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Cadmium, Cerium, Cobalt, Cesium,  
Distribution Coefficient, Iodine,  
Mercury, Neptunium, Pertechetate,  
Plutonium, Protactinium, Saltstone,  
Selenium, Solubility, Strontium,  
Technetium, Tin, Uranium, Vault 2  
concrete, Yttrium

**RETENTION:**  
**Permanent**

**SALTSTONE AND CONCRETE INTERACTIONS WITH  
RADIONUCLIDES: SORPTION ( $K_d$ ), DESORPTION, AND  
REDUCTION CAPACITY MEASUREMENTS**

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October 30, 2008

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**LIST OF ACRONYMS**

$\text{CaCO}_3$	Calcite
$\text{Ca(OH)}_2$	Portlandite
DDA	Deliquification, Dissolution, and Adjustment
DDI	Distilled deionized
$K_d$	Distribution coefficient
MSU	Modular Caustic Side Solvent Extraction Unit
PA	Performance assessment
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility

## 1.0 EXECUTIVE SUMMARY

The overall objective of this study was to measure a number of key input parameters quantifying geochemical processes in the subsurface environment of the Savannah River Site's (SRS's) Saltstone Facility. For the first time, sorption ( $K_d$ ) values of numerous radionuclides were measured with Saltstone and Vault 2 concrete. Particular attention was directed at understanding how Tc adsorbs and desorbs from these cementitious materials with the intent to demonstrate that desorption occurs at a much slower rate than adsorption, thus permitting the use of kinetic terms instead of (or along with) the steady state  $K_d$  term. Another very important parameter measured was the reduction capacity of these materials. This parameter is used to estimate the duration that the Saltstone facility remains in a reduced chemical state, a condition that maintains several otherwise mobile radionuclides in an immobile form. Key findings of this study follow.

- $K_d$  values for Am, Cd, Ce, Co, Cs, Hg, I, Np, Pa, Pu, Se, Sn, Tc, U, and Y for Saltstone and Vault 2 concrete were measured under oxidized and reduced conditions. Precipitation of several of the higher valence state radionuclides was observed. There was little evidence that the Vault 2 and Saltstone  $K_d$  values differed from previous SRS  $K_d$  values measured with reducing grout (Kaplan and Coates 2007). These values also supported a previous finding that  $K_d$  values of slag-containing cementitious materials, tend to be greater for cations and about the same for anions, than regular cementitious materials without slag. Based on these new findings, it was suggested that all previous reducing concrete  $K_d$  values be used in future PAs, except Np(V) and Pu(IV)  $K_d$  values, which should be increased, and I values, which should be slightly decreased in all three stages of concrete aging.
- The reduction capacity of Saltstone, consisting of 23 wt-% blast furnace slag, was 821.8 microequivalents per gram ( $\mu\text{eq/g}$ ). This value was approximately the same value as the one measured for 100% blast furnace slag. The cause for this approximately four-fold greater reduction capacity than anticipated is not known, but may be the result of the higher pH of Saltstone (pH ~11) compared to blast furnace slag (pH ~8), the presence of reducing minerals in the fly ash used to make the Saltstone, or to the Saltstone possibly having semi-conductor properties. These reduction capacity values will result in a near four-fold increase in the estimated duration that the Saltstone facility will remain in a reduced chemical state. The implication of this result is that oxidation-state-sensitive contaminants, such as Pu, Np, and Tc, will remain for a longer duration in a much less mobile form than previously believed. The reduction capacity of vault concrete, which consisted of 10 wt-% blast furnace slag, was 240  $\mu\text{eq/g}$ .
- Essentially all Am, Cd, Ce, Co, Cs, Hg, Sr, and Y was (ad)sorbed within four hours, whereas <3% of the adsorbed metals desorbed from these solids after 90 hours of continuous leaching. In particular, desorption of Tc (under oxidizing conditions) was  $>10^3$  fold slower than (ad)sorption (under reducing conditions). An important implication of this finding is that if groundwater by-passes or short-circuits the reduction capacity of the Saltstone by flowing along a crack, the ability of the oxygenated water to promote Tc desorption is appreciably less than that predicted based on the  $K_d$  value.
  - Relatively low Tc  $K_d$  values, 6 to 91 mL/g, were measured in these studies indicating that little if any of the Tc(VII) introduced into the Saltstone or Vault 2 concrete suspensions was reduced to Tc(IV). Such a reduction results in apparent  $K_d$  values on



the order of  $10^4$  mL/g. As such, these Tc sorption/desorption experiments need additional investigation to fully represent Saltstone environmental conditions.

It is important to understand the limits of these data. They do not provide insight into how radionuclides cured and immobilized in Saltstone will leach from the Saltstone. However they do provide insight into how radionuclides once released into porewater will interact with Saltstone or vault concrete. The use of these site-specific data would greatly improve the pedigree of the input data for the Saltstone performance assessment. Additionally, these studies provided important guidance and technical justification for the conceptual geochemical model to be used in the Saltstone performance assessment.

## 2.0 INTRODUCTION

### 2.1 SLAG REDUCTION CAPACITY IN CEMENTITIOUS MATERIALS

Saltstone is a concrete-like substance formed when the low-activity fraction of Savannah River Site (SRS) liquid waste is mixed with cement, flyash, and blast furnace slag. The weight percentage of cement, flyash, and slag is 10, 45, and 45, respectively. The nominal blend composition of Saltstone is 5 wt-% cement, 25 wt% flyash, 25 wt% blast furnace slag, and 45% salt solution (Heckrotte 1988). The addition of blast furnace slag to the Saltstone formulation provides a chemical reductant [iron(II)] and a precipitating agent (sulfide) that chemically binds several contaminants as insoluble species, thus reducing the tendency of these contaminants to leach from the solid waste form.

Experimentation has shown that leaching of chromium (Cr) and technetium (Tc) was effectively reduced to a level that enabled all projected salt solution composition to be processed into a slag-containing cementitious material (MMES 1992). Long-term lysimeter studies have shown that the addition of slag into the Saltstone formulation essentially stopped  $^{99}\text{Tc}$  leaching, but did not reduce nitrate leaching (MMES 1992).

Reduction capacity of a material is the amount of reductant in a materials. It has units of milliequivalents per gram of material. In this application, one milliequivalent is equal to one mmol of charge. The larger this value is, the greater the capacity of the material is to promote reducing conditions. Kaplan *et al.* (2005) measured the reduction capacity of the blast furnace slag used in Saltstone to be  $0.82 \pm 0.001$  meq/g, which agreed well with the measurement of Lukens *et al.* (2005), who reported a value of 0.82 meq/g. Kaplan *et al.* (2005) used this value to estimate the duration that buried Saltstone would remain reduced, thereby sequestering several key radionuclides, especially  $^{99}\text{Tc}$ . In these calculations, the slag in Saltstone became oxidized by oxygenated groundwater that moved through the Saltstone not by advection, but primarily by diffusion. Using two-dimensional reactive transport calculations, it was estimated that the Z-Area Saltstone waste form would maintain a reducing environment for well over 10,000 years. For example, it was calculated that only ~16% of the Saltstone reduction capacity would be consumed after 213,000 years.

For purposes of comparing this estimated Saltstone reduction duration, two additional calculations, based on entirely different assumptions, were made. The first calculation conducted by Lukens *et al.* (2005), was based on direct spectroscopy measurements of a Saltstone sample aged for ~1 year (without consideration of diffusion or aqueous transport considerations); it produced nearly identical results as above. The second calculation conducted as a first approximation and using unrealistically high groundwater flow rates, concluded that the Z-Area Saltstone waste form would likely maintain a reducing environment for more than 10,000 years (Kaplan and Hang 2003). Thus, the three calculations provide results that are in the same order of magnitude, namely that a vast majority (>90%) of the Saltstone would remain reduced after 10,000 years.

These calculations were based on reduction capacity measurements of slag, not directly of Saltstone containing slag. What was not known is how the reduction potential would change in a cementitious environment, *i.e.*, would the high pH promote or reduce the reduction capacity and whether the reduction capacity could be stoichiometrically estimated simply by determining the mass ratio of slag in the Saltstone (25 wt-% slag for the formulation described by Heckrotte, 1988).

## 2.2 PERTECHNETATE INTERACTION WITH SALTSTONE

Distribution coefficients ( $K_d$  values; a ratio of radionuclide solid phase concentration divided by aqueous phase concentration) are input parameters used in performance assessment (PA) calculations to provide a measure of radionuclide sorption to a solid phase; the greater the  $K_d$  value, the greater the sorption and the slower the estimated movement of the radionuclide through sediment.  $^{99}\text{Tc}$  is commonly found to be amongst the radionuclides posing the greatest potential risk at SRS waste disposal locations because it: 1) is believed to be highly mobile in its anionic form (pertechnetate,  $\text{TcO}_4^-$ ), 2) exists in relatively high concentrations in SRS waste, and 3) has a long half-life (213,000 years).

Kaplan *et al.* (2008) measured  $^{99}\text{TcO}_4^-$   $K_d$  values of 27 sediments from a well-boring core from E-Area. The sediment in this region of SRS is expected to be the same as that in Z-Area where the Saltstone facility is located. The mean  $K_d$  value was  $3.4 \pm 0.5$  mL/g and ranged from -2.9 to 11.2 mL/g. Kaplan and Coates (2007) measured  $\text{TcO}_4^-$   $K_d$  values of a cement recovered from a concrete slab in the SRS tank farm and exposed to the natural rainfall for 50 years. The measured  $K_d$  values were  $0.8 \pm 1.2$  and  $1.4 \pm 5.8$  mL/g for oxidizing aqueous  $\text{Ca(OH)}_2$  conditions (simulating a young cement porewater), and oxidizing  $\text{CaCO}_3$  conditions (simulating an older cement porewater), respectively. Under reducing aqueous  $\text{Ca(OH)}_2$  conditions the  $K_d$  value increased to  $3910 \pm 454$  mL/g. This behavior was likely the result of the  $\text{TcO}_4^-$  reducing to  $\text{Tc(IV)}$ , thereby becoming sparingly soluble. However, the  $K_d$  value for reducing conditions reported by Kaplan and Coates (2007), if converted to a solubility term, suggests that reducing conditions were only partially achieved during the study.

## 2.3 OBJECTIVES

The objectives of this study were to:

1. Measure Saltstone  $K_d$  values for  $^{241}\text{Am(III)}$ ,  $^{109}\text{Cd(II)}$ ,  $^{139}\text{Ce(III)}$ ,  $^{60}\text{Co(II)}$ ,  $^{137}\text{Cs(I)}$ ,  $^{230}\text{Hg(II)}$ ,  $^{129}\text{I(-I)}$ ,  $^{239}\text{Np(V)}$ ,  $^{238}\text{Pu(IV/V)}$ ,  $^{231}\text{Pa(V)}$ ,  $^{75}\text{Se(VI)}$ ,  $^{113}\text{Sn(IV)}$ ,  $^{89}\text{Sr(II)}$ ,  $^{99}\text{Tc(VII)}$ ,  $^{235}\text{U(VI)}$  and  $^{88}\text{Y(III)}$ <sup>1</sup>,
  - Measure  $K_d$  values simulating young Saltstone conditions and aged Saltstone conditions.
  - Measure (ad)sorption and desorption kinetics of a select group of isotopes
2. Measure the rate that Tc sorbs to Saltstone (presumably a measure of how rapidly  $\text{TcO}_4^-$  is reduced to  $\text{Tc(IV)}$ ) under reducing conditions and then how rapidly it desorbs under highly oxidizing conditions.

<sup>1</sup>  $K_d$  values do not differ for isotopes of a given element.

3. Measure the reduction capacity<sup>2</sup> of Saltstone.

### 3.0 MATERIALS AND METHODS

A detailed description of the various materials and methods are in Appendix A (Section 7.0), they include:

- Research and Development Instructions: Radionuclide Sorption to Cementitious Materials under Oxidizing and Reducing Conditions (Section 7.1),
- Research and Development Instructions: Sorption and Desorption Kinetics of  $\text{TcO}_4^-$  to and from Saltstone (Section 7.2), and
- Research and Development Instructions: Reduction Capacity of Solids by the  $\text{Ce(IV)} - \text{Fe(II)}$  Method (Section 7.2).

Details about the Saltstone formulations are also presented in Appendix A:

- Recipe for Simulants used in Saltstone Formulations (Section 7.4).

Following is a brief description of the materials and methods to provide sufficient guidance to the reader for interpreting the results.

### 3.1 MATERIALS

The same basic materials were used for all three studies:

- Solids:
  - Vault 2 simulant concrete (composition below in Section 3.1.1)
  - Saltstone samples (TR 431, TR 451, and TR 437; Section 7.4)
- Aqueous Phases:
  - Calcite ( $\text{CaCO}_3$ ) Saturated Solution: to simulate porewater in aged Saltstone (in reducing conditions)
  - Portlandite ( $\text{Ca(OH)}_2$ ) Saturated Solution: to simulate porewater in young Saltstone (oxygenated and deoxygenated)
- Radionuclides: gamma standard suite [ $^{241}\text{Am(III)}$ ,  $^{109}\text{Cd(II)}$ ,  $^{139}\text{Ce(III)}$ ,  $^{60}\text{Co(II)}$ ,  $^{137}\text{Cs(I)}$ ,  $^{230}\text{Hg(II)}$ ,  $^{113}\text{Sn(IV)}$ ,  $^{89}\text{Sr(II)}$ , and  $^{88}\text{Y(III)}$ ],  $^{75}\text{Se(VI)}$ ,  $^{14}\text{C(IV)}$ ,  $^{129}\text{I(-I)}$ ,  $^{238}\text{Pu(IV/V)}$ ,  $^{237}\text{Np(V)}$ ,  $^{231}\text{Pa(V)}$ ,  $^{99}\text{Tc(VII)}$ , and  $^{235}\text{U(VI)}$

#### 3.1.1 Cementitious Materials

Simulated Vault 2 concrete, as the name implies, is a simulant of the concrete that will be used to make Vault 2 at the Saltstone facility. The vault is the structure that will store the Saltstone. The

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<sup>2</sup> Reduction capacity is a measure of the total amount of reductant that a solid is composed of, in units of mol/L (or more precisely equivalents/L). In this application, the greater the reduction capacity, the longer it will take for groundwater to oxidize the solid.

composition of the concrete used in this study is presented in Table 1. From the stand point of radionuclide reactivity with the Vault 2 concrete, an important ingredient is the blast furnace slag that constitutes 268 lbs/yd<sup>3</sup> of simulated cement. It should be noted that during the time when these studies were being conducted, it was decided to use a slightly different formulation (Mix 2) than this one (Mix 1) for the simulated Vault 2 concrete. The only difference between these mixes is the amount of cementitious materials. Mix 1 had 670 lbs/yd<sup>3</sup> of cementitious materials and Mix 2 had 710 lbs/yd<sup>3</sup>. One may argue that Mix 2 should have greater sorption qualities than Mix 1 because there is more cementitious material per unit of salt waste in Mix 2 than in Mix 1.

**Table 1. Saltstone Vault 2, Mix 1 concrete formulation (670 lbs/cu yd cementitious material) (Class 3 sulfate resistant concrete)**

<b>Ingredient</b>	<b>Quantity (lbs/yd<sup>3</sup>)</b>
Type V cement (Lehigh T-V #2 ; ASTM C 150)	201
Grade 100 Blast furnace slag (Holcim Grade 100 Slag; ASTM C 989)	268
Silica Fume (W. R. Grace Silica Fume; ASTM C 1240)	44.7
Type F Fly ash (SEFA Class "F" Fly Ash; ASTM C 618)	156.3
Sand (Rinker Aggregates Company - Augusta Sand - Natural Washed Sand); ASTM C 33)	911
Aggregate (Rinker Aggregates Company - Dogwood Quarry - #67 Granite; ASTM C 33)	1850
Water (maximum; gal/ cu yd)	30.5
Maximum water to cementitious material ratio	0.38
Grace WRDA 35 (oz/cwt c+p)	5
Grace Darex II (oz/cwt c+p)	0.4 to 0.5
Grace Adva 380 (oz/cwt c+p)	3 to 4
Minimum compressive strength of at 28 days	5000 psig
Slump range/target of before Super-P	1 – 3 inches / 2 inches
Slump range/target of after Super-P	6 – 8 inches / 7 inches

The simulated Vault 2 concrete was received as a 3-inch diameter by 6-inch high cylinder. It was initially broken up with a chisel and hammer to ~1-cm particles. Then the ~1-cm particles were placed in a jaw crusher (Retsch Jaw Crusher Type BB51 with tungsten carbide plates) for ten minutes. The jaw crusher samples were then placed in a shatter box (Spec 8510 Shatterbox) for 10 seconds. The <1000-μm and >75-μm sieve fraction was used for these studies.

Simulated Saltstone samples were made with simulants of non-rad feed solutions. Recipes and formulations for TR 431, TR 451, and TR 437 are presented in Appendix A, Section 7.4. All simulated Saltstone formulations had a 0.6 water : premix ratio. The premix was composed of:

45 wt-% fly ash,  
45 wt-% slag, and  
10 wt-% cement.

The non-rad simulants were prepared by dissolving various salts into water to simulate different waste streams (also described in Appendix A, Section 7.4). Salts accounted for 22% of the Deliquification, Dissolution, and Adjustment (DDA) simulant, 29% of the Salt Waste Processing Facility (SWPF) simulant, and 32% of the Modular Caustic Side Solvent Extraction Unit (MCU) simulant. Expressed in different terms, the total salt concentrations in the: DDA simulant was 3.48 M, MCU simulant was 5.63 M, and SWPF simulant was 5.69 M. The three simulants received varying ratios of the same salts. They received 50% (of the added salt weight) as NaOH, and then varying amounts of NaNO<sub>3</sub>, NaNO<sub>2</sub>, NaCO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, aluminum nitrate, and sodium phosphate. The DDA simulant was used for most of the studies because it was believed to be representative of most of the waste stream going to the Saltstone facility.

### 3.1.2 Aqueous Phases

Portlandite (Ca(OH)<sub>2</sub>) Saturated Leaching Solution (oxygenated and deoxygenated): This solution was used in the sorption tests to simulate the first and second stages of cement aging.<sup>3</sup> During these cement aging stages, Ca(OH)<sub>2</sub> and calcium-silicate-hydrate gels are the key solid phases controlling aqueous leachate chemistry.

Because CO<sub>2</sub> in air is very soluble in water at high pH and the resulting dissolved carbonate (CO<sub>3</sub><sup>2+</sup>) will precipitate as calcite- (CaCO<sub>3</sub>) in the Ca(OH)<sub>2</sub>-saturated solution, care was taken to minimize contact of the solution with atmospheric air. Excess solid Ca(OH)<sub>2</sub> was undesirable because it would buffer the pH at an abnormally high pH level (the pH of the Ca(OH)<sub>2</sub>-saturated was 12.5 ± 1)

Distilled deionized (DDI) water was used for the preparation of both oxygenated and deoxygenated Ca(OH)<sub>2</sub>-saturated solutions. The DDI water was boiled for approximately 30 minutes and purged with high purity N<sub>2</sub> at approximately 25 ml/sec to remove dissolved CO<sub>2</sub> and O<sub>2</sub>. Approximately 1.35 g of reagent grade Ca(OH)<sub>2</sub> was added per liter of solution, followed by an ozone purge for approximately two minutes to restore dissolved O<sub>2</sub> to the oxygenated solution.

Calcite-Saturated Leaching Solution (oxygenated and deoxygenated): This solution was used in the sorption tests to simulate the third stage of cement aging. During this stage, Portlandite is assumed to be fully dissolved/reacted and the solubility or reactions of the calcium-silicate-hydrate gel with the infiltrating water controls the pH of the cement pore-water/leachate. The pH continues to decrease until it reaches the pH of the background sediment, pH 5.5 at the SRS. Radionuclides tend to sorb least during this stage.

By preparing the solution at a slightly elevated temperature the possibility of calcite precipitation during the test at room temperature was reduced. (Calcite undergoes retrograde solubility.) There was no need to minimize contact of this solution with the atmosphere. Calculated equilibrium values for this solution are: pH = 8.3, Ca<sup>2+</sup> = 20 mg/L, total inorganic carbon = 58 mg/L, PCO<sub>2</sub> = 0.0003 atm (fixed).

