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Impact of Cementitious Leachate on Se, Nb and Ra Partitioning

J.C. Seaman¹

Hyun-shik Chang²

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¹Senior Research Scientist
Assistant Director – Research/Quality Assurance
Savannah River Ecology Laboratory
The University of Georgia
Aiken, SC 29802
Phone: 803-725-0977
Email: seaman@uga.edu

²Assistant Research Scientist



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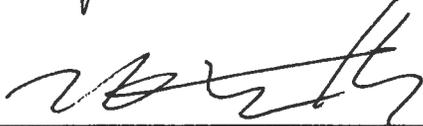
The University of Georgia
Savannah River Ecology Laboratory

REVIEWS AND APPROVALS

Authors:



John C. Seaman, SREL Associate Director-Research
Senior Research Scientist
9/5/13
Date



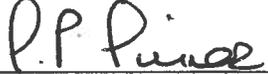
Hyun-shik Chang, Assistant Research Scientist
9/5/13
Date

Review:



Diana Soteropoulos – Research Coordinator
9/5/13
Date

Approval:



Steven Simner, SRR CTF
9/9/13
Date

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EXECUTIVE SUMMARY

The current study consisted of three separate objectives: (I) evaluating the partitioning (i.e., K_d values) of both selenium redox species (i.e., Se(IV) and Se(VI)) to subsurface sediments typical of those underlying the Saltstone Disposal Facility (SDF) under oxidizing and reducing conditions; (II) evaluating niobium (Nb) partitioning to the same SDF sediments under oxidizing and reducing conditions; and (III) evaluating radium (Ra) partitioning to reducing and non-reducing cementitious materials under oxidizing and reducing conditions. These three objectives were accomplished in three separate batch sorption experiments. In addition, a chromatography-based technique for determining the redox speciation of Se in aqueous samples was tested as part of Objective I.

The experimental conditions were chosen to be consistent with the Conceptual Geochemical Models for the Closed Radioactive Waste Tanks and the SDF as outlined by Kaplan (2010) in *Geochemical Data Package for Performance Assessment Calculations Related to the Savannah River Site* (SRNL-STI-2009-00473). Data from the current study can be used to provide direct and indirect information about radionuclide behavior related to the SDF and Tank Farm Performance Assessments (PAs).

For all three experiments, contaminant sorption was evaluated using four different background solution chemistries chosen to mimic various stages of saltstone/cement aging. Two alkaline treatment solutions (pH \approx 11-12), termed portlandite and saltstone leachate solution (SLS), were used to mimic the initial stages of cement weathering where leachate composition has the potential to dramatically alter contaminant partitioning to soils and sediments. The remaining two treatment solutions, termed artificial groundwater (AGW) and calcite-saturated solution (CSS), were used to evaluate contaminant partitioning after extensive weathering of the cementitious materials and/or dilution of the leachate with non-impacted Savannah River Site (SRS) groundwater. All partitioning experiments were conducted under oxic and anoxic (2% H₂ atmosphere) conditions to evaluate the overall impact of redox status on contaminant partitioning. For Objectives I and II, a site-specific soil material representing the soils and sediments underlying the SDF was used as a sorbent. For Objective III, reducing saltstone grout and non-reducing cement concrete were used as sorbents for evaluating radium (Ra) partitioning.

The notable results of the current study can be summarized as follows:

- Selenium partitioning to the SDF soil was consistent with previous batch results provided in Seaman and Chang (2013) that were determined using a mixed contaminant stock solution. Although changes in Se redox speciation are likely induced by the oxic and anoxic treatments, final K_d values were generally similar regardless of initial Se redox speciation at the onset of a given partitioning experiment. For example, both redox species,

Se(IV) and Se(VI), were highly sorbed ($K_d > 1400 \text{ mL g}^{-1}$) under background solution conditions (i.e., AGW with a pH ≈ 5). Se(VI) sorption was somewhat reduced at the higher pH of the CSS treatment (pH ≈ 6.2 -6.5), while Se(IV) partitioning for the CSS remained high, i.e., $K_d > 1400 \text{ mL g}^{-1}$. Selenium partitioning for both redox species was greatly reduced for both cementitious leachate treatments, with the lowest values observed for the SLS.

- The high performance liquid chromatography (HPLC) based method for speciating Se was generally effective for the AGW and CSS background treatment solutions; however, the residual aqueous-phase Se remaining after equilibration with the soil materials was generally close to the method detection limit, 1.5 ug L^{-1} . While generally qualitative in nature, chromatographs for the AGW and CSS treatments did indicate a sorption preference for Se(IV). Although significant aqueous-phase Se was present for the two high-pH (pH ≈ 11.5 -12.5) cementitious leachates, the background solutions were generally too caustic or too high in ionic strength for effective chromatographic separation.
- Niobium K_d values for the SDF soil were high ($K_d > 1200 \text{ mL g}^{-1}$) for all treatment solution chemistries, regardless of redox status.
- Radium K_d values were high ($K_d > 1500 \text{ mL g}^{-1}$) for both cementitious materials (i.e., reducing saltstone and conventional cement), regardless of background solution chemistry or redox status. This value is considerably higher than previous estimates ($K_d \approx 100 \text{ mL g}^{-1}$) for relatively young oxidizing and reducing cement materials and weathered/aged oxidizing and reducing cement materials ($K_d \approx 70 \text{ mL g}^{-1}$).

