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Iodine, Neptunium, Plutonium and Technetium Sorption to Saltstone and Cement Formulations Under Oxidizing and Reducing Conditions

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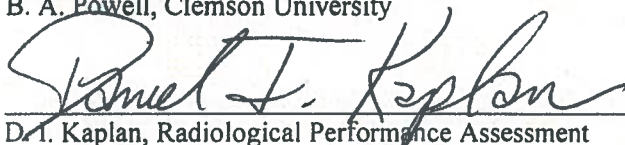
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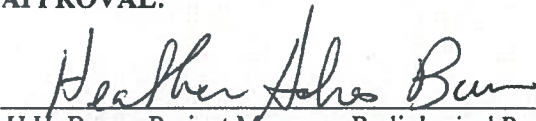
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EXECUTIVE SUMMARY

Sorption of ^{99}Tc , ^{127}I , ^{237}Np , and ^{242}Pu to two saltstone and two cementitious materials was examined. Np and Pu sorbed very strongly to all four cementitious formulations and appeared to reach steady state within 24 h. Based on the sorption behavior, there were some indications that partial reduction of Pu(IV) to Pu(III) and Np(V) to Np(IV) occurs in these systems. However, the K_d values for both Pu and Np remain $>10^5$ mL/g throughout the experiments. This value compares favorably with previously reported K_d values for Pu but is significantly higher than the previously reported value of 3000-4000 mL/g for Np (Kaplan *et al.* 2008).

In all experiments, regardless of the total concentration of Np and Pu in the system, a relatively constant aqueous phase concentration of both Np and Pu was observed. Therefore, it appears that the aqueous concentrations of Np and Pu are solubility controlled rather than sorption controlled. The measured concentrations for Np and Pu ranged from 10^{-11} mol/L to 10^{-13} mol/L. These values are consistent with precipitation of actinide hydrous oxide solid phases; consequently these tests strongly suggest that solubility (as described by solubility constants) and not sorption (as described by K_d values) will controlling Np and Pu aqueous concentration near the Saltstone Disposal Facility.

Sorption of both Tc and I do not appear to have reached steady state during the four day equilibration times used in these experiments. Similar to Np and Pu, surface mediated redox processes were affecting Tc and I sorption. However, this observation was based on changes in sorption behavior, not direct determination of Tc or I oxidation states. Calculated I K_d values of 7.66 and 7.25 mL/g for simulated Vault 2 concrete under oxidizing and reducing conditions, respectively, in the present work compare favorably with values of 8.94 and 7.15 mL/g under similar conditions reported by Kaplan *et al.* (2008). Although it appears steady state was not reached in Tc systems, conditional K_d values were calculated and were found to be a factor of ~ 5 higher than values previously reported by Kaplan *et al.* (2008). The fraction of reducing slag within each saltstone formulation appears to have an effect on Tc sorption. Tc K_d values under oxidizing conditions ranged from 2.75 to 5.08 mL/g. Saltstone formulations under reducing conditions had K_d values between 32 (0 dry wt-% slag) and 4,370 mL/g (45 dry wt-% slag), but the system had not achieved steady state conditions at the time of measurement, thus greater sorption may likely occur under natural conditions. Cementitious formulation did not influence Pu, Np, or I sorption. These data support the following changes in the SRS “best K_d ” geochemical data package used as input to SRS performance assessment calculations.

| | Present data ^(d) | | | This document | | |
|--|---------------------------------|-------------------|----------------|-----------------------------|-----------------------------|----------------------------|
| | Stage 1 ^(c) Young | Stage 2 Medium | Stage 3 Old | Stage 1 Young | Stage 2 Medium | Stage 3 Old |
| Reducing Concrete (mL/g) | | | | | | |
| I | 5 | 9 | 0 | 5 | 9 | 0 |
| Np | 4,000 | 4,000 | 3,000 | 10^{-13} M ^(a) | 10^{-13} M ^(a) | 5000 |
| Pu | 10,000 | 10,000 | 1,000 | 10^{-12} M ^(a) | 10^{-12} M ^(a) | 2000 |
| Tc | 5,000 | 5,000 | 5,000 | 5000 | 5000 | 1000 ^(b) |
| Oxidizing Concrete (mL/g) | | | | | | |
| I | 8 | 15 | 4 | 8 | 15 | 4 |
| Np | 1,600 | 1,600 | 250 | 10^{-12} M ^(a) | 10^{-12} M ^(a) | 5000 |
| Pu | 10,000 | 10,000 | 1,000 | 10^{-12} M ^(a) | 10^{-12} M ^(a) | 2000 |
| Tc | 0.8 | 0.8 | 0.5 | 0.8 | 0.8 | 0.5 |
| ^(a) Apparent solubility (units = M = mol/L). Below this concentration, K_d value of 10,000 mL/g is to be used. ^(b) A decrease in Tc K_d values with respect to previous values will be used because of the observation that Tc(IV) oxidizes readily under SRS conditions to Tc(VII) ^(c) Stages 1, 2, and 3 are conceptually based on mineral composition changes. The 1 st , 2 nd , and 3 rd stages are expected to last 50, 500, and 7000 pore volumes, respectively. A 2-ft slab of cement may be expected to last 740 yr in the 1 st stage, 7400 yr in the 2 nd and 103,600 yr in the 3 rd stage. ^(d) Kaplan (2007), Kaplan and Coates (2008), and Kaplan et al. 2008 | | | | | | |

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LIST OF ABBREVIATIONS

| | |
|----------------|--|
| DDI water | Distilled deionized water |
| ICP-MS | Inductively coupled plasma – mass spectrometer |
| K _d | Distribution coefficient |
| LSC | liquid scintillation counting |
| NOM | Natural organic matter |
| PA | Performance Assessment |
| ppb | parts per billion |
| ppq | parts per quadrillion |
| QA/QC | Quality Assurance/Quality Control |
| SA | Special Analyses |
| SRNL | Savannah River National Laboratory |
| SRS | Savannah River Site |

1.0 Introduction

Performance Assessments (PA) are risk calculations designed to determine: (1) the maximum amount of radioactivity that can be safely buried in a subsurface facility and (2) the potential human risk associated with disposing of radioactive waste in a subsurface facility. Special Analyses (SAs) are similar to PAs except that they are designed to address specific issues related to PAs, such as a new discovery since the PA was issued. Commonly, parameters describing the extent that a radionuclide interacts with solids at the source, vadose zone, and aquifer influence the extent of calculated human risk. The two parameters that the SRS use to represent radionuclide/solid interactions are K_d and apparent solubility values, together these parameters are referred to as sorption values. Sorption values vary with radionuclides, groundwater chemistry, and the type of solid phase (and for cementitious materials, by the age of the material during the calculation). In this work, K_d and apparent solubility values are reported for ^{99}Tc , ^{127}I , ^{237}Np , and ^{242}Pu sorption to various cementitious formulations.

2.0 Objectives

The objectives of this work were to:

1. Determine the influence of cementitious formulation on technetium (Tc), iodine (I), neptunium (Np), and plutonium (Pu) sorption under oxidizing conditions. The specific formulations that were evaluated included: 1) an aged cement recovered from a 30-year old outdoor concrete pad on the SRS, 2) Vault 2 concrete, 3) TR545 saltstone, and 4) TR547 saltstone (additional details are presented in Section 3.0 Materials and Methods).
2. Measure Tc, I, Np, and Pu sorption to the cementitious formulations under reducing conditions.

3.0 Materials and Methods

3.1 Preparation of ICP-MS Standards, Stock Solutions, and Working Solutions

3.1.1 ^{242}Pu

A National Institute of Standards and Technology, Standard Reference Material (NIST SRM 434H) was used to prepare a stock ^{242}Pu solution by dilution in 2% Aristar Optima HNO_3 . All volume additions were monitored gravimetrically. This working solution was then used to make a set of 0.01, 0.05, 1, 2, 5, 10 parts per billion (ppb) standards by dilution using 2% HNO_3 . Again all volume additions were monitored gravimetrically. These standards were used to calibrate the Thermo Scientific X Series 2 inductively coupled plasma – mass spectrometer (ICP-MS) for quantification of ^{242}Pu . A representative calibration curve for ^{242}Pu is shown in Figure 3.1. The instrument performance was monitored using ^{209}Bi , ^{232}Th , and ^{238}U as internal standards. The recovery of each sample during analysis was corrected based on the internal standard recovery. The internal standard recoveries remained within standard quality assurance/quality control QA/QC protocols for the instrument (between 80% and 120%).

A ^{242}Pu stock solution was prepared by dissolving 1mg of $\text{Pu}(\text{NO}_3)_4$ obtained as a Certified Reference Material from New Brunswick Laboratory (CRM 130). This CRM is >99.9% ^{242}Pu by atom percent. The CRM was dissolved in 20mL of 8M HNO_3 (Aristar Optima Grade). Because no chemicals or heat have been introduced to manipulate the Pu oxidation state, it can be assumed that Pu(IV) is the predominant oxidation state in this stock solution. A working solution to be used in spiking ^{242}Pu experiments was prepared by diluting 2.5 mL of the CRM stock solution with 100 mL 1.0 M Aristar Optima HNO_3 . The concentration of ^{242}Pu in this stock solution was determined using ICP-MS calibrated using the NIST SRM standards. The concentration of Pu in this stock solution was 1065 ppb. The total Pu

concentration was also determined using liquid scintillation counting using the isotopic ratios reported for CRM 130. These compared favorably with the ICP-MS results but are reported here as a rigorous standardization because the isotopic ratios of CRM 130 have not yet been certified.

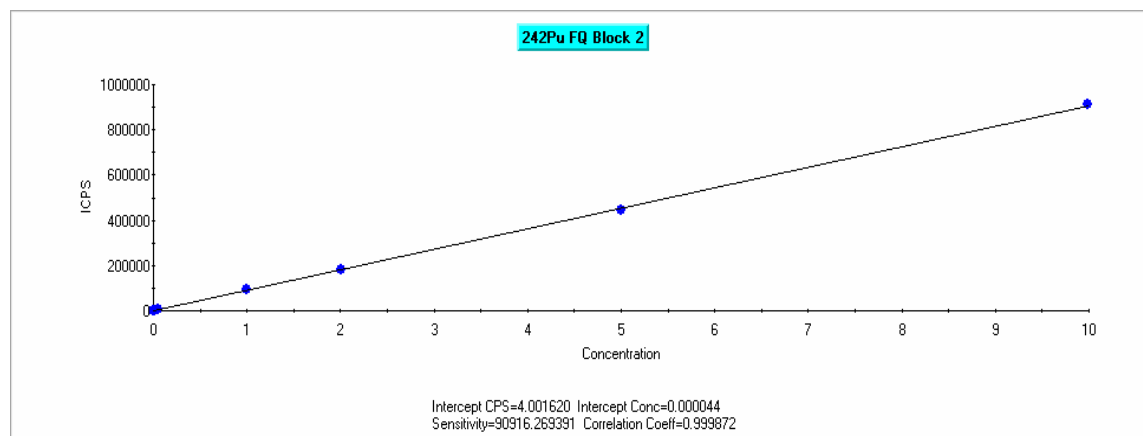


Figure 3.1: Screen capture of a typical ^{242}Pu calibration curve using Thermo PlasmaLab software to control the data collection and analysis. $R^2=0.999872$, Intercept Conc. (Detection Limit) = 0.000044 ppb.

3.1.2 ^{237}Np

A National Institute of Standards and Technology, Standard Reference Material (NIST SRM 4341) was used to prepare a stock ^{237}Np solution by dilution in 2% Aristar Optima HNO_3 . All volume additions were monitored gravimetrically. This working solution was then used to make a set of 0.01, 0.05, 1, 2, 5, 10 ppb standards by dilution using 2% HNO_3 . Again all volume additions were monitored gravimetrically. These standards were used to calibrate the Thermo Scientific X Series 2 ICP-MS for quantification of ^{237}Np . A representative calibration curve for ^{237}Np is shown in Figure 3.2. The instrument performance was monitored using ^{209}Bi , ^{232}Th , and ^{238}U as internal standards. The recovery of each sample during analysis was corrected based on the internal standard recovery. The internal standard recoveries remained within standard QA/QC protocols for the instrument (between 80% and 120%).

A compiled ^{237}Np stock solution from the Environmental Engineering and Earth Science (EE&ES) inventory (primarily purchased from Isotope Products, Valencia, CA) was evaporated to dryness then the residue was brought up in approximately 5mL 8.0 M HNO_3 . Then 1.0 M hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$, EMD Chemicals, ACS grade) and water were added to achieve a 3M HNO_3 /0.3M $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution. This solution was purified by extraction chromatography using Eichrom TEVA resin packed in a Bio-Rad poly-prep column. The 3M HNO_3 /0.3 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ neptunium solution was loaded on a 2 mL column and washed with 3 column volumes of 3 M HNO_3 . The Np(IV) was eluted with 0.02 M HCl + 0.2 M HF . The effluent was evaporated to dryness then redissolved in 1.0 M HNO_3 . Additional 1.0 M HNO_3 was added to maintain a approximately 10 mL then the solution was evaporated to incipient dryness and redissolved in a 5.0 mL of 1.0 M HNO_3 . An aliquot of the stock solution was evaporated to dryness on a stainless steel planchet and counted on the EG&G Ortec Alpha Spectrometer (Octete PC Detectors). No other alpha energies besides ^{237}Np were observed. The approximate concentration was determined using liquid scintillation counting and little ^{233}Pa was observed. The fuming in HNO_3 as performed at the end of the purification procedure will drive Np to the soluble pentavalent state. This is the stable oxidation state of Np under the experimental conditions. Therefore, experiments performed here can be assumed to be initially Np(V). The exact Np

concentration in this solution was determined using ICP-MS calibrated with a NIST standard as discussed in section 3.1.2 below.

A ^{237}Np working solution (Working Solution 1) was created by pipetting an aliquot of the ^{237}Np stock solution into a 100 mL Nalgene Teflon bottle and diluting with 2% BDH Aristar Ultra HNO_3 to give a working solution concentration of 820 ppb. All volumes were monitored gravimetrically. Analysis on the ICP-MS calibrated against NIST Standards as described below gave a concentration of 820 ppb in Working Solution 1.

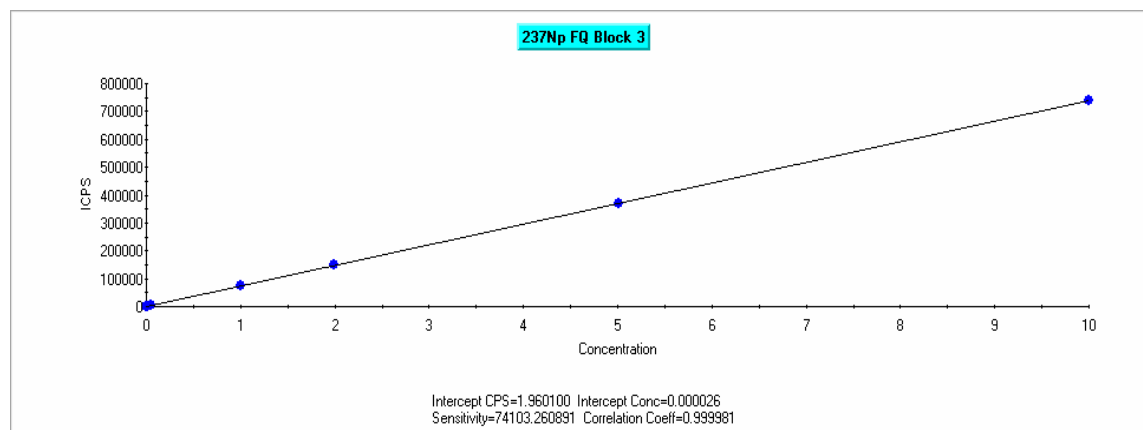


Figure 3.2: Screen capture of a typical ^{237}Np calibration curve using Thermo PlasmaLab software to control the data collection and analysis. $R^2=0.999981$, Intercept Conc. (Detection Limit) = 0.000026 ppb.

3.1.3 ^{99}Tc

A ^{99}Tc working solution was prepared by diluting a stock solution of ^{99}Tc (from the EE&ES inventory, purchased from Isotope Products, Valencia, CA) in distilled-deionized water (DDI, Resistivity $>18 \text{ M}\Omega\cdot\text{cm}$). The oxidation state of Tc was not measured. However, based on the aqueous concentration in the DDI water solution, Tc(VII) is the expected oxidation state. The reduced Tc(IV) oxidation state would not be soluble under these conditions. The expected concentration of 950 ppb based on the dilution was verified using liquid scintillation counting. The ^{99}Tc working solution was used to make 0.01, 0.05, 1, 2, 5, and 10 ppb standards by dilution using 2% HNO_3 . These standards were used to calibrate the Thermo Scientific X Series 2 ICP-MS for quantification of ^{99}Tc . A screen shot of a representative calibration curve is shown in Figure 3.3. The instrument performance was monitored by interpolating between ^{89}Y and ^{115}In internal standards. The recovery of each sample during analysis was corrected based on the internal standard recovery. The internal standard recoveries remained within standard QA/QC protocols for the instrument (between 80% and 120%).

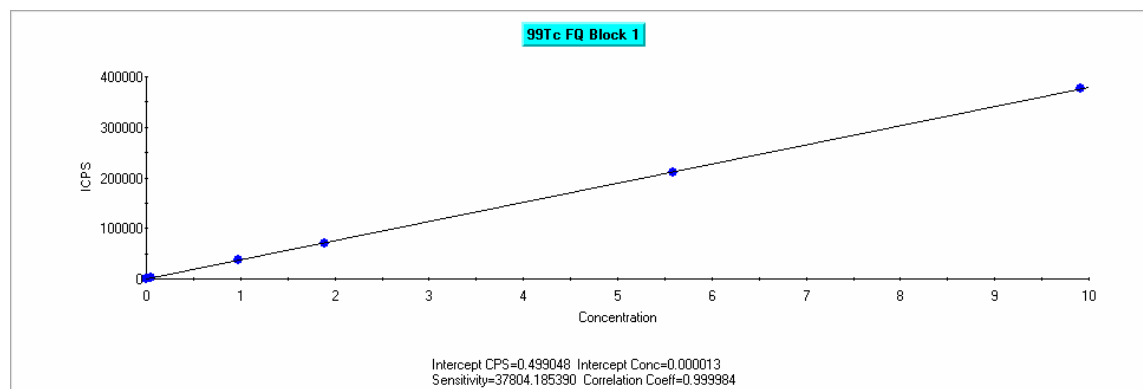


Figure 3.3: Screen capture of a typical ^{99}Tc calibration curve using Thermo PlasmaLab software to control the data collection and analysis. $R^2=0.999984$, Intercept Conc. (Detection Limit) = 0.000013 ppb.

3.1.4 ^{127}I

A 100 $\mu\text{g/mL}$ iodate (IO_3^-) stock solution from High Purity Standards (Charleston, SC) was used to make 1, 5, 10, 50, and 100 ppb standards by dilution using the “trap” solution (discussed in Section 3.2 below). These standards were used to calibrate the Thermo Scientific X Series 2 ICP-MS for quantification of ^{127}I . A screen shot of a representative calibration curve is shown in Figure 3.4. The use of a reducing, basic trap solution for iodine analysis limits the number of available internal standards that can be used to monitor ICP-MS instrument performance during iodine analysis. Experiments are underway to identify acceptable internal standards. However, the data presented in this work did not use any internal standards prior to rigorous testing and analysis of representative standards. As with the analyses for all isotopes (Tc, I, Np, and Pu), spiked QA/QC samples were frequently analyzed throughout the analysis as a check on instrument performance. While these values cannot be used to correct individual samples in the same manner that the internal standards can, they can be used to ensure accurate measurements of each isotope. In almost all cases, QA/QC standards were within 10% of the expected value. Because the average internal standard recovery ranges between 80% and 120% for the ICP-MS, the iodine QA/QC standard appears to be acceptable. However, a significant amount of ongoing work is testing various internal standards to improve the accuracy of iodine analysis using ICP-MS. In one experiment (discussed in detail below) the QA/QC standards deviated by an average value of 19.5%. This will be specifically discussed below.

Because experiments were performed with ^{127}I concentrations up to 1000 ppb, the 100 $\mu\text{g/mL}$ (ppm) stock iodate solution from High Purity Standards was used as the working solution.

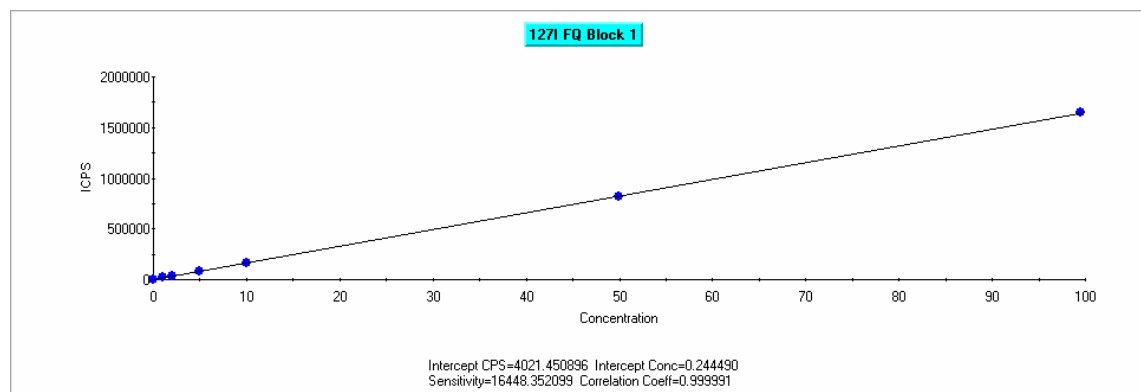


Figure 3.4: Screen capture of a typical ^{127}I calibration curve using Thermo PlasmaLab software to control the data collection and analysis. $R^2=0.999991$, Intercept Conc. (Detection Limit) = 0.24 ppb.

3.1.5 Cementitious Materials Selected for Experiments

There were four cementitious materials selected for this sorption study. The first, referred to as Aged Cement, is a 30 year old sample that does not contain any reducing slag. The aggregate from the Vault 2 cement had its aggregate removed prior to conducted tests in an effort to make subsamples more uniform. This was necessary because some of the aggregate were larger than the 0.5 g subsamples used in individual sorption tests. The Vault 2 cementitious material contained 17 dry wt-% reducing slag on a dry weight basis before the water was added to the mix (Table 3.1). The TR547 and TR545 saltstone formulations contain 45 dry wt-% and 90 dry wt-% reducing slag, respectively.

