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DISTRIBUTION COEFFICIENTS (K_d) GENERATED FROM A CORE SAMPLE COLLECTED FROM THE SALTSTONE DISPOSAL FACILITY

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LIST OF ACRONYMS

AA	Atomic Absorption spectroscopy
AD	Analytical Development
BFS	Blast Furnace Slag
$Ca(OH)_2$	Portlandite
DI	Deionized
DDA	Deliquification, Dissolution, and Adjustment
HTS	Haute Teneure en Silice
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
K_d	Distribution coefficient
PA	Performance Assessment
PHA	Pulse Height Analyzer
PVC	Polyvinyl chloride
ORP	Oxidation-Reduction Potential
SDF	Saltstone Disposal Facility
SHE	Standard Hydrogen Electrode
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
WAC	Waste Acceptance Criteria

1.0 EXECUTIVE SUMMARY

Core samples originating from Vault 4, Cell E of the Saltstone Disposal Facility were collected in September of 2008 and sent to the Savannah River National Laboratory (SRNL) to measure chemical and physical properties of the material including visual uniformity, mineralogy, microstructure, density, porosity, distribution coefficients (K_d), and chemical composition. The core samples were taken from grout placed in December of 2007. The saltstone is comprised of blast furnace slag, Class F fly ash, ordinary portland cement, and Deliquification, Dissolution, and Adjustment (DDA) Batch 2 radioactive salt solution. The core sample that was analyzed contained an olive green interior and a gray surface layer indicative that some oxidation had occurred prior to leaching studies. The oxidation condition of the core sample is important because it can impact the measured K_d values. For example, technetium will have lower K_d values or higher solubility values under sub-oxic conditions than under fully anoxic conditions.

In this report, results are presented from leaching experiments that were conducted with core sample 3-2 in conditions that are representative of saltstone performance. This study was designed to provide insight into how readily species immobilized in saltstone will leach from the saltstone under oxidizing conditions simulating the edge of a saltstone monolith and under reducing conditions (30 to 60 ppm O_2), targeting conditions within the saltstone monolith. Solubility and K_d values were obtained from measurement of the species present in the solid and the aqueous leachate. This work represents the first leaching study performed with a site-specific aged saltstone sample. As such, it represents the most representative solubility and K_d value data collected to date. Thirty-two K_d values were measured by desorption, 16 under oxidizing conditions and 16 under partially reducing conditions. The K_d values were compared to reported values (SRNL-STI-2009-00473). Some of the key differences between the previously reported K_d and solubility values are:

- Under oxidized conditions, Tc K_d values increased from 0.8 as reported in SRNL-STI-2009-00473 to 10 mL/g as measured in testing, Ba K_d values increased from 100 to 6000 mL/g, and Sr K_d values increased from 15 to 1000 mL/g (in both the young and middle aged cements).
- Under reducing conditions, Ba K_d values increased from 100 to 6000 mL/g, and Sr K_d values increased from 15 to 1000 mL/g (in both the young and middle aged cements). The increase is due to the presence of sulfate/sulfide that promotes precipitation.
- Solubility values of key risk driving radionuclides did not vary greatly. Tc solubility measured under reducing conditions were approximately the same as previously reported. Some proposed changes in solubility values include decreasing Al, Fe, and Th, and increasing Ba and Sr values.

2.0 INTRODUCTION

Core samples originating from Vault 4, Cell E of the Saltstone Disposal Facility (SDF) were collected in September of 2008 (Hansen and Crawford 2009, Smith 2008) and sent to SRNL to measure chemical and physical properties of the material including visual uniformity, mineralogy, microstructure, density, porosity, distribution coefficients (K_d), and chemical composition. Some data from these experiments have been reported (Cozzi and Duncan 2010). In this study, leaching experiments were conducted with a single core sample under conditions that are representative of saltstone performance. In separate experiments, reducing and oxidizing environments were targeted to obtain solubility and K_d values from the measurable species identified in the solid and aqueous leachate. This study was designed to provide insight into how readily species immobilized in saltstone will leach from the saltstone under oxidizing conditions simulating the edge of a saltstone monolith and under reducing conditions, targeting conditions within the saltstone monolith.

Core samples were taken from saltstone poured in December of 2007 giving a cure time of nine months in the cell and a total of thirty months before leaching experiments began in June 2010. The saltstone from Vault 4, Cell E is comprised of blast furnace slag, class F fly ash, portland cement, and Deliquification, Dissolution, and Adjustment (DDA) Batch 2 salt solution. The salt solution was previously analyzed from a sample of Tank 50 salt solution and characterized in the 4QCY07 Waste Acceptance Criteria (WAC) report (Zeigler and Bibler 2009). Subsequent to Tank 50 analysis, additional solution was added to the tank solution from the Effluent Treatment Project as well as from inleakage from Tank 50 pump bearings (Cozzi and Duncan 2010).

Core samples were taken from three locations and at three depths at each location using a two-inch diameter concrete coring bit (1-1, 1-2, 1-3; 2-1, 2-2, 2-3; 3-1, 3-2, 3-3) (Hansen and Crawford 2009). Leaching experiments were conducted with a section of core sample 3-2. All cores from location 3 were drilled without using water. Core sample 3-2 was drilled from approximately six inches to a depth of approximately 13 inches. Approximately six inches of the core was removed but it broke into two pieces during removal from the bit. At the time of drilling, core material appeared olive green in color (Smith 2008). The fact that the samples were cored as olive green and were received after storage with a gray outer layer is indicative that some oxidation had occurred prior to leaching studies.

3.0 EXPERIMENTAL

3.1 VAULT 4 CELL E CORE

In April 2009, core samples were removed from the stainless steel containers, inspected, and transferred to PVC tubes that were backfilled with nitrogen. The larger piece of core sample 3-2 was cut using a mitre box saw (for hydraulic conductivity measurements) at SRNL. The remainder of the sample was placed within the PVC container and backfilled with nitrogen in an effort to preserve the sample. When received for leaching studies, the sample consisted of two pieces. The pieces were gray in color except in places where the internal material was freshly exposed, giving an olive green color (Figure 1). The samples were removed from the PVC tube and placed in a glovebag connected to nitrogen (Figure 2).

