

Chemical Attenuation Coefficients for Selenium Species Using Soil Samples Collected from Selected Power Plant Sites

Laboratory Studies

Technical Report

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REPORT SUMMARY

Selenium is a trace constituent that is naturally enriched in fossil fuels and is further concentrated in fly ash. Field and laboratory studies have demonstrated that it can be present in coal combustion product (CCP) leachate. This report contains results of laboratory batch equilibrium studies for adsorption of selenium species by soils from three coal-fired power plant sites. This information can be used to more accurately predict long-term groundwater transport of selenium derived from CCP management facilities.

Background

If CCP leachate containing selenium is released to groundwater, selenium concentrations will be reduced by a number of factors, principally dilution by groundwater and attenuation by the soil and aquifer materials. The degree of attenuation is highly dependent on the selenium species present and soil characteristics. Understanding the species of selenium and its attenuation characteristics is necessary to predict the migration and potential risk associated with release to groundwater.

Objectives

- To determine selenium species-specific adsorption rates, using whole soils collected at the CCP management facilities and both simulated and CCP-derived leachate.
- To evaluate the factors that affect adsorption.

Approach

EPRI and the U.S. Department of Energy (DOE) designed this project to evaluate attenuation of selenite [Se(IV)] and selenate [Se(VI)] for soils at three coal-fired power plant sites from different U.S. geographical regions. One site was located in the Northeast, one in the Southeast, and one in the Midwest. Investigators developed adsorption isotherms and fit them to the Freundlich model for both Se(IV) and Se(VI). They obtained physical and chemical characterization data for the soils so that correlations between soil properties and adsorption of selenium species could be established. Specific experiments included 1) laboratory batch equilibrium experiments to construct adsorption isotherms and estimate adsorption coefficients for Se(IV) and Se(VI); 2) sequential batch leaching tests to characterize Se(IV) and Se(VI) release from the ash samples; and 3) laboratory batch adsorption tests to assess the effects of the ash leachate matrix on selenium species adsorption.

Results

Adsorption of selenium species was generally nonlinear with respect to concentration. For all three sites, adsorption of Se(IV) was significantly greater than Se(VI). The isotherms were best fit using the Freundlich model for the range in selenium concentrations used in the experiments. Linearized concentration-specific distribution coefficients (K_d^*)—calculated from adsorption isotherms at an initial solution concentration of 1 mg/L—ranged from 5 to approximately 500 L/kg for Se(IV) and from 2 to 18 L/kg for Se(VI) for the soils tested. The presence of sulfate decreases adsorption of selenium, with the effect being soil dependent but always greatest for Se(VI). The presence of calcium caused a small increase in Se(IV) adsorption, but had only a negligible effect on Se(VI) adsorption.

Adsorption of both species was strongly dependent on pH, with greatest adsorption in the acidic range. Se(VI) adsorption consistently decreased between pH 3 and 9. Se(IV) adsorption generally reached a maximum between pH 4 and 7, depending on soil type, and then decreased as pH increased. Decreasing sorption with increasing pH is characteristic for anion adsorption.

Linear and stepwise multiple linear regression analyses of the adsorption coefficients as well as soil chemical and physical properties indicate that 15-second dithionite-citrate-bicarbonate (DCB) extractable iron was the best single parameter correlation. However, reasonably good correlations for Se(VI) adsorption were also found with clay percentage. For both species, selenium adsorption was negatively correlated with soil isotherm pH. Combining pH with 15-sec DCB iron content of the soils resulted in the best correlation for adsorption of both Se(IV) and Se(VI).

EPRI Perspective

This research provides data that can be used to model and predict the migration of selenium in groundwater at CCP sites. Related studies characterized the attenuation of arsenic in groundwater (EPRI report 1005505) as well as the speciation of arsenic and selenium in CCP leachate (EPRI report 1012578). Knowledge of factors controlling the leachability and mobility of key constituents in groundwater is critical to predictive modeling for risk assessment and development of cost-effective CCP management practices that are protective of groundwater.

Keywords

Selenium Chemical Attenuation Adsorption Leaching Speciation

ABSTRACT

This report contains results of the laboratory batch equilibrium studies for chemical attenuation of selenium species by soils from three coal-fired power plant sites. Several soil samples were collected from three power plant sites to conduct the laboratory chemical attenuation studies. Adsorption isotherms and coefficients were developed for both selenium (IV) and selenium (VI). Physical and chemical characterization data for the soils were obtained so that correlations between soil properties and adsorption of selenium species can be established to the extent possible. Linear and Freundlich adsorption isotherm models were fitted to the data as appropriate.

Adsorption of selenium species was generally non-linear with respect to concentration. For all three sites, adsorption of Se(IV) was significantly greater than Se(VI). Linearized concentration-specific distribution coefficients calculated from adsorption isotherms at an initial solution concentration of 1 mg/L ranged from 5 to about 500 L/kg for Se(IV), and from 2 to 18 L/kg for Se(VI) for the soils tested. The presence of sulfate decreases adsorption of selenium with effects being soil dependent but always greatest for Se(VI). The presence of calcium had a small effect on Se(IV) adsorption, but a negligible effect on Se(VI) adsorption.

Linear and a step-wise multiple linear regression analyses of the adsorption coefficients and soil chemical and physical properties indicate that 15-second DC extractable iron was the best single parameter correlation; however, reasonably good correlations for Se(VI) adsorption were also found with clay percentage. For both species, selenium adsorption was negatively correlated with soil isotherm pH. Combining pH with 15 sec-DCB-Fe content of the soils resulted in the best correlation for adsorption of both Se(IV) and Se(VI).

These chemical attenuation data for the selenium species can be used to model selenium migration in groundwater at the coal ash management sites for the coal fired power plant sites.

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1 INTRODUCTION

Attenuation of selenium (Se) in the subsurface is highly dependent on the selenium species present and the characteristics of the soil. This project was designed to evaluate attenuation of selenite [Se(IV)] and selenate [Se(VI)] for soils at three coal-fired power plant sites from different geographical regions within the United States. One site is located in the northeastern United States (NE), one site is located in the Southeast (SE), and one site is located in the Midwest (MW). These data can be used to model selenium migration in groundwater at the sites and to compare to monitoring well data. This report presents the results of laboratory determinations of attenuation characteristics for soils collected at the three sites.

Objectives

The overall objectives of this research project were to:

- Collect soil samples from each of the three coal-fired power plant sites and characterize them for selected physical and chemical properties,
- Conduct laboratory batch equilibrium experiments to construct adsorption isotherms and estimate adsorption coefficients for Se(IV) and Se(VI) species with multiple soil samples from each of the three sites,
- Collect coal ash samples from the three power plants and perform sequential batch leaching tests to characterize Se(IV) and Se(VI) release from the ash samples, and
- Carry out laboratory batch adsorption tests with soils from the three sites to assess the effects of the ash leachate matrix on the attenuation of selenium species.

Literature Review

Although selenium is essential to humans and animal nutrition, it has been recognized to adversely impact aquatic ecosystems. Selenium in excess caused embryonic mortality and abnormalities of aquatic birds (Ohlendorf et al., 1986). Data in the late 1990s suggested that reproductive impairment in wildlife from Se pollution is more widespread than originally thought (Betts, 1998). Sources of selenium contamination associated with anthropogenic activities arise from application of agricultural pesticides, disposal of industrial wastes, and combustion of fuels. Selenium is naturally enriched in fossil fuels well above the level of abundance in the earth's curst of < 0.05 mg/kg (Bowen, 1979). Selenium is further concentrated in coal combustion by-products such as fly ash (e.g., 6.9 to 760 mg Se/kg ash) (Theis and Gardner, 1990). Approximately 45% of coal-derived fly ash is disposed of in landfills (USEPA, 1999; EPRI, 1997). Constituents present in ash landfills such as selenium may seep to adjacent water bodies or groundwater, thus potentially impacting the aquatic ecosystem (Carlson and

Introduction

Adriano, 1993; Eary et al., 1990). Selenium concentrations of 10 to 540 μ g/L were found in pore-water and leachate collected from typical ash disposal sites (Theis and Gardner, 1990 and references cited therein); and selenium concentrations of <1 to 2,360 μ g/L in a recent study of field leachate concentrations at 33 CCP management sites (EPRI, 2006).