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<sup>3</sup> Cement is described in the performance assessment as aging in three progressive stages. These stages have unique mineralogy and leachate chemical conditions. How cement aging is treated in the performance assessment is described by Kaplan (2006).

Calcite saturated solutions were prepared by adding excess powdered reagent grade calcite to distilled-deionized water and stirring for approximately 24 hr at a slightly elevated room temperature, approximately 25-30 °C. Solutions were filtered using 0.45 µm membranes. Solution pH was ~8.4. Deoxygenated calcite-saturated solutions were prepared as noted above after first purging the distilled-deionized water with high purity N<sub>2</sub> gas at a flow rate of 25 mL/sec for approximately 30 min for each 3-liter preparation. These solutions were filtered using the above apparatus under a N<sub>2</sub> blanket.

### 3.1.3 Radionuclides

Radionuclides used in this study were a gamma suite of standards (<sup>241</sup>Am(III), <sup>109</sup>Cd(II), <sup>139</sup>Ce(III), <sup>60</sup>Co(II), <sup>137</sup>Cs(I), <sup>230</sup>Hg(II), <sup>113</sup>Sn(IV), <sup>89</sup>Sr(II), and <sup>88</sup>Y(III)), <sup>129</sup>I(-I), <sup>238</sup>Pu(VI); but was likely converted to Pu(IV) once it came in contact with solids), <sup>237</sup>Np(V), <sup>75</sup>Se(VI), <sup>99</sup>Tc(VII), and <sup>233</sup>U(VI). They were purchased from Eckert & Ziegler Analytics (Atlanta Georgia), except <sup>238</sup>Pu, which originated from site activities and was provided by David Hobbs (SRNL).

I, Np, Pu, Se, Tc, and U were included in these tests because they were found to be important risk drivers in preliminary performance assessment calculations. Am, Cd, Ce, Co, Cs, Hg, Pa, Sr, Sn, and Y were included because they were present in a suite of gamma emitters and would provide a great deal of additional information with relatively little additional cost, *i.e.*, they could be independently measured within a single cocktail. These gamma emitting radionuclides were analyzed to provide information about the sorption of some radionuclides of interest to the performance assessment (*e.g.*, Co, Ce, Cs, Am, Pa, Sr, and Y), as well as to provide indirect information for surrogate radionuclides. For example, they provided insight into how monovalent cations (*e.g.*, Cs), divalent cations (*e.g.*, Hg, Co, and Sr), trivalent cations (*e.g.*, Ce and Am), and tetravalent cations (*e.g.*, Sn) sorb to cementitious materials.

## 3.2 BATCH SORPTION STUDY

### 3.2.1 Objectives – Batch Sorption

The objective of this experiment was to measure radionuclide K<sub>d</sub> values for the radionuclides listed in Section 3.1.3 under conditions appropriate for the Saltstone performance assessment. Experimental conditions were created to simulate an oxidizing cementitious environment early in its aging process (Stages 1 and 2) and later in its aging process (Stage 3) (these stages are described in more detail in Kaplan 2006). Similar tests were conducted with Vault 2 concrete.

### 3.2.2 Materials – Batch Sorption

- Cementitious Solid Phases: Vault 2 concrete (Mix 1), DDA Simulant Saltstone
- Aqueous phase chemistry: Portlandite and calcite saturated solutions to simulate Stages 1 and 2, and Stage 3 in the cement lifecycle, respectively,
- Radionuclides: <sup>241</sup>Am(III), <sup>109</sup>Cd(II), <sup>139</sup>Ce(III), <sup>60</sup>Co(II), <sup>137</sup>Cs(I), <sup>230</sup>Hg(II), <sup>125</sup>I(-I), <sup>237</sup>Np(V), <sup>238</sup>Pu(VI), <sup>75</sup>Se(IV), <sup>113</sup>Sn(IV), <sup>89</sup>Sr(II), <sup>99</sup>Tc(VII), <sup>233</sup>U(VI), and <sup>88</sup>Y(III).

### 3.2.3 Methods – Batch Sorption

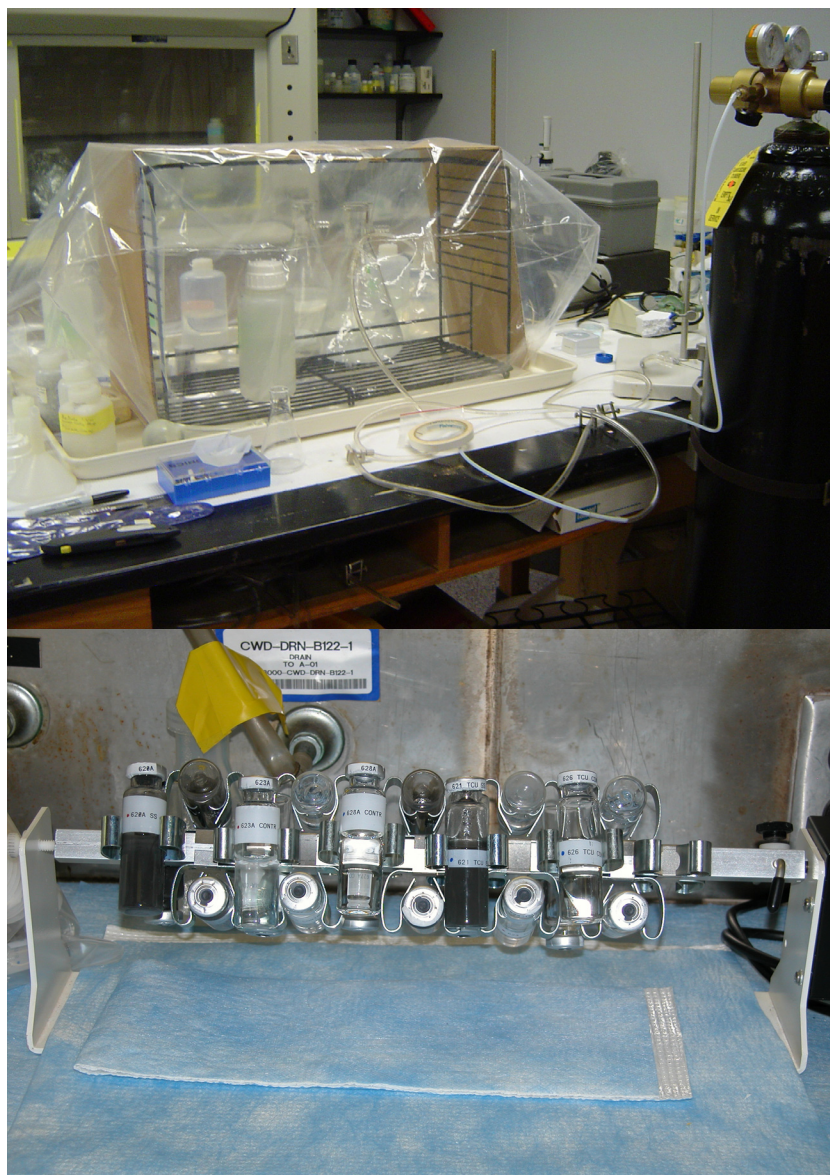
There were three nearly identical experiments conducted in which suites of different radionuclides were added to the same three cementitious materials. The radionuclides in these three experiments were:

1.  $^{125}\text{I}$ ,  $^{237}\text{Np}$ ,  $^{75}\text{Se}$ , and  $^{238}\text{Pu}$ ,
2.  $^{99}\text{Tc}$  and  $^{233}\text{U}$ , and
3. a suite of gamma-emitting radionuclides;  $^{241}\text{Am}$ ,  $^{109}\text{Cd}$ ,  $^{139}\text{Ce}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$ ,  $^{230}\text{Hg}$ ,  $^{113}\text{Sn}$ ,  $^{89}\text{Sr}$ , and  $^{88}\text{Y}$ .

Radionuclides were added in these groupings to ease analysis. Suite 1 was analyzed by low energy gamma spectroscopy. Suite 2 was analyzed by liquid scintillation counting. Suite 3 was measured by gamma spectroscopy. Each of these experiments was conducted in an oxidizing environment (on the lab counter top) and in a reducing environment. Clemson University created the reducing environment in a glove bag filled with  $\text{N}_2$  atmosphere. SRNL created the reducing environment by purging with  $\text{N}_{2(g)}$  each suspension containing serum vial. Photographs of the two approaches to creating reducing environments are presented in Figure 1.

Batch sorption tests were conducted in a suspension containing 0.5 g solid (DDA simulant Saltstone, partially oxidized DDA simulant Saltstone, or simulated Vault 2 concrete) and 10 mL solution (calcite-saturated or Portlandite-saturated solutions). Prior to adding the radiological spike solutions, each solid had been pre-equilibrated with the appropriate solutions in an effort to bring the suspension to a chemical steady state. Pre-equilibration was accomplished by adding 10 mL of the appropriate solution to the respective solids and shaking overnight, followed by decantation of the solution. This pre-equilibration was done for three consecutive days or until the suspension pH was stable. pH levels of the calcite-saturated suspensions generally reached the pH of the conditioning calcite solution (pH 10); whereas the Portlandite conditioned suspension generally stabilized at about pH 12, 0.5 pH units below the Portlandite solution. The resulting suspension was then spiked with  $\sim 330\ \mu\text{L}$  of a stock radiological solution. Spiked suspensions were placed on a rotator (Figure 1 bottom) and the samples were constantly mixed. At the end of this spike-equilibration period, the solids were permitted to settle for one hour and then the aqueous phase of each tube was passed through a  $0.1\ \mu\text{m}$  filter. These filtered solutions were analyzed for their respective radionuclides using traditional analytical techniques.





**Figure 1. Photographs of (top) N<sub>2</sub>-atmosphere glovebag and (bottom) N<sub>2</sub>-filled serum bottles used to create reducing environments for Saltstone batch sorption studies.**

All tests were conducted in duplicate or triplicate. A positive control was included with each set of experiments; “no-solids” control samples were used to determine if precipitation of the radionuclides occurred during the experiments. A negative control, “no spike” control, was included to determine if there was a problem with cross contamination or analytical problems.  $K_d$  values of Se, I, Np, Pu, Tc, and U were calculated using Equation 1, which calculates sorption by subtracting the concentration of radionuclide added from the concentration remaining in solution at the end of the one-week equilibration period:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times m_{solids}} \quad (\text{Eq. 1})$$

where  $C_i$  is the aqueous activities of the initial (from the “no solids” controls) and  $C_f$  is the final equilibrium activity of each radionuclide (dpm/mL);  $V$  = volume of liquid in the final equilibrated suspension (mL); and  $m_{solids}$  is the solids mass (g).  $C_i$  and  $C_f$  values of the gamma emitting radionuclides, Am, Cd, Co, Ce, Cs, Hg, Sn, Sr, and Y were measured directly.  $K_d$  value was calculated from direct measurements of the activity on the solids and activity in the liquids (Eq. 2):

$$K_d = \frac{C_{solids}}{C_f} \quad (\text{Eq. 2})$$

where  $C_{solids}$  is the radionuclide activity measured on the solids (dpm/g) and  $C_f$  is the radionuclide concentration in the aqueous phase at the end of the sorption experiment (dpm/mL).

### 3.3 APPROACH TO EQUILIBRIUM STUDY

#### 3.3.1 Objectives – Approach to Equilibrium

The objective of this study was to determine the rate that radionuclides sorb to the cementitious materials. The reason that these measurements were made was to determine if the assumption of steady-state partitioning of the radionuclides between the liquid and cementitious materials was reasonable. The measurements were also made to permit comparison of (ad)sorption and desorption rates (discussed in more detail below in Section 3.4). When using the  $K_d$  construct, it is assumed that adsorption and desorption rates are equal.

#### 3.3.2 Materials – Approach to Equilibrium

The solids used in this study were the simulated Vault 2 concrete (Mix 1, Table 1) and DDA simulant Saltstone. These materials were ground to pass a 1000- $\mu\text{m}$  sieve and be held by a 75- $\mu\text{m}$  sieve fraction. The aqueous phase in this study was the calcite-saturated solution. The radionuclides used in this study were the gamma suite ( $^{241}\text{Am}(\text{III})$ ,  $^{109}\text{Cd}(\text{II})$ ,  $^{139}\text{Ce}(\text{III})$ ,  $^{60}\text{Co}(\text{II})$ ,  $^{137}\text{Cs}(\text{I})$ ,  $^{230}\text{Hg}(\text{II})$ ,  $^{75}\text{Se}(\text{VI})$ ,  $^{113}\text{Sn}(\text{IV})$ ,  $^{89}\text{Sr}(\text{II})$ , and  $^{88}\text{Y}(\text{III})$ ). The solids, liquids, and radionuclides are described in more detail in Sections 3.1.1, 3.1.2, and 3.1.3, respectively.

#### 3.3.3 Methods – Approach to Equilibrium

A series of 42 samples were used in this study:

(2 cementitious materials x 6 contact durations x 3 replicates) + (1 “no-solids” control in calcite saturated solution x 3 replicates) + (“no spike” control x 3 replicates) = 42 samples.

45 mL of the appropriate equilibration solution was added to each triplicated simulated Vault 2 concrete and DDA simulant Saltstone sample. A 0.5 mL mixed gamma spike was added to each tube. This addition was quickly followed by adding a 0.501 mL 4 M NaOH for pH adjustment to the original solution pH (pH range of 8.8 and 9.4). At the appropriate contact time, solids were

separated from liquids by centrifuging at 2000 rpm for 15 min. 40 mL of the centrifugate were analyzed by traditional gamma spectroscopy for the concentrations of radionuclides. The controls were recovered after 24 hr.

### 3.4 DESORPTION STUDY

#### 3.4.1 Objectives – Desorption

The objective of this study was to determine if the rate of desorption was the same as the rate of (ad)sorption of radionuclides. This study is important because reactive transport studies implicitly assume that the two processes occur at the same rate when the  $K_d$  construct is used. Furthermore, if different rates exist, then it may be more accurate to describe radionuclide desorption from cementitious materials using a kinetic model, instead of a steady-state  $K_d$  model<sup>4</sup>.

#### 3.4.2 Materials – Desorption

The solids used in this study were DDA simulant Saltstone and simulated Vault 2 concrete. The liquid used was a calcite-saturated solution with the Vault 2 concrete and a deoxygenated calcite with the DDA simulant Saltstone. The radionuclides used in this study were the gamma suite (<sup>109</sup>Cd(II), <sup>60</sup>Co(II), <sup>139</sup>Ce(III), <sup>230</sup>Hg(II), <sup>113</sup>Sn(IV), <sup>137</sup>Cs(I), <sup>241</sup>Am(III) and <sup>89</sup>Sr(II)). All of these materials are described in more detail in Sections 3.1.1, 3.1.2, and 3.1.3.

#### 3.4.3 Methods – Desorption

Approximately 1 g of solid phase recovered from the Approach to Equilibrium Study (Contact time = ~7 days, Section 3.3) was removed from the appropriate centrifuge tubes and wet packed into 34 mm x 13 mm OD x 11 mm ID polypropylene chromatography columns. These columns were fitted with 1/8" x 1/16" a Kynar tube fitting (Cole Parmer 30303-14 and a 1/16" barb fitting, Upchurch Scientific P 854X). The column was connected to a peristaltic pump system (Cole Parmer Model 7553-80 fitted with an Easy Load Masterflex® pump head, Model 7518-10 and a Masterflex Speed Controller) with Norprene size-13 tubing. The pump was connected to a reservoir containing calcite-saturated solution, with air sparged (bubbled) through it to promote O<sub>2(g)</sub> saturation. Flow rates for the desorption study were 0.73 to 0.75 mL/min. This flow rate is greater than the expected flow rate at the Saltstone facility, especially within the Saltstone itself, but a faster rate was selected to maximize the tendency for sorbed radionuclides to enter the aqueous phase, especially those solutes precipitated on the solid phases.

The columns were connected to separate gamma detectors in the vertical position and held in place with the use of duct tape. "Total gamma" emissions for each of the sorbed radionuclides were converted to "gamma/sec" detected for an initial period and for an additional 12 intervals covering a time span of approximately 18 days.

Because some of the radionuclide concentrations changed appreciably during the counting duration, it was necessary to correct some of the counts to a single meaningful value. For

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<sup>4</sup> By using a  $K_d$  term instead of a slow desorption rate term, the risk will be overestimated (yielding a conservative estimate for the groundwater PA scenario).

example, Sr values had to be corrected because the rate of desorption was high and the amount on the column at the start of the counting period was significantly more than the concentration at the end of the counting period. Other radionuclides that did not desorb from the column at fast rates, such as Sn, Ce, and Am, did not require this correction.

### 3.5 Tc SORPTION/DESORPTION KINETICS

A detailed description of the procedure used in this study is presented in Appendix A, Section 7.2.

#### 3.5.1 Objective – Sorption/Desorption Kinetics

1. Measure  $^{99}\text{TcO}_4^-$  sorption kinetics to DDA simulant Saltstone and simulated Vault 2 concrete. This information provided  $K_d$  values as well as kinetic information for use in subsurface contaminant transport calculations.
2. Measure  $^{99}\text{TcO}_4^-$  desorption kinetics. It was anticipated that sorption would occur very quickly, on the order of <1 day, whereas desorption would occur over a much longer duration, on the order of months to years. If this assumption was true, it would be unnecessarily conservative to describe the reaction with a single  $K_d$  value.

#### 3.5.2 Materials – Sorption/Desorption Kinetics

Solids used in this study were simulated Vault 2 concrete (Mix 1, 180010 from Ken Dixon; Table 1) and DDA simulant Saltstone ground to pass a 1000- $\mu\text{m}$  sieve and be held by a 75- $\mu\text{m}$  sieve fraction.

Liquids used in this study were  $\text{CaCO}_3$  Saturated Solution: 1 L of distilled deionized water was placed on a stir/heating plate and the temperature of the solution was raised by 3 to 10°C from ambient room temperature. As the solution was stirred with a stir bar, 0.01 g of  $\text{CaCO}_3$  was added. The mixture was left on the stir/heating plate for 8 hr and then it was passed through a 0.45- $\mu\text{m}$  membrane.

$\text{N}_{2(g)}$  sparged,  $\text{CaCO}_3$ -Saturated Solution: Sparge 200 mL with house  $\text{N}_{2(g)}$  for 30 min and passed through a 0.45  $\mu\text{m}$  membrane filter prior to using.

#### 3.5.3 Methods – Sorption/Desorption Kinetics

During the adsorption portion of the study, a series of identical serum vials were set up containing 0.1 g DDA simulant Saltstone or simulated Vault 2 concrete and 12 mL of appropriate  $\text{CaCO}_3$  Saturated Solution. There were two  $\text{CaCO}_3$  Saturated Solutions. One was unsparged and was added to the serum vials designed to simulate oxidized conditions. The other solution was sparged with  $\text{N}_{2(g)}$  and was added to the serum vials design to simulate more reducing conditions (conditions of a younger Saltstone or Vault cement). These samples were brought to chemical equilibrium by pre-equilibrating overnight with the aqueous phase. The samples were then spiked with  $^{99}\text{TcO}_4^-$ . Several control samples were included (no solid spike samples). Samples were then placed on an end-over-end shaker, as shown in the bottom photograph in Figure 1. Duplicate samples were sacrificed 0.5hr, 1 hr, 2 hr, 6 hr, 24 hr, and 2

weeks after adding the  $^{99}\text{TcO}_4^-$ . At these durations, the samples were taken off the shaker, permitted to settle, and then the liquid phase was recovered and passed through a 0.1- $\mu\text{m}$  filter and saved for liquid scintillation counting.

There were 10 samples each of the simulant Saltstone and simulated Vault 2 solids that were equilibrated for two weeks with the  $\text{TcO}_4^-$ . These samples were then reused for the desorption experiment. After the 2 week (ad)sorption period, the liquid phase was removed and  $\text{N}_2$ -sparged or unsparged  $\text{CaCO}_3$  Saturated Solutions were added to each tube. The samples were placed on an end-over-end shaker and then 2 samples were analyzed at each of the following durations: 1 hr, 1 day, 7 days, 13 days, and 26 days. At these durations, the solids were separated from the liquids by settling. Liquids were then passed through a 0.1- $\mu\text{m}$  filter and analyzed for  $^{99}\text{TcO}_4^-$  activity by liquid scintillation counting.

