SREL Doc. R-13-0004
Ver. 1.0

Key Words:
Distribution Coefficient
Kd Values
Saltstone
Geochemistry

Impact of Cementitious Material Leachate on Contaminant Partitioning

J.C. Seaman[1]

Hyun-shik Chang[2]

September 4, 2013

[1] Senior 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

[2] Assistant Research Scientist

1785
The University of Georgia
Savannah River Ecology Laboratory

REVIEWS AND APPROVALS

Authors:

9/4/2013

John C. Seaman, SREL Associate Director-Research
Senior Research Scientist
Date

9/4/2013

Hyun-shik Chang, Assistant Research Scientist
Date

Reviewer:

9/4/2013

Diana Soteropoulus – Research Coordinator
Date

Approval:

9/4/2013

Steven Simner, SRR CTF
Date

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1.0 EXECUTIVE SUMMARY

Batch partitioning experiments were conducted to determine the impact of cementitious material leachate on the soil distribution coefficient (K_d) values for a disparate range of seventeen contaminants and non-radioactive chemical analogs (Cr, Ni, As, Se, Sr, Cd, I, Sb, Cs, Ba, La, Ce, Eu, Re, Tl, Th, and U). The experiments were designed to provide direct and indirect information about radionuclide behavior related to the Saltstone Disposal Facility (SDF) and Tank Farm Performance Assessments (PAs). Presently, there is limited information about the impact of cementitious material leachates on radionuclide partitioning in Savannah River Site (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.

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). A site-specific soil material representing the soils and sediments underlying the SDF was used for the current study. Two alkaline treatment solutions (pH ≈ 11-12), termed portlandite and saltwaste leachate solution (SLS), were chosen to mimic the initial stages of cement weathering where leachate composition has the potential to dramatically alter contaminant partitioning to SRS soils and sediments. The remaining two treatment solutions, termed artificial groundwater (AGW) and calcite-saturated solution (CSS), were used to approximate conditions for contaminant partitioning after extensive weathering of the cementitious materials and/or dilution with non-impacted SRS groundwater. All partitioning experiments were conducted under oxic and anoxic (2% H_2 atmosphere) conditions to evaluate the overall impact of redox status on contaminant partitioning to SRS soils and sediments in the absence of direct contact to reactive cementitious material.

Using the four test solutions, 136 site specific K_d values were estimated across a pH range from 4.8 to 12.2 under oxic and anoxic conditions. Sixteen of the elements tested were evaluated simultaneously using a “mixed contaminant” spike solution, while iodine (I) partitioning was evaluated in a separate experiment in order to simplify the analytical methodology. These results were then compared to values reported in the existing PA geochemical data package (Kaplan 2010; SRNL-STI-2009-00473), which includes both experimentally derived SRS K_d values and literature derived estimates that account for the impact of cement leachate. The results for fifteen of the elements tested (Ba, Cd, Ce, Cr, Cs, Eu, I, La, Ni, Re, Sb, Se, Sr, Th, and Tl) were consistent with baseline K_d values reported in SRNL-STI-2009-00473 or the discrepancies can

be readily explained in terms of the elements chemical speciation and/or the exact conditions of the test system. The baseline K_d values for As and U were considerably higher than expected. However, the general consistency of the current data set with baseline SRS K_d values supports the validity of the multi-element partitioning methodology used in the current study. In some cases, experimental K_d values generated in the presence of cement leachates differed greatly from estimated values, in many cases the values were considerably higher than previous non-site-specific estimates derived from the literature. The notable results of the current study can be summarized as follow:

- All baseline K_d values measured with site-specific SDF sediment were consistent or greater than those recommended for use in the SRS geochemical data package (SRNL-STI-2009-00473).
- Cementitious leachate impacted K_d values of the site-specific SDF sediment were generally consistent with or greater than those recommended for use in the SRS geochemical data package (SRNL-STI-2009-00473). Notable exceptions include As, Cr, Sb, and Se. Arsenic, Sb and Se had cement leachate impacted K_d values that were much lower (As - 13 to 14 mL g^{-1}, Sb - 5 to 7 mL g^{-1}, and Se - 17 to 19 mL g^{-1}) than the literature values reported in SRNL-STI-2009-00473 (As - 140 to 280 mL g^{-1}, Sb - 3500 mL g^{-1}, and Se - 1400 mL g^{-1}). For Cr, the lower cement leachate impact factor (i.e., 0.04 vs 1.4) reflects the much higher initial Cr partitioning under baseline conditions rather than a lower K_d value estimated by Kaplan (2010) for cement leachates.
- The K_d values for the alkaline earth metals, Ba and Sr (and Ra), were slightly higher than previously reported for baseline conditions. Barium and Sr partitioning was considerably higher for the portlandite solution, and higher still for SLS, possibly due to the high sulfur content in the cementitious leachate, as both cations form sparingly soluble sulfur compounds.
- The K_d values for the two divalent transition metals (i.e., Cd and Ni) were consistent with SRNL-STI-2009-00473 for background solution conditions, but much higher, >5000 and > 2000 mL g^{-1} for Cd and Ni, respectively, in the portlandite and SLS treatment solutions, regardless of redox conditions.
- Consistent with SRNL-STI-2009-00473, the K_d values for the trivalent cations, i.e., Ce, Eu, and La, remained quite high for all treatments, including the cementitious leachates, regardless of redox conditions. In addition, Cr displayed a much higher K_d than previously reported for SRS materials, which can be attributed to Cr being in the +III oxidation state (i.e., Cr^{3+}), with partitioning largely controlled by precipitation as oxy-hydroxides, rather than sorption of oxidized Cr, i.e., chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$).
- The K_d values for I were consistent with SRNL-STI-2009-00473 for background SRS conditions and the cementitious leachates (< 1 mL g^{-1}), regardless of redox status.
- The K_d value for Re, often used as a surrogate for Tc, was < 0.8 mL g^{-1} for all treatments, regardless of the redox status.
- The K_d value for Cs was consistent with SRNL-STI-2009-00473 for background SRS conditions (59 mL g^{-1}), but decreased somewhat in the presence of the portlandite and SLS

solutions, presumably due to greater competition for cation exchange sites and the general lack of 2:1 phyllosilicate clays in SRS soils that preferentially sorb Cs^+ and K^+.