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List of Acronyms and Abbreviations

AGW	Artificial Groundwater
CEC	Cation Exchange Capacity
CDB	Citrate Dithionite Bicarbonate
CSS	Calcite Saturated Solution
DIW	Deionized Water
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
HPLC	High Performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
K_d	Distribution Coefficient
LLW	Low Level Waste
PA	Performance Assessment
PSD	Particle Size Distribution
QA	Quality Assurance
QC	Quality Control
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SLS	Saltstone Leachate Solution
SREL	Savannah River Ecology Laboratory
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation, LLC
SRS	Savannah River Site
USDA	United States Department of Agriculture

1.0 INTRODUCTION

The Savannah River Site (SRS) Saltstone Disposal Facility (SDF) treats low-level radioactive and hazardous liquid waste remaining from the processing of radioactive materials. Such low level waste (LLW) derived from multiple SRS sources (i.e., Effluent Treatment Project, H Canyon, Actinide Removal Process/ Modular Caustic Side Solvent Extraction Unit) is stored in Tank 50 until transfer to the Saltstone Production Facility where it is used to make saltstone grout for long-term disposal in the SDF.

The overall objective of the current study was to resolve several gaps in our understanding of how various contaminants interact with cementitious materials or soils and sediments that have been impacted by cementitious material leachates. More specifically, the current study consisted of three separate objectives: (I) evaluating the partitioning (i.e., K_d values) of both selenium redox species (i.e., Se(IV) and Se(VI)) to subsurface sediments typical of those underlying the SDF under oxidizing and reducing conditions; (II) evaluating niobium (Nb) partitioning to the same SDF sediments under oxidizing and reducing conditions; and (III) evaluating radium (Ra) partitioning to reducing and non-reducing cementitious materials under oxidizing and reducing conditions. These three objectives were accomplished in three separate batch sorption experiments.

Presently, there is limited information about the impact of cementitious material leachates on radionuclide partitioning in SRS sediments, and as a result correction factors that account for the unique chemistry associated with cementitious material leachates have been derived from the literature. Therefore, contaminant sorption under four different background solution chemistries was evaluated to mimic various stages of saltstone/cement aging throughout the lifetime of the closed facility, from initial cementitious material formation and curing through weathering and eventual far-field leaching in the underlying soil environment.

A bulk sample of subsoil from the SDF was collected at the onset of this study for use in Objectives I and II to determine site specific soil K_d values. A simulated saltstone material and a weathered cement concrete sample supplied by Savannah River National Laboratory (SRNL) were used for evaluating Ra partitioning in Objective III. The empirically derived distribution coefficient (K_d) describes the partitioning of contaminants to the solid phase, i.e., soil or cementitious materials in the current study, in relation to the amount remaining in the background solution at equilibrium (1):

$$K_d = \frac{C_{solid}}{C_{liquid}} \quad (1)$$

where C_{solid} (mol g^{-1}) and C_{liquid} (mol mL^{-1}) represent the concentration of the contaminants associated with the solid and liquid phases, respectively. The K_d , with units of mL g^{-1} , is often used to describe the migration rate of a contaminant in relation to that of groundwater.

In the current study, two alkaline solution treatments, referred to as portlandite and the saltstone leachate solution (SLS), were chosen to represent the early stages of cement aging, i.e., Stage I/II. The portlandite treatment, made with Ca(OH)_2 , was chosen to mimic the initial high-pH ($\text{pH} \approx 12$) weathering phase of conventional cement where chemical equilibria is controlled by portlandite. The SLS treatment, described in greater detail in the Materials and Methods section, was chosen to mimic the early weathering stages of reducing grout materials, Stage I/II. Solution chemistry during Stage III of cement weathering is generally controlled by calcite, CaCO_3 (Kaplan, 2010). Therefore, a calcite saturated solution (CSS) was used to mimic Stage III. The Stage IV solution treatment, the artificial groundwater (AGW) simulant, was chosen to represent more-natural conditions within the SRS subsurface environment following extensive weathering of the cementitious materials and/or dilution with native groundwater.

Cement Leachate Impact Factors are used to address the differences observed between contaminant partitioning to soils and sediments under more-natural conditions compared to the same materials impacted by high pH cement leachates. The Impact Factor ($f_{Cement\ Leachate}$; unitless) is defined as

$$f_{Cement\ Leachate} = \frac{K_{d-Cement\ Leachate}}{K_d} \quad (2)$$

where K_d and $K_{d-Cement\ Leachate}$ represent the distribution coefficients derived under natural and cement leachate groundwater conditions, respectively (Kaplan, 2010). Due to lack of site specific data, Cement Leachate Impact Factors (i.e., $f_{Cement\ Leachate}$) used in PAs have been based on literature values (i.e., non-site specific data); thereby providing provisional guidance until site-specific laboratory measurements can be made under relevant chemical conditions.

$$K_{d-Cement\ Leachate} = f_{Cement\ Leachate} \times K_d \quad (3)$$

As noted above, a primary objective of the current study was to address select gaps in our current understanding of certain contaminants partitioning behavior as influenced by pore-water conditions indicative of cement leachate (i.e., $K_{d-Cement\ Leachate}$) using site-specific materials, typical of the soils and sediments underlying the SDF.