Toxicity

Considerable controversy between biologists and industries was spawned and has continued since the issuance of the 1987 chronic criterion of 5 parts per billion (ppb, $\mu g/L$) by US EPA (Renner, 1998; Renner, 2005). Both Se species are bio-accumulated in tissues and thus chronic exposure to even lower concentration may result in developmental abnormalities in embryos for wildlife and disturbed reproduction cycles for domestic animals (Dhillon and Dhillon, 2003). On the other hand, selenium constitutes an active site of selenoproteins such as glutathione peroxidase (Himeno and Imura, 2002). Of the all US EPA priority and non-priority pollutants, selenium toxicity is also dependent on its oxidation status. Elemental Se and selenide is essentially insoluble in water (aqueous solubility too low to determine with current analytical techniques). Release of selenium to water from these insoluble forms of selenium can occur slowly through microbial metabolism to more soluble forms (Losi and Frankenberger, 1998; Dowdle and Oremland, 1998). For most aquatic and terrestrial wildlife, Se(IV) is known to be more toxic than Se(VI) when exposed at equal concentration level (US EPA, 2004). However, the specific mechanism of selenium toxicity still remains unclear.

Speciation in fly ash leachate

It is difficult to determine the redox speciation of selenium in ash leachate based only on the well-known pE-pH relationship due to ash heterogeneity, kinetic barriers to equilibrium, and biological processes. Several studies have been carried out to determine selenium speciation in fly ash and subsequent leaching from fly ash, which may vary with coal origin, the coal combustion process, the ash weathering process, and leaching methodology. In batch leaching studies, it was reported that 5% to 100% of total water extractable selenium could exist as Se(IV) (Jackson and Miller, 1998; van der Hoek et al., 1996). In field leachates, it was reported that Se(IV) was the predominant form, although the proportion of Se(VI) was high in leachates at landfills receiving ash from subbituminous or lignite coals (EPRI, 2006).

Adsorption

The sorption behavior of Se is governed by various physical-chemical factors including oxidationreduction potential (pE), mineralogical composition of the soil, soil pH, and the solution matrix. Selenium exists in four oxidation states in natural systems: selenate (Se(VI)), selenite [Se(IV)], elemental Se [Se(0)], and selenide [Se(-II)]. Under the prevailing pH-pE range in soils, selenium is most mobile in the Se(IV) and Se(VI) forms, while elemental Se(0) and Se(-II) are present as stable metal forms (Neal et al., 1987a). Se(VI) is present as SeO₄²⁻ over the entire pH range of soils, while the major Se(IV) species is HSeO³⁻ (pK_a=2.68) at pH < 8.4 and SeO₃²⁻ (pK_a=8.4) at pH > 8.4 (Séby et al., 1998). The interaction of the inorganic Se species (VI and IV) with model soil components has been extensively studied (Goldberg and Glaubig, 1988; Hansmann and Anderson, 1985; Neal et al., 1987a; Neal et al., 1987b; Rajan and Watkinson, 1976; Su and Suarez, 2000; Zhang and Sparks, 1990); these studies found that iron/aluminum (hydro) oxides and allophane appear to have the greatest affinity for Se. In alkaline calcareous soils, adsorption of Se(IV) by calcite is important (Goldberg and Glaubig, 1988). Of the phyllosilicate minerals, kaolinite with variable charge edge sites tends to adsorb selenium more than montmorillonite, which has a negative surface charge (Bar-Yosef and Meek, 1987; Goldberg and Glaubig, 1988). However at high Se concentrations where precipitation may be induced, removal of Se(IV) from aqueous solutions may be greater with montmorillonite due to its higher surface area (surface area; 700 to 800 cm²/g) compared to kaolinite (surface area; 5 to 20 cm²/g) (Frost and Griffin, 1977). The precipitation or co-precipitation of selenium-metal complexes such as ferric selenite $Fe_2(SeO_3)_3$ ($K_s = 2.0 \pm 1.7 \times 10^{-31}$) and basic ferric selenite $Fe(OH)_4SeO_3$ ($K_s = 10^{-61.7}$), which both have extremely low aqueous solubilities, can also be important in the environmental cycling of selenium (Manning and Burau, 1995).

Generally, Se(VI) has been shown to behave like sulfate anion (e.g., outer-sphere surface complex) with relatively low adsorption and high mobility (Goldberg and Glaubig, 1988; Neal and Sposito, 1989; Rajan and Watkinson, 1976). However, inner-sphere complexation on iron or aluminum oxides/hydroxides has also been concluded from spectroscopic data (Peak and Sparks, 2002; Manceau and Charlet, 1994; Wijnja and Schulthess, 2000). Negligible adsorption of Se(VI) was observed for several calcareous, montmorillonitic, alluvial soils, and purified humic acids (Neal and Sposito, 1989; Goldberg and Glaubig, 1988; Saeki and Matsumoto, 1994). However, Se(VI) sorption was reported significant on oxides, kaolinite, and oxide-enriched soils, especially in the acidic pH range (Balistrieri and Chao, 1987; Bar-Yosef and Meek, 1987; You et al., 2001; Su and Suarez, 2000). Se(IV) is considered to behave more analogous to phosphate anion (e.g., inner-sphere surface complex) and to adsorb more than Se(VI) (Hansmann and Anderson, 1985; Zhang and Sparks, 1990). Experimental evidence for specific Se(IV) adsorption on metal oxide surfaces includes a decrease in the soil's zero point of charge (ZPC) following selenite adsorption (Bowden et al., 1980; Rajan, 1979), reduced electrolytic mobility (Su and Suarez, 2000), and spectroscopically observed structural characteristics (Hayes et al., 1987).

Adsorption of both Se(IV) and Se(VI) by several sorbents including metal oxides, clay soils (kaolinite, montmorillonite), oxidic soils, and montmorillonitic soils is pH-dependent (Bar-Yosef and Meek, 1987; Bowden et al., 1980; Goh and Lim, 2004; Neal et al., 1987a; Saeki et al., 1995; Zhang and Sparks, 1990). The selenium adsorption generally decreases with increasing pH characteristic of anion adsorption on soil surfaces (Bowden et al., 1980; Hingston et al., 1972). With increasing pH, the soil surface becomes increasingly more negative while the anionic fraction of selenium increases, thus increasing repulsive forces. Se(VI) adsorption is more sensitive to pH than Se(IV) (Bar-Yosef and Meek, 1987) with the magnitude of the slope or the position of the inflection point in the pH envelope (adsorption versus pH) being soil-dependent.

Several studies have been conducted to quantify the relationship between selenium adsorption capacity and soil properties. For 66 New Zealand soils (John et al., 1976) and 58 Japanese soils (Nakamura et al., 2005), Se(IV) adsorption correlated best with oxalate-extractable Fe and to less extent with Al. Limited information is available for correlating Se(VI) adsorption to specific soil properties. As previously stated, soil pH is known to influence selenium adsorption; however, differentiating the relative contributions of pH and oxide content to selenium adsorption in heterogeneous soil systems is currently lacking.

Introduction

Selenium retention by soils is impacted by the ionic composition of the solution phase similar to what has been observed for other oxyanions. Se(VI) adsorption is more sensitive than Se(IV) to the presence of competing anions (Dhillon and Dhillon, 2002; Goh and Lim, 2004; Balistrieri and Chao, 1987; Monteil-Rivera et al., 2000; Saeki et al., 1995; You et al., 2001). For example, adsorption of 0.2 mM Se(VI) decreased approximately 50% in the presence of 0.01 M sulfate (Goh and Lim, 2004) whereas sulfate did not significantly impact Se(IV) adsorption (Balistrieri and Chao, 1987; You et al., 2001). Se(IV) also outcompeted phosphate for adsorption sites when present at equimolar concentrations; however, at a 2:1 phosphate:Se(IV) ratio in solution, Se(IV) adsorption by goethite was suppressed by 70% (Balistrieri and Chao, 1987). The sequence of inhibitory effect of competing anions for selenium adsorption generally follows; phosphate > citrate > oxalate > sulfate (Balistrieri and Chao, 1987; Saeki et al., 1995). Chloride competition for both Se(IV) and Se(VI) is minimal (Neal et al., 1987b).

Selenium adsorption has been shown to be enhanced by divalent cations, and has been attributed to i) surface precipitation with Fe^{2+} or Cu^{2+} (Benjamin, 1983; Manning and Burau 1995); and ii) decreased negative (or increased positive) surface potential caused by Ca^{2+} sorption (Neal et al., 1987b). In both cases, the impact of the divalent cations on selenium adsorption was greater at alkaline pH values where adsorption of the divalent cations (Cu^{2+} and Ca^{2+}) is more favorable.