### 3.6 SALTSTONE REDUCTION CAPACITY

A detailed description of the materials and methods used for this measurement is presented in Appendix A, Sections 7.2.

#### 3.6.1 Objective –Reduction Capacity of Saltstone

The objective of this task was to measure the reduction capacity of DDA simulant Saltstone and to compare these results to those of pure SRS blast furnace slag, a 50-year old concrete, and SRS subsurface sediments.

#### 3.6.2 Materials – Reduction Capacity of Saltstone

1. Blast furnace slag
2. DDA Simulant Saltstone
3. Subsurface clayey sediments (Lysimeter Control Sediment)
4. Subsurface sandy sediment (from D. Kaplan's SRNL achieves)
5. 50-year old concrete recovered from D&D SRS site
6. 0.0500 M  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$  (FAS) solution
7. 0.0608 M Ce(IV) solution
8. 0.025M  $\text{Fe}(\text{o-phenanthroline})_3^{2+}$  solution

#### 3.6.3 Methods – Reduction Capacity of Saltstone

The reduction capacity was measured using a titration method developed by Angus and Glasser (1985).

The governing equation for this procedure is



The sample was ground to pass a 1000- $\mu\text{m}$  sieve and placed in an Erlenmeyer flask. Then, a 0.0608 M  $\text{Ce}^{4+}$  solution was added and the system was permitted to come to equilibrium. During this time, a fraction of the added  $\text{Ce}^{4+}$  was reduced to  $\text{Ce}^{3+}$  by the  $\text{S}^{2-}$  in the sample. A reaction-

neutral indicator solution, 0.025M Fe(o-phenanthroline)<sub>3</sub><sup>2+</sup>, was added and then the suspension was titrated with Fe<sup>2+</sup>, which is oxidized by the aqueous Ce<sup>4+</sup> that was not reduced by the solid sample.

In more detail, 0.5 g of sample were added to a 250-mL Erlenmeyer flask equipped with a stir bar. Then 25 mL of 0.06 M Ce(IV) (prepared from (NH<sub>4</sub>)<sub>4</sub>Ce(SO<sub>4</sub>)<sub>4</sub>•2H<sub>2</sub>O) were added to the sample. The contents of the flask were stirred with a magnetic stir bar for 1 hr at room temperature. Then 0.1 mL of 0.025M Fe(o-phenanthroline)<sub>3</sub><sup>2+</sup> solution were added, this solution is the indicator solution (It does not take part in the overall reactions and provides a colorimetric identification of the titration endpoint.). The 0.050 M (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)•6H<sub>2</sub>O solution was titrated until there was a change in color. This is the “Fe<sup>2+</sup>” in Equation 1. During titration, the solution goes from green to pale blue to lilac to pink. The reduction capacity was determined from the difference in the volume of Fe<sup>2+</sup> solution needed to titrate 25.0 mL of the Ce<sup>4+</sup> solution alone and with the blast furnace slag.

## 4.0 RESULTS

### 4.1 BATCH SORPTION STUDY

Before discussing the results, it is important to note that the K<sub>d</sub> values, as they are defined in Equations 1 and 2, include not only adsorption and absorption, but also (co)precipitation. Some (co)precipitation of the radionuclides was noted in the control samples that did not include any added solids. That is to say, aqueous radionuclide concentration decreases were observed in the absence of added solids. Therefore the measured decreases in aqueous radionuclides were due to causes other than the sorption of the radionuclides by the added solid phases. Instead, readily reversible reactions and some (co)precipitation were measured; (co)precipitation tends to have a much faster forward reaction (precipitation) than a backward reaction (dissolution). There will be more discussion about the precipitation noted in the controls below (Section 4.2).

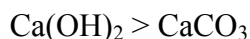
K<sub>d</sub> values measured with DDA simulant Saltstone, partially oxidized DDA simulant Saltstone, and simulated Vault 2 concrete are presented in Table 2. These measurements were done on a laboratory bench top, *i.e.*, under oxidizing conditions.

<sup>75</sup>Se K<sub>d</sub> values ranged from 29.7 to 78.5 mL/g and a ranking of the solids by their K<sub>d</sub> values shows:

Saltstone > partially oxidized Saltstone > Vault 2 concrete.

This ranking is the expected result, given that the blast furnace slag is expected to be a strong adsorbent because it contains elevated concentrations of Al and Fe phases for aqueous metals and anions to sorb to (Oguz 2004). And as mentioned above, it also contains mineral phases that are strong reductants, which may also play an important role. Oguz (2004) reported that blast furnace slag was an excellent material for removing phosphate (PO<sub>4</sub><sup>3-</sup>) from water. The chemistry of phosphate and selenate have many similarities given their anionic character, being oxyanions, and their proximity in the periodic table.

The solutions used in this study were  $\text{Ca}(\text{OH})_2$ -saturated water and  $\text{CaCO}_3$ -saturated water; used as surrogates for young cementitious pore water and aged cementitious pore water, respectively. A ranking of these solutions by Se  $K_d$  values were generally:



This ranking is expected for anionic radionuclides because the divalent  $\text{CO}_3^{2-}$  can out-compete many anions for sorption sites, especially monovalent anions (*e.g.*,  $\text{TcO}_4^-$ ). The difference in Se sorption between these two background solutions cannot be attributed to differences in pH, because the  $\text{Ca}(\text{OH})_2$  suspension generally had a pH of  $\sim 12$ , whereas the  $\text{CaCO}_3$  solutions had a pH of  $\sim 10$ . All the Se  $K_d$  values measured were less than literature Se  $K_d$  values and Se  $K_d$  values previously recommended (Kaplan 2007). However, these values are lower limits due to the filtrate activities being very low and close to the detection limits.

$\text{TcO}_4^-$   $K_d$  values were two orders of magnitude lower than Se  $K_d$  values, ranging from -0.02 to 0.93 mL/g Table 2. This result is not surprising given its “hard” chemical behavior and its valence state of negative 1. A ranking of the solid phase by  $\text{TcO}_4^-$   $K_d$  values was similar to that for Se  $K_d$  values, except that the partially oxidized DDA simulant Saltstone and the simulated Vault 2 concrete had similar  $K_d$  values. Like Se  $K_d$  values, Tc  $K_d$  values measure in the  $\text{Ca}(\text{OH})_2$  solution (young cement porewater) were generally greater than those measured in the  $\text{CaCO}_3$  solution. Perhaps most importantly, two of the six  $\text{TcO}_4^-$  values reported in Table 2 were non-zero values. This result supports the use of a non-zero  $\text{TcO}_4^-$   $K_d$  value for these solids.

Iodine was added as iodide,  $\text{I}^-$ , the likely form of iodine in these systems. The measured iodine  $K_d$  values were generally less than previously recommended iodine  $K_d$  values (Kaplan 2007). One possible reason that the measured  $K_d$  values are less than those previously recommended values is because the latter values came from the literature (primarily from Bradbury and Sarott, 1995), which in turn were taken from experiments typically conducted in distilled deionized water. Therefore, the amounts of competing anions ( $\text{OH}^-$  and  $\text{CO}_3^{2-}$ ) in the aqueous phase were likely appreciably less than those in this study. It could be argued that the experiments reported here were conducted under chemical conditions closer to conditions expected under field conditions than the experiments that used water.

Regretfully, no U  $K_d$  data were obtained. There was a problem measuring  $^{233}\text{U}$  in these experiments. The U peak in the spectra had shifted and could not be deconvoluted from the  $^{99}\text{Tc}$  peak. Oddly, the no-solids controls did not have this problem. One possible explanation is that the  $^{233}\text{U}$  took on a colloidal character (suspended solids), such as uranyl-carbonate or hydroxyl species.

Np  $K_d$  values were appreciably greater than literature values. It is quite likely that the Np, added as Np(V), was reduced to Np(IV), a strongly binding form of Np. Similarly, Pu  $K_d$  values were very high. These values, generally  $>100,000$  mL/g, are consistent with Pu  $K_d$  values measured with other SRS cementitious materials (Kaplan and Coates 2007). For oxidizing cementitious solids, Kaplan and Coates (2007) measured Pu  $K_d$  values ranging from 92,200 mL/g for older oxidized cementitious materials (in equilibrium with  $\text{CaCO}_3$ ) to 99,700 mL/g in young

cementitious porewater (in equilibrium with  $\text{Ca}(\text{OH})_2$ ). Pu  $K_d$  values with reducing grout were significantly less: in  $\text{Ca}(\text{OH})_2$  Pu  $K_d$  values were 5,760 mL/g and in  $\text{CaCO}_3$ , Pu  $K_d$  values were 11,055 mL/g. Bradbury and Sarott (1995) reported that there was no difference between Pu  $K_d$  values measured under oxidized or reducing conditions.

DDA simulant Saltstone  $K_d$  values were also measured under reducing conditions (Table 3). Iodine  $K_d$  values were about the same as those previously recommended by Kaplan (2006). Se activities in the aqueous fraction were very low and very near detection limits. As a result, Se  $K_d$  values were  $>35$  mL/g; this value is not especially informative because it was expected that Se  $K_d$  values would be much greater than this value. Consequently, no change in future recommendations to Se  $K_d$  values will be made based on these data. Np  $K_d$  values under reducing conditions were expected to be greater than those measure under oxidizing conditions because Np(IV) is well know to have lower solubility and  $K_d$  values than Np(V). Np  $K_d$  values under reducing conditions were 5,234 to 6,911 mL/g (Table 3), which are consistent with the Np  $K_d$  values measured under oxidizing conditions  $>4000$  mL/g (Table 2). It should be kept in mind that both the Vault and the Saltstone have blast furnace slag in them and even under oxidizing conditions, one could expect these solids to have ample amount of reductant to reduce many radionuclides. Had the Np remained as Np(V), the expected  $K_d$  value would have been on the order of 10 mL/g. Apparently, even under more oxidizing conditions, these solids could readily reduce Np(V) to Np(IV), yielding the large  $K_d$  values.



**Table 2.  $K_d$  values for simulated Vault 2 concrete, reducing Saltstone and partially oxidized Saltstone under oxidizing conditions (benchtop and exposed to air).**

Nuclide	Solid	Solution <sup>a</sup>	$K_d$ (mL/g)	Std. Dev. of 2 replicates	Value previously reported (mL/g) <sup>b</sup>
<sup>75</sup> Se	Vault 2	Ca(OH) <sub>2</sub>	29.7	4.3	300
		CaCO <sub>3</sub>	>36.5	24.7	150
	Reducing Saltstone	Ca(OH) <sub>2</sub>	>78.5	50.8	300
		CaCO <sub>3</sub>	>42.7	30.1	150
	Partially Oxidized Saltstone	Ca(OH) <sub>2</sub>	>65.0	26.0	300
		CaCO <sub>3</sub>	>39.8	25.3	150
<sup>99</sup> Tc	Vault 2	Ca(OH) <sub>2</sub>	0.23	0.02	5000
		CaCO <sub>3</sub>	0.17	0.01	5000
	Reducing Saltstone	Ca(OH) <sub>2</sub>	0.93 <sup>c</sup>	0.06 <sup>c</sup>	5000
		CaCO <sub>3</sub>	0.16	0.14	5000
	Partially Oxidized Saltstone	Ca(OH) <sub>2</sub>	0.25	0.02	5000
		CaCO <sub>3</sub>	-0.02	0.03	5000
<sup>125</sup> I	Vault 2	Ca(OH) <sub>2</sub>	8.94	7.02	2-10
		CaCO <sub>3</sub>	-0.01	5.89	4
	Reducing Saltstone	Ca(OH) <sub>2</sub>	7.15	4.40	2-10
		CaCO <sub>3</sub>	-5.29	2.79	4
	Partially Oxidized Saltstone	Ca(OH) <sub>2</sub>	3.94	1.89	2-10
		CaCO <sub>3</sub>	10.76	7.16	4
<sup>233</sup> U	Vault 2	Ca(OH) <sub>2</sub>	d		2500
		CaCO <sub>3</sub>	d		2500
	Reducing Saltstone	Ca(OH) <sub>2</sub>	d		2500
		CaCO <sub>3</sub>	d		2500
	Partially Oxidized Saltstone	Ca(OH) <sub>2</sub>	d		2500
		CaCO <sub>3</sub>	d		2500
<sup>237</sup> Np	Vault 2	Ca(OH) <sub>2</sub>	>4,358	1,977	3000
		CaCO <sub>3</sub>	>3,856	1,415	300
	Reducing Saltstone	Ca(OH) <sub>2</sub>	>3,847	1,370	3000
		CaCO <sub>3</sub>	>3,701	1,198	300
	Partially Oxidized Saltstone	Ca(OH) <sub>2</sub>	>4,218	1,326	3000
		CaCO <sub>3</sub>	>4,032	1,475	300
<sup>238</sup> Pu	Vault 2	Ca(OH) <sub>2</sub>	>97,138	56,695	5000
		CaCO <sub>3</sub>	>100,256	59,584	500
	Reducing Saltstone	Ca(OH) <sub>2</sub>	>105,863	11,385	5000
		CaCO <sub>3</sub>	>102,191	60,053	500
	Partially Oxidized Saltstone	Ca(OH) <sub>2</sub>	>96,965	62,347	5000
		CaCO <sub>3</sub>	>110,159	69,152	500

<sup>a</sup> = Ca(OH)<sub>2</sub> solution was used to represent the pore water of young cementitious materials, CaCO<sub>3</sub> solution was used to represent pore water from aged cementitious materials. The pH at the end of equilibration for the CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> treatments were pH ~10 and pH ~12, respectively.

<sup>b</sup> from Kaplan and Coates (2007): from Table 11, "Best" data for 1<sup>st</sup> & 2<sup>nd</sup> stage (Ca(OH)<sub>2</sub>; young and moderately aged stage) and 3<sup>rd</sup> stages (aged cement)

<sup>c</sup> = based on single measurement

<sup>d</sup> = The quality of the spectra generated for the <sup>233</sup>U analyses was compromised by a peak shift into the large <sup>99</sup>Tc region of the spectra.

**Table 3.  $K_d$  values for DDA simulated Saltstone under reducing conditions (purged with  $N_2$  and equilibrated for 19 days).**

Nuclide	Solution <sup>a</sup>	$K_d$ (mL/g)	Std. Dev. of 2 replicates	Value previously used <sup>b</sup> (mL/g)
<sup>75</sup> Se	Ca(OH) <sub>2</sub>	>35.1	35.6	300
	CaCO <sub>3</sub>	>56.7	41.1	150
<sup>99</sup> Tc	Ca(OH) <sub>2</sub>	91.3 <sup>c</sup>	114.6	5000
	CaCO <sub>3</sub>	6.5 <sup>c</sup>	2.6	5000
<sup>125</sup> I	Ca(OH) <sub>2</sub>	13.8	1.7	2
	CaCO <sub>3</sub>	-3.2	4.1	4
<sup>233</sup> U	Ca(OH) <sub>2</sub>	<sup>c</sup>	--	2500
	CaCO <sub>3</sub>	<sup>c</sup>	--	2500
<sup>237</sup> Np	Ca(OH) <sub>2</sub>	>5,234	2,782	3000
	CaCO <sub>3</sub>	>6,911	2,478	300
<sup>238</sup> Pu	Ca(OH) <sub>2</sub>	12,176	5,607	5000
	CaCO <sub>3</sub>	165,570	111,515	500

<sup>a</sup> = Ca(OH)<sub>2</sub> solution was used to represent the pore water of young cementitious materials, CaCO<sub>3</sub> solution was used to represent pore water from aged cementitious materials

<sup>b</sup> from Kaplan and Coates (2007): from Table 11, "Best" data for 1<sup>st</sup> & 2<sup>nd</sup> stage (Ca(OH)<sub>2</sub>; young and moderately aged stage) and 3<sup>rd</sup> stages (aged cement)

<sup>c</sup> quality of the spectra generated for the analyses was compromised by the <sup>233</sup>U peak shift into the <sup>99</sup>Tc region of the spectra

Based on the data in Table 2 and Table 3, recommended  $K_d$  values for reducing concrete are presented in Table 4 and Table 5. These latter tables also include previously recommended  $K_d$  values. It is our intention to change recommended  $K_d$  values as few times as possible. Changes will be made when there are major changes in measured versus recommended  $K_d$  values, the change is consistent with first principles of geochemistry, and a preponderance of evidence exist in support of the change. For this study, changes were recommended only when there was a greater than 2x change in measured versus recommended (Kaplan and Coates 2007)  $K_d$  values. Based on these criteria, Np and Pu greater recommended  $K_d$  values were warranted (also used for this analysis the raw data of Kaplan and Coates 2007). Conversely, I  $K_d$  values were reduced.

**Table 4. Recommended changes to  $K_d$  values based on the results of this study:  
Comparison to previous recommendations for Stages 1 and 2**

	Table 14, Stage 1 & 2 WSRC-STI-2006- 00004, Rev. 1 (Kaplan 2007)	Table 11, Stage 1 & 2 WSRC-STI-2007-00640 (Kaplan and Coates 2007)	New, this report, Stage 1 & 2 SRNS-STI-2008-00045
Sn	4,000	5,000	5,000
Am	5,000	5,000	5,000
Ce	5,000	5,000	5,000
Y	5,000	5,000	5,000
Cd	NA	5,000	5,000
Co	1,000	5,000	5,000
Hg	NA	1,000	1,000
Sr	1	0.5-3.0	0.5-3.0
U	5,000	2,500	2,500
Cs	2 - 4	0 - 2	0 - 2
Np(V)	2,000	3,000	<b>4,000</b>
Pa(V)	2,000	5,000	5,000
Pu	5,000	5,000	<b>10,000</b>
I	8 - 20	2 - 10	<b>5 - 9</b>
Tc(VII)	5,000	5,000	5,000
Se	300	300	300

<sup>(a)</sup> Bold values changed from Kaplan and Coates (2007) as a result of the data from this study.

**Table 5 . Recommended changes to  $K_d$  values based on the results of this study:  
Comparison to previous recommendations for Stage 3**

	Table 14 Stage 3, WSRC- STI-2006-00004, Rev. 1 (Kaplan 2007)	Table 11, Stage 3, WSRC- STI-2007-00640 (Kaplan and Coates 2007)	New, this report, Stage 3 SRNS-STI-2008-00045
Sn	2,000	2,000	2,000
Am	500	1,000	1,000
Ce	500	1,000	1,000
Y	500	1,000	1,000
Cd	NA	1,000	1,000
Co	500	1,000	1,000
Hg	NA	300	300
Sr	0.8	20	20
U	5,000	2,500	2,500
Cs	2	10	10
Np(V)	200	300	<b>3,000</b>
Pa(V)	200	500	500
Pu	500	500	<b>10,000</b>
I	0	4	<b>0</b>
Tc(VII)	5,000	5,000	5,000
Se	150	150	300

<sup>(a)</sup> Bold values changed from Kaplan and Coates (2007) as a result of the data from this study.

## 4.2 APPROACH TO EQUILIBRIUM STUDY

The approach to equilibrium study conducted with the gamma emitting suite of radionuclides ( $^{241}\text{Am}$ ,  $^{109}\text{Cd}$ ,  $^{139}\text{Ce}$ ,  $^{203}\text{Hg}$ ,  $^{113}\text{Sn}$ ,  $^{85}\text{Sr}$ ,  $^{137}\text{Cs}$ , and  $^{88}\text{Y}$ ) was unsuccessful. Precipitation of the radionuclides occurred when added to “no solids control” samples containing calcite-saturated and the Portlandite-saturate solutions. This behavior was noted in the “no-solid control” samples included as part of the quality assurance of this study (Table 6). There should be no precipitation in these control samples. The cause for this precipitation is not known and is surprising because last year, similar experiments were conducted (Kaplan and Coates 2007). The same background solutions (saturated- $\text{Ca}(\text{OH})_2$  and - $\text{CaCO}_3$  solutions) and radiological spike solutions were used, but negligible precipitation was observed in the no-solids controls. Results for the Approach to Equilibrium (Table 17 and Table 18) and the Batch  $K_d$  (Table 20, Table 21, and Table 21) studies with the gamma suite are presented in Appendix C. These results are presented in an appendix instead of the body of the text because the interpretation of the results is not straight forward owing to the fact that the no-solids control samples indicated that (homogeneous) precipitation had occurred.