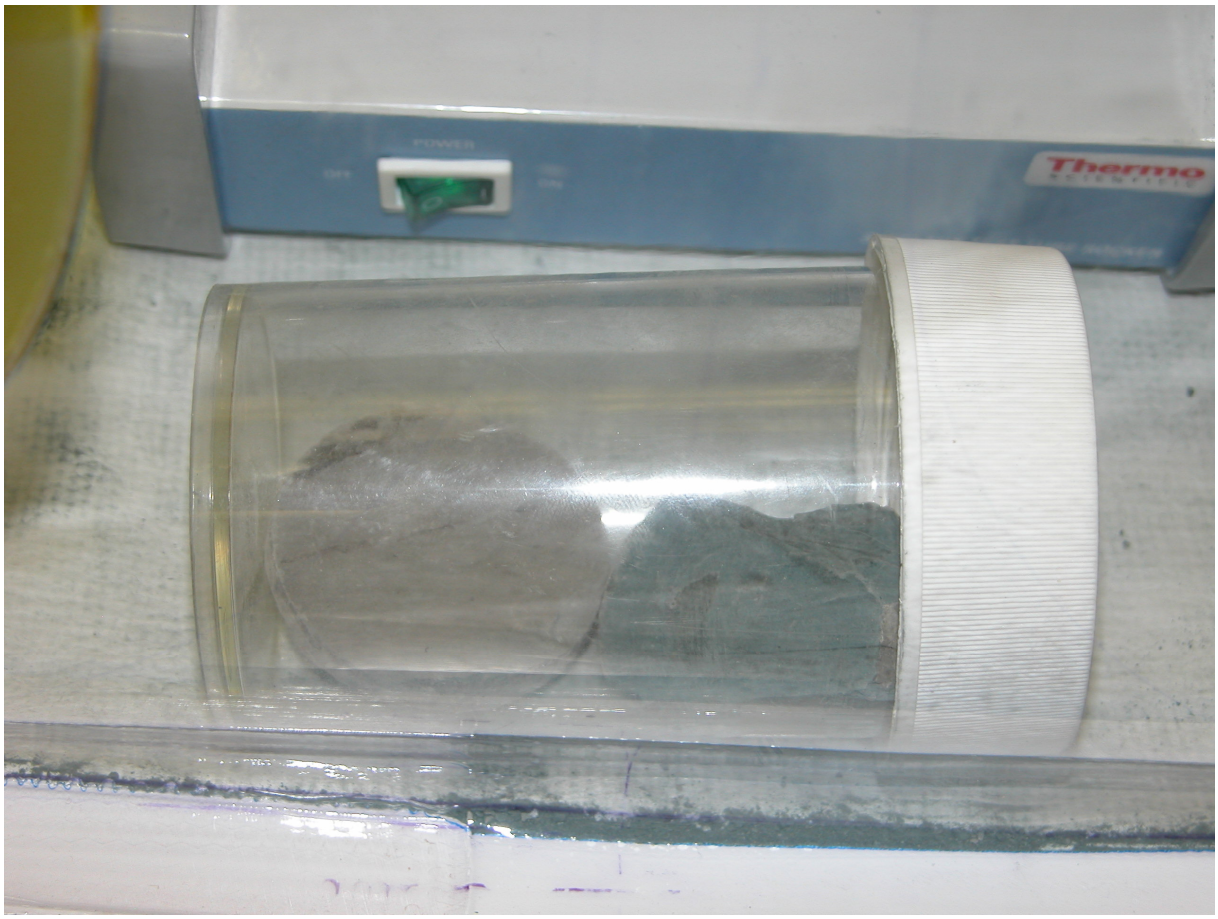

Figure 1. View of saltstone core sample 3-2 with gray (external) and olive green (internal) color from a freshly removed surface.

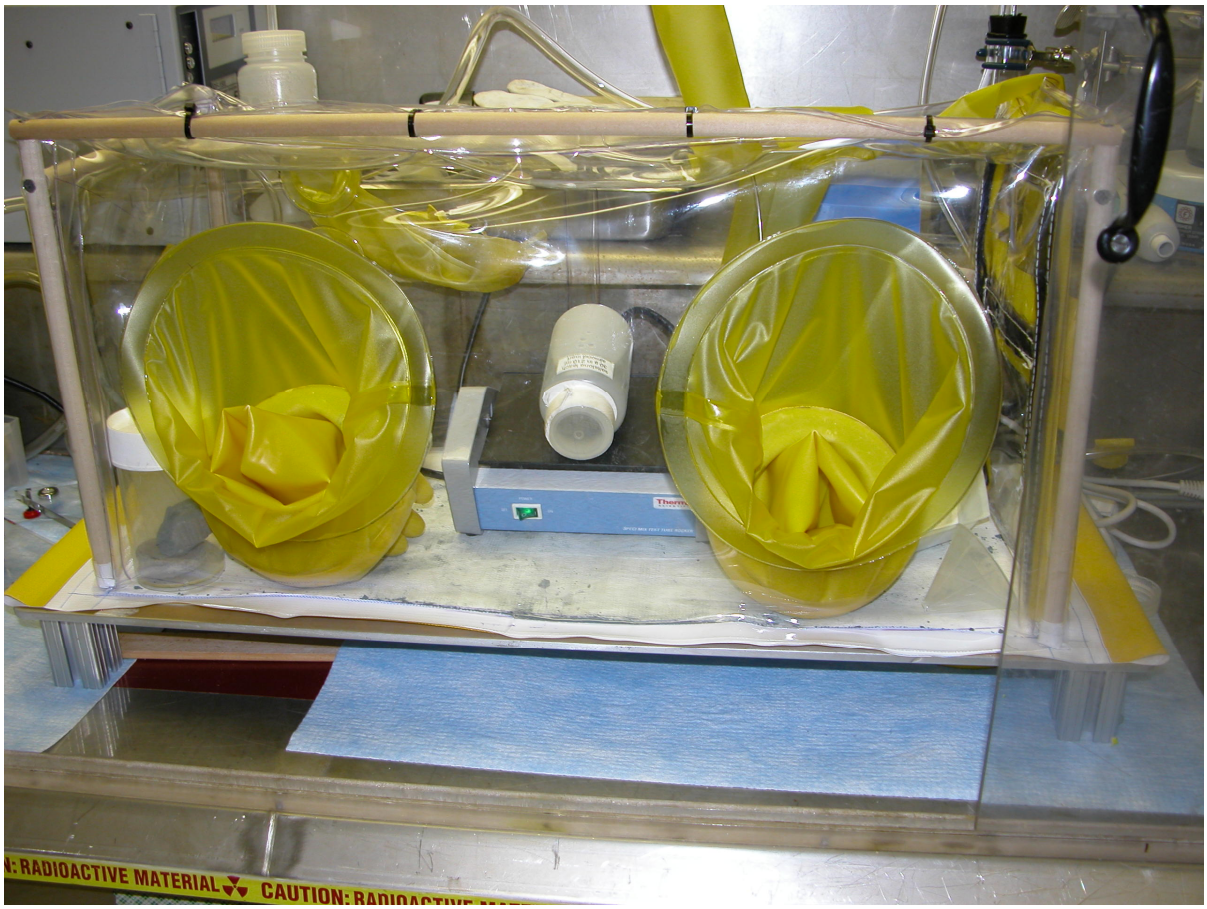

Figure 2. Photograph of the nitrogen atmosphere glovebag used to create a reducing environment for saltstone desorption studies.

Oxygen levels within the glovebag were monitored using a Delta F oxygen analyzer. The analyzer uses an electrochemical sensor and can measure oxygen below 10 ppm. The glovebag maintained a reduced oxygen environment of 30-60 ppm oxygen during the course of the experiments. However the levels rose above 1000 ppm temporarily during glovebag operations. This reduced oxygen environment was an attempt to simulate boundary conditions of the saltstone in the SDF, where oxygen levels are limited by diffusion (Smith and Walton 1993). One can think of the center of the saltstone monolith as maintaining an extremely low redox condition because of the high concentrations of sulfides and ferrous iron present from the slag (Harbour et al. 2006). The cementitious material's water-filled pores also provide very important secondary protection against oxygen diffusion and subsequent oxidation of redox-sensitive contaminants, such as Tc(IV). Similarly, in sample removal, we also can create a sample artifact related to affecting this moisture protection. Moisture in porous saltstone is subject to evaporation when taken out of its saturated environment.

Leaching experiments were performed in both reducing and oxidizing conditions to acquire distribution coefficients (K_d) and solubility values for the measurable elements present in the solid and aqueous leachate. The larger piece of core sample 3-2 weighing 154.3 g was used for the experiments. Approximately 30 grams of the sample were ground using a mortar and

pestle and then added to 210 mL of a saturated $Ca(OH)_2$ solution for each leaching experiment. For the reducing experiment, the sample was kept in the nitrogen glovebag. In the oxidizing experiment, air was continuously bubbled into the solution outside of the glovebag. As such, the oxidizing experiment leach solution is saturated with air, estimated at approximately 8 mg/L $O_{2(aq)}$. Leach solutions were contacted with the solid for 20 days and subsequently filtered using a 45 µm filter.

