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Chloride, Chromate, Silver, Thallium, and Uranium Sorption to SRS Soils, Sediments, and Cementitious Materials

John C. Seaman^{*} and Daniel I. Kaplan

^{*}Savannah River Ecology Laboratory
The University of Georgia, Aiken, SC 29802

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Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
Aiken, SC 29808

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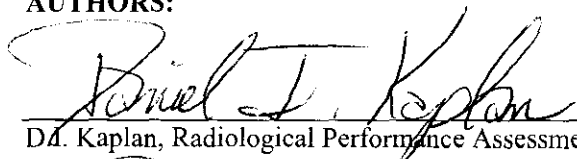
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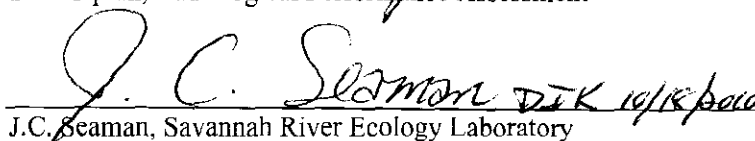
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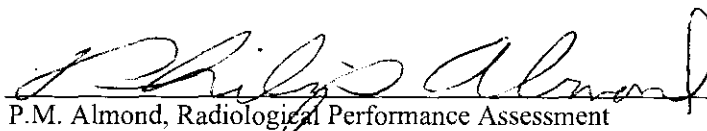
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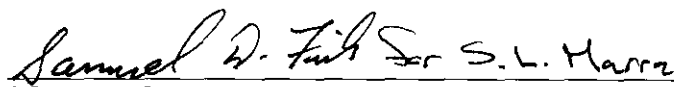
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 J.C. Seaman, Savannah River Ecology Laboratory Date

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 P.M. Almond, Radiological Performance Assessment Date

APPROVALS:

 _____
 D.A. Crowley, Manager, Radiological Performance Assessment Date

 S.L. Marra 19 Oct 2010
 S.L. Marra, Manager Date
 Environmental & Chemical Process Technology Research Programs

EXECUTIVE SUMMARY

The objective of this study was to measure sorption values for chloride (Cl^-), chromate (Cr(VI) or CrO_4^{2-}), silver (Ag), thallium (Tl), and uranium (U) to sediment and cementitious materials for the purpose of providing input values for use in risk models on the Savannah River Site (SRS). There have been few measurements quantifying the extent that these elements and compounds sorb to SRS sediments. For this reason, conservatively low K_d values have been used in modeling. Generally, the results from the current study showed greater sorption than have been reported in previous risk assessment models. For example, presently SRS commonly uses K_d of 200 mL g^{-1} and 300 mL g^{-1} for sandy and clayey sediments, respectively. In this study, we measured values of 2,000 and 17,000 mL g^{-1} , for sandy and clayey sediments, respectively. Similarly for Tl , estimated K_d values of 10 and 50 mL g^{-1} have been used in calculations for sandy and clayey sediments. In this study we measured K_d values for Tl of 80 and 90 mL g^{-1} , for sandy and clayey sediments, respectively. Cement K_d values were also higher than previously estimated. When the pH of the suspension was ≈ 11 -12, as is expected in the early period of cement aging (the first hundred to thousand years), U removal from solution was extremely high due to precipitation from solution. As expected, the U K_d decreased as the pH increased. Thallium and U sorption to sediment were especially sensitive to pH. Above pH 6.5 Tl appeared to precipitate out of solution. The K_d values for Ag were measured under two background solution conditions, a low ionic strength groundwater surrogate (referred to as Artificial Groundwater, AGW) and 1 mMol $\text{Ca(NO}_3)_2$. Results suggest that Ag partitioning in the AGW solution was controlled by the solubility of silver chlorides and sulfates, rather than the composition of the sediment materials, since both sediments yielded very similar K_d values, i.e., $\approx 350 \text{ mL g}^{-1}$. In contrast, the K_d values in the $\text{Ca(NO}_3)_2$ solution were considerably lower (≈ 11 -35 mL g^{-1}), possibly due to the higher ionic strength and competition with Ca , and varied with sediment texture. New site-specific K_d values are recommended for Cl^- , Cr(VI) , Ag , Tl , and U in sandy and clayey sediment, and for Tl and U in cementitious materials. Results from this research will reduce the uncertainty and provide greater technical justification for the selection of Cl^- , Cr(VI) , Tl , and U K_d values for risk models on the SRS.

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LIST OF ABBREVIATIONS

ACP	Area Completion Projects
AGW	Artificial Groundwater
CDB	Citrate Dithionite Bicarbonate
COC	Constituent of Concern
DOE	Department of Energy
DIW	Deionized Water
DWS	Drinking Water Standard
ICP-MS	Inductively Coupled Plasma – Mass Spectrometer
K_d	Distribution Coefficient
SREL	Savannah River Ecology Laboratory
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 INTRODUCTION

The objective of this effort was to measure chloride (Cl^-), chromate (CrO_4^{2-}), silver (Ag), thallium (Tl), and uranium (U) sorption to two cementitious materials and three SRS sediments. The contaminants are of interest to the Areas Completion Projects (ACP) either because they are risk drivers or because there is little site-specific data available to conduct reactive transport models. Sorption data, such as K_d values (the contaminant concentration in the solids divided by the residual concentration in the aqueous phase, i.e., $K_d = C_{\text{soil}}/C_{\text{groundwater}}$) is typically one of the most important input parameters in risk analysis. One reason for this is that there is often a wide potential range for K_d values, especially for chemically reactive species, such as Cr, Tl and U. Each of these elements has multiple oxidation states, and as such has a different sorption affinity to solid surfaces. In the case of thallium, the oxidized form sorbs much more strongly than the reduced form. The opposite is true for U and Cr. That is, Tl(III) sorbs more strongly than Tl(I), whereas U(IV) sorbs more strongly than U(VI) and Cr(III) sorbs more strongly than Cr(VI). In the literature, U, Cr, and Tl K_d values can vary as much as three orders of magnitude (USEPA 1999; Kaplan and Mattigod 1998). In an attempt to reduce uncertainty associated with a model's prediction and to improve a model's accuracy, this report focuses on the measurement of K_d values using site-specific conditions and materials.

The Cl^- , Cr(VI), and Ag sorption experiments were conducted at the Savannah River Ecology Laboratory (SREL). The Tl and U sorption research was conducted at the Savannah River National Laboratory (SRNL). Most of the solid phase characterization presented in this report was previously conducted by Kaplan (2010) and Kaplan et al. (2008). All solid phase characterization work was conducted at SRNL.

2.0 MATERIALS AND METHODS

2.1 Methods

A series of batch sorption experiments were conducted with Cl^- , Cr(VI), Ag, Tl, and U on the bench top. Five solid phases were evaluated: sandy surface soil, subsurface sandy sediment, subsurface clayey sediment, reducing grout, and a 50-year old weathered concrete sample (Table 1, Table 2, and Table 3). These materials are described in more detail in Section 2.2. Uranium (VI) (UO_2^{2+}), and thallium (I) (Tl^+) K_d values were measured in soil as a function of pH. The laboratory procedure for all tests was essentially the same, with procedural differences designed to optimize detection for the constituents of concern (COC). Appendices A and B provide detailed descriptions of the sorption test procedures used for the U and Tl, and the Ag, Cl^- and Cr(VI) sorption tests, respectively.

A series of tared and labeled 15-mL centrifuge tubes were set up and 0.1 to 1 g of solid phase sorbent (sediment or cement) was added, depending on which contaminant and which sorbent was added to tube. Next, 12 mL of liquid was added, and the exact amount of both the liquid and the solid phases was measured by weighing to within ± 0.0001 g. The solids were washed 2-3 times over night in 12 mL rinses of artificial groundwater (AGW) (Table 4) for successive days until the suspension pH did not change. This was done to bring the solid and the liquids into chemical equilibrium prior to adding the contaminant. A low concentration of the contaminant was then added to the solid-liquid suspension and the reaction tubes were sealed for equilibration.

