse replaced the existing two-stage collector system, and is capable of preventing more than 99.98 % of this fly ash carryover (Massingill, Energy Production Supt. III, personal communication, 2011). Following start-up of the baghouse, the average Se concentration in the effluent of the secondary ash pond have decreased from approximately $5 \mu\text{g Se L}^{-1}$ to non-detectable (ND) levels.

Fly ash collected in the silo is either sold or stored at the on-site ash landfill. Fly ash produced at Flint Creek is high in alkalinity, calcium content ($\sim 27 \%$), and exhibits pozzolanic properties, much like that of Portland cement (Helmuth, 1987; Wesche, 1991; Kiwerska, 2002). These characteristics allow the fly ash to be sold and utilized as an additive in concrete, improve soil structure and water-holding capacity, act as a neutralizer in acidic soils, and be an essential source of micronutrients for agricultural crops under the right conditions (Capp and Spencer, 1970; Martens et al., 1970; Helmuth, 1987; Wesche, 1991; Yeheyis, 2008). The quantity sold per year is dependent on current market conditions. For example, in 2005, approximately 55 % of the fly ash produced at Flint Creek was marketed for re-use. The unsold fly ash is transported from the storage silo to the landfill by semi-truck/trailers.

Class 3N Solid Waste Disposal Facility (Ash Landfill)

The Solid Waste Disposal Facility [Arkansas Department of Environmental Quality (ADEQ) Permit # 0273-S3N-R1], which from this point on will be referred to as the ash landfill, is located approximately 400 meters (1300 ft) northeast (N 36°, 15', 34''/ W 94°, 30', 48'') of the power plant (ADEQ, 2010). The ash landfill encompasses approximately 16 hectares (40 acres), and the area around the ash landfill is a relatively flat plateau surface (Burns and McDonnell, 1992). Property surrounding the ash landfill is owned by AEP-SWEPCO and leased out primarily as pasture for cattle and haying purposes (Figure 2-2; Carney, Plant Environmental Coordinator, personal communication, 2010). The land directly to the south of the landfill includes a two-lane highway (Swepeco Plant Road) that dead ends at the plant and a railroad track used for transporting coal and supplies to and from the plant. Just south of this railroad track is a small area of woods and the plant's primary ash settling pond. Approximately 800 meters (0.50 miles) to the west of the landfill is Swepeco Lake. This lake encompasses 215 hectares (531 acres) and was constructed to serve as a cooling water reservoir for the plant.

Upon initial power production in 1978, fly ash disposal began at the ash landfill (Burns and McDonnell, 1993). Fly ash was first disposed of on the northeast side of the landfill, and currently covers most of the landfill site (Burns and McDonnell, 1993; Wehling, Environmental and Safety Engineer I, personal communication, 2010). Stormwater runoff from the ash landfill is directed by surface water channels towards an earthen berm that surrounds the landfill (Burns and McDonnell, 1993; Terracon, 2006). The berms direct the stormwater runoff towards the southeast and southwest corners of the landfill where it passes underneath the road and railroad tracks through culverts. These culverts empty into a drainage ditch, transporting the surface runoff approximately 150 meters (~ 500 ft) before emptying into the plant's primary ash pond. The primary ash pond effluent flows into the secondary ash settling pond and then into Swepeco

Lake Reservoir. The discharge point from the secondary ash pond (N 36°, 15',03", W 94°, 31', 35") is regulated by a National Pollutant Discharge Elimination System (NPDES) permit (ADEQ Permit # AR-0037842).

Only Class 3 waste generated at the Flint Creek Power Plant is disposed at the ash landfill. Class 3 waste includes CCRs such as fly ash, bottom ash, bottom ash dredged from the settling ponds, slag, and grit blasting materials. Slag is a glassy, angular, non-crystalline material that accumulates in the boiler as the coal ash melts into a viscous liquid and is quenched for removal. Grit blasting is a non-hazardous material used to remove ash that has adhered to the interior surfaces of the boiler, ESPs, and duct work during plant outages (Terracon, 2006).

Ash Landfill – Daily Operations

The ash landfill is operated Monday through Friday from 0700 to 1700 (CST), unless conditions warrant extended operating times. There is only one entrance to the landfill and it is closed and locked during off hours. Only AEP-SWEPCO personnel and authorized contractors are allowed access to the landfill (Terracon, 2006). The ash landfill is operated by AEP-SWEPCO personnel, while an ash marketing contractor places ash upon the landfill under the direction and supervision of AEP-SWEPCO personnel. Ash is deposited and periodically graded to allow smooth and gradual slopes at all places. The current permit allows a 4:1 slope to a fill elevation of 370.33 meters above sea level (1215 ft above sea level) and then requires a 20:1 slope to the final fill elevation of 376.3 meters above sea level (1234.5 ft above sea level; Figure 2-3). Since fly ash has pozzolanic properties, water is applied to the ash after it has been deposited to control dust (Helmuth, 1987). The hardened fly ash fulfills the same requirements as daily and intermediate covers under the plants Title V air permit issued by ADEQ. Since the

ash landfill doesn't have common municipal landfill issues, such as vector control (e.g., flies, seagulls), blowing trash, and daily odor control, intermediate covers are not used (Carney, Plant Environmental Coordinator, personal communications, 2011).

Current Landfill Liner

When the plant was undergoing construction, Swepeco sought a permit for the ash landfill, but the State of Arkansas did not require permits to operate solid waste landfills at that time (Wehling, Environmental and Safety Engineer, personal communication, 2010). However, legislation and regulation changes required the landfill to be permitted, and in 1990 a pre-application for a permit was submitted and approved by the Arkansas Department of Pollution Control and Ecology (Burns and McDonnell, 1993).

Since construction was prior to the implementation of Arkansas regulation 22, the landfill did not have a clay liner installed before ash disposal began. In the western one-third of the landfill, the topsoil was removed down to the natural clay layer and the upper 15 cm (6 inches) of this natural clay layer was compacted to serve the purpose of a clay liner (Wehling, Environmental and Safety Engineer, personal communication, 2010). In the eastern two-thirds of the landfill, the topsoil was not removed before fly ash disposal began.

Current Sub-Surface Leachate Collection

Currently, a limited amount of sub-surface leachate discharging from a seep is collected in the southeast corner of the landfill and pumped into two 34,000 L (9,000 gal) storage tanks. As the storage tanks become full, the leachate is pumped into water trucks and transported to the

boiler where it is evaporated. Evaporation of the landfill's leachate was approved by the ADEQ Air Division on October 13, 2009 and placed in service in April 2010 (Miller, 2010).

Future Intermediate Liner and Leachate Collection System

In 2011, a permit modification was sent to the ADEQ requesting additional landfill storage capacity and approval to install an intermediate liner and leachate collection system at the Flint Creek ash landfill (Hull and Associates, 2011). This modification requests an additional 633,051 cubic meter (828,000 yd³) storage capacity, a 34.7 % increase from 1,189,647 to 1,822,699 cubic meters (1,556,000 to 2,384,000 yd³), and a final fill elevation of 400.8 meters (1315 ft above sea level) with a 4:1 slope. At current disposal rates, the modified landfill would be able to continue accepting ash for disposal until around the year 2045. However, the Flint Creek plant should have a dry flue gas scrubber installed and operational by the year 2016. This scrubber will reduce the life expectancy of the landfill by approximately 14 years due to the generation of an unmarketable calcium sulfite (CaSO₃) waste product during the sulfur dioxide (SO₂) removal process.

The proposed intermediate liner will consist of a 60-mil, high-density polyethylene (HDPE) geomembrane, which will be installed over the entire landfill in one phase. The leachate collection system will be installed in separate phases as the ash is deposited onto the liner. Separation berms will be constructed between the active phases to direct the leachate and prevent stormwater runoff from entering the leachate collection system. The leachate collection system will include a double-sided geocomposite drainage layer and a 30.5 cm (12 inch) HDPE leachate collection piping system. The leachate collection piping will be installed over the intermediate liner and have 0.9525 cm (0.375 inch) diameter holes to allow collection of the

leachate. The collected leachate will then gravity-feed to a leachate storage pond. This leachate storage pond will have a 1,099 cubic meter (290,244 gallon) capacity and be lined with a 0.61 meter (2.0 ft) compacted clay liner covered with a 60-mil, HDPE geomembrane liner. The leachate pond will be designed to hold seven days worth of leachate and a 25-year rainfall event directly on the pond. After collection, leachate can either be pumped to an on-site treatment facility (ABMet™ bioreactor) or removed by a tanker truck.

Stormwater runoff from the ash landfill will be collected by a contact water storage pond, which will act as a settling basin for total suspended solids (TSS) removal. The stormwater will travel from the landfill, to the contact pond, through a concrete-lined channel capable of handling a maximum flow rate of $1.59 \text{ m}^3 \text{ sec}^{-1}$ (418.9 gal sec^{-1}). The contact water pond will have an $11,010 \text{ m}^3$ (2,908,426 gal) capacity and will consist of the same liner system as the previously mentioned leachate storage pond. The contact water pond will be designed to contain a 25-year stormwater runoff event and a 25-year direct rainfall event on the pond. After settling, the effluent from the contact water pond will travel through a 76.2 cm (30 inch) diameter SaniTite® pipe to the plants primary ash pond. [Note: Previously mentioned information concerning the intermediate liner and leachate collection system was obtained from the “Permit Modification Application for the Intermediate Liner and Leachate Collection System” (Hull and Associates, 2011)].

ABMet™ Flint Creek - Treatment Technology

Selenium removal processes, such as iron co-precipitation, strongly basic anion resins, and constructed wetlands, were considered for the Flint Creek site. However, the ABMet™ system was chosen as the treatment process due to the high percentage of selenate (Se^{6+}) in the

ash landfill leachate. Unlike selenite (Se^{4+}), selenate (Se^{6+}) has proven difficult to remove from wastewater using conventional methods, such as ferrihydrite adsorption (Fujita et al., 2002; Hayashi et al., 2009; Smith et al., 2009). Selenite (Se^{4+}) is strongly adsorbed on the ferric hydroxide floc, while selenate (Se^{6+}) is loosely bound, resulting in poor removal rates (Hayashi et al., 2009). Strongly basic anion resins were not chosen due to the high operating costs, large amounts of sodium hydroxide needed for regenerations, and a large amount of waste regenerant that would need disposal. Constructed wetlands were also considered for a treatment option. However, wetlands would require a large footprint, still allow the potential for groundwater contamination, and could result in wildlife exposure to contaminated water without adequate reduction of selenium oxyanions.

Leachate from the Flint Creek ash landfill has an average total selenium concentration near $400 \mu\text{g Se L}^{-1}$, with selenate (Se^{6+}) accounting for approximately 95 % of this total selenium. Even though selenate (Se^{6+}) has proven difficult to remove with conventional methods, the ABMet™ system has proven capable of reducing selenate (Se^{6+}) with greater than 98 % reduction rates during full-scale operation (Lortie et al., 1992; Golder & Associates, 2009; Sonstegard et al., 2010). A study conducted by EPRI (2010) reported similar selenate (Se^{6+}) removal (> 99 %) from $182 \mu\text{g L}^{-1}$ to $1.3 \mu\text{g L}^{-1}$ from waste streams.

Prior to entering one of the three ABMet™ bioreactors, leachate from the Flint Creek ash landfill will enter a lined settling pond. This settling pond will facilitate TSS removal and aid with flow neutralization. The normal designed influent flow rate will be 56.8 L min^{-1} (15.0 gal min^{-1}). The leachate will then be pumped from the settling pond into a feed tank. Prior to entering the feed tank, sulfuric acid (93 %) will be mixed with the leachate at a feed rate of approximately 1.4 L hr^{-1} (0.37 gal hr^{-1}) to obtain an influent pH between 7.5 to 8.0. Sulfuric acid

must be added because the unprocessed leachate has a pH between 11.5 to 12.0. The neutralized leachate will then be pumped from the feed tank into the top of the bioreactors. Before entering the bioreactors, a nutrient mixture (molasses) will be injected into the bioreactor feed line, downstream from the feed pumps, at a rate of approximately 0.49 L hr^{-1} (0.13 gal hr^{-1}). Nutrient injection flow rates will be adjusted to maintain an effluent ORP of approximately -300 mV. The neutralized/nutrient-rich leachate will then enter the top of the bioreactors through a distribution lateral header. After spending approximately six hours gravity feeding down through the bioreactor, the processed leachate will exit through the effluent collection piping located at the bottom of each bioreactor, which is lined with a gravel sub-fill that acts as the support for the biomatrix (EPRI, 2010; Sonstegard et al., 2010).

Due to the reduction process, there will be accumulations of gases in the bed such as nitrogen and carbon dioxide (Harwood, GE Water, personal communication, 2010; Sonstegard et al., 2010). These gas pockets will be monitored by level and pressure transmitters within the bioreactor bed and effluent piping (Sonstegard et al., 2008). The frequency of “degas” backwashing, which from this point on will be referred to as degas, will vary depending on the constituent loading (e.g. nitrates and selenium oxyanions) of the bioreactor beds and the pressure differential within the bioreactor (Harwood, GE Water, personal communication, 2011). This degas sequence requires a high pressure pump, which will introduce water into the bottom of the reactor “lifting” the biomatrix at a design flow rate of $1,018 \text{ L min}^{-1}$ (269 gal min^{-1}). A degas does not send water out of the top of the bioreactor like a normal backwash. Instead, the degas is a high flow, short, “burp” of the bioreactor. This degas allows entrained gases to vent out of the bed, which prevents channeling and head-loss within the bioreactor (Sonstegard et al., 2008). If

the degas does not lower the head or differential pressure, then a solid backwash will need to be performed.

Approximately once per month, each bioreactor will need a solid backwash performed (Harwood, GE Water, personal communication, 2010). A solid backwash removes TSS, prevents clumping, and facilitates removal of the reduced metals (Pickett et al., 2006; Sonstegard et al., 2008). The TSS levels have a drastic effect on effluent quality and loading of the bioreactor beds (Harwood, GE Water, personal communication, 2010). High influent TSS levels will require frequent solid backwashing of the beds.

An increase in selenium effluent concentrations could also indicate a need for a solid backwash (Sonstegard et al., 2008; Sonstegard et al., 2010). This was noticed during full-scale operation at the Progress Energy Roxboro Station located near Roxboro, North Carolina (Sonstegard et al., 2010). A solid backwash lasts approximately 15 to 20 minutes at 2,040 L min⁻¹ (539 gal min⁻¹) flow rates. The backwash high flow rate will dislodge the entrained solids, which are carried out with the backwash water into a trough at the top of the bioreactor. From the trough, the backwash effluent will gravity-flow to the waste tanks. After settling, the backwash water will be pulled from the top of the tank and sent back to the feed tank for re-processing (Sonstegard et al., 2008). After approximately three backwash cycles, the settled “liquid” sludge will be removed from the two waste tanks and hauled off site for disposal. The waste sludge leftover from backwashing will contain mostly precipitated elemental metals, sulfides, and TSS (Sonstegard et al., 2008). Before proper disposal, the settled backwash sludge will be analyzed for hazardous waste constituents (Carney, Plant Environmental Coordinator, personal communications, 2011). Backwash solids from bench testing have passed the Toxicity Characteristic Leaching Procedure, which have shown that waste characteristics are below

concentrations which would cause the backwash solids to be classified as a hazardous waste (TCLP; Harwood, GE Water, personal communication, 2010). Based on an average influent of 30 mg L^{-1} TSS, there should be between a 0.5 to 2.0 % concentration of solids entrained in the backwash water (Harwood, GE Water, personal communication, 2011).

A certain amount of headspace is required within the bioreactor to allow for adequate expansion of the biomatrix during backwashing (Sonstegard et al., 2010). This headspace (Figure 2-4) must be maintained to prevent loss of the granular activated carbon (GAC) during backwashes, and will also be used as an indicator of the amount of gases and TSS developing within the bed (Sonstegard et al., 2010). Since the GAC is not being used as an adsorptive treatment mechanism, the GAC should only need topping off every 5 to 10 years replacing only what is backwashed out of the bioreactor (~ 0.5 % per year; Harwood, GE Water, personal communication, 2011). Degas and solid backwashes will need to use previously treated bioreactor effluent to prevent upsetting the microbes within the bioreactors because high oxidation-reduction potential (ORP) backwash water could upset the gradually reducing conditions inside the reactor (Sonstegard et al., 2010).

Previously treated effluent will also be used for bacteria seeding and for intermittent flow through the reactors when unit shutdown is required (EPRI, 2006b). If this is not done, an expected 24 hours would be needed for the ORP levels to come back down and the bacteria to re-stabilize (Dey and Kulkarni, 2010; Harwood, GE Water, personal communication, 2011). During this period, the selenium effluent concentrations may also increase slightly if non-processed water is used (Harwood, GE Water, personal communication, 2011). To compensate for this, extending retention times following upsets conditions should aid in the restabilization of

the bio-reduction process. A flow diagram for the ABMet™ at Flint Creek can be seen in Figure 2-5.

Any major abnormal operating condition “disruption”, such as mechanical, hydraulic, temperature, pH, or change in influent selenium concentrations, may cause an increase in effluent selenium concentrations until the microbes re-stabilize (Dey and Kulkarni, 2010; Harwood, GE Water, personal communication, 2010). The rate of disruption has showed to be more of concern than just the magnitude of disruption (Harwood, GE Water, personal communication, 2011). An increase in selenium effluent concentrations may also be encountered if the ABMet™ system is allowed to operate below design flow and/or cycled every few days (Harwood, GE Water, personal communication, 2011). Therefore, the bioreactors should be placed in service for an extended period of time and not taken in and out of service frequently. When a discontinuous-flow condition exists, the bioreactors must be shut down and placed into the maintenance mode.

Recent data from a full-scale ABMet™ system has shown that it is possible for selenium concentrations to remain at desired effluent levels following a long-term maintenance mode of 48 days (Harwood, GE Water, personal communication, 2011). During such an extended shutdown, the bioreactors will need to be placed in maintenance mode with an operator replacing a minimum of 25 % of the water/nutrient volume bi-weekly, within the bioreactor bed, to maintain proper conditions for bacteria survivability and prevent severe anaerobic conditions from developing within the bioreactors. This process of replacing a portion of the water within the bioreactors is termed “refreshing”. At Flint Creek, a 25 % displacement would equal approximately 1,579 L bioreactor⁻¹ (417 gal bioreactor⁻¹) that would need replacement bi-

weekly. Refreshing all three bioreactors weekly will require approximately 9,464 L (2,500 gallons) of leachate.