Previously, it was showed that with reducing grout and a 50-year-old concrete, it took less than one or two days for radionuclides to come to (ad)sorption steady state and months to years to come to desorption steady state (Kaplan and Coates 2007).

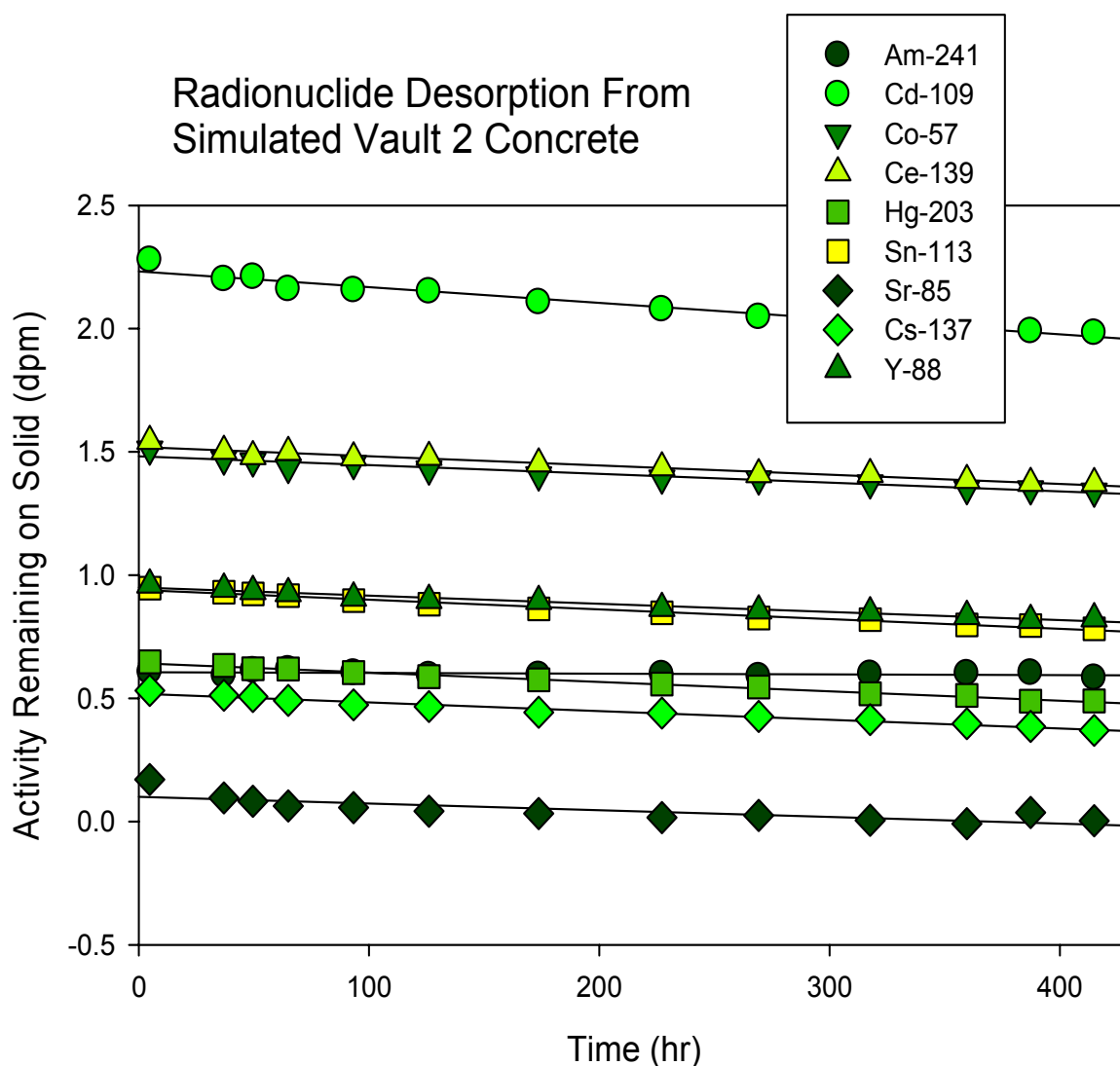
**Table 6. Percentage of radionuclide in the no-solids controls at end of experiment.**

	CaCO <sub>3</sub>		Ca(OH) <sub>2</sub>	
	Oxygenated	Deoxygenated	Oxygenated	Deoxygenated
Am-241 <sup>(a)</sup>	<0.2	<0.5	<0.2	0.5
Cd-109 <sup>(a)</sup>	1.6	0.3	2.3	0.3
Ce-139 <sup>(a)</sup>	<0.3	<0.5	<0.4	<0.5
Hg-203 <sup>(a)</sup>	37.1	41.3	25.8	36.3
Sn-113 <sup>(a)</sup>	4.3	2.8	10.1	10.8
Sr-85 <sup>(a)</sup>	71.5	77.8	70.1	74.5
Cs-137 <sup>(a)</sup>	84.2	88.7	83.9	86.3
Y-88 <sup>(a)</sup>	0.1	0.1	0.1	0.1
Co-60 <sup>(a)</sup>	0.2	0.2	4.9	0.6
Se-75	94	NA	132	NA
Pu-238	98	NA	103	NA
Np-237	93	NA	100	NA
Tc-99	87	NA	88	NA

<sup>(a)</sup> These gamma emitting isotopes were combined in one spiking solution for these tests.

### 4.3 DESORPTION STUDY

The objective of this task was to determine if radionuclide desorption was reversible. In the context of a chemical reaction, this behavior means that the rate of adsorption is equal to the rate of desorption. Another important objective of this work was to measure desorption kinetics. If the desorption rate is in fact slow, it may be more accurate to describe it with a kinetic term, rather than a steady state term, such as a  $K_d$  value. Our approach was to add a suite of gamma-emitting aqueous radionuclides to crushed DDA simulant Saltstone during a 7-day contact period. The DDA simulant Saltstone containing the (ad)sorbed radionuclides was then packed in a small column and the column placed directly on a gamma counter. Influent and effluent tubes were hooked up to the column and calcite-saturated water was slowly passed through the column. The flow rate was greater than that anticipated in the Z-Area Saltstone Facility, but it provided a bounding condition for optimal radionuclide desorption. Desorption was enhanced because the high flow rates (with respect to groundwater) would maintain the aqueous radionuclide concentrations low, promoting the solid phase radionuclides to desorb or dissolve into the aqueous phase.



**Figure 2. Desorption of radionuclides from simulated Vault 2 concrete as a function of time.**

The desorption from Simulated Vault 2 concrete (Figure 2) was much slower than the (ad)sorption, which was complete in less than one day (Appendix C: Table 17 and Table 18). It was expected that desorption would decrease with valence state. Instead, it was observed that the trivalent Am(III), and Y(III) desorbed at about the same rate as the divalent Co(II) and Cd(II). It is possible that chemical speciation had a role in the observed results as trivalent cations would be expected to form stronger hydroxyl complexes, which may have offset the electrostatic attraction differences between the trivalent and divalent cations. The largest decrease in activity during the 18 hr desorption period was seen for Sr(II) and Cs(I). Desorption of a radionuclide, RN, can be generically written as:



where  $\bullet S$  is a sorption site on a solid. A first-order description of Equation 4 can be expressed as:

$$\ln\left(\frac{RN \bullet S_t}{RN \bullet S_0}\right) = -kt \quad (\text{Eq. 5})$$

where  $RN \bullet S_t$  and  $RN \bullet S_0$  are the activity of the radionuclide on the solid phase at time  $t$  and time  $0$ , respectively. First-order fitted parameters for the data in Figure 2 are presented in Table 7. All the fits to the data to Equation 4 were highly statistically significant, except for Am, as shown by the “Significant F Value” and the correlation coefficient,  $R^2$ . As a demonstration of how these data can be used, Table 7 includes the percent of the radionuclide expected to remain on the Saltstone after 100 days. For example, after 100 days, 88.3% of the Am and 0% of the Sr are expected to remain on the solid after 100 days. The important point of this discussion is whereas (ad)sorption of these radionuclides required <1 day, desorption of these radionuclides was largely incomplete after 100 days.

**Table 7. First-order kinetic information related to the desorption of radionuclides from Vault 2 simulated concrete, as described in Equation 5.**

	Am	Cd	Co	Ce	Hg	Sn	Sr	Cs	Y
Slope (1/hr) <sup>a</sup>	-0.001	-0.007	-0.006	-0.006	-0.016	-0.011	-0.142	-0.018	-0.009
Significant F Value	<0.15	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0002	<0.0001	<0.0001
$R^2$	0.193	0.984	0.973	0.977	0.991	0.991	0.621	0.980	0.982
$\ln(A/A_0)$ , 100 d <sup>b</sup>	-0.12	-0.68	-0.56	-0.59	-1.61	-1.07	-14.19	-1.85	-0.87
% on solid, 100 d <sup>b</sup>	88.3	50.9	57.2	55.7	19.9	34.2	0.0	15.8	41.9

(a) Slopes are equal to  $k$  in Equation 5.

(b) Calculated value after 100 days, based on Equation 5 and  $k$  (negative value of the “Slope”) noted in the first row.  
 “% on solid” =  $A/A_0 \times 100$

Figure 3 contains similar data as above except for DDA simulant Saltstone. These experiments were not conducted for as long as those with simulated Vault 2 concrete and as a result it was not possible to calculate meaningful first-order kinetic information. However, the general trends are very similar to those for simulated Vault 2. The corresponding 1<sup>st</sup> order kinetic terms for the data in Figure 3 are presented in Appendix B, Table 16.

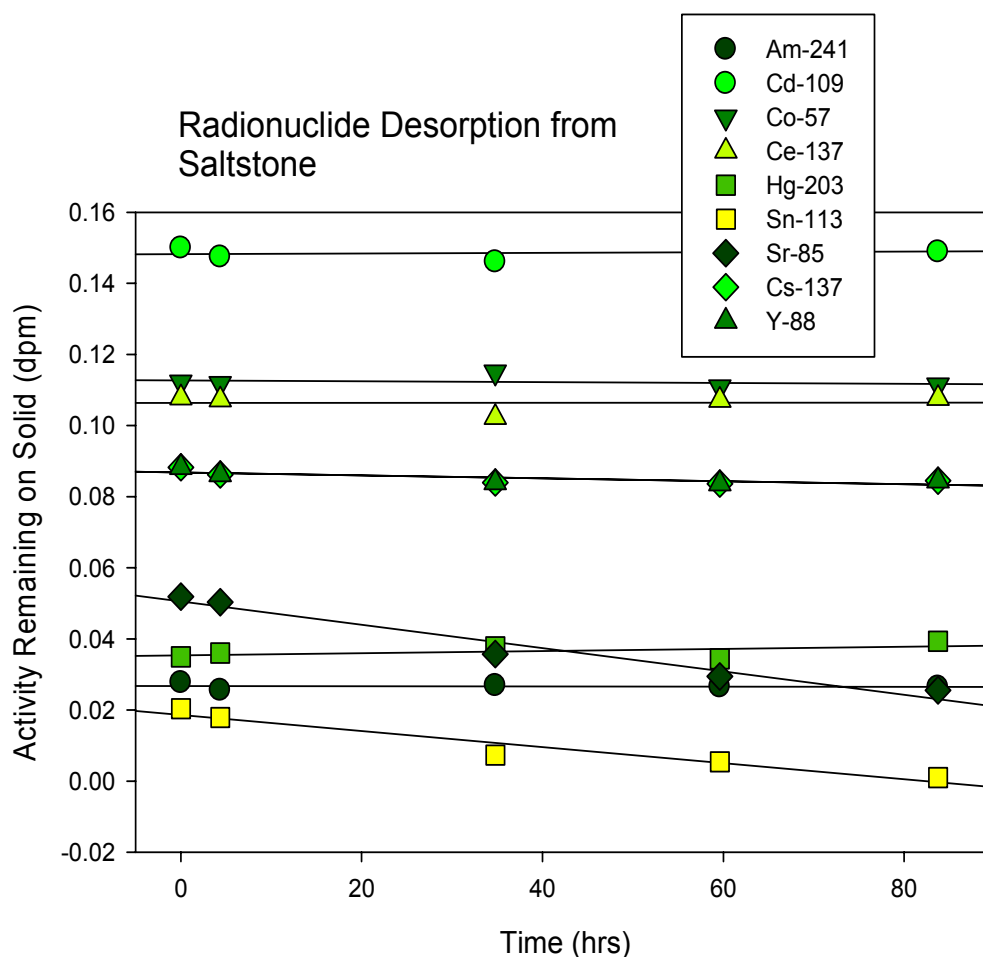


Figure 3. Desorption of radionuclides from DDA simulant Saltstone as a function of time.

#### 4.4 Tc SORPTION/DESORPTION KINETICS

The objective of this batch experiment was to compare the (ad)sorption kinetics to the desorption kinetics. It was anticipated that Tc would sorb much more quickly than it would desorb. The scenario that this experiment was designed to represent was one in which  $\text{TcO}_4^-$  comes in contact with and sorbs to Saltstone (under reducing conditions) or Vault 2 concrete (under oxidizing conditions), then cementitious porewater enters the system. This scenario was simulated by first permitting the solids to equilibrate in  $\text{CaCO}_3$ -saturated solution for about two weeks, with the intent of creating reducing conditions. Then  $\text{TcO}_4^-$  was added and permitted to equilibrate for 14 days. After 14 days, the solid phase was washed twice quickly to remove any interstitial Tc, and 14 mL of the  $\text{CaCO}_3$  saturated solution was added and left in contact with the solid phase. The amount of Tc that was desorbed in the following 26 days was monitored.

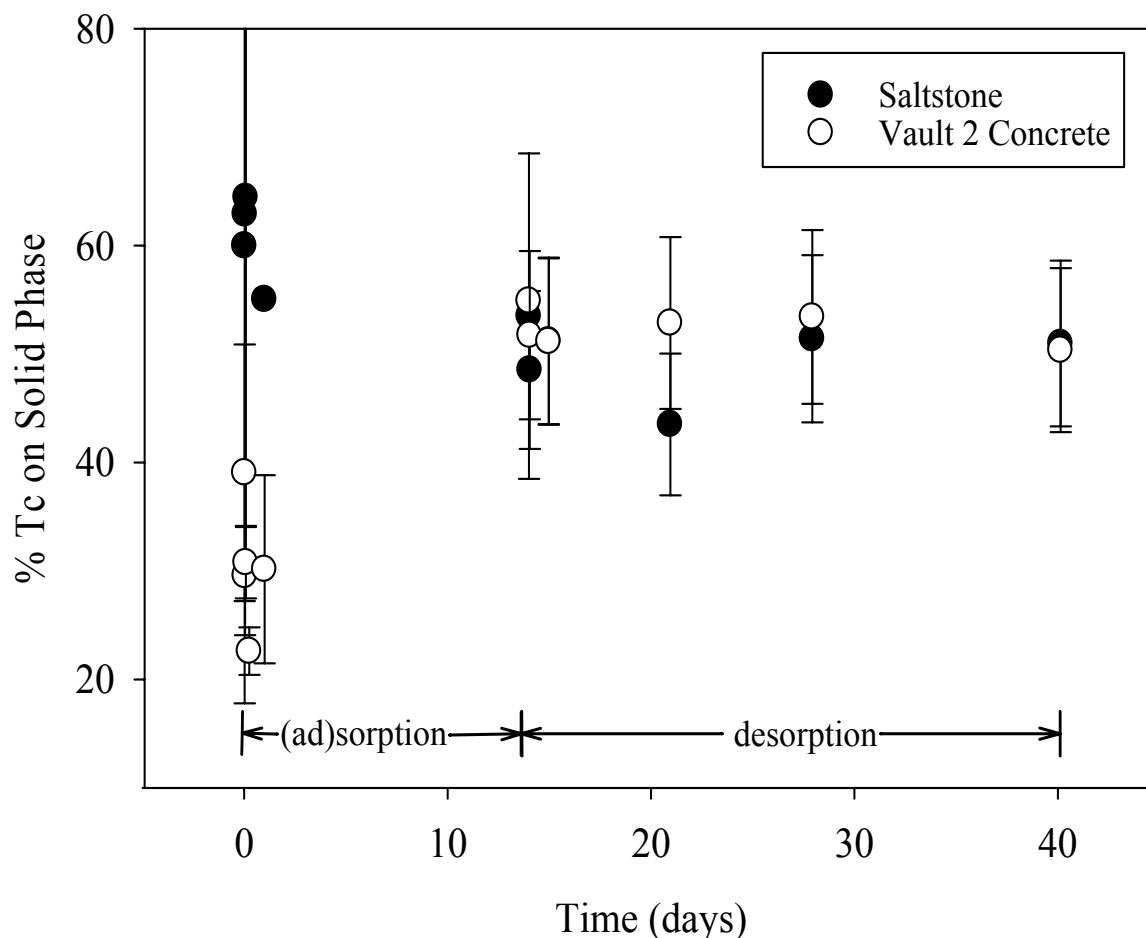
The first important point to make is that, even at its maximum, relatively little Tc was sorbed by the simulated Vault 2 concrete or the DDA simulant Saltstone (Figure 4). Expressed in terms of a  $K_d$  value, the Tc  $K_d$  value for the DDA simulant Saltstone was 13.0 mL/g and that for



simulated Vault 2 concrete was 28.1 mL/g. Tc  $K_d$  values for DDA simulant Saltstone measured in a separate task (Table 3) was  $6.5 \pm 2.6$  mL/g. Both Tc  $K_d$  values are more reflective of adsorption than precipitation, the latter being the expected Tc removal mechanism under reducing conditions. Had reduction of Tc(VII) to Tc(IV) occurred as expected, essentially all the Tc would have been removed from the aqueous phase due to precipitation of either  $\text{TcO}_{2(s)}$  or some Tc-Sulfide phase (Lukens *et al.* 2005). The cause for no or only partial reduction to occur is not known, but it is certain the material has a large reduction capacity and can generate very low redox conditions (Eh; discussed in greater detail in Section 3.6). One possible explanation for these results is that it takes more than the two weeks used in this study to create sufficiently reducing conditions to promote Tc(VII) reduction to Tc(IV). If this condition is the case, then the results arise from an experimental artifact because the true system would have many years to equilibrate.

$\text{TcO}_4^-$  sorption was essentially instantaneous (Figure 4). In fact, slightly more Tc was sorbed by the DDA simulant Saltstone after 34 min than after 14 days. This observation may be the result of Saltstone salts solubilizing into the aqueous phase, introducing competing anions for Tc sorption. Simulated Vault 2 sorbed about 30% of the Tc the first day, then sorbed an additional 25% after 14 days. Both DDA simulant Saltstone and simulated Vault 2 concrete sorbed about the same amount of Tc after 14 days,  $54.2 \pm 1.0$  % Tc.

Ten Saltstone and 10 Vault 2 concrete samples that had sorbed Tc for 14 days, were used in the desorption portion of this study (Figure 4). After 1 hr, Tc concentrations dropped in the Vault 2 suspensions by 6% and in the Saltstone suspensions by 3%. After that initial release of Tc (perhaps reflective of a very weakly bound form of Tc) there was a very slow release of Tc. After 26 days of desorption, an additional 4% of the Tc had desorbed from the DDA simulant Saltstone and an additional 2% had desorbed from the simulated Vault 2 concrete. Therefore, after 26 days, only 7 and 8 % of the sorbed Tc had desorbed from the DDA simulant Saltstone and simulated Vault 2 concrete, respectively. The most important conclusion from this work is that sorption of Tc was appreciably faster than desorption, as was the case with the other radionuclides (Am, Cd, Ce, Co, Cs, Hg, Sn, Sr, and Y) discussed in Section 4.3.