K_d values (mL/g) were calculated from direct measurements of the quantity of material in the solids and the quantity of material in the liquids.

$$K_d = \frac{C_{solids}}{C_f}$$

Where C_{solids} is the direct concentration (µg/g) or radionuclide activity (dpm/g) measured in the solids corrected for mass of element desorbed during equilibrium and C_f is the direct concentration (µg/mL) or radionuclide activity (dpm/mL) in the aqueous phase at the end of the sorption experiment.

A Portlandite ($Ca(OH)_2$) saturated leaching solution was used in the desorption tests to simulate young and moderately aged cementitious materials, defined in Kaplan 2009. During this cement aging stage, $Ca(OH)_2$ and calcium-silicate-hydrate gels are the key solid phases controlling aqueous leachate chemistry (Berner 1992), because CO_2 in air is very soluble in water at high pH, the resulting dissolved carbonate (CO_3^{2-}) will precipitate as calcite ($CaCO_3$) in the $Ca(OH)_2$ saturated solution. The pH of a $Ca(OH)_2$ saturated solution is approximately 12.5. Deionized (DI) water was used for the preparation of $Ca(OH)_2$-saturated solutions. Approximately 7.38 g of reagent grade $Ca(OH)_2$ was added to a liter of solution and stirred for one day. The solution was filtered using a 45 µm filter.

3.2 MATERIALS AND METHODS

The following is a brief description of the materials and methods used to obtain K_d and solubility values of core sample 3-2 under oxidizing and reducing conditions.

3.2.1 Materials

- The solids used in this study were from core sample 3-2 originating from Vault 4, Cell E.
- Portlandite ($Ca(OH)_2$) saturated leaching solution
- A glovebag supplied with N_2 gas
- Oxygen analyzer
- Hammer and chisel
- Mortar and pestle
- Test tube rocker
- pH/ORP meter

3.2.2 Methods

A Portlandite saturated leaching solution was prepared for use in the desorption tests to simulate young/moderately aged cement pore solution (Kaplan et al. 2008). DI water was used for the preparation of $Ca(OH)_2$-saturated solutions. Approximately 7.38 g of reagent grade $Ca(OH)_2$ was added to a liter of solution and stirred for one day. The solution was filtered using a 45 µm filter. Saltstone core sample 3-2 was received in two pieces and placed into the nitrogen glovebag. The larger piece weighed 154.3 g. The smaller piece weighed 35.5 g. Approximately 90 g of saltstone were removed from the larger piece of core sample 3-2. The sample was initially chipped using a hammer and chisel. Material size was further reduced by grinding with a mortar and pestle to generate 90 g of olive green powder.

30 g of the ground material were submitted to Analytical Development (AD) for total digestion and analysis. Saltstone was initially dissolved using Aqua Regia, yet solids remained. Therefore, a peroxide fusion method was used when necessary to prepare liquid sample for analysis, except for atomic absorption (AA) spectroscopy of mercury, selenium, and arsenic. Analyses also included Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Tc-99, Sr-90, and Se-79 Beta Liquid Scintillation, Pu-241 Liquid Scintillation, Cs-137 and I-129 gamma spectroscopy, Plutonium Alpha Pulse Height Analysis (PHA), and Americium/Curium counting (Tables 3 and 4). All AD data is archived in the Analytical Development's LIMS system.

To set up the leaching experiments, 30 g amounts of the ground saltstone were each added to a clean 250 mL polyethylene bottle for each of the oxidizing and reducing tests, and labeled with the date of sampling, and the identification of the core sampled (3-2). It is important to note that grinding samples versus working with a saltstone monolith may create experimental artifacts. For example, grinding may increase exposure to O_2 under sub-oxic experimental conditions. This would lead to lower K_d values. The leach solution for each experiment was purged with nitrogen for 30 minutes prior to adding 210 mL of solution to each bottle. For the reducing experiment, the first bottle was sealed with tape and placed on a test tube rocker for the duration of the experiment within the nitrogen glovebag. For the oxidizing experiment, the second bottle was continuously purged with air and stirred using a Teflon stir bar and stir plate. DI water was added to the oxidizing experiment when evaporation had occurred to replenish the initial solution volume, maintaining the 210 mL aqueous volume. A white precipitant, most likely $CaCO_3$, was observed to form after ~7 days within the oxidizing solution bottle on top of the ground saltstone solids. Each solution contacted the solids for 20 days. The solutions were subsequently filtered using a 45 µm filter. Approximately 200 mL of each solution was submitted to AD for analysis. The reduced solution had a pH of 12.05 while the oxidized solution had a pH of 11.46.

4.0 RESULTS AND DISCUSSION

From the analysis methods used for characterization of solids and liquids (Methods section), the elements identified in the saltstone core sample solid and in solution were aluminum, arsenic, barium, cesium, cobalt, iron, plutonium, potassium, silicon, strontium, technetium, and thorium.[1] Additional K_d values were calculated based on a lower detection limit denoted by a < or >. Results for leaching experiments under oxidizing and reducing experiments are presented in Table 1 and Table 2, respectively. In Table 1, calculated K_d values are presented and compared to the K_d 'best values' currently recommended (Kaplan 2009, Kaplan et al. 2011) under oxidizing conditions for young/middle aged cement. K_d (oxidizing) refers to the value obtained from the oxidation experiment with an air purge and in Table 2, calculated K_d values are compared to the best K_d currently recommended under reducing conditions for young/middle aged cement. K_d (reducing) refers to values obtained from reducing conditions within the nitrogen glovebag. The 'best value' refers to the best value suggested by a collection of reported data. K_d values are represented in mL/g. Solution concentrations for each element are presented in Tables 3 and 4 as apparent solubility values (moles/L) and compared to literature values for oxidizing and reducing conditions. A discussion of results by element follows. The "Proposed New Oxidizing Young/Middle K_d" are values that take into consideration previous values reported in a compendium of site specific geochemical data (Kaplan 2009) and values in this report.

[1] The Waste Acceptance Criteria (WAC) requires the characterization of >70 analytes. They are quantified in Ziegler and Bibler (2008).

Table 1. Analytical results and K_d values from desorption experiments under oxidizing conditions.

Element	Solid Concentration (µg/g) (except as noted)	Oxidizing Leachate (µg/mL) (except as noted)	Oxidizing K_d (mL/g)	Best Oxidizing Young/ Middle Cement K_d[§] (mL/g)	Proposed New Oxidizing Young/ Middle K_d (mL/g)	Comments
Aluminum (Al)	53200	6.34	8384	6000/6000	None	This is the first Al cement K_d measurement using SRS site specific materials. Aluminum sorption and solubility are strongly pH dependent. Trivalent cation K_d values for concrete exceed those for sediments (Atkins and Glasser 1992). The value of 8384 mL/g could be either precipitation or inner-sphere (strong) adsorption and is consistent with existing values.
Arsenic (As)	8.95	0.03	318	1000/1000	320	This is a first As cement measurement using SRS site specific materials. Previously arsenate was assumed to behave like phosphate. It is recommended that the As oxidized K_d value be reduced to 320 mL/g.
Barium (Ba)	399	<0.026	>15339	100/100	Saltstone = 6000/6000 Other cements = 100/100	Barium sulfate is highly insoluble in water and this insolubility is exploited in analytical sulfate tests (K_{sp} = 1E-10 M; Barium sulfide has only a slightly higher solubility value of K_{sp} = 5E-10). Sulfate was released from the saltstone slag and it promoted the precipitation of Ba from solution, thereby resulting in the incredibly high K_d value. For saltstone a uniquely high K_d will be assigned, that will not be used for other oxidized cementitious materials.
Boron (B)	<299	1.22	<238	---	None	
Cesium (Cs) (^{137}Cs)	1.26E-07 (Ci/g)	4.50E-09 (Ci/mL)	21	2/20	None	Cs K_d values in hardened HTS cement discs, pH 13.3 were close to 3 mL/g (Sarott et al. 1992). Wieland and Van Loon (2003) reviewed Cs K_d values of various cementitious materials and they had a very narrow range of 0.2 to 5 mL/g. Kaplan and Coates (2007) measured Cs K_d values in $Ca(OH)_2$-saturated and Ca-$CaCO_3$-saturated solutions in Ground, 40-year old concrete, simulating 1st/2nd and 3rd Stages, respectively. Measured K_d values were 21, and 17.6 mL/g, respectively. The desorption value of 21 mL/g measured in this test is consistent with existing values.
Cobalt (Co)	13.40	2.4E-03	5576	4000/4000	None	Using SRS materials, Kaplan and Coates (2007) measured Co(II) K_d values in Ca(OH)-saturated