- The K_d value for Tl was consistent for background conditions, but somewhat elevated for the portlandite and SLS cement leachate treatment solutions.
- Thorium displayed a K_d value > 730 mL g^{-1} regardless of treatment solution or redox conditions. The actual K_d value is likely much higher, as reported in SRNL-STI-2009-00473, but the current results were constrained by the high method detection limits (MDLs) observed for Th.
- Uranium K_d values were generally higher than previous estimates for background conditions and the portlandite treatment solution, with somewhat lesser (271-174 mL g^{-1}) than estimated values for the SLS treatment solution (i.e., 600 to 900 mL g^{-1}).

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List of Acronyms and Abbreviations

AGW	Artificial Groundwater
BFS	Blast Furnace Slag
CEC	Cation Exchange Capacity
CDB	Citrate Dithionite Bicarbonate
CDP	Cellulose Degradation Products
CSS	Calcite Saturated Solution
DIW	Deionized Water
EPA	Environmental Protection Agency
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IAEA	International Atomic Energy Agency
K_d	Distribution Coefficient
K_{sp}	Solubility Product
LLW	Low Level Waste
MDL	Method Detection Limit
NIST	National Institute of Standards and Technology
PA	Performance Assessment
PSD	Particle Size Distribution
QA	Quality Assurance
QC	Quality Control
SDF	Saltstone Disposal Facility
SLS	Saltstone Leachate Solution
SREL	Savannah River Ecology Laboratory
SRS	Savannah River Site
TMAH	Tetra Methyl Ammonium Hydroxide
USDA	United States Department of Agriculture
WAC	Waste Acceptance Criteria

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) is derived from multiple SRS sources (i.e., Effluent Treatment Project, H Canyon, Actinide Removal Process/ Modular Caustic Side Solvent Extraction Unit) and stored in Tank 50 until it is transferred to the SDF for treatment and disposal. The chemical composition of the saltwaste is typically measured on a quarterly basis to ensure that it meets the Waste Acceptance Criteria (WAC) for disposition as saltstone. The primary objective of the current study was to evaluate the relative partitioning behavior of a disparate set of contaminants using site-specific materials, typical of the soils and sediments underlying the SDF, under chemical conditions typical of the leachates derived from cementitious materials.

A bulk sample of subsoil from the SDF was collected at the onset of this study for use in determining a series of K_d values in the presence of cement leachate under oxic and anoxic conditions. The empirically derived distribution coefficient (K_d) is used to describe the migration rate of a contaminant in relation to that of groundwater. The K_d value describes the ratio of contaminant partitioning to the solid phase in relation to the amount remaining in solution at equilibrium (1):

$$K_d = \frac{C_{solid}}{C_{liquid}} \tag{1}$$

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 units for mass of contaminant cancel out to yield the units for K_d values of mL g^{-1}.

Although the K_d approach to estimating contaminant partitioning is empirical in nature, an understanding of the specific geochemical processes controlling solid-phase partitioning is critical in discerning the validity of K_d values that can be applied to a given system (Kaplan, 2010; Allison and Allison, 2005; USEPA, 1999a; USEPA, 1999b). K_d values vary greatly between contaminants depending on their specific chemical properties, and depend on both aqueous-phase (i.e., pH, redox status, contaminant concentration, competing ion concentration, etc.) and solid-phase chemistry. Therefore, determining site-specific K_d values under the unique chemical conditions associated with cement leachate is critical for using the linear partition coefficient to predict contaminant mobility in the subsurface environment.

Cementitious materials are often used as a media for the disposal of radioactive waste. In some cases, reducing agents such as blast furnace slag (BFS) may be added to cement formulations in order to reduce porosity, increase durability, and enhance contaminant sorption through the formation of insoluble sulfide (S) precipitates, and/or enhance the sorption/precipitation of redox sensitive contaminants, such as technetium (Tc) and chromium (Cr), which further complicates cement leachate chemistry when compared to natural groundwater conditions. The current study focuses on evaluating the solid-phase partitioning of saltwaste-derived contaminants to sediments underlying the SDF as a function of leachate composition associated with various stages of saltstone aging. Leachate derived from cementitiuos materials generally has a high pH and high ionic strength which changes as the material ages (Angus and Glasser, 1985; Bradbury and Sarott, 1995; Kaplan, 2010), quite different from the native soil pore waters and groundwater found on the SRS (Kaplan, 2010; Strom and Kaback, 1992). Therefore, background K_d values for contaminants derived under more-natural SRS groundwater conditions likely differ from K_d values associated with contaminant partitioning to sediments underlying the SDF facility because of the strong influence of cement leachate on pore-water chemistry.

Two alkaline solution treatments, referred to as the 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 (pH ≈ 12) weathering phase of conventional cement where chemical equilibria is controlled by portlandite. The SLS treatment described in greater detail below 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, $CaCO_3$, with a pH of ≈ 9.6 (Kaplan et al., 2010). The Stage IV solution treatment, the artificial groundwater (AGW) simulant, represents more-natural conditions within the subsurface environment following extensive weathering of cementitious materials and/or dilution with native groundwater.

Cement Leachate Impact Factors can be used to quantify the influence of cement leachate chemistry on contaminant partitioning when compared to natural groundwater conditions. The Impact Factor ($f_{Cement\ Leachate}$; unitless) is defined as

$$f_{Cement\ Leachate} = \frac{K_{d-Cement\ Leachate}}{K_d} \tag{2}$$

where K_d and $K_{d\text{-}Cement\ Leachate}$ represent the distribution coefficients derived under natural and cement leachate groundwater conditions, respectively (Kaplan, 2010). The $f_{Cement\ Leachate}$, often derived from literature or estimated based on an understanding of a particular elements chemical properties, can then be used as provisional guidance in adjusting existing K_d values in PAs until site-specific laboratory measurements can be made under relevant chemical conditions.

$$K_{d-Cement\ Leachate} = f_{Cement\ Leachate} \times K_d \tag{3}$$

The primary objective of the current study was to evaluate the relative partitioning behavior of a disparate set of contaminants under pore-water conditions indicative of cement leachate (i.e., $K_{d\text{-}Cement\ Leachate}$) 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 and Test Solutions

The characteristics of the new soil material, 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 material was air dried, homogenized, and passed through a 2-mm sieve before it was used in the current study. All test solutions were prepared with ultrapure de-ionized water (DIW; 18.2 MΩ cm^{-1} @ 25 °C) using reagent-grade chemicals.