2.0 MATERIALS AND METHODS

2.1 Characteristics of the SDF Soil Material used for Objectives I and II

The characteristics of the new soil material used in Objectives I and II, termed SDF soil (Table 1), are intermediate in terms of texture and clay mineralogy between the SRS “Clay” and “Sand” materials that have been used extensively to estimate contaminant partitioning on the SRS (Kaplan, 2010; Seaman and Kaplan, 2010). The SDF material is a Sandy Clay Loam, with a clay mineralogy dominated by kaolinite and Fe-oxyhydroxides, such as goethite. The soil material was air dried, homogenized, and passed through a 2mm sieve before it was used in the current study.

Table 1. Characteristics of the SDF soil compared to other SRS soil materials.

Soil/Sediment	SDF Soil ¹	Subsurface Red Clay ²	Subsurface Yellow Sandy ²
PSD ³			
% Sand	68.3	1.6	97
% Silt	4.1	40.6	2.9
% Clay	27.7	57.9	0.2
Texture Classification ⁴	Sandy Clay Loam	Silty Clay	Sand
pH _{DIW} ⁵	4.56 ± 0.39	4.55	5.1
CEC (cmol/kg) ⁶	1.01 ± 0.17	1.91 ± 0.15	0.091 ± 0.035
CDB ext. Fe (mg/gm) ⁷	12.82 ± 0.28	15.26 (17.43 ± 0.72)	7.06 (9.82 ± 0.21)
Clay Mineralogy ⁸	kaol, goe, ill	kaol, goe, hem	kaol, goe, ill

¹SDF Soil: Soil collected from the Saltstone Disposal Facility

²Soil materials commonly used in SRS PA studies (e.g. Kaplan, 2010; Seaman and Kaplan, 2010)

³PSD: Particle Size Distribution (Gee and Bauder, 1986).

⁴Textural classification based on the United States Department of Agriculture (USDA) classification scheme.

⁵pH in deionized water (DIW), 2/1 solution to soil ratio

⁶CEC, Cation exchange capacity determined using Ba saturation method (Rhoades, 1982).

⁷CDB ext. Fe: citrate dithionite bicarbonate extractable Fe (Jackson et al., 1986). Values in parentheses reflect additional CDB extractions conducted for the current study.

⁸Clay mineralogy of the ≤ 2 μ m fraction; kaol = kaolinite, goe = goethite, ill = illite, and hem = hematite.

2.2 Characteristics of the Cementitious Materials used for Objective III

Reducing Saltstone

All chemical solutions, including those used in making the reducing saltstone, were prepared with ultrapure de-ionized water (DIW; $18.2 \text{ M}\Omega \text{ cm}^{-1}$ @ $25 \text{ }^\circ\text{C}$) and reagent-grade chemicals. The reducing saltstone materials used as a sorbent for Ra were created using a saltwaste simulant recipe specified by Savannah River Remediation, LLC (SRR) (Table 2). The grout materials consisted of (1) Class F fly ash (The SEFA Group, Inc. Lexington, SC), (2) Grade 100 blast furnace slag (Holcim US, Inc. Birmingham, AL), and (3) Type II Portland cement (Holcim US, Inc. Birmingham, AL). All of the chemicals in Table 2, except for the NaOH solution, were combined with $\approx 1 \text{ L}$ of deionized water (DIW) in a 2-L volumetric polycarbonate flask. The NaOH was added as a 50% NaOH solution, and the flask was then filled to 2 L with DIW and allowed to stand overnight. The following day, the three powdered grout materials were weighed in three separate containers, i.e., 1350 g of Class F fly ash, 1350 g of Grade 100 blast furnace slag, and 300 g of Type II Portland cement. The three dry powdered materials were then mixed together in a single bucket. After thorough homogenization of the combined powders, the saltwaste simulant solution was slowly added to the dry materials while mixing at 250 rpm for 20 minutes. The saltwaste solution was added at a water to dry materials ratio of 0.6 (i.e., 1.8 kg of water added to 3 kg of dry materials).

Table 2. Composition of ARP/MCU solution used in making reducing saltstone.

Material	ARP/MCU Salt Simulant		
	Molarity (moles/L)	Mass (g/L)	Mass for 2 L (g)
Sodium Hydroxide, NaOH (50 wt.% by weight)	1.594	127.50	255
Sodium Nitrate, NaNO_3	3.159	268.48	536.96
Sodium Nitrite, NaNO_2	0.368	25.39	50.78
Sodium Carbonate, Na_2CO_3	0.176	18.65	37.3
Sodium Sulfate, Na_2SO_4	0.059	8.37	16.74
Aluminum Nitrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.054	20.33	40.66
Sodium Phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.012	4.67	9.34

After mixing, the grout material slurry was poured into a series of molds, and then cured for 28 days in a laboratory oven according to a prescribed temperature profile based on conditions recorded in Saltwaste Disposal Unit (SDU) 2B at an elevation of 10.5 ft above the SDU floor. A pan of water was placed in the oven in order to maintain high humidity conditions during the curing process.

After curing, grout materials used in the current study were initially pulverized with a hammer under ambient atmosphere and then homogenized into a fine powder with a Retsch PM 100 Planetary Ball Mill (Verder Scientific Inc). The <100 μm sieve fraction was used for these experiments.