The sealed samples were placed in the dark on a slow moving platform shaker to equilibrate. After one week, the solids were permitted to separate from the liquids by flocculation and settling. The liquids were passed through a 0.1- μ m pore-size filter, and then analyzed for Cl⁻ by the mercuric thiocyanate method, Cr_{total}, Ag, Tl, and U by ICP-MS according to the QA/QC protocols outlined in EPA Method 6020 (USEPA, 1994). The K_d values were then calculated by assuming that the amount of contaminant removed from the aqueous phase was sorbed to the sediment. More precisely, the amount of a spiked contaminant removed from the aqueous phase compared to the amount removed from a spiked control sample that was carried through the study (and accounted for any contaminant sorption to the tube walls or unexpected precipitation). The equation used to calculate K_d values from the raw experimental data is shown in Equation 1:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times M} \quad (1)$$

where C_i and C_f are the initial and the final concentration of the contaminant (mol/L), V is the liquid volume (mL), and M is the sediment mass (g). Included in these samples were positive controls (contaminant spikes with liquids but no solids) and negative controls (no contaminants w/solids + liquid). The positive controls were used as C_i in Equation (1) and the negative controls in all cases were acceptable.

2.2 Materials

There were three sediments used in these studies, a Subsurface Clayey Sediment, a Subsurface Sandy Sediment and a Surface Sand Sediment. The two subsurface sediments were selected to represent end members of the types of sediments found in the SRS subsurface. As the name implies, the Surface Sand sediment was recovered from a forested area behind the Savannah River Ecology Laboratory. The organic layer, diagnostically labeled the O horizon for the purposes of soil pedon description, was removed and the underlying mineral horizon sampled (i.e., A horizon).

Two cementitious solids were used in these studies: a reducing grout, that is a grout that contains 8 wt-% slag, a vitreous by-product of smelting ore, and an aged cement piece of concrete exposed to the weather for 50 years (the aggregate was removed from this sample and only the cement was analyzed) (Table 2 and Table 3).

Table 1. Sediment characterization.

Sediment	Subsurface Clay	Subsurface Sand	Surface Sand
Depth of Sample (m)	5	15	0.1 to 0.3
% sand (>53 μm)	57.9	97	93
% silt (53 – 2 μm)	40.6	2.9	6
% clay (<2 μm)	1.6	0.2	1
Textural classification	Silty clay	Sand	Sand
pH ^(a)	4.55	5.1	4.7 \pm 0.04
% OM ^(b)	NA	0	0.76
CEC (cmol/kg) ^(c)	1.09 \pm 0.31	-0.35 \pm 0.22	Not measured
AEC (cmol/kg)	1.58 \pm 0.61	0.06 \pm 0.19	0.61 \pm 0.02
BET surface area (m ² /g)	15.31	1.27	1.37
Single point surface area (m ² /g)	15.07	1.24	1.36
CDB extractable Fe (mg/g) ^(d)	15.26	7.06	
0.2 M NH ₄ Cl Extractable ^(d)			
Al (mg/kg)	63.59	16.64	
Na (mg/kg)	42.91	34.69	
Mg (mg/kg)	144.05	98.76	
Ca (mg/kg)	64.41	24.62	
K (mg/kg)	182.87	92.97	
Clay-size (<2 μm) Mineralogy	Kaolinite > goethite > Hem (no quartz or 14 angstrom)	Kaolinite > goethite > muscovite/14A (no quartz)	Chlorite/vermiculite > quartz > gibbsite Kaolin > illite (no goethite, very little Kaolin)

^(a) pH procedure from Chemical Analysis of Ecological Materials, Stewart E. Allen, pgs. 16-17.

^(b) OM procedure from Chemical Analysis of Ecological Materials, Stewart E. Allen, pgs. 15-16.

^(c) CEC/AEC procedure from Methods of Soil Analysis Part 3-Chemical Methods, D.L. Sparks pgs 1218-1220;

^(d) CDB procedure from Methods of Soil Analysis Part 3-Chemical Methods, D.L. Sparks pgs 1228-1220.

Ion extraction procedure using 0.2 M NH₄Cl from Methods of Soil Analysis Part 3-Chemical Methods, D.L. Sparks pgs 1218-1220.

Table 2. Reducing Grout* Formulation (OPDEXE-X-P-O-BS).

Ingredient	Quantity	Wt-%
Slag	210 lb/yd ³	5
Water	60 gallons/yd ³ (500 lbs/yd ³)	13
Portland cement	75 lb/yd ³	2
fly ash	375 lb/yd ³	10
Sand	2300 lb/yd ³	60
Adva-380	90 oz/yd ³	2
KelcoCrete	275 g/yd ³	7
sodium-thiosulfate	2.1 lb/yd ³	0

*Reducing Grout was prepared by Chris Langton (SRNL) and was identified as sample OPDEXE-X-P-O-BS.

The reducing Grout was initially broken up with a chisel and hammer to ~1-cm sized particles, then ~100 g of the 1-cm sized particles were placed in a jaw crusher (Retsch Jaw Crusher Type BB51 with tungsten carbide plates) for ten minutes. The crushed samples were then placed in a shatter box (Spec 8510 Shatterbox) for 10 seconds. Only the <1000- μm and >75- μm sieve fraction was used for these studies. The Brunauer, Emmett, Teller (BET) surface area, pH and Eh (redox) of the Reducing Grout are reported in (Table 3).

Aged Cement was collected from a 50 year old concrete core taken from a building pad located on the SRS. 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. After separation, 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. It is important to note that the cement and not the aggregate was used in these measurements.

Table 3. Characterization of the cementitious materials used in studies.

Cementitious Materials	BET surface Area (m^2/g)	pH (1:1 water:cement)	Eh (Ag/AgCl) (mV; 1:1 water:cement)
Reducing Grout	7.11 ± 0.02	11.16	36
Aged Cement	5.88 ± 0.02	11.99	347

Table 4. Artificial Groundwater Simulant

Constituent/Parameter	Artificial Groundwater^a
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

^aArtificial Groundwater: based on routine monitoring data for multiple non-impacted on the SRS (Strom and Kaback, 1992)

3.0 RESULTS

The results from the U and Tl studies are presented in Section 3.1, and the results for Cl⁻, Cr(VI), and Ag are discussed in Section 3.2.

3.1 Uranium and Thallium under Oxidizing Conditions

There has been a great need for U and Tl data for risk calculations. Existing values in the geochemical data package (Kaplan, 2010) have been largely based on non-site-specific data and have had to be conservative with lower K_d values. Table 5 provides the U (added to the sediment and cementitious materials as uranyl, UO_2^{2+}) and Tl (added as Tl^+) average and standard deviation of K_d values that were measured in triplicate. All values with the exception of the Reducing Grout K_d values were greater than those presently used in SRS risk calculations; i.e., greater than those reported in Kaplan (2010) (Table 6). The lower U K_d value with the Reducing Grout was unexpected because U(VI) can be easily reduced to U(IV), which has an appreciably lower aqueous solubility (and the aqueous U concentrations would be very low). But apparently, U(VI) reduction never occurred and limited sorption to the Reducing Grout was observed.

Table 5. Uranyl (UO_2^{2+}) and Tl^+ K_d values for sediments and cementitious materials measured under oxidized (bench top) conditions. Saturated CaCO_3 solutions were used to provide a matrix to mimic cementitious aging during Stage III, the oldest stage of cement aging. Saturated Ca(OH)_2 was used to provide a matrix to mimic cementitious material aging during Stage I and II.

Solid Phase	Aqueous Phase	Average pH	Ave. UO_2^{2+} K_d (mL/g)	Stdev. UO_2^{2+} K_d (mL/g)	Average Tl^+ K_d (mL/g)	Stdev. Tl^+ K_d (mL/g)
Surface Sand	Groundwater	6.86	157	136	71.4	9.1
Subsurface Sand	Groundwater	5.59	2,384	1,476	76.0	2.9
Subsurface Clay	Groundwater	5.51	17,719	-- ^(b)	86.0	5.0
Reducing Grout	Saturated CaCO_3	7.39	16	1	195.4	0.7
Aged Cement	Saturated CaCO_3	9.81	3,059	65	201.1	0.3
Reducing Grout	Saturated Ca(OH)_2	10.64	13,429	1,501	193.6	3.7
Aged Cement	Saturated Ca(OH)_2	11.23	11,105	2,261	197.8	2.2
No-Solid Controls		pH	UO_2^{2+} ($\mu\text{g/L}$)	Tl^+ ($\mu\text{g/L}$)		
Groundwater Control		5.30	7687	104		
CaCO_3 Control		4.21	7687	102.1		
Ca(OH)_2 Control		12.16	50 ^(a)	93.5		

^(a) It is important to note that in the No-Solids Controls 99.35% of the U precipitated out of solution due to solubility controls at this high pH of the solution. Thus, homogenous precipitation, and not solid phase sorption is responsible for U removal from the aqueous phase.