Table 3.1: Characteristics of saltstone formulations used in this work Kaplan *et al.* (2008)

| Sample | Percent Reducing Slag (dry wt-%) ^(c) | Percent Portland Cement (dry wt-%) ^(c) | Percent Fly Ash (dry wt-%) ^(c) | Percent Aggregate/sand (dry wt-%) ^(c) | Reducing Equivalents ($\mu\text{eq/g}$) |
|--------------------|---|---|---|--|---|
| Aged Cement | 0 | 10 | 45 | 45 | $85.5 \pm 10.1^{(a)}$ |
| Vault 2 Cement | 17 | 10 | 45 | 0 | $178^{(b)}$ |
| TR547 | 45 | 10 | 45 | 0 | $607^{(b)}$ |
| TR545 | 90 | 10 | 0 | 0 | $681^{(b)}$ |
| Blast furnace slag | 100 | 0 | 0 | 0 | $819^{(b)}$ |

^(a) Kaplan *et al.* (2008)

^(b) Roberts and Kaplan (2009)

^(c) All percentages of saltstone formulations are reported on a dry weight percentage basis, that is, the weight of the ingredients before water was added.

^(d) Based on Table 8 in Dixon *et al.* (2008; SRNL-STI-2008-00421), which shows the following quantity (lbs/cu yd) for saltstone Vault 2 Mix 1 concrete formulation: 201 cement (12.71 wt-%), 268 slag (16.95 wt-%), 44.7 silica fume (2.83 wt-%), 156.3 fly ash (9.89 wt-%), 911 fine sand (57.62 wt-%). The large aggregate was removed before the sorption tests were conducted. The large aggregate accounted for 75 wt-% of the original field sample, not the sample used in these test, before water was added to the mix.

TR547 is referred to as the Baseline by Dixon *et al.* (2008) and is described in more detail in Appendix C (Mix #2) by Dixon *et al.* (2008) (Control-BFS/PC) and #1 (Baseline).

TR545 saltstone contains 90% reducing slag, and it is Mix #1 in Dixon *et al.* (2008) and is described as:

“A control mix will be based on the baseline mix modified by exclusion of the Class F fly ash. Consequently, the cementitious materials premix will be a mixture of 90 % blast furnace slag and 10 % Portland cement. The degree of reaction will be much greater than with the normal premix and therefore should result in a lower porosity and a lower permeability. This bounding test at 0.60 w/cm ratio is expected to yield a hydraulic conductivity at or below the detection limit for the Mactec permeameter measurement system. Therefore, this test should demonstrate the lowest level of detection of the Mactec system as well as show a resolvable difference between measurements of the control mix and the control mix with the normal premix composition.”

3.2 ICP-MS Detection Limits

The PlasmaLab software platform determines a detection limit for each isotope based upon the intercept concentration. A new calibration curve was generated for each experimental run and curves were very similar. Using representative calibrations curves, the detection limits for each isotope were as listed in Table 3.2. Note the higher detection limit for ^{127}I is primarily due to the higher background count rate observed on the instrument. This is believed to be due to the minimum purity levels of chemicals required for the iodine “trap” solution as discussed in Section 3.3 below. Therefore, experiments were run with initial iodate concentrations higher than Tc, Np, and Pu to maintain analytical sensitivity.

Table 3.2: Detection limits for each isotope based on representative calibration curves generated in PlasmaLab software associated with the ICP-MS.

| Isotope | Detection Limit |
|-------------------|-----------------|
| ^{99}Tc | 0.000013 ppb |
| ^{127}I | 0.244 ppb |
| ^{237}Np | 0.000026 ppb |
| ^{242}Pu | 0.000044 ppb |

3.3 Experimental Methods

The experimental methods used in this work followed closely those previously described for experiments examining radionuclide sorption to saltstone (Kaplan *et al.*, 2007; Kaplan *et al.*, 2008). Brief descriptions of each method are provided below

Preparation of Calcite Solution: Using a hot/stirring plate, 1.0 L of distilled-deionized (DDI) water was heated to 3-10°C above room temperature. Then 0.01 g CaCO_3 (EM Science, ACS grade) was added to the solution and the resulting suspension was mixed for 24 hours at the elevated temperature. The solution was then vacuum filtered through a 0.45- μm filter to ensure no solid CaCO_3 remained in solution.

Preparation of 2% HNO_3 : Analysis of Tc, Np, and Pu on the ICP-MS required dilution in 2% HNO_3 . This was prepared by adding 28 mL of Aristar Optima HNO_3 from a clean graduated cylinder (designated to 2% HNO_3) into a 1 L volumetric flask (designated to 2% HNO_3) partially filled with DDI water, and then further diluted to volume.

Preparation of Trap Solution for Iodine Analysis: Analysis of I required the use of a reducing, basic solution that was capable of reducing iodate to iodine and holding the iodine in solution. This minimized the loss of I during sample analysis. A 1 L trap solution was prepared by weighing out 0.0500 g NaHSO₃ (Fisher Scientific, ACS Grade) on a calibrated Sartorius LA 230S scale and adding it to a 1L volumetric flask. Then 40 mL of 25% w/w tetramethylammonium hydroxide (Alfa Aesar, electronic grade) and 10 mL CFA-C solution (Spectrasol, Inc.) were added to the volumetric flask via a calibrated 1000-5000 µL Eppendorf Research pipette. The solution was then diluted to volume with DDI water.

3.4 Experimental Protocol for Sorption Experiments under Aerobic Conditions

Falcon BlueMax 15mL polypropylene vials were labeled and weighed to within 0.001 g on a calibrated Sartorius LA 230S scale. The scale was then zeroed and 0.25 +/- 0.01 g of a given solid were added to each tube, and the weight was recorded to within 0.001g.

For each of the four solids, three sets of triplicate samples were prepared. The three sets of samples were used to allow for experiments to be run with varying concentrations of each isotope. Target initial concentrations for ⁹⁹Tc, ²³⁷Np, and ²⁴²Pu samples were 1 ppb, 5 ppb, and 10 ppb. Target initial concentrations for the ¹²⁷I samples were 100 ppb, 500 ppb, and 1000 ppb. A set of no solids controls at initial concentrations of 1 ppb and 10 ppb for ⁹⁹Tc, ²³⁷Np, and ²⁴²Pu and initial concentrations of 100 ppb and 1000 ppb ¹²⁷I were also prepared by adding the calcite solution to pre-weighed, pre-labeled centrifuge tubes as discussed above.

The solids were equilibrated with the calcite solution before spiking with the radionuclides. This was done by adding 10 ± 0.1 mL of calcite solution to each tube, and recording the mass. The samples were then placed on a Thermo Scientific shaker overnight. After 24 hours, the solutions were allowed to settle for 1 hour. The pH was then measured and the samples were then centrifuged for 15 minutes at 8000 rpm to further separate the solids. The aqueous phase was then decanted and 10 ± 0.1 mL of calcite solution was added to each tube. The weight of the tube (labeled tube + solid + calcite solution) was measured to within 0.001g. During this washing process, the pH was monitored and held steady throughout the process. The pH ranged from 11-12 depending on the particular saltstone used. During the experiments, the exact pH for all samples at all equilibration times was measured and is reported in Appendix A and B.

The resulting suspensions were then spiked with ¹²⁷I, ²³⁷Np, ²⁴²Pu, and ⁹⁹Tc. It is important to note that all four isotopes were added to the same vial. Use of the ICP-MS to determine the concentration of each isotope allows for a single solution to contain all analytes of concern. This allowed for a greater variability in the sample set and increased replicates as opposed to running individual sorption tests for each isotope. For the systems with initial ⁹⁹Tc, ²³⁷Np, and ²⁴²Pu concentrations of 10 ppb and initial ¹²⁷I concentration of 100 ppb, a 100 µL aliquot of each radionuclide working solution was added to the first three tubes for each solid. The addition was made with the tube resting on a tared analytical balance so that the exact mass of each radionuclide solution added was recorded and the solution was gently swirled before the next radionuclide was added. The 5 ppb ²³⁷Np, ²⁴²Pu, and ⁹⁹Tc and 500 ppb ¹²⁷I samples were prepared in the same manner but adding 50 µL of the respective spike solutions. The final three tubes with initial ²³⁷Np, ²⁴²Pu, and ⁹⁹Tc concentrations of 1 ppb and 100 ppb ¹²⁷I were prepared by using 10 µL of the spike solutions for all four solids as well as a set of solid-free controls (No-Solids Controls). For clarity, this experimental matrix is shown in Table 3.3 below.

Table 3.3: Experimental Matrix of Sorption Experiments under Aerobic Conditions

| Experiment | Initial Concentration ⁹⁹ Tc, ²³⁷ Np, ²⁴² Pu | Initial Concentration ¹²⁷ I |
|----------------|---|--|
| Solids-Present | 1 ppb | 100 ppb |
| Solids-Present | 5 ppb | 500 ppb |
| Solids-Present | 10 ppb | 1000 ppb |
| Solids-Free | 1 ppb | 100 ppb |
| Solids-Free | 10 ppb | 1000 ppb |

After spiking the radionuclides, a precalculated amount of 10M NaOH was added to each sample to counter the acidic radionuclide spike solutions and the pH of one of the triplicate samples was measured to ensure the proper pH range was reached. The samples were then placed on an end-over-end shaker to mix at approximately 8 rpm. After 24 hours, the samples were removed from the shaker and the pH of each sample was measured using an Orion Ross semi-micro glass electrode calibrated against pH 4, 7, and 10 buffers (Thermo). The samples were then shaken and a transfer pipette was used to transfer 3.5 mL of a homogenous suspension to a 5mL syringe. The solution was then passed through a 100 nm nylon syringe filter. The first 0.25-0.50 mL of filtrate was discarded and the remaining filtrate was collected in a clean polyethylene vial. Then, 1.0 mL of the filtrate was removed and diluted in 9.0 mL 2% HNO₃. The mass of each phase was determined and recorded gravimetrically. Then, 1.0 mL of the remaining filtrate was transferred to a clean Falcon BlueMax 15mL vial and diluted with 9.0 mL of trap solution for ¹²⁷I analysis. Again, the volume of each phase was monitored gravimetrically. After the 24 hour sampling event, the samples were put back on the shaker to mix for three additional days. On day four, the above sampling procedure was repeated.

The ²³⁷Np, ²⁴²Pu, and ⁹⁹Tc samples can be run on the Thermo Scientific ICP-MS using the standard setup and procedure which included a standard flow glass nebulizer and bulb spray chamber. However, for the ¹²⁷I analysis, the ICP-MS must be reconfigured to accommodate the basic, reducing trap solution. This is to alleviate problems with iodine signal stability over time frequently observed in ICP-MS analysis. The reconfigured instrument uses an Elemental Science Microflow PFA-100 Teflon nebulizer with a flow rate of 100μL/min, along with a sapphire torch, and a Teflon spray chamber. This configuration must be run with a low pump speed to prevent back pressure on the system. Two 30 minute stability tests were performed using a 50 ppb iodate solution. Each experiment consisted of 40 separate measurements. After each experiment was completed the uncorrected mass counts were examined, and found to stay steady over the sampling period. The % relative standard deviation (% RSD) over all samples for each experiment was 1.866% and 1.460% respectively. This shows that there was no significant “memory” or loss of the iodine signal over time and that the reconfigured instrument has a stable iodine signal over time. However, as will be discussed below, some difficulty has been encountered in finding an adequate internal standard for iodine analysis.

3.5 Experimental Protocol for Sorption Experiments under Anerobic Conditions

In order to examine the effects of reducing conditions of sorption of each isotope to the various cementitious samples, a series of sorption experiments were performed in an anaerobic glovebox under a 2% H₂(g)/ 98% N₂(g) atmosphere. Based on the measured pH and E_H of these systems as discussed below, these systems were at the point of reducing water. Therefore, they are expected to represent a lower end of the possible range for reducing conditions expected in the porewater available within cementitious materials.

Preparation of Calcite for Reducing Conditions: Approximately 3.5 L of DDI water was boiled for 45 minutes. Argon was slowly bubbled through the water as it cooled. Once it cooled to below 50°C, approximately 3 g of calcite was added. This solution mixed overnight under a continuous Ar flow. After 12 hours the solution was moved into an oxygen free glove bag for filtration as described in 3.2.3.1. After filtration, the calcite solution was moved into the glove box.

Preparation of Working Solutions under Reducing Conditions: The calcite and solid solutions were prepared in the glove box using the previously mentioned procedure used under aerobic conditions. The radionuclide working solutions were transferred to the glovebox and stirred open to the reducing atmosphere for at least three days. The concentration of each isotope in the working solutions was measured to determine any change in the concentration due to evaporation while the solutions were equilibrating.

The preparation and spiking of samples for sorption experiments was performed exactly as described for the oxidizing conditions, except all sample handling was performed in the glovebox. After the 1 day and 4 day equilibration, the samples were filtered within the glovebox then transferred outside for dilution and ICP-MS analysis similar to the description provided about for the oxidizing conditions. For these experiments, only 4 mL of either 2% HNO₃ or trap solution were used to dilute the filtrate instead of the 9.0 mL used above for experiments performed under oxidizing conditions.

3.6 Examination of Sorption to Vial Walls for Solids and No Solids Controls

As will be discussed below, the solid-free controls samples indicated significant loss of Np and Pu. Once the one and four days samples were collected and run on the ICP-MS, it was necessary to determine the degree each radionuclide was sorbing to the vial walls. The remaining suspensions and controls were emptied into a waste container. Then 5 mL of the calcite solution was added to each vial using a calibrated pipette. The vials were sonicated for approximately one minute, and then emptied into the waste container. Another 5 mL of calcite solution was added for the second wash, and then discarded into the waste container. This procedure was expected to remove any soluble Pu from the system or Pu associated with colloidal particles. After each vial was washed, 10 mL of 2% HNO₃ was added using a calibrated pipette. The acid solution is expected to remove any Tc, Np, or Pu associated with the vial walls. This procedure has been shown to complete mass balances of Pu in similar sorption experiments using Pu (Powell *et al.*, 2002). This process was performed for both the solid suspension and the no solids controls. The samples were then run on the ICP-MS to determine the concentration of ⁹⁹Tc, ²³⁷Np, and ²⁴²Pu sorbed to the vial walls.

3.7 Data Analysis

The solubilities of ²⁴²Pu and ²³⁷Np were calculated by using the formula:

$$C_{sol} = \frac{C_{ICP-MS} * 10^{-6} \left(\frac{g_{nuclide}}{\mu g_{nuclide}} \right)}{M_{nuclide}} \quad \text{(Equation 3.1)}$$

C_{sol} = observed nuclide solubility (mol_{nuclide}/kg_{solution})

C_{ICP-MS} = aqueous concentration of nuclide from ICP-MS measurement (ppb, μg_{nuclide}/kg_{solution})

$M_{nuclide}$ = molecular mass of nuclide (g_{nuclide}/mol_{nuclide})

In order to determine the K_d values, one first needs to determine the concentration on the solid by using:

$$C_{solid} = \frac{\left[\frac{(C_{stock} * m_{spike})}{(m_{calcite} + m_{spike})} - C_{aq} \right] * (m_{spike} + m_{calcite})}{m_{solid}} \quad (\text{Equation 3.2})$$

C_{solid} = calculated solid phase concentration of the nuclide (ppb)

C_{stock} = concentration of the nuclide stock solution (ppb)

m_{spike} = mass of nuclide spiked into the saltstone suspension (g)

$m_{calcite}$ = total mass of calcite solution used in the saltstone suspension (g)

C_{aq} = aqueous concentration of nuclide from ICP-MS measurement (ppb)

m_{solid} = mass of the saltstone used in the suspension (g)

The K_d can be calculated using the equation:

$$K_d = \frac{C_{solid}}{C_{aq}} \quad (\text{Equation 3.3})$$

K_d = solid-water partitioning coefficient ($g_{solution}/g_{solid}$, assuming density of 1.0 g/mL traditional unit of mL_{solution}/g_{solid} can be obtained)

This K_d Equation (3.3) is numerically equivalent to the traditional K_d equation proposed in ASTM D-4646 which has been used in previous saltstone experiments (Kaplan *et al.*, 2007; Kaplan *et al.*, 2008).

4.0 Results and Discussion

4.1 Radionuclide Sorption to Cementitious Formulations under Oxidizing Conditions

Figure 4.1 shows Pu K_d values ranging from 10^4 to $>10^5$ mL/g. Generally for each solid, the K_d increases with increasing initial Pu concentrations, typical behavior of systems where the aqueous concentrations of the radionuclides are solubility controlled. This is not expected because the K_d expression indicates that the K_d value should remain constant with increasing total Pu concentrations. It was noted that aqueous phase concentration of Pu remained relatively constant in all samples (see discussion below regarding Pu solubility). Therefore, the sorption capacity of each solid phase for Pu has not been overcome. For each of these solid phases, it appears the solutions had reached equilibrium before the first samples were taken at 24 hours. In each case, the K_d values for the one day and four day are similar. A trend between the solid phases is not discernible. The aged cement with no reducing slag was expected to have the lowest K_d values, but in actuality it has the highest K_d . Also, there is no correlation with the concentration of reducing slag. The Vault 2 samples with 17 dry wt-% reducing slag has a K_d similar to that of the TR547 (45 dry wt-% slag), while the saltstone with the most slag TR545 (90 dry wt-% slag) has the lowest K_d value. Others have observed that Pu K_d values of cementitious materials are similar in the absence and presence of slag (Allard *et al.* 1984; Hoaglund *et al.* 1985).

It was observed that similar aqueous concentrations of Pu were observed regardless of the solid phase present. Figure 4.2 shows the average aqueous phase concentrations measured after one day and four days for all solids. As stated above, triplicate samples were prepared for each solid phase and each initial concentration. Therefore, each of the reported solubility values in Figure 4.2 is an average of nine measurements. Using the highest reported value with the expected maximum error (0.018 ppb for solid TR545), the maximum expected aqueous concentration of Pu in the pore water associated with the

saltstone formulations will be approximately 7×10^{-11} mol/L, as calculated using Equation 3.1. This is on the same order as the solubility of Pu hydrous oxide solid phases (Neck and Kim, 2001).

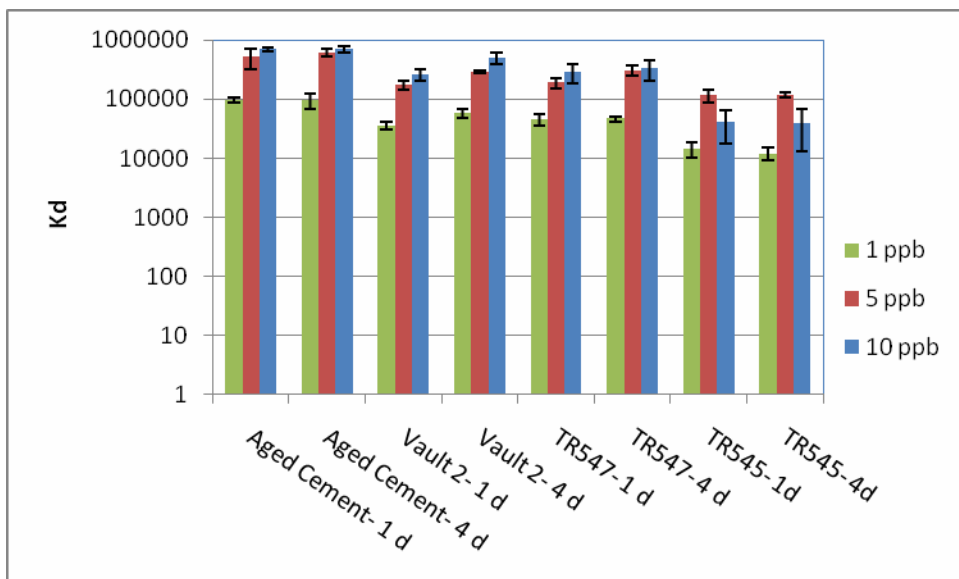


Figure 4.1: Plutonium K_d Values under Oxidizing Conditions. Plutonium K_d values for various saltstone formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. Total plutonium concentrations in each system were 1 ppb, 5 ppb, and 10 ppb. Sample prepared in triplicate and error bars represent standard deviation of samples except as follows: value for dataset TR547-4d 10 ppb is reported based on duplicate samples.

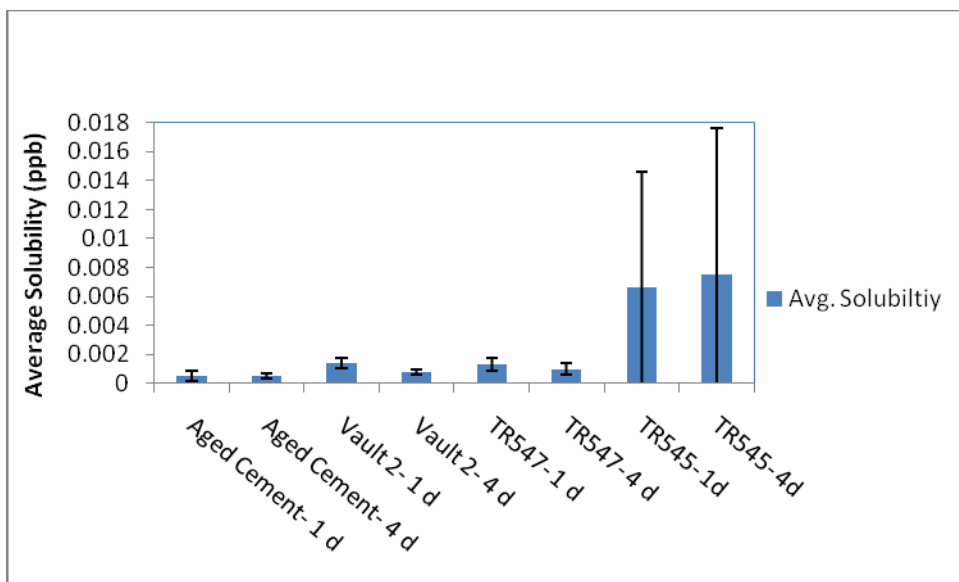


Figure 4.2: Plutonium solubility for various saltstone formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. Total plutonium concentrations in each system were 1 ppb, 5 ppb, and 10 ppb as noted. Samples prepared in triplicate, and an average of all samples (9) was used to determine average solubility. The error bars represent standard deviation of samples.

Overall, the K_d values for Np range from 10^5 to $>10^6$ with only a few outliers. The most significant outlier is the 1 ppb solution in the TR545 sample after the four-day equilibration. It drops two orders of magnitude, while the 5 and 10 ppb solutions remain constant. However, this result is most likely an analytical artifact from working at the detection limits of the ICP-MS. In the one-day equilibration samples, only one of the triplicates, S-2-E, had detectable Np, while in the four-day equilibration samples, only S-2-F had detectable amounts present. The graph also shows that with the exception of the 5 ppb sample in the aged cement, Np sorption to TR545 (90 dry-wt-% slag) and TR547 (45 dry wt-% slag) have K_d values approximately one order of magnitude over the aged cement (no slag) and Vault 2 (17 dry wt-% slag) samples.