There have also been concerns whether large temperature swings encountered in northwest Arkansas will affect the effluent selenium concentrations. As the wastestream becomes cooler, the microbes will slow down and a longer retention time (normal retention time is six hours) may be needed within the bioreactor beds. For example, during start-up of the Roxboro Plant in February 2008, the wastewater influent temperatures were near 9 °C (48 °F). During the sensitive inoculation and start-up period (first 2 weeks), the influent wastewater was pre-heated to maintain a reaction temperature greater than 27 °C (80 °F; Sonstegard et al., 2008). Increasing the temperature allowed for an increase in reaction rates and lower selenium effluent concentrations. After this start-up period, the bioreactors were able to accept influent wastewater at ambient temperatures. Similarly, warm summer temperatures at Flint Creek are not expected to be an issue due to anaerobic bacteria thriving at temperatures near 38 °C (100 °F; Smith et al., 2009). However, the upper tolerance limit specified by GE is 40 °C (104 °F). Therefore, the temperature will have to be monitored closely once inlet water temperatures rise above 38 °C (100 °F).

As part of a preventive maintenance program, the ABMet™ system should be shutdown once per week during continuous flow to refresh the water and nutrients in the reactor (Harwood, GE Water, personal communication, 2010). Before placing back in service, a backwash of the bioreactors is preferred. However, the bed can be placed back in service without a backwash if one is performed within 48 hours after startup (Harwood, GE Water, personal communication, 2011). The bioreactors should never be placed into a recirculation mode. Recirculation would

upset the stable ORP gradient zones within the bioreactor beds (Harwood, GE Water, personal communication, 2010).

Bioreactor effluent is not expected to need post-treatment at Flint Creek. The effluent will flow into the ash landfill's contact water pond (Carney, Plant Environmental Coordinator, personal communications, 2011). The contact water pond holds stormwater runoff collected from the fly ash landfill. The effluent from the contact water pond will be piped into the plant's primary ash pond. Under normal flow conditions, the bioreactor effluent will account for only 0.6 to 1.2 % of the total influent water into the primary ash pond.

The molasses carbon source should have an average cost of \$0.20 per 3,785 liters treated (\$0.20 per 1,000 gal), with total operation and maintenance costs averaging between \$0.35 to \$0.46 per 3,785 liters treated (\$0.35 to \$0.46 per 1,000 gal; Harwood, GE Water, personal communication, 2010; Sonstegard et al., 2010). An expected time of two weeks will be needed after installation before the correct reducing environment exists in the bed for proper selenium reduction (Harwood, GE Water, personal communication, 2010). Flint Creek's ABMet™ system will be designed for a maximum 95 L min^{-1} (25 gal min^{-1}) influent flow rate. However, the system should be able to handle flow rates between 19 to 38 L min^{-1} (5 to 10 gal min^{-1}) without negative effects on effluent quality (Harwood, GE Water, personal communication, 2010).

Groundwater Monitoring

The current groundwater monitoring system for the ash landfill consists of 18 monitoring wells and a leachate collection system (AEP, 2011). The wells and leachate collection system are sampled quarterly for parameters included in the Assessment Monitoring Constituent list

(AMC; Table 2-3; ADEQ, 2010). In addition to monitoring the parameters on the AMC list, once every three years, the wells are sampled for parameters in the Expanded Parameter (EP) list (Table 2-4; ADEQ, 2010). The sampling is performed by Eagle Environmental (Shreveport, LA) and sample analysis is performed by Environmental Testing Group (ETG) in Bentonville Arkansas, which is an ADEQ certified laboratory (Lab ID: 04-0574; Certification number: 10-063-0).

The initial groundwater monitoring wells were installed as part of the hydrogeologic site characterization that was conducted prior to landfill permitting in 1994 (Burns and McDonnell, 1992; AEP, 2010). Monitoring wells (B-01A, B-01B, B-02, B-04, and B-05) were installed in 1991 and are located at the approximate midpoint on each side of the landfill [B-01A and B-01B (North), B-02 (West), B-04 (East), and B-05 (South)] (Figure 2-6; Burns and McDonnell, 1992). Well B-06 was installed in 2001 just north of the northwest corner of the landfill. In May 2007, three additional wells were installed: B-07A, B-07C, and B-08 (AEP, 2010). Wells B-07A and B-07C are located just north of the northern edge of the landfill. Well B-08 is located to the west of the southwest corner of the landfill. From these wells, it has been determined that the general groundwater flow is to the west by northwest. On a few occasions, it has been observed to flow to the northeast.

In April 2009, groundwater monitoring well B-02 experienced an exceedence for Se ($50 \mu\text{g Se L}^{-1}$) under the Groundwater Protection Standard (GWPS; AEP, 2010). As part of a study to determine the nature and extent (NE) of the contamination plume, Flint Creek added three new groundwater monitoring wells down-gradient of well B-02, during the summer of 2009 (AEP, 2010). The three new wells were named NE-01, NE-02, and NE-3. Groundwater monitoring well NE-01 is located approximately 155 meters (510 ft) north-northwest of well B-02, well NE-

02 is located approximately 122 meters (400 ft) west-northwest of well B-02, and well NE-03 is located approximately 140 meters (460 ft) southwest of well B-02 (AEP, 2010). Hydraulic conductivity values for wells B-01B, B-02, B-04, B-05, B-06, NE-1, NE-2, and NE-3 are presented in Table 2-5 and the procedure used is described in Appendix A.

Due to Se being detected at levels above the Groundwater Protection Standard (GWPS) at well NE-3, six new groundwater monitoring wells were installed down-gradient of current monitoring wells NE-1, NE-2, and NE-3 as part of the Nature and Extent Workplan (ADEQ Permit # 273-S3N-R1; Document # 59665). During June 2011, these new wells were installed north (NE-4), northwest (NE-5), west-northwest (NE-6), west (NE-7S and NE-7D), and west-southwest (NE-8) of current monitoring well NE-3 (See Appendix B for drilling technique and Figure 2-6 for aerial view of well locations). Quarterly sampling of these wells began on July 19, 2011 with testing performed by the ETG laboratory. Data suggest that the Se plume has not reached this area.

While installing well NE-7D, the drilling crew believed that this well was not capable of producing enough water for installing the well (i.e., setting). Therefore, well NE-7S was installed adjacent to NE-7D. However, after 24 hours, it was determined that well NE-7D would produce enough water for final setting of the well. Therefore, sampling of wells NE-7S and NE-7D are rotated every quarter. Another notable comment is that during drilling of well NE-5, a void in the bedrock was encountered at a depth of 6.10 to 6.86 meters (20 to 22.5 ft), which is below the top of the groundwater table. Water was encountered at a depth of 5.5 meters (18 ft) below the ground surface at this well (NE-5). After sitting overnight, water had risen to a depth of 2.2 meters (7 ft 6 inches) below the ground surface, which indicated that there is a substantial

amount of head on this well. Soil samples during drilling were obtained using the “split-spoon” method.

Local Geology/Hydrology

The Flint Creek ash landfill is located on the relatively flat, southward extension of the Springfield Plateau (Figure 2-7). The Springfield Plateau is located on the southwestern side of the Ozark Highlands, which is an irregular, flattened, dome-like structure known as the Ozark uplift (Sargent and Lundy Engineers, 1974). The Ozark uplift’s history has been marked by the ingression and regression of shallow seas. However, during most of its history, the Ozark Highlands has stood high enough to serve as a source of sediments.

The Springfield Plateau is a sub-division of the Ozark Highland Province and differentiates itself from the rest of the Ozarks by being underlain by rocks of Mississippian age (Fenneman, 1938). Topography in the area around the ash landfill consists of a relatively flat plateau with a general slope of 0.3 to 0.4 % to the southwest (Sargent and Lundy Engineers, 1974). The Springfield Plateau, in the area around the ash landfill, can be divided into three stratigraphic units: the Boone formation, the St. Joe formation, and the Chattanooga Shale formation (Figure 2-8).

Boone Formation

Regolith around the ash landfill is a mixture of iron-rich clay, chert, and limestone fragments, with clay comprising greater than 50 % of the total volume of the regolith (Doheny-Skubic, 2006). Regolith is an insoluble material that is formed from the downward weathering of cherty limestone (Doheny-Skubic, 2006). From soil boring logs, it has been determined that

there is approximately 6.1 to 12.2 meters (20 to 40 ft) of regolith overlying the Boone formation at the ash landfill site.

The Boone formation is a gray limestone of lower-Mississippian age interbedded with varying types and amounts of chert (Martin, 1993; Al-Qinna, 2003). The Boone formation is characterized by a block-like chert and limestone that weathers into a reddish-colored regolith (McFarland, 1975). Due to this in-situ weathering, the Boone formation around the landfill consists of cherty limestone mixed with red to brown clay seams (Burns and McDonnell, 1992). The Boone formation lies almost horizontally in the area around the ash landfill and has an average thickness of 61 to 76 meters (200 to 250 ft). The Boone formation can be separated into lower and upper divisions due to the presence of two separate types of chert: diagenetic and penecontemporaneous.

The upper division of the Boone contains a white to tan diagenetic chert. This upper division can contain up to 70 % chert that often shows signs of being calcitized, making it easy to identify (Martin, 1993; Al-Qinna, 2003). This diagenetic chert was formed as silica-rich groundwater replaced the original carbonate limestone.

The lower division of the Boone contains 45 to 65 % of a gray to blackish blue penecontemporaneous chert (Al-Qinna, 2003; Laubhan, 2007). In the field, the lower Boone division will appear as nodules, discontinuous bands, and anastomosing bodies that divide and reconnect. In both the upper and lower divisions, groundwater can possibly become perched by the bedding of the chert (Smith, 1992). At locations where the chert beds intersect the ground surface, springs can form (Smith, 1992). Underlying the Boone formation is the St. Joe formation.

St. Joe Formation

The St. Joe formation is a relatively pure Mississippian-age limestone, with an average thickness of 14 meters (45 ft) in the area around the ash landfill (Martin, 1993). It is the switch from a persistent dark chert to a light gray chertless limestone that differentiates the Boone from the St. Joe. In some areas, the St. Joe can be differentiated from the Boone formation by a greenish shale bed that is less than 15 cm (< 6 inches) thick (Shanks, 1976). The St. Joe limestone has experienced less erosional degradation than the Boone limestone (McFarland, 1975). However, many karst features, such as caves, are formed in the St. Joe limestone due to carbonate dissolution from the slightly acidic, circulating groundwater.

The United States Geological Survey (USGS) recognizes the St. Joe as a basal member of the Boone formation and not its own independent formation (Laubhan, 2007). However, the St. Joe has been generally accepted as its own formation independent from that of the Boone due to previous investigations in this area by McFarland (1975) and Shanks (1976). Underlying the St. Joe formation is the Chattanooga Shale formation.

Chattanooga Shale Formation

The Chattanooga formation is of Devonian age and ranges from 15 to 17 meters (50 to 55 ft) thick in the area surrounding the landfill (Martin, 1993; Al-Qinna, 2003). The top of the shale is approximately 274 meters (900 ft) above sea level, with the average elevation of the ground surface ranging from 357 to 363 meters (1170 to 1190 ft) above sea level. The Chattanooga formation is a thick gray to black clay-like shale that serves as the regional confining unit for groundwater in this area with low permeability and primary porosity (Al-Qinna, 2003; Laubhan, 2007). The dark black color of the shale is due to the presence of pyrite and other carbonaceous

material (Duncan, 1983). In some areas of northwest Arkansas, the shale is exposed at the ground surface. At these weathered locations, the shale will appear black, have a distinct petroleum odor, and may have an orange staining due to pyrite oxidation within the shale (Duncan, 1983). In the area around the landfill, the shale is deeply buried beneath the Boone and St. Joe formations with no exposure sights nearby.

The Chattanooga Shale restricts the transportation of contaminants to the lower aquifer, thus providing an important protection barrier for the lower Ozark aquifer (Al-Rashidy, 1999). When the groundwater reaches the shale, it will move laterally until reaching an outlet where the shale is exposed. Since groundwater in the vicinity of the landfill is confined by the shale, there is no need for further discussion on any of the geological formations below the Chattanooga Shale. The perched groundwater above the Chattanooga Shale is known as the Springfield aquifer and below the Chattanooga Shale is the Ozark aquifer.

Hydrology - Springfield Plateau Aquifer

The Springfield Plateau aquifer lies within the Boone and St. Joe formations and is the primary drinking water source for rural residents in Benton County (Smith, 1992). In most areas, the aquifer is unconfined and permeable due to fractures in the limestone. However, the Springfield aquifer can become perched (Figure 2-9) if the chert is impermeable or if the limestone is shaley, which decreases the vertical hydraulic conductivity (Willis, 1978). The Springfield aquifer tends to have low well-water yields of 7.5 to 75.7 liters min⁻¹ (2 to 20 gal min⁻¹).

The top of the Springfield aquifer is also the top of the local groundwater table around the landfill. Recharge to the Springfield aquifer comes from infiltration of precipitation through the

vadose zone. The landfill receives on average 120 cm (47 inches) of precipitation annually (NOAA, 2011). From this 120 cm (47 inches), it has been estimated that roughly 25 cm (10 inches) percolates downward and recharges the aquifer (Imes and Emmett, 1994). The amount of recharge into the aquifer is aided by thin soils, gentle sloping topography, fracturing of the bedrock, and secondary permeability (Smith, 1992). The Boone formation is known to be extensively fractured in this study area. This fracturing allows the infiltrating rainwater to interact and dissolve the soluble CaCO_3 -rich limestone, which leads to the formation of karst features, such as sinkholes, caves, and channels (Bolyard, 2007). Concentrated groundwater flow is governed by the size and number of karst features in an area. However, in the area directly around the landfill, there is a limited amount of karst features present (Dr. Van Brahana, University of Arkansas, personnel communication, 2011).

Once precipitation reaches the groundwater table, the water will move laterally and discharge into streams, seeps, or could possibly move downward towards the regional groundwater system (Imes and Emmett, 1994). According to Imes and Emmett (1994), determining the quantity of water reaching the groundwater system can be difficult and nearly impossible due to the varying thickness of the aquifer and the complexity of the lithology and geologic formations. This downward percolation of groundwater could eventually allow water to reach the underlying Ozark aquifer if the Chattanooga Shale confining unit was fractured in this area (Rankin, 1998).

Local Soils

Soils at the ash landfill are derived from weathering of the Boone formation. The Boone-derived soils consist of sand, gravel, or cobble-sized pieces of chert in a clay matrix (Phillips and

Harper, 1977). Soils of this origin can serve as important temporary groundwater reservoirs, slowly releasing water into the fractures of the Boone formation below. The current ash landfill has ash deposited over the entire 16 hectares (40 acres). Construction of the ash landfill occurred prior to the implementation of EPA Subtitle D and Arkansas Regulation 22. Therefore, no liner was constructed at the ash landfill. Instead, the ash was deposited directly on the topsoil in the eastern two thirds of the landfill. In the western one third of the landfill, the topsoil was removed down to the natural clay chert layer and compacted. Due to the topsoil being present under the majority of the ash and a leachate Se plume extending to the west of the landfill, it is relevant to discuss the soils and their characteristics underlying the landfill site (Figure 2-10) and directly to the west of the landfill due to the westerly migration of the Se plume (Figure 2-11).

The soil directly below the ash landfill is comprised of five different soil series: Linker (LrC- 79.1 %), Nixa (Nfc- 7.9 %), Elsah (Eg- 5.8 %), Captina (CnB- 5.7 %), and Noark (NoD- 1.6 %). Linker soils have a moderate water infiltration rate when thoroughly wet, moderate permeability, low available water capacity, and are considered unfavorable for landfill use (NRCS, 2011). Linker soils tend to exist as a thin covering of the regolith with an average depth of only 0.66 meters (26 inches; Phillips and Harper, 1977). Descriptions of the remaining soils are summarized in Appendix C.

Preliminary Data

Previous groundwater sampling has provided this study with a good source of background information. Groundwater in wells B-02 and NE-3 have exceeded the groundwater protection (GWP) standard of $50 \mu\text{g Se L}^{-1}$, while well B-05 has been experiencing a steady increase in the Se concentration since 2005 followed by a leveling off below the GWP standard

(Figure 2-12). All non-detect (ND) values were reported as $5.0 \mu\text{g Se L}^{-1}$ to maintain consistency in the results.

Sampling of the private groundwater drinking well (Bartley Well), which is approximately 500 meters (0.31 miles) to the west of the landfill, has occurred intermittently since 2009. All samples have been reported as either NDs or values less than $3.3 \mu\text{g Se L}^{-1}$, with one sample having a reported value of $57.8 \mu\text{g Se L}^{-1}$. However, this sample will be considered an outlier because of probable contamination in the field or laboratory. Swepeco Lake is located approximately 800 meters (0.5 miles) to the west of the landfill and has also been sampled intermittently since 2009. All values reported have been NDs or values less than $1.0 \mu\text{g Se L}^{-1}$, except for one sample with a reported value of $40.7 \mu\text{g Se L}^{-1}$. This sample will also be considered an outlier due to probable contamination in the field or the laboratory.

Selenium speciation analysis was performed on samples from the ash landfill seep via ion chromatography inductively coupled plasma dynamic reaction cell mass spectrometry (IC-ICP-DRC-MS). Samples collected on February 27, 2009 were sent to Applied Speciation and Consulting, LLC (Bothell, Washington). In these samples, selenite (Se^{4+}) was reported as having a value of $17.3 \mu\text{g L}^{-1}$ and selenate (Se^{6+}) a value of $329 \mu\text{g L}^{-1}$. Samples collected on April 15, 2009 were sent to the AEP-Dolan laboratory, in which selenite (Se^{4+}) was reported as having a value of $18.5 \mu\text{g L}^{-1}$ and selenate (Se^{6+}) a value of $285 \mu\text{g L}^{-1}$.

Treatments

Fly ash samples were collected at the Flint Creek plant via grab samples by an InterSystems Model XE0118 automated collection device (InterSystems, Omaha, Ne) installed on the fly ash collection piping on the outlet of the hot-side ESP. The ash collector took

approximately 5 g of ash sample, every 10 minutes, for a total of 30 days during normal plant operation. In-situ fly ash samples were collected randomly from the fly ash landfill at a depth of approximately 1.0 m (3.28 ft) using a backhoe. The actual age of the weathered samples is unknown due to the disposal methods of the ash. However, weathered samples were collected from an area of the landfill that is believed to have the oldest ash.