Microbial reduction and oxidation of selenium

Microbial transformation of selenium includes both reduction and oxidation processes and appears to be similar to the biological cycling of sulfur (Losi and Frankenberger, Jr., 1997a). Mechanisms for microbial transformations include assimilatory reduction (used as a nutrient source), dissimilarity reduction (terminal electron acceptors in energy metabolism), and detoxification (e.g., biomethylation to volatile forms). The reductive microbial processes include reduction of Se(VI) to Se(IV) or further to elemental selenium, depending on microbial species and growth time (Lortie et al., 1992; Losi and Frankenberger, Jr., 1997b; Maiers et al., 1988). Both pH and redox potential can also affect the microbial transformation of selenium (Masscheleyn et al., 1990). From an environmental perspective, microbial reduction processes are favorable, because the reduced Se forms [e.g., Se(0) or Se(IV)] are less soluble and more easily adsorbed by soils than Se(VI) (the oxidized form). Less is known about microbial oxidation of selenium; however, it appears to be primarily a slow biotic process and the major mechanism by which solubilization of Se(0) occurs (Losi and Frankenberger, 1998). Dowdle and Oremland (1998) reported that 17% Se(0) was transformed into Se(IV) over a 25-day period in a soil slurry system with transformation rates being 3 to 4 orders-of-magnitude smaller than the rates of reduction of Se(IV) to Se(0). Similarly, only 2% to 13% of Se(0) spiked into soil at 100 mg/kg Se(0) was oxidized within a 125-day period in studies by Losi and Frankenberger (1998), and the amount of selenium oxidized appeared correlated with prior exposure of the soil to selenium.

Understanding adsorption behavior is critical for assessing the amount of selenium that may be released from ash disposal facilities and the ability for soils surrounding the facilities to attenuate transport towards near-by water bodies. Such information is critical in assessing the true risk potential of Se contamination from ash disposal facilities. In order to establish a theoretical framework for predicting selenium attenuation by soil, this study focused on the following objectives: (1) quantifying the adsorption of Se(VI) and Se(IV) onto soils from coal-fired power plant sites having a wide range of physical and chemical properties; (2) establishing a range of

distribution coefficients that may be used in assessing selenium mobility in ash leachate; (3) characterizing the competitive effects of Ca and SO_4 on the adsorption of Se(VI) and Se(IV); and (4) characterizing pH effects on selenium adsorption by soils.

2 METHODS AND MATERIALS

Soil Sampling and Characterization

Soils samples were collected from several depths at each of the three sites by spilt spoon sampling equipment with a plastic insert. Two to three soil borings were advanced within about 200 ft of the downgradient edge of the ash fill using a hollow stem auger, and samples were collected at five to ten foot intervals. The two-foot sections were sealed with end caps for transport to the laboratory in chilled coolers. Ash samples from the landfill site were collected in a similar manner for the NE and SE sites. A sample of bulk ash was taken at the MW site.

Upon arrival at the laboratory at Purdue University, soil and ash samples were transferred to plastic bins, and stored moist at 4°C. A soil pH and texture screening of samples received was performed to select a subset of samples considered representative of the site for use in detailed studies. For the soil samples selected and all the ash samples, moisture content was determined gravimetrically by the loss of water after heating at 105 °C for 24 h and cooled in a desiccator. For each soil sample selected, a subsample (• 200 g) was air dried, sieved to particle diameter less than 2 mm, and thoroughly homogenized prior to characterization and use. Each processed soil sample was characterized for the following physical and chemical properties: particle size distribution by the hydrometer method (Gee and Bauder, 1996), pH of 1:1 (5 g soil: 5 mL H,O) soil suspensions, organic carbon content by combustion (Nelson and Summers, 1996), cation exchange capacity (CEC) (Sumner and Miller, 1996), dithionite-citrate-bicarbonate (DCB) extractable iron and aluminum (Loeppert and Inskeep, 1996), acid ammonium oxalate extractable iron and aluminum (Loeppert and Inskeep, 1996), X-ray diffraction analysis of clay minerals, and timed DCB extractions of Fe and Al. Quick (15-sec) releasable DCB extraction of Fe was measured with methods previously reported (EPRI, 2004). Characterization of the dominant clay mineralogy in each of the soil samples was performed by X-ray diffraction analysis. Details with regard to X-ray slide preparation, mineral identification and characterization were also previously reported (EPRI, 2004).

Adsorption Isotherms on Site Soils

Adsorption isotherms were constructed independently for both Se(IV) and Se(VI) in an ionic matrix of 1 mM CaSO₄ using four to eight Se concentrations plus a zero Se concentration control. Applied solution concentrations generally ranged from 0.11 to 2.7 mg/L in the case of Se(IV), and 0.11 to 1.0 mg/L for Se(VI). Selenium solutions were added to 50-mL polypropylene centrifuge tubes containing 0.5 g to 1 g of soil resulting in soil to solution ratios of 20 g/L for Se(IV) and 50 g/L for Se(VI). Soil suspensions were then allowed to equilibrate at $22 \pm 2^{\circ}$ C on a rotary shaker (≈ 45 rpm) for 16 h for Se(IV) and 48 h for Se(IV). Selenium

Methods and Materials

concentrations in solution were measured after equilibration (C_w , mg/L), and sorbed concentrations (C_s , mg/kg) were estimated by the difference in the Se mass applied and the Se mass remaining in solution after equilibration with soil.

Equilibration times were selected to achieve near equilibrium without having significant shifts in the redox state of the Se remaining in solution; the redox state of adsorbed Se was assumed to be the same as what was measured in solution. Suspensions containing Se(IV) were equilibrated for a shorter period of time (\approx 16 h) due to concerns that a significant amount of Se(IV) would oxidize to Se(VI) within a 48-h equilibration period. Preliminary studies performed with NE1 25-30, NE2 10-15, and MW3 23 soils and applied solution concentrations of 1.5 µmol L⁻¹, 15 µmol L⁻¹, or 30 µmol L⁻¹ at 50 g/L showed that within a 16-h equilibration period, less than 10% of the Se(IV) was oxidized. This subset of soils represented the highest and almost the lowest K_r values, high and low values of pH, extractable iron, extractable aluminum, organic matter, and clay content of the soils used in this study. Balistrieri and Chao (1987) found that the Se(IV) adsorption from aqueous solutions reaches apparent equilibrium in 2 h and without oxidizing to Se(VI) over an additional 22-h time period.

After equilibration, the pH of the soil suspensions was measured using a double junction glass pH electrode. A 10-mL aliquot of the suspension was collected from each sample and filtered using a 10-mL plastic syringe with a 0.45 μ m regenerated cellulose luer-lock syringe filter. Filtered samples were preserved by adding 0.1 mL of concentrated NiNO₃ for total selenium or HCl for Se(IV). Analysis of selenium concentrations in the filtered samples was performed using an automated Shimadzu graphite furnace atomic absorption spectrometry (GFAA).

pH Effects

The effect of pH on Se(IV) and Se(VI) adsorption was characterized by measuring adsorption isotherms from pH adjusted 1 mM CaSO₄ solutions for selected soils from each site (NE1 25-30, SE1 48.5-50, and MW1 17-19 soils). Pre-determined amounts of diluted HCl or NaOH were added to 1 mM CaSO₄ solution to obtain pH values of equilibrated soil suspensions between 3 and 9. Duplicated initial concentrations of 0.52 mg/L for Se(IV) and 0.41 mg/L for Se(VI) were equilibrated with soils at a soil to solution ratio of 20 g/L and 50 g/L, respectively. Equilibration times, sample preparation, and selenium analysis were identical to those previously described.

Matrix Effects

The effect calcium (Ca²⁺) and sulfate (SO₄²⁻) concentrations on adsorption of Se(IV) and Se(VI) from a fixed concentration of 1.39 mg/L for Se(IV) and 0.53 mg/L for Se(VI) was investigated on NE1 25-30 soil. Ca²⁺ or SO₄²⁻ concentrations were 0, 0.1, 0.5, 1, 5, and 10 mM prepared with CaCl₂ and K₂SO₄ solutions at a constant ionic strength (I) of 0.03 by adding appropriate concentrations of KCl. For example, 0 mM Ca²⁺ (or SO₄²⁻) solution was prepared by 30 mM KCl solution yielding an I = 0.03; 5 mM Ca²⁺ (or SO₄²⁻) solution was prepared by 15 mM CaCl₂ (or K₂SO₄) mixed in 15 mM KCl yielding an I = 0.03; 10 mM Ca²⁺ (or SO₄²⁻) solution was prepared by 10 mM CaCl₂ (or K₂SO₄) yielding an I = 0.03 without addition of a KCl solution. (Note I = 0.5Σ c_i z_i² were c_i is the molar concentration of the ith ion and z is the charge of the ith ion).

The competitive effects of Ca^{2+} and SO_4^{2-} were furthered investigated by measuring multiconcentration isotherms from 1 mM KCl (I = 0.001), 1 mM CaCl₂ (I=0.003), 1 mM K₂SO₄ (I=0.003), and 1 mM CaSO₄ (I=0.004)) for selected soils (NE1 25-30, NE2 10-15, SE1 48.5-50, and MW1 17-19). To minimize the effect of the pH shifts that occur with different ionic solutions, pre-determined amounts of diluted HCl or NaOH solution were added such that pH was relatively constant for the four electrolyte solutions. Ionic strength of the equilibrating solutions was not controlled; however, ionic strength effects on selenium adsorption are small (Neal et al., 1987b, Peak and Sparks, 2002).