^(b) Only one replicate

Table 6. Present K_d values being used by some SRS risk models (from Kaplan 2010).

Solid Phase and Environment	Tl	U
	(mL/g)	(mL/g)
Subsurface Sand – Oxidizing	10	200
Subsurface Clay – Oxidizing	50	300
Cement Oxidizing (Stage 1 – Young)	2	250
Cement Oxidizing (Stage 2 – Mid)	20	250
Cement Oxidizing (Stage 3 – Old)	10	70
Cement Reducing (Stage 1 – Young)	2	2500
Cement Reducing (Stage 2 – Mid)	10	2500
Cement Reducing (Stage 3 – Old)	10	2500

3.1.1 Key Conclusions from the Sediment U and Tl K_d Data

1. Sediment U K_d values are high with respect to those presently used in risk calculations on the SRS (Table 6). The Subsurface Sand and Clay U K_d values of 2384 ± 1476 and $17,719$ (one replicate) mL g^{-1} , respectively (Table 5) are considerably greater than the conservative values for the sand and clay of 200 and 300 mL g^{-1} proposed in Table 6. Similarly, Tl K_d values measured in the Subsurface Sand and Clay also had large K_d values of 76 ± 3 and 86 ± 5 mL g^{-1} , respectively. These are appreciably greater than the present values used in SRS risk calculations: Tl Sand K_d is 10 mL g^{-1} and Tl Clay K_d is 50 mL g^{-1} .
2. Such high U K_d values are supported by *in situ* measurements in wetland sediments (6493, 2110, 1297, 1237, and 170 mL g^{-1} ; Kaplan et al. 2000) and in situ aquifer measurement made in F-Area (generally in the 1000s mL g^{-1} Serkiz and Johnson, 1994; Serkiz et al., 2007).
3. Variability for U K_d values was unexpectedly high. Cause for this variability is not entirely known. It is not due to experimental error (discussed below), it is due to sorption mechanism, and sample variability.
4. Tl sediment K_d values are very high, much higher than expected based on potassium (K^+) as a chemical analogue.
5. Tl K_d values have very low variability, which shows that variability of U partitioning is due to sorption.
6. The sediment No-solid Controls showed that the amount measured in solution is consistent with the initial spike concentration.

3.1.2 Cement

1. Saturated aqueous CaCO_3 was used in these studies to mimic the third stage, or oldest stage, of cementitious material aging. Saturated Ca(OH)_2 was used to mimic the first two stages. More details about these stages of aging are presented in Bradbury and Sarott (1995) and Kaplan 2010.

2. As the No-Solids Controls demonstrate, there was a massive amount of U that precipitated out of solution in the saturated $\text{Ca}(\text{OH})_2$ solution at pH 12, as expected. Thus much of the sorption can be attributed to homogeneous precipitation (precipitation without the presence of a solid.) The risk calculations should take "credit" for this and since K_d is the only chemistry term in the model, this is the best place to account for loss of U from solution (see the footnote to Table 5).
3. Reducing Grout showed an exceptionally low K_d value for U, but the Tl K_d is similar to the other three tests. All three triplicates were similarly very low. Previously Roberts and Kaplan (2008) showed that an identical sample had similarly very low C-14 sorption (where regular Portland cement had a C-14 K_d of $>2850 \text{ mL g}^{-1}$, this reducing grout had a C-14 K_d of only 39 mL g^{-1}). The cause for this is not known. Testing needs to be repeated under reducing conditions that are more similar to field conditions.

3.1.3 Sorption as a Function of pH

Thallium and U sorption to the Subsurface Sandy and Subsurface Clayey Sediments were measured as a function of pH (Figure 1). Thallium sorption to the Clayey Sediment was appreciably greater at lower pH levels than it was to the Sandy Sediment. But perhaps the most profound effect was that in both soils, above pH 6, Tl was below ICP-MS detection limit ($\sim 2 \text{ ppb}$). The fact that it occurred for both sediments at the same critical pH suggests that the aqueous phase pH is contributing to the loss of Tl from solution and that precipitation is likely a mode of sorption. Thus, the use of the K_d construct to describe this phenomena at higher pH levels is not appropriate. Additional work is required to confirm the mode of sorption at higher pH levels. In cementitious environments it would be expected that Tl would have extremely high K_d values based on these findings and those in Table 5.

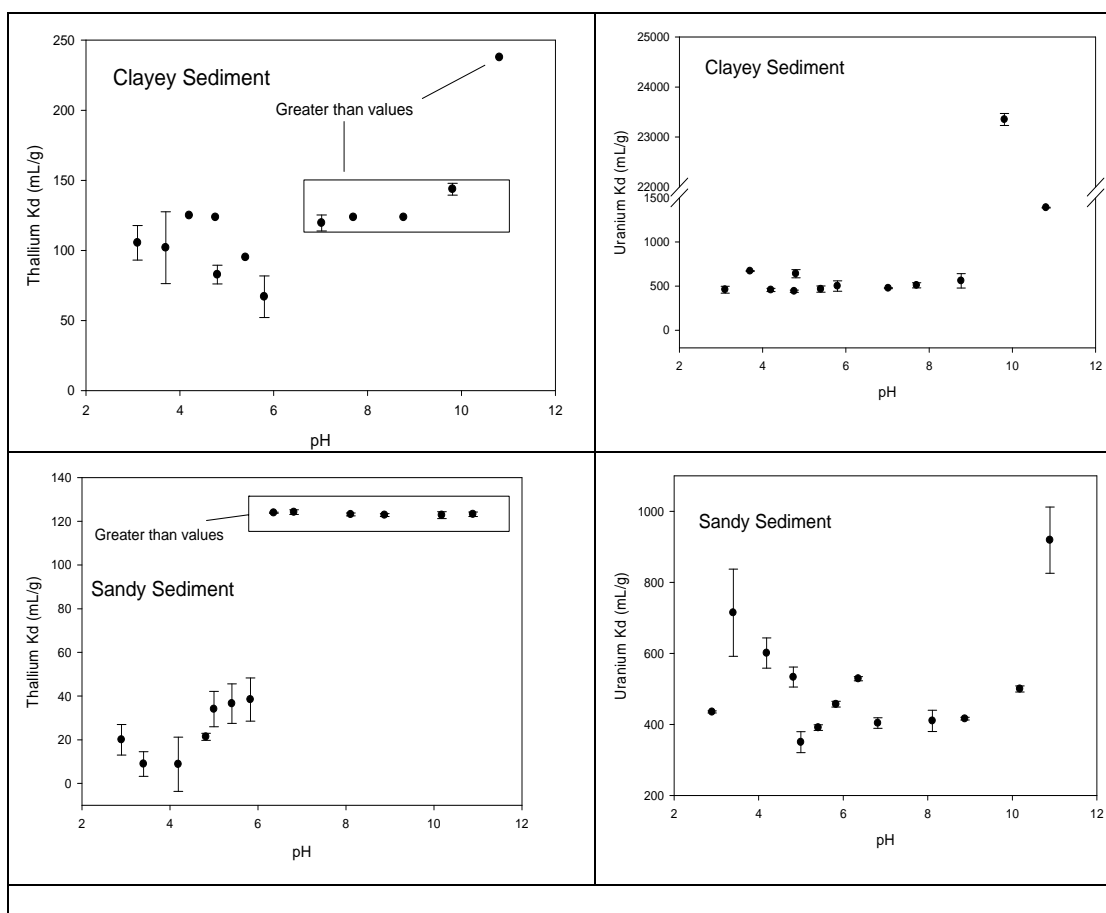


Figure 1. Thallium and uranium K_d values as a function of pH in Subsurface Clayey Sediment (Top) and Subsurface Sandy Sediment (Bottom). Each value is an average of two values; 0.5 g: 15 mL. 0.5 g sediment: 15 mL SRS artificial groundwater.

Uranium sorption did not show the classic sigmoidal increase at lower levels, starting at pH 4, plateauing near pH 8 to 9, then starting to decline around pH 10. Rather the Clayey Sediment had a rather consistent U K_d until pH 9.81, when it increased sharply to an “apparent K_d value” of 23,351 mL g⁻¹. This steep increase in removal of U from the aqueous phase has been attributed to U precipitation. As the pH value increases to 10.8, the U solid phase solubilizes, and the apparent K_d decreases to 1389 mL g⁻¹. This general trend is commonly seen in the literature (USEPA, 1999). What was not seen in this data set was the smooth sigmoidal curve at the low pH levels.