The gravimetric water content of the fly ash was determined by oven drying the ash at 105 °C for 24 h. After drying, weathered fly ash samples were manually ground and sieved to less than 2 mm. Fresh samples did not need to be ground and sieved. Pre-extraction pH and EC of the ash samples were measured using a 1:10 solid/solution ratio of ten grams of fly ash and 100 mL of DI water. Organic matter was determined by loss-on-ignition (LOI) by oven drying the ash at 750 °C for 1 hour. Fresh and weathered fly ash acid-recoverable Se, As, Cr, Sb, Ba, Be, Cd, Pb, Hg, Ni, Ag, and V were determined following EPA Method 200.7/6010B at the AEP Analytical Chemistry Services Laboratory (Shreveport, LA) using the Varian VistaPro inductively coupled plasma-optical emission spectrometer (ICP-OES; Agilent Technologies, Santa Clara, CA; EPA, 2007a). Chemical analysis (e.g., silicon dioxide, aluminum oxide, iron oxide, calcium oxide, magnesium oxide, sulfur trioxide, sodium oxide, and potassium oxide) of the fly ash samples were performed by the Analytical Testing Service Laboratories (Joplin, MO) using American Society for Testing and Materials (ASTM) standard method C-311 (ASTM, 2006). Fresh and weathered fly ash sample analyses were based on three replications. The Applied Speciation and Consulting, LLC (Bothell, WA) laboratory performed fresh and weathered ash speciation analysis via ion chromatography, inductively coupled plasma, collision-reaction-cell, mass spectrometry (IC-ICP-CRC-MS) using an Agilent 7700 Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Agilent Technologies, Santa Clara,

CA), on four replications of each ash type. The speciation analysis was a 2-hour alkaline extraction based on previous research by Jackson and Miller (2000).

The water-extraction treatments consisted of a 10:1 extractant-to-fly ash dilution ratio (30 mL extractant to 3 g fly ash) for all three extractant types at ambient room temperature, which is consistent with previous studies (Wang et al., 2007, McDonald et al., 2009, Daigh et al., 2010). Extraction was conducted using a 30 revolutions per minute (rpm) end-over-end shaker for 2 and 6 hours. Post-extraction pH and EC were measured potentiometrically before centrifuging the samples at 6000 rpm (11.5 G) for 10 minutes, followed by filtration using a 0.45- μ m Suppor-450 membrane filter (Pall Life Science, Port Washington, NY).

The filtrate was then preserved with Fisher® Optima Grade nitric acid to maintain a pH less than 2. The combination of the pH < 2 and the presence of the nitrate ions will keep the majority of the metals in solution preventing the formation of metal oxides and hydroxides in the presence of oxygen. The samples were cooled to a temperature of 4 °C (39.2 °F) for storage and shipment. Samples were labeled noting the date, time, analysis required, collection location, preservation method, person sampling, extraction time and extractant type. Duplicate treatment blanks were prepared to ensure proper quality assurance and quality control (QAQC). A chain of custody (COC) form was filled out with one copy being kept in the Flint Creek laboratory and one being sent with the samples. A total of 60 (e.g., 2 fly ash types x 3 extractants x 2 extractant times x 5 replications) water-extractant treatment samples and 12 treatment blanks (e.g., 3 extractants x 2 extractant times x 2 replications) were sent to the ETG lab for Se, As, and Cr analyses by Agilent 7500 Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Agilent Technologies, Santa Clara, CA). The ETG laboratory is certified by the Arkansas Department of Environmental Quality (Lab ID: 04-0574; Certification number: 10-063-0) for Se,

As, and Cr analyses. United States EPA Method 200.8/6020 was used as the procedure guidelines for the proper calibration and analysis of the samples (EPA, 1994; EPA, 2007b).

Water-Extractant Collection

Rainwater was collected in an agricultural field (e.g., pasture) in Washington County, AR during a single event, using multiple open containers. The groundwater sample was collected from an uncontaminated private well located adjacent to the landfill at a depth of approximately 61 meters (200 feet). Deionized water was collected from the outlet of the Flint Creek demineralizer. The Flint Creek demineralizer consists of a strong-acid cation and strong-base anion bed, followed by a mixed-bed polishing unit. Outflow from this design consistently produces ion concentrations of $<1 \mu\text{g L}^{-1}$. Water-extractant samples were stored at 4 °C and until the Se, As, and Cr concentrations of the extractant solution could be determined at the ETG laboratory based on three replications. The pH and EC were measured potentiometrically at the Flint Creek laboratory. AEP Analytical Chemistry Services Laboratory (Shreveport, LA) analyzed the water-extractant samples to determine the remaining metal and water-parameter values present.

Statistical Analyses

Using Minitab (version 13.31, Minitab Inc., State College, Penn.), a two-factor *t*-test was performed to determine differences between the fresh and weathered ash sample properties. One-factor analysis of variance (ANOVA) was performed using SAS (version 9.3, SAS Institute, Inc., Cary, NC) to compare differences in initial water-extractant characteristics and to identify possible contamination of treatment blanks. Two-factor ANOVA was used to determine the

effects of ash type, Se species, and their interaction on Se concentrations. Two-factor ANOVA was used to evaluate the effects of extraction time, extractant type, and their interaction on pH, EC, Se, As, and Cr concentrations in the blank samples. Three-factor ANOVA was used to evaluate the effects of ash type, extraction time, water-extractant type, and their interaction on pH, EC, Se, As, and Cr concentrations in the water-extractable treatment samples. Reported values were considered significantly different if the means were separated by least significant difference (LSD) at the 0.05 alpha level. Linear correlations were used to evaluate the effects of water extractant, extractant property, and extraction time on the relationship between suspension pH and EC, and water-soluble Se, As, and Cr concentrations for the weathered ash using Microsoft Excel (version 2010, Microsoft Corporation, Redmond, WA), with correlation coefficient (r) being significant at the 0.05 alpha level.

RESULTS AND DISCUSSION

Initial Ash Characteristics

Several initial chemical and physical characteristics differed between the two ash types (i.e., fresh and weathered). The fresh ash had lower water content (0.001 g g^{-1}) compared to the weathered ash (0.361 g g^{-1} ; $P < 0.001$; Table 2-6), which was expected due to the environmental exposure of each ash. Fresh ash was collected from the outlet piping of the ESPs where the fresh ash had been exposed to temperatures of approximately 400°C (752°F), while weathered ash was exposed to environmental weathering in the ash landfill. Organic matter differed ($P < 0.001$) between the fresh (0.39 %) and weathered ash (6.40 %; Table 2-6), which is consistent with the Class C fly ash organic matter concentration range of 0.32 to 17.52 % reported by Lou et al. (2011). At Flint Creek, normal plant operation results in fresh ash organic matter concentration that is consistently below 1.0 %; however, fresh ash organic matter was reported as high as 5.4 % for a short period in 1986, possibly due to poor pulverizer performance. Furthermore, exposure to environmental conditions (i.e., wind-blown organic matter as dust) at the landfill could contribute to the increased organic matter of the weathered ash. However, differences in initial ash organic matter concentration were not suspected to have affected the water-extractabilities of the trace metals because research by Lopez-Anton et al. (2006) reported that organic matter in fly ash does not significantly influence As or Se adsorption/retention onto the fly ash.

As expected, pH differed ($P < 0.001$) 0.4 units between the fresh (pH = 11.6) and weathered ash (pH = 11.2; Table 2-6). Previous studies (EPRI, 1998, 2012) investigating eastern bituminous, western subbituminous, low-sulfur bituminous, subbituminous, lignite, and subbituminous PRB fly ash reported that the most alkaline (pH = 11.05 to 12.57) ash suspension

was from subbituminous PRB ash. Environmental weathering and leaching of Ca, Fe, and S may have contributed to the lower pH of the weathered ash, which is supported by previous findings that fly ash with a Fe/Ca ratio > 3 produce acidic suspensions, while ratios < 3 generate alkaline suspensions (Mattigod et al., 1990). The fresh and weathered ash had Fe/Ca ratios of 0.21 and 0.20, respectively. Furthermore, fly ashes with Ca/S ratios < 2.5 produce acidic suspensions, while ratios > 2.5 generate alkaline suspensions (EPRI, 1987). The fresh and weathered ash had Ca/S ratios of 19.3 and 17.2, respectively. Both the Fe/Ca and Ca/S ratio comparisons supported the observations that weathering and leaching resulted in a lower pH for the weathered ash compared to the fresh ash.

Similarly, EC differed ($P < 0.001$) between ash types with EC being approximately two times greater for the fresh than weathered ash (Table 2-6), likely due to the leaching of major ash constituents such as Na, SO_4^{2-} , and B from the weathered ash, due to its environmental exposure. Due to the effects of time and exposure to water, major constituents can be released from the ash when exposed to water percolating downward through the ash. Comparing EC between studies can be difficult due to the wide array of solid/solution ratios, agitation times, and initial elemental concentrations; therefore, the EC difference between fresh and weathered ash is likely of more importance than the magnitude of the EC itself.

As expected, there were several differences in the oxide concentrations between ash types. Due to the suspected leaching and formation of secondary ash products, ferric oxide ($P < 0.01$), magnesium oxide ($P < 0.001$), and sodium oxide ($P < 0.001$) concentrations were lower for the weathered than fresh ash (Table 2-6). The sulfur trioxide concentration also differed ($P < 0.05$) between ash types; however, the weathered ash had a greater sulfur trioxide concentration (1.53 %) than the fresh ash (1.39 %; Table 2-6). Unexpectedly, the calcium oxide concentration

did not differ between ash types and averaged 26.6 % (Table 2-6). Silica was also greater ($P < 0.01$) in the fresh (34.9 %) than in the weathered ash (32.0 %; Table 2-6). Results from this study are consistent with the ASTM classification of Class C fly ash, which requires a minimum of 50 % SiO_2 , Al_2O_3 , and Fe_2O_3 and 20 % CaO, compared to Class F fly ash, which has a minimum SiO_2 , Al_2O_3 , and Fe_2O_3 concentration of 70 % and normal CaO concentration of < 10 % (ASTM, 2006).

Total acid-extractable Se and As concentrations did not differ between ash types and averaged $4.0 \text{ mg Se kg}^{-1}$ and $6.4 \text{ mg As kg}^{-1}$ between ash types (Table 2-6), which were similar to subbituminous PRB ash concentrations reported by Lou et al. (2011) and Seshadri et al. (2011), which ranged from 2.2 to $15.0 \text{ mg Se kg}^{-1}$ and from 1.8 to $26.9 \text{ mg As kg}^{-1}$. In comparison, research by EPRI (1987) reported mean bituminous ash Se and As concentrations of 12.3 and 219 mg kg^{-1} , respectively. Coals with large sulfur concentrations (i.e., bituminous) are expected to contain greater As concentrations compared to low-sulfur coals (i.e., subbituminous PRB) because As is associated with Fe sulfides and sulfide minerals in the coal (EPRI, 1998). In contrast, the acid-extractable Cr concentration was lower ($P < 0.05$) in the fresh (49.2 mg kg^{-1}) than in the weathered ash (52.0 mg kg^{-1} ; Table 2-6), which was similar to that for subbituminous ash Cr reported by EPRI (1987), with a mean of 73 mg kg^{-1} and a range from 41 to 108 mg kg^{-1} . Other acid-extractable metals that differed ($P < 0.05$) between ash types were Be, Cd, Pb, Hg, and V (Table 2-6). Unexpectedly, of these metals (i.e., Be, Cd, Pb, Hg, and V) only Be had a greater concentration in the fresh compared to the weathered ash.

The acid-extractable Cr concentration being greater in the weathered ash may be due to the coal mining location and/or combustion conditions that produced the ash (Lou et al., 2011). Even if the coal was from the same mine, differences can exist between the seams of coal.

Similarly, varying combustion conditions could affect trace metal release and re-precipitation onto the surface of the fly ash. Therefore, when trying to explain differences in trace metal concentrations between fresh and weathered ash, not only should leaching of trace elements be considered, but also factors such as coal source (i.e., differential coal seams) and combustion conditions. Furthermore, trying to compare ash trace metal concentrations among different studies can also be difficult because of the differences in power plant operating systems. For example, the coal source type (i.e., lignite, sub-bituminous, bituminous, anthracite), furnace design (i.e., wall-, tangential-, or cyclone-fired furnace), combustion conditions (i.e., combustion temperature, flue-gas duct temperature, ash/element reaction time, and post-combustion oxygen concentration), and differences in equipment design/environmental upgrades (i.e., cold- or hot-side ESPs, wet- or dry-ash handling system, activated-carbon injection, wet- or dry-scrubber, and selective catalytic reduction equipment) can have a dramatic effect on initial ash characteristics.

Another factor that may contribute to initial ash variability, but is seldom mentioned, is the collection location and resulting differences in relative enrichment of Se onto the fly ash particles. As fly ash particles pass through the multiple ESP fields, the ash particle size decreases resulting in increased fly ash surface area and increased Se adsorption (Huang et al., 2004). The first two fields of the Flint Creek ESP collect the majority of the larger diameter (i.e., 30 to 7.5 micron) fly ash particles, while fields three through eight capture the remaining ash particles (i.e., 7.5 to 3.5 micron). Therefore, as the fly ash passes through the eight fields of the Flint Creek ESP, greater Se adsorption, per volume of ash, should occur in the later fields. The first two fields will remove approximately 83 % of the ash particles (Neundorfer Particulate Knowledge, personal communication, 2013); however, per volume, greater Se adsorption should be occurring in the later fields. Adsorption rates differing among fields is important because if

samples are collected from an ash hopper underneath one of the later fields, then Se may be greatly enriched compared to that collected from an earlier field. Andren and Klein (1975) reported a fresh ash Se concentration of $28.0 \mu\text{g L}^{-1}$ at the inlet of the precipitator and concentration of $88.3 \mu\text{g Se L}^{-1}$ at the outlet. Therefore, reporting the exact fly ash collection location would provide useful insight in future studies. Collecting fly ash from an automated collection device installed on the outlet piping of the precipitator hoppers, or from a fly ash silo, may help reduce variability between initial trace metal concentrations in future studies.

As hypothesized, there were differences between fresh and weathered ash selenite (Se^{4+}) and selenate (Se^{6+}) concentrations. Selenite (Se^{4+}) was greater ($P < 0.001$) in the fresh (3.85 mg kg^{-1}) than in the weathered ash (0.70 mg kg^{-1}), while selenate (Se^{6+}) was lower ($P < 0.001$) in the fresh (0.48 mg kg^{-1}) than in weathered ash (0.67 mg kg^{-1} ; Table 2-6). Huggins et al. (2007) reported similar results with selenite (Se^{4+}) as the dominate species present in both fresh bituminous and subbituminous PRB ash. Comparing speciation across ash types, fresh ash selenite (Se^{4+}) was greater ($P < 0.001$; 3.85 mg kg^{-1}) than fresh ash selenate (Se^{6+} ; 0.48 mg kg^{-1}). In contrast, speciation did not differ between weathered ash selenite (Se^{4+}) and selenate (Se^{6+} ; 0.70 and 0.67 mg kg^{-1} ; respectively). When compared to total-acid extractable Se concentrations, the ash speciation extraction recovered 103 % of the fresh ash total Se, while only 36 % of the weathered ash total Se was recovered, based on the assumption that all Se species were present as selenite (Se^{4+}) and selenate (Se^{6+}). The difference between fresh and weathered ash speciation recovery was likely due to the lack of selenite (Se^{4+}) recovery in the weathered ash.

The differences between fresh and weathered ash selenite (Se^{4+}) concentrations were likely due to the formation of ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} - 26\text{H}_2\text{O}$] and calcium selenite

(CaSeO₃) precipitate following hydration (Lecuyer et al., 1996; Baur and Johnson, 2003; Huggins et al., 2007). Wang et al. (2007) reported similar conclusions that highly alkaline washed ash acted as a sink for selenite (Se⁴⁺) through ettringite formation or precipitation with Ca; however, almost all of the selenate (Se⁶⁺) remained in the soluble phase. Baur and Johnson (2003) reported that the precipitation of CaSeO₃ limited the solubility of selenite (Se⁴⁺) through the formation of inner-sphere complexes, while selenate (Se⁶⁺) has a lower affinity for Ca-oxide surfaces and forms weakly bound outer-sphere complexes. Furthermore, Solem-Tishmack et al. (1995) and Baur and Johnson (2003) reported that selenate (Se⁶⁺) was more readily leachable when bound to ettringite than selenite (Se⁴⁺). Selenite (Se⁴⁺) sorption by ettringite was found to be five times greater than sorption of selenate (Se⁶⁺; Baur and Johnson, 2003).

Formation of secondary hydrated products (i.e., ettringite and CaSeO₃) may take up to several months to allow equilibrium conditions to occur (Hassett and Pflughoeft-Hassett, 2002). Therefore, hydration during the 2-hour speciation extraction was not likely long enough to allow formation of the secondary hydrated products within the fresh ash that binds selenite (Se⁴⁺), which allows the selenite (Se⁴⁺) to become solubilized during the alkaline extraction. However, the pre-hydrated weathered ash (water content = 0.361 g g⁻¹; Table 2-6) would have stabilized the weathered ash ettringite and CaSeO₃ and prevented solubilization of selenite (Se⁴⁺; Lecuyer et al., 1996; Wang et al., 2009).

Initial Water-Extractant Characteristics

As expected, there were several differences among initial water extractants (i.e., deionized water, rainwater, and groundwater) used for the laboratory extractions. The pH differed ($P < 0.05$) among all three water extractants with deionized water having the most

alkaline pH (8.22), groundwater having a slightly alkaline, intermediate pH (7.64), and rainwater having the most acidic pH (5.24; Table 2-7). Similarly, EC differed between all three water extractants with groundwater being approximately 336 times greater and rainwater 4.5 times greater than that of deionized water (Table 2-7). Selenium, As, and Cr concentrations were all below instrument detection limits for all three water extractants (i.e., < 0.005 , < 0.005 , and $< 0.001 \text{ mg L}^{-1}$, respectively; Table 2-7). Sodium was the only other initial water-extractant property that differed ($P < 0.05$) between all three water-extractants, while Mn and TSS concentrations did not differ among the three water extractants (Table 2-7). The remaining initial water-extractant characteristics (i.e., Al, Ba, Ca, Cu, Mg, K, Sr, Zn, HCO_3 , total alkalinity, N, SiO_2 , and total dissolved solids) did not differ between the deionized water and rainwater; however, groundwater Al, Ba, Ca, Cu, Mg, K, Sr, Zn, HCO_3 , total alkalinity, N, SiO_2 , and total dissolved solid concentrations were all greater ($P < 0.05$) compared to deionized water and rainwater (Table 2-7).

Treatment Effects on Extractable Fly-Ash Properties

All extractable fly-ash properties evaluated were affected by one or more treatment factors examined. Suspension pH and EC differed ($P < 0.01$) between ash types, among extraction times, and across extractant types (Table 2-8). In contrast to suspension pH and EC, water-soluble Se and As concentrations differed ($P < 0.05$) between ash types across extractant types, while water-soluble Cr concentration differed between ash types among extraction times ($P < 0.01$) and differed between ash types across extractant types ($P = 0.02$; Table 2-8).

As expected, fresh ash suspension pH and EC extracted with deionized water, rainwater, and groundwater for 2- and 6-hours was greater ($P < 0.05$) than for weathered ash extracted over

the same treatments (Figure 2-13). Characteristics of the initial fresh and weathered ash, such as the Fe/Ca and Ca/S ratios, were likely responsible for the lower weathered ash suspension pH. Similarly, due to the suspected leaching of major elements from the weathered ash from environmental exposure, greater fresh-ash suspension EC occurred. Increasing the fresh and weathered ash extraction time from 2- to 6-hours across extractant types resulted in greater suspension pH and EC for all water extractants, except for the weathered ash EC extracted with groundwater, which did not differ between extraction times (Figure 2-13).