It was observed that similar aqueous concentrations of Np were observed regardless of the solid phase present. Figure 4.4 shows the average aqueous phase concentrations measured after one day and four-day equilibrations for all solids. As stated above, triplicate samples were prepared for each solid phase and each initial concentration. Therefore, each of the reported solubility values in Figure 4.4 is an average of nine measurements of Np concentration unless stated otherwise. Using the highest reported value with the expected maximum error (0.0026 ppb for solid TR545), the maximum expected aqueous concentration of Pu in the pore water associated with the saltstone formulations will be approximately 2×10^{-11} mol/L.

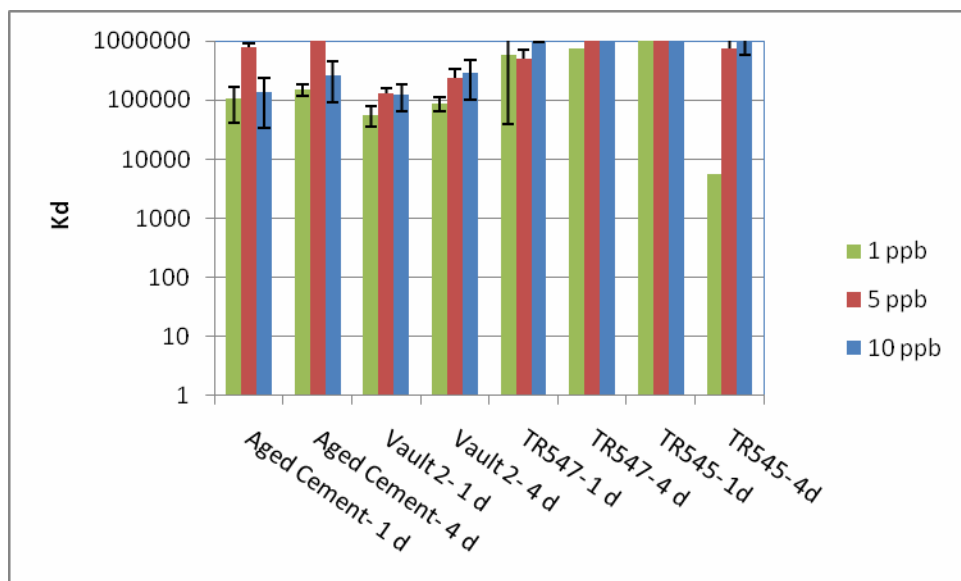


Figure 4.3: Neptunium K_d values under oxidizing conditions. Neptunium K_d values for various saltstone formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. Total plutonium concentrations in each system were 1 ppb, 5 ppb, and 10 ppb as noted. Samples prepared in triplicate and error bars represent standard deviation of samples except as follows: value for datasets TR545-1d 1ppb, TR545-4d 1ppb, TR547 4d 1ppb, TR545-4d 10 ppb, TR547-1d 1ppb, TR547-4d, 10 ppb are reported based on a single sample and for dataset TR545-1d 5ppb is reported based on duplicate samples. K_d values limited to $>10^6$ were at instrumental background.

The K_d values for Tc are significantly lower than that of Pu or Np. As a whole, the values are comparable. The values for the one-day and four-day equilibrations solutions in the Vault 2 (17 dry wt-% slag) and TR545 (90 dry wt-% slag) remained constant within reasonable error with just a slight increase from the one-day to four-day equilibration. However, the Aged Cement (no slag) and TR547 (45 dry wt-% slag) showed a noticeable decrease from day one to day four (Figure 4.5).

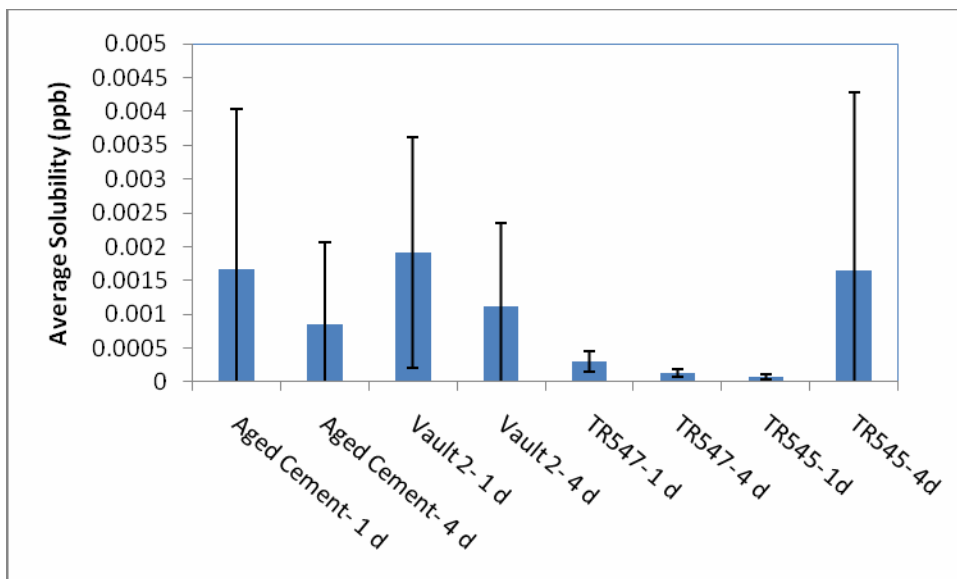


Figure 4.4: Average solubility of Np under oxidizing conditions. Neptunium solubility for various saltstone formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. Total Np concentrations in each system were 1 ppb, 5 ppb, and 10 ppb. Samples prepared in triplicate, and an average of all samples (9) was used to determine average solubility except as follows: TR545-1d is based on 6 samples, TR545- 4d on 5 samples, TR547-1d on 7 samples, and TR547- 4d on 5 samples. The error bars represent standard deviation.

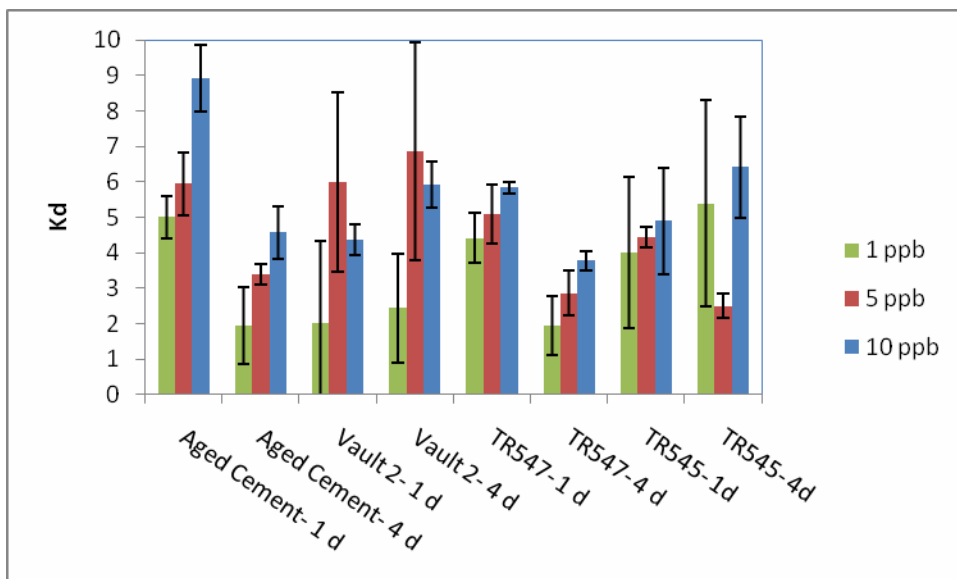


Figure 4.5: Technetium K_d values under oxidizing conditions. Tc K_d values for various saltstone formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. Total Tc concentrations in each system were 1 ppb, 5 ppb, and 10 ppb as noted above. Samples were prepared in triplicate and the error bars represent standard deviation of samples except as follows: data sets for Vault 2-1d 1ppb were duplicates, and TR547- 4d 10 ppb is based on a single dataset.

Similar to the Tc K_d values, the ^{127}I K_d values are much lower than those of Pu and Np. The amount of reducing slag present in each of the solids does not appear to have a drastic effect on the ^{127}I K_d values. In fact, the initial (one day) Aged Cement (0% slag) samples had a K_d almost two orders of magnitude above those with reducing slag. The cause of this behavior is not known, but it has been shown that iodate, IO_3^- , the oxidized form of iodine, sorbs more strongly than iodide, I^- to charged surfaces (Schwehr *et al.* 2009; Yoshida *et al.* 1992; Fukui *et al.* 1996). It is possible that the slag is reducing the iodine to the I^- form, converting it to a species that is less likely to sorb to saltstone. Additional work would be required to confirm the oxidation state of iodine when associated with saltstone.

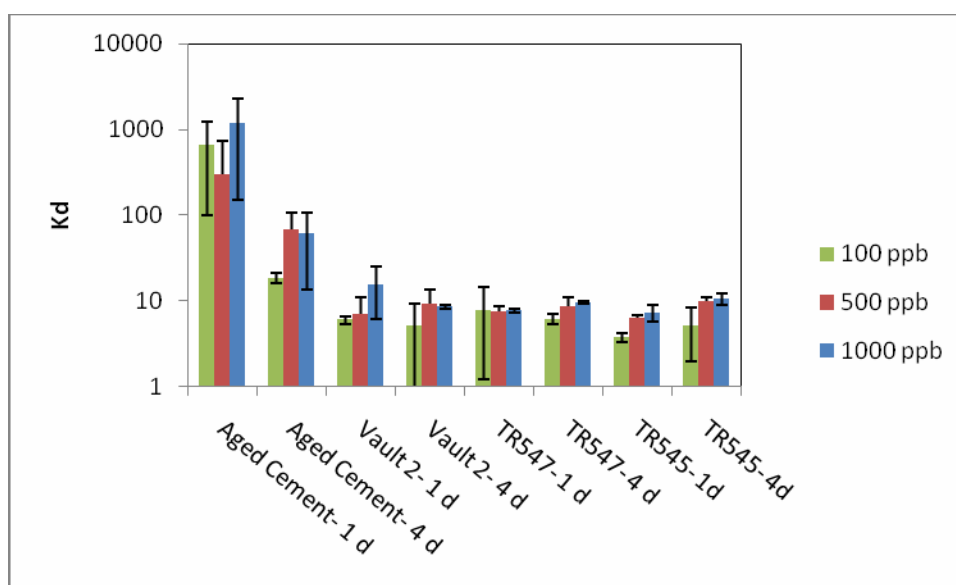


Figure 4.6: Iodine K_d Values under Oxidizing Conditions. Iodine K_d values for various cementitious formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. Total iodine concentrations in the systems were 100ppb, 500 ppb, and 1000 ppb as noted above. Samples were prepared in triplicate and the error bars represent standard deviation of samples except as follows: duplicates were used for dataset TR545- 1d 100ppb.

4.2 Radionuclide Sorption to Vial Walls Under Oxidizing Conditions

Figure 4.7 shows the aqueous fractions found in the no-solids controls. It provides a measure of the solubility of each radionuclide as well as examines the fraction of each radionuclide sorbed to the vial walls. After one day, only 25% of the Pu remained in solution and the concentration decreased even more after four days. The loss of Pu from the aqueous phase may be due to sorption of Pu to the vial walls or precipitation of a Pu hydrous oxide solid (discussed with respect to Figure 4.9. below). Additional experiments would be required to examine the solubility of the Pu in high pH, calcite saturated solutions.

After one day, about 80% of the Np remained in solution. However, the aqueous concentration in the initially 1-ppb solution was significantly reduced after four days. Approximately 60% of the Np remained soluble in the initially 10-ppb solution. Once again this drop could be due to sorption to the vial wall. The Tc present after one day ranged from about 88% to about 95% and was virtually 100% after four days. These values are consistent with internal standards used to monitor Tc detection performance on the ICP-MS. Greater than 50% of the I remained in solution after the one-day and four-day equilibrations. As shown in Figure 4.8, the standard deviation between the triplicate I control samples was

quite large. Additional control samples are required to understand the mechanism by which I is being lost from the aqueous phase in these samples.

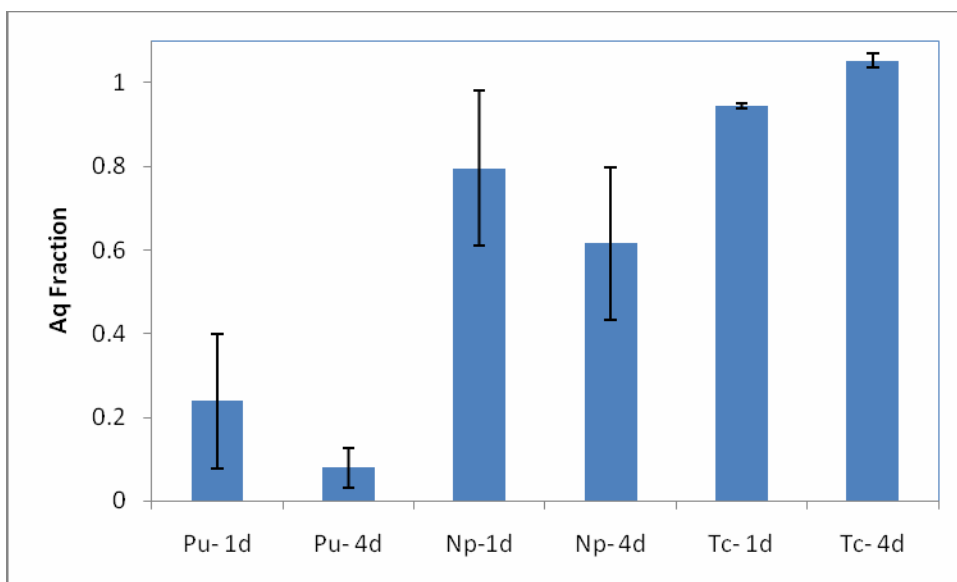


Figure 4.7: Plutonium, Neptunium, and Technetium Aqueous Fractions. Fraction of Pu, Np, and Tc remaining in the aqueous phase for the No Solids controls after a one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. The total concentration for each radionuclide 10 ppb as noted above. Samples were prepared in triplicate and the error bars represent the standard deviation of the samples.

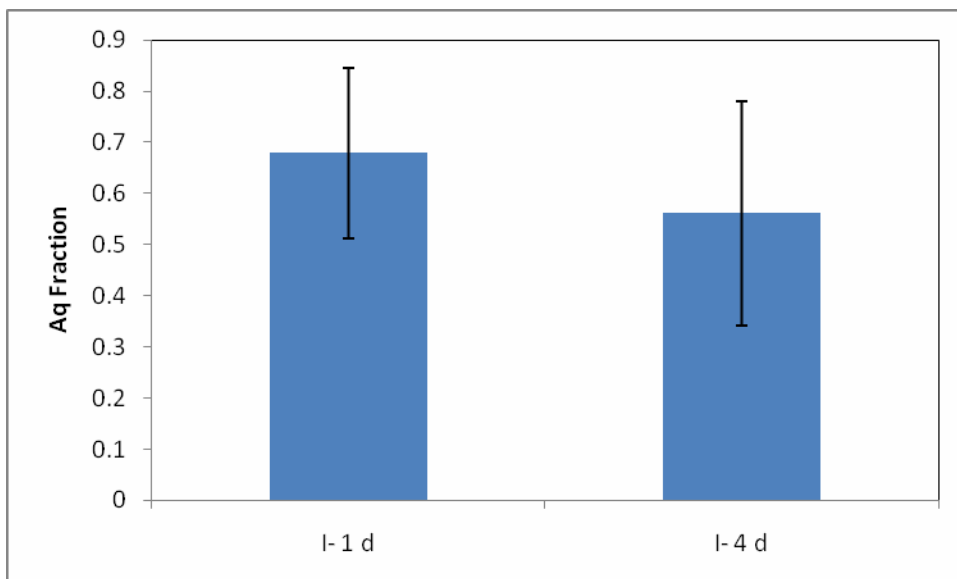


Figure 4.8: Iodine Aqueous Fraction. Iodine aqueous fraction for the no-solids controls after a one-day equilibration (1d) and four-day equilibration (4d) under oxidizing conditions. The total concentration of iodine was 1000 ppb as noted above. Samples were prepared in triplicate and the error bars represent the standard deviation of the samples.

As discussed above, the loss of Np and Pu from the no-solids control (Figure 4.7) could be due to precipitation of Np and Pu hydrous oxides or sorption to the vial walls. To quantify the differences between these possible sinks, the vials were washed as described in Section 3.6. The data in Figure 4.9 indicate that significant sorption of Np and Pu to the vial walls may occur. When combining the mass of Np represented in Figure 4.7 and Figure 4.9, there is almost 100% mass recovery of the Np sorbed to the vial wall and the aqueous fraction measured. Therefore, no precipitation of Np is expected. However, because 100% recovery was not achieved for Pu, a Pu hydrous oxide phase could be precipitating which was washed out of the vial during the cleaning procedure. The data in Figure 4.7 represent the no-solids control samples where there was no solid phase present for Np or Pu to sorb to besides the vial walls. However, when a cementitious solid phase is present in the sample, there will be competition between the vial walls and the cement for sorption of Np and Pu. Based on the affinity of metals for metal oxide surfaces as opposed to the polypropylene surface and the much higher surface site density expected for the cementitious samples, it is assumed that the cementitious samples will out-compete the vial walls for sorption sites. This thesis was tested by taking one of the triplicate samples from each sorption experiment with a solid phase present, removing the solid phase from the tubes, and leaching any sorbed Np and Pu from the tubes with acid as described in Section 3.6. Figure 4.10 and Figure 4.11 show that although some of the Pu and Np sorbed to the vial walls of the samples, this amount accounted for less than 2% in all samples. Therefore, sorption of Np and Pu to the vial walls does not appear to be a significant factor in experiments where the solid phase is present. Note these results do not discount the possibility that Pu hydrous oxide precipitates were forming in both the no-solid control experiments and experiments with cement formulations present. *Based on the observation of a constant aqueous phase concentration of Pu regardless of the initial Pu concentration, the presence of a solubility limiting Pu phase cannot be discounted based on these data.* Further experiments examining the solubility of Pu in high pH, calcite saturated solutions are required.

Like Pu, Np shows little affinity for the vial walls in the presence of a solid phase. In each case tested, there was significantly less than 1% of the total Np sorbed to the vial walls. This behavior is consistent with the ~100% mass balance on Np achieved in the solid-free controls. The majority of Np remained soluble in the solid-free control experiments. Therefore, it is expected that sorption of Np to the vial walls was the primary reason for the loss of Np from the aqueous phase in the no-solids systems, rather than precipitation of a Np solid phase similar to the process discussed for Pu above. This assumption is based on the relative solubility of Np(V) as compared with Pu(IV).

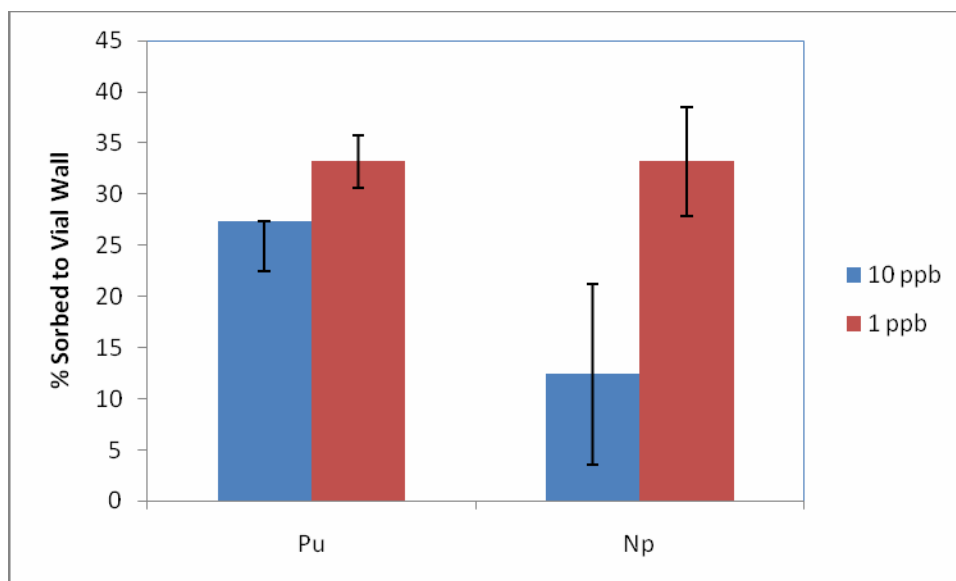


Figure 4.9: Percent Pu and Np sorbed to vial walls of the no solids controls after the aqueous phases were discarded and the vials were washed. Both the 10 ppb and 1 ppb datasets were prepared in triplicate, and the error bars show the standard deviation.

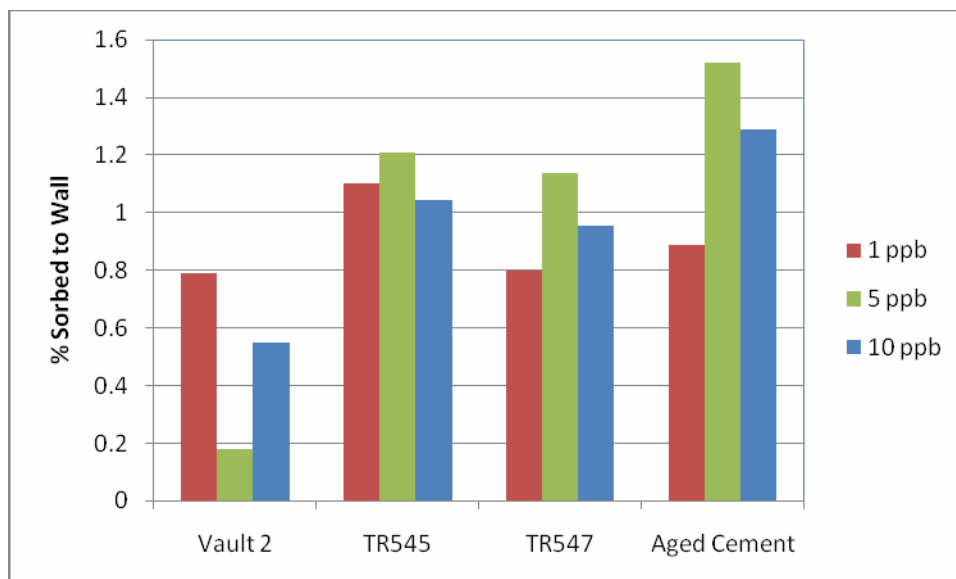


Figure 4.10: Percent Pu sorbed to vial walls after the solids and aqueous phases were removed and the vials were washed. The graph illustrates one sample from each of the 1 ppb, 5 ppb, and 10 ppb systems. Therefore, no error bars are present.