3.2 Chloride, Chromate, and Silver

3.2.1 Silver

Initial batch partitioning experiments for Ag in the AGW background solution yielded essentially the same K_d value for both SRS soil materials, suggesting that solubility limitations were controlling Ag partitioning (Table 7). (See Appendix B for detailed

descriptions of the methods used in these experiments.) The average residual Ag concentration after equilibration was ≈ 284 and $280 \mu\text{g L}^{-1}$ for the clayey and sandy subsurface materials, respectively. Potential solubility constraints were evaluated using the EPA equilibrium chemical speciation model, MINTEQA2 (ver. 1.50) (USEPA, 1997). Initial solution conditions for equilibrium modeling were based on the AGW treatment solution plus the added AgNO_3 spike. Modeling results indicated that the combined solution was supersaturated with respect to cerargyrite, i.e., $\text{AgCl}_{(s)}$. In fact the residual Ag levels were quite close to the MINTEQA2 predicted value in equilibrium with $\text{AgCl}_{(s)}$, i.e., $222 \mu\text{g Ag L}^{-1}$. Therefore, a second Ag batch partitioning experiment was conducted using $1 \text{ mMol Ca(NO}_3)_2$ as the background solution. A difference between the two materials was apparent in the second partitioning experiment, with the clayey ($33.8 \pm 13 \text{ mL g}^{-1}$) sediments displaying a higher K_d than the sandy subsurface material ($10.6 \pm 2.5 \text{ mL g}^{-1}$).

3.2.2 Chromate

Redox reactions play a large role in controlling Cr partitioning in soil and aquifer systems (USEPA, 1999). In nature, Cr occurs primarily in one of two redox states, the relatively benign and immobile trivalent form, Cr(III), and the toxic, more mobile, hexavalent forms, chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$). Despite different toxicities, current EPA regulations fail to account for redox state in the drinking water standard (DWS) for dissolved Cr set at 0.1 mg L^{-1} ($\approx 1.9 \mu\text{M}$). However, Cr(III) solubility can exceed DWS under moderately acidic conditions. Variable charge minerals such as Fe- and Al-oxides (e.g., goethite, ferrihydrite, gibbsite, etc.) commonly found in SRS soils and subsurface sediments can act as sorbents of Cr(VI) and limit migration in soil and aquifer systems. As such, soil pH is an important factor governing Cr(VI) sorption to variable charge minerals. Organic acids and inorganic anions commonly present in groundwater, such as SO_4^{2-} , PO_4^{3-} , and to a lesser degree NO_3^- and Cl^- , are effective competitors for Cr(VI) sorption sites (Hutchison et al., 2003; Kent et al., 1995; Seaman et al., 1999; Stollenwerk and Grove, 1985; USEPA, 1999). Previous studies evaluating the mobility of Cr(VI) in subsurface materials from the SRS have indicated limited inherent capacity for the abiotic reduction of Cr(VI), so only total soluble Cr (Cr_{total}) was quantified in the current batch sorption experiments rather than using the colorimetric method for quantifying Cr(VI) specifically.

In the current study, the K_d values for Cr(VI) were 1214 ± 149 and $411 \pm 84 \text{ mL g}^{-1}$ for the clayey and sandy subsurface materials, respectively (Table 7). These results are consistent with limited SO_4^{2-} concentration (0.73 mg L^{-1}) in the background AGW solution, and the citrate dithionite bicarbonate (CDB) extractable Fe content for the two subsurface sediments, i.e., 15.26 and 7.06 mg g^{-1} Fe for the clayey and sandy subsurface materials, respectively (Table 1). The K_d value for the clayey material is higher than the range previously reported in Looney et al. (1987).

Table 7. Batch derived K_d and pH for silver (Ag), chromate (Cr(VI)), and chloride (Cl⁻).

COC***	Background Solution	Soil Materials**			
		Subsurface Clay		Subsurface Sand	
		$K_d = \text{mL/g}$ Mean \pm SD	pH Mean \pm SD	$K_d = \text{mL/g}$ Mean \pm SD	pH Mean \pm SD
Ag(I)	AGW*	338 \pm 17	5.34 \pm 0.20	339 \pm 17	5.92 \pm 0.11
Ag(I)	1 mMol Ca(NO ₃) ₂	33.8 \pm 12.6	4.73 \pm 0.07	10.6 \pm 2.5	5.55 \pm 0.16
Cl ⁻	1 mMol Ca(NO ₃) ₂	8.5 \pm 0.5	4.56 \pm 0.09	1.8 \pm 1.1	6.03 \pm 0.11
Cr(VI)	AGW	1214 \pm 149	5.32 \pm 0.15	411 \pm 84	6.86 \pm 0.29

*Artificial Groundwater Simulant

**Sediment characteristics provided in Appendix A

***Constituents of Concern

3.2.3 Chloride

In most instances Cl⁻ sorption is considered to be minimal in soils and aquifer sediments because of the presence of clay minerals that possess a net negative charge, and therefore generally repel anions. When observed, such electrostatic repulsion can result in anions migrating at a velocity greater than water, a process commonly called anion exclusion (Hoehn and Roberts, 1982; Melamed et al., 1994). However, several field and laboratory studies have reported high levels of anion retardation for the highly weathered soils and sediments of the SRS (e.g., Korom, 2000; Seaman, 1998; Seaman et al., 1995; Seaman et al., 1996; Seaman et al., 2007). In the current study, the K_d values observed for Cl⁻ were 8.5 \pm 0.4 and 1.8 \pm 1.1 mL g⁻¹ for the clayey and sandy subsurface materials, respectively (Table 7). The high standard deviation observed for the sandy material may reflect inherent sample heterogeneity despite efforts to homogenize the sediment materials, and is somewhat typical of analytical limitations in cases where relatively minor amounts of sorption are observed. However, the relatively high K_d values observed in the current study for Cl⁻ and Cr(VI) have important implications to the transport of other anionic contaminants (i.e., ¹²⁹I and ⁹⁹Tc) that are generally considered to be transported in a conservative manner (move at the same rate as water) for environmental assessment purposes with little or no retardation.

4.0 CONCLUSIONS

Based on the data from these tests some best estimates can be provided for modeling on the SRS. Based on the data in Table 5 and Figure 1, and consideration of the site specific data presented in Kaplan (2010), best estimates were provided for Tl and U (Table 8).

Similarly, best estimate K_d values for silver, chloride, and chromate based on the data from Table 7 are presented in Table 9.

Table 8. New recommended uranium and thallium K_d values under oxidizing conditions based on this work and previous site work compared to existing K_d values (Kaplan 2010).

Solid Phase and Environment	Tl K_d (mL/g)		U K_d (mL/g)	
	Existing (Kaplan 2010)	New Recommended	Existing (Kaplan 2010)	New Recommended
Surface Sand - Oxidizing	NA	NA	NA	150
Subsurface Sand – Oxidizing	10	25	200	300
Subsurface Clay – Oxidizing	50	70	300	400
Cement Oxidizing (Stage 1 – Young)	2	150	250	1000
Cement Oxidizing (Stage 2 – Mid)	20	150	250	1000
Cement Oxidizing (Stage 3 – Old)	10	150	70	100
Cement Reducing (Stage 1 – Young)	2	NA	2500	NT
Cement Reducing (Stage 2 – Mid)	10	NA	2500	NT
Cement Reducing (Stage 3– Old)	10	NA	2500	NT

NT = Not tested; NA = Not available

Table 9. Recommended silver, chloride, and chromate K_d values under oxidizing conditions based on this work.

Sediment – Environment	Ag(I) (mL/g)	Cl ⁻ (mL/g)	Cr(VI) (mL/g)
Subsurface Sand – Oxidizing	10	1	1000
Subsurface Clay – Oxidizing	30	8	400

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Appendix A: Detailed Methodology for Batch Sorption Experiments: Uranium and Thallium

Research and Development (R&D) Directions: Measuring Uranium (U) and Thallium (Tl) K_d Values of Sediments and Cementitious Materials of Interest to SRS Risk Assessments

PI:

Dan Kaplan

HAP:

SRNL-EST-2006-00093

Hazards:

Radionuclides

Hazards Mitigation:

Radionuclides: Follow training of Advanced Rad Worker

Objective:

Determine Tl(I) and U(VI) K_d values under oxidizing conditions for a Surface Sand, Subsurface Sand, Subsurface Clay, Reducing Grout, and an ordinary (oxidizing) 50-year-old cement.