Non-Reducing Cement Concrete

The non-reducing cement concrete was provided by SRNL. The sample was collected from a 40 year old concrete core taken from a pad supporting a non-rad tank in P-Area located on the SRS (Kaplan and Coates, 2007). To separate the aggregate from the cement, a portion of the 3-inch diameter core was crushed with a hammer and then the cement was loosened from the aggregate with the use of an awl and screw driver. The cement phase was broken up into smaller more uniform particles with a Spex 8510 Shatterbox. The <1000 μm and >75 μm sieve fraction was used for these experiments.

2.3 Batch Treatment Solutions

Four distinct background solutions, chosen to mimic various stages of saltstone and cement weathering, were used in evaluating contaminant partitioning for all three test objectives. The two alkaline solutions described below were chosen to reflect the initial weathering (i.e., Stage I/II) of two distinctly different cementitious materials (i.e., portlandite cement and reducing saltstone grout) at a time when their leachates may dramatically impact contaminant partitioning to SRS soils and sediments. A $\text{Ca}(\text{OH})_2$ -saturated leaching solution (referred to as portlandite) and a solution created using ground up saltstone (referred to as the saltstone leachate solution, labeled SLS) were used to mimic the leachates derived from portlandite cement and saltstone grout, respectively. A calcite saturated solution, CaCO_3 (labeled CSS), and an AGW surrogate were chosen to reflect the contaminant partitioning after significant weathering of the cementitious materials and dilution with non-impacted pore waters (i.e., weathering Stages III and IV, respectively).

The “portlandite” test solution was created by adding 1.26 g L^{-1} of $\text{Ca}(\text{OH})_2$ to CO_2 purged DIW. Further contact with the atmosphere was minimized by storing under N_2 until the solution was used. The CSS test solution was created by adding an excess of CaCO_3 to a liter of warm DIW

and stirring overnight. After 24 hrs the calcite solution is then passed through a 0.45 µm pore-size filter to remove any residual calcite. The SLS was created by equilibrating ground saltstone with DIW for 24 hrs at a 1/10 (g/g) saltstone to DIW ratio. After equilibration, the solution was vacuum filtered (0.45 µm pore size) before use. The composition of the AGW test solution (Table 3) was based on the typical groundwater composition for non-impacted water-table wells on the SRS (Strom and Kaback, 1992).

Table 3. Composition of the artificial groundwater (AGW) simulant.

Constituent/Parameter	AGW ¹
pH	5.0
	(mg L ⁻¹)
Na	1.39
K	0.21
Ca	1.00
Mg	0.66
Cl	5.51
SO ₄	0.73

¹AGW based on routine monitoring of non-impacted groundwater on the SRS derived from natural infiltration (Strom and Kaback, 1992).

2.4 Selenium Partitioning Experiments

Oxic Treatments

Two separate batch experiments were conducted to evaluate the impact of Se redox speciation (selenate Se^{VI}O₄²⁻ and selenite Se^{IV}O₃²⁻) on partitioning to SDF soil materials under oxidizing and reducing conditions, with the only difference being how the samples were initially spiked with Se. In both experiments, triplicate 2.0 ± 0.10-g of air-dried SDF soil samples were suspended in 30 ± 0.1-mL of the appropriate background solution (i.e., AGW, CSS, SLS, and portlandite) in 50-mL polypropylene Oak Ridge centrifuge tubes. In addition, three replicate no-soil control tubes were included for each of the four test solutions. The same set of solution treatments was also replicated for anoxic test conditions described in the following Anoxic Treatments section. Both the oxic and anoxic test suspensions were shaken overnight on a horizontal orbital shaker (~100 rpm) to equilibrate with the specific test solution. After the pre-equilibration step, the samples were centrifuged using a Sorvall RC 5B plus centrifuge equipped with a Sorvall SS-34 rotor for 15 minutes at 10,000 rpm. Then 25 mL of the supernatant was removed from each tube and the tubes were re-weighed to obtain residual soil + solution mass. Twenty four milliliters of the appropriate test solution was then added to each tube, for a total solution volume of 29 mL.

Two analytical redox standards [i.e., Se(IV) and Se(VI)] supplied by Inorganic Ventures, Inc. (Christiansburg, VA) were used as stock contaminant solutions for spiking the various batch treatments. The Se(VI) (selenate) standard was provided by Inorganic Ventures, Inc. in DIW, while the Se(IV) (selenite) standard was provided in a 2% HNO₃ background solution. In the first Se partitioning experiment, 0.5 mL of the 10 µg mL⁻¹ Se(IV) stock solution and 0.5 mL of the 10 µg mL⁻¹ Se(VI) stock solution were added to each tube for a final total volume of 30 mL. The same mixture of contaminant spikes was added to the no-sorbent controls as well. In the second Se partitioning experiment, two complete sets of soil treatment replicates (i.e., four treatment solutions, two redox conditions, three replicates, and soil/no soil controls) were created for spiking with either 1 mL of 10 µg mL⁻¹ Se(IV) stock solution or 1 mL of 10 µg mL⁻¹ Se(VI) stock solution. In both experiments the initial Se concentration was ≈ 333 µg L⁻¹.