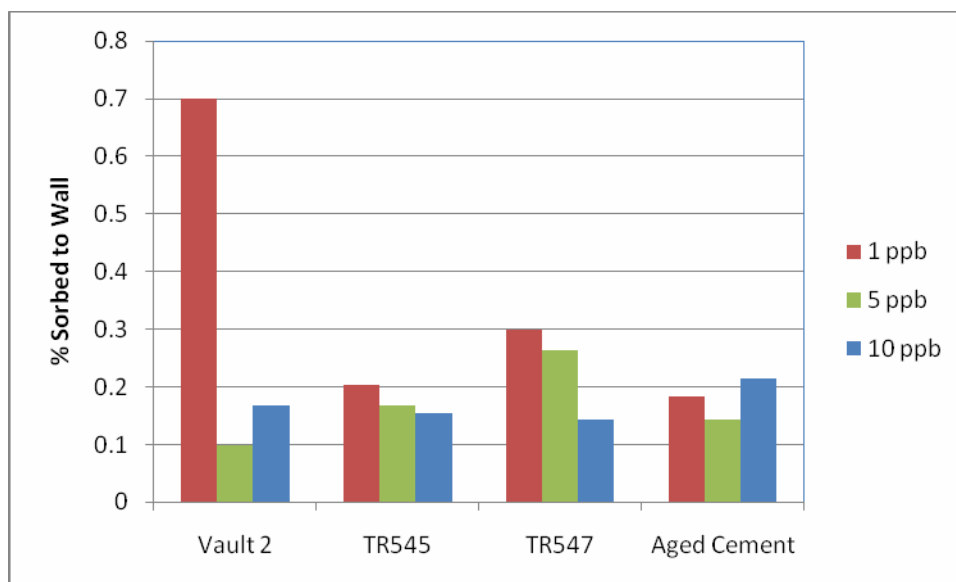


Figure 4.11: Percent Np sorbed to vial walls after the solids and aqueous phases were removed, and the vials were washed. The graph illustrates one sample from each of the 1 ppb, 5 ppb, and 10 ppb systems. Therefore, no error bars are present.

4.3 Radionuclide Sorption to Cementitious Formulations under Reducing Conditions

Similar to the Pu K_d values under oxidizing conditions, Pu K_d values ranged from 10^4 to $>10^5$ under reducing conditions (Figure 4.12). Also similar to the results under oxidizing conditions, the K_d increases with increasing initial Pu concentration. Again, this behavior is indicative of the aqueous phase concentration of Pu being controlled by solubility of Pu rather than by sorption. In each case the samples appeared to reach steady state within 24 hours. This equilibration is evident because the K_d values after one day and four days are very similar. Also, it appears that the amount of reducing slag does not make a significant difference in the K_d value. In fact the TR547 solid consists of 45% reducing grout, but produces approximately the same K_d values of the aged cement, which does not have any reducing grout. Each of these K_d values are higher than the TR545, which is 90% reducing grout. These findings are in agreement with those conducted by Allard *et al.* (1984) and Hoglund *et al.* (1985) who reported that concrete containing reducing agents (slag, similar to that used in our study) did not have greater Pu K_d values than those that did not contain slag.

Similar aqueous concentrations of Pu were observed regardless of the solid phase present. Figure 3.6 shows the average aqueous phase concentrations measured after one day and four days for all solids. As stated above, triplicate samples were prepared for each solid phase and each initial concentration. Therefore, each of the reported solubility values in Figure 4.12 is an average of up to nine measurements of the Pu aqueous concentrations. *Using the highest reported value with the expected maximum error (0.0045 ppb for solid Vault 2), the maximum expected aqueous concentration of Pu in the pore water associated with the cementitious formulations will be approximately 2×10^{-11} mol/L (calculated from Equation 3.1).* This value is on the same order as the solubility of Pu hydrous oxide solid phases (Neck and Kim, 2001). *A best value would be 10^{-12} mol/L.*

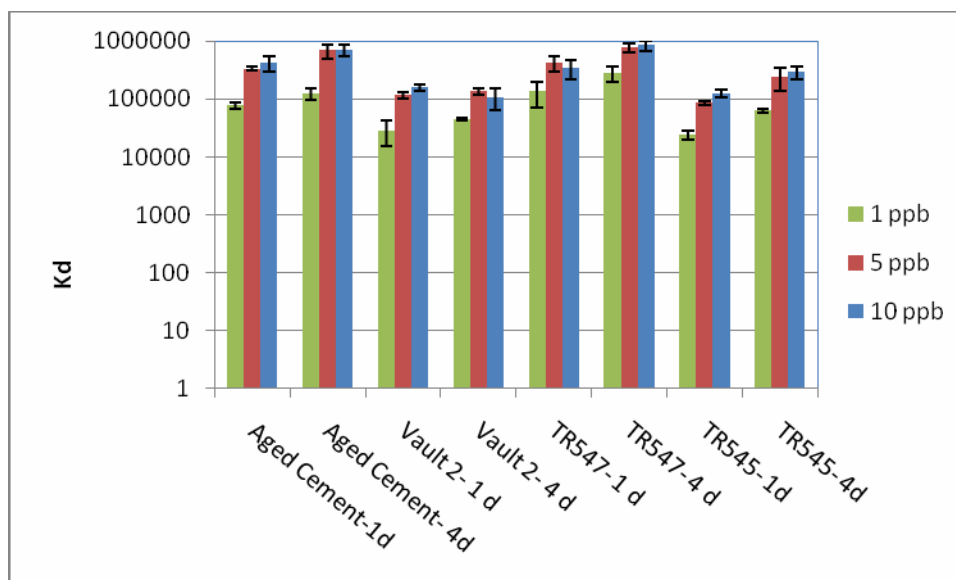


Figure 4.12: Pu K_d Values under Reducing Conditions. Plutonium K_d values for various cementitious formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under reducing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb. Samples prepared in triplicate and error bars represent standard deviation.

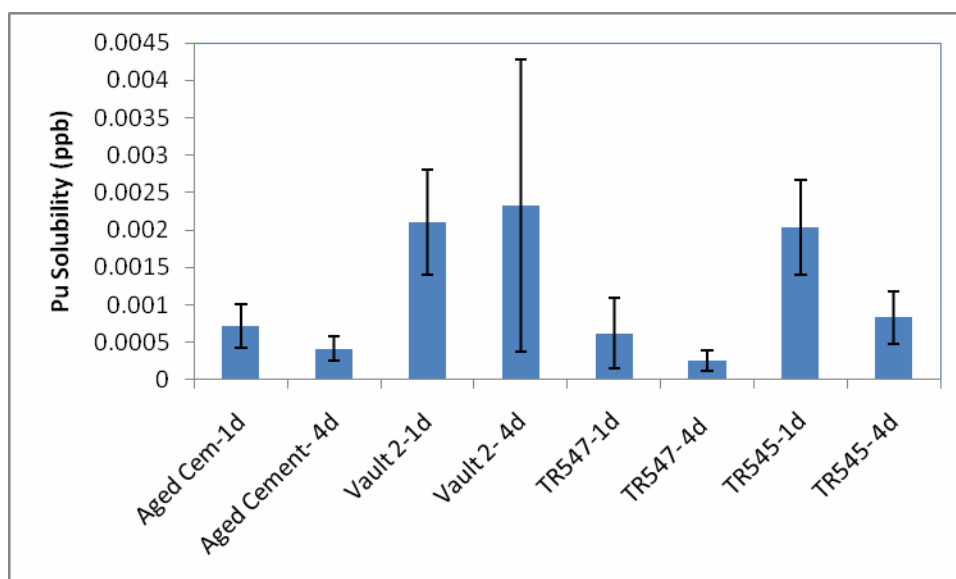


Figure 4.13: Average Solubility of Plutonium under Reducing Conditions. Plutonium solubility for various cementitious formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under reducing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Samples prepared in triplicate, and an average of all samples (9) was used to determine average solubility. The error bars represent standard deviation of samples.

The Np K_d values reported in Figure 4.14 obtained under reducing conditions are very similar to those obtained under oxidizing conditions. In each case the samples appeared to reach steady state within 24 hours. This equilibration is evident because the K_d values between the one-day and four-day equilibrations are similar. As was the case with Pu, the amount of slag present in each solid does not

seem to have a significant effect on the K_d values. Again, the aged cement with no slag has as high a K_d as the TR545 with 90% reducing slag.

Similar aqueous concentrations of Np were observed regardless of the solid phase present. Figure 3.14 shows the average aqueous phase concentrations measured after one day and four days for all solids. All K_d values were $> 10^5$ mL/g, which is considerably larger than those reported by Kaplan and Coates (2007), who reported Np K_d values to 1300 to 1600 mL/g. This difference can be attributed to two important experimental differences: 1) the experiment was designed to permit larger K_d values to be measured (e.g., solid to liquid ratios and spike concentrations), and more importantly, 2) a more sensitive analytical method, ICP-MS, was used instead of conventional low-energy gamma spectroscopy or liquid scintillation counting (LSC) analysis. As stated above, triplicate samples were prepared for each solid phase and each initial concentration. Therefore, each of the reported solubility values in Figure 4.15 is an average of up to nine measurements. *Using the highest reported value (to provide the most conservative, most soluble values) with the expected maximum error (0.0045 ppb for solid TR545), the maximum expected aqueous concentration of Np in the pore water associated with the cementitious formulations will be approximately 2×10^{-11} mol/L. A best value, taking into consideration the less-than values, which are depicted in Figure 4.14 as running off the top of the plot would be 10^{-12} mol/L.*

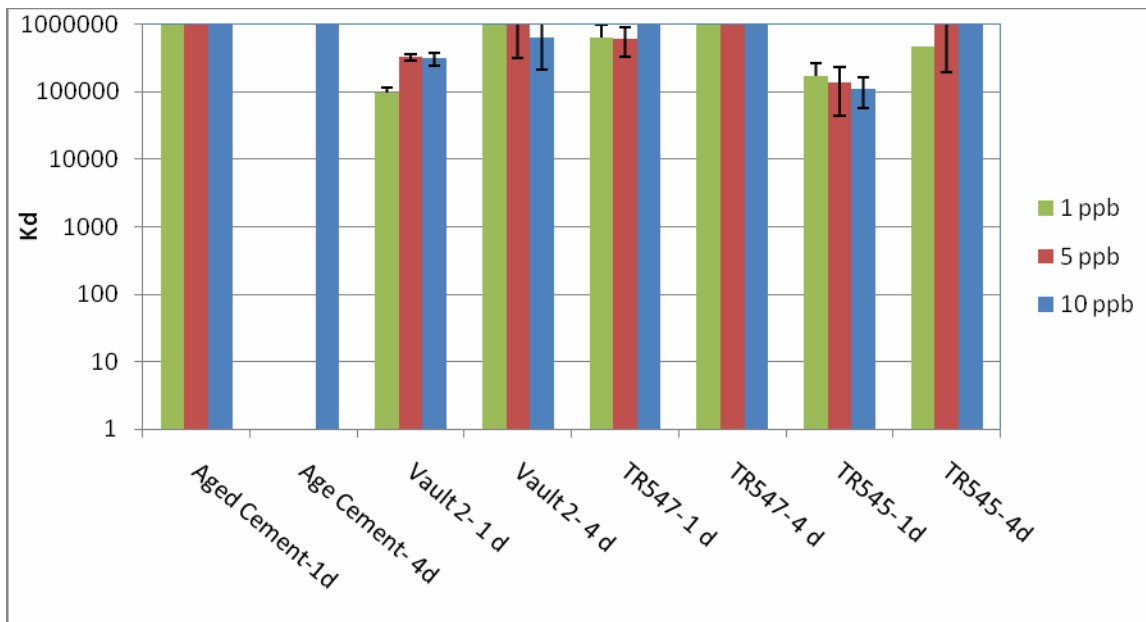


Figure 4.14: Np K_d Values under Reducing Conditions. Neptunium K_d values for various cementitious formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under reducing conditions. Total Np concentrations in each system were 1 ppb, 5 ppb, and 10 ppb. Samples were prepared in triplicate and the error bars represent standard deviation. K_d values limited to $>10^6$ were at instrumental background.

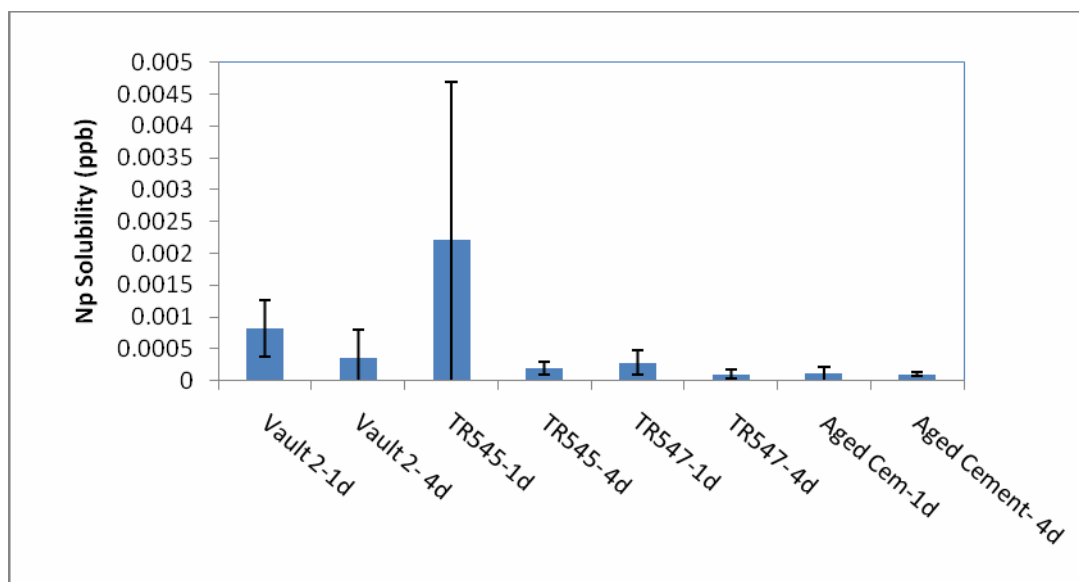


Figure 4.15: Average Solubility of Neptunium under Reducing Conditions. Neptunium solubility for various cementitious formulations measured after one day equilibration (1d) and four day equilibration (4d) under reducing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb. Samples prepared in triplicate, and an average of all samples (9) was used to determine average solubility. The error bars represent standard deviation.

A plot of the Tc K_d values for each cementitious formulations under reducing conditions is shown in Figure 4.16 (log y-axis) and Figure 4.17 (reduced scale linear y-axis). The K_d values for each of the initial Tc concentrations are relatively similar. This behavior is consistent with the K_d expression. However, the increasing K_d values from the one-day to four-day day equilibrations for each solid indicate that steady state was not reached within one day and it is unclear whether steady state was reached after four days. A possible explanation for this behavior is that Tc(VII) was being reduced to Tc(IV) in these systems due to the reducing conditions. As Tc(VII) was reduced, the K_d would increase based on the high affinity of Tc(IV) for solid phases. This proposed mechanism was observed by Lukens *et al.* (2005) using an SRS saltstone material, similar but not identical to TR547. Using synchrotron X-ray absorption fine structure spectroscopy they observed over a 45.3 month period that Tc(VII) incorporated into SRS saltstone slowly converted to Tc(IV) and that the nearest neighbor was initially predominantly oxygen and eventually became predominantly sulfur (described as a Tc(IV) phase: TcS_x). Lacking in Lukens *et al.* (2005) is quantification of the solubility of Tc. This analysis still needs to be completed, along with re-oxidation studies (*i.e.*, what is the rate that reduced Tc reoxidizes under ambient natural saltstone conditions).

Unlike Np and Pu, Tc K_d values changed with the amount of slag included in the formulation: Tc K_d values noticeable increase as the amount of slag in the formulation increased. TR547 (45 dry-wt-% slag) K_d value is visibly higher than the Aged Cement and Vault 2 K_d values, while the most reducing TR545 (90 dry wt-% slag) K_d value is significantly higher than the others. Following a similar trend, the reduction capacity, that is the total quantity of reductant in the saltstone on a mass basis (units of milliequivalents of charge per g), of TR547 had slightly greater or equal reduction capacity to that of TR545 (Roberts and Kaplan 2009).

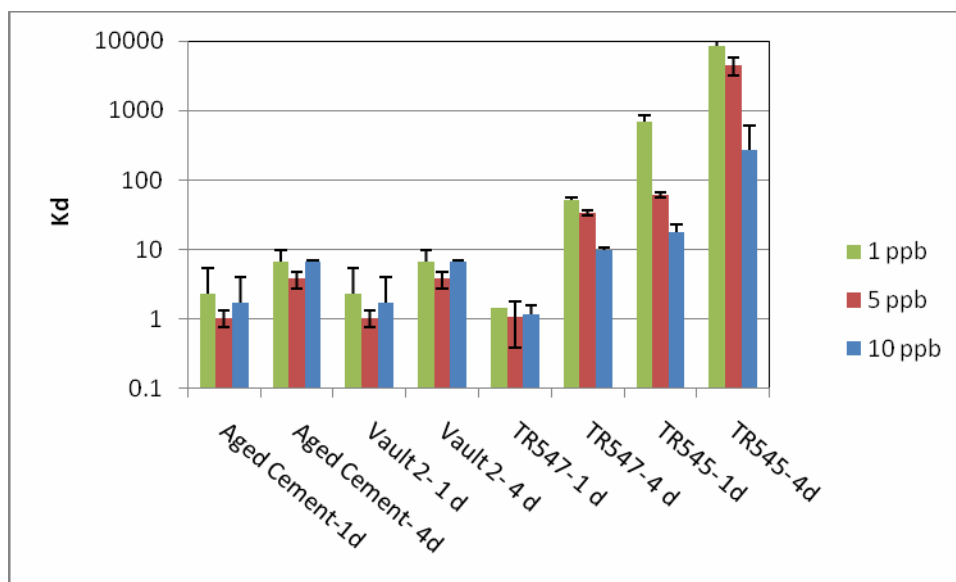


Figure 4.16: Tc K_d Values under Reducing Conditions. Tc K_d values for various cementitious formulations measured after one-day equilibration (1d) and four-day equilibration (4d) under reducing conditions. Total Tc concentrations in each system were 1 ppb, 5 ppb, and 10 ppb. Sample prepared in triplicate and error bars represent standard deviation except as follows: TR547-1d 1 ppb is based on a single dataset and datasets Vault 2-1d 5 ppb, Vault 2- 4d 1 ppb, Aged Cement-1d 5 ppb, and Aged Cement-4d 1 ppb are duplicates.

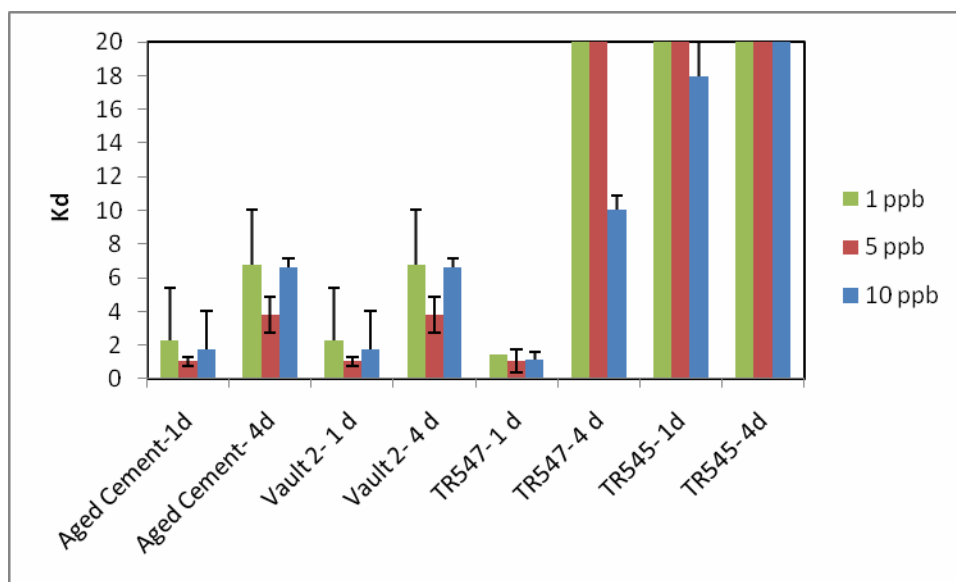


Figure 4.17: Data from Figure 4.16 replotted on a reduced linear scale for easier viewing. Each sample was prepared in triplicate except as follows: TR547-1d 1 ppb is based on a single dataset; Vault 2-1d 5 ppb, Vault 2- 4d 1 ppb, Aged Cement-1d 5 ppb, and Aged Cement-4d 1 ppb are duplicate datasets.

The calculated K_d values for I sorption to cementitious samples under reducing conditions are shown in Figure 4.18. Before discussing the data, it should be noted that spiked QA/QC samples which were analyzed on the ICP-MS along with the samples used to generate the data in Figure 4.18 were off by an average of 19.5%, with one outlier of approximately 40%. This dataset did not include the use of internal standards as discussed in Section 3.1 above.¹ Due to a lack of an internal standard, the iodine results presented in this report should be considered with a minimum error estimate of 20%.

The iodine K_d values under reducing conditions are different from those observed under oxidizing conditions. Under oxidizing conditions, it appears they are at a steady state by day one. However, under reducing conditions, there is a noticeable difference between days one and four, indicating steady state was not reached by day one and possibly not by day four. Another interesting observation is that the K_d values are decreasing from day one to four. A possible reason for this behavior may be due to redox chemistry of iodine in this system. If iodine partially or entirely exists in the form as iodate (IO_3^-), it is possible it could be reduced to iodide, I^- , within the reducing cementitious system. These two iodine species sorb differently, iodate sorbing to minerals more strongly than iodide (Denham *et al.* 2009; Schwehr *et al.* 2009; Fukui *et al.* 1996; Yoshida *et al.* 1992). It is hypothesized that the reducing environment of the saltstone is sufficient to reduce iodate ions to the more weakly binding form of iodine, iodide.

This is one of the few datasets (along with Tc) in this study where there may be a difference between the various solids. The degree of iodate reduction would be expected to increase as the slag content increases. As mentioned above, reduction of iodate to iodide should result in a decrease in sorption. Therefore, higher K_d values should be observed for solids with less slag, such as the Aged Cement (0 dry wt-% slag), and Vault 2 (17 dry wt-% slag). This is generally the case in Figure 4.18 where the highest K_d values are reported for the Aged Cement and the lowest values are for solid TR547. However, this trend does not hold completely, where the saltstone sample containing 90% slag (TR545) has generally equal or higher K_d values than the saltstone containing 45 dry wt-% slag (TR547).