Fresh-ash suspension EC after 2 hours of extraction differed among all water extractants; EC averaged $2800 \mu\text{S cm}^{-1}$ from rainwater, $2710 \mu\text{S cm}^{-1}$ from deionized water, and $2500 \mu\text{S cm}^{-1}$ from groundwater (Figure 2-13). In contrast, the suspension EC for the weathered ash extracted for 2 hours did not differ ($P > 0.05$) among water extractants and averaged $1638 \mu\text{S cm}^{-1}$ (Figure 2-13). Both the fresh and weathered ash extracted with deionized water and rainwater for 6 hours resulted in similar suspension EC, but was 1.31 (fresh) and 1.07 (weathered) times greater than the suspension EC with groundwater after 6-hr extraction (Figure 2-13). The likely reason for differences between 2- and 6-hour suspension EC was that extraction for 2 hours was not long enough to allow maximum extraction to occur. Furthermore, the low ionic strength of the deionized water and rainwater, and resulting gradient difference with the ash, could possibly explain the greater suspension EC when deionized water or rainwater was used compared to groundwater.

Evaluating the fresh ash extracted for 2 hours, the suspension pH was lower ($P < 0.05$) when rainwater (pH = 11.84) and groundwater (pH = 11.82), which did not differ, were used as the extractants compared to deionized water (pH = 11.89; Figure 2-13). Similar to suspension EC, suspension pH for fresh ash extracted for 6 hours was similar between extraction with

deionized water and rainwater, but was 0.14 (deionized water) and 0.15 (rainwater) pH units greater than extraction with the environmentally representative groundwater (Figure 2-13). When comparing among water-extractant types for the 2 hour extraction of weathered ash, suspension pH was also greater with deionized water (pH = 11.41) and rainwater (pH = 11.40) as the extractant type, which did not differ, compared to extraction with groundwater (pH = 11.31; Figure 2-13). Weathered ash extracted for 6 hours resulted in a slightly decreasing suspension pH when deionized water (pH = 11.55), rainwater (pH = 11.51), and groundwater (pH = 11.41) were used (Figure 2-13). Consequently, deionized water should be used for any combination of ash type and extraction time to obtain maximum suspension pH. However, to ensure maximum fresh and weathered ash suspension pH and EC, it is recommended to perform a 6-hour extraction with deionized water even though several of the treatment factors did not differ between extraction with deionized water and rainwater. Using deionized water should ensure maximum suspension pH and EC and is readily available as compared to the collection of rainwater. Therefore, when focused exclusively on pH and EC, extraction with environmentally representative rainwater and groundwater offered no distinct benefits when compared to deionized water as the extractant of choice.

Averaged over extraction times, weathered ash Se and As concentrations differed among water-extractant types, while fresh ash Se and As concentrations did not differ between water-extractant types (Figure 2-14). Fresh ash extractable Se and As concentrations were reported at or near the minimum detection limit (MDL) for all three water-extractant types, possibly explaining the lack of difference between the three water-extractant types. The extractable As concentration in the weathered ash was greater ($P < 0.05$) with rainwater ($0.45 \mu\text{g L}^{-1}$) than with deionized water ($0.36 \mu\text{g L}^{-1}$), while the extractable As concentration from extraction with

groundwater was intermediate ($0.41 \mu\text{g L}^{-1}$) and similar ($P > 0.05$) to that from both rainwater and deionized water (Figure 2-14). In contrast, the extractable Se concentration from the weathered ash was greater ($P < 0.05$) with groundwater ($60.1 \mu\text{g L}^{-1}$) and rainwater ($59.8 \mu\text{g L}^{-1}$), which did not differ, than extraction with deionized water ($57.6 \mu\text{g L}^{-1}$; Figure 2-14). The Se and As results are consistent with previous research by Wang et al. (2009) who used a 10:1 dilution ratio of deionized water and subbituminous ash and reported that As was not detected under most experimental factors and that Se was more readily leachable than As.

When comparing extractable As between ash types and across water-extractant types, the reported results could be misleading because all of the mean extractable As concentrations were $< 0.5 \mu\text{g L}^{-1}$ (Figure 2-14). Since these concentrations are at and near the MDL of $0.2 \mu\text{g L}^{-1}$, it may be difficult to differentiate and compare reported As results with any type of confidence. Wang et al. (2009) reported that As did not leach from subbituminous ash until a 2:1 deionized water dilution ratio was used for a total of 30 days using a 180-revolutions-per-minute (rpm) shaker. Therefore, a longer extraction time and lower dilution ratio may be required to obtain more relevant data pertaining to water-soluble As concentrations.

Averaging over water-extractant types, weathered ash water-soluble Cr concentration increased as the extraction increased from 2 hours ($166.9 \mu\text{g L}^{-1}$) to 6 hours ($174.7 \mu\text{g L}^{-1}$; Figure 2-15). For comparison, EPRI (1994) reported that the water-soluble Cr fraction over a one-week laboratory extraction was 42.3 % (0.25 hr), 42.3 % (24 hr), 11.5 % (48 hr), and 3.9 % (168 hr) using a 10:1 dilution ratio. Therefore, it is recommended that, if Cr is the trace metal of interest, extraction occur for at least 24 hours to extract the majority of the water-soluble Cr from weathered ash. Water-soluble Cr concentration in the fresh ash was unaffected by extraction time and averaged $1.2 \mu\text{g Cr L}^{-1}$ (Figure 2-15). Similar to Se and As, fresh ash water-soluble Cr

concentration, averaged over extraction times, did not differ between water-extractant types as would be expected since measured concentrations were at or near the MDL (Figure 2-14).

However, for the weathered ash, extraction with groundwater resulted in a greater ($P < 0.05$) extractable Cr concentration ($176.3 \mu\text{g Cr L}^{-1}$) compared to that from rainwater ($170.1 \mu\text{g Cr L}^{-1}$) and deionized water ($166.0 \mu\text{g Cr L}^{-1}$), which did not differ (Figure 2-14).

Possible reasons for why weathered ash Se and Cr extraction was greatest with groundwater include differences in suspension pH and EC between the water extractants (Figure 2-13). Selenium and Cr can be incorporated into ettringite by substitution with the sulfate ion at $\text{pH} > 11.5$, but become unstable at a $\text{pH} < 10.7$ (Hassett and Pflughoeft-Hassett, 2002; EPRI, 2006c). Weathered ash extraction with groundwater resulted in the lowest suspension pH when compared to rainwater and deionized water (Figure 2-13). Therefore, a greater amount of Se or Cr could have been incorporated into the ettringite, due to the greater weathered ash suspension pH from extraction with deionized water and rainwater. The ettringite can act as a sink for Se or Cr and prevent solubilization (Lecuyer et al., 1996; Wang et al., 2007).

Furthermore, 6-hour extraction with deionized water and rainwater resulted in greater weathered ash suspension EC compared to that from groundwater (Figure 2-13). However, there was no difference in suspension EC between the water extractants for the 2-hour extraction. Increased suspension EC was likely a result of increased solutes dissolved in suspension. A portion of these solutes will be negatively charged, which may cause the negatively charged Se and Cr oxyanions to be repulsed at a greater extent in the weathered ash suspension. Repulsion between negatively charged anions should reduce the solubility of weathered ash Se and Cr, assuming that Cr was present in solution as the chromate oxyanion (CrO_4^{2-} ; Cr^{6+}) and not as the trivalent cation (Cr^{3+} ; EPRI, 2011). However, more evidence is needed to determine why greater

weathered ash Se and Cr extraction occurred with environmentally representative groundwater. Furthermore, previous explanations do not explain why weathered ash Se extraction with rainwater and groundwater did not differ. Weathered ash suspension pH and EC did not differ between rainwater and deionized water, except for the 6-hour extraction suspension pH (Figure 2-13).

From these results, it is clear that a significant difference existed between fresh and weathered ash Se and Cr water-soluble concentrations, with possible differences between fresh and weathered ash water-soluble As concentrations. Information regarding oxidation state (i.e., speciation) is essential in understanding and predicting Se, As, and Cr behavior and may help explain the extraction differences between ash types (EPRI, 1998). For example, selenite (Se^{4+}), arsenate (As^{5+}), and trivalent (Cr^{3+}) Cr are known to be less water-soluble than selenate (Se^{6+}), arsenite (As^{3+}), and hexavalent (Cr^{6+}) Cr (EPRI, 2006a). When examining speciation, the initial speciation within the coal is not important because virtually all of the Se, As, and the majority of the Cr is volatilized into the gas phase during combustion; therefore, the initial coal speciation has no effect on post-combustion speciation (Huggins et al., 2007).

As fly ash weathers, trace metal speciation may also change, resulting in a change in leaching behavior. For example, selenate (Se^{6+}) is very soluble, while selenite (Se^{4+}) only sparingly soluble and limited by adsorption to hydrous oxide surfaces. EPRI (2006a) reported that Se in weathered sub-bituminous ash landfill leachate was almost entirely in the selenate (Se^{6+}) form. However, Wang et al. (2009) reported that fresh sub-bituminous PRB ash exhibited low-leaching potential, which is consistent with Se in the selenite (Se^{4+}) form; therefore, the field-derived data may indicate conversion from selenite (Se^{4+}) to selenate (Se^{6+}) from environmental exposure in the landfill. Speciation may explain the differences noted between

fresh and weathered ash water-soluble Se concentrations. Assuming that all Se species were present as selenite (Se^{4+}) and selenate (Se^{6+}), fresh ash Se was predominately in the less-water-soluble selenite (Se^{4+}) form (88.9 %), compared to selenate (Se^{6+} ; 11.1 %), likely explaining why fresh ash water-extractable Se concentrations were at or below MDL for all three water-extractants (Figure 2-14). Similarly, Narukawa et al. (2005) reported fresh ash water-soluble Se concentrations were present predominately as selenite (Se^{4+}), but the coal source was not reported.

Mattigod and Quinn (2003) reported that selenite (Se^{4+}) from subbituminous ash was completely oxidized to selenate (Se^{6+}) after one week using a 4:1 dilution ratio. In contrast, Wang et al. (2009) reported that an extraction time of 30 days had no effect on Se speciation conversion from selenite (Se^{4+}) to selenate (Se^{6+}) under natural conditions (i.e., exposed to air), regardless of dilution ratio. Therefore, in some instances, 30 days may not be enough exposure to stimulate a change in Se speciation. Environmental weathering in the landfill may have affected Se speciation, promoting the oxidation of selenite (Se^{4+}) to selenate (Se^{6+}). The highly water-soluble selenate (Se^{6+}) concentrations were greater ($P < 0.001$) in the weathered (0.67 mg kg⁻¹) than the fresh ash (0.48 mg kg⁻¹), while selenite (Se^{4+}) concentrations were less ($P < 0.001$) in the weathered (0.70 mg kg⁻¹) than in the fresh ash (3.85 mg kg⁻¹). Therefore, speciation likely explains the greater water-extractable weathered ash Se concentrations across all three water-extractants (Figure 2-14).

Compared to As, Wang et al. (2009) reported no significant change in speciation of As during a 30 day extraction. Wang et al. (2009) also reported non-detectable As concentrations for the fresh subbituminous PRB ash except with a 2:1 dilution ratio and 30-day extraction, which resulted in water-soluble As concentrations of 20 µg L⁻¹, which was primarily in the

arsenate (As^{5+}) form. Narukawa et al. (2005) reported fresh ash water-soluble As concentrations were dominated by the less mobile and less toxic arsenate (As^{5+}) form, but did not report the coal source. Huggins et al. (2007) reported similar results with arsenate (As^{5+}) as the dominate species present in both fresh bituminous and subbituminous PRB ash, thereby likely explaining the fresh ash water-extractable As concentrations being at or the near the MDL across all three extractants.

Minimal water-extractable weathered ash As concentrations may be explained by the high-calcium content of the ash, which may have attributed to As precipitation with the Ca, or substitution with ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} - 26\text{H}_2\text{O}$]. Selenium, As, and Cr can be incorporated (i.e., substituted) into ettringite at pHs > 11.5, but become unstable at a pH < 10.7 (EPRI, 2006c), which is consistent with measured suspension pH values from this study (Figure 2-13). However, ettringite formation has been reported by Hassett et al. (2005) as a long-term process (i.e., > 18 hours) between water and ash; therefore, fresh ash extraction should not have been affected by ettringite formation because the fresh ash was not exposed to water prior to extraction in this study.

Speciation may also explain increased water-extraction from the weathered ash. In fresh ash samples, Stam et al. (2011) reported that the less mobile trivalent (Cr^{3+}) Cr was the dominate species present. However, the alkaline pH suspension of subbituminous PRB ash promotes conversion of trivalent (Cr^{3+}) Cr to the more water-soluble hexavalant (Cr^{6+}) Cr (EPRI, 1986, 2011). Similarly, in a study of 29 landfill leachates, EPRI (2006a) reported hexavalant (Cr^{6+}) Cr as the dominate species present when pH was greater than 6, with concentrations of 0.5 to 5,100 $\mu\text{g Cr L}^{-1}$. Although Cr speciation analyses was not performed, a comparison can be made between Se and Cr because of mobility similarities, results from previous research, and

differences between fresh and weathered ash water-extractable Cr concentrations which indicate that trivalent (Cr^{3+}) Cr was the likely the dominant Cr species in the fresh ash and the hexavalent (Cr^{6+}) Cr was the likely dominant species in the weathered ash.

Water-Soluble Se, As, and Cr Fractions

To better characterize fly ash trace metals, Narukawa et al. (2005) and Yuan (2009) performed a chemical fractionation that distributed trace metals into five fractions: water-soluble, acid-soluble (i.e., bound to carbonates; extracted with acetic acid), reducible (i.e., bound to Fe-Mn oxides), oxidizable (i.e., bound to organic matter), and residual (i.e., bound to silica; extracted with HNO_3 and HCl). Of these, the water-soluble fraction is the most readily available fraction that can be easily released into the environment through contact with rainwater and groundwater. Averaged over extraction time and extraction type, the total water-soluble fraction of Se, As, and Cr was determined for fresh and weathered ash. The fresh ash water-soluble fraction for Se (0.05 %), As (< 0.01 %), and Cr (< 0.01 %) were very low since concentrations were at, or near, MDL values. The weathered water-soluble fraction for Se, As, and Cr was 1.6, 0.01, and 0.33 %, respectively, which is lower than reported fresh-ash results by Narukawa et al. (2005) and Yuan (2009). However, ash samples from Narukawa et al. (2005) and Yuan (2009) were collected at eight different locations throughout the world and exhibited different initial ash characteristics than those in this study.

Correlations among Ash Properties

Linear correlations were used to evaluate the effects of water extractant, extractant property, and extraction time on the relationship between suspension pH, and EC, and water-

soluble Se, As, and Cr concentrations. Only weathered ash data were analyzed since the fresh ash water-soluble Se, As, and Cr concentrations were all reported at or near the MDL. Water-soluble Se concentration was positively correlated ($r = 0.95$; $P < 0.01$) with suspension EC for weathered ash extracted for 6 hours with rainwater (Table 2-9). Similarly, weathered ash water-soluble Se concentrations was positively correlated ($r = 0.96$; $P < 0.01$) with suspension pH for the 2-hour extraction with deionized water (Table 2-9).

In contrast to Se, weathered ash As and Cr concentrations were unrelated to suspension pH. Weathered ash water-soluble As concentration was inversely related ($r = -1.00$; $P < 0.001$) to suspension EC for the 2-hour extraction with rainwater (Table 2-9); however, four of the five replicate concentrations were $0.5 \mu\text{g L}^{-1}$, with the other being $0.4 \mu\text{g L}^{-1}$, possibly skewing the data. Therefore, in contrast to the statistical data, no linear relationship between water-soluble As and suspension EC was suspected. Extraction for 2 hours with deionized water resulted in an inverse relationship ($r = -0.93$; $P < 0.05$) between weathered ash water-soluble Cr concentration and suspension EC (Table 2-9).

Although some of the data appear to support a linear relationship between weathered ash properties for various treatments (i.e., water extractant and extraction time), several underlying variables/factors may be skewing this data since there appears to be little to no consistency within combinations. For example, previous research (EPRI, 2006a; Wang et al. 2007) has reported a strong linear relationship between water-soluble Se and pH; however, these data were collected over a wide pH range (i.e., 2-12), while site-specific, weathered ash suspension pH from this study only varied by 0.26 units. Therefore, treatment effects on linear relationships among weathered ash properties can neither be proved nor disproved for this body of work.

Environmental Implications

The relatively long lag period (~24 years) before Se became mobilized and transported with the groundwater past the boundaries of the landfill was likely due to the low moisture content of fresh ash deposited at the landfill (Table 2-6). Since the ash moisture content was extremely low compared to the underlying soils, minimal drainage from the ash would have occurred until the ash approached or surpassed field moisture capacity (EPRI, 2002; Hillel, 2004). Fresh ash continually deposited in the landfill would also have prolonged this lag period (EPRI, 2002). However, eventually the moisture content increased until the ash was moist enough to allow infiltration into the ash and drainage through the material in the landfill (EPRI, 2002; Hillel, 2004).

Following installation of the intermediate liner and leachate collection system, contact between percolating rainwater and the fly ash underneath the intermediate liner should be eliminated. However, immediate mitigation will not occur because accumulated moisture within the fly ash will likely continue to leach out the readily available water-soluble Se, and other trace metals, in the weathered ash (Figure 2-14; EPRI, 2001). Once the moisture source is eliminated, the fly ash will reach field capacity and recharge beneath the landfill should be eliminated (EPRI, 2002; Hillel, 2004). It is unknown what the lag time will be before Se concentrations are reduced below the GWPS of $50 \mu\text{g Se L}^{-1}$. Previous research by EPRI (2002), reported effective remediation (i.e., groundwater concentrations $< 5 \mu\text{g Se L}^{-1}$) of Se from groundwater within four years after installation of a 60 mil HDPE liner. Hydraulic conductivity values between the EPRI (2002) research site (i.e., $2.4 \times 10^{-3} \text{ cm s}^{-1}$) and the Flint Creek site (Table 2-5) are similar; however, groundwater Se concentrations were lower ($\sim 60 \mu\text{g Se L}^{-1}$) at the EPRI (2002) research site. Eliminating the Se source should reduce groundwater Se concentrations and

prevent concentrations from increasing down gradient of the plume through adsorption to soil, biological reduction, and dilution processes.