Materials:

1. SRS Surface Sandy Sediment
2. SRS Subsurface Sandy Sediment
3. SRS Subsurface Clayey Sediment
4. Reducing Grout (note which specific sample you use), ground to pass a 100 μ m sieve
5. 50-year-old cement, ground to pass a 100 μ m sieve
6. Artificial SRS Groundwater: Prepare by diluting 1 mL of AGW Stock Solution up to 1 L total volume in DI water. AGW stock is presented in Table 1.

Table 1. Artificial SRS Groundwater (AGW) Stock Solution. Combine the salts below and bring up to one liter. Using litmus paper check that the pH is between 5 – 6.

Salt	g/L
CaCl ₂ ·2H ₂ O	3.677
Na ₂ SO ₄	1.073
KCl	0.400
NaCl	2.653
MgCl ₂ ·6H ₂ O	3.094

7. Ca(OH)₂-Saturated Leaching Solution:

Background: Because CO₂ in air is very soluble in water at high pH and the resulting dissolved carbonate will precipitate as calcite in the Ca(OH)₂-saturated solution, care will be taken to minimize contact of the solution with atmospheric air. Excess solid Ca(OH)₂ is undesirable because it will buffer the pH at a higher than expected value.

Procedure: Deoxygenate ~1-L of D.I. water by boiling and then purge with N₂ gas for 30 min. After purging with N₂, place water in a Teflon bottle (because this material has a low air diffusion coefficient). Add a sufficient quantity of fresh Ca(OH)₂ (~1.26 g/L @ 25°C) to the deoxygenated water to just saturate the solution. To minimize exposure to air, purge head space with N₂ and if necessary periodically skim off any precipitates that may form. Using litmus paper, measure approximate pH of solution. Skim-off any precipitate with a spatula.

7. Calcite-Saturated Leaching Solution:

Explanation: By preparing the solution at a slightly elevated temperature the possibility of calcite precipitation during the test at room temperature will be minimized. (Calcite undergoes retrograde solubility, i.e., it is *more* soluble at low temperatures.) There will be no need to minimize contact of this solution with the atmosphere. After the solution is prepared, the pH value and calcium and carbonate concentrations will be measured and compared to expected equilibrium values and concentrations [pH = 8.3, Ca²⁺ = 20 mg/L, TIC = 58 mg/L, PCO₂ = 0.0003 atm (fixed)].

8. Procedure: Put 1 L of DI water on a stir/heating plate and raise the temperature of the solution by 3 to 10 °C from ambient room temperature. As solution is being stirred with a stir bar, add 0.01 g of CaCO₃ to the heated DI water. Leave mixture on stir/heating plate for 24 hr. The calcite-saturated solution will be prepared by adding excess powdered calcite to deionized water and stirring or shaking the mixture for 24 hours. Pass through a 0.45-μm membrane.
9. 0.2-μm syringe filters
10. 1000 mg/L U Standard solution: Borrow ~15 mL from ADS, ICP-AE standard (located in B-159, Building 773A)
11. 10,000 ppm Thallium in 5% Nitric Acid Custom Plasma STD (SPEX Industries Inc.): Borrow ~5 mL from the ADS's Mobile Lab

Method for Preliminary Study to Determine Appropriate Spike Concentration:

1. Record "Tube Tare (g)" weight to within 0.001g of labeled 20-mL serum vials with cap as identified in Column F of Table 2.
2. Add 0.5 ± 0.01-g of solid to each tube. Weigh and record "Solid (g)" weight to within 0.001g in Column G.
3. Prepare following spike solutions.
4. 1000 mg/L U Standard solution (note units): Borrow some from ADS
 - i. 1,000,000 ppb U (for making the **8,400 ppb U** spike suspension): Combine 5 mL of 1000 mg/L U Standard solution.
 - ii. 120,000 ppb U (for making the **1000 ppb U** spike suspension): Combine 0.6 mL of 1,000,000 ppb U solution + 4.4 mL water.
 - iii. 12,000 ppb U (for making the **100 ppb U** spike suspension): Combine 0.05 mL of 120,000 ppb U spike solution + 4.95 mL water.

5. 1,000 ppm Thallium in 5% Nitric Acid Custom Plasma STD (SPEX Industries Inc.):
 - i. 20,000 ppb Tl Working Solution: Add 2.0mL of the 1,000 ppm Tl STD and bring up to 100 mL in a volumetric flask. Move to a storage container.
 - ii. 12,000 ppb Tl (for making the **100 ppb** Tl suspensions): Combine 3 mL of the 20,000 ppb Tl Working Sol'n + 2 mL water.
 - iii. 6000 ppb Tl (for making the **50 ppb** Tl suspensions): Combine 2.5 mL of the 12,000 ppb Tl Solution + 2.5 mL water.
 - iv. 1200 ppb Tl (for making the **10 ppb** Tl suspension): Combine 1 mL of the 6000 ppb Tl Spike Solution + 4 mL water.
6. Add 12 mL of the appropriate liquid as defined in Table 2 to your solids. Shake well.
7. Measure pH with litmus paper enter data in Column D.
8. Move tubes and Tl spikes into hood.
9. Add 100µL of the appropriate Tl spike and 100 µL of the U spike. First add least concentrated spike to the most concentrated spike solutions so that you don't have to change pipette tips.
10. Check pH with litmus paper. Add 0.1 M NaOH to bring back to pH noted in Column D, the original pH. Note volume of base added in Column H. The pH of the cement samples (sample >#304) should not change greatly).
11. Put on rotating shaker for 2 days.
12. Let solids settle (or centrifuge at 4000 rpm for 10 min).
13. Pass liquids through a 0.2 µm syringe filter; collecting filtrate in sample bottle to be submitted to Curtis Johnson in Analytical Development for ICP-MS. Submit for expedited return.

Table 2. Treatments and Tube weights for the Preliminary test.

A	B	C	D	E	F	G	H
Tube #	Solid	Liquid	pH	Spike Trt. (Uppb/Tlppb)	Tube Tare (g)	Solids (g)	Vol 0.1 (mL)
301	Subsurf. Clay	AGW		8,400/100			
302				1,000/50			
303				100/10			
304	Cement	Ca(OH) ₂		8,400/100			
305				1,000/50			
306				100/10			
307	Red.Grout	CaCO ₃		8,400/100			
308				1,000/50			
309				100/10			

Methods for Main Experiment

1. Label tubes and record tare weights (without caps) as shown in Table 3
2. Add 0.5 ± 0.001g of soil material (Tubes 310 – 336). Weigh and enter "Solid Wt." into Table 3.
3. **Equilibrating solids to the aqueous phase.** *Solid Phase Chemical Conditioning:*
The cementitious material will be equilibrated with appropriate Ca(OH)₂ or CaCO₃ solutions prior to spiking with the radionuclide mixture. This pre-equilibration will help to minimize "shocking the chemistry" of the spiked radionuclide and facilitate approximate steady state conditions.
 1. Add 12 ± 0.1-mL of appropriate solution to each tube as defined in Table 3. Put on shaker overnight. Let settle for 1 hr. Decant liquid. If solids do not separate from the liquid, centrifuge at 15 min 6000 rpm, then decant liquid.

Throw away liquid. Error on the side of leaving liquid in tube rather than accidentally losing fines down the drain.

2. Add 12 ± 0.1 mL of appropriate liquid to each tube as defined in Table 3, including the No-Solids Controls. Measure pH. Record weight to within 0.001g of each tube in "Tube + soils + Equil + GW (g)"
4. **Adding Tl and U Spike Solution to suspensions.** Move rack of tubes to rad hood. Add 100 μ L of the Tl and U Spike Solution identified in the preliminary experiments to each tube. Also add this to the No-Solids Controls.
5. **pH adjust suspension.** Because the spike solution is in an acid solution, you will need to add base to bring the suspensions back to their native pH. Based on the preliminary study, this may not be necessary for the cements. Record "Base vol added" in Table 3, Column H.
6. **Equilibrating radionuclides with cement suspension.** Leave samples in rad hood for a minimum of 7 days.
7. **Analyzing for Tl and U in Aqueous Phase by ICP-MS:** At end of equilibrium period, collect liquids by drawing liquids into a syringe and then passing liquid through a 0.2- μ m filter. Submit the aqueous phase for Tl and U analyses by ICP-MS.