Element	Solid Concentration (µg/g) (except as noted)	Oxidizing Leachate (µg/mL) (except as noted)	Oxidizing K_d (mL/g)	Best Oxidizing Young/ Middle Cement K_d[§] (mL/g)	Proposed New Oxidizing Young/ Middle K_d (mL/g)	Comments
						and $CaCO_3$-saturated solutions in ground, 40-yr old concrete, simulating 1st/2nd and 3rd Stages, respectively. The measured Co(II) Kd values were 4343 mL/g in Ca(OH)-saturated solutions and 3994 mL/g in $CaCO_3$-saturated solutions. Measured desorption value is consistent with previous values.
Iron (Fe)	19300	0.27	71740	6000/6000	None	This is the first time that Fe K_d values were measured in saltstone. It appears that the Fe was +3 and that it precipitated due to the high pH environment. This is consistent with basic geochemical principles. Measured desorption value is consistent with previous values.
Lithium (Li)	<138	2.31	<53	---	None	
Molybdenum (Mo)	<341	0.72	<464	300/300	None	
Phosphorus (P)	<677	5.23	<122	---	None	
Plutonium (Pu) (^{238}Pu)	4.36E-10 (Ci/g)	9.46E-14 (Ci/mL)	4607	10,000/10,000	None	Concrete containing reducing agents (blast furnace slag, BFS) did not have greater Pu K_d values (solubility values) than those that did not contain BFS. High K_d values are attributed more to a low solubility of Pu in high pH systems than to adsorption or absorption processes. Pu K_d values ranged from 1,000 to 12,000 mL/g (Allard et al. 1984, Hoglund et al. 1985). Kaplan and Coates (2007) measured Pu K_d values added as Pu(VI) but likely reduced to Pu(IV) in Ca(OH)-saturated and $CaCO_3$-saturated solutions in ground, 40-yr old concrete, simulating 1st/2nd and 3rd Stages, respectively. The measured K_d values were 99,700 and 92,200 mL/g, respectively.
Potassium (K)	10500	261	33	2/20	None	This is the first K K_d value measured in cement using SRS site-specific materials. Some of the K in solid phase is tied up in the mineral structure of the silicates and other minerals as impurities, and as such, will never enter into the aqueous phases. The result from this measurement is consistent with previous values.

Element	Solid Concentration (µg/g) (except as noted)	Oxidizing Leachate (µg/mL) (except as noted)	Oxidizing K_d (mL/g)	Best Oxidizing Young/ Middle Cement K_d[§] (mL/g)	Proposed New Oxidizing Young/ Middle K_d (mL/g)	Comments
Silicon (Si)	124000	42.4	2918	---	None	This is the first Si K_d (solubility) value measured in cement.
Strontium (Sr)	390	0.07	5728	15/15	Saltstone = 1000/1000 Other cements = 15/15	Sr typically has a moderately low K_d in cementitious environments, however when sulfate concentration are high, $SrSO_4$ precipitates, as was likely the case here. $SrSO_4$ has a solubility of 3.2E-07 M (strontium sulfite solubility product is even lower, $SrSO_3$ K_{sp} = 4E-08 M). Additional research needs to be performed with actual SDF samples because Sr solubility is not detected when Sr is simply added to saltstone. Large Sr sorption noted under reducing conditions also. Jakubick et al. (1987) reported Sr K_d values of 0.8 to 1.6 mL/g for high density and normal density concretes, and 1.3 to 3 mL/g for the same concretes, but in lower ionic strength solutions. Ewart et al. (1986) reported K_d values between 1 and 4 mL/g. Kato and Yanase (1993) reported a Sr K_d value of 56 mL/g for an experiment involving 24 h contact time, dried cement powder, pH 11 cement equilibrated water. Previously, we elected to disregard this value because it is an order-of-magnitude greater than those reported by other researchers and the nature of the solid phase was not clearly described by the author. In 1st Stage K_d values were decreased because high ionic strength likely results in competitive exchange (desorption). Kaplan and Coates (2007) measured Sr K_d values in Ca(OH)-saturated and $CaCO_3$-saturated solutions in ground, 40-yr old concrete, simulating 1st/2nd and 3rd Stages, respectively. The measured K_d values were 28.1 and 39.1 mL/g, respectively.
Technetium (Tc) (^{99}Tc)	5.36E-11 (Ci/g)	2.82E-12 (Ci/mL)	12	0.8/0.8	Saltstone = 10/10 Other cements = 0.8/0.8	An appreciable amount of Tc remained associated with the saltstone, suggesting that values are in fact greater than previously expected based on short-term (ad)sorption studies conducted at SRS (Kaplan and Coates 2007, K_d = 0.8 to 1.4 in various cements)

Element	Solid Concentration (µg/g) (except as noted)	Oxidizing Leachate (µg/mL) (except as noted)	Oxidizing K_d (mL/g)	Best Oxidizing Young/ Middle Cement K_d[§] (mL/g)	Proposed New Oxidizing Young/ Middle K_d (mL/g)	Comments
						(Lilley et al. 2009, K_d =2.75 to 5.08 in saltstone) or reported in the literature (Allard et al. 1984; K_d = 1 – 10 mL/g). The desorption value is significantly higher than the (ad)sorption values mentioned above. The proposed new values are increased because the cementitious chemistry unique to saltstone (perhaps sulfide/sulfur or Fe) may be influencing Tc desorption under oxidizing conditions. But this is likely not typical of other cements.
Thorium (Th) (^{232}Th)	3.20E-12 (Ci/g)	<9.01E-16 (Ci/mL)	>3548	10,000/10,000	None	Using three 65-yr-old crushed concrete samples and seven fresh concrete samples, Th K_d values were 2,500 to 5,500 mL/g (Allard et al. 1984; Hoglund et al. 1985). Th K_d values were consistently less than Am K_d values, greater than U K_d values, and very similar to Np and Pu K_d values (Allard et al. 1984; Hoglund et al. 1985). Using a sulfate resistant portland cement, Th K_d values were measured to be 100,000 mL/g (Wieland and Van Loon 2003). The value of >3548 mL/g suggests solubility controls and is consistent with existing values.

[§] SRNL-STI-2009-00473

Table 2. Analytical results and K_d values from desorption experiments under reducing conditions.