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

[1] SDF Soil: Soil collected from the Saltstone Disposal Facility
[2] Soil materials commonly used in SRS PA studies (e.g. Kaplan, 2010; Seaman and Kaplan, 2010)
[3] PSD: Particle Size Distribution (Gee and Bauder, 1986).
[4] Textural classification based on the USDA classification scheme.
[5] pH in deionized water (DIW), 2/1 solution to soil ratio
[6] CEC, Cation exchange capacity determined using Ba saturation method (Rhoades, 1982).
[7] CDB ext. Fe: citrate dithionite bicarbonate extractable Fe (Jackson et al., 1986). Values in parentheses reflect additional CDB extractions conducted for the current study.
[8] Clay mineralogy of the ≤2 μm fraction; kaol = kaolinite, geo = goethite, ill = illite, and hem = hematite.

Four distinct background solutions, initially chosen to mimic various stages of saltstone and cement weathering, were used in evaluating contaminant partitioning. 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 $Ca(OH)_2$-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 ($CaCO_3$) saturated solution (CSS) and an artificial ground water (AGW) surrogate, the final composition of which is specified in Table 2, 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).

Table 2. 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

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

The “portlandite” test solution was created by adding 1.26 g L^{-1} of $Ca(OH)_2$ 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 was based on the typical groundwater composition for unimpacted water-table wells on the SRS (Strom and Kaback, 1992).

A list of the seventeen contaminants or radioactive contaminant analogs evaluated in the current study is provided in Table 3, with important chemical properties that impact partitioning summarized in Table 4. The “mixed contaminant” spike solution consisted of an National Institute of Science and Technology (NIST) traceable (SM-2042-002, Lot#1309802; High Purity Standards, Inc.) custom-mixed solution (2% HNO_3) containing 10 mg L^{-1} of the following elements: antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), cerium (Ce), cesium (Cs), chromium (Cr), europium (Eu), lanthanum (La), nickel (Ni), rhenium (Re), selenium (Se), strontium (Sr), thallium (Tl), thorium (Th), and uranium (U). The components of the test solution were chosen to reflect a disparate range of elements of interest for the SDF. An additional potential contaminant, iodine (I), was evaluated in a separate sorption experiment to avoid potential analytical interferences associated with its analysis by inductively coupled plasma – mass spectrometry (ICP-MS). A 15 mg L^{-1} iodide (I^-) stock solution was created by dissolving reagent grade potassium iodide (KI; Thermo Fisher Scientific, Waltham, MA) in DIW.

Table 3. Contaminants evaluated in the current study listed in increasing atomic number.

AN	Element	AW	Symbol	Notes
24	Chromium	52	Cr	
28	Nickel	58.7	Ni	Surrogate for Pb and Co
33	Arsenic	74.9	As	
34	Selenium	78.9	Se	
38	Strontium	87.6	Sr	
48	Cadmium	112.4	Cd	Surrogate for Pb and Co
51	Antimony	121.8	Sb	
53	Iodine	126.9	I	
55	Cesium	133	Cs	
56	Barium	137	Ba	Alkaline Earth element, e.g., Ra, Sr
57	Lanthanum	139	La	Lanthanides are generally used as surrogate for tri-valent actinides, e.g. (Ac(III)
58	Cerium	140	Ce	Surrogate for plutonium (Pu)
63	Europium	152	Eu	Surrogate for americium (Am) and curium (Cm)
75	Rhenium	186	Re	Surrogate for techetium (Tc)
81	Thalium	204	Tl	
90	Thorium	232	Th	Surrogate for tetravalent actinides U(IV), Np(IV), and Pu(IV)
92	Uranium	238	U	

Table 4. Radionuclides of interest and their assumed oxidation state under varying environments (Modified from SRNL-STI-2009-00473).

	Chemical Grouping [(b)]	Sandy Sediment, Clayey Sediment, Cementitious Leachate Impacted Sandy/Clayey Sediment, CDP Impacted Sandy/Clayey Sediment	Oxidizing Cement	Reducing Cement
tritium (T)		HTO	HTO, OH^-	HTO, OH^-
Inorganic C		CO_3^{2-}, HCO_3^-	CO_3^{2-}, HCO_3^-	CO_3^{2-}, HCO_3^-
Ag, **Tl**	Monovalent soft metal	+1	+1	+1
Al	Trivalent metal	+3	+3	+3
As, Sb	Divalent Oxyanion	XO_4^{2-}	+5	+3
Co, **Cd**, **Ni**, Pt	Divalent Transition	+2	+2	+2
Cr		CrO_4^{2-}	+6	+3
Cu			+2	+1
Fe		Fe^{+3}	+3	+2
Mn			+4	+2
Mo			+6	+4
N		NO_3^-/NO_2^-	+5/+3	-3
Se, Te	VIB Elements	XO_4^{2-}, $XO_3^{2-(c)}$	XO_4^{2-}, XO_3^{2-}	XO_3^{2-}
Kr, Rn, Ar	Noble Gas	0	0	0
Sr, Ra, **Ba,** Ca	Alkali-earth metals	+2	+2	+2
Zr, **Th**	Group VI Elements	+4	+4	+4
Nb		$Nb(OH)_6^-$	$Nb(OH)_6^-$	$Nb(OH)_4^{-(a)}$
Tc, **Re**	$XO_4^{-(c)}$	XO_4^-	XO_4^-	X^{4+}
Sn		+4	+4	+4
Cl, F, **I**, At	VIIB, Halides	-1	-1	-1
Cs, Fr, K, Na, Rb	Alkali metals	+1	+1	+1
La	Lanthanides	+3	+3	+3
Ac, Am, Bk, Bi, **Ce**, Cf, Cm, **Eu**, Gd, Lu, Sm, Y	Trivalent Actinides & Rare Earth Elements	+3	+3	+3
Hg, Pb, Po	Soft, divalent cation	+2	+2	+2
U		UO_2^{2+}	UO_2^{2+}	U^{4+}
Np, Pa		$XO_3^{-(c)}$	XO_3^-	X^{4+}
Pu		$Pu^{VI}O_2^{2+}$, $Pu^{V}O_2^{+}$, colloid	$Pu^{VI}O_2^{2+}$, $Pu^{V}O_2^{+}$, colloid	Pu^{4+}, colloid

The elements evaluated in the current study are in bold type.