¹ . Clemson University is presently investigating appropriate internal standards for iodine analyses for ICP-MS. Of those tested, rhenium and molybdenum have shown some promise.

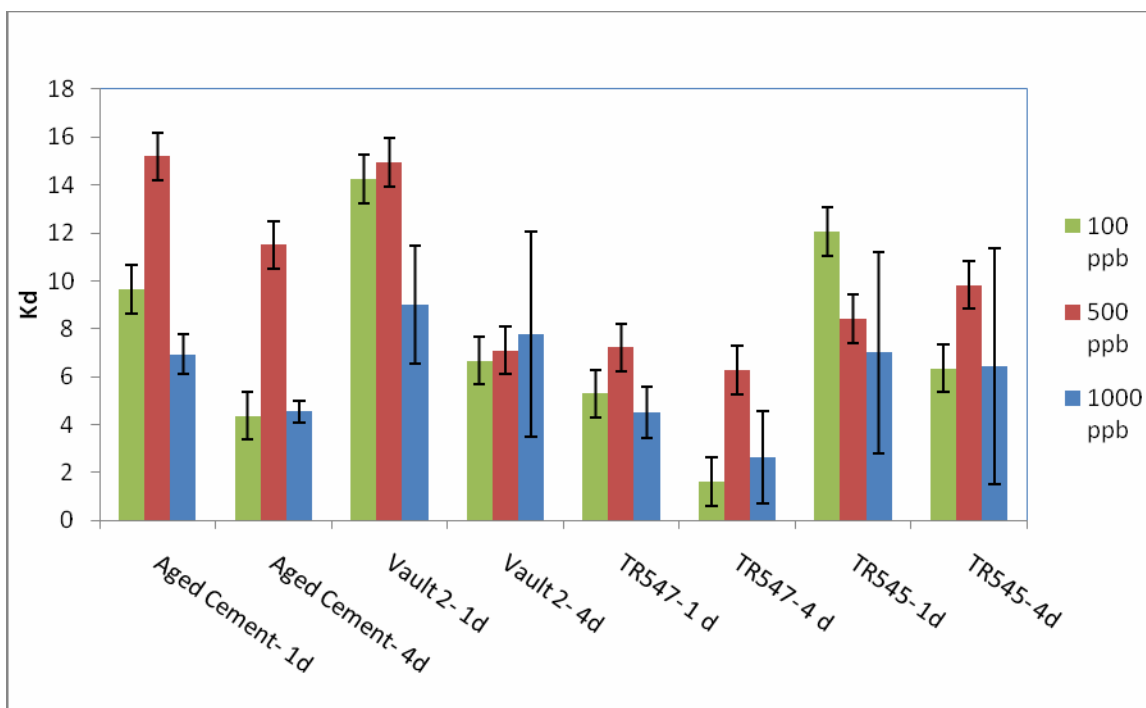


Figure 4.18: Iodine K_d Values under Reducing Conditions. I K_d Values for various cementitious formulations measured after one day equilibration (1d) and four day equilibration (4d) under reducing conditions. Total iodine concentrations in each system were 100 ppb, 500 ppb, and 1000 ppb as noted. Sample prepared in triplicate and error bars represent standard deviation of samples except as follows: Vault 2-4 d 100 ppb is a single dataset, while the datasets for Vault 2-1 d 100 ppb, 4 d 1000 ppb, TR545-4 d 1000 ppb, 100 ppb, TR547-4 d 1000 ppb, 500 ppb, 100 ppb, and Aged Cement- 4 d 1000 ppb, and 100 ppb are all based on duplicates.

4.4 Radionuclide Sorption to Vial Walls under Reducing Conditions

The aqueous concentrations for Pu, Np, and Tc in the no solids controls are shown in Figure 4.19. The results are similar to those presented for experiments performed under oxidizing conditions above. The 1 ppb Pu aqueous fraction is approximately three times greater than the 10 ppb fraction at day one. This fraction decreases over time, and by day four they are approximately equal when taking error into account. This behavior is similar to the aqueous fraction under oxidizing conditions. The 1 ppb Np aqueous fraction is significantly higher on both day one and day four than the aqueous fraction of the 10 ppb samples. However, each remained constant from day one to day four. The 10 ppb aqueous fraction is twice as low as under oxidizing conditions, which suggests either higher sorption to the vial walls, or more precipitating out under the reducing conditions. Like Pu and Np, Tc shows a decrease from day one to day four, especially for the 1 ppb samples. The decrease in the 10 ppb sample is minimal, and the aqueous fraction remains around 0.9. This value is slightly lower than that under oxidizing conditions.

To examine the degree of sorption to the vial walls, the tubes were washed again as performed for the experiments under oxidizing conditions above and similar results were found. Ninety percent of the 1 ppb Pu sample was sorbed to the vial wall upon completion of the experiment, which gives a 100% mass recovery when comparing this value to that found in Figure 4.19. However, this result is not the case with the 10 ppb samples, where approximately 75% of the mass remains unaccounted. It is noteworthy that approximately 25% of the Pu from the 10 ppb solution sorbed to the vial walls under both oxidizing

and reducing conditions. Np follows the same trend as Pu, while less than 0.05% of the Tc sorbed to the wall.

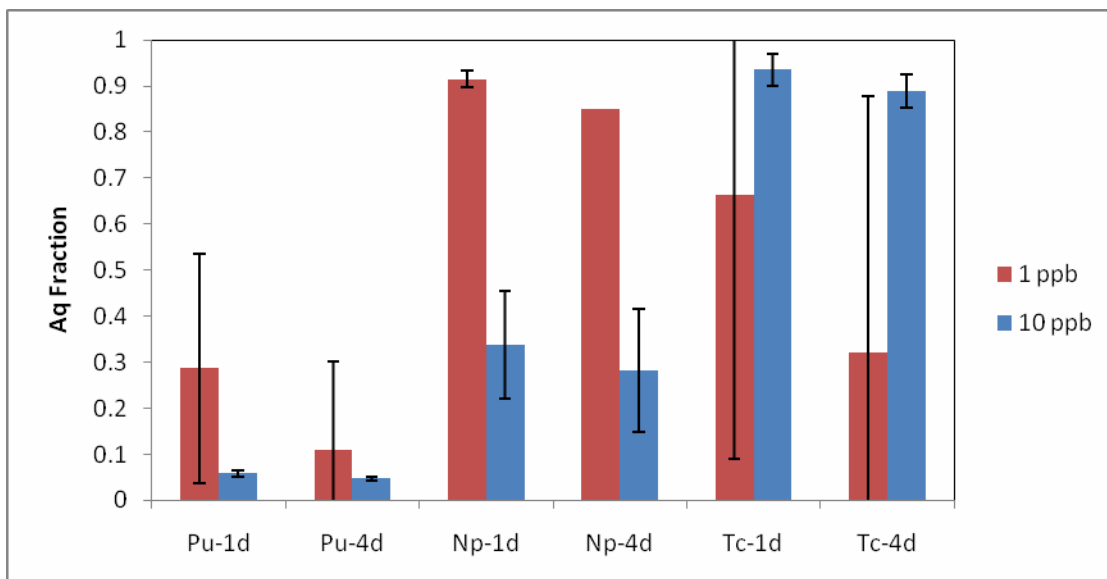


Figure 4.19: Plutonium, Neptunium, and Technetium No-Solids Aqueous Fractions under Reducing Conditions. Pu, Np, and Tc aqueous fractions of No Solids controls after a one-day equilibration (1d) and four-day equilibration (4 d) under reducing conditions. Total concentration for each radionuclide was 1 ppb and 10 ppb. Samples were prepared in triplicate and the error bars represent the standard deviation.

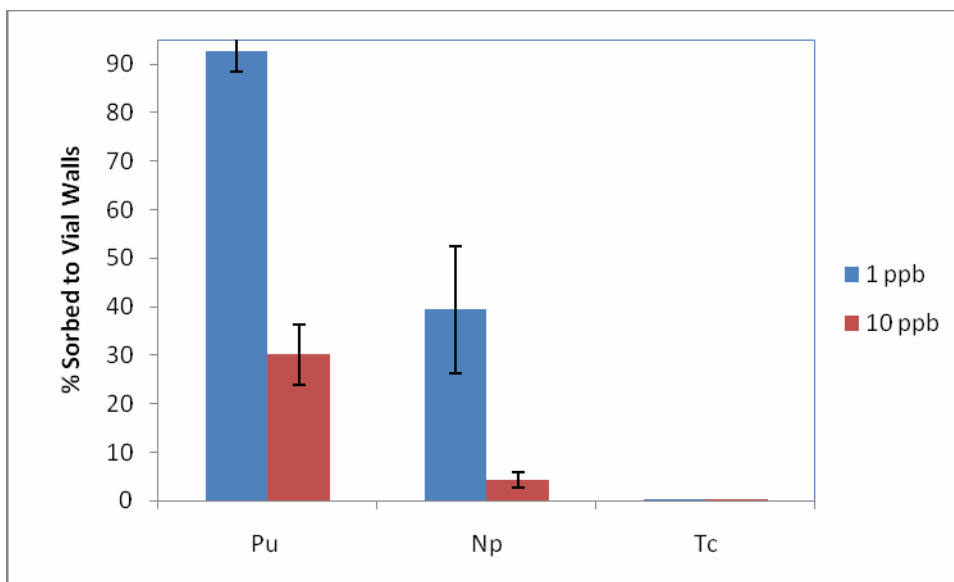


Figure 4.20 Percent of Pu, Np, and Tc sorbed to the vial walls of the No Solids control samples under reducing conditions. Each the 1 ppb and 10 ppb samples were prepared in triplicate, and the error bars represent the standard deviations of triplicate samples.

Under reducing conditions the fraction of I remaining in the aqueous phase was around 90%, with almost 100 % mass recovery of the 100 ppb I after the four-day equilibration. These graphs show that

under reducing conditions, there will only be a small fraction of I sorbing to the vial wall or coming out of solution. This result is a much better mass recovery than under oxidizing conditions (Figure 4.8), which had a mass recovery of approximately 65% after four days. This result is also consistent with the interpretation that there may be a iodine speciation change between the two redox treatments.

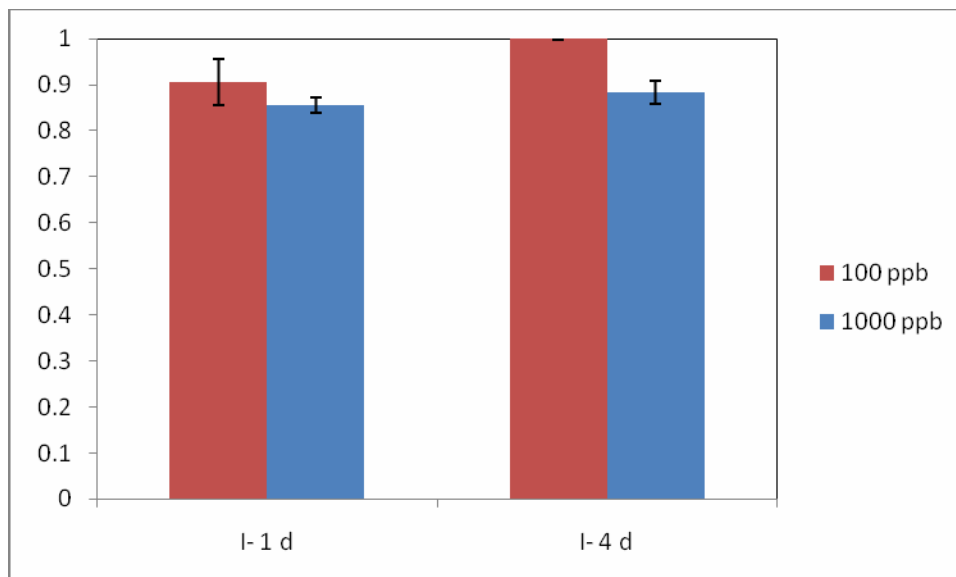


Figure 4.21: Iodine No-Solids Aqueous Fractions under Reducing Conditions. I aqueous fractions of No-Solids controls after a one-day equilibration (1d) and four-day equilibration (4d) under reducing conditions. The total concentration for each system was 100 ppb and 1000 ppb. Samples were prepared in triplicate and the error bars represent the standard deviation.

5.0 Comparison of Radionuclide Sorption under Oxidizing and Reducing Conditions.

In the following figures (Figure 5.1 through Figure 5.4), the data shown above has been replotted to allow comparison between the oxidizing and reducing conditions for each cementitious formulation. General observations based on these data follow.

Vault 2 Observations (Figure 5.1):

- Pu K_d s are greater than 10^4 under both oxidizing and reducing conditions and Pu K_d s are slightly lower under reducing conditions. This could possibly be due to reduction of Pu(IV) to Pu(III). However, no oxidation state analysis was performed in this work.
- Np K_d s are generally greater than 10^4 under both oxidizing and reducing conditions. Interestingly, Np K_d s are higher under reducing conditions by almost an order of magnitude. This could possibly be due to reduction of Np(V) to Np(IV). However, no oxidation state analysis was performed in this work.
- Regardless of the initial Np or Pu concentration, similar aqueous phase concentrations of Np or Pu were observed in all samples. This trend indicates that “sorption” of Np and Pu in these systems may be a combination of adsorption, absorption, and (co)precipitation processes.
- Tc appears to reach a steady state within four days under oxidizing conditions. This behavior does not appear to be the case under reducing conditions. After four days similar K_d values are reached under both oxidizing and reducing conditions. It is unclear

whether the K_d value of Tc will continue to increase under reducing conditions consistent with reduction of Tc(VII) to Tc(IV). The similarity in K_d values under both oxidizing and reducing conditions is an interesting observation and certainly warrants additional studies.

- I K_d values are similar under both oxidizing and reducing conditions. However, reducing condition systems may not be at steady state after four days while systems under oxidizing conditions appeared to reach a steady state. The difference in rates may be due to reduction of iodate to iodine.
- For all isotopes examined, the sorption behavior to each of the solid phases is very similar.

TR545 and TR547 Observations (Figure 5.2 and Figure 5.3):

- Similar to the discussion above with respect to Vault 2, Pu, Np, and Tc all appear to reach a steady state under oxidizing conditions and approach steady state slower under reducing conditions.
- Np and Pu K_d values are greater than 10^4 for all systems and time steps. The aqueous phase concentrations of Np and Pu appear to be better described as a solubility in terms of the aqueous phase concentration of Np and Pu. Similar aqueous phase concentrations of both Np and Pu were reached. The data indicate that the initial Np and Pu concentration generally does not affect the aqueous phase concentration at an apparent steady state. The presence of each solid phase appears to limit the aqueous phase concentration of both Np and Pu on the order of 10^{-11} mol/L.
- Tc shows significantly higher K_d values under reducing conditions versus oxidizing conditions.
- For all isotopes examined, the sorption behavior to each of the solid phases is very similar.

Aged Cement Observations (Figure 5.4):

- Pu appears to be close to steady state for each solid by day one with similar K_d values reached on between day one and day four.
- Np has a higher K_d under reducing conditions than oxidizing (10^5 under oxidizing conditions and $>10^5$ under reducing conditions).
- Neither set of Tc data was at steady state by day one and rates of sorption/desorption reactions appear to be different. Tc K_d s decrease from day one to four under oxidizing conditions, but increase under reducing conditions.
- The K_d values for I under oxidizing conditions were considerably higher than those measured for I with any other solid. Similar K_d values obtained for the same solids under reducing conditions indicate that the reported K_d values under oxidizing conditions appear to be suspect. However, analysis of the raw data gives no indication of an experimental artifact. As discussed above, these observations may be explained based upon the amount of slag contained within the solids which will affect the reducing capacity (i.e. No reducing slag is in the aged cement, which could be reason the reduction of iodate to iodide (speculated in other samples) is not evident).
- The difference in sorption behavior of iodine to the aged cement between oxidizing and reducing conditions also indicates that the reducing conditions of the solution may affect I redox behavior in addition to any reactivity expected in the solid phases.

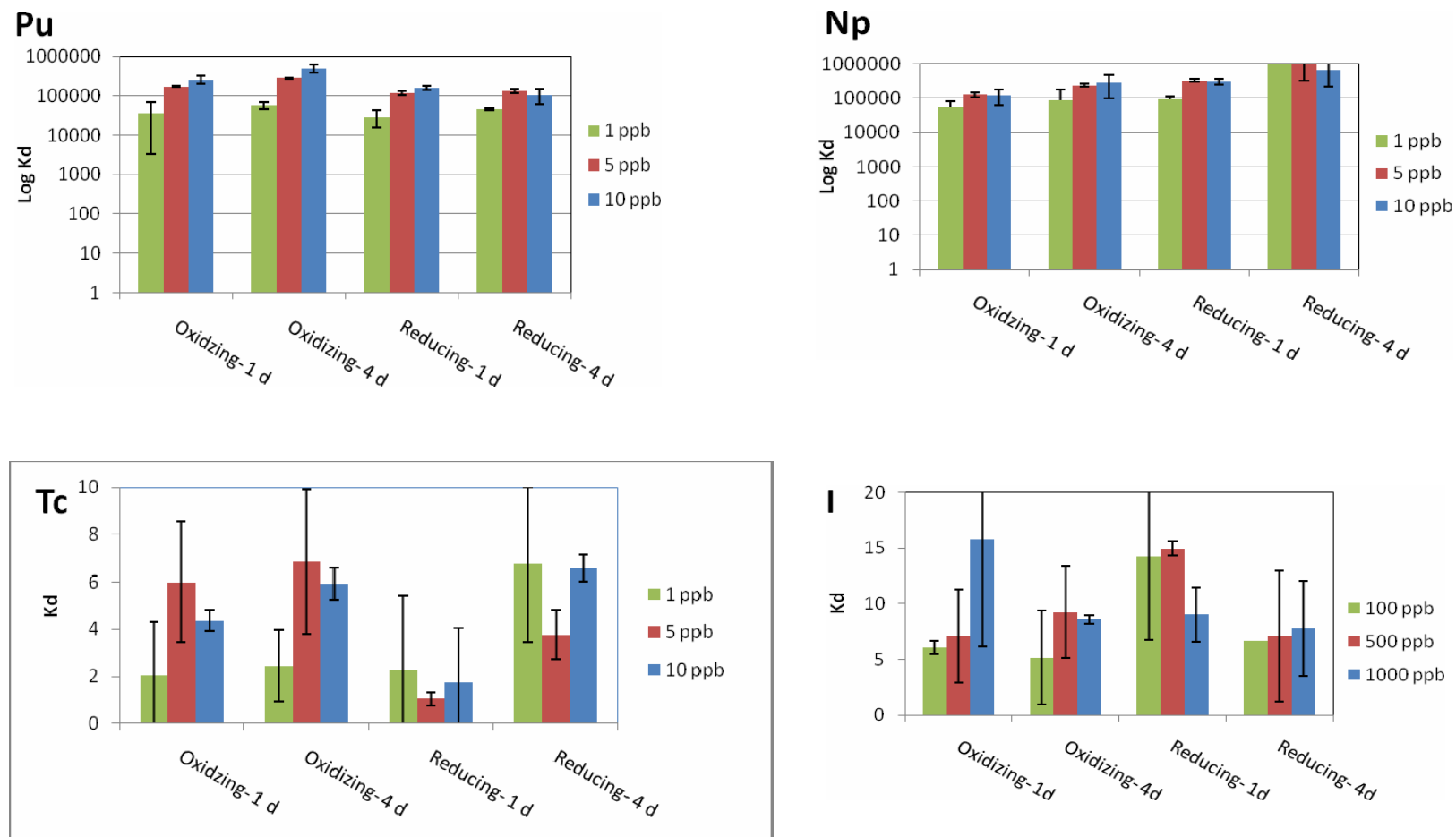


Figure 5.1: Comparison of Tc, I, Np, and Pu sorption to Vault 2 solid under oxidizing and reducing conditions

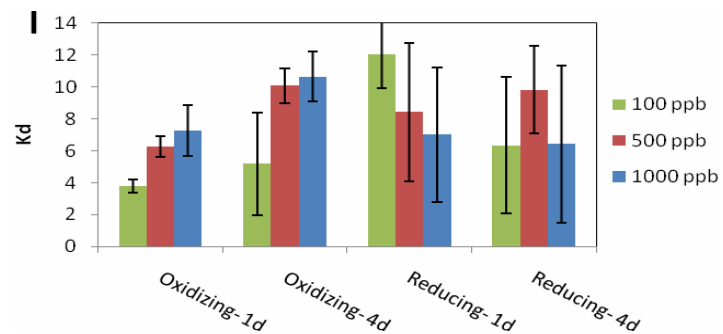
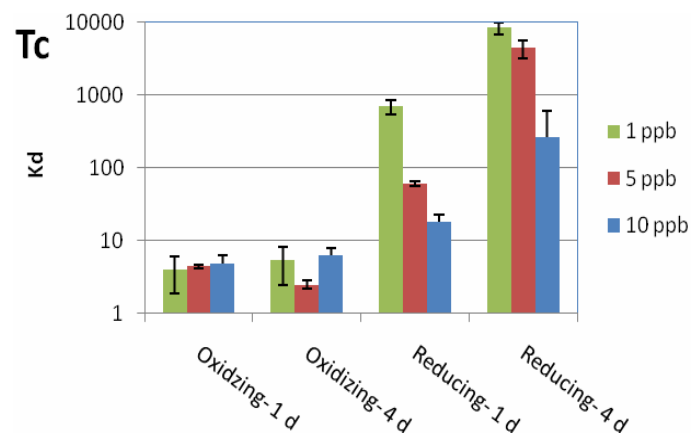
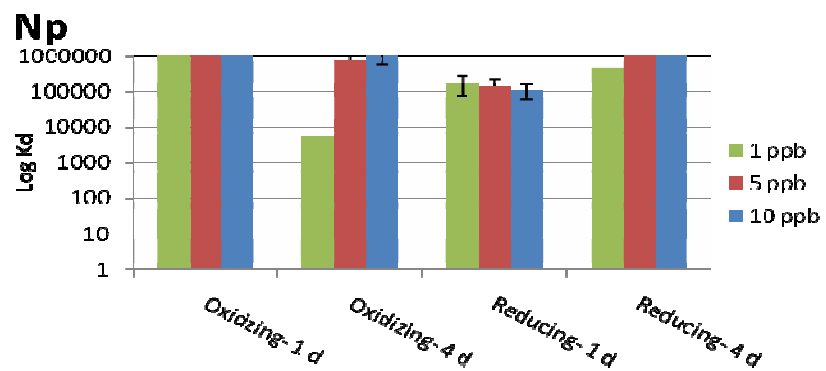
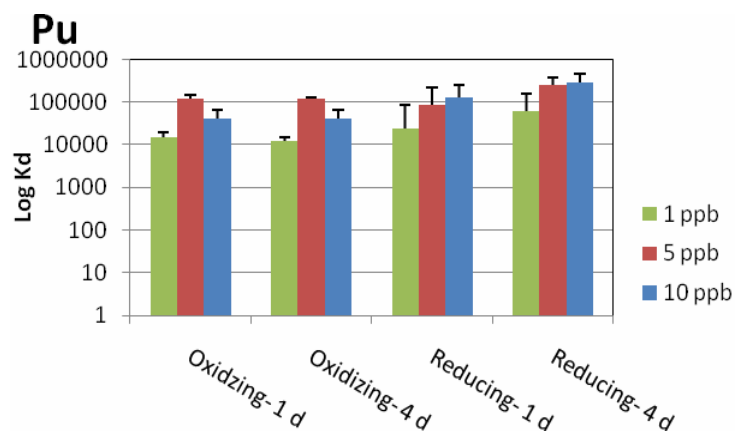


Figure 5.2: Comparison of Tc, I, Np, and Pu sorption to TR 545 solid under oxidizing and reducing conditions.