Table 3. Batch sorption experiment parameters for Tl and U, and various SRS subsurface solid phases.

A	B	C	D	E	F	G	H
Sample ID	Solid	Liquid	Rep	Tare Wt (g)	Tare+Solid+Liq wt (g)	pH	0.1M NaOH added (mL)
310	Surf Sand	AGW	1				
311			2				
312			3				
313	Sub Sand	AGW	1				
314			2				
315			3				
316	Sub Clay	AGW	1				
317			2				
318			3				
319	Red Grout	CaCO ₃	1				
320			2				
321			3				
322	Cement	CaCO ₃	1				
323			2				
324			3				
325	Red Grout	Ca(OH) ₂	1				
326			2				
327			3				
328	Cement	Ca(OH) ₂	1				
329			2				
330			3				
331	No solids AGW Cont	AGW	1				
332			2				
333	No Solids CaCO ₃ Cont	CaCO ₃	1				
334			2				
335	No Solids Ca(OH) ₂ Cont	Ca(OH) ₂	1				
336			2				

Research and Development (R&D) Directions: Measuring U and Thallium (Tl) K_d Values of Sediments as a Function of pH under Oxidizing Conditions

PI:

Dan Kaplan

HAP:

SRNL-L3100-2009-00216. Rev 0

Hazards:

Radionuclides
Strong acids

Hazards Mitigation:

Radionuclides: Follow training of Advanced Rad Worker
Strong acids: use limited volumes (~1mL); add strong acid to dilute aqueous solution, (NOT in the opposite order). Proper protective equipment, eyeware, proper gloves,

Objective:

Determine Tl(I) and U(VI) sorption to sediments as a function of pH under oxidizing conditions.

Materials:

1. SRS Subsurface Sandy Sediment
2. SRS Subsurface Clayey Sediment
3. 0.2- μ m syringe filters
4. 15-mL tubes
5. 1000 mg/L U Standard solution: Borrow ~15 mL from ADS, ICP-AE standard (located in B-159, Building 773A)
6. 1,000 ppm Thallium in 5% Nitric Acid Custom Plasma Standard STD (SPEX Industries Inc.): Borrow ~5 mL from the AD's Mobile Lab.
7. 12,000 ppb Tl spike solution: Add 0.24 mL of 1000 ppm Thallium Standard and bring up to 20.0 mL with water. (use a balance to make this solution).
8. 0.1 M NaOH (50 mL of 1M NaOH and bring up to 500 mL with H₂O)
9. 1 M NaOH (20 mL 5 M NaOH and bring up to 100 mL with H₂O)
10. 0.01 M NaOH: Add 5 mL 1M NaOH to a 500 mL volumetric flask. Bring to volume with water.
11. 0.1 M HCl

Table 1. Amount of acid, base, ionic strength salt and distilled water necessary to establish a 15-mL aliquot consisting of a sequential pH change.

A	B	C	D	E	F	G	H	I	J	K	L
ID	Solids	0.005 M HCl (mL)	0.01 M NaOH (mL)	0.02 M NaCl (mL)	Distilled Water (mL)	Rep	Tare Wt (g)	Tare + Soil (g)	pH before spike	Tube wt. before spike (g)	Target pH (Dan)
450	Sub- Sand	7.5	0	5.64	1.86	1					
451						2					
452		4.5	0	6.36	4.14	1					
453						2					
454		2.4	0	6.9	5.7	1					
455						2					
456		1.2	0	7.2	6.6	1					
457						2					
458		0.6	0	7.35	7.05	1					
459						2					
460		0.15	0	7.44	7.41	1					
461						2					
462		0	0	7.5	7.5	1					
463						2					
464		0	0.15	7.44	7.41	1					
465						2					
466		0	0.6	7.35	7.05	1					
467						2					
468		0	1.2	7.2	6.6	1					
469						2					
370		0	2.4	6.9	5.7	1					
471						2					
472		0	4.5	6.36	4.14	1					
474						2					
474		0	7.5	5.64	1.86	1					
475						2					
476	Sub- Clay	7.5	0	5.64	1.86	1					
477						2					
478		4.5	0	6.36	4.14	1					
479						2					
480		2.4	0	6.9	5.7	1					
481						2					
482		1.2	0	7.2	6.6	1					
483						2					
484		0.6	0	7.35	7.05	1					
485						2					
486		0.15	0	7.44	7.41	1					
487						2					
488		0	0	7.5	7.5	1					
489						2					

A	B	C	D	E	F	G	H	I	J	K	L
ID	Solids	0.005 M HCl	0.01 M NaOH	0.02 M NaCl	Distilled Water	Rep	Tare Wt	Tare + Soil	pH before spike	Tube wt. before spike (g)	Target pH (Dan)
490		0	0.15	7.44	7.41	1					
491						2					
492		0	0.6	7.35	7.05	1					
493						2					
494		0	1.2	7.2	6.6	1					
495						2					
496		0	2.4	6.9	5.7	1					
497						2					
498		0	4.5	6.36	4.14	1					
499						2					
500	No- Solids Control					1					
		0	7.5	5.64	1.86						
501		7.5	0	5.64	1.86	1					
502		4.5	0	6.36	4.14	1					
503		2.4	0	6.9	5.7	1					
504		1.2	0	7.2	6.6	1					
505		0.6	0	7.35	7.05	1					
506		0.15	0	7.44	7.41	1					
507		0	0	7.5	7.5	1					
508		0	0.15	7.44	7.41	1					
509		0	0.6	7.35	7.05	1					
510		0	1.2	7.2	6.6	1					
511		0	2.4	6.9	5.7	1					
512		0	4.5	6.36	4.14	1					
513		0	7.5	5.64	1.86	1					

Methods:

1. Number tubes as shown in Table 1 and record tare weight in **Column H**.
2. Add 0.5 g of either subsurface sandy sediment or subsurface clayey sediment as directed by Table 1. Don't add any sediment to Tubes 400-513, which are No-Solid Controls. Record Tare and Soil Weight (or if you prefer only Soil Weight) in **Column I**.
3. Add the volume of 0.005 M HCl to each tube as directed by column C.
4. Add the volume of 0.01 M NaOH as directed by Column D.
5. Add the volume of 0.02 M NaCl as directed by Column E.
6. Add the volume of distilled water as directed by Column F.
7. Put on shaker for at least 2 days then measure pH of one tube for each rep and assume that the pH of the other tube is the same and record in **Column J** in EXCEL file.
8. Send to Dan and he will set up target pH range in **Column L**.
9. Only to tubes with sediment in them (tubes 450-499), add drops of HCl and NaOH to pH adjust ± 0.2 of the target pH; monitor for pH with a meter. Put tubes on platform shaker. Adjust pH everyday for first two day, then every other day. Alternate which rep you take pH measurement of each time you make a pH measurement.

10. Record chemical additions and pH measurements in EXCEL. Dan will prepare EXCEL file – note how much and which acid/base solutions were used for pH adjustment.
11. No pH adjustment for samples 462, 263, 488, & 489. These are the 4 samples that did not receive any acid or base initial treatment.
12. Once Dan determines pH is stable in pH-adjusted suspensions for 3 days, proceed to next step.
13. Weigh tube and record total weight in EXCEL spreadsheet.
14. **Spike Tl & U:** Weigh tubes and record in **Column K**. Move tubes into hood. Add 200 μL of 12,000 ppb Tl spike solution (#7 in Materials) and add 100 μL of 1000 ppm U spike solution (#5 Materials) to each tube.
15. **pH adjust suspension after adding acidic spike.** Add base to compensate for acidic spike and bring suspension back to target pH. As always, record in EXCEL spreadsheet how much liquid you add to tube.
16. **Equilibrating radionuclides with suspension.** Leave samples shaking in rad hood for a minimum of 4 days.
17. **Analyzing for Tl and U in Aqueous Phase by ICP-MS:** At end of equilibrium period, measure final pH and record in EXCEL file, collect liquids by drawing liquids into a syringe and then passing liquid through a 0.2- μm filter. Add 50- μL of concentrated HNO_3 to each sample vial (to preserve sample and make sure Tl and U does not stick to the labware). Submit the aqueous phase for Tl and U for analyses by ICP-MS.