**Figure 4. Tc sorption for 14 days followed by 26 days of desorption from DDA simulant Saltstone and simulated Vault 2 concrete. Experiment was conducted in a saturated  $\text{CaCO}_3$  solution.**

#### 4.5 SALTSTONE REDUCTION CAPACITY

The reduction capacities of various materials are presented in Table 8. A sample of 100% blast furnace slag was included in the samples as a control because there are no nationally recognized standards for this measurement. Instead, the 100% blast furnace slag is the only material that has been measured by more than one laboratory. Lukens *et al.* (2005), from Lawrence Berkeley National Laboratory, reported a SRS blast furnace slag reduction capacity of 820  $\mu\text{eq/g}$  (micro-equivalents/gram). Using the identical materials, two years later Kaplan *et al.* (2005) measured a near identical reduction capacity of  $817 \pm 1.4 \mu\text{eq/g}$ . The value reported in Table 8,  $832.4 \pm 4.9 \mu\text{eq/g}$ , is in excellent agreement with those previous measurements and provides some assurance of the data quality.

An unexpected result from this work was that the DDA simulant Saltstone sample had the same reduction capacity as the 100% blast furnace slag, even though it contained only 23 wt-% blast furnace slag. Five possible explanations for this result are advanced.

- One possible explanation is that for the higher pH Saltstone system, more  $\text{Ce}^{4+}$  was sorbed by the Saltstone during the measurement of the reduction capacity, producing the illusion that more reduction existed in the sample than in reality. This effect would be an experimental artifact. But it should be noted that the  $\text{Ce}^{4+}$  species used in this study,  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , was carefully selected for this procedure because it has weak interactions with surfaces.
- This result may be due to the difference in pH of the Saltstone, pH 11.85, and the blast furnace slag, pH 8.1. Slag is a glassy (amorphous) silicate that likely has inclusions of iron sulfides and other reducing iron phases. At the high pH of the Saltstone system, the silicate matrix may have dissolved, making the reducing inclusions more available to the aqueous phase.
- The Saltstone is behaving as a semi-conductor, permitting electrons to readily travel through it when a potential exists at the surface (*e.g.*, when  $\text{TcO}_4^-$  lies on the Saltstone surface, it may create a potential between the interior slag-Fe(0/II) and the  $\text{TcO}_4^-$ ). A number of Fe-(oxy)hydroxides (goethite, hematite, and ferrihydrite) have been shown recently to behave as semi-conductors, materials in which electron transfer occurred between solid phase-interior and -exterior Fe ions (see references in Williams and Scherer 2004).
- It is very likely that some of the minerals in the fly ash used to make the Saltstone also contained some reducing capacity, for example, pyrrhotite and magnetite (Yossifova et al. 2007).
- Finally, it is possible that the Saltstone has a greater microporosity than the slag alone. The greater microporosity may have been produced when the slag dissolved into the Ca-Si-hydroxide gel of the Saltstone. The result is that the reaction surface area of the reducing components in the Saltstone might be much higher than the slag alone.

Of the possible explanations, the last four are the most likely. Importantly, whatever the cause for the extraordinarily high Saltstone reduction capacity, it was reproducible in the laboratory, as indicated by the low standard deviation value (Table 8).

Similarly, the simulated Vault 2 concrete (Mix 1) used in these studies had only 10 wt-% blast furnace slag, yet its reduction capacity,  $239.8 \pm 31.1 \mu\text{eq/g}$ , *i.e.*, ~30% that of pure blast furnace slag (Table 8). The reduction potential of typical subsurface “red clay” sediment commonly found in SRS Upper Vadose Zones had a potential of  $24.4 \pm 0.7 \mu\text{eq/g}$ . The reduction potential in SRS sediments originates almost entirely from the Fe-(oxy)hydroxides. The sediment reduction potential is relatively quite low, but given the enormous amount of sediment with which a plume may come in contact, this reduction capacity may prove important for maintaining contaminants in a less-mobile reduced form once they leave the engineered barrier.

**Table 8. Reduction capacity of various materials.**

<b>Sample</b>	<b>Reducing Equivalents (<math>\mu\text{eq/g}</math>)</b>	<b>Percent blast furnace slag in formulation (wt-%)</b>
DDA simulant Saltstone	$821.8 \pm 8.1$	23
Vault 2 concrete (mixture 1)	$239.8 \pm 31.1$	10
Blast furnace slag	$832.4 \pm 4.9^{(a)}$	100
Subsurface Red Sediment	$24.4 \pm 0.7$	NA
Subsurface Sandy Sediment	$81.2 \pm 12.1$	NA
Cement from 50 yr Old SRS Concrete	$85.5 \pm 10.1$	NA

<sup>(a)</sup> Lukens *et al.* (2005) reported blast furnace slag reduction capacity by the Ce(IV) method to be  $820 \mu\text{eq/g}$ . Kaplan *et al.* (2005) also measured the reduction capacity of this material and reported essentially the identical value,  $817 \pm 1.4 \mu\text{eq/g}$ . The value reported for this study is in excellent agreement with these previous reported values.

Some measurements were also made of the redox condition of the system, as measured by an Eh probe. This instrument measures an intensity term, compared to reduction capacity, which is a measure of capacity of the system. The two measurements are related in a similar way as pH is to total acidity, the former is an intensity term and the latter is a capacity term. Eh, like pH, is useful for conducting thermodynamic calculations and is strongly related to the speciation of many radionuclides. Air-sparged  $\text{CaCO}_3$ -saturated solution (simulating an aged groundwater in a cementitious environment) was passed through a column of partially oxidized DDA simulant Saltstone (BioRad Econo-pak column; length = 6 cm, diameter = 1.5 cm) (Figure 5). The aqueous phase Eh was initially extremely low, -750 mV. This Eh value is well below that necessary to promote the reduction of  $\text{Tc}^{\text{VII}}\text{O}_4^-$  to  $\text{Tc}^{4+}$ . As soon as the oxygenated aqueous phase was passed through the partially oxidized DDA simulant Saltstone, the effluent became increasing oxygenated. There was an initial rapid increase in Eh to  $\sim 0$  mV, then the Eh continued to rise, but at a much slower rate. Concurrent with the rise in Eh was a decrease in pH. This is a common pH-Eh relationship that can be ascribed in a general manner to the following equation:



Log transforming Equation 6 produces:

$$\log(\text{H}^+) + \log(\text{e}^-) = \frac{1}{2} \log \text{H}_2(\text{g}) \quad (\text{Eq. 7})$$

or

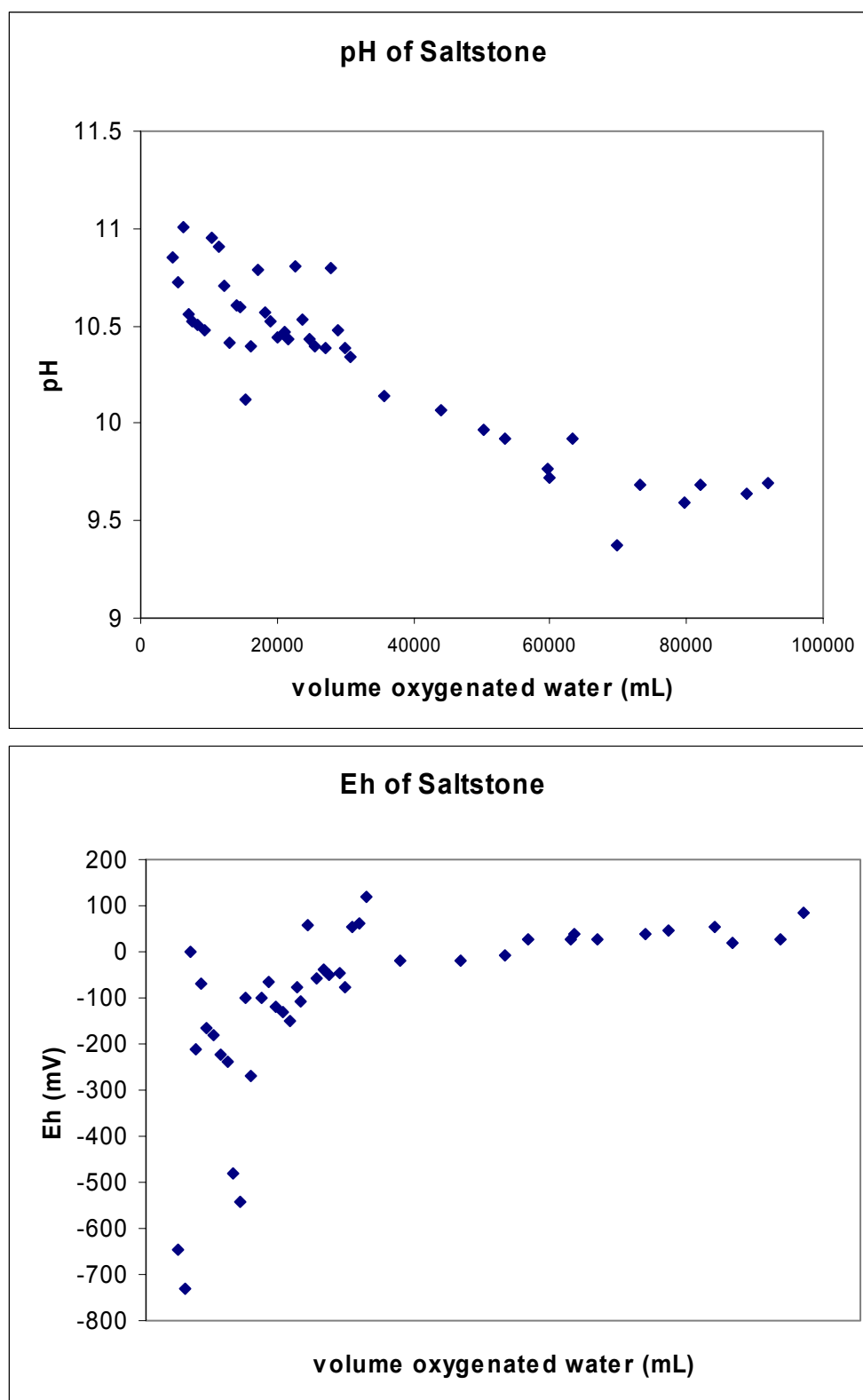
$$\text{pe} + \text{pH} = -\frac{1}{2} \log \text{H}_2(\text{g}) \quad (\text{Eq. 8})$$

where  $pe$  is the negative log of the electron activity and  $pH$  is the negative log of the  $H^+$  activity. Finally the relationship between  $pe$  and  $Eh$  is:

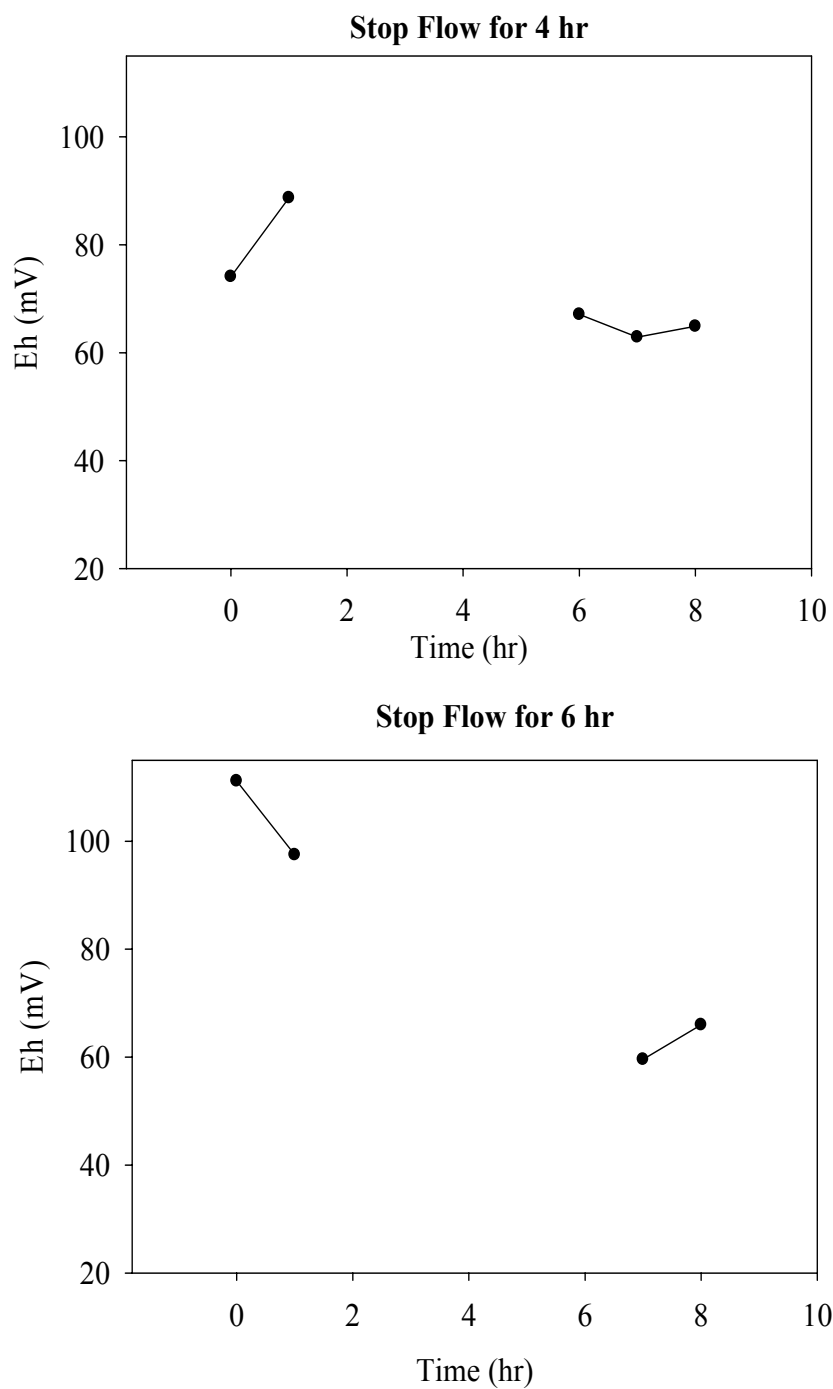
$$Eh \text{ (millivolts)} = 59.2pe \quad (\text{Eq. 9})$$

So when  $H_2(g)$  is constant, as is the case under steady state conditions, increases in  $Eh$  (or increases in  $pe$  and decreases in  $e^-$ ) result in concurrent decreases in  $pH$  (or increases in  $H^+$  activity).

After 100,000 mL were passed through the column, which is equal to about  $3.0 \times 10^5$  pore volumes, the effluent was still not at steady state, as suggested by the slight but continued increase in  $Eh$  and decrease in  $pH$  values at the end of the study. This result is not surprising given that the aqueous phase was pumped at a relatively fast rate compared to anticipated groundwater or cementitious porewater flow rates. This accelerated flow rate was selected to deliver a large amount of oxidant (in this case  $O_2(aq)$ ) to the partially oxidized Saltstone. To demonstrate that this system was not at steady state, two stop-flow experiments were conducted in which the water flow set at 14 mL/min was stopped for 4 or 6 hours (Figure 6). After the flow had been stopped for 4 hours, the  $Eh$  dropped 21 mV; when stopped for 6 hr, the  $Eh$  dropped 37 mV. These results demonstrate that, in fact, the Saltstone is much better poised to buffer  $Eh$  changes than Figure 5 suggests. Stated differently, this demonstrates that the  $Eh$  will change much less than Figure 5 suggests when flow rates are slower and more representative of those expected at the Saltstone facility.



**Figure 5. Redox condition (Eh) and pH of effluent from a column of DDA simulant Saltstone (flow rate = 14 mL/min; column diameter = 1.5 cm, column length = 6 cm).**



**Figure 6. Stop-flow experiments demonstrating that system at the high flow rates used in Figure 5 are not at steady state. Top: Stop flow for 4 hr, Bottom: Stop flow for 6 hr. Note that the system becomes increasingly more reduced the longer the flow has been interrupted.**

## 5.0 CONCLUSIONS

The key findings from this study follow.

- There was little evidence that the simulated Vault 2 and DDA simulant Saltstone  $K_d$  values differed from previous SRS  $K_d$  values measured with reducing grout (Kaplan and Coates 2007). These values also supported a previous finding that  $K_d$  values of slag-containing cementitious materials, tend to be greater for cations and about the same for anions, than regular cementitious materials without slag. Based on these new finding, it was suggested that all previous reducing concrete  $K_d$  values be used in future PAs, except Np(V) and Pu(IV)  $K_d$  values, which should be increased, and I values, which should be slightly decreased in all three stages of concrete aging.
- The reduction capacity of the DDA simulant Saltstone, consisting of 23 wt-% blast furnace slag, was 821.8  $\mu\text{eq/g}$ . This was approximately the same value as the one measured for 100% blast furnace slag. The cause for this approximately four-fold greater reduction capacity than anticipated is not known, but may be the result of the higher pH of Saltstone (pH  $\sim 11$ ) compared to blast furnace slag (pH  $\sim 8$ ), the presence of reducing minerals in the fly ash used to make the Saltstone, or to the Saltstone possibly having semi-conductor properties. These reduction capacity values will result in a near four-fold increase in the estimated duration that the Saltstone facility will remain reduced. The implication of this result is that oxidation-state-sensitive contaminants, such as Pu, Np, and Tc, will remain for a longer duration in a much less mobile form than previously believed. The reduction capacity of vault concrete, which consisted of 10 wt-% blast furnace slag, was 240  $\mu\text{eq/g}$ .
- Essentially all Am, Cd, Ce, Co, Cs, Hg, Sr, and Y was (ad)sorbed within four hours, whereas  $<3\%$  of the adsorbed metals desorbed from these solids after 90 hours of continuous leaching. In particular, desorption of Tc (under oxidizing conditions) was  $>10^3$  fold slower than (ad)sorption (under reducing conditions). An important implication of this finding is that if groundwater by-passes or short-circuits the reduction capacity of the Saltstone by flowing along a crack, the ability of the oxygenated water to promote Tc desorption is appreciably less than that predicted based on the  $K_d$  value.
  - Relatively low Tc  $K_d$  values, 6 to 91 mL/g, were measured in these studies indicating that little if any of the Tc(VII) introduced into the Saltstone or Vault 2 concrete suspensions was reduced to Tc(IV). Such a reduction results in apparent  $K_d$  values in the order of  $10^4$  mL/g. As such, these Tc sorption/desorption experiments need additional investigation to fully represent Saltstone environmental conditions.

It is important to understand the limits of these data. They do not provide insight into how radionuclides cured and immobilized in Saltstone will leach from the Saltstone. However they do provide insight into how radionuclides once released into porewater will interact with Saltstone or vault concrete. The use of these site-specific data would greatly improve the pedigree of the input data for the Saltstone performance assessment. Additionally, these studies provided important guidance and technical justification for the conceptual geochemical model to be used in the Saltstone performance assessment.



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## **7.0 APPENDIX A: MATERIALS AND METHODS**

## 7.1 DETAILED DESCRIPTION OF THE RESEARCH AND DEVELOPMENT INSTRUCTIONS: RADIONUCLIDE SORPTION TO SALTSTONE AND CEMENTITIOUS MATERIALS UNDER OXIDIZING AND REDUCING CONDITIONS

### 7.1.1 Objective

Determine I, Np, Pu, Se, Tc, and U  $K_d$  values of three cementitious materials (Saltstone, partially oxidized Saltstone, and Vault concrete) in an oxidizing or reducing environment with a  $\text{Ca}(\text{OH})_2$  solution (to simulate the pore water of a young cementitious material) and  $\text{CaCO}_3$  solution (to simulated a pore water of an older cementitious material). Conditions simulating the Saltstone Facility will be used during these experiments.

### 7.1.2 Approach

There will be two near identical experiments conducted: one in which I, Np, Se, and Pu will be tested, and the other in which Tc and U will be tested. They are separated in this manner to ease analytical detection of the radionuclides. Additionally, each of these experiments will be conducted under two environments: 1) oxidizing and 2) reducing.