(a)Nb likely exists as Nb(III) under reducing conditions, but little sorption data is available for this species (Baes and Mesmer 1976).

(b) These groupings of radionuclides will be used in the following Kd and solubility limit value tables in the absence of experimental data. These groupings are based on the basic chemical considerations including periodicity and basic aqueous chemical properties.

(c) X = generic metal.

2.2 Oxic Partitioning Treatments

Triplicate 2.0 ± 0.10-g of air-dried SDF soil samples were suspended in 30 ± 0.1-mL of the appropriate background solution 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 suspensions were shaken overnight on a horizontal orbital shaker (~100 rpm) to equilibrate with the specific test solution. Afterwards, the pre-reaction set was centrifuged using a Sorvall RC 5B plus centrifuge 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.

The samples were then filled with 24-mL of the appropriate background solution and 1 mL of the "mixed-contaminant" spike solution for a total volume of 30 mL. In order to neutralize acid from the "contaminant" spike, a sufficient amount of NaOH was added to each tube based on preliminary titrations of the contaminant spike. The exact same procedure was used for the iodine partitioning experiment, except the "mixed-contaminant" spike solution was replaced with the KI solution (i.e., 15 mg L^{-1} I^-) described previously, and there was no need to add NaOH to address any acidity associated with the I^- spike solution.

The 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, Massachusetts) into a labeled 15-mL metal-free polypropylene tube (VWR, Radnor, PA), and acidified with trace metal grade HNO_3 to 2% of sample volume. Instead of acidification, samples for I^- analysis were preserved by addition of 0.4 mL of 25% tetra-methyl ammonium hydroxide (TMAH) solution to each 10 mL filtered sample. Then remaining supernatants in the 50-mL Oak Ridge tubes for both the "mix contaminant" and iodine experiments were analyzed for pH and Eh.

2.3 Anoxic Partitioning Treatments

As noted for the oxic treatments, three replicate no-soil control tubes were included for each of the four test solutions. All background solutions were prepared with N_2-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 O_2 for 30 to 60 minutes before filling with 30 ± 0.1-mL of the appropriate background solution and resealing. The anoxic environment in the glove box was maintained by addition of a 95% N_2/5% H_2 gas mixture to establish a consistent 2% H_2 atmosphere. The samples were then secured on an orbital shaker at 100 rpm inside the glove box and reacted overnight. The pre-reaction set was then removed from the glove box and centrifuged as noted above 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 1 mL of the “mixed-contaminant” spike solution for a total volume of 30 mL. As noted previously, a sufficient amount of NaOH was added to each tube in order to neutralize the acidity associated with the contaminant spike solution. The exact same anoxic procedure was used for the iodine partitioning experiment, except the “mixed-contaminant” spike solution was replaced with the KI solution (i.e., 15 mg L^{-1} I^-) described previously, and there was no need to add NaOH to address any acidity associated with the I^- spike solution.

The spiked samples were then placed on the orbital shaker (~100 rpm) 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, Massachusetts) into labeled 15-mL metal-free polypropylene tubes (VWR, Radnor, PA), and acidified with trace metal grade HNO_3 to 2% of sample volume. Instead of acidification, samples for I^- analysis were preserved by addition of 0.4 mL of 25% TMAH solution to each 10 mL filtered sample. Then remaining supernatants in the 50-mL Oak Ridge tubes for both the “mix contaminant” and iodine experiments were analyzed for pH and Eh.

2.3 Sample Analysis

The concentration of contaminants remaining in solution after equilibration was determined by ICP-MS in accordance with the quality assurance (QA) and quality control (QC) protocols of EPA method 6020A (USEPA, 2007). Samples and standards for iodine analysis were prepared in a 1% TMAH, 0.01% Trition X solution for ICP-MS analysis using Re as internal standard (Zheng et al., 2012).

3.0 RESULTS

A complete summary of all 136 SDF soil-specific K_d values generated in the current study is provided in Table 5. Initially, the CSS and AGW treatment solutions were chosen to mimic Stages III and IV of cementitious material weathering, respectively. However, the CSS, with an initial pH of ≈ 9, provided insufficient buffering capacity in the presence of the SDF soils, with CSS treatments yielding final equilibrated pH values (pH ≈ 5.2) that were only slightly higher than the AGW solution treatments (pH ≈ 4.9). Therefore, both the CSS and AGW treatment results were combined for the purposes of discussion, and generally reflect partitioning conditions associated with Stage IV of cement material weathering, after significant dilution with native groundwater.

In Table 6, the current K_d values for the SDF soil are compared to the most appropriate (i.e., "best values") values provided in Kaplan (2010; SRNL-STI-2009-00473) under various SDF leaching scenarios, including background solution conditions and adjusted K_d estimates based on the Cementitious Leachate Impact Factors, i.e., $f_{Cement\ Leachate}$. For comparison, the SDF K_d values reported in Table 6 for the current study represent the range observed for a given solution treatment. For the portlandite and SLS solution treatments, the reported range reflects the K_d values observed under oxic and anoxic conditions, respectively. Summarized in Table 7, the K_d values derived for this study were used to calculate Cementitious Leachate Impact Factors for the SLS treatment solution for comparison with the Cementitious Leachate Impact Factors reported by Kaplan (2010; SRNL-STI-2009-00473).

As noted earlier, K_d results for fifteen of the seventeen elements (Ba, Cd, Ce, Cr, Cs Eu, I, La, Ni, Re, Sb, Se, Sr, Th, and Tl) under background solution conditions (i.e., AGW/CSS treatment solutions) were consistent with SRNL-STI-2009-00473, or differences can be readily explained in terms of the chemical speciation of the specific contaminant and/or the exact conditions of the experimental system. The K_d values for As and U under background soil conditions were clearly higher than expected. In contrast, far more discrepancies were observed when comparing the K_d values determined in the two alkaline treatment solutions compared to estimates based on the Cement Impact Factor. A discussion of the results for each of the elements evaluated in the current study is provided below. In some instances, elements with similar chemical properties noted in Table 4 have been grouped together for the purposes of discussion.