Element	Solid Concentration (µg/g) (except as noted)	Reducing Leachate (µg/mL) (except as noted)	Reducing K_d (mL/g)	Best Reducing Young/ Middle Cement K_d[§] (mL/g)	Proposed New Reducing Young/Middle K_d (mL/g)	Comments
Aluminum (Al)	53200	26.4	2008	7000/7000	None	See comments in Table 1.
Arsenic (As)	8.95	0.04	240	1000/1000	200/200	This is the first As cement measurement using SRS site specific materials. Under oxidizing conditions (Table 1) As K_d was 318 mL/g and the assumed dominant form of As is arsenate. Under reducing conditions arsenite will be more abundant, and it is known to sorb more weakly, hence the lower recommended K_d value compared to oxidized conditions. It is recommended that the As reduced K_d value be changed to 200 mL/g.
Barium (Ba)	399	0.054	7382	100/100	Saltstone = 6000/6000 Other cements = 100/100	See comments in Table 1.
Boron (B)	<299	0.615	<479	---	None	
Cesium (Cs) (^{137}Cs)	1.26E-07 (Ci/g)	4.95E-09 (Ci/mL)	18	2/20	None	Note similar K_d value whether measured under oxidizing (Table 1) or reducing conditions. The desorption value of 18 mL/g measured in this test is consistent with existing values.
Cobalt (Co)	13.40	7.8E-3	1702	5000/5000	None	See comments in Table 1.
Iron (Fe)	19300	0.21	92781	7000/7000	None	See comments in Table 1.
Lithium (Li)	<138	2.22	<55	---	None	
Molybdenum (Mo)	<341	0.66	<511	300/300	None	
Phosphorus (P)	<677	4.12	<157	---	None	
Plutonium (Pu) (^{238}Pu)	4.36E-10 (Ci/g)	<1.73E-13 (Ci/mL)	>2510	10,000/10,000	None	See comments in Table 1
Potassium (K)	10500	279	31	2/20	None	See comments in Table 1.
Silicon (Si)	124000	9.79	12659	---	None	
Strontium (Sr)	390	0.52	737	15/15	Saltstone = 1000/1000 Other cements = 15/15	See comments in Table 1.

Element	Solid Concentration (µg/g) (except as noted)	Reducing Leachate (µg/mL) (except as noted)	Reducing K_d (mL/g)	Best Reducing Young/ Middle Cement K_d[§] (mL/g)	Proposed New Reducing Young/Middle K_d (mL/g)	Comments
Technetium (Tc) (^{99}Tc)	5.36E-11 (Ci/g)	3.68E-13 (Ci/mL)	139	5000/ 5000	1000/ 1000	The Tc K_d value does not suggest that it is being controlled by a Tc-sulfide phase solubility, as has been used in defense of using high solubility values. The glovebag had very low atmospheric O_2 concentrations of between 30 to 60 ppm, but the Eh of the suspensions were between 140 and 400 mV S.H.E., suggesting that only moderately reducing conditions were obtained. A concern is that the slightest amount of O_2 oxidizes the Tc(IV) to Tc(VII). In a kinetic study, Kaplan et al. (2011) measured steadily increasing Tc K_d values from 2 to 900 mL/g as the contact time of Tc(VII) increased from 1 to 56 days. In these latter studies, a glovebox was used and atmospheric O_2 was maintained much lower, <0.5 ppm, and suspension Eh was typically -250 mV. Background: $Tc^{VII}O_4^-$ gets reduced to Tc^{4+}, which like other tetravalent cations sorbs strongly to surfaces. Lukens et al. (2005) conducted fundamental studies using SRS slag and grout mixtures. In their study, they added Tc(VII) to a reducing grout and using X-ray Absorption Spectroscopy, specifically, XANES, they observed the slow transformation of Tc(VII) to $Tc^{VII}O_2$-H_2O to $Tc^{IV}S_x$. This process was monitored in the grout over a course of 45 months. The solubility of the $Tc^{IV}O_2$ is low but that of $Tc^{IV}S_x$ is extremely low, 1E-20 M in alkaline systems (2.4E-08 pCi/L ^{99}Tc; (MMES 1992; Table D.3-3). The high K_d values selected for these conditions are to reflect the low solubility of Tc under these conditions. Lilley et al. (2009) measured $Tc^{VII}O_4^-$ sorption to two SRS saltstone simulants containing 45% slag, but did not reach steady state. In one formulation they measured a K_d of 18 in the other formulation they measured a K_d of 3660 mL/g. Recommended values are based on several values (Kaplan et al. 2011), including literature values and site specific values. One reason these values were discounted was because the partial pressure of oxygen was

Element	Solid Concentration (µg/g) (except as noted)	Reducing Leachate (µg/mL) (except as noted)	Reducing K_d (mL/g)	Best Reducing Young/ Middle Cement K_d[§] (mL/g)	Proposed New Reducing Young/Middle K_d (mL/g)	Comments
						slightly higher (30 to 60 ppm) than is expected in a reducing cement, such as saltstone (<0.5 ppm O_2). When O_2 <0.5 ppm, Tc K_d = 1000 mL/g (Kaplan et al. 2011). This K_d value of 139 mL/g represents the K_d near the oxygen front.
Thorium (Th) (^{232}Th)	3.20E-12 (Ci/g)	2.98E-15 (Ci/mL)	1067	5000/5000	None	See comments in Table 1

[§] SRNL-STI-2009-00473

Table 3. Apparent solubility values from field saltstone samples compared to existing values under oxidizing conditions.

Element	Method	Oxidizing Leachate (ug/mL) (except as noted)	Solubility (mol/L)	Existing Apparent Solubility§ (mol/L)	Proposed change to Solubility Value (mol/L)	Comments
Aluminum (Al)	ICP-ES	6.34	2.35E-04	1E-11	1E-04	This is the first solubility measurement for Al. The existing solubility values were never calculated by thermodynamics or measured. They were estimated based on chemical analogues.
Arsenic (As)	AA	0.03	3.67E-07	---	1E-07	This is the first solubility measurement for As.
Barium (Ba)	ICP-ES	<0.026	<1.89E-07	1E-05	Saltstone =1E-08 Other cements =1E-05	Assuming that solubility is partially controlled by solubility of $BaSO_3$ and/or $BaSO_4$
Boron (B)	ICP-ES	1.22	1.13E-04	---	None	
Cesium (Cs) (^{137}Cs)	Gamma Scan	4.50E-09 (Ci/mL)	3.78E-10	---	None	
Cobalt (Co)	ICP-MS	2.4E-03	4.07E-08	1E-07	None	
Iron (Fe)	ICP-ES	0.27	4.82E-06	1E-11	1E-06	This is the first solubility measurement for Fe. The existing solubility values were never calculated by thermodynamics or measured. They were estimated based on chemical analogues.
Lithium (Li)	ICP-ES	2.31	3.33E-04	---	None	
Molybdenum (Mo)	ICP-ES	0.72	7.55E-06	---	None	
Phosphorus (P)	ICP-ES	5.23	1.69E-04	---	None	
Plutonium (Pu) (^{238}Pu)	Alpha PHA	9.46E-14 (Ci/mL)	2.32E-14	1E-12	None	See comments in this table for Th.
Potassium (K)	ICP-ES	261	6.68E-03	---	None	
Silicon (Si)	ICP-ES	42.4	1.51E-03	---	None	
Strontium (Sr)	ICP-ES	0.07	7.76E-07	1E-05	Saltstone =1E-06 Other cements = 1E-05	Assuming that solubility is partially controlled by solubility of $SrSO_3$ and/or $SrSO_4$.