### 7.1.3 Materials

1. Vault concrete (Vault 2, Mix 1 cement) , ground to pass a 100 $\mu\text{m}$  sieve
2. Saltstone (DDA stimulant), ground to pass a 100 $\mu\text{m}$  sieve
3. Partially oxidized Saltstone: Place ~10g Saltstone in column assembly. Pump oxygenated water (bubble air into it) through column very slowly. Continue adding water until pH & Eh become steady.
4. 100 20-mL serum glass vials with caps
5. House  $\text{N}_2$  gas
6.  $\text{Ca}(\text{OH})_2$ -Saturated Leaching Solution:  
Background: Because  $\text{CO}_2$  in air is very soluble in water at high pH and the resulting dissolved carbonate will precipitate as calcite in the  $\text{Ca}(\text{OH})_2$ - saturated solution, care will be taken to minimize contact of the solution with atmospheric air. Excess solid  $\text{Ca}(\text{OH})_2$  is undesirable because it will buffer the pH at a higher than expected value.  
Procedure:
  - a. Deoxygenate ~1-L of D.I. water by boiling and then purge with  $\text{N}_2$  gas for 30 min. After purging with  $\text{N}_2$ , place water in a Teflon bottle (because this material has a low air diffusion coefficient).
  - b. Add a sufficient quantity of fresh  $\text{Ca}(\text{OH})_2$  (~1.35 g/L @ 25°C) to the deoxygenated water to just saturate the solution.
  - c. To minimize exposure to air, purge head space with  $\text{N}_2$  and if necessary periodically skim off any precipitates that may form. Using litmus paper, measure approximate pH of solution.
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,  $\text{Ca}^{2+}$  = 20 mg/L, TIC = 58 mg/L,  $\text{PCO}_2$  = 0.0003 atm (fixed)].

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  $\text{CaCO}_3$  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- $\mu\text{m}$  membrane.

8. 0.1- $\mu\text{m}$  syringe filters
9. 1-M NaOH for pH adjustment of samples
10. 1 N HCl for pH adjustment of samples
11.  $^{125}\text{I}$  Spike Solution (0.01  $\mu\text{Ci/mL}$   $^{125}\text{I}$ ).<sup>5</sup>
  - Add 0.11 mL of Eckert & Ziegler's 1.25  $\mu\text{Ci/mL}$   $^{125}\text{I}$  stock (note that this stock solution has gone through ~2 half lives since it was purchase at a concentration of 10  $\mu\text{Ci/mL}$ ).
  - Add 13.09mL water
12.  $^{75}\text{Se}$ ,  $^{237}\text{Np}$  &  $^{238}\text{Pu}$  Spike Solution (1.52  $\mu\text{Ci/mL}$   $^{238}\text{Pu}$ , 0.0385  $\mu\text{Ci/mL}$   $^{237}\text{Np}$ , 5.51e-4  $\mu\text{Ci/mL}$   $^{75}\text{Se}$ )
  - Add 9.76 mL of 7.53e-4  $\mu\text{Ci/mL}$   $^{75}\text{Se}$  stock (from Dave Diprete) to spike solution
  - Add 0.90 mL of ~20  $\mu\text{Ci/mL}$   $^{238}\text{Pu}$  stock (David Hobbs) to spike solution
  - Add 2.54 mL of 0.2  $\mu\text{Ci/mL}$   $^{237}\text{Np}$  stock (Eckert & Ziegler) to spike solution
13.  $^{99}\text{Tc}$  and  $^{233}\text{U}$  Spike Solution (0.182 $\mu\text{Ci/mL}$   $^{99}\text{Tc}$  & 0.182 $\mu\text{Ci/mL}$   $^{233}\text{U}$ ):
  - Add 4.0 mL of 0.5  $\mu\text{Ci/mL}$   $^{233}\text{U}$  stock (Eckert & Ziegler) to spike solution.
  - Add 0.12mL of 0.198  $\mu\text{Ci/mL}$   $^{99}\text{Tc}$  stock (Eckert & Ziegler ) to spike solution
  - Add 9.08 mL water to spike solution.

#### 7.1.4 Methods for Measuring I, Np, Pu, & Se Sorption under Oxidizing Conditions (Samples #601a – 624a)

1. Record "Tube Tare (g)" weight to within 0.001g of labeled 20-mL serum vials with cap as identified in Table 1.
2. Add  $0.5 \pm 0.01$ -g of solid to each tube. Weigh and record "Solid (g)" weight to within 0.001g.
3. **Equilibrating solids to the aqueous phase.** *Solid Phase Chemical Conditioning:* The cementitious material will be equilibrated with appropriate  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$  solutions prior to spiking with the radionuclide mixture. This pre-equilibration will help to minimize "shocking the chemistry" of the spiked radionuclide and facilitate approximating steady state conditions.
  - a. Add  $12 \pm 0.1$ -mL of appropriate solution to each tube as defined in Table 1. Put on shaker for overnight. Let settle for 1 hr. Decant liquid. If solids do not

<sup>5</sup> I-125 has a half life of ~59 days. This spike solution is ~3 half lives old. So the 10  $\mu\text{Ci/mL}$  stock is now 1.3  $\mu\text{Ci/mL}$ . We want a 0.01  $\mu\text{Ci/mL}$  stock solution.  $(1.3\mu\text{Ci/mL})(x \text{ mL}) = (13.2 \text{ mL})(0.01\mu\text{Ci/mL})$ ;  $x = 0.101\text{mL}$

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.

- b. Add  $12 \pm 0.1$  mL of appropriate liquid to each tube as defined in Table 1, including the No-Solids Controls. Measure pH. Record weight to within 0.001g of each tube in “Tube + soils + Equil + GW (g)”
4. **Adding  $^{75}\text{Se}$ ,  $^{237}\text{Np}$  &  $^{238}\text{Pu}$  Spike Solution to suspensions.** Move rack of tubes to rad hood. Add 330  $\mu\text{L}$  of  $^{75}\text{Se}$ ,  $^{237}\text{Np}$  &  $^{238}\text{Pu}$  Spike Solution to each tube. Also add this to the No-Solids Controls. Gently shake or swirl tube containing the concrete samples suspensions in each tube.
5. **pH adjust suspension.** Because the spike solution is in a  $\sim 1$  M HCl solution, you will need to add base to bring the suspensions back to their native pH. Do a non-rad set of dummy runs to determine the volume of 0.1 M NaOH to add. This is being done because it will not be possible to measure the pH of the sealed vials after the spike is added. Record “Base vol added” in Table 1.
6. **Add  $^{125}\text{I}$  Spike Solution to suspensions.** Add 330  $\mu\text{L}$  of “ $^{125}\text{I}$  Spike Solution” to each tube. There is no need to pH adjust.
7. **Equilibrating radionuclides with cement suspension.** Leave samples in rad hood for minimum of 5 days. During this equilibration period, place tubes on a gentle platform shaker or shake by hand 2x/day.
8. At end of equilibrium period, collect liquids by drawing liquids into a syringe and then passing liquid through a 0.1- $\mu\text{m}$  filter.
9. **Gamma Analysis.** Submit to Analytical Development for low energy gamma spec analysis. Note in your order, Travel Copy, that this is a routine turn-around-time order, and the rads of interest are I-125, Se-75, U-233, Np-237.
10. **Data Management.** Enter them into an EXCEL spreadsheet. Calculated  $K_d$  values as suggested in ASTM D-4646, using the following equation:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times m_{\text{soil}}}$$

where  $C_i$  and  $C_f$  are the aqueous concentrations of the initial spike (the average of samples 621-A, -B, and -C) and the final equilibrium concentration of each radionuclide ( $\text{Ci/mL}$  or  $\text{dpm/mL}$ );  $V$  = volume of liquid in the final equilibrated suspension ( $\text{mL}$ ); and  $m_{\text{soil}}$  is the soil mass ( $\text{g}$ ). All data will be achieved in the Analytical Development’s LIMS system, and on my computer and its independent computer backup system. A hard copy will be kept on file of the original gamma results.

#### 7.1.5 Methods For Measuring I, Np, Pu, & Se Sorption under Reducing Conditions (Samples #619a – #630a)

1. Record “Tube Tare (g)” weight to within 0.001g (with cap) of labeled 20-mL serum vials as identified in Table 1.
2. Add  $0.25 \pm 0.01$ -g of Saltstone to each tube. Weigh and record “Solid (g)” weight to within 0.001g.

3. **Equilibrating solids with the aqueous phase. Solid Phase Chemical Conditioning:**  
The ground cementitious material will be equilibrated with appropriate solutions prior to spiking with the radionuclide mixture. We will conduct this pre-equilibration in two steps, the first pre-equilibration (steps a – b) is designed to promote the macro-chemistry to come to steady state, the second pre-equilibration (steps c – e) is designed to bring the redox into steady state.
  - a. Add  $12 \pm 0.1$ -mL of  $N_{2(g)}$ -sparged solution ( $\sim 0.5$  hour) to each vial as identified in Table 1, including the No-Solids Controls. Loosely cover serum bottle with cap (because we will need to remove cap to pre-equilibrate again for redox).
  - b. Mix by hand 2x/day for one day. Let settle for 1 hr and dispose of aqueous phase.
  - c. Add  $12 \pm 0.1$ -mL of  $N_{2(g)}$ -sparged solution ( $\sim 0.5$  hour) to each tube as identified in Table 1, including the No-Solids Controls. Crip caps onto serum bottles. Record weight to within 0.001g of each tube in “Tube + soils + Equil + GW (g)”.
  - d. Place two syringes through septum, one as an exhaust and the other attached to  $N_{2(g)}$ . Make sure the first syringe (exhaust) is above the water and the second syringe (sparge) reaches to the bottom or near bottom of bottle to maximize sparging. Sparge  $\sim 2$  min with  $N_{2(g)}$ . After sparging, remove both syringes from septum.
  - e. Put on shaker or mix by hand 2x/day for 2 week.
4. **Adding  $^{75}\text{Se}$ ,  $^{237}\text{Np}$  &  $^{238}\text{Pu}$  Spike Solution to suspensions.** Move rack of tubes to rad hood. Using a syringe, add 330  $\mu\text{L}$  of “ $^{75}\text{Se}$ ,  $^{237}\text{Np}$  &  $^{238}\text{Pu}$  spike solution” to each tube. Also add this to the No-Solids Controls. Shake or swirl vials.
5. **pH adjust suspension.** Because the capped vials do not permit measuring the pH, we will assume the pH needs to be adjusted similarly to the oxidized experiments. Add approximately the same amount of base as used in the “oxidized” experiment. Record “Base vol added” in Table 1.
6. **Add  $^{125}\text{I}$  Spike Solution to suspensions.** Add 330  $\mu\text{L}$  of “ $^{125}\text{I}$  Spike Solution” to each tube. There is no need for additional pH adjustment.
7. **Equilibrating radionuclides with cement suspension.** Leave samples in rad hood for minimum of 5 days. During this equilibration period, place tubes on a gentle platform shaker or shake by hand 2x/day.
8. At end of equilibrium period, collect liquids by drawing liquids into a syringe and then passing liquid through a 0.1- $\mu\text{m}$  filter.
9. **Gamma Analysis.** Submit to Analytical Development for low-energy gamma spec analysis. Note in the Travel Copy, that this is a routine turn-around-time order, and the radionuclides of interest are  $^{237}\text{Np}$ ,  $^{238}\text{Pu}$ ,  $^{125}\text{I}$ , &  $^{75}\text{Se}$ .

#### 7.1.6 Methods for Measuring Tc-99 and U-233 Sorption under Oxidizing Conditions (Sample #601Tc – #618Tc) and Reducing Conditions (Samples #619Tc – #630Tc)

Same as “I, Np, Se, and U Study” above except:

- Enter data into Table 2.
- Skip step 6 because all radionuclides will be spiked at the same time.
- Step 8. Request that ADS does liquid scintillation counting of these samples and that the radionuclides of interest are  $^{99}\text{Tc}$  and  $^{233}\text{U}$ .

**Safety, Hazards Assessment Package (HAP):**

The HAP number is SRNL-EST-2006-00-93 and it is located in lab notebook number WSRC-NB-2003-00251 in Building 773-43A, Room 215.

**Hazards:**

1. radionuclides
2. ~3 mL of strong acids
3. ~3 mL of strong base
4. sharps (syringes)

**Hazards Mitigation:**

1. Radionuclides: Follow training of Rad Worker II or Advanced Rad Worker
2. Strong Acid: wear appropriate gloves and as always protective eye ware
3. Strong Base: wear appropriate gloves and as always protective eye ware
4. Sharps: syringes will be used in these studies; it will be necessary to develop a lab technique whereby the hand holding the serum bottle in which the syringe will be pushed into, will never be below the point of the syringe tip. Rack will be used that holds 20ml vial so that only hand holding syringe will be needed and each vial will not be held individually, thereby minimizing the risk of syringe contact with fingers/hands.



**Table 1.** Cement sample descriptions and weights for I-125, Np-238, Pu-238, and Se-75  $K_d$  measurements.

Tube #	Solid <sup>(a)</sup>	Rep	Water	Solids pH-H <sub>2</sub> O (1:1)	Tube Tare (g)	Soils (g)	Tube + Solids + Equil + GW (g)	Base vol. added ( $\mu$ L)
Method Step				(Step 3b)	(Step 1)	(Step 2)	(Step 3b)	(Step 5)
<b>Oxidized Experiment</b>								
601a	Vault	1	Ca(OH) <sub>2</sub>					
602a		2						
603a	Vault	1	CaCO <sub>3</sub>					
604a		2						
605a	Ox Saltstone	1	Ca(OH) <sub>2</sub>					
606a		2						
607a	Ox Saltstone	1	CaCO <sub>3</sub>					
608a		2						
609a	Saltstone	1	Ca(OH) <sub>2</sub>					
610a		2						
611a	Saltstone	1	CaCO <sub>3</sub>					
612a		2						
613a	Control (no concrete)	1	Ca(OH) <sub>2</sub>					
614a		2						
615a		3						
616a	Control (no concrete)	1	CaCO <sub>3</sub>					
617a		2						
618a		3						
<b>Reducing Experiment</b>								
619a	Saltstone	1	Ca(OH) <sub>2</sub>					
620a		2						
621a	Saltstone	1	CaCO <sub>3</sub>					
622a		2						
623a	Control (no concrete)	1	Ca(OH) <sub>2</sub>					
624a		2						
625a		3						
626a	Control (no concrete)	1	CaCO <sub>3</sub>					
627a		2						
628a		3						

**Table 2.** Cement sample descriptions and weights for Tc-99 and U-233  $K_d$  measurements.

Tube #	Solid <sup>(a)</sup>	Rep	Water	Solids pH-H <sub>2</sub> O (1:1)	Tube Tare (g)	Solids (g)	Tube + Solids + Equil + GW (g)	Base vol. added ( $\mu$ L)
Method Step				(Step 3b)	(Step 1)	(Step 2)	(Step 3b)	(Step 5)
<b>Oxidized Experiment</b>								
601TcU	Vault	1	Ca(OH) <sub>2</sub>					
602TcU		2						
603TcU	Vault	1	CaCO <sub>3</sub>					
604TcU		2						
605TcU	Ox Saltstone	1	Ca(OH) <sub>2</sub>					
606TcU		2						
607TcU	Ox Saltstone	1	CaCO <sub>3</sub>					
608TcU		2						
609TcU	Saltstone	1	Ca(OH) <sub>2</sub>					
610TcU		2						
611TcU	Saltstone	1	CaCO <sub>3</sub>					
612TcU		2						
613TcU	Control (no concrete)	1	Ca(OH) <sub>2</sub>					
614TcU		2						
615TcU		3						
616TcU	Control (no concrete)	1	CaCO <sub>3</sub>					
617TcU		2						
618TcU		3						
<b>Reducing Experiment</b>								
619TcU	Saltstone	1	Ca(OH) <sub>2</sub>					
620TcU		2						
621TcU	Saltstone	1	CaCO <sub>3</sub>					
622TcU		2						
623TcU	Control (no concrete)	1	Ca(OH) <sub>2</sub>					
624TcU		2						
625TcU		3						
626TcU	Control (no concrete)	1	CaCO <sub>3</sub>					
627TcU		2						
628TcU		3						

## 7.2 DETAILED DESCRIPTION OF THE RESEARCH AND DEVELOPMENT

### INSTRUCTIONS: SORPTION AND DESORPTION KINETICS OF $^{99}\text{TcO}_4^-$ FROM CEMENTITIOUS MATERIALS

**Hazards Analysis Plan:** SRNL-ECP-2007-00009

**Hazards:** Radionuclides and sharps

**Hazards Mitigation:** Radionuclides: Follow training of Advanced Rad Worker

Sharps: Syringes will be used in these studies. Prior to initiating this work, it will be necessary to develop a lab technique whereby the hand holding the serum bottle in which the syringe will be pushed into, will never be below the point of the syringe tip. Rack will be used that holds 20ml vial so that only hand holding syringe will be needed and each vial will not be held individually, thereby minimizing the risk of syringe contact with fingers/hands.

#### 7.2.1 Objective:

3. Measure  $^{99}\text{TcO}_4^-$  sorption kinetics to Saltstone and Vault 2 cementitious material. We will also evaluate whether  $^{99}\text{Tc}$  sorption should be described using a  $K_d$  or a solubility value. This information will provide  $K_d$  values as well as kinetic information for use in subsurface contaminant transport calculations.
4. Measure  $^{99}\text{TcO}_4^-$  desorption kinetics. It is anticipated that sorption occurs very quickly, in the order of <1 day, whereas desorption occurs over a much longer duration, in the orders of months. If this is true, it would be unnecessarily conservative to describe the reaction with a single  $K_d$  value.

#### 7.2.2 Matierials:

1. Vault 2 (Mix 1, 180010-3D from John Harbor), ground to pass a 100 $\mu\text{m}$  sieve
2. Saltstone (TR 451 from John Harbor), ground to pass a 100 $\mu\text{m}$  sieve
3. 0.94  $\mu\text{Ci}$   $^{99}\text{TcO}_4^-$  spike solution (in 1 mM KCl – stock solution = 100  $\mu\text{Ci}$ ; Eckert & Ziegler). Add 0.15 mL of stock to 16 mL of water. Label spike solution “0.94  $\mu\text{Ci}$   $^{99}\text{Tc}$ ; Saltstone spike; date; name”.
4. 100 20-mL serum glass vials with caps
5. 10-mL disposable syringes
6. Saturated  $\text{CaCO}_3$  solution: 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  $\text{CaCO}_3$  to the heated DI water. Leave mixture on stir/heating plate for 8 hr. Pass through a 0.45- $\mu\text{m}$  membrane.
7. Ar-sparged Saturated  $\text{CaCO}_3$  solution: Sparge 200mL with house Ar for 30 min prior to using. Pass through a 0.45- $\mu\text{m}$  membrane.
8. 0.1- $\mu\text{m}$  syringe filters

### 7.2.3 Methods:

#### Sorption Tests (Objectives 1)

This experiment will include

- 6 durations (10 min (ASAP), 30 min, 1 hr, 6 hr, 24 hr, and 214 hr (1 wk).
  - Duplicate samples
  - 2 solids (Vault 2 and Saltstone)
1. Label tubes and record tare weights in Table 1.
  2. Add  $0.1 \pm 0.001\text{g}$  of Saltstone (Tubes 701 – 720) or  $0.5 \pm 0.001\text{g}$  of Vault 2 (tubes 721 – 740) into 20mL serum vials. Weight and enter “Solid Wt.” into Table 1.
  3. **Equilibrating solids to the aqueous phase.** *Solid Phase Chemical Conditioning:* We will conduct this pre-equilibration in two steps. The first pre-equilibration [steps 1) & 2)] is designed to promote the macro-chemistry ( $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$  ...) to come to steady state. The second pre-equilibration [steps 3) – 5)] is designed to bring the redox into steady state.
    - 1) Add  $12 \pm 0.1\text{-mL}$  of the appropriate Saturated  $\text{CaCO}_3$  Solution to each tube as identified in Table 1. Add 12 mL of “not sparged Saturated  $\text{CaCO}_3$  solution” to the No-Solids Control. Loosely cover serum bottle with cap (because we will need to remove cap to pre-equilibrate again for redox).
    - 2) Mix by hand 2x/day for one day or put on a platform shaker. Let settle for 1 hr and dispose of aqueous phase.
    - 3) Add another  $12 \pm 0.1\text{-mL}$  of the appropriate Saturated  $\text{CaCO}_3$  Solution to each tube as identified in Table 1, including the No-Solids Controls.
    - 4) For the Saltstone samples with Ar-sparged  $\text{CaCO}_3$  solution, place two syringes through septum, one as an exhaust and the other attached to  $\text{Ar}_{(g)}$ . Make sure the first syringe (exhaust) is above the water and the second syringe (sparge) reaches to the bottom or near bottom of bottle to maximize sparging. Sparge  $\sim 1$  min with  $\text{Ar}_{(g)}$ . After sparging, remove both syringes from septum. Put on shaker or mix by hand 2x/day for 2 week.  
For the Vault 2 samples containing unsparged  $\text{CaCO}_3$  solution, place on shaker for overnight.
    - 5) Weigh and record in column designated “Tube + soils + Equil + aq (g)” in Table 1.
  4. **Spike Addition:** Move pre-equilibrated solids to rad hood. Using a syringe, add 0.33mL of the  $^{99}\text{Tc}$  spike solution. Initially mix very well and then place on an end-over-end shaker. Note that time = 0 hours is after adding the spike and shaking vigorously.
  5. **Equilibration with Tc:** During equilibration with the Tc, shake the tubes 2x/day or leave on a shaker.
  6. **Recover Aqueous Phase:** After the appropriate duration, removing caps from tubes to be sacrificed, withdraw aqueous phase using a syringe, and pass through a  $0.1\text{ }\mu\text{m}$  filter. Record “stop date/time” in Table 1. (Replace cap of samples #711 – 720 ASAP

to minimize reoxidation. You will want to start the Desorption Experiment immediately after sacrificing the 1 week sorption samples).