Appendix B: Detailed Methodology for Batch Sorption Experiments: Silver, Chromate, and Chloride

PI: John Seaman

Hazards:

Metals and acidic solutions

Hazards Mitigation:

Standard SREL laboratory protocols

Objective:

Determine Ag, Cl, and Cr(VI) K_d values for two SRS subsurface materials.

Materials:

1. SRS Subsurface Sandy Sediment
2. SRS Subsurface Clayey Sediment
3. Artificial SRS Groundwater: Prepare by diluting 1 mL of AGW Stock Solution up to 1 L total volume in DI water. AGW stock is presented in Table 1.
4. 1 mMol $\text{Ca}(\text{NO}_3)_2$ solution
5. Ag spike solution ($\approx 100 \text{ mg L}^{-1}$ Ag in DIW) derived from AgNO_3
6. Cr(VI) spike solution ($\approx 52 \text{ mg L}^{-1}$ Cr(VI) in AGW) derived from potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)
7. Cl spike solution ($\approx 57 \text{ mg L}^{-1}$ Cl in 1 mMol $\text{Ca}(\text{NO}_3)_2$ solution derived CaCl_2

Table 1 AGW stock solution

Salt	gm/L
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (148 g/mol)	3.68
Na_2SO_4 (142 g/mol)	1.07
KCl	0.40
NaCl (58.4 g/mol)	2.65
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (203 g/mol)	5.51

Table 2. Artificial Groundwater Simulant.

Constituent/Parameter	AGW ^a
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

^aArtificial Groundwater: non-impacted groundwater derived from natural infiltration (Strom and Kaback, 1992)

Methods:

Partitioning coefficient (K_d) values Ag, Cl, and Cr(VI) were determined using a modified version (exceptions noted below) of the PNNL K_d method outlined in Krupka et al. (1999). Sorbent materials were sieved to remove particles $> 2\text{mm}$ and then thoroughly homogenized. Prior to the sorption experiments, all samples will be equilibrated with an artificial groundwater (AGW) simulant based on the average composition of groundwater collected from several non-impacted wells screened in the water table aquifer on the SRS (Tables 1 and 2 above). In general batch treatments consisted of either 1 or 5 gm (± 0.1 gm) of sorbate and 30 mL (i.e., 30/1 or 30/5 solution/solid ratio) of equilibrating solution contained within an Oak Ridge centrifuge tube. Specific differences in methodology for a given test constituent are noted below.

Silver Partitioning in AGW

1. Label 10 Oak Ridge centrifuge tube tubes and record tare weights. Five reps with two different sorbent materials equals 10 tubes.
2. Weigh 1 gm (± 0.01 gm) of the appropriate sorbate material (i.e., sandy or clayey subsurface material) into each tube and record the weight.
3. Add 30 mL (i.e., 30/1 solution/solid ratio) of AGW to each tube and shake for 1 hour (wash 1).
4. Remove the tubes from the shaker, record the pH of each tube, and then centrifuge for 20 minutes at 10,000 rpm.
5. Decant most of the supernatant, filter the supernatant (0.2 μ m pore size) into a labeled storage bottle (wash 1, sample name), and then acidify the filtered sample for future analysis.
6. Record the weight of each tube, i.e., residual soil and solution, tube and cap, to determine the mass of residual water in each sample.
7. Add enough AGW solution to each tube to bring the total tube solution volume back to 30 mL, and return the samples to the shaker.
8. Allow the tubes to shake for 1 hour, then repeat steps 4-7 above (sample storage bottles labeled wash 2, sample name).
9. Repeat 3 through 8 above to generate wash sample 3. Record the final weight of each tube, i.e., residual soil and solution, tube and cap, to determine the mass of residual water in each sample.
10. Add sufficient AGW to return to original 30/1 solution/solid ratio.
11. Add Ag spike to each tube (0.1 mL of $\approx 1,075$ mg L⁻¹ for a final treatment concentration of 3.58 mg L⁻¹) and equilibrate for 24 hours on end-over-end shaker.
12. Remove the tubes from the shaker, record the pH of each tube, and then centrifuge for 20 minutes at 10,000 rpm.
13. Decant most of the supernatant, filter the supernatant (0.2 μ m pore size) into a labeled storage bottle (wash 1, sample name), and acidify (1% Nitric Acid) the filtered sample for ICP-MS analysis.
14. Analyze for Ag by inductively coupled plasma-mass spectrometry (ICP-MS; Elan DRC, Perkin Elmer, Inc., Waltham, MA 02451) following the QA/QC protocols outlined in EPA method 6020.

		A	B	B	C	D	E	F	G	H	I	J		
Ag in AGW		ICP-MS Results												
Soil	Rep	Soil Weight	An1	An2	An Avg	dil	An Avg	dissolved	mg added	sorbed	sorbed	Kd	Avg	Std.
Clayey Soil		gm	ppb	ppb	ppb		mg/L	mg/tube			mg/kg	L/kg		Dev
	1	1.06	236.4	283.4	259.9		0.260	0.0078	0.1075	0.0996	93.91	361.3		
	2	1.01	286.8	291.1	289.0		0.289	0.0087	0.1075	0.0988	97.59	337.7		
	3	1.07	291.5	295.0	293.2		0.293	0.0088	0.1075	0.0986	92.18	314.4		
	4	1.00	289.1	293.3	291.2		0.291	0.0088	0.1075	0.0987	98.70	339.0		
	5	1.02	285.4	289.6	287.5		0.288	0.0087	0.1075	0.0988	96.87	336.9	337.9	16.59
Sandy Soil								0.0000						
	1	1.06	296.6	299.8	298.2		0.298	0.0090	0.1075	0.0985	92.91	311.6		
	2	1.01	275.1	280.6	277.8		0.278	0.0084	0.1075	0.0991	98.12	353.2		
	3	1.03	274.5	276.8	275.7		0.276	0.0083	0.1075	0.0992	96.28	349.3		
	4	1.07	268.0	270.0	269.0		0.269	0.0081	0.1075	0.0994	92.87	345.2		
	5	1.05	278.6	279.5	279.0		0.279	0.0084	0.1075	0.0991	94.35	338.1	339.5	16.55

- A. Soil weight (gm).
- B. ICP results (μ g L⁻¹) for various isotopes of the element of interest, i.e., 107 and 109 for Ag.
- C. Average ICP results for each sample based on multiple isotopes.
- D. Dilution factor prior to ICP-MS analysis.
- E. ICP-MS results in mg L⁻¹.
- F. Total mass of Ag for each tube remaining solution after equilibration.
- G. Mass of Ag added to each tube.
- H. Total mass of Ag sorbed for each tube.

- I. Mass of Ag sorbed per mass of sorbent, i.e., clayey or sandy subsurface materials.
- J. Calculated partition coefficient (K_d):

$$K_d = \frac{\text{sorbed concentration } \left(\frac{\text{mg}}{\text{kg}} \right)}{\text{dissolved concentration } \left(\frac{\text{mg}}{\text{L}} \right)} = \frac{\text{L}}{\text{kg}}$$

Silver Partitioning in 1 mMol Ca(NO₃)₂

The methods for evaluating Ag partitioning were the same as above, except 1 mMol Ca(NO₃)₂ was used instead of AGW as the background equilibration solution to avoid the possible precipitation of AgCl_(s). As before, the subsurface materials were equilibrated with the background solution before Ag was added.