Data Analysis

The amount of selenium adsorbed (C_s , mg/kg) was calculated by the difference in selenium masses present in the applied solution and aqueous phase (C_w , mg/L) after equilibration with the soil. Selenium isotherms were fit with the Freundlich adsorption model;

$$C_{\rm s} = K_{\rm f} C_{\rm w}^{\rm N}$$
 Eq. 2-1

where K_f is the Freundlich adsorption coefficient (mg^{1-N} L^N kg⁻¹) and N (unitless) is a measure of isotherm linearity. Adsorption model parameter (K_f and N) optimization (nonlinear fits) and statistical regression analysis were performed using SAS/STAT program (SAS institute, 1989).

The Freundlich model is often the best approach to predicting adsorption as a function of concentration when adsorption is substantially nonlinear over the concentration range of interest and the specific adsorption mechanisms are not known. Problems arise using this approach when predictive transport models only allow for the input of a linear adsorption coefficient (K_d , L kg⁻¹ = C_s [mg/kg]/ C_w [mg/L]). In the latter case, the model can estimate a linearized concentration-specific K_d^* value using the Freundlich isotherm model coefficients (K_f and N) as follows:

$$K_{\rm d}^{*} = K_{\rm f} C_{\rm w}^{\rm N-1}$$
 Eq. 2-2

Note K_d^* is equal to K_f when $C_w = 1$ mg/L.

Fly Ash Leaching

Sequential Leaching

Sequential leaching experiments were performed in triplicate for ash samples collected from each site to imitate the recurrent flushing of disposed fly ash with water flow through the disposal site. For NE site, two ash samples were collected from 15-20 feet below ground surface (bgs) in cores NE3 and NE4 (labeled NE3 15-20 and NE4 15-20, respectively). For the SE site, four cores were collected from depths of 5-7 feet, 7-9 feet, 23.5-25.5 feet, and 33.5-37.5 feet in core SE1. Ash samples were combined to result in only 2 samples for leaching by mixing the samples collected at 5-7 feet with 7-9 feet for one representative sample labeled SE1 5-9, and samples 23.5-25.5 feet and 33.5-37.5 feet for a second representative sample labeled SE1 23.5-

37.5. For the MW site, ash was obtained from a bulk ash depository awaiting landfill placement. Approximately 9 g of ash and 35 mL of reagent-grade water were added to 80-mL Nalgene polycarbonate tubes. Tubes were rotated end-over-end for 24 h, followed by centrifugation at 2,700 rpm for 1 h. Aqueous equilibrium pH was measured after equilibration followed by removal and filtration of the supernatant using a 20 mL luer-lock syringe with 0.45 µm cellulose filter. Filtered solutions were divided into two subsamples with one acidified with HNO₃/NiNO₃ for total selenium analysis and the other acidified with HCl for Se(IV) analysis. Reagent-grade water was then added to the ash remaining in the tube to replace the solution removed, and the sequential leaching procedure was repeated approximately 15-25 times. Total selenium concentration in supernatants were determined after oxidizing Se(IV) to Se(VI), and Se(IV) was estimated by hydride vapor generation atomic absorption spectrometry (HVGAA). Se(VI) was estimated by subtracting Se(IV) concentrations from total selenium concentrations (Fio and Fujii, 1990).

Leaching Kinetics

A kinetic assay was performed on the same ash samples as used in the sequential leaching study to model the effect of varying residence times of water in ash disposal sites on the concentration of Se. Approximately 3 g of ash and 30 mL of reagent-grade water were added to acid-washed 80-mL Nalgene polycarbonate tubes. Tubes were rotated end-over-end. For each time increment, a set of triplicate bottles were removed, centrifuged at 2,700 rpm for 1 h, and the supernatant sampled and filtered for selenium analysis as previously described. Sampling times were as follows: 2 h, 4 h, 8 h, 1 d, 2 d, 4 d, 8 d, 12 d, 20 d, and 30 d. Supernatants were analyzed for total Se and Se(IV) as previously described.

Leachate Selenium Attenuation by Site Soils

An attenuation study was performed to assess the degree to which soils present at the site of disposal would attenuate Se present in the fly ash leachate compared to the 1 mM CaSO₄ solution which was considered to represent typical ash leachate and used in the standard adsorption studies. Leachate of SE1 5-9, SE1 23.5-37.5, and MW ashes was tested for site soils. Because of similar Se adsorption behavior between SE1 48.5-50 and SE1 60-62 soils, two soils were mixed (shown as SE1 48.5 + SE1 60) for this experiment and suspended with SE ash leachate. Ash leachate generated by one 24-hour equilibration cycle (i.e., a first sequential leaching) was spiked with Se(IV) or Se(VI) at 0, 100, or 250 μ g/L. One gram of soil and 10 mL spiked leachate were mixed in 15-mL Nalgene polycarbonate test tubes. The tubes were rotated end-over-end for 24 h, centrifuged at 4000 rpm for 20 min, and the supernatant sampled and filtered for selenium analysis as previously described. Se(IV) and Se(VI) were analyzed as previously described.

3 SELENIUM ADSORPTION ON SITE SOILS

NE Site

Soil Characterization Data

Selected soil properties for six soils representative of the NE site are shown in Table 3-1. NE site soils contained 13 to 29% clay composed predominantly of illite and mica with minor amounts of kaolinite. The soils contained less than 1% organic matter and their soil-water pH values ranged from 4.8 to 5.5. Selective Fe dissolution of the soils resulted in DCB-extractable Fe (intended to estimate total reducible Fe oxides) levels ranging from approximately 6,000 to 32,000 mg/kg, and DCB-extractable Al levels ranging from 270 to 1,300 mg/kg. Ranges in oxalate-extractable Fe and Al were less variable, with Fe ranging from 320 to 5,465 mg/kg, and Al ranging from 240 to 513 mg/kg. Based on the assumption that the oxalate extraction primarily dissolves amorphous Fe and Al oxides, the differences between DCB and oxalate extractable Al is amorphous. Fe extracted in 15 seconds with DCB ranged from 270 to 1,618 mg/kg, and was intended to estimate the most reactive portion of Fe oxides (i.e., Fe oxides exposed to solution and readily available for reaction). Of the 3 sites sampled in this study, the NE site has soils that are generally more acidic, have higher % clay, and have the higher upper range in DCB-extractable and oxalate-extractable Fe and Al than all other site soils.

Soil		рН	Sand	Silt	Clay	CECª	DCB⁵-Fe	DCB-AI	Ox°-Fe	Ox-Al	DCB-Fe 15 sec	Dominant Clay
	H ₂ O CaCl ₂ % cmol/kg						mg/kg	Winerals				
NE1 25-30	5.3	5.1	33	50	17	15.5	5,928	270	320	240	270	I, K, V
NE1 35-40	5.0	4.7	40	35	25	12.6	6,030	610	5,465	525	651	I, K, V
NE2 10-15	4.8	4.4	60	23	17	4.7	31,800	1,200	1,575	513	992	Ι, Κ
NE2 16-21	5.0	4.6	59	28	13	2.45	11,370	630	1,090	364	534	Ι, Κ
NE3 50-54	5.0	4.9	9	62	29	13.2	22,470	1,070	1,750	475	1,618	Ι, Κ
NE4 46-50	5.5	5.5	57	28	15	5.8	18,330	1,300	1,590	500	1,044	I, K

Table 3-1 Selected Properties of Six Soils Representative of the NE Site.

^a cation exchange capacity

^b dithionite-citrate bicarbonate extractable

°oxalate extractable

^d I = illite, K = kaolinite, V = vermiculite

Selenium Adsorption on NE Site Soils

Adsorption data for Se(IV) and Se(VI) on the six soils representative of the NE sites were measured and fit with the Freundlich isotherm model. Se(IV) and Se(VI) isotherms are plotted in Figures 3-1 and 3-2, and modeling fits are summarized in Table 3-2. K_r adsorption coefficients (mg^{1-N} L^N kg⁻¹) ranged between 40.4 and 107 for Se(IV), and between 6.69 and 13.3 for Se(VI). Nonlinearity was greater for Se(IV) with Freundlich N values ranging from 0.249 to 0.436 compared to Se(VI) with N values ranging from 0.859 to 0.982. Adsorption of Se(IV) is also consistently much higher than that observed for Se(VI) with Freundlich K_r values being 6 to 11 times higher those for Se(IV). To exemplify the overall selenium adsorption behavior observed for the six representative samples of the NE site, Se(IV) and Se(IV) isotherms for the lowest and highest adsorption profiles are shown in the upper graphs of Figure 3-3. Also shown in Figure 3-3 (lower graphs) is the concentration-specific K_d^* values as a function of concentration that could be used to estimate site-specific transport at a given ash leachate concentration. Note that the more nonlinear the sorption isotherms, the larger the range in the concentration-specific K_d^* values (e.g., compare the more nonlinear Se(IV) profiles with the Se(VI) profiles).