3.1 Antimony (Sb), Arsenic (As), and Selenium (Se)

Arsenic displayed unexpectedly high K_d values (i.e., > 1900 mL g^{-1} compared to 100 to 200 mL g^{-1}) for the AGW/CSS treatments (pH < 6), even when considering the capacity of highly-weathered, Fe oxide-rich SRS soils and sediments to electrostatically retain anions (Seaman et al., 1995; Seaman et al., 1999). In contrast, Sb and Se partitioning for the AGW/CSS solution treatments was generally consistent with expectations. The K_d value for As remained high for the Portlandite treatment (> 1900 mL g^{-1}), above the Cement Impact Factor adjusted value, but was considerably less for the SLS treatment. Partitioing in the presence of the SLS treatment was somewhat impacted by As and Se present in the SLS treatment solution, likely derived from the fly ash and BFS used in making the cementitiuos material. Therefore, the K_d values reported in Tables 5 and 6 have been adjusted to account for the additional As and Se present in the SLS treatment. Compared to the background solution treatments and the Cement Leachate Factor estimates, the K_d values for Sb and Se were much lower for the portlandite treatment, and even lower still in the SLS. Of the elements tested, Sb and Se displayed the largest decreases in K_d values compared to the Cement Leachate Impact Factor estimates for both alkaline solution treatments, while the As K_d value was only reduced significanlty for the SLS treatment. A comparision of the estimated Cement Leachate Impact Factors provided by Kaplan (2010) with the current data is provided in Table 7.

3.2 Barium (Ba) and Strontium (Sr)

As alkaline earth metals (along with Mg, Ca and Ra), Ba and Sr are present in the soil environment in the +II oxidation state. As with other alkaline earth cations, Ba and Sr partitioning in soil is generally controlled by cation exchange with soil clays and competition with other common exchangeable cations (i.e., Ca, Mg, Na, K, etc.) (USEPA, 1999b). On an equivalence basis, cation exchange experiments generally show the following preference trend, i.e., Ra > Ba> Sr > Ca > Mg (Seaman and Roberts, 2012). The alkaline earth metals form sparingly soluble phosphates, and form carbonates under alkaline conditions. The solubility products (K_{sp}) for alkaline earth phosphates are typically $\leq 1 \times 10^{-23}$ M. Further, the alkaline earth metals are also subject to varying degrees of precipitation with sulfur, either sulfate (SO_4^{2-}) or sulfide (S^{2-}), with Ba and Ra sulfates being much less soluble than Ca and Sr sulfates. Under highly alkaline conditions, the hydroxides of Sr, Ba and Ra are much more soluble than Ca (Lehto and Hou, 2011).

The K_d values for Ba are higher than expected for the portlandite treatment solution (152-186 mL g^{-1}). Despite pH values similar to the portlandite treatments, the Ba K_d for SLS treatments under oxic and anoxic conditions were > 2000 ml g^{-1}. The higher Ba partitioning in the SLS solution treatment may reflect the high sulfur content of the leachate derived from the saltstone BFS, with both $BaSO_4$ [K_{sp} 1E-10 M] and BaS [K_{sp} 5E-10 M] being fairly insoluble (Almond and Kaplan, 2011). Unlike Ba, the K_d for Sr did not increase for the portlandite treatment, possibly due to greater competition with Ca for exchange sites, but did increase for the SLS treatment (303 and 492 ml g^{-1}, for the oxic and anoxic SLS treatments, respectively), but not as much as observed for Ba, possibly due to the somewhat higher solubility of Sr sulfur compounds, $SrSO_4 \approx K_{sp}$ 1E-7 M. The higher K_d under anoxic conditions may also reflect the lower Sr solubility observed for reduced sulfur species (Almond and Kaplan, 2011; Lehto and Hou, 2011; Seaman and Roberts, 2012). The impact of the high K_d values observed for the SLS treatment solution on the calculated Cement Leachate Impact Factors is reported in Table 7.

Table 5. Summary of pH, Eh, and K_d values for the SDF soil derived under various treatment environments.

Treatment Sol.	**AGW**		**CSS**		**Saltstone Leachate Solution** Reducing Cement**		**Portlandite Leachate Solution Oxidizing Cement**	
Cement Weathering Stage	**Baseline Leaching Conditions: Stage IV***				**Stage I/II**		**Stage I/II**	
Redox State	**Oxic**	**Anoxic**	**Oxic**	**Anoxic**	**Oxic**	**Anoxic**	**Oxic**	**Anoxic**
pH	4.8	4.9	5.3	5.1	12.1	11.9	12.0	12.0
Eh (mV)	626.0	-51.0	629.0	-99.0	228.0	-705.0	299.0	-670.0
Contaminants	**Kd (mL/g)**				**Kd (mL/g)**		**Kd (mL/g)**	
As	>1900	>1900	>1900	>1900	13	14	>1900	>1900
Ba	18	30	44	50	>2000	>2000	152	186
Cd	14	23	37	42	>5000	>5000	>5000	>5000
Ce	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000
Cr	>1400	>1400	>2400	>2400	309	503	>2400	>2400
Cs	40	46	59	60	14	14	21	22
Eu	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000
I* **	<1	<1	<1	<1	<1	<1	<1	<1
La	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000
Ni	14	21	36	30	>1100	>1100	>1100	>1100
Re	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
Sb	>1200	>1200	>1200	>1200	7	5	190	190
Se	>1400	>1400	>1400	>1400	17	19	19	29
Sr	14	22	31	43	303	492	3	15
Th	>730	>730	>730	>730	>730	>730	>730	>730
Tl	28	34	49	45	133	1125	134	123
U	776	1207	>2500	>2500	271	174	>2500	>2500

*AGW and CSS treatments were grouped together as Leachate Stage IV because the final pH of the CSS treatment was similar to that of the AGW because of the soils buffering capacity, far less than a calcite-saturated system.