Element	Method	Oxidizing Leachate (ug/mL) (except as noted)	Solubility (mol/L)	Existing Apparent Solubility[§] (mol/L)	Proposed change to Solubility Value (mol/L)	Comments
Technetium (Tc) (^{99}Tc)	Tc-99 Liquid Scintillation	2.82E-12 (Ci/mL)	1.68E-09	---	None	Upon exposure to oxygen, Tc(IV) readily oxidizes to TcO_4^-, a highly soluble species that does not sorb to minerals that comprise the cement waste form (Gilliam 1990).
Thorium (Th) (^{232}Th)	ICP-MS	<9.01E-16 (Ci/mL)	<3.54E-08	1E-12	1E-08	Assumed solubility controlling phases are hydroxide/hydrous oxides for Th, Zr, Pu and hydroxycarbonates for Pb. The following is from (Ewart et al. 1992) and was conducted by adding Th(IV) to water equilibrated with concrete and pH adjusted: solubility ranged from 1E-08 M to 4E-09 M as pH increased from 8.3 to 12.9. In essence, the solubility didn't change for Th. Because there are so few Th cement solubility measurements, other +4 elements were considered for estimating solution of Th. Following is a discussion of these considerations. Lilley et al. (2009) measured Pu(IV) K_d values in Vault 2 cement containing 25% slag and 2 saltstone samples under reducing and oxidizing conditions. In both oxidizing and reducing conditions he measured 10^{-12} M solubility levels. One of the main reasons they could measure such low levels was because they used an ICP-MS rather than conventional radiometric analytical methods. Sn exists in the tetravalent state, (Sn(IV)), under the cementitious conditions and readily hydrolyses in the pH range >8. It sorbed to the same extent as Th(IV) to sulfate resistant portland cement (Ewart et al. 1992). In a recent exhaustive review of Th K_d values and solubilities in various cementitious materials, Wang et al. (2009; section 4.8.2) calculated the solubility of Th to be in cementitious leachate to be 1E-09 M and it agreed well with measured values.

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Table 4. Apparent solubility values from field saltstone samples compared to existing values under reducing conditions.

Element	Method	Reducing Leachate (ug/mL) (except as noted)	Solubility (mol/L)	Existing Apparent Solubility[§] (mol/L)	Proposed change to Solubility Value (mol/L)	Comments
Aluminum (Al)	ICP-ES	26.4	9.78E-04	1E-11	1E-04	See comment for aluminum in Table 3.
Arsenic (As)	AA	0.04	4.85E-07	---	1E-07	See comment for arsenic in Table 3.
Barium (Ba)	ICP-ES	0.054	3.93E-07	1E-05	1E-08	See comment for barium in Table 3.
Boron (B)	ICP-ES	0.615	5.69E-05	---	None	
Cesium (Cs) (^{137}Cs)	Gamma Scan	4.95E-09 (Ci/mL)	4.16E-10	---	None	
Cobalt (Co)	ICP-MS	7.8E-03	1.33E-07	1E-07	None	
Iron (Fe)	ICP-ES	0.21	3.72E-06	---	1E-06	See comment for iron in Table 3.
Lithium (Li)	ICP-ES	2.22	3.20E-04	---	None	
Molybdenum (Mo)	ICP-ES	0.66	6.86E-06	---	None	
Phosphorus (P)	ICP-ES	4.12	1.33E-04	---	None	
Plutonium (Pu) (^{238}Pu)	Alpha PHA	<1.73E-13 (Ci/mL)	<4.37E-14	1E-12	None	Lilley et al (2009) measured Pu(V) K_d values in Vault 2 cement containing 25% slag and 2 saltstone samples under reducing and oxidizing conditions. In both oxidizing and reducing conditions he measured 10^{-12} M solubility levels. The Pu(V) presumably quickly reduced to Pu(IV) (or perhaps less likely Pu(III)) in these experiments. Pu(IV) solubility measured by adding Pu(IV) spike into concrete rinsate under reducing conditions without solid phase and adjusting pH: from 9 to 11 the solubility was 1E-10 to 5E-11; essentially not changing (Ewart et al. 1992). Assumed $Pu(OH)_4$ controlled solubility. Based on thermodynamic calculations, solubility limits under reducing cementitious conditions were estimated to be less than 10^{-9} to 10^{-10} M Pu (Brady and Kozak 1995). It is assumed that the cementitious materials remain reducing throughout all three

Element	Method	Reducing Leachate (ug/mL) (except as noted)	Solubility (mol/L)	Existing Apparent Solubility[§] (mol/L)	Proposed change to Solubility Value (mol/L)	Comments
						stages. Lilley et al. (2009) measured Pu(V) K_d values in Vault 2 cement containing 25% slag and 2 saltstone samples under reducing and oxidizing conditions. In both oxidizing and reducing conditions he measured 1E-12 M solubility levels. Pu(combo) is a single geochemical parameter for Pu taking into account its many oxidation states. For this system, all Pu is assumed to exist in the +4 oxidation state.
Potassium (K)	ICP-ES	279	7.14E-03	---	None	
Silicon (Si)	ICP-ES	9.79	3.49E-04	---	None	
Strontium (Sr)	ICP-ES	0.52	5.98E-06	1E-05	1E-06	See comment for strontium in Table 3.
Technetium (Tc) (^{99}Tc)	Tc-99 Liquid Scintillation	3.68E-13 (Ci/mL)	2.19E-10	1E-10	None	Bayliss et al. (1991) adsorbed Tc onto portland cement or concrete in an anoxic glove box with 0.05 M dithionite in 1.5 M NaCl for 28 days in 50:1 water:crushed cement: K_d = 5000 mL/g and measured Tc solution concentration was 1E-11 M. Assuming Tc_2S_7 as the solubility controlling phase, MMES (1992; Appendix D) calculated that reducing grout used in the SRS saltstone program would maintain Tc at a concentration of 1.4E-20 M (2.4E-08 pCi/L). Allard (1984) calculated that reducing concrete would maintain Tc at a concentration <1E-10 M. It is assumed that the SRS cementitious materials containing blast furnace slag remain reducing throughout all three stages. The 3rd stage has a lower solubility only to permit some Tc to release into the environment due to oxidation of phase, not because the phase is believed to have change into a form that is more soluble (a way to release Tc into the aqueous phase).
Thorium (Th) (^{232}Th)	ICP-MS	2.98E-15 (Ci/mL)	1.17E-07	1E-12	1E-08	See comment for Th in Table 3.

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4.1 ALUMINUM

This is the first aluminum cement K_d measurement using SRS site specific materials. The K_d value of 8384 mL/g (oxidizing) and 2008 mL/g (reducing) were measured, compared to a best value of 10,000 (oxidizing) and 7000 (reducing) mL/g (Tables 1 and 2). Aluminum sorption and solubility are strongly pH dependent. Trivalent cation K_d values for concrete exceed those for sediments (Atkins and Glasser 1992). The value of 8384 mL/g suggests there could be either precipitation or inner-sphere adsorption. The reported values are consistent with existing recommended values (Kaplan 2009).

2.35E-04 (oxidizing) and 9.78E-04 mol/L (reducing) are the first solubility measurements for aluminum under these conditions (Tables 3 and 4). The existing solubility values have not been previously measured or calculated by thermodynamics. They were estimated based on chemical analogues. A proposed change of the solubility value to 1E-04 mol/L is recommended for oxidizing and reducing conditions.

4.2 ARSENIC

This is the first arsenic cement K_d measurement using SRS site specific materials. Previously, arsenate was assumed to behave like phosphate, which has been assigned a very high K_d value due to its propensity to precipitate metals. Therefore, a best value oxidizing K_d of 1,000 was suggested previous to this work (Tables 1 and 2). Under oxidizing conditions the arsenic K_d was 318 mL/g, where the assumed dominant form of arsenic is arsenate. Under reducing conditions the K_d was measured at 240 mL/g. Under reducing conditions, arsenite will be more abundant, where it is known to sorb more weakly. Therefore a lower K_d value is warranted compared to oxidized conditions. It is recommended that the arsenic K_d (oxidizing) value be lowered to 318 mL/g and the arsenic K_d (reducing) be lowered to 200 mL/g, compared to the original K_d value of 1000 mL/g.