Table 3-2
Freundlich Isotherm Fits for Selenite [Se(IV)] and Selenate [Se(VI)] Adsorption From 1 mM
CaSO, for NE Site Soils.

Soil			Se(IV)		Se(VI)				
	рНª	K, ^b	Ν	r ²	pН	K,	Ν	r²	
NE1 25-30	5.24	40.4 (1.6)°	0.436 (0.037) [°]	0.970	5.34	6.69 (1.37)	0.952 (0.107)	0.965	
NE1 35-40	5.52	71.0 (2.6)	0.331 (0.028)	0.951	5.62	10.8 (1.0)	0.904 (0.054)	0.987	
NE2 10-15	4.78	107 (4)	0.312 (0.024)	0.959	4.68	10.1 (1.3)	0.982 (0.070)	0.986	
NE2 16-21	4.85	75.0 (2.7)	0.339 (0.028)	0.952	4.89	6.77 (0.92)	0.871 (0.071)	0.977	
NE3 50-54	4.95	83.2 (3.1)	0.249 (0.020)	0.956	4.88	13.3 (1.4)	0.859 (0.063)	0.981	
NE4 46-50	5.51	101 (3.1)	0.400 (0.025)	0.977	5.47	11.5 (2.5)	0.946 (0.122)	0.950	

^a average aqueous pH values in which isotherm was measured

^b $K_{\rm f} = {\rm mg}^{(1-N)} {\rm L}^{\rm N} {\rm kg}^{-1}$

[°] numbers in parentheses are standard errors



Figure 3-1 Se(IV) Adsorption Isotherms for NE Site Soils.



Figure 3-2 Se(VI) Adsorption Isotherms for NE Site Soils.



Figure 3-3

Se(IV) and Se(VI) adsorption profiles (upper graphs) for NE site soils using NE3 50-54 soil (solid line) and NE1 25-30 soil (dashed line); and effect of nonlinearity and Se concentration on concentration-specific Kd* values (lower graphs)

SE Site

Soil Characterization Data

Selected soil properties for six soils representative of the SE site are shown in Table 3-3. The SE site soils contained <5% clay, which was dominated by kaolinite and illite, with kaolinite being the dominant clay mineral in all soils except SE3 38.5 and SE2 23.5. Soils contained less than 1% organic matter and their soil-water pH values ranged from 5.6 to 6.4. Selective Fe dissolution of the soils resulted in DCB-extractable Fe levels ranging from approximately 5,243 to 14,948 mg/kg, and DCB-extractable Al levels ranging from 150 to 900 mg/kg. Ranges in oxalate-extractable Fe and Al were less variable, with oxalate extractable Fe ranging from 245 to 757 mg/kg, and oxalate extractable Al ranging from 228 to 486 mg/kg. Based on the assumption that the oxalate extraction primarily dissolves amorphous Fe and Al oxides, the differences

between DCB and oxalate extracts indicate that 4 to 8% of extractable Fe in the soils is amorphous, and that half to all of extractable Al is amorphous. Fe extracted in 15 seconds with DCB ranged from 56 to 330 mg/kg, and was intended to estimate the most reactive portion of Fe oxides (i.e., Fe oxides exposed to solution and readily available for reaction). Of the 3 sites sampled in this study, the SE site soils represent the middle range for pH, % clay, and DCBextractable and oxalate-extractable Fe and Al range.

Selenium Adsorption on SE Site Soils

Adsorption data for Se(IV) and Se(VI) on the six soils representative of the SE site were measured and fit with Freundlich and Langmuir isotherm models. Se(IV) and Se(VI) isotherms are plotted in Figures 3-4 and 3-5, and modeling fits are summarized in Table 3-4. K, adsorption coefficients (mg^{1-N} L^N kg⁻¹) ranged between 25.0 and 84.2 for Se(IV) adsorption, and between 3.91 and 9.27 for Se(VI), which are lower than observed for NE site soils. Similar to the NE site soils, Se(IV) was more adsorbed and isotherms more nonlinear than Se(VI), but overall adsorption nonlinearity was less for SE site soils with Freundlich N values of 0.332 to 0.570 for Se(IV) and 0.935 to 1.03 for Se(VI). Freundlich K_{e} values for Se(IV) are 5.4 to 11 times higher than observed for Se(VI). To exemplify the overall selenium adsorption behavior at the SE site, Se(IV) and Se(VI) isotherms for the lowest and highest adsorption observed for the six soils considered representative of the site are shown in Figure 3-6, as well as the effect of nonlinearity on the concentration-specific K_d^* values that would be used to estimate site-specific transport. Note that the lowest sorption was observed for Se(VI) with an N values of 1.032, which is not statistically different than unity; however, this slightly greater than unity N value resulted in a slight decline in concentration-specific K_d^* values with decreasing C_w values, which is the opposite of what is observed when N<1. Nevertheless, there is essentially a negligible effect of concentration on the K_d^* value for this soil, because sorption is nearly linear.

Soil	i	рH	Sand	Silt	Clay	CEC [®]	DCB⁵-Fe	DCB-AI	Ox°-Fe	Ox-Al	DCB-Fe 15 sec	Dominant Clay
3011	H₂O		l ₂ %		cmol/kg		mg/kg					
SE1 48.5-50	5.7	5.4	62	33	5	4.3	7,105	450	576	486	150	K, I
SE1 60-62	6.0	5.8	56	39	5	4.8	14,948	900	757	423	330	K, I
SE2 23.5-25.5	6.1	6.1	66	31	3	4.1	8,399	182	413	305	56	K, I
SE2 33.5-35.5	6.4	6.2	60	35	5	2.7	5,243	280	245	228	60	K, I
SE3 5.5-7.5	5.6	5.4	66	29	5	3.1	6,209	280	226	395	84	K, I
SE3 38.5-40.5	6.2	6.1	62	35	3	4.1	6,647	150	500	243	73	K, I

Table 3-3			
Selected Pro	perties of Six Soil	s Representative	of the SE Site.

^a cation exchange capacity

^b dithionite-citrate bicarbonate extractable

° oxalate extractable

^d K = kaolinite, I = illite



Figure 3-4 Se(IV) Adsorption Isotherms for SE Site Soils.



Figure 3-5 Se(VI) Adsorption Isotherms for SE Site Soils.
Table 3-4
Freundlich Isotherm Fits for Selenite [Se(IV)] and Selenate [Se(VI)] Adsorption From 1mM
CaSO₄ for SE Site Soils.

Soil			Se(IV)		Se(VI)					
	рН°	K ^b _f	Ν	r ²	pН	K,	Ν	r²		
SE1 48.5-50	4.67	84.2 (1.7) [°]	0.570 (0.026)°	0.991	4.47	7.67 (1.7)	0.968 (0.118)	0.958		
SE1 60-62	4.89	68.7 (1.6)	0.480 (0.026)	0.985	4.70	9.27 (1.2)	0.945 (0.071)	0.982		
SE2 23.5-25.5	5.34	48.0 (1.3)	0.524 (0.029)	0.988	5.20	4.52 (0.32)	0.977 (0.036)	0.996		
SE2 33.5-35.5	5.42	26.7 (1.8)	0.522 (0.045)	0.969	5.53	3.91 (0.55)	1.032 (0.069)	0.988		
SE3 5.5-7.5	4.51	61.0 (2.2)	0.332 (0.025)	0.961	4.56	7.18 (0.89)	0.952 (0.070)	0.982		
SE3 38.5-40.5	5.84	25.0 (1.7)	0.368 (0.047)	0.933	5.62	4.64 (0.64)	0.935 (0.067)	0.985		

^a average aqueous pH values in which isotherm was measured ^b $K_{\rm f} = {\rm mg}^{(1-N)} {\rm L}^{\rm N} {\rm kg}^{-1}$ ^c numbers in parentheses are standard errors



Figure 3-6

Se(IV) and Se(VI) adsorption profiles (upper graphs) for SE site soils using SE1 48.5-50 soil (solid line) and SE2 33.5-35.5 soil (dashed line); and effect of nonlinearity and Se concentration on concentration-specific Kd* values (lower graphs).