The Se spiked samples were then placed on the horizontal orbital shaker (~100 rpm) for 5 days. At the end of the equilibration period, the samples were centrifuged as described above, and a 10-mL aliquot was removed, passed through a 0.2-µm pore-size hydrophilic PTFE filter (Millipore, Billerica, MA) split into two labeled 15-mL metal-free polypropylene tubes (VWR, Radnor, PA). One set of the tubes was acidified (2% HNO₃) for total Se analysis (i.e., Se_{total}). The remaining filtered fraction of each sample was stored at 4 °C for preservation until subsequent Se speciation analysis using the procedure described below in the Se Analysis section, while the remaining supernatant in the 50-mL Oak Ridge tubes was analyzed for pH and Eh.

Anoxic Treatments

As noted for the oxic treatments, three replicate no-soil control tubes were included for each of the four test solutions. All anoxic background solutions were prepared with N₂-sparged ultrapure DIW using reagent-grade chemicals. The anoxic sample tubes with 2.0 ± 0.10-g of air-dried SDF soil were opened inside of a glove box (Coy Vinyl Anaerobic Chambers, Grass Lake, MI) and allowed to equilibrate in the absence of O₂ for 30 to 60 minutes before filling with 30 ± 0.1-mL of the appropriate background solution and resealing. The anoxic/reducing environment in the glove box was maintained by addition of a 95% N₂/5% H₂ gas mixture to establish a consistent 2% H₂ atmosphere. The samples were then secured on an orbital shaker at 100 rpm inside the glove box and reacted overnight. After pre-equilibration, the tubes were removed from the glove box and centrifuged as noted previously for 15 minutes at 10,000 rpm. The centrifuged tubes were returned to the glove box and 25 mL of the supernatant was removed from each tube. The samples were then resealed and removed from the glove box and re-weighed to obtain residual soil + solution mass.

The samples were then allowed to equilibrate with the anoxic atmosphere and then filled with 24 mL of the appropriate background solution and the appropriate Se spike solution(s) was added to

each tube. As noted above, two different experiments were conducted, one using an equivalent mixture of Se(IV) and Se(VI) as the initial Se source within a given soil tube and the second experiment in which either Se(IV) or Se(VI) was added to a given soil tube.

The samples were then placed on the orbital shaker (~100 rpm) in the glove box and equilibrated for 5 days. At the end of the equilibration period, the samples were centrifuged for 15 minutes at 10,000 rpm, and then returned to the anoxic chamber. Inside the anoxic chamber, a 10-mL aliquot was removed, passed through 0.2- μm pore-size hydrophilic PTFE filters (Millipore, Billerica, MA) and split into two sub-samples for analysis, one of which was acidified (2% HNO_3) and the second which was stored at 4 °C for preservation prior to Se speciation analysis. The remaining supernatant in the 50-mL Oak Ridge tubes was analyzed for pH and Eh.

Se Analysis

Two methods were used for Se analysis. The acidified sample fractions were analyzed for Se_{total} by inductively coupled plasma-mass spectrometry (ICP-MS) in accordance with the quality assurance (QA) and quality control (QC) protocols of Environmental Protection Agency (EPA) Method 6020A (USEPA, 2007). Selenium redox speciation in the unacidified sample fractions was determined using HPLC (Flexar LC, Perkin Elmer, Inc., Waltham, MA) as a coupled, in-line means of separating Se(IV) and Se(VI) prior to analysis by ICP-MS (Neubauer et al., 2006). The coupled HPLC-ICP-MS protocol uses reverse-phase ion pairing with a mobile phase consisting of 0.1mM tetrabutyl-ammonium hydroxide (TBAOH), 0.15 mM ammonium acetate and 0.15 mM ethylenediaminetetraacetic acid (EDTA), with an adjusted pH of ≈ 6.9 to 7.2 (Neubauer et al., 2006)

2.5 Niobium (Nb) Partitioning Experiments

For Objective II, niobium (Nb) partitioning to the SDF soil material was evaluated as a function of leachate composition and redox status, i.e., oxic and anoxic conditions. The laboratory batch procedure was essentially the same as that described for Se, except that a single $10 \mu\text{g mL}^{-1}$ Nb stock solution was used for all treatments (High Purity Standards, Inc. Charleston, SC) and all of the resulting filtered samples after equilibration were acidified (2% HNO_3) prior to analysis by ICP-MS. The remaining supernatant in the 50-mL Oak Ridge tubes after equilibration was analyzed for pH and Eh.

2.6 Radium Partitioning to Cementitious Materials

For Objective III, Ra partitioning to two types of cementitious materials was evaluated using the same four background solutions under oxidizing and reducing conditions described for Objectives I and II. A 0.5 ± 0.01 -g sample of pulverized saltstone or cement was weighed into a

series of 30 mL polypropylene centrifuge tubes, with three replicates for each treatment. Fifteen mL of appropriate treatment solution described above was added to each tube. The tubes were then equilibrated overnight under the appropriate atmosphere. After equilibration, the cementitious material suspensions were allowed to settle for 1 hr and 10-12 mL of clear supernatant was removed. A sufficient volume of the appropriate treatment solution was then added to each tube to bring the final solution volume back up to 14.5 mL.