Following installation of the liner, percolating rainwater will have considerably less contact with the fly ash deposited on top of the liner. This will especially be true within the years directly after installation of the liner because the depth at which the fly ash will be deposited on top of the intermediate liner will be substantially less compared to the average thickness (i.e., 10.7 m; 35 feet) of the current weathered ash. With less contact between the ash and percolating rainwater, the speciation could be different and the release of Se could be lower than compared to the characteristics of the pre-liner leachate. The reaction kinetics of the oxidation of selenite (Se^{4+}) to selenate (Se^{6+}) are not well understood, but appear to be a slow process (Seby et al., 1998). Therefore, results from this extraction study may also provide insight into the post-liner leachate Se concentrations entering the ABMet™ bioreactors.

SUMMARY AND CONCLUSIONS

When performing an environmental assessment of the potential environmental impact of trace elements in fly ash, the total concentration is not nearly as important as knowing the water-soluble and speciation fractions. The water-soluble fraction is the most likely fraction to be released into the environment and the speciation is what determines the mobility and toxicity once released. Fresh and weathered subbituminous PRB fly ash had significantly different water-soluble Se, As, and Cr leaching characteristics, with fresh ash water-soluble concentrations at or very near the MDL across all treatments. Differences between fresh and weathered ash were likely due to the speciation present in the ash. Selenite (Se^{4+}) was shown to be the dominate species present in the fresh ash, likely preventing the release of Se during the water-

extraction study. Once landfilled, environmental weathering promotes the oxidation of selenite (Se^{4+}) to the highly mobile, water-soluble selenate (Se^{6+}).

Although Cr and As speciation analyses was not performed, differences between fresh and weathered ash water-soluble Cr concentrations indicate that the less water-soluble trivalent (Cr^{3+}) Cr was likely dominate in the fresh ash and the more water-soluble hexavalent (Cr^{6+}) Cr was likely dominate in the weathered ash. Weathered ash water-soluble Se and Cr concentrations indicate that there is still a significant amount of Se and Cr readily available to be released into the environment if allowed to come in contact with rainwater or groundwater. Fresh and weathered ash water-soluble As concentrations at or near the MDL were likely due to As existing and remaining in the arsenate (As^{5+}) form. Previous research indicates that the less water-soluble arsenate (As^{5+}) is the dominate species present in fresh subbituminous PRB ash and it is unlikely that the arsenate (As^{5+}) is being reduced to the more water-soluble arsenite (As^{3+}) in the landfill (Huggins et al., 2007). Therefore, results from this study indicate that speciation is likely responsible for the differences between extraction behavior of fresh and weathered ash Se, As, and Cr concentrations.

Weathered ash water-soluble Se concentrations were greatest when extraction occurred with environmentally representative rainwater and groundwater. Similarly, weathered ash water-extractable Cr concentration was greatest with groundwater. Selenium and As extraction was unaffected by extraction time; however, weathered ash water-soluble Cr concentration increased as the extraction time increased from 2- to 6-hours. This research was not able to demonstrate if 6 hours was enough time to ensure maximum Cr extraction; therefore, a 24-hour extraction is recommended for Cr (EPRI, 1994). Water-soluble As concentrations were too near the MDL to make an informed decision for both fresh and weathered ash. Therefore, a longer extraction time

and lower dilution ratio may be required to obtain measurable water-extractable As concentrations from a Class C fly ash (Wang et al., 2009). To obtain maximum fresh and weathered ash suspension pH and EC, it is recommended to perform at minimum a 6-hour extraction with deionized water for both fresh and weathered ash. Extraction with environmentally representative rainwater and groundwater offered no distinct benefits when compared to deionized water as the extractant of choice for suspension pH and EC.

It should be re-iterated that results from this study were derived from the extraction of a Class C fly ash produced from the combustion of a subbituminous PRB coal and may not be comparable to extraction from Class F fly ash, whereas the goal of this study was to better understand the behavior of a site-specific fly ash and not fly ash in a holistic sense.

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Table 2-1. Analysis of sub-bituminous coal used at the Flint Creek Power Plant for electrical generation.[†]

Parameter	Values
Proximate Analysis (wt %)	
Moisture	28.4
Ash, dry	6.4
Volatile Matter, dry	43.8
Fixed Carbon, dry	49.8
Ultimate Analysis (wt %)	
Carbon	69.7
Hydrogen	4.8
Nitrogen	0.9
Chlorine	< 0.01
Sulfur	0.31
Ash	6.4
Oxygen	17.89
Trace Elements (mg kg ⁻¹)	
Arsenic	< 1
Barium	346
Beryllium	0.2
Boron	27
Cadmium	< 0.2
Chlorine	13
Chromium	4
Copper	11
Fluorine	70
Lead	2
Manganese	7
Mercury	0.06
Molybdenum	< 2
Nickel	3
Selenium	< 1
Silver	< 0.2
Strontium	160
Thallium	< 1
Tin	< 1
Vanadium	10
Zinc	7
Zirconium	14

[†]Samples were collected and analyzed at the Rochelle/ North Antelope mine (Wyodak-Anderson Seam in Wyoming.

Table 2-2. Flint Creek fly ash samples analyzed for leaching using the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Precipitation Leaching Procedure (SPLP).

Parameter	TCLP Metals	SPLP Metals
Arsenic (mg L ⁻¹)	< 0.02	< 0.02
Barium (mg L ⁻¹)	3.22	14.6
Cadmium (mg L ⁻¹)	< 0.001	< 0.001
Chromium (mg L ⁻¹)	0.17	< 0.01
Lead (mg L ⁻¹)	< 0.02	< 0.02
Mercury (mg L ⁻¹)	< 0.05	< 0.05
Selenium (mg L ⁻¹)	0.22	< 0.02
Silver (mg L ⁻¹)	< 0.001	< 0.001

Table 2-3. Assessment monitoring constituent (AMC) list for the groundwater protection standard (GWPS) sampled quarterly (AEP, 2010; EPA, 2011).

Constituent	GWPS
Arsenic, total (mg L ⁻¹)	0.01
Barium, total (mg L ⁻¹)	2.0
Boron, total (mg L ⁻¹)	7.3
Cadmium, total (mg L ⁻¹)	0.005
Chloride (mg L ⁻¹)	Standard not applicable
Chromium, total (mg L ⁻¹)	0.1
Copper, total (mg L ⁻¹)	1.3
Fluoride (mg L ⁻¹)	4.0
Iron, total (mg L ⁻¹)	11.0
Lead, total (mg L ⁻¹)	0.015
Manganese, total (mg L ⁻¹)	1.7
Mercury, total (mg L ⁻¹)	0.002
Molybdenum, total (mg L ⁻¹)	0.18
pH (field)	3.79 to 9.0
Selenium, total (mg L ⁻¹)	0.05
Silver, total (mg L ⁻¹)	0.18
Sulfate (mg L ⁻¹)	1200
Total Dissolved Solids (mg L ⁻¹)	Standard not applicable
Turbidity (field)	Standard not applicable
Zinc, total (mg L ⁻¹)	11.0

Table 2-4. Expanded Parameter (EP) list for the groundwater protection standard (GWPS) sampled once every three years (AEP, 2010; EPA, 2011).

Constituent	GWPS
Aluminum, total (mg L ⁻¹)	37.0
Antimony, total (mg L ⁻¹)	0.006
Arsenic, total (mg L ⁻¹)	0.01
Barium, total (mg L ⁻¹)	2.0
Beryllium, total (mg L ⁻¹)	0.004
Boron, total (mg L ⁻¹)	7.3
Cadmium, total (mg L ⁻¹)	0.005
Chloride (mg L ⁻¹)	Standard not applicable
Chromium, total (mg L ⁻¹)	0.1
Cobalt, total (mg L ⁻¹)	0.73
Copper, total (mg L ⁻¹)	1.3
Flouride, total (mg L ⁻¹)	4.0
Iron, total (mg L ⁻¹)	0.015
Manganese, total (mg L ⁻¹)	1.7
Mercury, total (mg L ⁻¹)	0.002
Molybdenum, total (mg L ⁻¹)	0.18
Nickel, total (mg L ⁻¹)	0.73
pH (field)	3.79 to 9.0
Potassium, total (mg L ⁻¹)	Standard not applicable
Selenium, total (mg L ⁻¹)	0.05
Silver, total (mg L ⁻¹)	0.18
Sodium (mg L ⁻¹)	Standard not applicable
Strontium, total (mg L ⁻¹)	22.0
Sulfate (mg L ⁻¹)	1200
Sulfide (mg L ⁻¹)	Standard not applicable
Thallium (mg L ⁻¹)	0.002
Tin, total (mg L ⁻¹)	22.0
Total dissolved solids (mg L ⁻¹)	Standard not applicable
Total suspended solids (mg L ⁻¹)	Standard not applicable
Vanadium, total (mg L ⁻¹)	0.037
Zinc, total (mg L ⁻¹)	11.0

Table 2-5. Hydraulic conductivity values for groundwater monitoring wells located at the Flint Creek ash landfill based on slug tests.

Groundwater Monitoring Well	Hydraulic Conductivity (cm sec ⁻¹)	Hydraulic Conductivity (feet sec ⁻¹)	Hydraulic Conductivity (feet yr ⁻¹)
B-01B [†]	1.18E-06	3.87E-08	1.2
B-02 [†]	7.31E-03	2.40E-04	7,563
B-04 [†]	4.02E-03	1.32E-04	4,159
B-05 [†]	9.64E-05	3.16E-06	100
B-06 [†]	5.59E-03	1.83E-04	5,784
NE-1 [‡]	6.30E-04	2.07E-05	652
NE-2 [‡]	1.91E-03	6.27E-05	1,976
NE-3 [‡]	2.48E-02	8.14E-04	25,659

[†]Slug tests were performed during March 2005.

[‡]Slug tests were performed during September 2009.

Table 2-6. Two-sample t-test summary of the initial ash characteristics used in the laboratory extractions. Mean (n = 3) values (Standard error) are reported.

Ash property	Weathered ash	Fresh ash
Water Content (g g ⁻¹)	0.361 (0.00)	0.001 (< 0.01) ***
Fineness (> 325 Mesh; %)	65.80 (1.15)	22.83 (0.43)***
Organic Matter (%)	6.40 (0.02)	0.39 (0.00) ***
Electrical Conductivity (μS cm ⁻¹)	810 (8.57)	1682 (5.36) ***
pH	11.2 (0.01)	11.6 (0.01) ***
Antimony (mg kg ⁻¹)	< 0.25 [†]	< 0.25 [†]
Arsenic (mg kg ⁻¹)	5.82 (0.08)	6.93 (0.26)
Barium (mg kg ⁻¹)	209 (5.77)	405 (77.49)
Beryllium (mg kg ⁻¹)	2.41 (0.05)	2.66 (0.05) *
Cadmium (mg kg ⁻¹)	1.02 (0.01)	0.88 (0.00) **
Chromium (mg kg ⁻¹)	51.97 (0.49)	49.23 (0.12) *
Lead (mg kg ⁻¹)	26.30 (0.22)	23.97 (0.12) **
Mercury (mg kg ⁻¹)	0.01 (0.00)	< 0.01 [†] ***
Nickel (mg kg ⁻¹)	37.83 (0.43)	38.83 (0.35)
Selenium (mg kg ⁻¹)	3.81 (0.08)	4.21 (0.15)
Selenite (mg kg ⁻¹)	0.70 (0.01)	3.85 (0.30)***
Selenate (mg kg ⁻¹)	0.67 (0.01)	0.48 (0.01)***
Silver (mg kg ⁻¹)	< 0.05 [†]	< 0.05 [†]
Vanadium (mg kg ⁻¹)	193.7 (1.86)	173.3 (1.20) ***
Silica (%)	32.04 (0.34)	34.92 (0.19)**
Aluminum Oxide (%)	21.55 (0.15)	21.69 (0.09)
Ferric Oxide (%)	5.20 (0.05)	5.55 (0.03)**
Sulfur Trioxide (%)	1.53 (0.03)	1.39 (0.02)*
Calcium Oxide (%)	26.3 (0.22)	26.8 (0.17)
Magnesium Oxide (%)	5.14 (0.05)	5.69 (0.03)***
Sodium Oxide (%)	1.73 (0.02)	1.87 (0.00)***
Potassium Oxide (%)	0.39 (0.07)	0.41 (0.01)
Available Alkalies as NaO (%)	1.31 (0.01)	1.50 (0.02)***

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

[†]Values were below detection limits, and therefore no SE is reported.

Table 2-7. Analysis of variance summary of the initial water extractant characteristics used during the laboratory extractions. Mean (n = 3) values (Standard error) are reported. For the purpose of conducting statistical analyses, concentrations below instrument detection limits were reported as the detection limit value.

Extractant property	Extractant		
	Deionized water	Rainwater	Groundwater
Electrical Conductivity ($\mu\text{S cm}^{-1}$)	0.88 (< 0.01)a [†]	4.11 (< 0.01)b	295.6 (0.58)c
pH	8.22 (0.01)a	5.24 (0.02)b	7.64 (0.02)c
Aluminum (mg L^{-1})	< 0.005 [‡] a	< 0.005 [‡] a	0.007 (0.00)b
Arsenic (mg L^{-1})	< 0.005 [‡]	< 0.005 [‡]	< 0.005 [‡]
Barium (mg L^{-1})	< 0.001 [‡] a	< 0.001 [‡] a	0.031 (0.00)b
Calcium (mg L^{-1})	0.025 (0.01)a	0.193 (0.014)a	71.85 (0.55)b
Chromium (mg L^{-1})	< 0.001 [‡]	< 0.001 [‡]	< 0.001 [‡]
Copper (mg L^{-1})	0.001 (0.00)a	< 0.001 [‡] a	0.002 (0.00)b
Hardness, Ca (mg L^{-1})	0.06 (0.01)a	0.481 (0.035)a	179.5 (1.50)b
Hardness, Mg (mg L^{-1})	< 0.04 [‡] a	0.055 (0.01)a	3.21 (0.02)b
Hardness, Total (mg L^{-1})	0.075 (0.01)a	0.532 (0.039)a	182.5 (1.50)b
Magnesium (mg L^{-1})	< 0.01 [‡] a	0.01 (0.00)a	0.780 (0.01)b
Manganese (mg L^{-1})	0.002 (0.00)	< 0.001 [‡]	< 0.001 [‡]
Potassium (mg L^{-1})	< 0.01 [‡] a	0.02 (0.00)a	0.487 (0.01)b
Selenium (mg L^{-1})	< 0.005 [‡]	< 0.005 [‡]	< 0.005 [‡]
Sodium (mg L^{-1})	< 0.01 [‡] a	0.06 (0.00)b	1.77 (0.02)c
Strontium (mg L^{-1})	< 0.001 [‡] a	< 0.001 [‡] a	0.036 (0.00)b
Zinc (mg L^{-1})	< 0.005 [‡] a	< 0.005 [‡] a	0.015 (0.00)b
Bicarbonate (mg L^{-1})	10 (0.00)a	10 (0.00)a	161.5 (0.50)b
Total Alkalinity (mg L^{-1})	10 (0.00)a	10 (0.00)a	161.5 (0.50)b
Nitrate-N (mg L^{-1})	< 1.0 [‡] a	< 1.0 [‡] a	1.2 (0.00)b
Residue, Total (mg L^{-1})	9.50 (2.50)a	31.5 (23.50)a	202 (2.00)b
Silica (mg L^{-1})	< 0.1 [‡] a	< 0.1 [‡] a	8.3 (0.00)b
Total Dissolved Solids (mg L^{-1})	9.00 (3.00)a	12 (4.00)a	199.5 (4.50)b
Total Suspended Solids (mg L^{-1})	< 1 [‡]	< 1 [‡]	< 1 [‡]

[†]Means followed by different letters in a row are significantly different at the 0.05 level.

[‡]Values were below detection limits, and therefore no SE is reported.

Table 2-8. Analysis of variance summary of the effects of ash type, extraction time, extractant type, and their interaction on suspension pH and electrical conductivity (EC), and water-extractable selenium (Se), arsenic (As), and chromium (Cr) concentrations.

Source of Variation	pH	EC	Se <i>P</i>	As	Cr
Ash Type (Ash)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Extraction Time (Time)	< 0.01	< 0.01	0.41	0.86	0.01
Extractant Type (Extractant)	< 0.01	< 0.01	0.03	0.44	< 0.01
Ash x Time	0.69	< 0.01	0.41	0.39	< 0.01
Ash x Extractant	0.62	< 0.01	0.03	0.04	0.02
Time x Extractant	< 0.01	< 0.01	0.80	0.44	0.68
Ash x Time x Extractant	< 0.01	< 0.01	0.80	0.22	0.99

Table 2-9. Summary of the effects of water extractant and extractant property on linear correlations (r) between suspension pH and EC, and water-soluble selenium (Se), arsenic (As), and chromium (Cr) concentrations for the weathered ash samples.