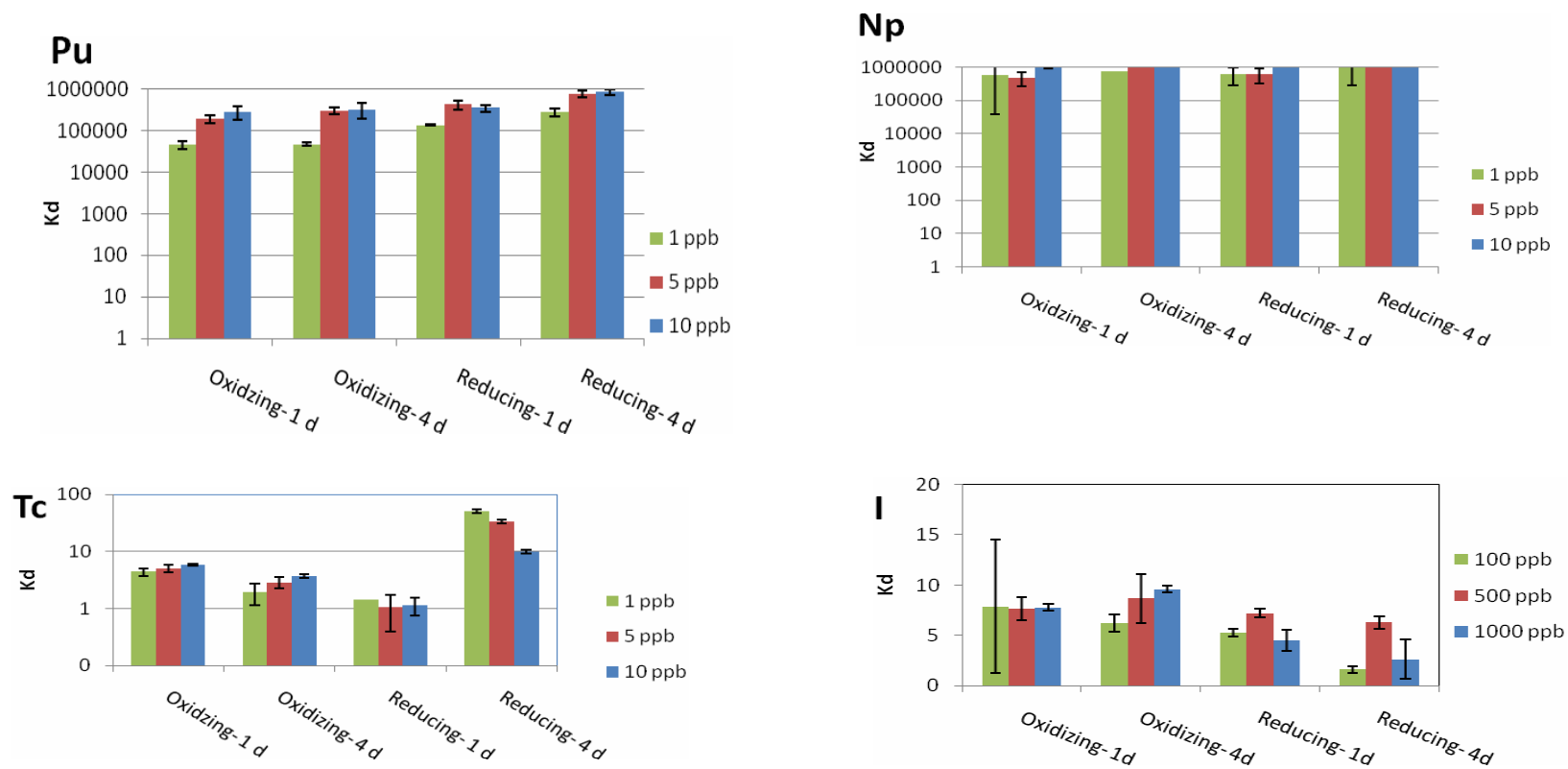


Figure 5.3: Comparison of Tc, I, Np, and Pu sorption to TR547 solid under oxidizing and reducing conditions.

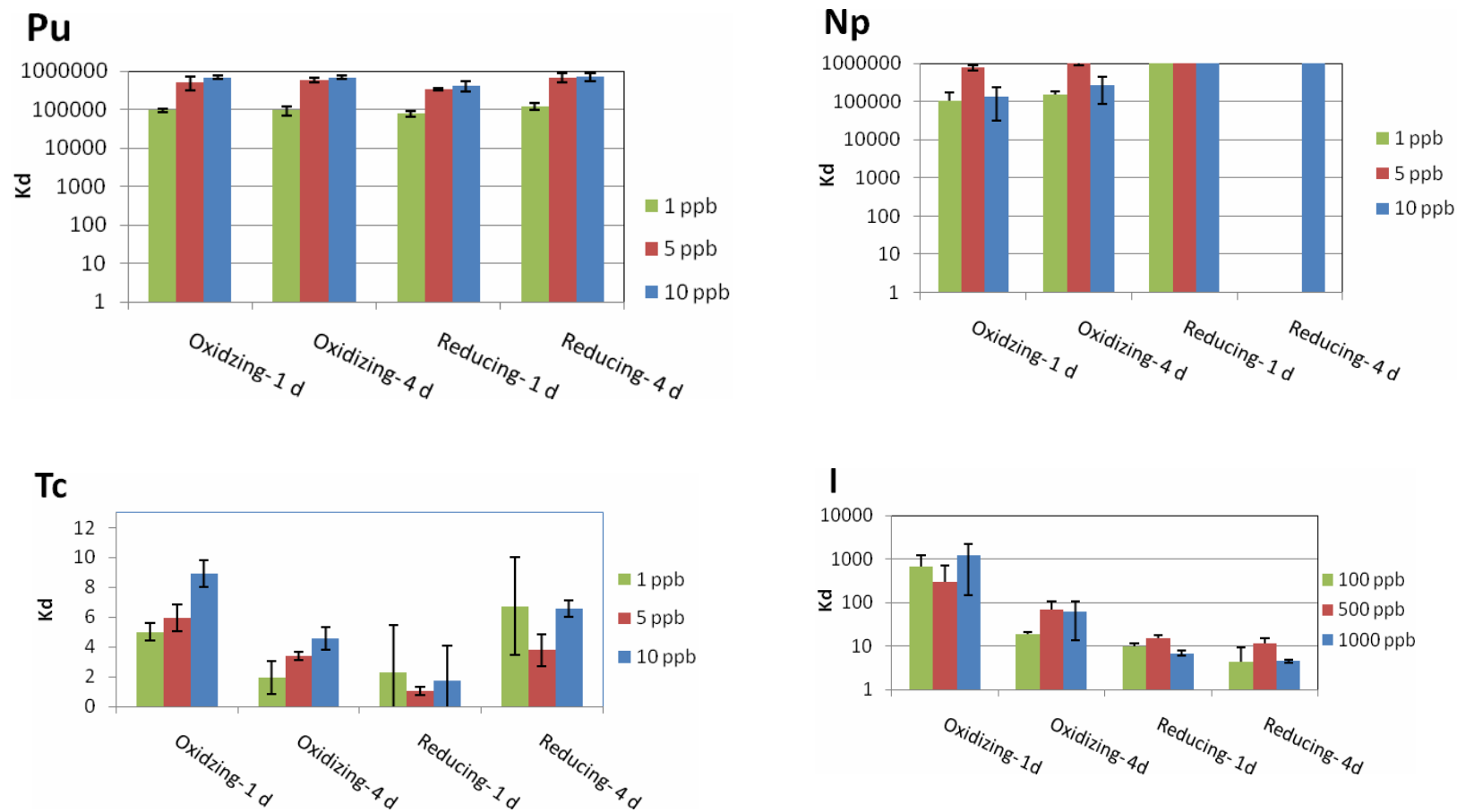


Figure 5.4: Comparison of Tc, I, Np, and Pu sorption to Aged Cement under oxidizing and reducing conditions.

6.0 Comparison of Radionuclide Sorption and Solubility under Oxidizing and Reducing Conditions

To further summarize the data, the following tables provide either the average solubility (for Np and Pu) or average K_d (for Tc and I) determined under both oxidizing and reducing conditions for each cementitious formulation. Each table lists the average value, standard deviation, and the number of replicate samples used to calculate the reported values.

The solubility of Pu in the presence of each solid under oxidizing and reducing conditions is shown in Table 6.1 (this is taken from experiments equilibrated for four days, not one day). Under oxidizing conditions, the apparent solubility values associated with the Aged Cement (0 dry wt-% slag), Vault 2 (17 dry wt-% slag), and TR547 (45 dry wt-% slag) are all similar with only a slight increase in solubility as the amount of reducing slag increases. There is a significant increase of almost an order of magnitude for the most reducing saltstone, TR545 (90 dry wt-% slag). However, these samples also have a standard deviation on the same order of magnitude as the solubility itself, which when taken into account brings the solubility back into the range of the others. Under reducing conditions the apparent solubility values are slightly lower than under oxidizing conditions. In this set of samples, the Vault 2 saltstone with 10 dry wt-% reducing slag had the highest apparent solubility, but once again when considering the standard deviation, the values are similar.

Table 6.1: Comparison of plutonium apparent solubility values under oxidizing and reducing conditions.

| Cement | Oxidizing Solubility (M) | Std. Dev | # of Replicates | Reducing Solubility (M) | Std. Dev | # of Replicates |
|--------------------|---------------------------------|-----------------|------------------------|--------------------------------|-----------------|------------------------|
| Aged Cement | 2.08E-12 | 5.65E-13 | 9 | 1.71E-12 | 6.61E-13 | 9 |
| Vault 2 | 3.35E-12 | 6.71E-13 | 9 | 9.60E-12 | 8.08E-12 | 9 |
| TR545 | 3.12E-11 | 4.14E-11 | 9 | 3.44E-12 | 1.44E-12 | 9 |
| TR547 | 4.09E-12 | 1.54E-12 | 8 | 1.07E-12 | 5.75E-13 | 9 |

Table 6.2 lists the apparent solubility values of Np in the presence of each cementitious formulation under both oxidizing and reducing conditions. Under oxidizing conditions, the cementitious formulation does not appear to have a dramatic effect on the solubility. The apparent solubility values are similar to those of Pu under similar conditions, except the Np standard deviations are much higher. The high standard deviations are an analytical artifact since the measured concentrations were close to or at the detection limit of the ICP-MS. There does appear to be a slight decrease in Np solubility under reducing conditions. However, the statistical significance of this decrease was not calculated.

Table 6.2: Comparison of neptunium apparent solubility values under oxidizing and reducing conditions.

| Cement | Oxidizing Solubility (M) | Std. Dev | # of Replicates | Reducing Solubility (M) | Std. Dev | # of Replicates |
|--------------------|---------------------------------|-----------------|------------------------|--------------------------------|-----------------|------------------------|
| Aged Cement | 3.49E-12 | 5.06E-12 | 9 | 4.24E-13 | 1.39E-13 | 3 |
| Vault 2 | 4.62E-12 | 5.10E-12 | 9 | 1.43E-12 | 1.84E-12 | 9 |
| TR545 | 6.80E-12 | 1.09E-11 | 6 | 7.80E-13 | 4.22E-13 | 7 |
| TR547 | 5.34E-13 | 2.40E-13 | 6 | 4.07E-13 | 2.98E-13 | 7 |

Unlike the apparent solubility values of Pu and Np, the aqueous/atmospheric conditions and cementitious formulation seem to have an effect on the Tc K_d values (Table 6.3). Under oxidizing conditions, there is not a discernible difference among the different cementitious formulations, especially when taking the respective standard deviations into account. However, when experiments were run under reducing conditions, the specific formulation had a noticeable effect. The two saltstone samples with the least amount of reducing slag Aged Cement (0 dry-wt-% slag) and Vault 2 (17 dry wt-% slag) had K_d values which were similar to those observed under oxidizing conditions. However, the TR547 (45 dry-wt-% slag) increased by almost an order of magnitude, while the TR545 (90 dry wt-% slag) increased by about three orders of magnitude. Although the respective standard deviations are large, the higher K_d values do appear to be significant.

Table 6.3: Comparison of technetium K_d values under oxidizing and reducing conditions.

| Cement | Oxidizing K_d | Std. Dev | # of Replicates | Reducing K_d | Std. Dev | # of Replicates |
|--------------------|-----------------------------------|-----------------|------------------------|----------------------------------|-----------------|------------------------|
| Aged Cement | 3.30 | 1.33 | 9 | 5.57 | 2.03 | 8 |
| Vault 2 | 5.08 | 2.66 | 9 | 5.569 | 2.03 | 8 |
| TR545 | 4.77 | 2.39 | 9 | 4.37E+03 | 3.66E+03 | 9 |
| TR547 | 2.75 | 0.948 | 8 | 3.16E+01 | 1.82E+01 | 9 |

Unlike Tc, I does not seem to be as affected by cementitious formulation and redox status (Table 6.4). The only treatment (possible outlier) that does not follow this trend is the Aged Cement under oxidizing conditions. This K_d value is higher than the others, but also has a much higher standard deviation, which when accounted for, gives a value similar to the others. All other treatments had near identical K_d values, irrespective of solid phase or redox condition. But again, the Aged Cement data cannot be discounted at this time given the possibility of the influence that redox may have on iodine speciation and the strong influence I speciation has on sorption to cementitious materials.

Table 6.4: Comparison of iodine K_d values under oxidizing and reducing conditions.

| Cement | Oxidizing K_d | Std. Dev | # of Replicates | Reducing K_d | Std. Dev | # of Replicates |
|--------------------|-----------------|----------|-----------------|----------------|----------|-----------------|
| Aged Cement | 49.5 | 38.0 | 9 | 7.47 | 4.82 | 7 |
| Vault 2 | 7.66 | 3.53 | 9 | 7.25 | 4.19 | 6 |
| TR545 | 8.64 | 3.21 | 9 | 7.86 | 3.61 | 7 |
| TR547 | 8.17 | 1.98 | 9 | 3.71 | 2.38 | 6 |

7.0 Summary and Recommendations for Future Work

7.1 Comparison with Previous Data

The increased sensitivity of the ICP-MS over conventional low-energy gamma spectroscopy or liquid scintillation counting (LSC) analysis allowed for much more accurate K_d values and apparent solubility values in this work than were previously obtainable. Generally, radioanalytical detection methods start with activities on the order of 10^3 to 10^4 counts per minute (cpm) and approach background levels of 1 to 5 cpm for strongly sorbing radionuclides. Therefore, the accuracy of the K_d value will be the difference in analytical sensitivity when the initial aqueous activity decreases by a factor of approximately 5000 (*i.e.*, the aqueous activity drops from approximately 5000 cpm to the instrument background of 1 cpm following almost complete sorption). As a result, the reported K_d values can only be reliably reported up for a K_d of 10^3 to 10^4 . This constraint is believed to be the difference between the observed K_d values for ^{237}Np of $> 10^5$ observed in this work when compared with the K_d values between 3,000 and 4,000 reported by Kaplan *et al.*, (2008). A similar observation was made for Pu because ^{242}Pu was used for ICP-MS analysis and ^{238}Pu was used in the work of Kaplan *et al.* (2008). This constraint may account for the different K_d value of $>10^4$ reported in Kaplan *et al.* (2008) compared with the value of $>10^5$ observed in this work.

In the case of Tc, Kaplan *et al.*, (2008) reported a K_d of 0.23 mL/g for Vault 2 under oxidizing conditions, and 0.93 mL/g under reducing conditions, while the above experiment determined the Vault 2 K_d to be 5.05 mL/g under oxidizing conditions, and 5.57 mL/g under reducing conditions.

Unlike the discrepancy in the K_d values for Np, Pu, and Tc between the above findings and those in Kaplan *et al.* (2008), the reported K_d values for iodine are similar. For Vault 2, Kaplan *et al.* (2008) found ^{125}I to have a K_d of 8.94 mL/g under oxidizing conditions and 7.15 mL/g under reducing conditions. These values are similar to the K_d values of 7.66 mL/g and 7.25 mL/g observed under oxidizing and reducing conditions, respectively, in this work. These findings appear to confirm the previously accepted K_d values of 0-10 mL/g depending on the cementitious formulation.

7.2 Suggested Future Work

The above data demonstrate several areas that require further examination. The increasing Tc K_d values over time dataset suggest that steady state had not been achieved. It would be beneficial to determine the amount of time required to reach steady state and allow determination of a more accurate K_d value (an assumption of the K_d construct is that it be measured at steady state). Also, kinetic studies of both Tc and I are needed to better understand their respective interactions with the different cementitious formulations. As for the I, additional

tests should be performed to test the hypothesis that iodine may in part exist as iodate which may initially sorb to the saltstone, then undergo reduction to iodine or iodide, and then desorbs causing a decrease in K_d .

A final area of future work is to examine the possible causes for the similar behavior of each cementitious formulation despite the different slag content. This discrepancy is not only observed in the above experiments, but also in Kaplan *et al.* (2008), which is illustrated in Table 3.1 and by recent work in measurements of saltstone reduction capacity (Roberts and Kaplan 2009). The reduction capacity (units in milli-equivalents/g solid) equivalents of the Aged Cement with no slag is 85.5 ± 10.1 , and adding 10% slag gives a reducing equivalent of 239.8 ± 31.1 . However, increasing the slag content to 23% causes the reducing capacity to increase to 821.8 ± 8.1 , which is almost equivalent to the 832.4 ± 4.9 of the 100% slag. Understanding the chemistry behind the reducing capacity of each cementitious formulation will help to define what reactions are important for controlling radionuclide release from the saltstone.

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9.0 Appendix A: Data Tables of Radionuclide Sorption to Saltstone under Oxidizing Conditions

The following tables represent data collected for the no solids controls, each saltstone, and testing of radionuclide sorption to the vial walls. The no solids controls tables include the concentration (ppb) of the radionuclide spiked into the sample, along with the concentration of the radionuclide (ppb) measured in the aqueous phase after the given equilibration time. The pH at the time the sample was taken is also recorded, along with the fraction of the radionuclide which stayed in the aqueous phase. The tables for the cementitious formulation data include the data above, along with the addition of a K_d value. The tables of the data for the radionuclides sorbed to the vial walls include the initial concentration (ppb) of the spike, the concentration (ppb) of the radionuclide that had sorbed to the vial wall during the experiment, and the percentage of the total concentration this represents.

Important Notes:

BDL- Below Detection Limit

<0.1* denotes no notable sorption occurred

9.1 Data Tables for No Solid Controls

Table 9.1: Plutonium no solids control after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 10.98124271 | 0.588738002 | 12.06 | 0.053613058 |
| B | 10.98518068 | 3.623675578 | 11.68 | 0.329869456 |
| C | 10.95633227 | 3.667254562 | 11.71 | 0.33471553 |
| D | 1.084337349 | 0.224089715 | 11.96 | 0.206660515 |
| E | 1.062853037 | 0.217987352 | 11.84 | 0.205096419 |
| F | 1.072807061 | 0.187059704 | 11.85 | 0.174364721 |
| G | 10.47554375 | 0.245110331 | 11.52 | 0.02339834 |
| H | 0.98857645 | 0.053735822 | 11.54 | 0.054356769 |

Table 9.2: Plutonium no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 10.9812427 | 0.278151513 | 12.02 | 0.025329694 |
| B | 10.9851807 | 1.179747464 | 11.7 | 0.107394452 |
| C | 10.9563323 | 1.149191187 | 11.74 | 0.104888311 |
| D | 1.08433735 | 0.061646445 | 11.86 | 0.056851721 |
| E | 1.06285304 | 0.051767732 | 11.86 | 0.048706387 |
| F | 1.07280706 | 0.04514876 | 11.85 | 0.042084697 |
| G | 10.4755438 | 0.271974836 | 11.5 | 0.025962837 |
| H | 0.98857645 | 0.056143201 | 11.48 | 0.275117656 |

Table 9.3: Neptunium no solids control after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 9.689771741 | 5.635730545 | 12.06 | 0.58161644 |
| B | 9.847322158 | 8.815567839 | 11.68 | 0.895224884 |
| C | 9.749375678 | 8.872066318 | 11.71 | 0.910013791 |
| D | 1.154111059 | 1.139541421 | 11.96 | 0.987375879 |
| E | 0.998383266 | 0.716244157 | 11.84 | 0.717404009 |
| F | 0.973220964 | 0.598731247 | 11.85 | 0.615205867 |
| G | 9.760929917 | 0.375956436 | 11.52 | 0.038516457 |
| H | 0.982585077 | 0.01870128 | 11.54 | 0.019032734 |

Table 9.4: Neptunium no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 9.68977174 | 4.815179672 | 12.02 | 0.496934273 |
| B | 9.84732216 | 8.11967814 | 11.7 | 0.824556972 |
| C | 9.74937568 | 5.125187481 | 11.74 | 0.525693916 |
| D | 1.15411106 | 0.064698249 | 11.86 | 0.056058946 |
| E | 0.99838327 | 0.006926236 | 11.86 | 0.006937452 |
| F | 0.97322096 | 0.012723741 | 11.85 | 0.013073846 |
| G | 9.76092992 | 0.397124158 | 11.5 | 0.040685074 |
| H | 0.98258508 | 0.03846849 | 11.48 | 0.039150289 |

Table 9.5: Technetium no solids control after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 9.970293475 | 8.758010503 | 12.06 | 0.878410503 |
| B | 10.35795579 | 9.223444824 | 11.68 | 0.890469607 |
| C | 9.756181039 | 8.68137711 | 11.71 | 0.88983354 |
| D | 0.990946387 | 0.9571545 | 11.96 | 0.965899379 |
| E | 1.000848286 | 0.958642075 | 11.84 | 0.957829561 |
| F | 1.000219419 | 0.954324935 | 11.85 | 0.954115584 |
| G | 10.15650402 | 0.86718206 | 11.52 | 0.085381944 |
| H | 1.001427944 | 0.917354471 | 11.54 | 0.916046409 |

Table 9.6: Technetium no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 9.97029348 | 9.681302845 | 12.02 | 0.971014832 |
| B | 10.3579558 | 10.39736502 | 11.7 | 1.00380473 |
| C | 9.75618104 | 9.652179907 | 11.74 | 0.989339975 |
| D | 0.99094639 | 1.047989563 | 11.86 | 1.057564341 |
| E | 1.00084829 | 1.047120027 | 11.86 | 1.046232522 |
| F | 1.00021942 | 1.027134282 | 11.85 | 1.026908959 |
| G | 10.156504 | 9.612163266 | 11.5 | 0.946404712 |
| H | 1.00142794 | 1.000804551 | 11.48 | 0.999377496 |

Table 9.7: Iodine no solids control after one day.