A 0.5 mL aliquot of a ^{226}Ra spike solution (20,000 pCi mL⁻¹ in 1% HNO₃; Eckert & Ziegler Analytics, Inc. Atlanta, GA) was then added to each tube ($\approx 10,000$ pCi/tube) for a total volume of 15 mL. The same 0.5 mL ^{226}Ra spike was also added to the no-sorbent controls. Sufficient base was added to each tube to neutralize the acidity associated with the spike solution. Essentially the same methodology was used for the anoxic samples, except N₂(g)-sparged treatment solutions were used instead. The spiked samples were then equilibrated on an orbital shaker for five days under the appropriate atmosphere, i.e., ambient laboratory conditions (oxidizing) and 2% H₂ (reducing).

After equilibration, the samples were allowed to settle overnight and 10 mL of clear supernatant was removed and placed in a 20mL glass scintillation vial. The scintillation vials were then acidified (1% HNO₃) for preservation. The remaining supernatant in each 30 mL centrifuge tube was then analyzed for pH and Eh. The residual ^{226}Ra remaining in solution after equilibration was determined by EPA Method 901.1 using known dilutions of the initial ^{226}Ra stock solution as standards (USEPA, 1980; Kohler et al., 2002; Lehto and Hou, 2011).

3.0 RESULTS

The batch partitioning results will be discussed in terms of each specific contaminant under evaluation, and when appropriate, the current data will be compared to K_d values reported in Seaman and Chang (2013) and Kaplan (2010). Measured redox potentials determined at the end of sample equilibration are provided to illustrate the relative difference in redox status between the oxic (ambient laboratory conditions) and anoxic/reducing (i.e., 2% H₂ atmosphere) treatments.

3.1 Selenium (Se)

In the first batch Se sorption experiment, both Se(IV) and Se(VI) were added in equivalent concentrations to evaluate changes in Se redox speciation and the impact of such changes on soil partitioning. After equilibration in the presence of SDF soil, samples for Se speciation analysis were stored at 4 °C in an unacidified state until they could be analyzed by the coupled HPLC-ICP-MS technique described in Neubauer et al. (2006). Samples for conventional Se analysis (i.e., Se_{total}) by ICP-MS were acidified after filtration. Examples of the chromatographs

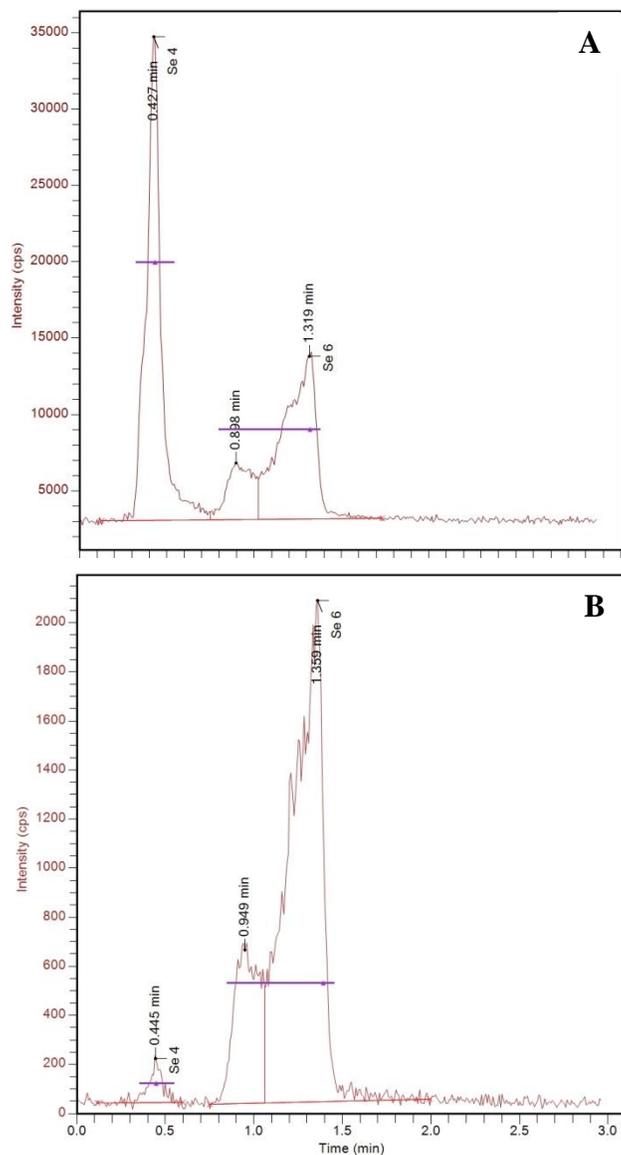
generated during speciation analysis are provided in Figure 1. Figure 1A represents the chromatograph for an analytical standard with equivalent concentrations of Se(IV) and Se(VI), while Figure 1B represents the residual aqueous-phase Se after equilibration with the SDF soil materials.

Two analytical limitations were encountered during the first Se partitioning experiment. For sample treatments displaying significant Se sorption, i.e., AGW and CSS under both oxidizing and reducing conditions, residual aqueous-phase Se_{total} levels were generally at or below the method detection limit ($1.5 \mu\text{g L}^{-1}$). For the two treatment solutions used to mimic high pH cement leachates, i.e., portlandite and SLS, the samples were generally too caustic and/or too high in ionic strength for effective chromatographic separation, even with significant dilution. In addition, the estimates of total Se recovery based on the sum of both species were generally well below the Se_{total} (i.e., 60-70%). Despite such limitations, the chromatographs for all of the AGW and CSS treatments indicate that the soil had a preference for sorbing Se(IV) rather than Se(VI) (see Figure 1B).