3.67E-07 (oxidizing) and 4.85E-07 mol/L (reducing) are the first solubility measurements for arsenic under these conditions (Tables 3 and 4). The existing apparent solubility values were never calculated by thermodynamics or measured (Kaplan 2009). They were estimated based on chemical analogues. A proposed change of the apparent solubility value to 1E-07 mol/L is recommended for oxidizing and reducing conditions based on these measured values.

4.3 BARIUM

Barium sulfate is highly insoluble in water and this insolubility is exploited in analytical sulfate tests (K_{sp} = 1E-10 M). Sulfate was released from the saltstone slag and it promoted the precipitation of barium from solution, thereby resulting in the high K_d value of 7382 mL/g for the reducing experiment (Tables 1 and 2). For saltstone a uniquely high K_d will be assigned of 6000 mL/g based on these measured values, while for other oxidized cementitious materials the value of 100 mL/g.

A solubility value of 3.93E-07 mol/L (reducing) was measured (Tables 3 and 4). The solubility of barium may be partially controlled by the solubility of $BaSO_3$ and/or $BaSO_4$. A proposed change of the apparent solubility value to 1E-08 mol/L is recommended for oxidizing and reducing conditions for saltstone.

4.4 CESIUM

The K_d values of 21 mL/g and 18 mL/g were measured for oxidizing and reducing (Tables 1 and 2), respectively in this test and are consistent with reported values (Kaplan 2009). Cesium K_d values in hardened HTS cement discs (Haute Teneure en Silice, a French sulphate resistant cement), pH 13.3 were close to 3 mL/g (Sarott et al. 1992). Wieland and Van Loon (2003) reviewed Cs K_d values of various cementitious materials and they had a very narrow range of 0.2 to 5 mL/g. Kaplan and Coates (2007) measured cesium K_d values in $Ca(OH)_2$-saturated and Ca-$CaCO_3$-saturated solutions in ground, 40-year old concrete, simulating $1^{st}/2^{nd}$ and 3rd Stages, respectively. Measured K_d values were 21, and 17.6 mL/g, respectively.

4.5 COBALT

The K_d value of 5576 (oxidizing) and 1702 mL/g (reducing) were measured, compared to a best value of 4000 (oxidizing) and 5000 (reducing) mL/g (Tables 1 and 2). The measured desorption value is consistent with previous values (Kaplan 2009). Using SRS materials, Kaplan and Coates (2007) measured Co(II) K_d values in Ca(OH)-saturated and $CaCO_3$-saturated solutions in ground, 40-yr old concrete, simulating $1^{st}/2^{nd}$ and 3rd Stages, respectively. The measured Co(II) K_d values were 4343 mL/g in Ca(OH)-saturated solutions and 3994 mL/g in $CaCO_3$-saturated solutions.

4.6 IRON

This is the first time that iron K_d values were measured in saltstone. It appears that the Fe(III) precipitated due to the high pH environment giving extremely high K_d values of 71740 mL/g for oxidizing and 92781 mL/g for reducing experiments (Tables 1 and 2). These results are consistent with basic geochemical principles. The measured desorption value is consistent with previous values (Kaplan 2009).

4.82E-06 (oxidizing) and 3.72E-06 mol/L (reducing) are the first solubility measurements for iron under these conditions (Tables 3 and 4). The existing apparent solubility values reported were never calculated by thermodynamics or measured (Kaplan 2009). They were estimated based on chemical analogues. A proposed change of the apparent solubility value to 1E-06 mol/L is recommended for oxidizing and reducing conditions.

4.7 PHOSPHORUS

The K_d values of <122 mL/g (oxidizing) and <157 mL/g (reducing) were measured (Tables 1 and 2). No recommendations are made for phosphorus at this time.

4.8 PLUTONIUM

The desorption value of 4607 mL/g and >2510 mL/g for oxidizing and reducing experiments, respectively in this test compared to a best value of 10,000 mL/g (Tables 1 and 2) and is consistent with previous values (Kaplan 2009). Previous results show that concrete containing reducing agents such as blast furnace slag did not have greater plutonium K_d values (solubility values) than those that did not contain BFS. High K_d values are attributed more to a low solubility of plutonium in high pH systems, than to adsorption or absorption processes. Plutonium K_d values ranged from 1,000 to 12,000 mL/g (Allard et al. 1984, Hoglund et al. 1985). Kaplan and Coates (2007) measured plutonium K_d values added as Pu(VI) but likely reduced to Pu(IV) in Ca(OH)-saturated and $CaCO_3$-saturated solutions in ground, 40-yr old concrete, simulating $1^{st}/2^{nd}$ and 3rd stages, respectively. The measured K_d values were 99,700 and 92,200 mL/g, respectively.

A solubility value of 2.32E-14 mol/L (oxidizing) was measured (Table 3). Lilley et al. (2009) measured Pu(V) K_d values in Vault 2 cement containing 25% slag and two saltstone samples (simulant TR545 (95% slag) and TR547 (45% slag)) under reducing and oxidizing conditions. In both oxidizing and reducing conditions they measured 1E-12 M solubility levels. The Pu(V) presumably quickly reduced to Pu(IV) (or perhaps less likely Pu(III)) in these experiments. Pu(IV) solubility was measured by adding a Pu(IV) spike into concrete rinsate under reducing conditions without a solid phase and adjusting pH: from 9 to 11 the solubility was 1E-10 to 5E-11; essentially not changing (Ewart et al. 1992). It is assumed that $Pu(OH)_4$ controlled the solubility. Based on thermodynamic calculations, solubility limits under reducing cementitious conditions were estimated to be less than 1E-09 to 1E-10 M plutonium (Brady and Kozak 1995). It is assumed that the cementitious materials remain reducing throughout all three stages. Lilley et al. (2009) measured Pu(V) K_d values in Vault 2 cement containing 25% slag and two saltstone samples under reducing and oxidizing conditions. In both oxidizing and reducing conditions they measured 1E-12 M solubility levels. Pu(combo) is a single geochemical parameter for plutonium taking into account its many oxidation states. For this system, all plutonium is assumed to exist in the +4 oxidation state.

4.9 POTASSIUM

The desorption values of 33 mL/g and 31 mL/g were measured for oxidizing and reducing experiments, respectively (Tables 1 and 2). These are the first K_d values measured in SRS saltstone. Some of the potassium in solid phase is most likely tied up in the mineral structure of the silicates and other minerals as impurities, and as such, will mitigate release into the aqueous phases. The result from this measurement is consistent with previous values (Kaplan 2009).

4.10 SILICON

The desorption values of 2918 mL/g and 12659 mL/g were measured for oxidizing and reducing experiments, respectively (Tables 1 and 2). These are the first silicon cement K_d measurement using SRS site specific materials. No recommendations are made at this time.