Extractant Property	Extractant	2 hr			6 hr		
		Se	As	Cr	Se	As	Cr
pH	DI	0.96**	-0.64	0.54	-0.45	0.40	-0.29
	RW	0.19	0.78	0.69	0.85	0.33	0.08
	GW	-0.34	-0.27	0.37	-0.72	0.34	-0.86
EC [†] ($\mu\text{S cm}^{-1}$)	DI	-0.72	0.45	-0.93*	0.59	0.09	0.31
	RW	0.29	-1.00***	-0.23	0.95**	0.64	0.59
	GW	-0.22	0.12	-0.29	0.80	-0.06	0.46

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

[†]Electrical conductivity

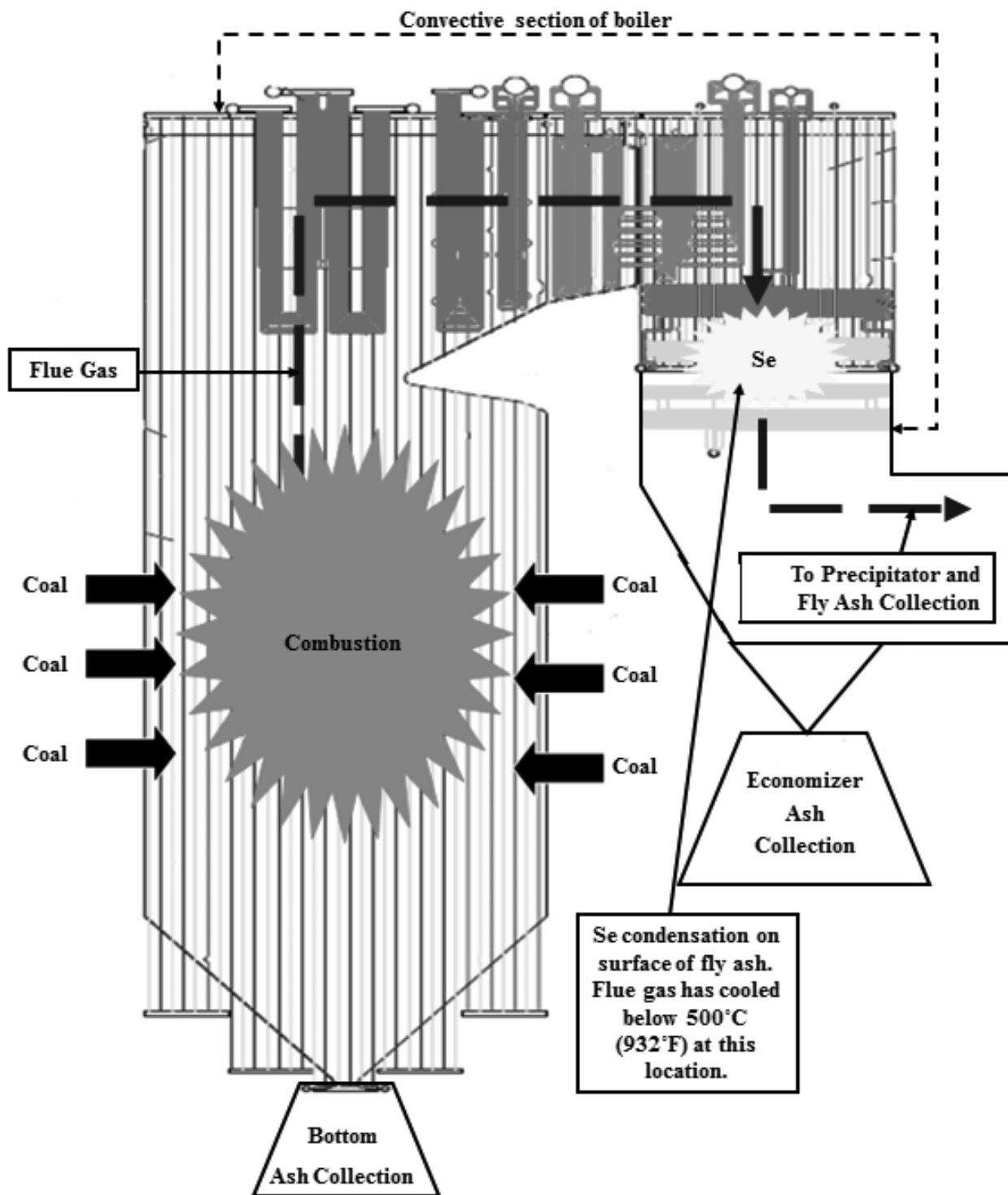


Figure 2-1. Basic diagram of the boiler at the Flint Creek Power Plant. Selenium that is naturally enriched in the coal volatilizes upon combustion and is carried with the flue gas stream through the convective section of the boiler. The flue gas enters the convective section around 1371 °C (2500 °F) and cools to a temperature of 399 °C (750 °F) before exiting the convective section. Selenium will condense on the surface of the fly ash at temperatures below 500 °C (932 °F; Sargent and Lundy Engineers, 1974).

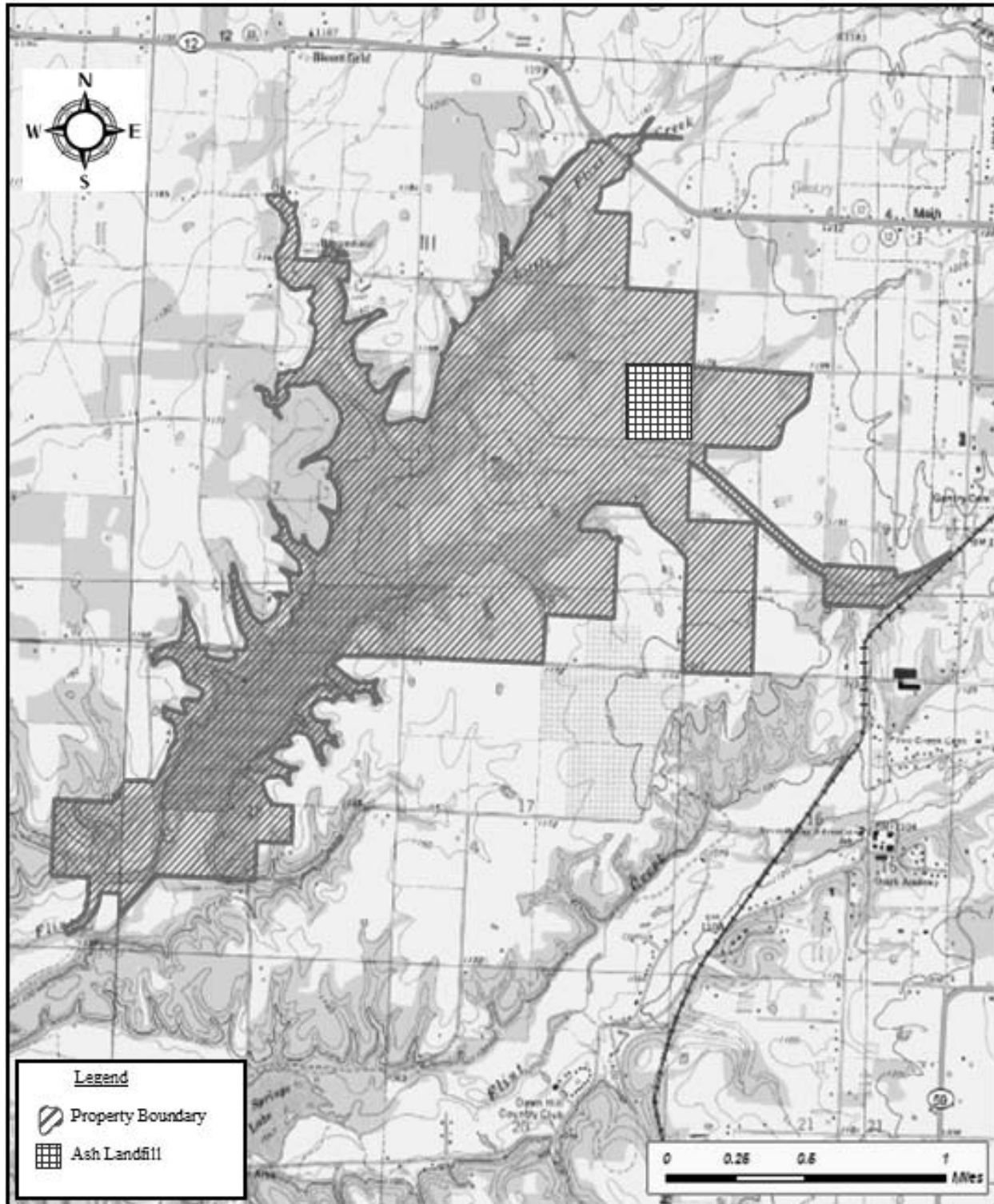


Figure 2-2. Topographic map showing the property boundary for the Flint Creek Power Plant in relation to the ash landfill. Total property owned by American Electric Power (AEP) is approximately 607 hectares (1,500 acres). Modified from AEP Real Estate Asset Mgmt. Dept. (2010).

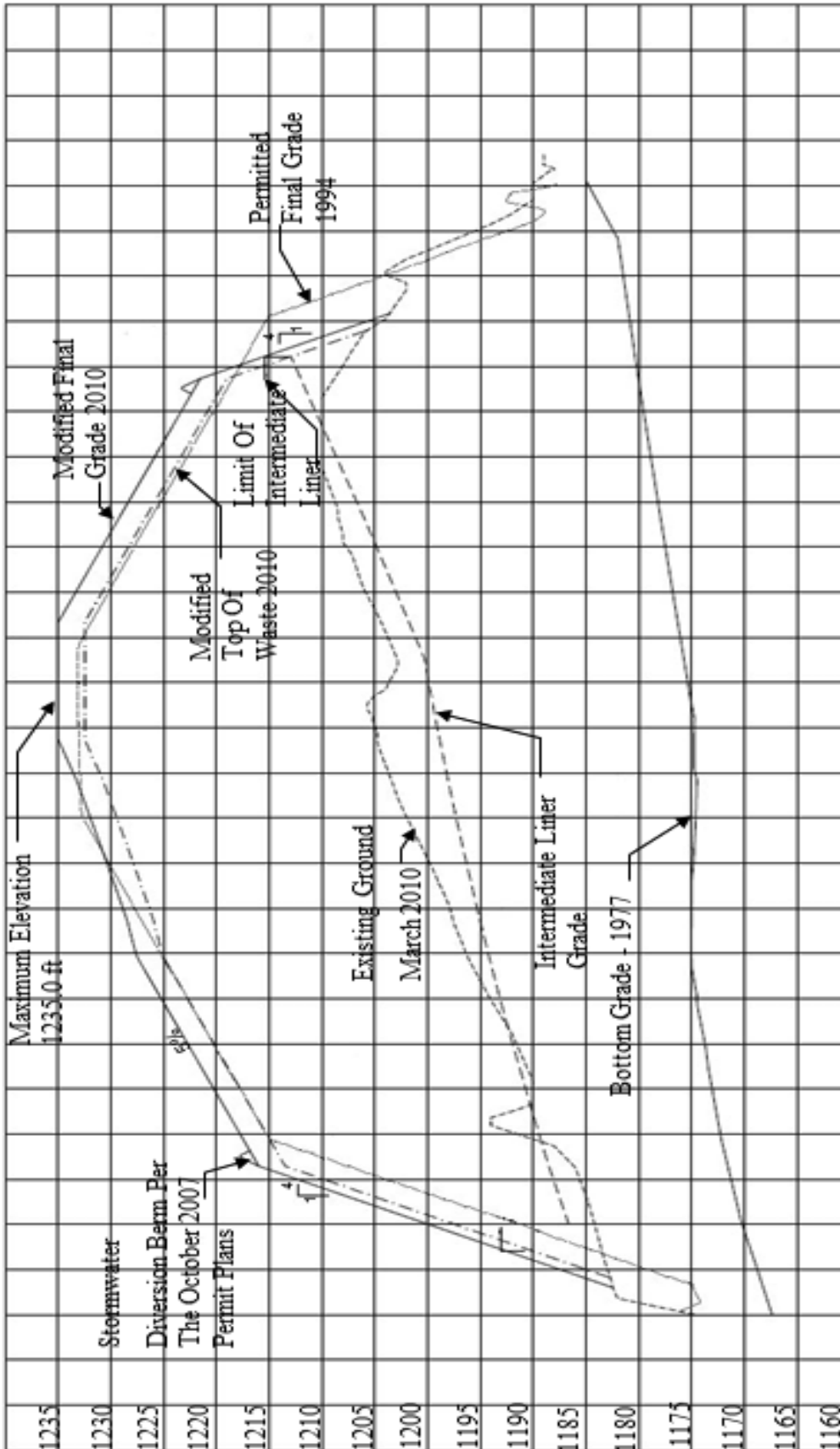


Figure 2-3. Cross-section map of the ash landfill showing the final grade, top of waste, intermediate liner, existing ash and bottom grade elevations; modified from AEP (2011). Elevations listed on left and right y-axis are in feet above sea level.

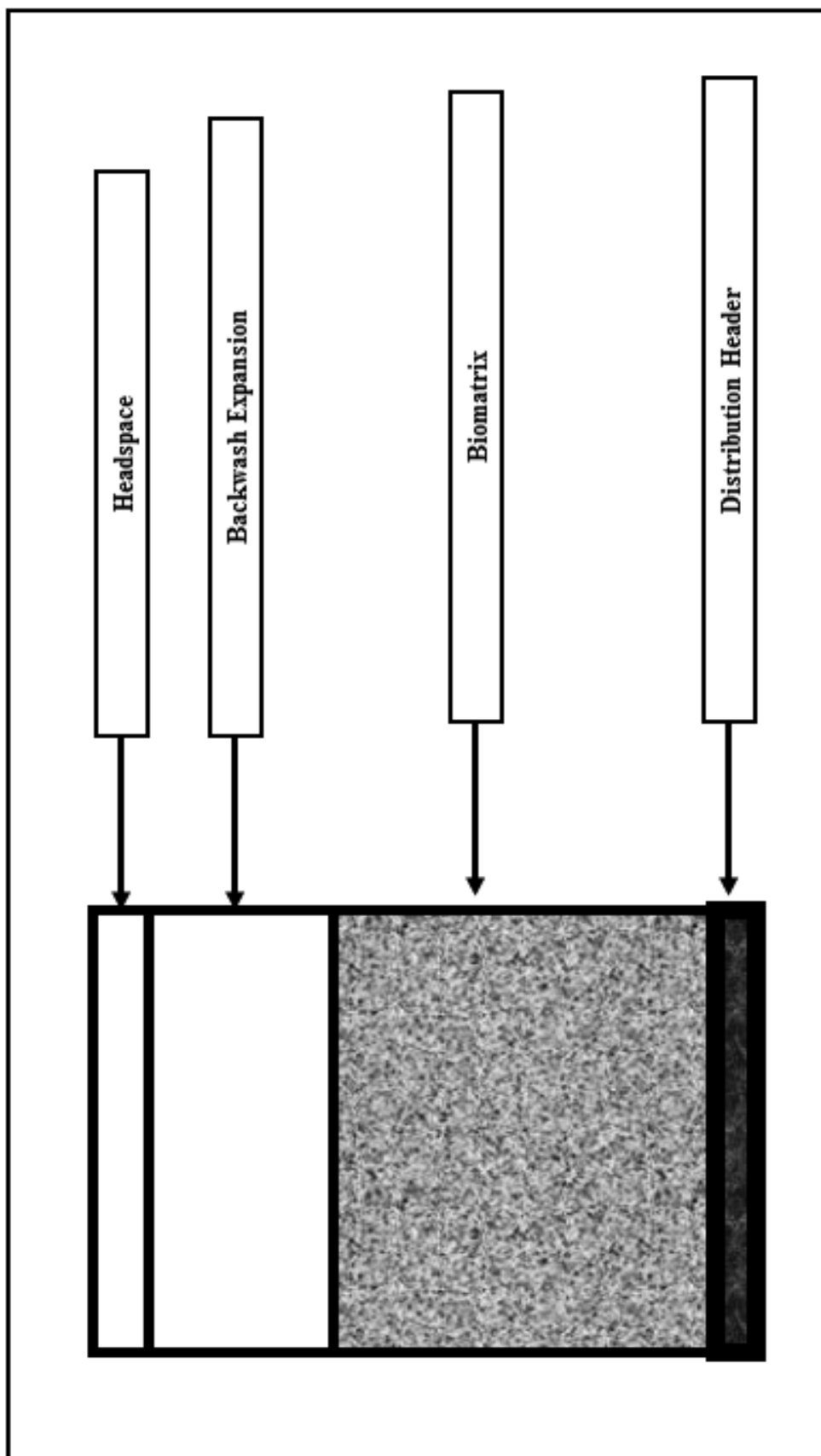


Figure 2-4. Simplified cross-section of the ABMet™ bioreactor. Enough free-board must be maintained within the bioreactor to allow for adequate expansion of the biomatrix during the backwash sequence to prevent washout of the biomatrix.

Legend:

- = Influent Leachate
- = H_2SO_4 / Molasses
- = Backwash Water
- = Treated Effluent
- = Backwash Effluent
- = Emergency Leachate

Process Flow:

- Landfill Leachate enters the Leachate Collection Pond.
- Leachate flows from the Leachate Collection Pond to the Feed Tank.
- Feed Tank output goes through a Feed Pump(s) into Bioreactor 1.
- Nutrient Tank and Acid Injection feed into Bioreactor 1.
- Backwash Pump(s) return water from Bioreactor 1 to the Feed Tank.
- Bioreactor 1 output goes to the Effluent Tank.
- Effluent Tank output goes through an Effluent Pump(s) to the Contact Pond.
- Contact Pond discharges into the Primary Ash Pond.
- Emergency Leachate Tank and Waste Tank are connected to the main flow lines via pumps.

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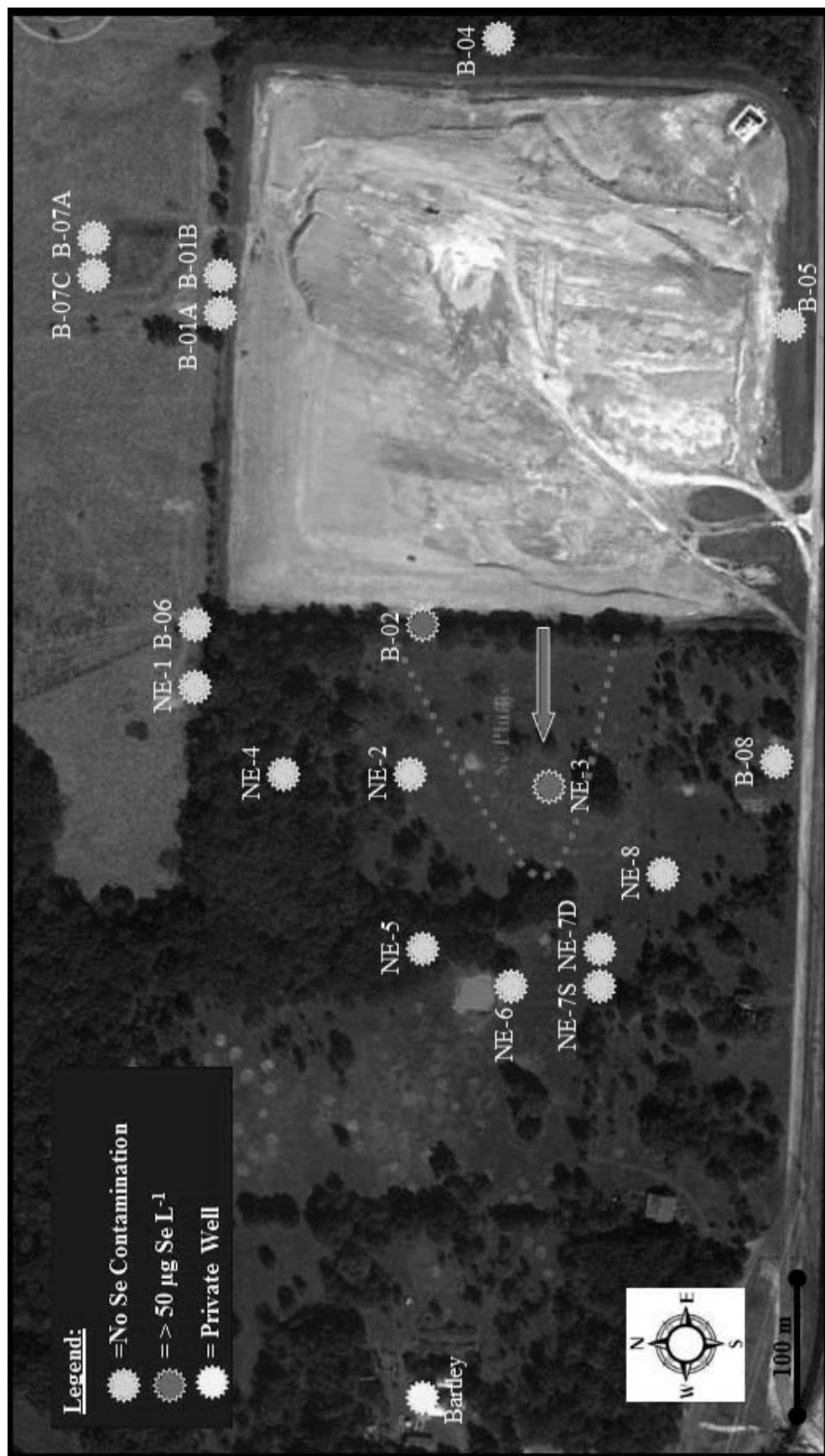


Figure 2-6. Aerial image of the groundwater monitoring wells in relation to the ash landfill. Monitoring wells that have exceeded the Groundwater Protection Standard of $50 \mu\text{g Se L}^{-1}$ are indicated in red. Wells with no Se contamination are indicated in green, including the private well indicated in yellow. The assumed migration of the Se plume is indicated by the dashed red line.