A second Se partitioning experiment was conducted to address some of the analytical limitations encountered during the first experiment, i.e., the inability to quantify Se speciation in the high-pH cementitious leachate treatment solutions. Instead of using both Se(IV) and Se(VI) in the same treatment solution, the second batch experiment used either Se(IV) or Se(VI) as the initial treatment spike, with only Se_{total} measured at the end of equilibration. The results from the second Se experiment are included in Table 4 along with the K_d values reported by Seaman and Chang (2013) under similar experimental conditions. In general, high K_d values ($> 1400 \text{ mL g}^{-1}$) were observed for both Se(IV) and Se(VI) treatments for the AGW background solution. These K_d values are consistent with the background values reported by Kaplan (2010) for typical SRS “Sand” and “Clay” materials. The K_d value for Se(VI) in the CSS treatment solution was lower (152 and 99 mL g^{-1} for oxic and anoxic conditions, respectively) in the present study than the reported for Seaman and Chang (2013), but the pH of the CSS treatment solution after equilibration for the current study is higher than the final equilibration pH (i.e., 5.1 to 5.3) reported in Seaman and Chang (2013), which may account for the higher Se sorption in the earlier study.

The Se K_d values for the two high-pH treatment solutions were considerably lower than the values observed for the AGW or CSS treatment solutions in the current study, regardless of the initial redox state of Se, with only limited partitioning observed ($K_d \approx 1$ to 5 mL g^{-1}) for the SLS treatment solution. These results are consistent with trends reported by Seaman and Chang (2013) under similar experimental conditions and indicate that Se redox speciation is not a major factor controlling partitioning under various leaching scenarios relevant to the SDF. Because low K_d observed in the presence of the cementitious leachate materials, the calculated Cement Leachate Impact Factor for Se is low, 0.01 (Table 6).

Figure 1. HPLC-ICP-MS chromatograph for a mixture of equivalent amounts ($15 \mu\text{g L}^{-1}$ each) of Se(IV) and Se(VI), and (B) residual Se(IV) and Se(VI) in solution after equilibration with SDF soil in the CSS background solution.



3.2 Niobium (Nb)

Niobium, a 4d transition metal with oxidation states ranging from +II to +V, is generally found in the +V oxidation state except under extremely reducing conditions. Niobium is considered fairly insoluble and Nb₂O₅ (oxidation state V) is the most stable oxide, which generally requires hydrofluoric acid (HF) for dissolution. Because of its high oxidation state, Nb(V) forms an oxy cation, niobyl (NbO₃⁺), under acidic conditions and various anionic complexes (e.g., NbO₃⁻), especially with halides such as fluoride, at pH values above neutrality (Echevarria et al., 2005; Lehto and Hou, 2011).

Limited data is available concerning the behavior of Nb in soils. Niobium is likely to form insoluble Nb(V) oxides and hydroxides in the pH and Eh ranges typically encountered in soils. Echevarria et al. (2005) reported similar K_d values ($K_d \approx 103 \text{ mL g}^{-1}$) after three days of equilibration for three French soils with pHs ranging from 6.2 to 7.0. Rhodes (1957) reported a Nb K_d of $> 1980 \text{ mL g}^{-1}$ for a sandy calcareous soil. The site specific K_d observed in the current study ($> 1200 \text{ mL g}^{-1}$) for the SDF soil material is far greater than the default value reported in Kaplan (2010) based on its anionic speciation (Table 5). Additionally, the high K_d was observed for all treatment solutions, regardless of redox conditions. The Cement Leachate Impact Factor for Nb is ≥ 1 because of the high degree of Nb sorption observed for all solution treatments (Table 6).

3.3 Radium (Ra)

Radium (Ra) is an alkaline earth metal (+II oxidation state) with properties similar to calcium (Ca), barium (Ba) and strontium (Sr). In the soil environment, Ra may co-precipitate as various sulfate and carbonate minerals, and readily sorbs to phyllosilicate clays and Fe and Al oxides via cation exchange mechanisms (USEPA, 2004; Seaman and Roberts, 2012). However, the present study focused on partitioning to various cementitious materials, including reducing and non-reducing cements. Radium-226, a beta/gamma emitter with a 1600 yr half-life, was used as sorbate for the current study.

Results for the current study are summarized in Table 7. Although the same four treatment solutions used for Objectives I and II were used in the present study (Objective III), the final high solution pH observed for all four treatment solutions indicates that the sorbent material strongly influenced solution chemistry regardless of the initial background solution treatment. For all sorbent treatments, typical Ra recoveries were quite low ($< 2.5\%$ of the ²²⁶Ra spike for all treatments). A high degree of sorption ($> 1500 \text{ mL g}^{-1}$) was observed for both cementitious materials, regardless of the solution treatment or redox status. The current K_d is considerably higher than the values reported by Kaplan (2010) for “Young” and “Middle” age (100 mL g^{-1}) and “Old” age (70 mL g^{-1}) cement materials based on the values reported by Bayliss et al. (1989) and Berry et al. (1988) for portland cement.