MW Site

Soil Characterization Data

Selected soil physical-chemical properties for six soil samples representative of the MW site are shown in Table 3-5. The MW soils are predominately sands (93 to 97% sand) with <1% clay; therefore, clay type analysis was not pursued. Soils contained less than 0.5% organic matter and their soil-water pH values ranged from 6.8 to 8.1. Selective Fe dissolution of the soils resulted in DCB-extractable Fe levels ranging from 2,718 to 4,540 mg/kg, and DCB-extractable Al levels ranging from 175 to 610 mg/kg. Ranges in oxalate extractable Fe and Al were less variable, with oxalate-extractable Fe ranging from 217 to 570 mg/kg, and oxalate-extractable Al ranging from 78 to 456 mg/kg. Based on the assumption that the oxalate extraction primarily dissolves amorphous Fe and Al oxides, the differences between DCB and oxalate extracts indicate that 4 to

13% of extractable Fe in the soils is amorphous, and 39 to 100% of extractable Al is amorphous. Fe extracted in 15 seconds with DCB ranged from 8 to 69 mg/kg, and was intended to estimate the most reactive portion of Fe oxides (i.e., Fe oxides exposed to solution and readily available for reaction). Of the 3 sites sampled in this study, the MW site soils have the highest sand content by far, the higher soil pH range (neutral to alkaline pH values), and the lowest levels of DCB-extractable Fe relative to all other site soils.

Selenium Adsorption on MW Site Soils

Adsorption data for Se(IV) and Se(VI) on the six soil samples representative of the MW site were measured and fit with Freundlich isotherm model. Se(IV) and Se(VI) isotherms are plotted in Figures 3-7 and 3-8, and modeling fits are summarized in Table 3-6. K_f adsorption coefficients (mg^{1-N} L^N kg⁻¹) ranged between 8.16 and 15.8 for Se(IV), and between 1.96 and 3.12 for Se(VI), which are the lowest observed for any of the three sites. Adsorption was lowest on the MW site soil samples, but adsorption isotherms exhibited less nonlinearity, with Freundlich N values of 0.489 to 0.750 for Se(IV) and 0.772 to 0.989 for Se(VI). Similar to the NE and SE sites, adsorption of Se(IV) is consistently higher on these soils than that observed for Se(VI) with Freundlich K_f values being 2.5 to 7.4 times higher than for Se(VI), although differences between Se(IV) and Se(VI) were much less than observed for soil samples from the other two other sites. The overall selenium adsorption behavior at the MW site is exemplified in Figure 3-9, with Se(IV) and Se(VI) isotherms for the lowest and highest adsorption observed for the six soils shown as well as the effect of nonlinearity on the concentration-specific K_d^* values that would be used to estimate site-specific transport.

Soil		рН		Silt	Clay	CEC ^a	DCB⁵-Fe	DCB-AI	Ox°-Fe	Ox-Al	DCB-Fe 15 sec
	H₂O	CaCl ₂		%		cmol/kg			mg/kg		
MW1 17-19	8.1	7.3	93	4	3	3	4540	610	570	456	69
MW1 33-35	7.7	6.9	95	4	1	1.4	3781	198	145	78	15
MW2 17-19	7.5	6.2	95	4	1	1.4	3312	382	261	253	28
MW2 25-27	6.8	6.3	97	2	1	1.4	3143	175	217	95	12
MW3 17-19	7.7	6.8	95	4	1	1.7	2718	389	299	384	23
MW3 23-25	8.0	6.8	95	4	1	1.4	2964	105	241	105	8

Table 3-5Selected Properties of Six Soils Representative of the MW Site.

^a cation exchange capacity

^b dithionite-citrate bicarbonate extractable

°oxalate extractable

0.877 (0.055)

0.918 (0.076)

0.989 (0.053)

0.787 (0.070)

0.828 (0.059)

0.983

0.971

0.988

0.963

0.977

Freundlich Isotherm Fits for Selenite [Se(IV)] and Selenate [Se(VI)] Adsorption From 1mM CaSO₄ for MW Site Soils.										
Seil		9	Se(IV)	Se(VI)						
501	рН°	K, ^b	Ν	r²	рН	K,	Ν	r²		
MW1 17-19	7.63	15.8 (0.8)°	0.646 (0.030)°	0.992	7.35	2.51 (0.37)	0.772 (0.041)	0.987		

0.977

0.939

0.971

0.953

0.953

6.74

6.38

6.53

6.89

6.78

1.96 (0.31)

2.18 (0.43)

2.91 (0.33)

3.12 (0.75)

2.06 (0.39)

0.750 (0.062)

0.489 (0.062)

0.468 (0.040)

0.655 (0.074)

0.506 (0.054)

Table 3-6

11.3 (1.0) ^a average aqueous pH values in which isotherm was measured

14.5 (1.5)

7.93 (0.87)

8.16 (0.6)

10.8 (1.4)

^b $K_{\rm f} = {\rm mg}^{(1-N)} {\rm L}^{\rm N} {\rm kg}^{-1}$

MW1 33-35

MW2 17-19

MW2 25-27

MW3 17-19

MW3 23-25

 $^{\circ}$ numbers in parentheses are standard error

7.06

6.45

6.57

6.98

6.84



Figure 3-7 Se(IV) Adsorption Isotherms on MW Site Soils.



Figure 3-8 Se(VI) Adsorption Isotherms on MW Site Soils.



Figure 3-9

Se(IV) and Se(VI) adsorption profiles (upper graphs) for MW site using MW1 17-19 soil (solid line) and MW2 17-19 soil (dashed line; and effect of nonlinearity and Se concentration on concentration-specific Kd* values (lower graphs).

4 FACTORS AFFECTING SELENIUM ADSORPTION

Effects of Solution pH on Selenium Adsorption

The adsorption of selenium was expressed quantitatively as the percentage of selenium adsorbed (removed from the initial solution) relative to the applied concentration. Adsorption envelopes produced for each selenium species as a function of pH are shown in Figures 4-1, 4-2, and 4-3 for one soil sample from each site (NE1 25-30, SE1 48.5-50, and MW1 17-19). The initial concentration of spiked selenium of 0.52 mg/L for Se(IV) and 0.41 mg/L for Se(VI) is approximately mid range of the concentrations used in the multi-concentration isotherm measurements from 1 mM CaSO₄ system. Two arrows shown in each figure indicate the range of equilibrium pH values observed when soils were mixed with water, 1 mM CaCl₂, and 1 mM CaSO₄ solutions (no pH adjustments).

It is evident that selenium adsorption of selenium species is strongly dependent on pH with the greatest adsorption occurring in the acidic pH range. For Se(IV), the apparent adsorption maxima varies with soil type with NE1 25-30, SE1 48.5-50, and MW1 17-19 exhibiting apparent maxima or adsorption plateaus at pH < 4.5, pH < 5.5, and pH < 7, respectively. Adsorption of Se(VI) is pH-dependent over the entire pH range studied (approximately 3 to 9) with sorption consistently decreasing with increasing pH. The increase in adsorption with decreasing pH of the soil is characteristic of anion adsorption. Similar pH-dependent Se(IV) adsorption was reported for oxides, pure clay minerals, and natural soils (Balistrieri and Chao, 1987; Hingston et al., 1972; Neal et al., 1987a). Increased protonation of soil surface functional groups ($\equiv OH_2^+$) with decreasing pH is expected to increase the anion exchange capacity, and therefore, increase the amount of anions sorbed on the soil particles. Frequent observations that Se(IV) adsorption maxima (μ mol/g) greater than expected from surface positive charge of sorbent suggests that Se(IV) can replace the uncharged OH₂ surface groups (ligand exchange) (Rajan, 1979).

Soil solution pH may change as the ash leachate plume moves through soils down gradient of an ash landfill, thus affecting selenium mobility. The potential changes in soil solution pH will depend on the natural soil pH, the buffer capacity of the soil, the pH and buffer capacity of the ash leachate, and residence time. For the NE soils, the range in soil pH in water and 1 mM CaCl₂ is between 4.4 and 5.5, and the ash pH associated with that site ranged between 5.5 and 6.2 (Section 5). Therefore, assuming the pH envelope for NE1 25-30 is representative of the NE site, substantial changes in mobility of Se(VI) only may be expected as a worse case scenario, which assumes that the buffer capacity of the ash is much greater than the soil buffer capacity.







Figure 4-2 pH Effects on Se Adsorption on SE1 48.5 Soil (C, is the applied Se concentration).





Given that the NE soils contain about 1% carbon, significant % clay, and high extractable Fe and Al, the soil is likely to have a reasonable capacity to buffer pH changes. For the SE soils, the range in soil pH in water and 1 mM CaCl₂ is between 5.4 and 6.4, and the ash associated with that site has a pH \approx 6 (Section 5). Assuming the pH envelope for SE1 48.5 is representative of the SE site, soil solution pH and therefore selenium adsorption is unlikely to change much over time. For the MW soils, the range in soil pH in water and 1 mM CaCl₂ is between 6.2 and 8.1; however, the ash associated with this site yields a leachate with a much higher pH of 11 to 12 (Section 5). Soils at this MW site are also very sandy (93 to 97% sand), thus have little buffer capacity or adsorption capacity. Therefore, enhanced mobility of both Se(IV) and Se(VI) is likely as ash leachate plume passes through the soil.