**SLS K_d values adjusted to account for As and Se present in the SLS treatment solution.

***Iodine K_d values determined in separate partitioning experiment.

Table 6. Summary of K_d values for the SDF soil compared to the values reported in Kaplan (2010) for the SRS "Sandy" and "Clayey" sediments.

Rad	Best Sand *Kd*	**SDF *Kd Background***	Best Clay *Kd*		Best Sand *Kd* (Cement Leachate)	**SDF *Kd Saltstone Leachate***	Best Clay *Kd* (Cement Leachate)		Best Sand *Kd* (Cement Leachate)	**SDF *Kd Portlandite Leachate***	Best Clay *Kd* (Cement Leachate)
	(mL/g)	**(mL/g)**	(mL/g)		(mL/g)	**(mL/g)**	(mL/g)		(mL/g)	**(mL/g)**	(mL/g)
		All Values				**oxic to anoxic**				**oxic to anoxic**	
pH		**5**				**12.1 to 11.9**				**12**	
Eh (mV)		**555**				**228 to -705**				**299 to -670**	
As	100	**>1900**	200		140	**13 to 14**	280		140	**>1900**	280
Ba	5	**18 to 50**	17		15	**>2000**	51		15	**152 to 186**	51
Cd	15	**14 to 42**	30		45	**>5000**	90		45	**>5000**	90
Ce	1100	**>2000**	8500		1650	**>2000**	12750		1650	**>2000**	12750
Cr	4	**>2400**	10		6	**309 to 503**	14		6	**>2400**	14
Cs	10	**40 to 60**	50		10	**14**	50		10	**21**	50
Eu	1100	**>2000**	8500		1650	**>2000**	12750		1650	**>2000**	12750
I	0.3	**<1**	0.9		0.0	**<1**	0.1		0.0	**<1**	0.1
La		**>2000**				**>2000**				**>2000**	
Ni	7	**14 to 36**	30		22	**>1100**	96		22	**>1100**	96
Re	0.6	**<0.80**	1.8		0.1	**<0.80**	0.2		0.1	**<0.80**	0.2
Sb	2500	**>1200**	2500		3500	**7 to 5**	3500		3500	**190**	3500
Se	1000	**>1400**	1000		1400	**17 to 19**	1400		1400	**19 to 29**	1400
Sr	5	**14 to 43**	17		15	**303 to 492**	51		15	**3 to 15**	51
Th[***]	900	**>730**	2000		1800	**>730**	4000		1800	**>730**	4000
Tl	10	**28 to 49**	50		10	**133 to 1125**	50		10	**134 to 123**	50
U	200	**776 to >2500**	300		600	**271 to 174**	900		600	**>2500**	900

*Kd values in bold represent the current study.

**Kd values adjusted to account for As and Se present in the SLS treatment solution.

***Thorium Kd values reported in the current study are constrained by analytical limitations. Actual values may be much greater.

Table 7. Calculated Cement Leachate Impact Factors for the saltstone leachate solution compared to the values reported in Kaplan (2010).

			Calculated Oxic Impact Factor			Calculated Anoxic Impact Factor	Kaplan 2010 Impact Factor ; Table 13
Contaminant	**AGW oxic**	**Saltstone Leachate Stage I/II-Oxic**		**AGW-Anoxic**	**Saltstone Leachate Stage I/II/ Anoxic**		**Oxic**
As	>1900	13	0.01	>1900	14	0.01	1.4
Ba	18	>2000	111	30	>2000	67	3
Cd	14	>5000	357	23	>5000	217	3
Ce	>2000	>2000	≥1*	>2000	>2000	≥1	1.5
Cr	>1400	309	0.22	>1400	503	0.04	1.4
Cs	40	14	0.35	46	14	0.30	1
Eu	>2000	>2000	≥1	>2000	>2000	≥1	3.2
I	<1	<1	**	<1	<1	**	0.1
La	>2000	>2000	≥1	>2000	>2000	≥1	NA
Ni	14	>1100	79	21	>1100	52	3.2
Re	<0.80	<0.80	**	<0.80	<0.80	**	0.1
Sb	>1200	7	0.01	>1200	5	0.004	1.4
Se	>1400	17	82	>1400	19	0.01	1.4
Sr	14	303	22	22	492	22	3
Th	>730	>730	≥1	>730	>730	≥1	2
Tl	28	133	5	34	1125	33	3
U	776	271	0.35	1207	174	0.14	3

*Cement Impact Factors for elements displaying a high degree of sorption regardless of treatment solution (i.e., Ce, Eu, La and Th) are reported as ≥1 since the reported K_d value represents the absolute minimum degree of sorption under all relevant conditions.

**The limited sorption observed for I and Re for all treatment solutions precludes calculating a Cement Impact Factor.

3.3 Divalent Transition Metals: Cadmium (Cd) and Nickel (Ni)

Cadmium and Ni are found in the +II oxidation state, and can serve as surrogates for other potential metal contaminants in the +II oxidation state, such as lead (Pb) and cobalt (Co). The range in K_d values obtained in the current study under background conditions, 14 to 42 and 14 to 36 mL g^{-1} for Cd and Ni, respectively, are similar to the values reported by Kaplan (2010). However, the observed K_d values for both transition metals are much greater (i.e., >5000 and >1100 mL g^{-1} for Cd and Ni, respectively) when in the presence of the portlandite or SLS treatment solution, regardless of oxidation state (Table 6). The high K_d values observed for the two alkaline treatment solutions results in much higher Cement Leachate Impact Factors than originally estimated in Kaplan (2010) (see Table 7).

3.4 Cerium (Ce), Europium (Eu), and Lanthanum (La)

Cerium, a lanthanide that is generally found in the +III oxidation state as a trivalent cation (i.e., Ce^{3+}), displays similar traits to actinium (Ac), americium (Am), bismuth (Bi), californium (Cf), curium (Cm), Eu, and La (Lehto and Hou, 2011). A K_d value of > 2,000 mL g^{-1}, defined by the MDL in the current study, was observed for all solution treatments (Table 5), regardless of the redox conditions. This value is consistent with the range reported in Kaplan (2010; SRNL-STI-2009-00473) for Sandy (1,100 mL g^{-1}) and Clayey sediments (8,500 mL g^{-1}) (Table 6). The observed K_d also falls within the range estimated for SRS soil systems under the influence of cement leachate.