The high Ra K_d is not surprising for the reducing saltstone material as Seaman and Chang (2013) reported a high soil K_d for Ba ($>2000 \text{ mL g}^{-1}$) in the presence of the SLS treatment solutions derived from similar materials, which they attributed to sulfur present in the SLS leachate. However, the same high K_d was also observed for the conventional cement under both the oxidizing and reducing treatments.

4.0 DISCUSSION

The experiments discussed in the current report were successful in generating site-specific K_d values for three saltwaste contaminants, i.e., Se, Nb and Ra. The high degree of Se partitioning to the SDF soil under typical background solution conditions was consistent with previous reports [Seaman and Chang (2013) and Kaplan (2010)]; however, Se sorption was greatly reduced in both high-pH cementitious material leachates, as noted previously in Seaman and Chang (2013). In general, apparent differences in the partitioning of the two Se redox species were fairly minor when compared to the overall impact of the high-pH leachates in reducing sorption of either species to the SDF soil material.

Niobium partitioning to the SDF soil material was high ($>1200 \text{ mL g}^{-1}$), regardless of the background solution or redox conditions. The high soil K_d value was generally consistent with the limited number of studies available in the scientific literature, but much higher than previous estimates based on Nb speciation chemistry (Kaplan, 2010).

Radium partitioning to the two cementitious materials was also much higher than earlier estimates. The high K_d value observed for the reducing saltstone is consistent with high soil K_d values observed for the partitioning of other alkaline earth metals (i.e., Ba $>2000 \text{ mL g}^{-1}$ and Sr $>730 \text{ mL g}^{-1}$) in a saltstone derived background solution, i.e., the SLS treatment solution (Seaman and Chang, 2013). Radium sorption in the presence of the non-reducing cement was also much higher than previous reported values (Kaplan, 2010).

Table 4. Summary of pH, Eh and Se K_d values for SDF soil derived under various treatment environments (Objective I).

Treatment Sol.		Artificial Groundwater (AGW)		Calcite Saturated Solution (CSS)		Saltstone Leachate Solution (SLS)		Portlandite Leachate Solution (portlandite)	
Cement Weathering Stage		IV		III		I/II		I/II	
		Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
Se (IV)	pH	5.7	5.1	6.5	6.2	11.8	11.5	12.5	12.2
	Eh (V)	518	-251	465	-261	146	-169	153	-71
	K_d (mL/g)	>1400	>1400	>1400	>1400	2	3	30	41
Se (VI)	pH	4.9	5.0	6.1	6.5	11.7	11.5	12.5	12.2
	Eh (V)	493	-194	416	-242	149	-180	143	-19
	K_d (mL/g)	>1400	>1400	152	99	1	5	16	41
Se*		>1400	>1400	>1400	>1400	17	19	19	29

*Se K_d values from Seaman et al. 2013 under similar experimental conditions.

Table 5. Summary of pH, Eh, and Nb K_d values for partitioning to the SDF soil derived under various treatment environments (Objective II).

Treatment Solution	Artificial Groundwater (AGW)		Calcite Saturated Solution (CSS)		Saltstone Leachate Solution (SLS)		Portlandite Leachate Solution (portlandite)	
Cement Weathering Stage	IV		III		I/II		I/II	
Redox State	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
pH	5.6	5.5	8.5	8.1	11.8	11.7	11.9	12.1
Eh (mV)	380	-145	404	-353	167	-567	182	-238
K_d (mL/g)	>1200	>1200	>1200	>1200	>1200	>1200	>1200	>1200

Table 6. Calculated Cement Leachate Impact Factors Se and Nb in the saltstone leachate solution compared to the values reported in Kaplan (2010).

Contaminant	Saltstone Leachate Stage I/II		Calculated Impact Factor		Kaplan 2010 Impact Factor ; Table 13	
	AGW Oxic	AGW Anoxic	Oxic	Anoxic	Oxic	Anoxic
Nb	>1200	>1200	≥1*	>1200	1.4	>1200
Se	>1400	17	0.01	>1400	1.4	19

*Cement Impact Factor for Nb is reported as ≥1 since the reported K_d value represents the absolute minimum degree of sorption under all relevant conditions.

Table 7. Summary of pH, Eh, and K_d values for Ra partitioning to reducing and non-reducing cementitious materials in various treatment solutions (Objective III).

Treatment Sol.	Oxidation Status	Artificial Groundwater (AGW)		Calcite Saturated Solution(CSS)		Saltstone Leachate Solution (SLS)		Portlandite Leachate Solution (portlandite)	
		Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
Reducing Saltstone Grout	Ra K_d	>1500	>1500	>1500	>1500	>1500	>1500	>1500	>1500
	pH	11.6	10.8	11.7	10.9	12.0	11.0	12.2	11.6
	Eh (mV)	422	-535	274	-581	240	-560	321	-618
Non-Reducing Cement	Ra K_d	>1500	>1500	>1500	>1500	>1500	>1500	>1500	>1500
	pH	11.2	10.4	11.5	10.6	11.9	11.0	12.0	11.7
	Eh (mV)	247	-560	240	-573	206	-523	198	-555

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