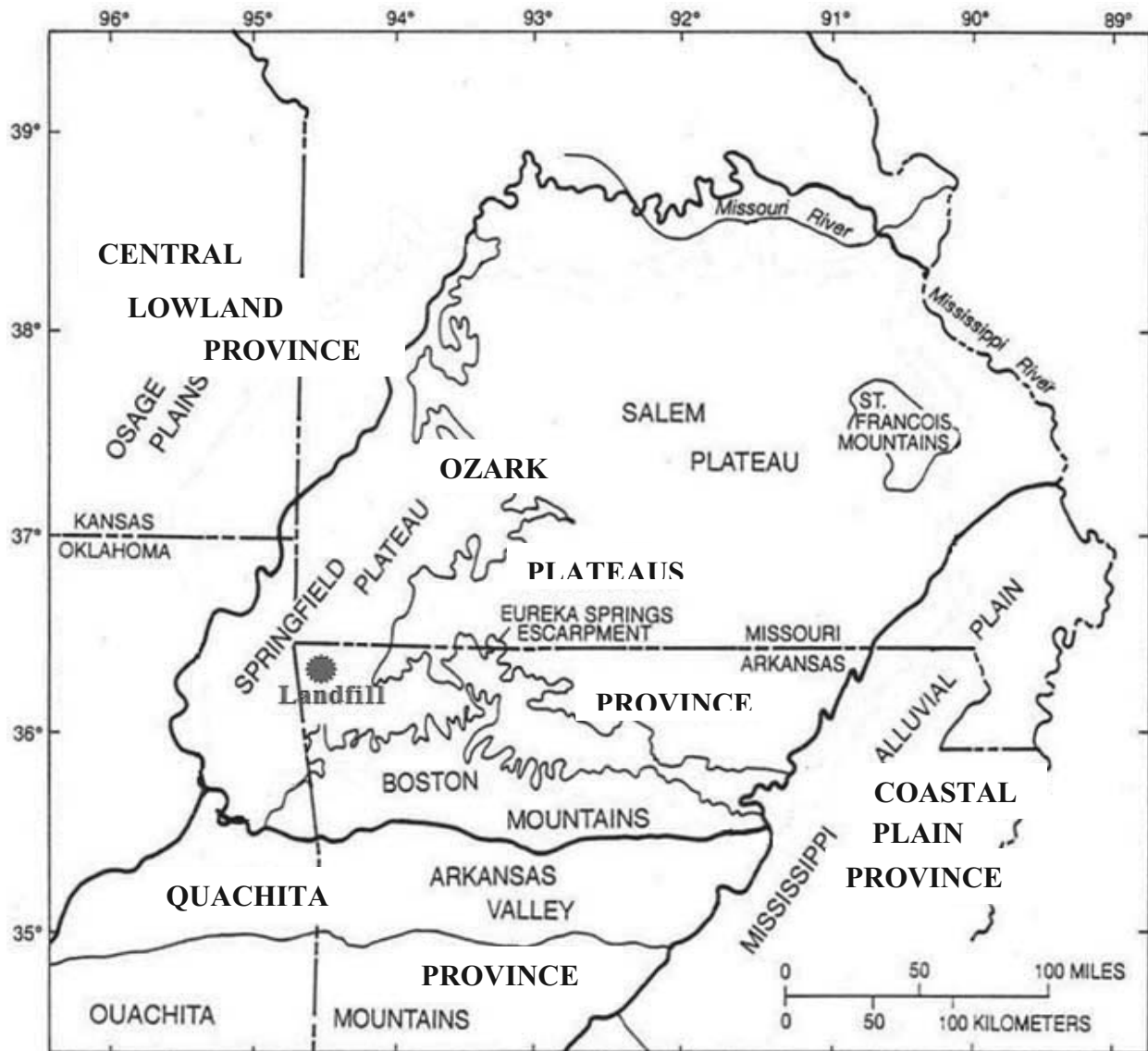


Figure 2-7. Physiography map of the area surrounding the Flint Creek ash landfill. The ash landfill is located on the relatively flat, southward extension of the Springfield Plateau. Modified from Fenneman (1938).

Regolith

(6 to 12 meters thick)

Chert, limestone fragments,
and clay

Boone Formation

(61 to 76 meters thick)

Upper Boone Division

Thick bedded limestone with 40 to
75 % insoluble, light colored chert

Lower Boone Division

Thick bedded limestone with 45 to
65 % nodular, dark-colored chert

St. Joe Formation

(~ 14 meters thick)

Thinly bedded pure gray limestone;
karst and caves form in this area

Chattanooga Shale

(15 to 17 meters thick)

Regional confining unit

Figure 2-8. Stratigraphy of the Flint Creek ash landfill; modified from Doheny-Skubic (2006) and Brahana (2011; personal communication).

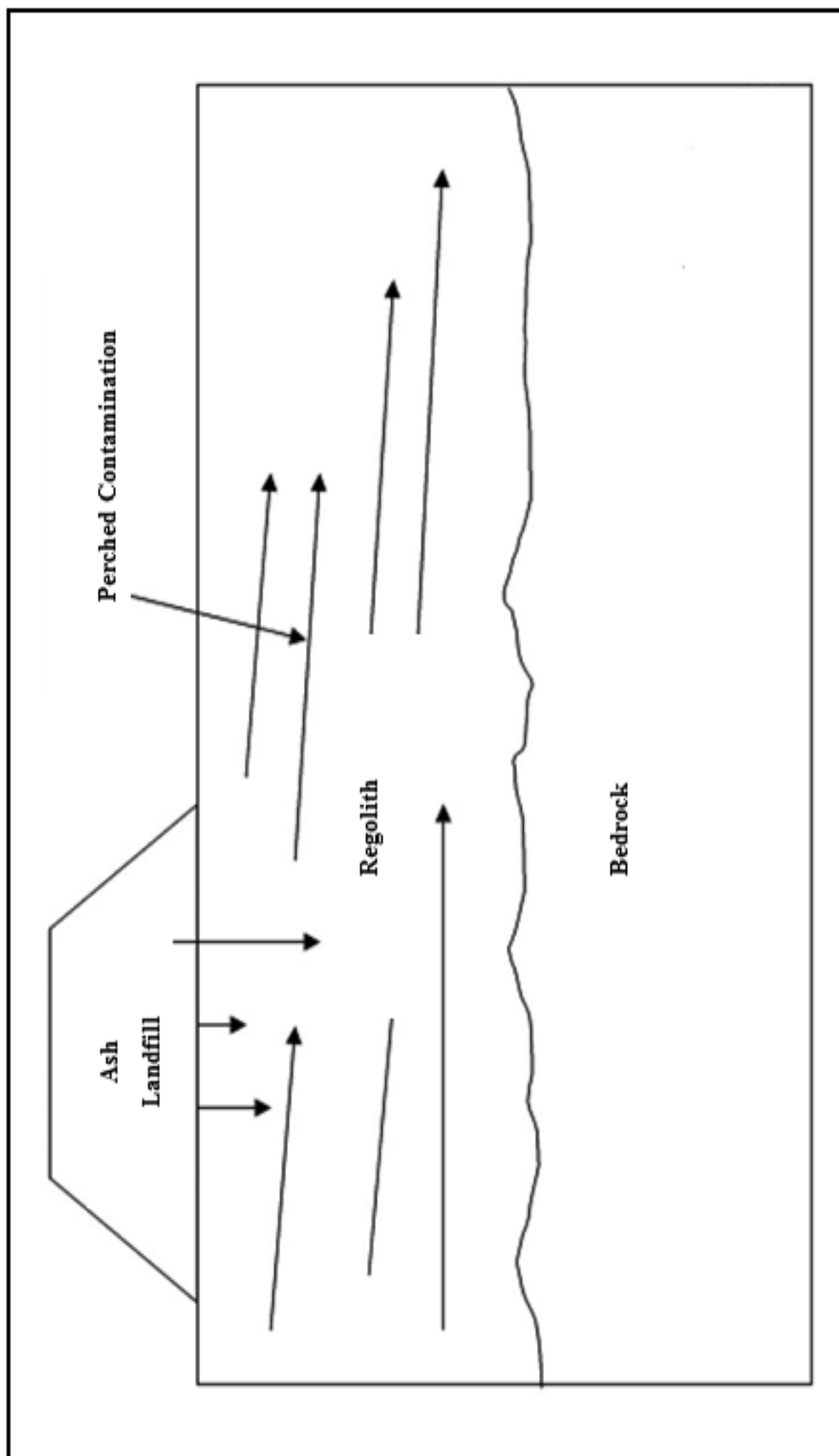


Figure 2-9. Cross-sectional schematic of the perched selenium contamination in the regolith at the Flint Creek ash landfill; not drawn to scale.



Figure 2-10. Underlying soils map of the Flint Creek ash landfill area. Linker fine sandy loam (LrC), Nixa very gravelly silt loam (NfC), Captina silt loam (CnB), Elsah soils (Eg), and Noark very gravelly silt loam (NoD) are soil series located beneath the ash landfill. Modified from NRCS- Natural Resources Conservation Services.

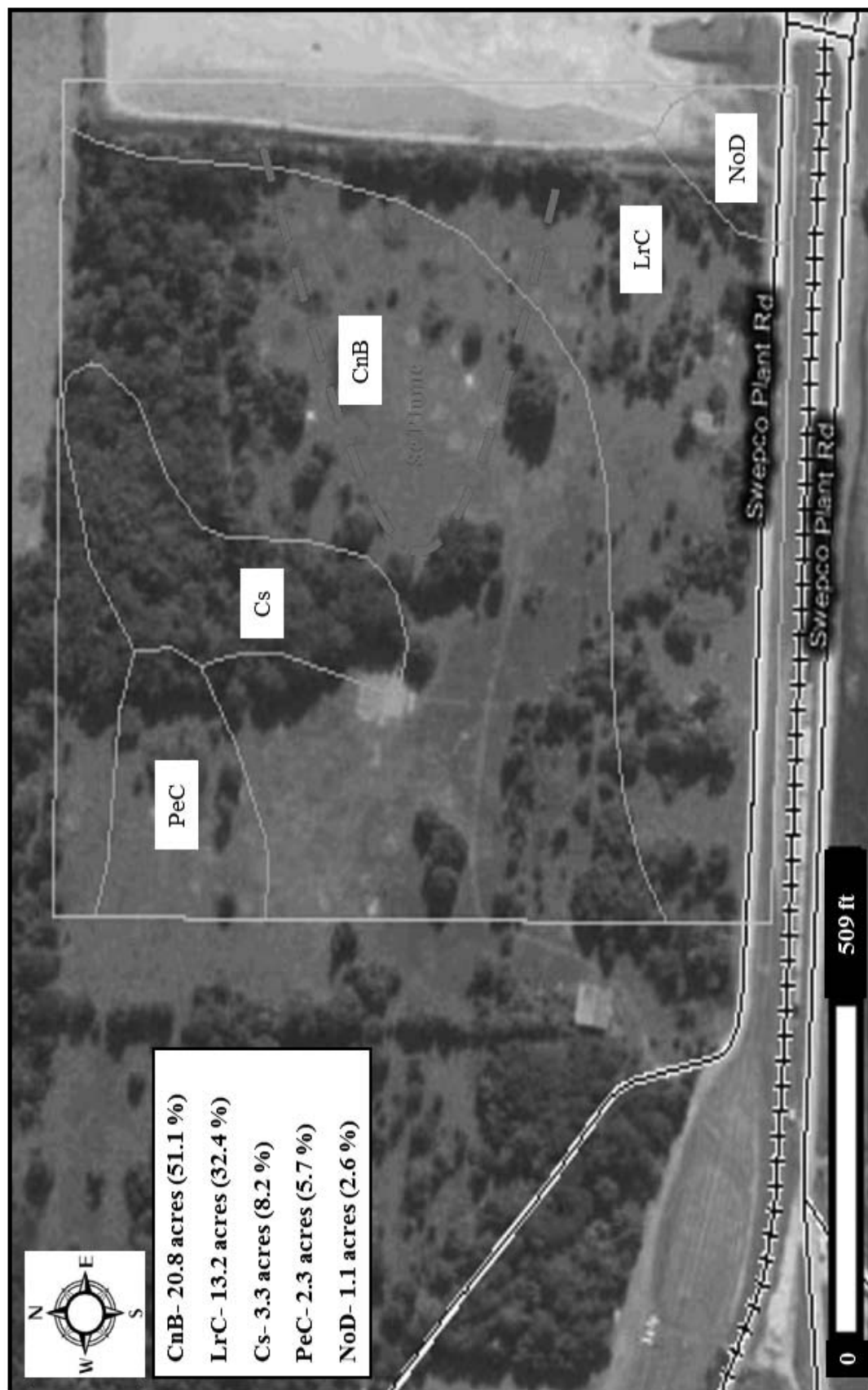


Figure 2-11. Underlying soils map of the land directly west of the Flint Creek ash landfill in relation to the selenium plume. Captina silt loam (CnB), Linker fine sandy loam (LrC), Cherokee silt loam (Cs), Peridge silt loam (PeC), and Noark very gravelly silt loam (NoD) are soil series located in this area. Modified from NRCS- Natural Resources Conservation Services.

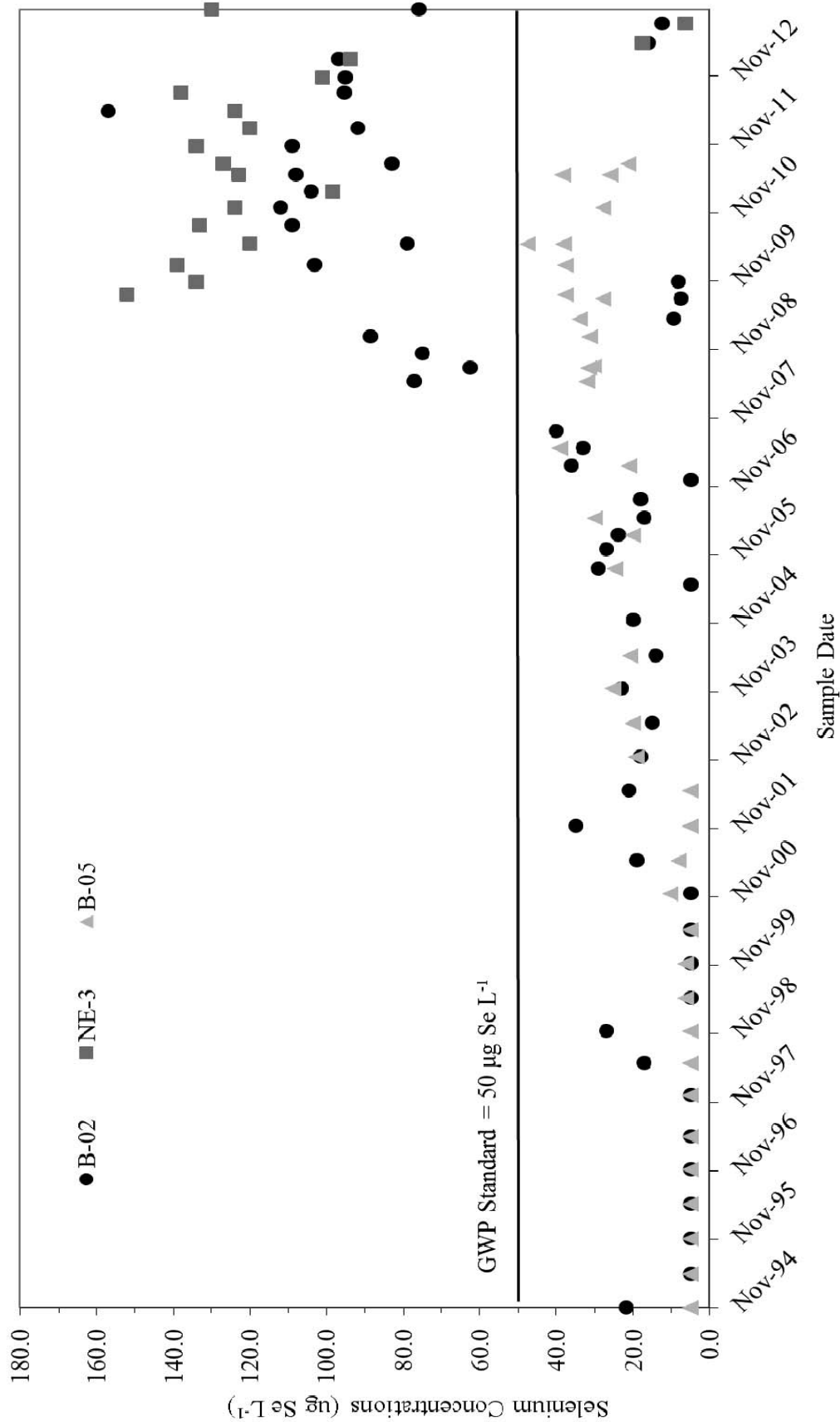


Figure 2-12. Groundwater Se concentrations (µg Se L⁻¹) as monitored at three wells (B-02, NE-3, and B-05) over a 12-yr period at the Flint Creek coal ash landfill. B-02 experienced an exceedence of the groundwater protection (GWP) standard in January 2009 after four consecutive readings greater than 50 µg Se L⁻¹. After the exceedence, monitoring well NE-3 was installed to determine the nature and extent of the Se plume down-gradient of well B-02.