Europium, also found as a trivalent cation, shows the same trends in partitioning behavior with respect to pH and redox conditions as reported above for Ce (Table 5). A K_d value of > 2,000 mL g^{-1}, again defined by the MDL in the current study, was observed for all solution treatments (Table 5), regardless of the redox conditions. This value is consistent with the range reported in Table 6 by Kaplan (2010) for Sandy (1,100 mL g^{-1}) and Clayey (8,500 mL g^{-1}) SRS sediments. Furthermore, the observed K_d also falls within the range reported for SRS soil systems under the influence of cement leachate (Table 6).

Lanthanum, the first member of the Lanthanide series extending from La to Lu and conventionally considered a rare-earth metal, is typically found in the +III oxidation state (i.e., La^{+3}), behaving much the same as other trivalent metals, Ce and Eu (Lehto and Hou, 2011). In the present study, La behaves very similar to Ce and Eu, with K_d values >2000 mL g^{-1}, regardless of solution treatment or redox state, consistent with data from Kaplan (2010) reported in Table 6.

For all three elements, it is difficult to derive an appropriate Cementitious Leachate Impact Factor when the K_d values for all treatment solution is limited by the MDL of the study.

3.5 Cesium (Cs)

Cesium, a poorly hydrated, monovalent alkali metal, tends to irreversibly sorb to certain 2:1 layered phyllosilicate soil clays, i.e., micas and vermiculites, restricting migration in the subsurface environment. The International Atomic Energy Association (IAEA) reports a a mean soil K_d value for all soils of 1,200 ml g^{-1} (IAEA, 2010; Seaman and Roberts, 2012). However, the soils of the southeastern US, including the SRS, are somewhat deficient in such 2:1 clays, resulting in lower reported partitioning coefficients (Seaman and Bertsch, 1999; Seaman et al., 2001).

The Cs K_d values generated in the current study for the AGW/CSS solution treatments (i.e., 40 to 60 mL g^{-1}) are consistent with the range of 10 to 50 mL g^{-1} for Sand and Clay (Table 6), respectively. The current values for the portlandite and SLS (i.e., 21 and 14 mL g^{-1}, respectively) are also consistent with Kaplan (2010), and similar to the values reported for Cs release from actual Saltstone cores (Almond and Kaplan, 2011), showing no increase in sorption for either high pH treatment. In fact, the values decrease somewhat when compared to background soil conditions, which may reflect greater competition for cation exchange sites at the higher ionic strength of the two high-pH treatment solutions.

3.6 Chromium (Cr)

Chromium displayed a much higher K_d than previously reported for SRS materials under background conditions (Table 5), which can be attributed to Cr being in the +3 redox state (i.e., Cr^{3+}), with partitioning largely controlled by precipitation as oxy-hydroxides, rather than the sorption behavior of the oxidized Cr(VI) species, i.e., chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) (Seaman et al., 1999). The Cr K_d values in the presence of the portlandite (>2400 mL g^{-1}) and SLS treatment (309 to 503 mL g^{-1}) solutions were also much higher than the Cement Leachate Impact Factor estimates (Table 6).

3.7 Iodine (I)

The current study focused on I^- rather than the oxidized iodate (IO_3^-) species because Hu et al. (2005) observed that significant IO_3^- reduction occurred in the presence of SRS soils and sediments under oxic conditions, including SRS subsoils and sediments that are rich in Fe oxy-hydroxides such a goethite. The K_d values observed for I in the current study (< 1.0 mL g^{-1}) are consistent with the values reported by Hu et al. (2005), and by Kaplan (2010; SRNL-STI-2009-00473) for Sandy (0.3 mL g^{-1}) and Clayey (0.9 mL g^{-1}) sediments under baseline solution conditions. The same low K_d (< 1.0 mL g^{-1}) was also observed for the other three treatment solutions, regardless of redox conditions. The limited degree of sorption observed for all treatment solutions makes it difficult to quantify major changes in I^- partitioning resulting from the cementitious leachates. However, a general decrease in I^- K_d would be expected for the two alkaline treatment solutions, i.e., the portlandite and SLS treatments.

3.8 Rhenium (Re)

Rhenium, a third row transition metal with oxidation states of +IV and +VII, is often considered a chemical analog for ^{99}Tc. Like Tc, Re generally forms oxyanions (ReO_4^-) and tetravalent cations (Re^{4+}), the latter of which is subject to hydrolysis and precipitation. Re displayed very limited partitioning under all treatment solution and redox conditions, with a K_d of < 0.8 mL g^{-1}. This is consistent with the K_d values reported by Kaplan (2010; SRNL-STI-2009-00473) for Sandy (0.6 mL g^{-1}) and Clayey (1.8 mL g^{-1}) sediments, as well as sediments impacted by cement leachate.

Under similar glove box conditions to those used in the current study (i.e., 2% H_2 atmosphere), Kaplan et al. (2011) found that extended exposure (> 8 days) to low anoxic conditions in the presence of reductive saltstone was required for significant Tc sorption (K_d 10,000 mL g^{-1}) to occur. In addition, significant Tc reduction and sorption to non-reducing cement was also noted after prolonged equilibration (56 days) under anoxic conditions. This suggests that the limited equilibration time used in the current study was insufficient to observe Re reduction in the anoxic treatments.

3.9 Thallium (Tl)

The SDF K_d value for Tl (47 mL g^{-1}), a soft monovalent metal, falls within the reported range for SRS Sand (10 mL g^{-1}) and Clay materials (50 mL g^{-1}) (Table 6). However, the K_d values in the presence of the portlandite are approximately three times higher (130 mL g^{-1}) than based line values, and even higher still (>1100 mL g^{-1}) in the presence of SLS under anoxic conditions. This supports an increase in the Cement Leachate Impact Factor from previous estimates in Kaplan (2010) (see Table 7).

3.10 Thorium (Th)

Thorium exists primarily in the +IV redox state, forming both carbonate and hydroxide species in the soil environment (USEPA, 1999b). The reported K_d values for Th were consistently limited by the MDLs, with a minimum reported value for the current study of > 730 mL g^{-1}, regardless of background solution composition, pH, or redox status (Table 5). This is comparable to the values reported by Kaplan (2010) for Sand (900 mL g^{-1}) and Clay (2000 mL g^{-1}) under background conditions, but far less than the estimated values for cement leachate, i.e., 1800 and 4000 mL g^{-1} for Sand and Clay, respectively.