7. **Submit to ADS for liquid scintillation counting for  $^{99}\text{Tc}$ .** On the Travel Copy please note we need the samples analyses in a routine turn-around-time. Also provide the following estimates of solution activity:
  - Samples 701–720, 50 dpm/mL;
  - Samples 721 – 740, 500 dpm/mL;
  - Samples 741-743, 10,000 dpm/mL.

### Desorption Tests (Objectives 2)

8. **Quick Rinse/Dilute Samples:** Move tubes 711 – 720 and 731 – 740 into the same rack. Re-label them as shown in Table 2 (e.g., 801 – 820). Add 15 mL of appropriate Saturated  $\text{CaCO}_3$  Solution, as designated in Table 2. Place cap, but do not crimp onto vial. Shake sample vigorously by hand for 5 seconds. Let settle. Pour out as much of the liquids as possible without losing solids. It's OK to leave some liquid in tubes.
9. Add another 6 mL of appropriate solution. Crimp on cap. Shake. Weigh and record weight in Table 2, in column "TARE+ SOLID+INTER AFTER ADSORP. (G)"
10. Shake by hand 2 or 3 times a day.
11. To sacrifice a sample, let solids settle to separate solids from liquids. Remove crimped cap. Quickly siphon supernatant from vials, pass through a  $0.1\mu\text{m}$  syringe filter, and collect filtrate in sample bottle.
12. On the Travel Copy please note we need the samples analyses in a routine turn-around-time. Also provide the following estimates of solution activity:
  - Samples 801–810 near detection limit;
  - Samples 811-820 50 dpm/mL

**Table 1.** Tc Sorption sample identification and weight data

ID	solid	Time	Rep	Sat. CaCO <sub>3</sub> Sol'n	Tare Wt (g)	Solid Wt (g)	Tare+Solid+ Equi + Aq (g)	Start date/ time	Stop date/tim e
	Instruction Step #				1	2	6	7	11
701	Saltstone	t=10min	1	Sparged					
702			2						
703		t=0.5h	1						
704			2						
705		t=1h	1						
706			2						
707		t=6h	1						
708			2						
709		t=24h	1						
710			2						
711		t=214h	1						
712			2						
713			3						
714			4						
715			5						
716			6						
717			7						
718			8						
719			9						
720			10						
721	Vault 2	t=10min	1	Not Sparged					
722			2						
723		t=0.5h	1						
724			2						
725		t=1h	1						
726			2						
727		t=6h	1						
728			2						
729		t=24h	1						
730			2						
731		t=214h	1						
732			2						
733			3						
734			4						
735			5						
736			6						
737			7						
738			8						
739			9						
740			10						
741	No-Solids Controls	t=214h	1	Not Sparged					
742			2						
743			3						

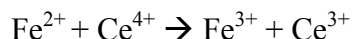
**Table 2.** Desorption Experiment

ID	ID in Table 1	Solid	Sat. CaCO <sub>3</sub> Sol'n	Desorption Duration (day)	Rep	Tare+ Solid+Inter after Adsorp. (g)
<b>Step</b>						<b>(9)</b>
801	711	Saltstone	Sparged	0.04	1	
802	712				2	
803	713			1	1	
804	714				2	
805	715			7	1	
806	716				2	
807	717			14	1	
808	718				2	
809	719			30	1	
810	720				2	
811	731	Vault 2	Not sparged	0.04	1	
812	732				2	
813	733			1	1	
814	734				2	
815	735			7	1	
816	736				2	
817	737			14	1	
818	738				2	
819	739			30	1	
820	740				2	

### 7.3 DETAILED DESCRIPTION OF THE RESEARCH AND DEVELOPMENT INSTRUCTIONS: REDUCTION CAPACITY OF SOLIDS BY THE CE(IV)-FE(II) METHOD

(Adapted from Angus and Glasser, 1985, Mat. Res. Soc. Symp. Proc. 50:547–556)

The governing equation for this procedure is



#### 7.3.1 Preparation of Solutions and Samples:

##### 1. Preparation of 0.0500 M $(\text{NH}_4)_2\text{Fe}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$ (FAS) (primary standard)

- 4.902 g of FAS weighed into a 250 mL volumetric flask
- 100 mL  $\text{H}_2\text{O}$  and 10 mL  $\text{H}_2\text{SO}_4$  added in quick succession
- Filled with  $\text{H}_2\text{O}$
- Allowed to cool to RT (~2 hours)
- Added  $\text{H}_2\text{O}$  to make 250.0 mL

##### 2. Preparation of 0.0608 M Ce(IV) solution

- 9.615 g of  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  weighed into a 250 mL volumetric flask
- Added 150 mL  $\text{H}_2\text{O}$  and 25 mL  $\text{H}_2\text{SO}_4$  in quick succession
- Filled flask to 250 mL and added a stirbar
- Magnetically stirred for 2 hours ( $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  dissolves slowly)
- Stirbar removed and water added to make 250 mL
- Titrated with FAS to determine the actual Ce(IV) concentration (0.059 M, in this case)

##### 3. Preparation of 0.025M $\text{Fe}(\text{o-phenanthroline})_3^{2+}$ (aka Ferroin)

- 0.069 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 0.131 g of 1,10-phenanthroline weighed into a 10 mL volumetric flask
- $\text{H}_2\text{O}$  added to make 10.0 mL
- Dark red solution

##### 4. Preparation of Solid Samples

- ~0.5 g of sample was added to a 250 mL Erlenmeyer flask equipped with a stirbar
- 25.0 mL of ~0.05 M Ce(IV) solution was added by volumetric pipette
- The contents of the flask were stirred magnetically for 1 hour at room temp.
- Added 0.100 mL 0.025M  $\text{Fe}(\text{o-phenanthroline})_3^{2+}$  (solution acquires a greenish tint)

#### 7.3.2 Measurements:

##### 2.1 Calibration of Ce(IV) Concentration

- 25.0 mL Ce (IV) solution added to a 250 mL Erlenmeyer flask
- Added 0.100 mL Ferroin indicator (solution acquires a greenish tint)
- Titrated with 0.050 M  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$  until solution remained lilac colored.



## 2.2 Ce(IV) Titration of Samples

- Titrated with 0.050 M  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$  until solution remained lilac colored
- During titration, solution goes from green to pale blue to lilac to pink

### 7.3.3 Calculations:

#### 1. Ce(IV) Calibration

- Ce(IV) concentration is determined from the volume of FAS added to reach endpoint

*Example:* 25.0 ml Ce(IV) solution was titrated with 0.03021 L of 0.050 M FAS  
 $(0.03021 \text{ L}) \times (0.05 \text{ M FAS}) \times 1 \text{ mol Fe(II)}/1 \text{ mol Ce(IV)} = 1.5 \times 10^{-3} \text{ mol Fe(II)}$   
 $1.5 \times 10^{-3} \text{ mol Fe(II)} \times 1 \text{ mol Ce(IV)}/1 \text{ mol Fe(II)} / 0.025 \text{ L} = 0.060 \text{ M Ce(IV)}$

#### 2. Determining the Total Number of Oxidizing Equivalents in Ce(IV) Solutions

- The total number of oxidizing equivalents in the Ce(IV) solution is determined from the Ce(IV) concentration established in 3.1

*Example:* 0.025 L of Ce(IV) solution titrated  
 $0.025 \text{ L Ce(IV)} \times 0.060 \text{ M Ce(IV)} = 1.5105 \times 10^{-3} \text{ mole } e^- \text{ Ce(IV)}$

#### 3. The Number of Reducing Equivalents of Fe(II) Needed to Neutralize Ce(IV) after it Reacts with Sample

*Example:* Unknown Ce(IV) solution was titrated with 0.02202 L of FAS  
 $0.02202 \text{ L FAS} \times 0.050 \text{ M Fe(II)} \times (1 \text{ mol Fe(II)} / 1 \text{ mol FAS}) = 1.101 \times 10^{-3} \text{ Mole } e^- \text{ Fe(II)}$

#### 4. Determining the Reducing Equivalents in the Solid Sample

- The reducing equivalents in the solid sample are determined from the difference between the total oxidizing equivalents in the Ce(IV) solution (3.2) and the number of reducing equivalents needed to neutralize the Ce(IV) solution after it reacted with the sample (3.3)

*Example:*

$$1.310 \times 10^{-3} - 1.101 \times 10^{-3} = 4.095 \times 10^{-4} \text{ mole } e^-$$

#### 5. Reducing Equivalents per Gram

- The reducing equivalents per gram are calculated by dividing the reducing equivalents in the solid sample (3.4) by the mass of the sample.

*Example:* The reducing equivalents in a 0.5015 g sample were determined to be  $4.095 \times 10^{-4}$  mole  $e^-$

$$4.095 \times 10^{-4} / 0.5015 \text{ g sample} = 8.16 \times 10^{-4} \text{ mole } e^-/\text{g or } 0.816 \text{ meq/g or } 816 \text{ } \mu\text{eq/g}$$

## 7.4 RECIPE FOR SIMULANTS USED IN SALTSTONE FORMULATIONS

### 7.4.1 SWPF (TR 451) Simulant

Compound	TARGET Molarity Moles/Liter	MW grams/mole	REFERENCE Amt / Liter grams	TARGET Amt / 2 liters grams
50% by Weight NaOH	2.866	40.00	229.28	458.57
NaNO <sub>3</sub>	1.973	84.99	167.66	335.31
NaNO <sub>2</sub>	0.485	68.99	33.43	66.87
Na <sub>2</sub> CO <sub>3</sub>	0.118	105.99	12.46	24.92
Na <sub>2</sub> SO <sub>4</sub>	0.055	142.04	7.84	15.67
Aluminum Nitrate (9 H <sub>2</sub> O)	0.114	375.13	42.90	85.80
Sodium Phosphate (12 H <sub>2</sub> O)	0.007	380.12	2.76	5.51
Total Salt mass			361.59	
Total Na Molarity	5.69			
Notes Make 2 two liter batches and combine				

Trial Run	PreMix (grams)	Simulant (grams)	April 22, 2008	H <sub>2</sub> O (grams)	H <sub>2</sub> O/Premix	Grout (grams)
Use SWPF Simulant PA 022508, Temperature of 22°C						
TR449	867.38	732.62		520.43	0.60	1600
SWPF	Salt grams/Liter 361.59	Water grams/Liter 886.81	Salt + Water grams/Liter 1248	Water g/g simulant 0.71	Salt g/g simulant 0.29	Total 1
Premix		Target	Actual	Batch	Out of Bucket	
fly ash	0.45	390.32		PA-2	2	fly ash
slag	0.45	390.32		PA-2	2	slag
cement	0.10	86.74		PA-1	1	cement
total	1.00	867.38				
MIXING METHOD: PADDLE BLADE						
	Initial	final		Batched by		
RPM			Density of Simulant	1.2484		
Temperature			Wt % Solids	28.88		

## 7.4.2 MCU (TR 437) Simulant

Compound	TARGET Molarity Moles/Liter	MW grams/mole	REFERENCE Amt / Liter grams	TARGET Amt / 2 liters grams
50% by Weight NaOH	1.594	40.00	127.50	255.01
NaNO <sub>3</sub>	3.159	84.99	268.48	536.97
NaNO <sub>2</sub>	0.368	68.99	25.39	50.78
Na <sub>2</sub> CO <sub>3</sub>	0.176	105.99	18.65	37.31
Na <sub>2</sub> SO <sub>4</sub>	0.059	142.04	8.37	16.73
Aluminum Nitrate (9 H <sub>2</sub> O)	0.054	375.13	20.33	40.66
Sodium Phosphate (12 H <sub>2</sub> O)	0.012	380.12	4.67	9.34
Total Salt mass			398.21	
Total Na Molarity	5.63			
Notes				
Make 2 two liter batches and combine				

Trial Run	PreMix (grams)	Simulant (grams)	March 31, 2008	H <sub>2</sub> O (grams)	H <sub>2</sub> O/Premix	Grout (grams)
Use MCU Simulant PA 022008, Temperature of 22°C						
TR435	852.43	747.57		511.46	0.60	1600
DDA	Salt grams/Liter 398.21	Water grams/Liter 862.59	Salt + Water grams/Liter 1261	Water g/g simulant 0.68	Salt g/g simulant 0.32	Total 1
Premix		Target	Actual	Batch	Out of Bucket	
fly ash	0.45	383.59		PA-1		fly ash
slag	0.45	383.59		PA-1		slag
cement	0.10	85.24		PA-1		cement
total	1.00	852.43				
MIXING METHOD: PADDLE BLADE				Batched by		
	Initial	final				
RPM			Density of Simulant	1.2608		
Temperature			Wt % Solids	31.54		

## 7.4.3 DDA (TR 431) Simulant

Compound	TARGET Molarity Moles/Liter	MW grams/mole	REFERENCE Amt / Liter grams	TARGET Amt / 2 liters grams
50% by Weight NaOH	0.769	40.00	61.52	123.04
NaNO <sub>3</sub>	2.202	84.99	187.15	374.30
NaNO <sub>2</sub>	0.110	68.99	7.56	15.12
Na <sub>2</sub> CO <sub>3</sub>	0.145	105.99	15.36	30.72
Na <sub>2</sub> SO <sub>4</sub>	0.044	142.04	6.31	12.61
Aluminum Nitrate (9 H <sub>2</sub> O)	0.071	375.13	26.63	53.27
Sodium Phosphate (12 H <sub>2</sub> O)	0.008	380.12	3.22	6.43
Total Salt mass			263.66	
Total Na Molarity	3.48			

Trial Run	PreMix (grams)	Simulant (grams)	March 18, 2008	H <sub>2</sub> O (grams)	H <sub>2</sub> O/Premix	Grout (grams)
Use DDA Simulant PA 021408, Temperature of 22°C						
TR429	901.88	698.12		541.13	0.60	1600
	Salt	Water	Salt + Water	Water	Salt	Total
DDA	grams/Liter	grams/Liter	grams/Liter	g/g simulant	g/g simulant	
	263.66	908.84	1173	0.7751301	0.2248699	1
Premix	Target	Actual	Batch	Out of		
fly ash	0.45	405.85	PA-1	Bucket		fly ash
slag	0.45	405.85	PA-1			slag
cement	0.10	90.19	PA-1			cement
total	1.00	901.88				
MIXING METHOD: PADDLE BLADE				Batched by		
RPM		Density of Simulant	1.17252			
Temperature		Wt % Solids	22.33			

## **8.0 APPENDIX B: DETAILED DATA**

**Table 9. Data from Tc-99 sorption experiments on Saltstone and Vault 2 concrete as a function of time under reducing conditions (N<sub>2</sub> purged).**

ID		solid	Time	Rep	Sat.	Tare Wt	Solid Wt	Tare+Solid+Eq. + Aq	li-liquid	Start	Stop	time actual	Tc-99	1 sigma
	ADS #		target		CaCO <sub>3</sub>	(g)	(g)	(g)	(g)	date/ time	date/time	(d:h:min)	(dpm/mL)	%Unc
701	300252253	Saltstone	10min	1	Sparged	16.5381	0.101	26.1234	9.4843	8/6/2008 9:11	8/6/2008 9:45	0:0:34	9420.000	0.022
702	300252254			2		16.7406	0.1002	26.7762	9.9354	8/6/2008 9:12	8/6/2008 9:47	0:0:35	10300.000	0.022
703	300252255		0.5h	1		16.5805	0.1008	26.7021	10.0208	8/6/2008 9:13	8/6/2008 10:15	0:1:02	9500.000	0.022
704	300252256			2		16.6233	0.1001	26.555	9.8316	8/6/2008 9:13	8/6/2008 10:17	0:1:04	10900.000	0.022
705	300252257		1h	1		16.6026	0.1004	26.6559	9.9529	8/6/2008 9:14	8/6/2008 11:16	0:2:02	10000.000	0.022
706	300252258			2		16.6564	0.1002	26.6796	9.923	8/6/2008 9:15	8/6/2008 11:18	0:2:03	9090.000	0.022
707	300252259		6h	1		16.2901	0.1005	25.9669	9.5763	8/6/2008 9:16	8/6/2008 15:22	0:6:06	11900.000	0.022
708	300252260			2		16.6273	0.0999	26.8917	10.1645	8/6/2008 9:16	8/6/2008 15:24	0:6:08	10200.000	0.022
709	300252261		24h	1		16.6893	0.1004	26.7706	9.9809	8/6/2008 9:17	8/7/2008 9:24	1:0:07	9710.000	0.022
710	300252262			2		16.5865	0.1009	26.7307	10.0433	8/6/2008 9:18	8/7/2008 9:26	1:0:08	10600.000	0.022
711	300252921		214h	1		16.6544	0.101	27.1396	10.3842	8/6/2008 9:40	8/20/2008 9:45	14:0:05	10000.000	0.022
712	300252922			2		16.6973	0.0992	27.0548	10.2583	8/6/2008 9:40	8/20/2008 9:45	14:0:05	9530.000	0.022
713	300252923			3		16.6286	0.0997	27.1814	10.4531	8/6/2008 9:40	8/20/2008 9:45	14:0:05	9970.000	0.022
714	300252924			4		16.6129	0.0999	26.8121	10.0993	8/6/2008 9:40	8/20/2008 9:45	14:0:05	10600.000	0.022
715	300252925			5		16.7077	0.0999	26.9991	10.1915	8/6/2008 9:40	8/20/2008 9:45	14:0:05	9230.000	0.022
716	300252926			6		16.6169	0.0996	26.4864	9.7699	8/6/2008 9:40	8/20/2008 9:45	14:0:05	7850.000	0.022
717	300252927			7		16.6116	0.1007	26.6238	9.9115	8/6/2008 9:40	8/20/2008 9:45	14:0:05	9660.000	0.022
718	300252928			8		16.6228	0.0991	26.5317	9.8098	8/6/2008 9:40	8/20/2008 9:45	14:0:05	12200.000	0.022
719	300252929			9		16.7221	0.0991	26.9542	10.133	8/6/2008 9:40	8/20/2008 9:45	14:0:05	9300.000	0.022
720	300252930			10		16.6964	0.0994	26.8612	10.0654	8/6/2008 9:40	8/20/2008 9:45	14:0:05	10100.000	0.022