Effects of Solution Matrix on Selenium Adsorption

The effect of calcium (Ca²⁺) and sulfate (SO₄²⁻) in solution on adsorption of Se(IV) and Se(VI) on NE1 25-30 soils is shown in Figure 4-4 from a fixed concentration of 1.39 mg/L for Se(IV) and 0.53 mg/L for Se(VI). The impact of increased sulfate concentration on both Se(IV) and Se(VI) adsorption is much greater than impact of calcium over the range of concentrations (0 to 10 mM). From sulfate free to 10 mM SO_4^{2} solutions, Se(IV) adsorption decreased from 43.8 mg/kg to 27.9 mg/kg, and Se(VI) adsorption decreased from 7.22 mg/kg to 1.49 mg/kg for Se(VI), which corresponds to a 36% and 79% decrease, respectively. The greater decrease in Se(VI) adsorption relative to Se(IV) is in agreement with the hypothesis that Se(VI) forms outer-sphere complexes similar to sulfate, whereas Se(IV) tends to form inner-sphere complexes more like phosphate (Neal et al., 1987b). Increases in adsorption with increasing calcium concentrations up to 10 mM were small and similar for both selenium species with a 17.4% and 17.9% increase in sorption for Se(IV) and Se(VI), respectively. Similar increases in selenium adsorption in the presence of Ca have been reported for several soils (Neal et al., 1987b); however, little information is currently available concerning the specific mechanism of this enhanced adsorption. Plausible explanations for this phenomenon include: (1) sorption of Ca^{2+} to negatively charged surface sites making the electrical potential at those sites less negative, thereby increasing the adsorption of selenium anions; (2) intramolecular bridging of Ca^{2+} between an oxyanion and negatively charged surface site; and (3) co-precipitation. The latter is unlikely given the relatively low concentration of selenium in solution used in this study.





Impact of Concentration of Ca and SO₄ on Se Adsorption on NE1 25-30 (C_i is the applied Se concentration).

In Figures 4-5 and 4-6, the multi-concentration isotherms measured from 1 mM KCl, 1 mM CaCl₂, 1 mM K₂SO₄, and 1 mM CaSO₄ are shown for Se(IV) and Se(VI), respectively. For Se(VI), only SO_4^{2} appears to affect sorption significantly, thus sorption is similar and suppressed in CaSO₄ and K₂SO₄ and higher but similar in CaCl₂ and KCl (Figure 4-6). Se(IV) sorption is also reduced by SO_4^{2-} ; but in addition, Ca²⁺enhanced sorption resulting in the following trends for all three soils investigated: $1 \text{ m}M \text{ CaCl}_2 > 1 \text{ m}M \text{ CaSO}_4 > 1 \text{ m}M \text{ KCl} > 1 \text{ m}M \text{ K}_2\text{SO}_4$ (Figure 4-6). This phenomena supports the conclusion derived from Figure 4-4 with the one exception that the effects of sulfate on Se(IV) adsorption is much greater than calcium, yet adsorption of Se(IV) from 1 mM CaSO, is greater or similar to 1 mM CaCl, Se(IV) adsorption from 1 mM K_3SO_4 is less than 1 mM KCl, but the difference is less than expected. Also in all cases, increases in Se(IV) adsorption from 1 mM CaSO₄ and 1 mM CaCl₂ relative to 1 mM KCl are much greater. The less than expected differences between Se(IV) adsorption from 1 mM K₂SO₄ and 1 mM KCl, and the larger than expected differences between Se(IV) adsorption in 1 mM CaSO₄ and 1 mM CaCl₂ relative to 1 mM KCl may partially be due to the differences in solution ionic strength. Ionic strength increased as follows: 1 mM KCl (I = 0.001) < 1 mM $K_2SO_4 = 1 \text{ mM CaCl}_2$ (I = 0.003) < 1 mM CaSO₄ (I=0.004). Ionic strength was not controlled in the multi-concentration isotherms experiment, because the differences in ionic strength (0.001 to 0.004) were hypothesized to be small based on existing literature (Neal et al., 1987b; Peak and Sparks, 2002). However, based on Se(IV) adsorption from 1 mM K₂SO₄ and 1 mM CaCl₂ at a constant and where Ca^{2+} and SO_{4}^{2-} coexist in equal concentrations, Ca^{2+} has the greater impact on Se(IV).







Figure 4-6 Ionic Matrix Effects on Se(VI) Adsorption on NE1 25-30 and NE2 10-15 Soils.

Adsorption Data versus Soil Characteristics for All Sites

Evaluating the main soil factors involved in adsorption mechanism of selenium in soil and quantifying correlations between sorption and key soil properties can be useful in making approximate a priori predictions of selenium mobility at a site. Towards this goal, simple and multiple linear regression analyses were performed between Se(IV) and Se(VI) adsorption and several soil properties. For both the simple and the multiple linear regression analyses, similar results were obtained using either K_f adsorption coefficients or concentration-specific K_d^* values estimated using equation 2-2 with different concentrations. The results of the simple linear regression analysis for both Se(IV) and Se(VI) using the K_f adsorption coefficients and K_d^* values calculated at $C_w = 100 \mu g/L$ are shown in Tables 4-1 and 4-2, respectively.

From the simple linear regression analysis, soil clay and oxide contents were found to show the best positive correlations. For the oxide data, the best correlation was found with easily reducible Fe for both Se(IV) and Se(VI) (shown as15-sec DCB-Fe in Tables 4-1 and 4-2) as exemplified in Figure 4-7. For both species, selenium adsorption was negatively correlated with soil isotherm pH, supporting the general trend of decreasing adsorption with increasing pH shown in Figures 4-1 through 4-3. Based on the simple linear regression analysis, pH, clay content, and 15-sec DCB-Fe appear to be the most important soil properties affecting selenium adsorption from a constant solution matrix (1 mM CaSO₄).

A summary of the stepwise multiple linear regression analyses using K_d^* values for both Se(IV) and Se(VI) calculated at $C_w = 100 \mu g/L$ (Table 4-3) shows that correlations are improved when clay and oxide contents were combined with pH. The best prediction for selenium adsorption in this study was made using 15 sec-DCB-Fe content in combination with isotherm pH with r^2 being 0.884 and 0.818, for Se(IV) and Se(VI), respectively. Combining pH and clay content also gave good predictions for Se(IV) and Se(VI) adsorption with $r^2 = 0.802$ and 0.836, respectively. Note that the fraction of oxides will be present in the clay fraction (< 2 µm); however, not all clays are oxides; therefore, the relatively high correlation coefficients for clay is a little surprising. Both pH and clay content are easily measured on any soil sample making this particular correlation appealing for predicting adsorption characteristics of selenium species by a soil. Note that correlations using simultaneously both clay and oxides parameters also appear good, but since the oxides are within the clay fraction, this in part, gives weight to the same parameter twice.

Table 4-1

Summary of simple linear regressions between various soil parameters and the massbased Freundlich isotherm adsorption coefficients (Kf, $mg^{1-N} L^N kg^{-1}$) estimated in 1 mM CaSO₄.

Specie	Regression	рН°	Clay	DC - Fe	DC - AI	Ox - Fe	Ox - Al	15-sec DCB-Fe			
	Falameter		%	mg/kg							
Se(IV)	slope	-28.40	2.68	0.003	0.057	0.013	0.139	0.053			
	intercept	210	25.4	19.9	18.9	36.4	1.90	30.0			
	R²	0.635	0.479	0.499	0.385	0.212	0.339	0.514			
Se(VI)	slope	-2.76	0.351	0.0003	0.006	0.002	0.016	0.007			
	intercept	22.0	3.25	3.39	3.14	4.58	1.06	4.00			
	R²	0.530	0.727	0.439	0.377	0.368	0.373	0.685			

^a equilibrium pH values of adsorption isotherm

Table 4-2

Summary of simple linear regressions between various soil parameters and the concentration-specific selenium adsorption coefficients (Kd*,L/kg; Cw=100 μ g/L) estimated in 1 mM CaSO₄.

Specie	Regression	pH°	Clay	DC - Fe	DC - AI	Ox - Fe	Ox - Al	15-sec DCB-Fe			
	Farameter		%	%mg/kg							
Se(IV)	slope	-129	15.2	0.017	0.302	0.072	0.684	0.303			
	intercept	931	65.7	38.8	39.3	127.4	-34.0	90.9			
	R²	0.556	0.652	0.641	0.460	0.295	0.350	0.712			
Se(VI)	slope	-3.019	0.448	0.0003	0.007	0.002	0.019	0.008			
	intercept	24.4	3.66	4.26	3.76	5.37	1.15	4.62			
	R ²	0.382	0.786	0.372	0.360	0.398	0.370	0.740			

^a equilibrium pH values of adsorption isotherm





Linear Correlation for Se(IV) and Se(IV) Between Concentration Specific Kd* Values and Easily Reducible Fe Assayed Using a 15-second DCB Extraction Method.