4.11 STRONTIUM

The K_d (oxidizing) value of 5728 and 737 mL/g compares to a best value of 15 mL/g (Tables 1 and 2). Strontium typically has a moderately low K_d in cementitious environments; however, when sulfate concentrations are high, $SrSO_4$ precipitates, as was likely the case here. $SrSO_4$ has a solubility of 3.2E-07 M (strontium sulfite solubility product is even lower, $SrSO_3$ K_{sp} = 4E-08 M). Large Sr sorption was also noted under reducing conditions. Jakubick et al. (1987) reported strontium K_d values of 0.8 to 1.6 mL/g for high density and normal density concretes, and 1.3 to 3 mL/g for the same concretes, but in lower ionic strength solutions. Ewart et al. (1986) reported K_d values between 1 and 4 mL/g. Kato and Yanase (1993) reported a strontium K_d value of 56 mL/g for an experiment involving 24 h contact time, dried cement powder, pH 11 cement equilibrated water. Previously, we elected to disregard this value because it is an order-of-magnitude greater than those reported by other researchers and the nature of the solid phase was not clearly described by the author. In 1st Stage K_d values were decreased because high ionic strength likely results in competitive exchange (desorption). Kaplan and Coates (2007) measured strontium K_d values in Ca(OH)-saturated and $CaCO_3$-saturated solutions in ground, 40-yr old concrete, simulating 1st/2nd and 3rd Stages, respectively. The measured K_d values were 28.1 and 39.1 mL/g, respectively.

Solubilities of 7.76E-07 (oxidizing) and 5.98E-06 mol/L (reducing) for strontium are reported (Tables 3 and 4). The solubility of strontium may be partially controlled by solubility of $SrSO_3$ and/or $SrSO_4$. A proposed change of the apparent solubility value to 1E-06 mol/L is recommended for oxidizing and reducing conditions.

4.12 TECHNETIUM

A K_d value for the oxidizing experiment was 12 mL/g compared to a best value of 0.8 mL/g, while under reducing conditions the K_d value was 139 mL/g, compared to a best value of 5000 mL/g (Tables 1 and 2) found in the literature (Kaplan 2009). Under oxidizing conditions, an appreciable amount of technetium remained associated with the saltstone, suggesting that the values are in fact greater than previously expected based on short-term (ad)sorption studies conducted at SRS (Kaplan and Coates 2007, K_d = 0.8 to 1.4 in various cements) (Lilley et al 2009, K_d = 2.75 to 5.08 in saltstone) or reported in the literature (Allard et al. 1984; K_d = 1 – 10 mL/g). The desorption value is significantly higher than the (ad)sorption values mentioned above. The proposed new values are increased to 10 mL/g because the cementitious chemistry unique to saltstone (perhaps sulfide/sulfur or iron) may be influencing technetium desorption under oxidizing conditions. But this is likely not typical of other cements.

In the reducing experiment, the technetium K_d value does not suggest that it is being controlled by a Tc-sulfide phase solubility, as has been used in defense of using high solubility values. The glovebag had very low atmospheric O_2 concentrations of between 30 to 60 ppm, but the Eh of the suspensions were between 140 and 400 mV S.H.E., suggesting that only moderately reducing conditions were obtained. A concern is that this demonstrates that only a small concentration of O_2 needs to be present for oxidation of Tc(IV) to occur. Lukens et al. (2005) conducted fundamental studies using SRS slag and grout mixtures. In their study, they added Tc(VII) to a reducing grout and using X-ray Absorption Spectroscopy, specifically, XANES, they observed the slow transformation of Tc(VII) to $Tc^{IV}O_2$-H_2O to $Tc^{IV}S_x$ without oxygen exposure to the sample. However, starting with $Tc^{IV}S_x$, appreciable oxidation to Tc(VII) occurred over the course of 45 months with some exposure of the grout to air. Previous desorption studies by Kaplan et al. (2008) reported K_d values similar to those measured for this report where they measured a K_d in an oxidizing environment of 0.93 mL/g and a reduced value of 91.3 mL/g, although there is some question to the validity of the latter value because of interference in the analytical data used to calculate the K_d (Kaplan et al. 2008). In a kinetic study, Kaplan et al. (2011) measured steadily increasing technetium K_d values from 2 to 900 mL/g as the contact time of Tc(VII) increased from 1 to 56 days. In these latter studies, a glovebox was used and atmospheric O_2 was maintained much lower <0.5 ppm, (this work 30-60 ppm), and suspension Eh was typically -250 mV. Lilley et al (2009) measured TcO_4^- sorption to two SRS saltstone simulants containing 45% slag, but did not reach steady state. In one formulation they measured a K_d of 18 in the other formulation they measured a K_d of 3660 mL/g. It is recommended that the K_d value for technetium be lowered to better reflect the behavior of technetium in saltstone in young cement containing BFS. It is recommended that the best value technetium K_d be lowered to 1000 mL/g for reducing conditions. The recommended values are based on several values (Kaplan et al. 2011), including literature values and site specific values. One reason these values were discounted was because the partial pressure of oxygen was slightly higher (30 to 60 ppm) than is expected in a reducing cement, such as saltstone (<0.5 ppm O_2). When O_2 <0.5 ppm, Tc K_d = 1000 mL/g (Kaplan et al. 2011). This K_d value of 139 mL/g represents the K_d near the oxygen front.

Based on previous literature, BFS can be very effective in reducing the release rate of redox sensitive species such as technetium by reducing TcO_4^- to Tc(IV). However, as oxygen diffuses into concrete, the reduced species can become oxidized leading to degraded performance of the waste form. The diffusion of oxygen into BFS-containing concrete, modeled as a "shrinking core", results in the formation of an outer zone of oxidized concrete and a shrinking core of reduced intact concrete (Smith and Walton 1993). The physical and chemical properties of the outer oxidized zone differs significantly because of interactions between oxygen and solids in the concrete. While TcO_4^- is initially reduced from the presence of BFS in the cement to some extent, exposure of the cement to some amount of atmospheric oxygen can reoxidize Tc(IV) to TcO_4^-. This is evidenced by the lower K_d values measured under the oxidizing vs. the reducing experiment.

Solubilities of 1.68E-09 (oxidizing) and 2.19E-10 (reducing) mol/L were measured (Tables 3 and 4). Under reducing conditions within saltstone, the amount of technetium in solution

should be solubility controlled by the formation of TcO_2 and $Tc(IV)S_x$ solids. Exposure to oxygen will reoxidize Tc(IV) to TcO_4^-, increasing technetium concentration in solution.

4.13 THORIUM

The desorption value of >3548 mL/g and 1067 mL/g for oxidizing and reducing experiments, respectively compared to a best value of 10,000 mL/g oxidizing and 5000 mL/g for reducing conditions (Tables 1 and 2). The value of >3548 mL/g suggests solubility controls and is consistent with previous values (Kaplan 2009). Using three 65-yr-old crushed concrete samples and seven fresh concrete samples, thorium K_d values were 2,500 to 5,500 mL/g (Allard et al. 1984; Hoglund et al. 1985). Thorium K_d values were consistently less than Am K_d values, greater than U K_d values, and very similar to Np and Pu K_d values (Allard et al. 1984; Hoglund et al. 1985). Using a sulfate resistant portland cement, thorium K_d values were measured to be 100,000 mL/g (Wieland and Van Loon 2003).

A solubility value of 1.17E-07 mol/L was measured under reducing conditions (Table 4). The assumed solubility controlling phases are hydroxide/hydrous oxides for thorium, zirconium, and plutonium. Ewart et al. (1992) added Th(IV) to water equilibrated with concrete, and measured a solubility range of 1E-08 M to 4E-09 M as pH increased from 8.3 to 12.9.

5.0 CONCLUSIONS

The results from this study provide desorption K_d and solubility values obtained from measurement of species identified in the core sample and aqueous leachate. The majority of the 32 K_d measurements supported previous values. However, there were a few exceptions and the details of these differences are identified in Tables 1 and 2. This data represents the first K_d measurements from a site-specific sample obtained from the Saltstone Disposal Facility. Furthermore, K_d data had not been previously reported for many of these elements in cement/saltstone. The data was collected from a single saltstone core and as such it does not provide a measure of variability within the Saltstone Disposal Facility. These K_d and solubility values provide additional site-specific information about the desorption characteristics of saltstone.

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