3.11 Uranium (U)

Uranium is generally found in one of two redox states, with U(IV) and U(VI) dominating under reducing and oxidizing conditions, respectively. Uranium (IV) is generally much less soluble than U(VI). Under oxidizing conditions, U(VI) hydrolyzes instantly to form the uranyl cation, UO_2^{2+}. Uranyl forms soluble complexes with carbonate under neutral to alkaline conditions. In the absence of carbonates, UO_2^{2+} forms various hydrolysis species in response to pH, with soil parameters such as organic matter content and pH playing a strong role in controlling soil partitioning (Seaman and Roberts, 2012; USEPA, 1999b). While the background K_d values are higher than the "Best" values for Sand and Clay reported in Table 6, they are consistent with high U K_d values reported in other SRS studies, especially under reducing conditions (Seaman and Kaplan, 2010; Serkiz and Johnson, 1994; Serkiz et al., 2007). However, the U K_d values for the SLS treatment solution were somewhat less than expected (i.e., 271 and 174 mL g^{-1} for the oxic and anoxic treatments, respectively), while the portlandite K_d values were quite high (>2500 mL g^{-1}).

4.0 DISCUSSION

The current study demonstrates the ability to simultaneously derive K_d values for a disparate range of contaminants and non-radioactive chemical analogs under conditions designed to mimic the impact cement leachate on contaminant partitioning. In addition to measuring the impact of cement leachate on contaminant partitioning, this is the first study using site-specific soil materials collected at the SDF. Utilizing the low detection limits of ICP-MS enabled the determination of K_d values for multiple chemical analogs of radioactive contaminants at concentrations that are environmentally relevant. Although more analogous to actual waste conditions, evaluating the partitioning of multiple contaminants from within a single stock treatment can complicate the eventual interpretation of the results because of the potential for the contaminants to interact. However, most of the initial K_d values determined in the current study under background chemical conditions were consistent with previously reported values, which serves as general validation for the current experimental methodology, or can be explained based on contaminant speciation.

In all, 138 site specific K_d values were estimated in the current study across a pH range from 4.8 to 12.2 under oxic and anoxic conditions. While the partitioning of certain elements (i.e., As, Se, and Sb) was somewhat reduced in the presence cement leachate when compared to previous Impact Factor estimates, the partitioning values for several other elements of interest were much higher than previous estimates, with consistent partitioning trends generally observed for elements with similar chemical properties, regardless of solution treatment. This general consistency should help in refining Cement Leachate Impact Factors for other elements that lack sufficient relevant data.

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

- All baseline K_d values measured with site-specific SDF sediment were consistent or greater than those recommended for use in the SRS geochemical data package (SRNL-STI-2009-00473).
- Cementitious leachate impacted K_d values of the site-specific SDF sediment were generally consistent with or greater than those recommended for use in the SRS geochemical data package (SRNL-STI-2009-00473). Notable exceptions include As, Cr, Sb, and Se. Arsenic, Sb and Se had cement leachate impacted K_d values that were much lower (As - 13 to 14 mL g^{-1}, Sb - 5 to 7 mL g^{-1}, and Se - 17 to 19 mL g^{-1}) than the literature values reported in SRNL-STI-2009-00473 (As - 140 to 280 mL g^{-1}, Sb - 3500 mL g^{-1}, and Se - 1400 mL g^{-1}). For Cr, the lower cement leachate factor (i.e., 0.04 vs 1.4) reflects the much higher initial Cr partitioning under baseline conditions rather than a lower K_d value than estimated by Kaplan (2010) for cement leachates.
- The K_d values for the alkaline earth metals, Ba and Sr (and Ra), were slightly higher than previously reported for baseline conditions. Barium and Sr partitioning was considerably higher for the portlandite solution, and higher still for SLS, possibly due to the high sulfur content in the cementitious leachate, as both cations form sparingly soluble sulfur compounds.
- The K_d values for the two divalent transition metals (i.e., Cd and Ni) were consistent with SRNL-STI-2009-00473 for background solution conditions, but much higher, >5000 and > 2000 mL g^{-1} for Cd and Ni, respectively, in the portlandite and SLS treatment solutions, regardless of redox conditions.
- Consistent with SRNL-STI-2009-00473, the K_d values for the trivalent cations, i.e., Ce, Eu, and La, remained quite high for all treatments, including the cementitious leachates, regardless of redox conditions. In addition, Cr displayed a much higher K_d than previously reported for SRS materials, which can be attributed to Cr being in the +III oxidation state (i.e., Cr^{3+}), with partitioning largely controlled by precipitation as oxy-hydroxides, rather than sorption of oxidized Cr, i.e., chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$).
- The K_d values for I were consistent with SRNL-STI-2009-00473 for background SRS conditions and the cementitious leachates (< 1 mL g^{-1}), regardless of redox status.
- The K_d value for Re, often used as a surrogate for Tc, was < 0.8 mL g^{-1} for all treatments, regardless of the redox status.
- The K_d value for Cs was consistent with SRNL-STI-2009-00473 for background SRS conditions (59 mL g^{-1}), but decreased somewhat in the presence of the portlandite and SLS solutions, presumably due to greater competition for cation exchange sites and the general lack of 2:1 phyllosilicate clays in SRS soils that preferentially sorb Cs^+ and K^+.
- The K_d value for Tl was consistent for background conditions, but somewhat elevated for the portlandite and SLS cement leachate treatment solutions.
- Thorium displayed a K_d value > 730 mL g^{-1} regardless of treatment solution or redox conditions. The actual K_d value is likely much higher, as reported in SRNL-STI-2009-

00473, but the current results were constrained by the high method detection limits (MDLs) observed for Th.

- Uranium K_d values were generally higher than previous estimates for background conditions and the portlandite treatment solution, with somewhat lesser (271-174 mL g^{-1}) than estimated values for the SLS treatment solution (i.e., 600 to 900 mL g^{-1}).

5.0 ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of S. Buettner, S. Harris and D. Soteropoulos with completion of the laboratory studies and production of this report.

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