Table 4-3

Summary of Multiple Linear Regression Analyses Between Various Soil Parameters and the Concentration-Specific Selenium Adsorption Coefficients (Kd*,L/kg; Cw=100 μ g/L)

											r²
Se(IV)	-78.0	pН	+	10.8	Clay	+	548				0.802
	-79.0	рН	+	0.012	DCB-Fe	+	536				0.796
	-104	рН	+	0.227	DCB-AI	+	674				0.794
	-113	рН	+	0.052	Ox-Fe	+	794				0.700
	-106	рН	+	0.432	Ox-Al	+	656				0.678
	-80.0	рН	+	0.229	15sec-Fe	+	573				0.884
	5.35	clay	+	0.213	15sec-Fe	+	76.4				0.730
	0.02	DCB-Fe	-	0.030	DCB-AI	+	42.8				0.643
	0.05	Ox-Fe	+	0.511	Ox-Al	-	19.7				0.456
	-88.7	рН	+	0.007	DCB-Fe	+	0.117	DCB-AI	+	581	0.811
	-101	рН	+	0.040	Ox-Fe	+	0.300	Ox-Al	+	635	0.751
	9.80	clay	+	0.013	DCB-Fe	-	0.082	DCB-AI	+	29.9	0.807
	14.6	clay	+	0.018	Ox-Fe	+	0.301	Ox-Al	-	12.7	0.707
Se(VI)	-1.24	рН	+	0.387	Clay	+	11.2				0.836
	-2.03	рН	+	0.0002	DCB-Fe	+	16.8				0.499
	-2.40	рН	+	0.006	DCB-AI	+	18.1				0.584
	-2.53	рН	+	0.002	Ox-Fe	+	20.0				0.656
	-2.24	рН	+	0.014	Ox-Al	+	15.5				0.552
	-1.50	рН	+	0.007	15sec-Fe	+	13.5				0.818
	0.29	clay	+	0.003	15sec-Fe	+	3.84				0.814
	0.0002	DCB-Fe	+	0.003	DCB-AI	+	3.80				0.392
	0.002	Ox-Fe	+	0.013	Ox-Al	+	1.64				0.542
	-2.81	рН	-	0.0002	DCB-Fe	+	0.008	DCB-AI	+	20.5	0.598
	-2.15	рН	+	0.002	Ox-Fe	+	0.008	Ox-Al	+	15.4	0.709
	0.41	clay	+	0.00001	DCB-Fe	+	0.001	DCB-AI	+	3.25	0.795
	0.42	clay	-	0.0002	Ox-Fe	+	0.007	Ox-Al	+	1.84	0.824

5 ATTENUATION OF SELENIUM IN ASH LEACHATE

Leaching and adsorption experiments were performed using leachate generated from site ash samples to evaluate the effect of the leachate matrix on selenium adsorption. One or two ash samples from each site were used in sequential and kinetic leaching studies. Ash samples were selected based on their location with respect to the water table. For each site, if appropriate, one ash was selected that resided predominantly above the water table (unsaturated) and one ash was selected that resided predominantly below the water table (saturated).

Sequential Leaching

Average pH values measured for sequential leaching of ash samples obtained from each site are summarized in Figure 5-1 (upper figure). In all but the high pH of MW ash, pH values were lowest in the first leaching and then stabilized at slightly higher pH values for subsequent leachings, with NE 4 15-20 exhibiting the largest increase in pH of one unit from the first to third sequential leaching. All ashes stabilized at pH values between 6 and 6.4 except the MW ash, which had a pH of about 11.7 in the first leaching and 11.3 by the 15th sequential leaching.

Selenium concentrations over the sequential leaching series are shown on Figure 5-2. In all cases Se(VI) is the primary form of selenium in sequential leaching. Total selenium was less than 50 μ g/L in all ashes except NE3 15-20, in which Se(IV) approaches 20 µg/L for several leachings. For the NE and MW ash, selenium concentrations in the first leachate were 0 to $<20 \mu g/L$ (ash dependent) followed by increasing concentration up to approximately the 5th leaching and then remained at this concentration of 35 to 50 µg/L (ash dependent) for the remaining 10 leachings. The 2 ashes from the SE site behaved distinctly different from each other as well as the other ashes. SE1 5-9 had the highest concentration in the first leachate ($\approx 32 \,\mu g/L$) and then decreased rapidly to approximately 5 μ g/L by the 6th leaching and remained at that concentration for the next 10 leachings. The other SE ash (SE1 23.5-37.5) had constant and relatively high concentrations (\approx 32 µg/L) through the first 6 leachings and then increased to a plateau concentration of just over 50 µg/L for the remaining leachings. The difference in leaching patterns implies possible differences in the mineral form of Se as well as the location of Se in the ash particles (on the ash surface versus within the internal volume of the ash). The sequential leaching pattern for SE1 23.5-27.5 is indicative of a change in the solubility control as various inorganic constituents are leached. The complex or precipitate that has the lowest solubility product for a given pH-redox condition will limit the Se concentrations that can exist in solution. As the lower solubility limit precipitate is washed away, another complex or precipitate of higher solubility will become the new limiting factor. Whereas, the sequential leaching pattern of SE1 5-9 is indicative of an easily removed fraction of Se, perhaps surface associated followed by mass transfer constrained release from within the ash particle. Changes in pH and redox state can also contribute to concentration changes with sequential leachings; however, after the first leaching, pH was relatively constant with leaching.



Figure 5-1 pH Profile Over Sequential and Kinetic Leaching Series for Ash Samples Collected From SE Site and NW Site



Figure 5-2

Total selenium (IV+VI) and Se(IV) profiles over sequential leaching series for ash samples collected from NE, SE, and MW sites. Total Se are the average values of triplicate and the standard deviations are shown as error bars.

Leaching Kinetics

Average pH values measured for leaching kinetics of ash samples obtained from each site are summarized in Figure 5-1 (lower figure). Total selenium and Se(IV) leaching profiles over time for ash samples are shown in Figure 5-3. The average pH values and selenium concentrations were similar to what was observed in the sequential leaching study with one exception. SE1 23.5-37.5 only reached 35 μ g/L over the 2 month period whereas 50 μ g/L was observed in the sequential leaching. However, Se concentrations in the first 6 leachings are around 32 μ g/L (Figure 5-2), which is comparable to the upper concentration reached within the 60 day time frame in the kinetics study (Figure 5-3) before a change in the solubility control occurred. Therefore, even in the absence of mass transfer constraints, maximum observed concentrations in a kinetic study, where no leachate replacement occurs, may likely not compare well to what is observed in the field. For all ashes, Se concentrations appear to increase over the time frame of the study with the initial rate of increase being orders of magnitude greater than at later times with the exception of MW ash. For the latter, Se concentrations continued to rise at what appears to be a steady rate of increase for the entire 2 months. Although laboratory leaching studies can be insightful, several factors including residence time and release kinetics, ash mass to solution volume ratio, total pore volumes passed, and microbial activity will contribute to differences of the maximum concentrations observed in a laboratory study compared to a field scenario.

Leachate Selenium Attenuation by Onsite Soils

Attenuation of selenium by the SE and MW soils from ash leachate collected at those sites is shown for Se(IV) in Figure 5-4 and for Se(VI) in Figure 5-5 along with the multi-concentration selenium isotherms measured from 1 mM CaSO₄. Se(IV) and Se(VI) present in the ash leachate were significantly attenuated through adsorption by the site soils in a manner consistent with the isotherms developed using 1 mM CaSO₄. Therefore, the use of 1 mM CaSO₄ for selenium adsorption matrix appear to be a reasonably good simulated leachate matrix for conducting laboratory equilibrium adsorption test.



Figure 5-3

Batch kinetic Leaching of Total Selenium (IV+VI) and Se(IV) From SE and MW Ash Samples. Total Se Are the Average Values of Duplicate and the Data Ranges Are Shown as Error Bars.



Figure 5-4 Attenuation of Se(IV) by Soil Adsorption Present in Ash Leachate by SE and MW Site Soils, Along With Multi-Concentration Se(IV) Isotherms Measured From 1 mM CaSO,



Figure 5-5 Attenuation of Se(VI) by soil Adsorption Present in Ash Leachate by SE and MW Site Soils, Along With Multi-Concentration Se(VI) Isotherms Measured From 1 mM CaSO₄.

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