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 1033.096997 | 518.501178 | 12.06 | 0.501890122 |
| B | 1033.465548 | 727.6930444 | 11.68 | 0.704128982 |
| C | 1035.728144 | 860.0139369 | 11.71 | 0.830347174 |
| D | 99.81932702 | 8.482630391 | 11.96 | 0.08497984 |
| E | 98.80042315 | 5.447287368 | 11.84 | 0.055134251 |
| F | 99.73570039 | 9.041153475 | 11.85 | 0.090651125 |
| G | 1003.615011 | 435.3607551 | 11.52 | 0.43379259 |
| H | 94.86339671 | 5.683679634 | 11.54 | 0.059914359 |

Table 9.8: Iodine no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| A | 1033.097 | 325.5083399 | 12.02 | 0.315080133 |
| B | 1033.46555 | 652.0607126 | 11.7 | 0.630945767 |
| C | 1035.72814 | 763.7322674 | 11.74 | 0.737386806 |
| D | 99.819327 | BDL | 11.86 | NA |
| E | 98.8004231 | BDL | 11.86 | NA |
| F | 99.7357004 | BDL | 11.85 | NA |
| G | 1003.61501 | 343.8150241 | 11.5 | 0.342576606 |
| H | 94.8633967 | 2.530184962 | 11.48 | 0.026671878 |

9.2 Data Tables for Vault 2

Table 9.9: Vault 2- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.62367044 | 0.001733701 | 11.01 | 0.000163192 | 257380.6 |
| B | 10.65611835 | 0.00212538 | 11.05 | 0.000199452 | 206799.6 |
| C | 10.14798459 | 0.001323578 | 11.01 | 0.000130428 | 327843.3 |
| D | 1.035694085 | 0.001381959 | 11.34 | 0.001334331 | 30344.26 |
| E | 1.132618376 | 0.001099997 | 11.35 | 0.000971199 | 41080.91 |
| F | 1.005505809 | 0.001101291 | 11.4 | 0.001095261 | 36860.45 |
| G | 5.364163602 | 0.001194136 | 11.2 | 0.000222614 | 178142 |
| H | 5.370393851 | 0.001095256 | 11.23 | 0.000203943 | 202974.1 |
| I | 5.494303637 | 0.001659554 | 11.25 | 0.00030205 | 137974.3 |

Table 9.10: Vault 2- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.62367 | 0.0011705 | 11.09 | 0.0001102 | 381237.3 |
| B | 10.656118 | 0.0008583 | 11.11 | 8.055E-05 | 512147.4 |
| C | 10.147985 | 0.0007166 | 11.09 | 7.062E-05 | 605548.4 |
| D | 1.0356941 | 0.000788 | 11.26 | 0.0007609 | 53245.05 |
| E | 1.1326184 | 0.0008703 | 11.22 | 0.0007684 | 51934.16 |
| F | 1.0055058 | 0.0005765 | 11.3 | 0.0005734 | 70450.16 |
| G | 5.3641636 | 0.0007065 | 11.19 | 0.0001317 | 301136.7 |
| H | 5.3703939 | 0.0007858 | 11.23 | 0.0001463 | 282939.6 |
| I | 5.4943036 | 0.0008239 | 11.28 | 0.00015 | 277947.8 |

Table 9.11: Vault 2- neptunium after one day

| Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------------------|------------------------|-------|-------------|----------------|
| 9.21692635 | 0.005957077 | 11.01 | 0.000646319 | 65041.88 |
| 9.170432784 | 0.00306662 | 11.05 | 0.000334403 | 123477.6 |
| 9.096163751 | 0.002111663 | 11.01 | 0.000232149 | 184471.9 |
| 0.968314926 | 0.000867507 | 11.34 | 0.000895894 | 45223.52 |
| 0.994314793 | 0.000898163 | 11.35 | 0.000903298 | 44178.52 |
| 0.969777681 | 0.000484972 | 11.4 | 0.000500086 | 80796.96 |
| 3.929661216 | 0.001578688 | 11.2 | 0.000401736 | 98671.72 |
| 3.911007939 | 0.001115352 | 11.23 | 0.000285183 | 145101.4 |
| 4.054091025 | 0.001146601 | 11.25 | 0.000282826 | 147323.3 |

Table 9.12: Vault 2- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.2169263 | 0.0043124 | 11.09 | 0.0004679 | 89862.73 |
| B | 9.1704328 | 0.0012261 | 11.11 | 0.0001337 | 308879.3 |
| C | 9.0961638 | 0.0008395 | 11.09 | 9.229E-05 | 464093.3 |
| D | 0.9683149 | 0.000481 | 11.26 | 0.0004967 | 81594.77 |
| E | 0.9943148 | 0.0005631 | 11.22 | 0.0005664 | 70485.87 |
| F | 0.9697777 | 0.0003397 | 11.3 | 0.0003503 | 115357 |
| G | 3.9296612 | 0.000686 | 11.19 | 0.0001746 | 227125.1 |
| H | 3.9110079 | 0.0004796 | 11.23 | 0.0001226 | 337488.4 |
| I | 4.054091 | 0.0011432 | 11.28 | 0.000282 | 147761.1 |

Table 9.13: Vault 2- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.256597482 | 8.294548724 | 11.01 | 0.896068857 | 6.565531 |
| B | 9.220605132 | 8.284935394 | 11.05 | 0.898524042 | 6.31461 |
| C | 9.328322619 | 8.280953522 | 11.01 | 0.887721604 | 7.274366 |
| D | 1.041945759 | 0.974835903 | 11.34 | 0.935591795 | 2.958653 |
| E | 1.023734743 | 0.961438092 | 11.35 | 0.939147663 | 2.759052 |
| F | 0.97395176 | 0.832434488 | 11.4 | 0.854697864 | 7.034554 |
| G | 4.880291057 | 4.145068165 | 11.2 | 0.849348557 | 7.809823 |
| H | 4.837797242 | 4.288579455 | 11.23 | 0.886473583 | 6.107532 |
| I | 4.738827116 | 3.781772577 | 11.25 | 0.798039786 | 11.37228 |

Table 9.14: Vault 2- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.2565975 | 7.8650338 | 11.09 | 0.8496679 | 9.123867 |
| B | 9.2206051 | 8.0394456 | 11.11 | 0.8719 | 7.715476 |
| C | 9.3283226 | 8.120385 | 11.09 | 0.8705086 | 8.226739 |
| D | 1.0419458 | 0.9591407 | 11.26 | 0.9205284 | 3.667817 |
| E | 1.0237347 | 0.9375635 | 11.22 | 0.9158266 | 3.841864 |
| F | 0.9739518 | 0.8407776 | 11.3 | 0.8632641 | 6.565308 |
| G | 4.8802911 | 4.0565827 | 11.19 | 0.8312174 | 8.828343 |
| H | 4.8377972 | 4.2645053 | 11.23 | 0.8814973 | 6.371143 |
| I | 4.7388271 | 3.6819451 | 11.28 | 0.7769739 | 12.78797 |

Table 9.15: Vault 2- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 994.6530213 | 668.522424 | 11.01 | 0.644950246 | 21.9202 |
| B | 984.2972041 | 682.7479432 | 11.05 | 0.665719094 | 20.79681 |
| C | 1370.633906 | 1289.25931 | 11.01 | 0.899565656 | 4.668908 |
| D | 93.27895369 | 95.78419326 | 11.34 | 1.022618541 | <0.1* |
| E | 99.39172266 | 85.63510014 | 11.35 | 0.857892433 | 6.496328 |
| F | 94.41369098 | 83.0634865 | 11.4 | 0.876223604 | 5.620694 |
| G | 484.1170487 | 434.1708968 | 11.2 | 0.879296934 | 5.525112 |
| H | 482.8043618 | 450.2906342 | 11.23 | 0.914490246 | 3.871429 |
| I | 500.263811 | 395.9869628 | 11.25 | 0.775848285 | 11.76974 |

Table 9.16: Vault 2- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 994.65302 | 849.29996 | 11.09 | 0.8193535 | 8.778888 |
| B | 984.2972 | 845.31183 | 11.11 | 0.8242284 | 8.832374 |
| C | 1370.6339 | 1200.3449 | 11.09 | 0.8375266 | 8.112402 |
| D | 93.278954 | 90.828797 | 11.26 | 0.9697134 | 1.27742 |
| E | 99.391723 | 89.516549 | 11.22 | 0.8967768 | 4.514156 |
| F | 94.413691 | 76.23566 | 11.3 | 0.8041979 | 9.687715 |
| G | 484.11705 | 415.71485 | 11.19 | 0.8419192 | 7.557309 |
| H | 482.80436 | 428.01299 | 11.23 | 0.8692468 | 6.227932 |
| I | 500.26381 | 380.02219 | 11.28 | 0.7445689 | 13.9756 |

Table 9.17: TR545- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.46580588 | 0.026580976 | 11.81 | 0.002539793 | 17022.63 |
| B | 10.4436762 | 0.010478566 | 11.83 | 0.001003341 | 42594.87 |
| C | 10.49080459 | 0.006700641 | 11.8 | 0.000638716 | 63660.25 |
| D | 1.13124665 | 0.004242148 | 12 | 0.003749977 | 10734.92 |
| E | 1.174037402 | 0.003429046 | 11.99 | 0.00292073 | 13453.71 |
| F | 1.101694915 | 0.002227889 | 11.98 | 0.002022238 | 19403.59 |
| G | 5.448687281 | 0.002419858 | 11.86 | 0.000444118 | 93896.51 |
| H | 5.342234695 | 0.001490989 | 11.88 | 0.000279095 | 147892.8 |
| I | 5.388454776 | 0.002074015 | 11.89 | 0.0003849 | 108704.2 |

9.3 Data tables for saltstone TR545

Table 9.18: TR545- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.465806 | 0.0330348 | 11.88 | 0.0031565 | 13688.79 |
| B | 10.443676 | 0.0114086 | 11.85 | 0.0010924 | 39119.24 |
| C | 10.490805 | 0.0062925 | 11.85 | 0.0005998 | 67791.61 |
| D | 1.1312466 | 0.0044912 | 11.97 | 0.0039702 | 10137.34 |
| E | 1.1740374 | 0.0029871 | 12 | 0.0025443 | 15449.78 |
| F | 1.1016949 | 0.0040505 | 12.06 | 0.0036766 | 10655.01 |
| G | 5.4486873 | 0.0020968 | 11.96 | 0.0003848 | 108370.4 |
| H | 5.3422347 | 0.0019612 | 11.96 | 0.0003671 | 112422.5 |
| I | 5.3884548 | 0.0017107 | 11.94 | 0.0003175 | 131795.5 |

Table 9.19: TR545- neptunium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.264165178 | 4.02285E-05 | 11.81 | 4.34238E-06 | 9980817 |
| B | 9.352537276 | 0.000110618 | 11.83 | 1.18276E-05 | 3616813 |
| C | 9.363541597 | 7.05331E-05 | 11.8 | 7.53273E-06 | 5401186 |
| D | 0.993110568 | BDL | 12 | NA | NA |
| E | 0.977247222 | 3.00794E-05 | 11.99 | 3.07797E-05 | 1280331 |
| F | 0.962441315 | BDL | 11.98 | NA | NA |
| G | 4.059128499 | BDL | 11.86 | NA | NA |
| H | 4.065161486 | 7.05198E-05 | 11.88 | 1.73473E-05 | 2380003 |
| I | 4.116819691 | 0.000110748 | 11.89 | 2.69014E-05 | 1555864 |

Table 9.20: TR545- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.2641652 | NA | 11.88 | NA | NA |
| B | 9.3525373 | 0.0001935 | 11.85 | 2.069E-05 | 2067199 |
| C | 9.3635416 | 4.119E-05 | 11.85 | 4.4E-06 | 9247818 |
| D | 0.9931106 | BDL | 11.97 | NA | NA |
| E | 0.9772472 | BDL | 12 | NA | NA |
| F | 0.9624413 | 0.0066817 | 12.06 | 0.0069424 | 5624.21 |
| G | 4.0591285 | 0.0003289 | 11.96 | 8.103E-05 | 514827.4 |
| H | 4.0651615 | 0.0025316 | 11.96 | 0.0006228 | 66257.37 |
| I | 4.1168197 | 0.0001018 | 11.94 | 2.474E-05 | 1692126 |

Table 9.21: TR545- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.655146069 | 8.20460082 | 11.81 | 0.849764546 | 8.998984 |
| B | 9.356176321 | 7.703053505 | 11.83 | 0.823312135 | 10.51242 |
| C | 9.114122586 | 7.978297395 | 11.8 | 0.875377451 | 7.062663 |
| D | 1.042349157 | 0.853053814 | 12 | 0.818395456 | 9.099556 |
| E | 0.983206046 | 0.871198263 | 11.99 | 0.886079033 | 5.196709 |
| F | 0.905148405 | 0.803451372 | 11.98 | 0.887646013 | 5.098696 |
| G | 4.950156706 | 4.275082341 | 11.86 | 0.863625658 | 7.213934 |
| H | 4.889067068 | 4.173762594 | 11.88 | 0.853693053 | 7.687519 |
| I | 4.854463762 | 4.147024058 | 11.89 | 0.854270268 | 7.771045 |

Table 9.22: TR545- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.6551461 | 8.0911855 | 11.88 | 0.8380179 | 9.713902 |
| B | 9.3561763 | 7.4410368 | 11.85 | 0.7953075 | 12.34203 |
| C | 9.1141226 | 7.5881085 | 11.85 | 0.832566 | 9.452625 |
| D | 1.0423492 | 0.8195966 | 11.97 | 0.7862975 | 11.11505 |
| E | 0.983206 | 0.8251481 | 12 | 0.8392422 | 7.678853 |
| F | 0.9051484 | 0.8066411 | 12.06 | 0.89117 | 4.923541 |
| G | 4.9501567 | 4.4733496 | 11.96 | 0.9036784 | 5.072867 |
| H | 4.8890671 | 4.3558824 | 11.96 | 0.8909435 | 5.665444 |
| I | 4.8544638 | 4.3264547 | 11.94 | 0.8912323 | 5.739026 |

Table 9.23: TR545- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 971.2446639 | 845.8491376 | 11.81 | 0.835627421 | 7.856457 |
| B | 992.1185946 | 857.5189634 | 11.83 | 0.829335063 | 8.520183 |
| C | 995.5720475 | 917.4749665 | 11.8 | 0.884380649 | 5.450116 |
| D | 102.2494888 | 105.4151374 | 12 | 1.026487576 | <0.1* |
| E | 100.3068795 | 92.53307262 | 11.99 | 0.918551075 | 3.480297 |
| F | 89.52017188 | 81.48352848 | 11.98 | 0.906576684 | 4.096805 |
| G | 494.0393083 | 434.9637713 | 11.86 | 0.862852934 | 6.406294 |
| H | 484.0176398 | 434.9559364 | 11.88 | 0.880930756 | 5.580958 |
| I | 499.1209221 | 436.2736266 | 11.89 | 0.856667235 | 6.817707 |

Table 9.24: TR545- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 971.24466 | 815.45995 | 11.88 | 0.8056055 | 9.637661 |
| B | 992.11859 | 794.82276 | 11.85 | 0.7686995 | 12.45818 |
| C | 995.57205 | 838.67718 | 11.85 | 0.8084252 | 9.879 |
| D | 102.24949 | 98.946711 | 11.97 | 0.9635008 | 1.54859 |
| E | 100.30688 | 86.788315 | 12 | 0.8615244 | 6.3087 |
| F | 89.520172 | 75.300141 | 12.06 | 0.837781 | 7.697785 |
| G | 494.03931 | 413.51764 | 11.96 | 0.8203095 | 8.828858 |
| H | 484.01764 | 394.21041 | 11.96 | 0.7984075 | 10.42559 |
| I | 499.12092 | 401.22049 | 11.94 | 0.7878369 | 10.97334 |

9.4 Data Tables for Saltstone TR547

Table 9.25: TR547- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.48950046 | 0.002141023 | 11.49 | 0.000204111 | 211228.1 |
| B | 10.39943573 | 0.001770549 | 11.57 | 0.000170254 | 246048.7 |
| C | 10.84651695 | 0.001127533 | 11.53 | 0.000103953 | 401491.8 |
| D | 1.088686867 | 0.001201087 | 11.72 | 0.001103244 | 35645.24 |
| E | 1.119673887 | 0.000783288 | 11.77 | 0.000699568 | 57098.97 |
| F | 1.045722787 | 0.000914861 | 11.81 | 0.00087486 | 44953.24 |
| G | 5.387981131 | 0.001444832 | 11.69 | 0.000268158 | 149471.5 |
| H | 5.412748988 | 0.001143483 | 11.69 | 0.000211257 | 196574.9 |
| I | 5.373948758 | 0.0010003 | 11.64 | 0.000186139 | 228047.2 |

Table 9.26: TR547- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.4895 | NA | 11.6 | NA | NA |
| B | 10.399436 | 0.001828 | 11.65 | 0.0001758 | 238313.2 |
| C | 10.846517 | 0.0010788 | 11.64 | 9.946E-05 | 419615.9 |
| D | 1.0886869 | 0.0009131 | 11.84 | 0.0008388 | 46897.78 |
| E | 1.1196739 | 0.0010624 | 11.89 | 0.0009488 | 42089.28 |
| F | 1.0457228 | 0.0007967 | 11.91 | 0.0007619 | 51625.8 |
| G | 5.3879811 | 0.0007915 | 11.73 | 0.0001469 | 272899.3 |
| H | 5.412749 | 0.0008355 | 11.75 | 0.0001544 | 269064.1 |
| I | 5.3739488 | 0.0006103 | 11.74 | 0.0001136 | 373789.2 |

Table 9.27: TR547- neptunium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.589772032 | 0.000454463 | 11.49 | 4.73903E-05 | 911633.5 |
| B | 9.293228768 | 0.000260081 | 11.57 | 2.7986E-05 | 1499475 |
| C | 10.08725504 | 0.000302018 | 11.53 | 2.99405E-05 | 1397125 |
| D | 0.952173007 | 0.00019177 | 11.72 | 0.000201403 | 195460.3 |
| E | 0.992224074 | BDL | | NA | NA |
| F | 0.967815522 | 4.02137E-05 | 11.81 | 4.1551E-05 | 947469.9 |
| G | 4.068405786 | 0.000222282 | 11.69 | 5.46361E-05 | 733698.6 |
| H | 4.09543171 | 0.000531619 | 11.69 | 0.000129808 | 319915.2 |
| I | 4.017406611 | 0.000410123 | 11.64 | 0.000102086 | 415780.7 |

Table 9.28: TR547- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.589772 | NA | 11.6 | NA | NA |
| B | 9.2932288 | 0.0002145 | 11.65 | 2.308E-05 | 1818463 |
| C | 10.087255 | 0.0001628 | 11.64 | 1.614E-05 | 2591215 |
| D | 0.952173 | BDL | 11.84 | NA | NA |
| E | 0.9922241 | BDL | | NA | NA |
| F | 0.9678155 | 5.107E-05 | 11.91 | 5.277E-05 | 746037.5 |
| G | 4.0684058 | 0.0001336 | 11.73 | 3.284E-05 | 1220544 |
| H | 4.0954317 | 8.151E-05 | 11.75 | 1.99E-05 | 2086795 |
| I | 4.0174066 | 0.0001322 | 11.74 | 3.292E-05 | 1289605 |

Table 9.29: TR547- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.466799266 | 8.233850788 | 11.49 | 0.869760788 | 8.220086 |
| B | 9.439556236 | 8.17653394 | 11.57 | 0.866198975 | 8.165745 |
| C | 9.383493063 | 8.086024379 | 11.53 | 0.861728604 | 8.430884 |
| D | 1.061939876 | 0.919992065 | 11.72 | 0.866331594 | 6.241759 |
| E | 0.991827343 | 0.836511397 | 11.77 | 0.843404251 | 7.590958 |
| F | 0.971981155 | 0.839862696 | 11.81 | 0.864073024 | 6.354378 |
| G | 4.883337077 | 4.14858839 | 11.69 | 0.849539633 | 7.903986 |
| H | 4.691440077 | 3.996173112 | 11.69 | 0.851800949 | 8.038249 |
| I | 4.86993937 | 4.291285586 | 11.64 | 0.881178442 | 6.558707 |

Table 9.30: TR547- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.4667993 | NA | 11.6 | NA | NA |
| B | 9.4395562 | 8.5812109 | 11.65 | 0.9090693 | 5.885474 |
| C | 9.3834931 | 8.4622373 | 11.64 | 0.9018217 | 6.279204 |
| D | 1.0619399 | 0.9580683 | 11.84 | 0.9021869 | 4.435663 |
| E | 0.9918273 | 0.8881507 | 11.89 | 0.8954691 | 4.835506 |
| F | 0.9719812 | 0.9036489 | 11.91 | 0.929698 | 3.138862 |
| G | 4.8833371 | 4.490415 | 11.73 | 0.9195382 | 4.312104 |
| H | 4.6914401 | 4.2054182 | 11.75 | 0.8964024 | 5.612948 |
| I | 4.8699394 | 4.3843193 | 11.74 | 0.9002821 | 5.536503 |

Table 9.31: TR547- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 994.4920441 | 881.3152965 | 11.49 | 0.886196427 | 7.38241 |
| B | 995.6006121 | 874.7156303 | 11.57 | 0.878580848 | 8.007767 |
| C | 982.2152291 | 866.4470934 | 11.53 | 0.882135674 | 7.988892 |
| D | 100.2391846 | 93.33490632 | 11.72 | 0.931121963 | 3.368509 |
| E | 99.18273427 | 66.25075445 | 11.77 | 0.667966607 | 15.51748 |
| F | 99.18175056 | 89.31364957 | 11.81 | 0.900504872 | 4.773862 |
| G | 516.6570628 | 444.5386532 | 11.69 | 0.860413387 | 7.961604 |
| H | 484.7821413 | 410.447427 | 11.69 | 0.84666367 | 8.664303 |
| I | 485.0381381 | 426.6693706 | 11.64 | 0.879661489 | 6.413801 |