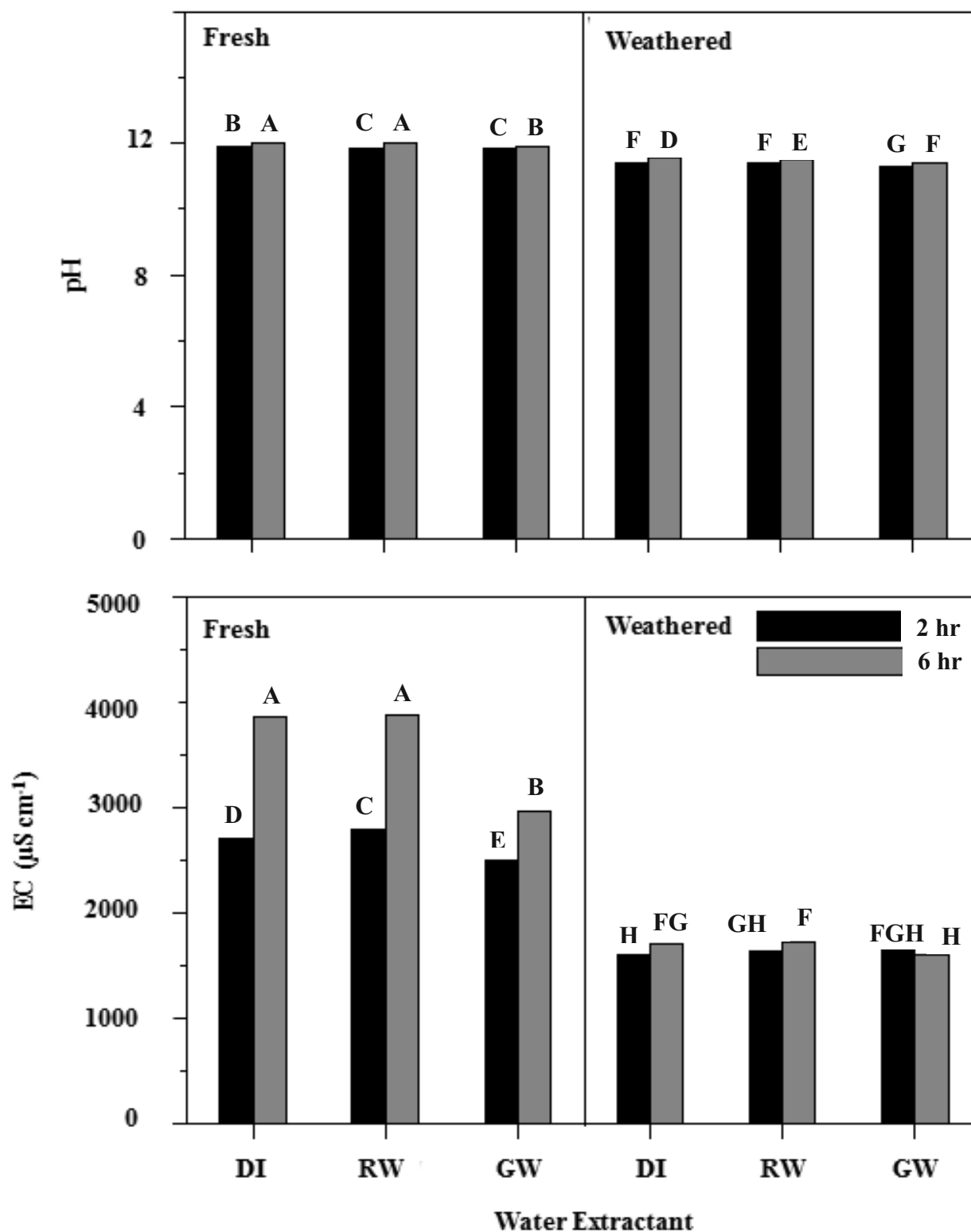


Figure 2-13. Suspension pH and electrical conductivity (EC) as affected by ash type (fresh and weathered), extraction time (2 and 6 hr), and water-extractant type [deionized water (DI), rainwater (RW), and groundwater (GW)]. Different letters atop bars within a property are significantly different at the 0.05 level.

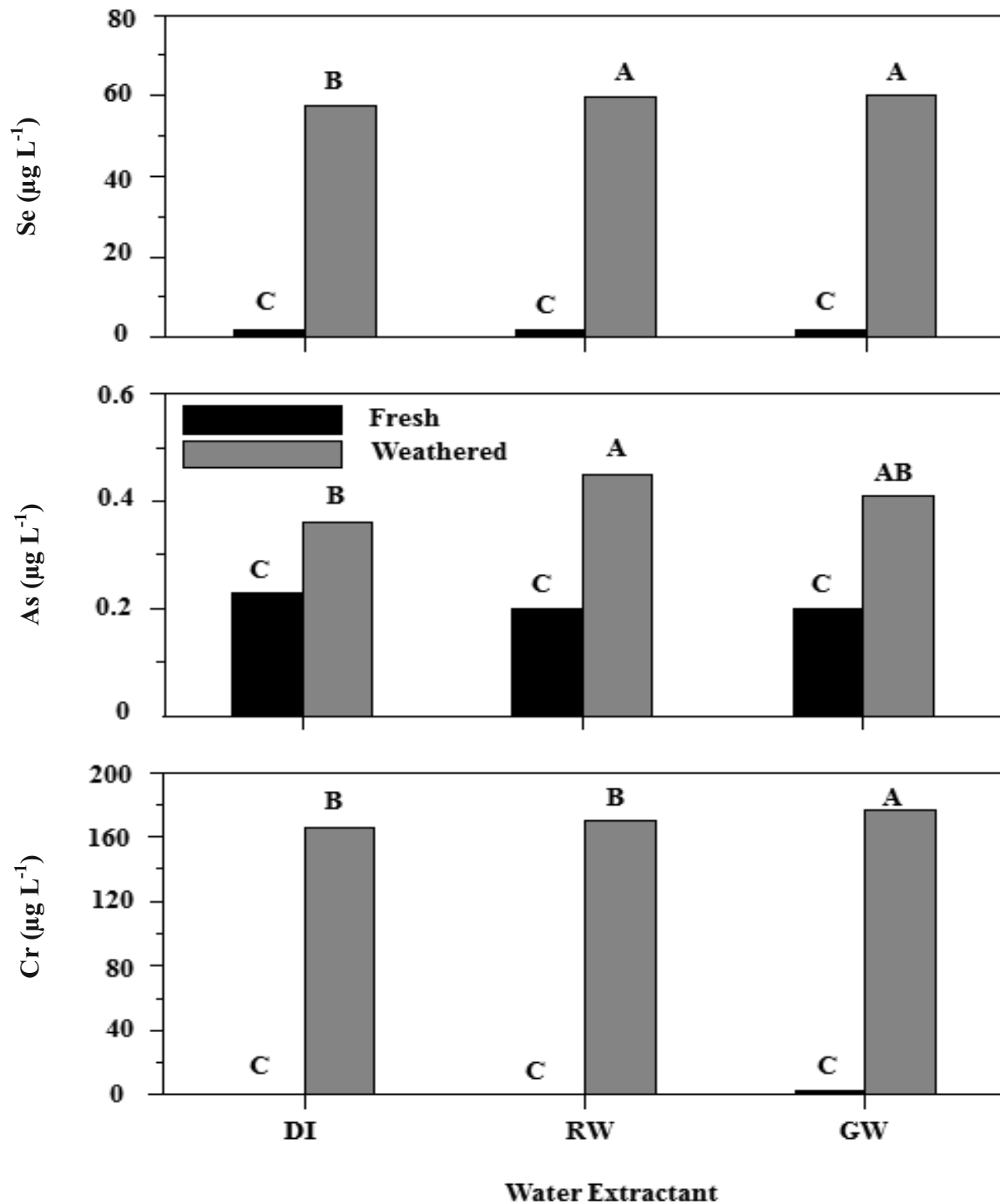


Figure 2-14. Water-soluble selenium (Se), arsenic (As), and chromium (Cr) concentration differences between ash types (fresh and weathered) across water-extractant types [deionized water (DI), rainwater (RW), and groundwater (GW)], averaged over extraction times. Different letters atop bars within a property are significantly different at the 0.05 level.

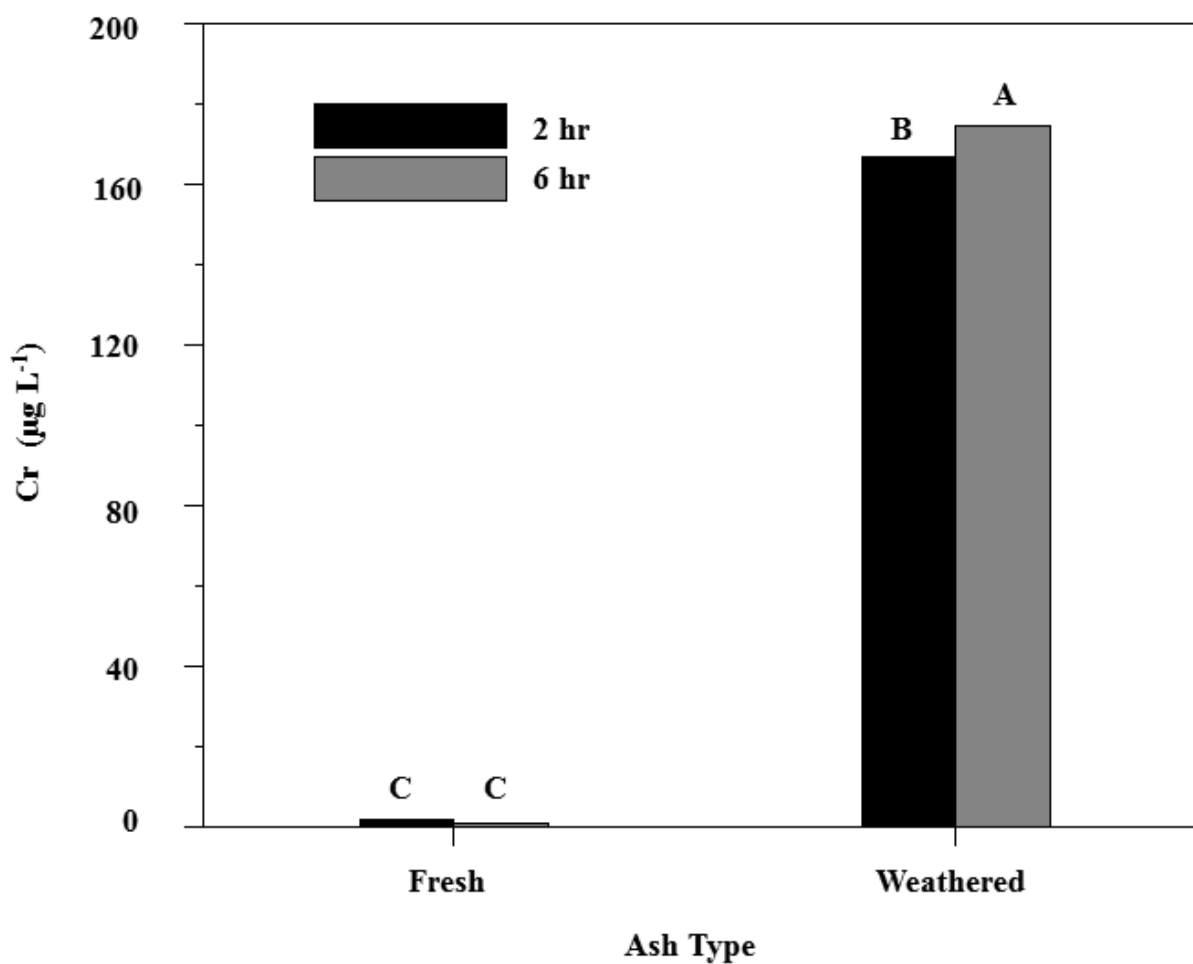


Figure 2-15. Water-soluble chromium (Cr) concentration differences between ash types (fresh and weathered) among extraction times (2 and 6 hr), averaged over water-extractant types. Different letters atop bars are significantly different at the 0.05 level.

APPENDICES

Appendix A

AEP-Engineering has determined the hydraulic conductivity values for the groundwater monitoring wells B-01B, B-02, B-04, B-05, B-06, NE-1, NE-2, and NE-3 based on slug tests. These slug tests were performed by placing a Solinst LevelloggerII (serial number 1016823) at the bottom of the groundwater monitoring wells (AEP, 2010). There were two types of PVC slugs used during the testing; 1.52 meter x 3.18 cm (5 ft x 1.25 inch) and 1.52 meter x 2.54 cm (5 ft x 1.00 inch). The LevelloggerII measures the water pressure inside the groundwater monitoring well before and after insertion of the PVC slug and converts this measured pressure to a water depth value (AEP, 2010). To perform the necessary calculations, Aqtesolv® software was used. It should be noted that slug tests for groundwater monitoring wells NE-1, NE-2, and NE-3 were performed during September 2009 and slug tests for groundwater monitoring wells B-01B, B-02, B-04, B-05, and B-06 were performed during March 2005.

Appendix B

New groundwater monitoring wells west of the ash landfill were constructed during June 2011 by Terracon. As part of the Nature and Extent Report, Terracon followed ASTM D5092 “Standard Practice for Design and Installation of Groundwater Monitoring Wells in Aquifers” Regulation 22.1103. Below is a brief description of the techniques used to install the monitoring wells.

An auger was used to drill down until weathered limestone was encountered. After auger refusal, a 7.6 cm (3 inch) diameter Tri-cone air bit was then used to drill through the bedrock until groundwater was encountered. When at least 3.1 meters (10 ft) of water was present in the monitoring well, setting of the wells began. To allow groundwater penetration, the bottom 4.6 meters (15 ft) of each well utilized 5.1 cm (2 inch) diameter 0.254 mm (0.010 inch) machine slotted PVC well screen. This procedure was followed by placing a 5.1 cm (2 inch) diameter threaded, flush-joint PVC riser pipe to the ground surface. The well was then lined with pre-sieved 12/20 grade silica sand around the well screen from the bottom of the boring to approximately 0.6 meters (2 ft) above the top of the well screen. Above the sand liner, 0.6 meters (2 ft) of hydrated bentonite pellets were used to seal off the monitoring well to prevent intrusion of surface water. The remainder of the well was lined with Portland cement/bentonite slurry to the ground surface. All wells are protected with monument type protective covers.

Appendix C

(Information below was derived from Phillips and Harper, 1977; NRCS, 2008).

The soil directly below the ash landfill is comprised of five different soil series: Linker (LrC- 79.1 %), Nixa (Nfc- 7.9 %), Elsah (Eg- 5.8 %), Captina (CnB- 5.7 %), and Noark (NoD- 1.6 %). Linker soils cover approximately 13.8 hectares (34.1 acres) under the weathered fly ash and are classified with a “B” hydrologic soil group rating (moderate water infiltration rate when thoroughly wet). Linker soils are formed from weathering of sandstone (i.e, residuum), consist of a fine sandy loam that is well-drained at the surface, has moderate permeability, low available water capacity, and is considered unfavorable for landfill use.

Nixa soils cover approximately 1.4 hectares (3.4 acres) and have a “C” hydrologic soil group rating (slow water infiltration rate when thoroughly wet). Nixa soils are formed from weathering of cherty limestone (i.e., residuum), have very slow permeability, medium available water capacity, and are very favorable for landfill use.

Elsah soils cover approximately 1.0 hectares (2.5 acres) and have a “B” hydrologic soil group rating (moderate water infiltration rate when thoroughly wet). Elsah soils are formed from sediment being washed from cherty upland soils (i.e., alluvium, colluvium), have moderately rapid permeability, low available water capacity, and are unfavorable for landfill use.

Captina soils cover approximately 1.0 hectares (2.5 acres) and have a “C” hydrologic soil group rating (slow water infiltration rate when thoroughly wet). Captina soils are formed from loamy material overlying cherty limestone (i.e., residuum), have low water permeability, medium available water capacity, and are moderately favorable for landfill use.

Noark soils cover approximately 0.3 hectares (0.7 acres) and have a “B” hydrologic soil group rating (moderate water infiltration rate when thoroughly wet). Noark soils are a very

gravelly silty loam at the surface, well-drained, formed from weathering of cherty limestone (i.e., residuum), have moderate water permeability, medium available water capacity, and are moderately favored for landfill use.

CONCLUSION

When performing an environmental assessment of the potential environmental impact of trace elements in fly ash, the total concentration is not nearly as important as knowing the water-soluble and speciation fractions. The water-soluble fraction is the most likely fraction to be released into the environment and the speciation is what determines the mobility and toxicity once released. Fresh and weathered subbituminous PRB fly ash had significantly different water-soluble Se, As, and Cr leaching characteristics, with fresh ash water-soluble concentrations at or very near the MDL across all treatments. Differences between fresh and weathered ash were likely due to the speciation present in the ash. Selenite (Se^{4+}) was shown to be the dominate species present in the fresh ash, likely preventing the release of Se during the water-extraction study. Once landfilled, environmental weathering promotes the oxidation of selenite (Se^{4+}) to the highly mobile, water-soluble selenate (Se^{6+}).

Although Cr and As speciation analyses was not performed, differences between fresh and weathered ash water-soluble Cr concentrations indicate that the less water-soluble trivalent (Cr^{3+}) Cr was likely dominate in the fresh ash and the more water-soluble hexavalent (Cr^{6+}) Cr was likely dominate in the weathered ash. Weathered ash water-soluble Se and Cr concentrations indicate that there is still a significant amount of Se and Cr readily available to be released into the environment if allowed to come in contact with rainwater or groundwater. Fresh and weathered ash water-soluble As concentrations at or near the MDL were likely due to As existing and remaining in the arsenate (As^{5+}) form. Previous research indicates that the less water-soluble arsenate (As^{5+}) is the dominate species present in fresh subbituminous PRB ash and it is unlikely that the arsenate (As^{5+}) is being reduced to the more water-soluble arsenite (As^{3+}) in the landfill (Huggins et al., 2007). Therefore, results from this study indicate that

speciation is likely responsible for the differences between extraction behavior of fresh and weathered ash Se, As, and Cr concentrations.

Weathered ash water-soluble Se concentrations were greatest when extraction occurred with environmentally representative rainwater and groundwater. Similarly, weathered ash water-extractable Cr concentration was greatest with groundwater. Selenium and As extraction was unaffected by extraction time; however, weathered ash water-soluble Cr concentration increased as the extraction time increased from 2- to 6-hours. This research was not able to demonstrate if 6 hours was enough time to ensure maximum Cr extraction; therefore, a 24-hour extraction is recommended for Cr (EPRI, 1994). Water-soluble As concentrations were too near the MDL to make an informed decision for both fresh and weathered ash. Therefore, a longer extraction time and lower dilution ratio may be required to obtain measurable water-extractable As concentrations from a Class C fly ash (Wang et al., 2009). To obtain maximum fresh and weathered ash suspension pH and EC, it is recommended to perform at minimum a 6-hour extraction with deionized water for both fresh and weathered ash. Extraction with environmentally representative rainwater and groundwater offered no distinct benefits when compared to deionized water as the extractant of choice for suspension pH and EC.

It should be re-iterated that results from this study were derived from the extraction of a Class C fly ash produced from the combustion of a subbituminous PRB coal and may not be comparable to extraction from Class F fly ash, whereas the goal of this study was to better understand the behavior of a site-specific fly ash and not fly ash in a holistic sense.

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Huggins, F., C.L. Senior, P. Chu, K. Ladwig, and G.P. Huffman. 2007. Selenium and arsenic speciation on fly ash from full-scale coal-burning utility plants. *Environ. Sci. Technol.* 41:3284-3289.

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