		A	B	B	C	D	E	F	G	H	I	J		
Ag in Ca-Nitrate		ICP-MS Results												
Soil	Rep	Soil Weight	An1	An2	An Avg	dil	An Avg	dissolved	mg added	sorbed	sorbed	K _d	Avg	Std.
Clayey Soil		gm	ppb	ppb	ppb		mg/L	mg/tube			mg/kg	L/kg		Dev
	1	1.02	153.0	153.7	153.3	10	1.533	0.0462	0.1075	0.0613	60.11	39.2		
	2	1.04	186.6	158.5	172.5	10	1.725	0.0519	0.1075	0.0555	53.40	31.0		
	3	1.01	199.7	236.0	217.9	10	2.179	0.0656	0.1075	0.0419	41.47	19.0		
	4	1.05	126.3	126.4	126.4	10	1.264	0.0380	0.1075	0.0694	66.12	52.3		
	5	1.00	155.1	218.7	186.9	10	1.869	0.0563	0.1075	0.0512	51.21	27.4	33.8	12.64
Sandy Soil					0.0	10								
	1	1.03	291.4	291.8	291.6	10	2.916	0.0878	0.1075	0.0197	19.12	6.6		
	2	1.05	262.2	263.0	262.6	10	2.626	0.0791	0.1075	0.0284	27.06	10.3		
	3	1.05	251.0	253.6	252.3	10	2.523	0.0759	0.1075	0.0315	30.01	11.9		
	4	1.02	257.5	259.8	258.6	10	2.586	0.0779	0.1075	0.0296	29.03	11.2		
	5	1.02	247.6	247.9	247.7	10	2.477	0.0746	0.1075	0.0329	32.25	13.0	10.6	2.47

Cr(VI) Partitioning in AGW

1. Label 10 Oak Ridge centrifuge tube tubes and record tare weights. Five reps with two different sorbent materials equals 10 tubes.
2. Weigh 5 gm (±0.01 gm) of the appropriate sorbate material (i.e., sandy or clayey subsurface material) into each tube and record the weight.
3. Add 30 mL (i.e., 30/5 solution/solid ratio) of AGW to each tube and shake for 1 hour (wash 1).
4. Remove the tubes from the shaker, record the pH of each tube, and then centrifuge for 20 minutes at 10,000 rpm.
5. Decant most of the supernatant, filter the supernatant (0.2 µm pore size) into a labeled storage bottle (wash 1, sample name), and then acidify the filtered sample for future analysis.
6. Record the weight of each tube, i.e., residual soil and solution, tube and cap, to determine the mass of residual water in each sample.
7. Add enough AGW solution to each tube to bring the total tube solution volume back to 30 mL, and return the samples to the shaker.
8. Allow the tubes to shake for 1 hour, then repeat steps 4-7 above (sample storage bottles labeled wash 2, sample name).
9. Repeat 3 through 8 above to generate wash sample 3. Record the final weight of each tube, i.e., residual soil and solution, tube and cap, to determine the mass of residual water in each sample.
10. Add sufficient AWG to return to original 30/5 solution/solid ratio.

11. Add Cr(VI) spike to each tube (0.1 mL of $\approx 1,075 \text{ mg L}^{-1}$ for a final treatment concentration of 3.58 mg L^{-1}) and equilibrate for 24 hours on end-over-end shaker.
12. Remove the tubes from the shaker, record the pH of each tube, and then centrifuge for 20 minutes at 10,000 rpm.
13. Decant most of the supernatant, filter the supernatant (0.2 μm pore size) into a labeled storage bottle (wash 1, sample name), and acidify (1% Nitric Acid) the filtered sample for ICP-MS analysis.
14. Analyze for Cr_{total} by inductively coupled plasma-mass spectrometry (ICP-MS; Elan DRC, Perkin Elmer, Inc., Waltham, MA 02451) following the QA/QC protocols outlined in EPA method 6020.

		A	B	B	C	D	E	F	G	H	I	J		
Cr(VI) in AGW		ICP-MS Results												
Soil	Rep	Soil Weight	An1				An Avg	dissolved	ug added	sorbed	sorbed	Kd	Avg	Std.
Clayey Soil		gm	ppb				ug/L	ug/tube	ug/tube	ug/tube	ug/kg	L/kg		Dev
	1	5.00	0.372				0.372	0.0115	2.2410	2.2295	445.90	1200		
	2	5.00	0.361				0.361	0.0112	2.2410	2.2298	445.96	1235		
	3	5.02	0.348				0.348	0.0108	2.2410	2.2302	444.27	1277		
	4	5.00	0.456				0.456	0.0141	2.2410	2.2269	445.37	977		
	5	5.00	0.323				0.323	0.0100	2.2410	2.2310	446.20	1383	1214	149
Sandy Soil														
	1	5.01	0.826				0.826	0.0256	2.2410	2.2154	442.19	535		
	2	5.00	1.278				1.278	0.0396	2.2410	2.2014	440.27	344		
	3	5.00	1.094				1.094	0.0339	2.2410	2.2071	441.42	404		
	4	5.01	1.340				1.340	0.0415	2.2410	2.1995	439.02	328		
	5	5.03	0.989				0.989	0.0307	2.2410	2.2103	439.43	444	411	84

- Soil weight (gm).
- ICP results ($\mu\text{g L}^{-1}$) for various isotopes of the element of interest.
- Average ICP results for each sample based on multiple isotopes.
- Dilution factor prior to ICP-MS analysis.
- ICP-MS results in $\mu\text{g L}^{-1}$.
- Cr_{total} for each tube remaining solution after equilibration.
- Mass of Cr(VI) added to each tube.
- Total mass of Cr(VI) sorbed for each tube.
- Mass of Cr(VI) sorbed per mass of sorbent, i.e., clayey or sandy subsurface materials.
- Calculated partition coefficient (Kd):

$$K_d = \frac{\text{sorbed concentration } \left(\frac{\mu\text{g}}{\text{kg}} \right)}{\text{dissolved concentration } \left(\frac{\mu\text{g}}{\text{L}} \right)} = \frac{\text{L}}{\text{kg}}$$

Cl Partitioning in 1 mMol $\text{Ca}(\text{NO}_3)_2$

1. Label 10 Oak Ridge centrifuge tube tubes and record tare weights. Five reps with two different sorbent materials equals 10 tubes.
2. Weigh 5 gm (± 0.01 gm) of the appropriate sorbate material (i.e., sandy or clayey subsurface material) into each tube and record the weight.
3. Add 30 mL (i.e., 30/5 solution/solid ratio) of 1 mMol $\text{Ca}(\text{NO}_3)_2$ to each tube and shake for 1 hour (wash 1).
4. Remove the tubes from the shaker, record the pH of each tube, and then centrifuge for 20 minutes at 10,000 rpm.
5. Decant most of the supernatant, filter the supernatant (0.2 μm pore size) into a labeled storage bottle (wash 1, sample name), and then acidify the filtered sample for future analysis.

6. Record the weight of each tube, i.e., residual soil and solution, tube and cap, to determine the mass of residual water in each sample.
7. Add enough 1 mMol $\text{Ca}(\text{NO}_3)_2$ solution to each tube to bring the total tube solution volume back to 30 mL, and return the samples to the shaker.
8. Allow the tubes to shake for 1 hour, then repeat steps 4-7 above (sample storage bottles labeled wash 2, sample name).
9. Repeat 3 through 8 above to generate wash sample 3. Record the final weight of each tube, i.e., residual soil and solution, tube and cap, to determine the mass of residual water in each sample.
10. Add sufficient 1 mMol $\text{Ca}(\text{NO}_3)_2$ to return to original 30/5 solution/solid ratio.
11. Add Cl spike to each tube equilibrate for 24 hours on end-over-end shaker.
12. Remove the tubes from the shaker, record the pH of each tube, and then centrifuge for 20 minutes at 10,000 rpm.
13. Analyze Cl by the mercuric thiocyanate method.

		A	B	B	C	D	E	F	G	H	I	J		
Cl in Ca-Nitrate														
Soil	Rep	Soil Weight	Anl				An Avg	dissolved	mg added	sorbed	sorbed	Kd	Avg	Std.
Clayey Soil		gm	ppm				mg/L	mg/tube			mg/kg	L/kg		Dev
	1	5.01	0.750				0.750	0.0233	0.0570	0.0338	6.74	9.0		
	2	5.02	0.790				0.790	0.0245	0.0570	0.0325	6.48	8.2		
	3	5.03	0.780				0.780	0.0242	0.0570	0.0328	6.52	8.4		
	4	5.01	0.750				0.750	0.0233	0.0570	0.0338	6.74	9.0		
	5	5.03	0.800				0.800	0.0248	0.0570	0.0322	6.40	8.0	8.5	0.45
Sandy Soil														
	1	5.00	1.280				1.280	0.0397	0.0570	0.0173	3.46	2.7		
	2	5.00	1.450				1.450	0.0450	0.0570	0.0121	2.41	1.7		
	3	5.03	1.400				1.400	0.0434	0.0570	0.0136	2.70	1.9		
	4	4.99	1.830				1.830	0.0567	0.0570	0.0003	0.05	0.0		
	5	5.02	1.250				1.250	0.0388	0.0570	0.0183	3.64	2.9	1.8	1.14

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