ID		solid	Time	Rep	Sat.	Tare Wt	Solid Wt	Tare+Solid+Eq. + Aq	li-liquid	Start	Stop	time actual	Tc-99	1 sigma
	ADS #		target		CaCO <sub>3</sub>	(g)	(g)	(g)	(g)	date/ time	date/time	(d:h:min)	(dpm/mL)	%Unc
721	300252215	Vault 2	10min	1	Not Sparged	16.623	0.5003	28.4861	11.3628	8/6/2008 9:20	8/6/2008 9:49	0:0:29	5040.000	0.022
722	300252216			2		16.6588	0.5004	28.5454	11.3862	8/6/2008 9:20	8/6/2008 9:52	0:0:32	6630.000	0.022
723	300252217		0.5h	1		16.5803	0.4999	28.1765	11.0963	8/6/2008 9:21	8/6/2008 10:20	0:0:59	9140.000	0.022
724	300252218			2		16.7685	0.4994	28.3663	11.0984	8/6/2008 9:22	8/6/2008 10:23	0:1:01	6910.000	0.022
725	300252219		1h	1		16.6318	0.4999	28.736	11.6043	8/6/2008 9:23	8/6/2008 11:20	0:1:57	6280.000	0.022
726	300252220			2		16.6157	0.5004	28.443	11.3269	8/6/2008 9:24	8/6/2008 11:22	0:1:58	6880.000	0.022
727	300252221		6h	1		16.5863	0.4993	28.208	11.1224	8/6/2008 9:25	8/6/2008 15:26	0:6:01	7730.000	0.022
728	300252222			2		16.7518	0.5007	28.8059	11.5534	8/6/2008 9:26	8/6/2008 15:28	0:6:02	7150.000	0.022
729	300252223		24h	1		16.582	0.5003	28.2508	11.1685	8/6/2008 9:28	8/7/2008 9:29	1:0:01	7410.000	0.022
730	300252224			2		16.7506	0.5003	28.5687	11.3178	8/6/2008 9:29	8/7/2008 9:20	0:23:51	6130.000	0.022
731	300252931		214h	1		16.6263	0.4997	28.3206	11.1946	8/6/2008 9:50	8/20/2008 9:45	13:23:55	4340.000	0.022
732	300252932			2		16.669	0.5004	28.3234	11.154	8/6/2008 9:50	8/20/2008 9:45	13:23:55	4560.000	0.022
733	300252933			3		16.7211	0.4992	28.8819	11.6616	8/6/2008 9:50	8/20/2008 9:45	13:23:55	4020.000	0.022
734	300252934			4		16.6784	0.5004	28.6438	11.465	8/6/2008 9:50	8/20/2008 9:45	13:23:55	5160.000	0.022
735	300252935			5		16.613	0.5001	28.5331	11.42	8/6/2008 9:50	8/20/2008 9:45	13:23:55	4690.000	0.022
736	300252936			6		16.6161	0.499	28.2684	11.1533	8/6/2008 9:50	8/20/2008 9:45	13:23:55	3770.000	0.022
737	300252937			7		16.6825	0.4998	28.43	11.2477	8/6/2008 9:50	8/20/2008 9:45	13:23:55	3980.000	0.022
738	300252938			8		16.7283	0.4999	28.8549	11.6267	8/6/2008 9:50	8/20/2008 9:45	13:23:55	4090.000	0.022
739	300252939			9		16.6089	0.4995	28.3423	11.2339	8/6/2008 9:50	8/20/2008 9:45	13:23:55	4010.000	0.022
740	300252940			10		16.6958	0.4999	28.3376	11.1419	8/6/2008 9:50	8/20/2008 9:45	13:23:55	4710.000	0.022
741		No-Solids Controls	214h	1	Not Sparged	16.4511		27.2151	10.764	8/6/2008 9:11	8/20/2008 9:45	14:0:34		
742				2		16.5778		27.3032	10.7254	8/6/2008	8/20/2008	14:0:34		

ID		solid	Time	Rep	Sat.	Tare Wt	Solid Wt	Tare+Solid+Eq.	li-liquid	Start	Stop	time actual	Tc-99	1 sigma
	ADS #		target		CaCO <sub>3</sub>	(g)	(g)	(g)	(g)	date/ time	date/time	(d:h:min)	(dpm/mL)	%Unc
										9:11	9:45			
743				3		16.639		26.4423	9.8033	8/6/2008 9:11	8/20/2008 9:45	14:0:34		



**Table 10. Tc-99 desorption from Saltstone and Vault 2 concrete as a function of time.**

ID	ID in Table 1	ADS #	Solid	Sat. CaCO <sub>3</sub> Sol'n	Desorption Duration (day)	Rep	Tare+ Solid+Inter after Adsorp. (g)	wt soln for desorption	Start time	Stop time	Tc-99 (dpm/mL)	1 Sigma %Unc
811	711	300252941	Saltstone	Sparged	0.04	1	23.756	7.0006	8/20/2008 11:05	8/20/2008 12:00	1.03E+02	4.82%
812	712	300252942				2	23.058	6.2615	8/20/2008 11:05	8/20/2008 12:00	1.55E+01	19.40%
813	713	300252943			1	1	23.099	6.3707	8/20/2008 11:05	8/21/2008 10:15	4.86E+01	7.72%
814	714	300252944				2	22.877	6.1642	8/20/2008 11:05	8/21/2008 10:15	2.99E+01	11.10%
815	715	300252945			7	1	22.995	6.1874	8/20/2008 11:05	8/27/08 11:00	3.87E+02	2.87%
816	716	300252946				2	23.27	6.5535	8/20/2008 11:05	8/27/08 11:00	2.03E+03	2.29%
817	717				14	1	23.562	6.8497	8/20/2008 11:05	9/3/2008 9:30		
818	718					2	23.544	6.8221	8/20/2008 11:05	9/3/2008 9:30		
819	719				30	1	23.85	7.0288	8/20/2008 11:05			
820	720					2	22.979	6.1832	8/20/2008 11:05			
831	731	300252947	Vault 2	Not sparged	0.04	1	23.993	6.867	8/20/2008 11:10	8/20/2008 12:02	9.52E+01	5.07%
832	732	300252948				2	24.209	7.0396	8/20/2008 11:10	8/20/2008 12:02	1.56E+02	3.94%
833	733	300252949			1	1	24.197	6.9767	8/20/2008 11:10	8/21/2008 10:15	1.18E+02	4.51%
834	734	300252950				2	23.938	6.7592	8/20/2008 11:10	8/21/2008 10:15	1.43E+02	4.10%
835	735	300252951			7	1	23.989	6.8759	8/20/2008 11:10	8/27/08 11:05	5.84E+01	6.89%
836	736	300252952				2	25.879	8.7639	8/20/2008 11:10	8/27/2008 11:05	2.04E+02	3.53%
837	737				14	1	24.525	7.3427	8/20/2008 11:10	9/3/2008 9:30		
838	738					2	23.948	6.7198	8/20/2008 11:10	9/3/2008 9:30		
839	739				30	1	23.958	6.8496	8/20/2008 11:10			
840	740					2	23.85	6.6543	8/20/2008 11:10			

**Table 11. Data for sorption of Se-75, I-129, Np-237 and Pu-238 on Saltstone, Vault 2 concrete and oxidized Saltstone under oxidizing conditions.**

ADS#	Tube #	solid	rep	soln	tube tare (g)	soils (g)	tube +solids (g)	tube+sol+ soln+tracer (g)
300251616	601a	Vault	1	Ca(OH) <sub>2</sub>	16.7152	0.501	17.2162	28.92
300251617	602a		2		16.5669	0.5	17.0669	28.954
300251618	603a	Vault	1	CaCO <sub>3</sub>	16.6441	0.4998	17.1439	30.12
300251619	604a		2		16.6469	0.4999	17.1468	30.24
300251620	605a	Oxidized Saltstone	1	Ca(OH) <sub>2</sub>	16.6248	0.5012	17.126	28.974
300251621	606a		2		16.7611	0.4988	17.2599	29.675
300251622	607a	Oxidized Saltstone	1	CaCO <sub>3</sub>	16.6967	0.5	17.1967	30.363
300251623	608a		2		16.4785	0.4992	16.9777	30.01
300251624	609a	Saltstone	1	Ca(OH) <sub>2</sub>	16.8044	0.5004	17.3048	29.338
300251625	610a		2		16.7007	0.4997	17.2004	29.178
300251626	611a	Saltstone	1	CaCO <sub>3</sub>	16.6783	0.5008	17.1791	30.137
300251627	612a		2		16.6959	0.5009	17.1968	29.363
300251628	613a	Control (no concrete)	1	Ca(OH) <sub>2</sub>				27.279
300251629	614a		2					26.714
300251630	615a		3					26.895
300251631	616a	Control (no concrete)	1	CaCO <sub>3</sub>				28.143
300251632	617a		2					27.922
300251633	618a		3					28.071

**Table 12. Data for sorption of Tc-99 and U-233 on Saltstone, Vault 2 concrete and oxidized Saltstone under oxidizing conditions.**

ADS#	Tube #	solid	rep	soln	tube tare (g)	soils (g)	tube+solid(g)	tube+sol+soln+tracer
300252001	601TcU	Vault	1	Ca(OH) <sub>2</sub>	16.6945	0.5011	17.1956	28.778
300252002	602TcU		2		16.6037	0.5002	17.1039	28.862
300252003	603TcU	Vault	1	CaCO <sub>3</sub>	16.5939	0.5014	17.0953	29.791
300252004	604TcU		2		16.6394	0.5	17.1394	29.852
300252005	605TcU	Oxidized Saltstone	1	Ca(OH) <sub>2</sub>	16.6757	0.5008	17.1765	28.952
300252006	606TcU		2		16.7968	0.4991	17.2959	28.99
300252007	607TcU	Oxidized Saltstone	1	CaCO <sub>3</sub>	16.6939	0.5	17.1939	30.064
300252008	608TcU		2		16.6184	0.5012	17.1196	29.929
300252009	609TcU	Saltstone	1	Ca(OH) <sub>2</sub>	16.6685	0.4992	17.1677	29.064
300252010	610TcU		2		16.6529	0.4996	17.1525	29.094
300252011	611TcU	Saltstone	1	CaCO <sub>3</sub>	16.6521	0.4993	17.1514	30.125
300252012	612TcU		2		16.6709	0.5002	17.1711	30.182
300252048	613TcU	Control (no concrete)	1	Ca(OH) <sub>2</sub>				27.704
300252049	614TcU		2					27.675
300252050	615TcU		3					27.777
300252051	616TcU	Control (no concrete)	1	CaCO <sub>3</sub>				29.076
300252052	617TcU		2					28.993
300252053	618TcU		3					28.318

**Table 13. Sorption of Se-75, Np-237, and Pu-238 on Saltstone under reducing (N<sub>2</sub> purged) conditions.**

ADS#	Tube #	solid	rep	sol'n	tube tare (g)	soils (g)	tube + solids (g)	tube+sol+ soln+tracer(g)
300252225	619a	Saltstone	1	Ca(OH) <sub>2</sub>	16.5597	0.2507	16.8104	30.265
300252226	620a		2		16.668	0.2506	16.9186	29.866
300252227	621a	Saltstone	1	CaCO <sub>3</sub>	16.7938	0.2510	17.0448	30.232
300252228	622a		2		16.5337	0.2499	16.7836	29.825
300252229	623a	Control (no concrete)	1	Ca(OH) <sub>2</sub>				27.986
300252230	624a		2					27.776
300252231	625a		3					27.93
300252232	626a	Control (no concrete)	1	CaCO <sub>3</sub>				29.466
300252233	627a		2					29.693

**Table 14. Sorption of Tc-99 and U-233 on Saltstone under reducing (N<sub>2</sub> purged) conditions.**

<b>ADS#</b>	<b>Tube #</b>	<b>solid</b>	<b>rep</b>	<b>soln</b>	<b>tube tare (g)</b>	<b>soils (g)</b>	<b>tube +solids</b>	<b>tube+sol+ soln+tracer</b>
300252235	619TcU	Saltstone	1	Ca(OH) <sub>2</sub>	16.4988	0.2503	16.7491	28.142
300252236	620TcU		2		16.6187	0.2498	16.8685	28.416
300252237	621TcU	Saltstone	1	CaCO <sub>3</sub>	16.5451	0.2498	16.7949	29.44
300252238	622TcU		2		16.6678	0.2492	16.917	29.555
300252239	623TcU	Control (no concrete)	1	Ca(OH) <sub>2</sub>				27.67
300252240	624TcU		2					27.52
300252241	625TcU		3					27.401
300252242	626TcU	Control (no concrete)	1	CaCO <sub>3</sub>				29.012
300252243	627TcU		2					29.207

**Table 15. Sorption of I-129 on Saltstone under reducing (N<sub>2</sub> purged) conditions.**

<b>ADS#</b>	<b>Tube #</b>	<b>solid</b>	<b>rep</b>	<b>soln</b>	<b>tube tare (g)</b>	<b>soils (g)</b>	<b>tube +solids</b>	<b>tube+sol+ soln</b>
300252989	619I	Saltstone	1	Ca(OH) <sub>2</sub>	16.6201	0.2501	16.8702	30.2337
300252990	620I		2		16.6396	0.25	16.8896	29.4
300252991	621I	Saltstone	1	CaCO <sub>3</sub>	16.6626	0.2499	16.9125	27.374
300252992	622I		2		16.6714	0.25	16.9214	27.4424
300252993	623I	Control (no concrete)	1	Ca(OH) <sub>2</sub>	16.6491			28.8372
300252994	624I		2		16.6984			28.8545
300252995	625I		3		16.6329			28.7838
300252996	626I	Control (no concrete)	1	CaCO <sub>3</sub>	16.5303			28.3947
300252997	627I		2		16.6762			28.5721

**Table 16. First-order kinetic information related to the desorption of radionuclides from Vault 2 concrete, as described in Equation 5.**

	<b>Am</b>	<b>Cd</b>	<b>Co</b>	<b>Ce</b>	<b>Hg</b>	<b>Sn</b>	<b>Sr</b>	<b>Cs</b>	<b>Y</b>
Slope <sup>a</sup>	-0.0090	0.0096	-0.0158	0.0252	0.0203	-0.0115	-0.9918	-0.1639	0.0029
Significant F Value	0.19	0.53	0.40	0.27	0.81	0.25	0.25	0.05	0.59
R <sup>2</sup>	0.914	0.459	0.653	0.830	0.091	0.849	0.852	0.994	0.366
ln(A/A <sub>0</sub> ), 100 d <sup>b</sup>	-0.90	0.96	-1.58	2.52	2.03	-1.15	-99.18	-16.39	0.29
% on solid, 100 d <sup>b</sup>	40.8	259.9	20.7	1237.4	759.3	31.5	0.0	0.0	133.5

<sup>(a)</sup> Slopes are equal to  $k$  in Equation 5.

<sup>(b)</sup> Calculated value after 100 days, based on Equation 5 and  $k$  noted in the first row. “% on solid” =  $A/A_0 \times 100$

Note: Statistics indicate that there is a poor fit to data in Figure 3.

## **9.0 APPENDIX C: APPROACH TO EQUILIBRIUM AND BATCH $K_d$ VALUES FOR THE GAMMA-SUITE OF RADIONUCLIDES**



**Table 17.** Aqueous phase concentration of radionuclides (dpm) in contact with Vault 2 concrete: Approach to equilibrium study.

	<b>Time (day)</b>				
	<b>0</b>	<b>0.17</b>	<b>2</b>	<b>4</b>	<b>8</b>
Am-241	0.24	4.5E-05	Bdl	bdl	bdl
Cd-109	0.99	5.6E-04	Bdl	bdl	bdl
Co-57	0.64	2.2E-04	4.1E-05	bdl	bdl
Ce-139	0.65	1.3E-04	Bdl	bdl	bdl
Hg-203	0.31	8.0E-05	Bdl	bdl	bdl
Sn-113	0.45	1.3E-04	Bdl	bdl	bdl
Sr-85	0.35	4.3E-03	4.3E-03	4.0E-03	4.2E-03
Cs-137	0.41	3.4E-03	2.7E-03	2.6E-03	2.7E-03
Y-88	0.50	1.4E-04	Bdl	bdl	bdl
Co-60	0.45	1.4E-04	2.5E-05	bdl	bdl
Co-60	0.40	1.1E-04	1.5E-05	bdl	bdl
Y-88	0.31	7.7E-05	Bdl	bdl	bdl

bdl = below detection limit

**Table 18.** Aqueous phase concentration of radionuclides (dpm) in contact with Saltstone: Approach to equilibrium study.

	<b>Time (day)</b>				
	<b>0</b>	<b>0.17</b>	<b>2</b>	<b>4</b>	<b>8</b>
Am-241	0.2	9.3E-06	bdl	6.9E-06	bdl
Cd-109	1.0	8.4E-05	bdl	7.5E-06	bdl
Co-57	0.6	4.5E-05	1.8E-05	1.8E-05	6.7E-06
Ce-139	0.7	3.3E-05	bdl	bdl	5.2E-06
Hg-203	0.3	3.9E-05	bdl	1.7E-05	7.9E-06
Sn-113	0.4	5.1E-05	2.1E-05	1.6E-05	bdl
Sr-85	0.3	2.7E-03	2.5E-03	2.6E-03	1.5E-03
Cs-137	0.4	3.1E-03	3.0E-03	3.1E-03	1.8E-03
Y-88	0.5	5.8E-05	1.4E-05	bdl	1.5E-05
Co-60	0.5	1.3E-05	7.7E-06	1.2E-05	bdl
Co-60	0.4	2.0E-05	bdl	bdl	bdl
Y-88	0.3	1.5E-05	1.6E-05	bdl	bdl

bdl = below detection limit

**Table 19.** Batch  $K_d$  values of gamma suite of radionuclides measured in this study compared to previously measured values and recommended values for cementitious materials: Vault, Calcite-saturated, Reducing.

	<b>Vault <math>K_d</math> (mL/g)</b>	<b>Measured <math>K_d</math> Oxidized <math>\text{Ca}(\text{OH})_2</math> grout (mL/g; young concrete; taken from Kaplan and Coates 2007, Table 3, Stages 1 and 2 Reducing)</b>	<b>"Best" <math>K_d</math> value as reported in Kaplan (2006) for oxidizing cement Stage 1 &amp; 2) (mL/g)</b>
Am-241	>39,481	42,887	5,000
Cd-109	236,878	297,300	500
Ce-139	>173,457	103,840	5,000
Hg-203	108,738	1,173	500
Sn-113	73,634	71,762	4,000
Sr-85	1,256	3	0.2 - 0.5
Cs-137	1,327	-2	2 - 4
Y-88	404,648	64,821	5,000
Co-60	272,594	1,000	15,065

**Table 20.** Batch  $K_d$  values of gamma suite of radionuclides measured in this study compared to previously measured values and recommended values for cementitious materials: Saltstone, Calcite-saturated, Reducing.

	<b>Saltstone <math>K_d</math> (mL/g)</b>	<b>Measure <math>K_d</math> with grout Stage 3 reducing (Kaplan and Coates 2007; Table 3) (mL/g)</b>	<b>"Best" <math>K_d</math> value as reported in Kaplan (2006) for reducing cement Stage 1 &amp; 2) (mL/g)</b>
Am-241	>458,330	4,112	500
Cd-109	582,495	3,180	250
Ce-139	>213,346	4,652	500
Hg-203	133,590	568	250
Sn-113	266,177	3,360	2,000
Sr-85	768	39	1
Cs-137	358	18	2
Y-88	NA	4,738	500
Co-60	573,318	3,994	500

Table 21. Batch  $K_d$  values of gamma suite of radionuclides measured in this study compared to previously measured values and recommended values for cementitious materials: Saltstone, Portlandite-saturated, Reducing.

	<b>Saltstone <math>K_d</math> (mL/g)</b>	<b>Measure <math>K_d</math> with grout Stage 3 reducing (Kaplan and Coates 2007; Table 3) (mL/g)</b>	<b>“Best” <math>K_d</math> value as reported in Kaplan (2006) for reducing cement Stage 1 &amp; 2) (mL/g)</b>
Am-241	>352,270	17,113	500
Cd-109	247,087	17,510	250
Ce-139	>260,452	4,564	500
Hg-203	112,133	1,095	250
Sn-113	284,837	5,520	2,000
Sr-85	556	55	1
Cs-137	230	15	2
Y-88	501,547	5,336	500
Co-60	474,158	6,539	500

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