Table 9.32: TR547- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 994.49204 | 840.78927 | 11.6 | 0.845446 | 9.304586 |
| B | 995.60061 | 843.39692 | 11.65 | 0.8471237 | 9.547302 |
| C | 982.21523 | 828.21547 | 11.64 | 0.8432118 | 9.915886 |
| D | 100.23918 | 89.006508 | 11.84 | 0.8879413 | 5.357117 |
| E | 99.182734 | 84.480287 | 11.89 | 0.851764 | 7.03665 |
| F | 99.181751 | 85.844767 | 11.91 | 0.8655299 | 6.384908 |
| G | 516.65706 | 418.57945 | 11.73 | 0.8101688 | 10.46071 |
| H | 484.78214 | 400.68924 | 11.75 | 0.8265347 | 9.670412 |
| I | 485.03814 | 432.18665 | 11.74 | 0.8910364 | 5.894162 |

9.5 Data Tables for Aged Cement

Table 9.33: Aged cement- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.49661917 | 0.00057716 | 11.67 | 5.49853E-05 | 757083.3 |
| B | 10.44676116 | 0.000712674 | 11.54 | 6.82196E-05 | 634071 |
| C | 10.40494422 | 0.000659215 | 11.63 | 6.33559E-05 | 685779.5 |
| D | 1.069574815 | 0.000501161 | 11.81 | 0.000468561 | 87438.06 |
| E | 1.119884926 | 0.000459622 | 11.82 | 0.000410419 | 96118.08 |
| F | 1.132798521 | 0.000428241 | 11.84 | 0.000378038 | 105626.4 |
| G | 5.494249954 | 0.000427061 | 11.7 | 7.77287E-05 | 528785.4 |
| H | 5.407466468 | 0.000325564 | 11.69 | 6.02064E-05 | 699373.6 |
| I | 5.3502419 | 0.000692442 | 11.7 | 0.000129423 | 321010.2 |

Table 9.34: Aged cement- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 10.496619 | 0.0007248 | 11.67 | 6.905E-05 | 602873.5 |
| B | 10.446761 | 0.0005881 | 11.61 | 5.629E-05 | 768392.4 |
| C | 10.404944 | 0.0006194 | 11.61 | 5.953E-05 | 729854.9 |
| D | 1.0695748 | 0.0005383 | 11.84 | 0.0005033 | 81398.48 |
| E | 1.1198849 | 0.0005656 | 11.87 | 0.000505 | 78106.96 |
| F | 1.1327985 | 0.0003573 | 11.88 | 0.0003154 | 126606.3 |
| G | 5.49425 | 0.0003353 | 11.77 | 6.103E-05 | 673465.7 |
| H | 5.4074665 | 0.0003576 | 11.76 | 6.612E-05 | 636796.5 |
| I | 5.3502419 | 0.0004411 | 11.76 | 8.244E-05 | 503954.1 |

Table 9.35: Aged cement- neptunium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.280093212 | 0.007108181 | 11.67 | 0.00076596 | 54392.88 |
| B | 9.320139831 | 0.004011335 | 11.54 | 0.000430394 | 100629.7 |
| C | 9.508541493 | 0.00166325 | 11.63 | 0.000174922 | 248828 |
| D | 0.97028876 | 0.000726172 | 11.81 | 0.000748408 | 54737.5 |
| E | 1.081890779 | 0.000520905 | 11.82 | 0.000481476 | 81948.95 |
| F | 0.994472941 | 0.000224317 | 11.84 | 0.000225563 | 177080.3 |
| G | 4.062063373 | 0.000183026 | 11.7 | 4.50574E-05 | 912048.6 |
| H | 4.091295968 | 0.000223825 | 11.69 | 5.47076E-05 | 769603.6 |
| I | 4.079362752 | 0.000254574 | 11.7 | 6.24054E-05 | 665753.7 |

Table 9.36: Aged cement- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.2800932 | 0.0038179 | 11.67 | 0.0004114 | 101304.2 |
| B | 9.3201398 | 0.0016426 | 11.61 | 0.0001762 | 245800.9 |
| C | 9.5085415 | 0.0009139 | 11.61 | 9.611E-05 | 452898 |
| D | 0.9702888 | 0.0002133 | 11.84 | 0.0002198 | 186450.4 |
| E | 1.0818908 | 0.0002982 | 11.87 | 0.0002756 | 143179.3 |
| F | 0.9944729 | 0.0003267 | 11.88 | 0.0003285 | 121583 |
| G | 4.0620634 | 0.0001016 | 11.77 | 2.501E-05 | 1642830 |
| H | 4.091296 | 0.0001998 | 11.76 | 4.884E-05 | 862107.8 |
| I | 4.0793628 | 8.206E-05 | 11.76 | 2.012E-05 | 2065348 |

Table 9.37: Aged cement- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.416663483 | 7.667114947 | 11.67 | 0.814207172 | 11.17916 |
| B | 9.465319299 | 7.556377889 | 11.54 | 0.798322555 | 12.66251 |
| C | 9.569149292 | 7.922749629 | 11.63 | 0.827947123 | 10.7987 |
| D | 1.004295601 | 0.866599278 | 11.81 | 0.862892635 | 6.684472 |
| E | 1.031694856 | 0.865518891 | 11.82 | 0.838929152 | 7.750351 |
| F | 0.984134558 | 0.828238515 | 11.84 | 0.841590724 | 7.688585 |
| G | 4.895111728 | 4.051996638 | 11.7 | 0.827763872 | 9.366864 |
| H | 4.862204917 | 4.190616825 | 11.69 | 0.861875815 | 7.58057 |
| I | 4.886868983 | 4.145489943 | 11.7 | 0.848291607 | 8.251034 |

Table 9.38: Aged cement- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 9.4166635 | 8.2267024 | 11.67 | 0.8736324 | 7.702806 |
| B | 9.4653193 | 8.5780661 | 11.61 | 0.9062627 | 6.210837 |
| C | 9.5691493 | 8.5417433 | 11.61 | 0.8926335 | 6.996406 |
| D | 1.0042956 | 0.9416563 | 11.84 | 0.9376286 | 2.898204 |
| E | 1.0316949 | 0.9196854 | 11.87 | 0.8914316 | 4.979791 |
| F | 0.9841346 | 0.886981 | 11.88 | 0.9012802 | 4.545372 |
| G | 4.8951117 | 4.3441484 | 11.77 | 0.8874462 | 6.02818 |
| H | 4.8622049 | 4.3653822 | 11.76 | 0.8978195 | 5.625012 |
| I | 4.886869 | 4.3948285 | 11.76 | 0.8993138 | 5.472433 |

Table 9.39: Aged cement- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 987.5081178 | 478.2787653 | 11.67 | 0.484328945 | 46.01018 |
| B | 955.1280827 | 19.17864389 | 11.54 | 0.020079657 | 2112.282 |
| C | 983.6817804 | 28.50427319 | 11.63 | 0.028977128 | 1457.909 |
| D | 99.43520802 | 53.54401206 | 11.81 | 0.53848142 | 35.30201 |
| E | 99.2014285 | 3.303880468 | 11.82 | 0.033304767 | 1145.599 |
| F | 100.4016064 | 4.562722289 | 11.84 | 0.045444714 | 839.1729 |
| G | 485.6028999 | 298.1077404 | 11.7 | 0.61389201 | 26.6613 |
| H | 487.1988025 | 24.55078723 | 11.69 | 0.050391723 | 794.1965 |
| I | 487.7095245 | 173.01515 | 11.7 | 0.354750402 | 76.38668 |

Table 9.40: Aged cement- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | K _d |
|-----------|-----------------------|------------------------|-------|-------------|----------------|
| A | 987.50812 | 449.61824 | 11.67 | 0.4553059 | 51.48943 |
| B | 955.12808 | 681.3704 | 11.61 | 0.7133812 | 19.11392 |
| C | 983.68178 | 277.08852 | 11.61 | 0.2816851 | 112.5817 |
| D | 99.435208 | 71.523103 | 11.84 | 0.7192935 | 16.16758 |
| E | 99.201429 | 67.909668 | 11.87 | 0.6845634 | 18.35712 |
| F | 100.40161 | 65.826354 | 11.88 | 0.6556305 | 21.15061 |
| G | 485.6029 | 274.20191 | 11.77 | 0.5646628 | 32.49713 |
| H | 487.1988 | 185.38966 | 11.76 | 0.3805216 | 69.37195 |
| I | 487.70952 | 138.93489 | 11.76 | 0.2848722 | 105.1135 |

9.6 Data Tables for Sorption to Vial Walls

Table 9.41: % Plutonium sorbed to vial wall in no solids control

| Sample ID | Initial Conc. | Conc. In Wash of Vial (ppb) | % Sorbed to Walls |
|-----------|---------------|-----------------------------|-------------------|
| NS-A | 0.110121 | 0.03628 | 32.94558 |
| NS-B | 0.110228 | 0.0268 | 24.31335 |
| NS-C | 0.110121 | 0.02735 | 24.83632 |
| NS-D | 0.010863 | 0.00335 | 30.83863 |
| NS-E | 0.01065 | 0.0035 | 32.86385 |
| NS-F | 0.010757 | 0.00386 | 35.88528 |
| NS-G | 0.111719 | 0.01536 | 13.74878 |
| NS-H | 0.010544 | 0.00313 | 29.68513 |

Table 9.42: % Neptunium sorbed to vial wall in no solids control

| Sample ID | Initial Conc | Conc. In Wash of Vial (ppb) | % Sorbed to Walls |
|-----------|--------------|-----------------------------|-------------------|
| NS-A | 0.09717 | 0.0121 | 12.4524 |
| NS-B | 0.09881 | 0.00345 | 3.491549 |
| NS-C | 0.09799 | 0.0208 | 21.22666 |
| NS-D | 0.011562 | 0.00333 | 28.80125 |
| NS-E | 0.010004 | 0.00316 | 31.58737 |
| NS-F | 0.009758 | 0.00382 | 39.14737 |
| NS-G | 0.097744 | 0.04938 | 50.51972 |
| NS-H | 0.00984 | 0.00559 | 56.80894 |

10.0 Appendix B: Data Tables of Radionuclide Sorption to Saltstone Under Reducing Conditions

The following tables represent data collected for the no solids controls, each cementitious solid, and testing of radionuclide sorption to the vial walls. The no solids controls tables include the concentration (ppb) of the radionuclide spiked into the sample, along with the concentration of the radionuclide (ppb) measured in the aqueous phase after the given equilibration time. The pH at the time the sample was taken is also recorded, along with the fraction of the radionuclide which stayed in the aqueous phase. The tables for the cementitious solids' data include the data above, along with the addition of a K_d value. The tables of the data for the radionuclides sorbed to the vial walls include the initial concentration (ppb) of the spike, the concentration (ppb) of the radionuclide that had sorbed to the vial wall during the experiment, and the percentage of the total concentration this represents.

Important Notes:

BDL= Below Detection Limit

<0.1* denotes no notable sorption occurred

10.1 Data Tables for No-Solid Controls

Table 10.1: Plutonium no solids control after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 9.865515956 | 0.583283525 | 11.78 | 0.059123469 |
| NS-B | 9.899624212 | 0.663485207 | 11.76 | 0.067021252 |
| NS-C | 9.800690365 | 0.539915704 | 11.77 | 0.055089558 |
| NS-E | 1.082582721 | 0.431846663 | 11.66 | 0.398904079 |
| NS-F | 1.032892193 | 0.000301866 | 11.73 | 0.000292253 |
| NS-G | 1.052776412 | 0.488809417 | 11.71 | 0.464305061 |

Table 10.2: Plutonium no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 9.865515956 | 0.545394 | 11.83 | 0.055283 |
| NS-B | 9.899624212 | 0.468747 | 11.79 | 0.04735 |
| NS-C | 9.800690365 | 0.439191 | 11.80 | 0.044812 |
| NS-E | 1.082582721 | 0.358897 | 11.61 | 0.331519 |
| NS-F | 1.032892193 | 0.000111 | 11.71 | 0.000107 |
| NS-G | 1.052776412 | 4.55E-05 | 11.65 | 4.32E-05 |

Table 10.3: Neptunium no solids control after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 9.784205654 | 2.227968645 | 11.78 | 0.227710733 |
| NS-B | 9.774386849 | 3.506033589 | 11.76 | 0.358696013 |
| NS-C | 9.748642055 | 4.599509164 | 11.77 | 0.471810242 |
| NS-E | 0.990926695 | 0.923435978 | 11.66 | 0.931891312 |
| NS-F | 1.059013829 | BDL | 11.73 | NA |
| NS-G | 1.015695951 | 0.920736194 | 11.71 | 0.906507694 |

Table 10.4: Neptunium no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 9.784205654 | 1.843735 | 11.83 | 0.18844 |
| NS-B | 9.774386849 | 2.360655 | 11.79 | 0.241514 |
| NS-C | 9.748642055 | 4.40653 | 11.80 | 0.452015 |
| NS-E | 0.990926695 | 0.846694 | 11.61 | 0.854447 |
| NS-F | 1.059013829 | BDL | 11.71 | NA |
| NS-G | 1.015695951 | BDL | 11.65 | NA |

Table 10.5: Technetium no solids control after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 8.794409081 | 8.777467999 | 11.78 | 0.998073653 |
| NS-B | 9.132734292 | 8.531262277 | 11.76 | 0.93414108 |
| NS-C | 8.608231557 | 8.553778159 | 11.77 | 0.993674264 |
| NS-E | 0.907236499 | 0.898199858 | 11.66 | 0.990039376 |
| NS-F | 0.916275429 | 0.000368379 | 11.73 | 0.00040204 |
| NS-G | 0.915720325 | 0.925888607 | 11.71 | 1.011104135 |

Table 10.6: Technetium no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 8.794409081 | 8.337459 | 11.83 | 0.948041 |
| NS-B | 9.132734292 | 8.065824 | 11.79 | 0.883177 |
| NS-C | 8.608231557 | 8.155761 | 11.80 | 0.947437 |
| NS-E | 0.907236499 | 0.877529 | 11.61 | 0.967255 |
| NS-F | 0.916275429 | 0.000146 | 11.71 | 0.000159 |
| NS-G | 0.915720325 | 0.000238 | 11.65 | 0.00026 |

Table 10.7: Iodine no solids control after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 959.726097 | 843.2881472 | 11.78 | 0.878675853 |
| NS-B | 959.688424 | 851.3714171 | 11.76 | 0.887133153 |
| NS-C | 962.4703316 | 875.7645753 | 11.77 | 0.909913321 |
| NS-E | 96.24816906 | 86.36792982 | 11.66 | 0.897346211 |
| NS-F | 95.26296152 | 91.98116117 | 11.73 | 0.965550091 |
| NS-G | 96.16691794 | 83.27792058 | 11.71 | 0.865972648 |

Table 10.8: Iodine no solids control after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|-----------------------|------------------------|-------|-------------|
| NS-A | 959.726097 | 865.0033 | 11.83 | 0.901302 |
| NS-B | 959.688424 | 9343.247 | 11.79 | 9.735709 |
| NS-C | 962.4703316 | 902.5099 | 11.80 | 0.937702 |
| NS-E | 96.24816906 | 94.18273 | 11.61 | 0.978541 |
| NS-F | 95.26296152 | 116.0028 | 11.71 | 1.217711 |
| NS-G | 96.16691794 | 92.7704 | 11.65 | 0.964681 |

10.2 Data Tables for Vault 2

Table 10.9: Vault 2- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.4058918 | 0.002841681 | 11.05 | 0.000302117 | 140393.6 |
| B | 9.602498 | 0.002282224 | 11.10 | 0.00023767 | 178325.2 |
| C | 9.630618675 | 0.002608744 | 11.04 | 0.00027088 | 157169.7 |
| D | 4.945396384 | 0.002082692 | 11.25 | 0.000421137 | 100991.1 |
| E | 4.964945192 | 0.001703548 | 11.28 | 0.000343115 | 120299.9 |
| F | 4.441601383 | 0.00165649 | 11.20 | 0.000372949 | 127140 |
| G | 1.079602045 | 0.001250199 | 11.29 | 0.001158019 | 37399.33 |
| H | 1.031512133 | 0.003222175 | 11.32 | 0.003123739 | 13179.61 |
| I | 0.939293925 | 0.001224667 | 11.33 | 0.001303816 | 36320.54 |

Table 10.10: Vault 2- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.405892 | 0.007019 | 11.1 | 0.000746258 | 56812.06 |
| B | 9.602498 | 0.003294 | 11.17 | 0.000342992 | 123554 |
| C | 9.630619 | 0.002936 | 11.14 | 0.000304893 | 139631.8 |
| D | 4.945396 | 0.001795 | 11.3 | 0.000363011 | 117168.8 |
| E | 4.964945 | 0.001373 | 11.31 | 0.000276484 | 149301.5 |
| F | 4.441601 | 0.001516 | 11.3 | 0.000341219 | 138967.4 |
| G | 1.079602 | 0.001109 | 11.42 | 0.001027508 | 42155.19 |
| H | 1.031512 | 0.000883 | 11.43 | 0.000855983 | 48205.76 |
| I | 0.939294 | 0.000978 | 11.43 | 0.001040992 | 45502.55 |

Table 10.11: Vault 2- neptunium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq |
|-----------|--------------------------|---------------------------|-------|-------------|
| A | 9.425042625 | 0.001709054 | 11.05 | 0.000181331 |
| B | 9.611386476 | 0.001184125 | 11.10 | 0.0001232 |
| C | 9.579553607 | 0.001155517 | 11.04 | 0.000120623 |
| D | 4.974000414 | 0.000672325 | 11.25 | 0.000135168 |
| E | 4.916731623 | 0.000675371 | 11.28 | 0.000137362 |
| F | 4.373142817 | 0.000570681 | 11.20 | 0.000130497 |
| G | 0.943366414 | 0.000389738 | 11.29 | 0.000413136 |
| H | 1.011745587 | 0.000565648 | 11.32 | 0.000559081 |
| I | 0.865252712 | 0.000379545 | 11.33 | 0.000438653 |

Table 10.12: Vault 2- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|--------------------------|---------------------------|-------|-------------|----------|
| A | 9.425043 | 0.001341 | 11.1 | 0.000142314 | 298567.4 |
| B | 9.611386 | 0.000792 | 11.17 | 8.23889E-05 | 515339.4 |
| C | 9.579554 | 0.000363 | 11.14 | 3.79197E-05 | 1124764 |
| D | 4.974 | 6.56E-05 | 11.3 | 1.31798E-05 | 3231076 |
| E | 4.916732 | 0.000212 | 11.31 | 4.3111E-05 | 958475.6 |
| F | 4.373143 | 0.000252 | 11.3 | 5.75681E-05 | 824464 |
| G | 0.943366 | 3.55E-05 | 11.42 | 3.75857E-05 | 1153591 |
| H | 1.011746 | 3.53E-05 | 11.43 | 3.49083E-05 | 1183195 |
| I | 0.865253 | 2.02E-05 | 11.43 | 2.33004E-05 | 2035123 |

Table 10.13: Vault 2- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|--------------------------|---------------------------|-------|-------------|----------|
| A | 8.426518355 | 8.33290075 | 11.05 | 0.98889012 | 0.476492 |
| B | 8.638001423 | 7.823321167 | 11.10 | 0.905686487 | 4.413063 |
| C | 9.323317745 | 9.25927516 | 11.04 | 0.993130923 | 0.294664 |
| D | 4.42651005 | 4.300859603 | 11.25 | 0.971614106 | 1.242837 |
| E | 4.426849405 | 4.336992073 | 11.28 | 0.979701742 | 0.855315 |
| F | 3.929483125 | 3.938204338 | 11.20 | 1.00221943 | <0.1* |
| G | 0.817864386 | 0.81693181 | 11.29 | 0.998859743 | 0.049487 |
| H | 0.878958929 | 0.792412508 | 11.32 | 0.901535306 | 4.510199 |
| I | 0.772205665 | 0.871436364 | 11.33 | 1.128502941 | <0.1* |

Table 10.14: Vault 2- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 8.426518 | 7.387328 | 11.1 | 0.876676186 | 5.966258 |
| B | 8.638001 | 7.419385 | 11.17 | 0.858923768 | 6.960547 |
| C | 9.323318 | 8.036996 | 11.14 | 0.862031802 | 6.818523 |
| D | 4.42651 | 3.962629 | 11.3 | 0.895203859 | 4.979995 |
| E | 4.426849 | 4.090424 | 11.31 | 0.92400338 | 3.395329 |
| F | 3.929483 | 3.698764 | 11.3 | 0.941285083 | 2.958172 |
| G | 0.817864 | 0.742066 | 11.42 | 0.907321016 | 4.428077 |
| H | 0.878959 | 0.720997 | 11.43 | 0.820285656 | 9.047228 |
| I | 0.772206 | 0.788286 | 11.43 | 1.020823931 | <0.1* |

Table 10.15: Vault 2- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 876.0849289 | 764.9889866 | 11.05 | 0.873190442 | 6.159384 |
| B | 892.6622427 | 715.8886295 | 11.10 | 0.801970326 | 10.46384 |
| C | 894.4822597 | 719.172491 | 11.04 | 0.804009787 | 10.37675 |
| D | 466.7085975 | 437.9235651 | 11.25 | 0.93832333 | 2.796427 |
| E | 450.0417953 | 333.1662008 | 11.28 | 0.740300577 | 14.4803 |
| F | 404.412292 | 305.1584708 | 11.20 | 0.754572689 | 15.42407 |
| G | 125.7756141 | 104.2917052 | 11.29 | 0.829188598 | 8.933914 |
| H | 95.15163608 | 64.58872226 | 11.32 | 0.678797811 | 19.54128 |
| I | 81.92282988 | 86.40513157 | 11.33 | 1.054713707 | <0.1* |

Table 10.16: Vault 2- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 876.0849 | 787.583 | 11.1 | 0.898980219 | 4.765962 |
| B | 892.6622 | 5032.039 | 11.17 | 5.637113657 | <0.1* |
| C | 894.4823 | 713.4714 | 11.14 | 0.79763622 | 10.79982 |
| D | 466.7086 | 458.9269 | 11.3 | 0.983326499 | 0.72138 |
| E | 450.0418 | 374.5656 | 11.31 | 0.832290717 | 8.317575 |
| F | 404.4123 | 321.4176 | 11.3 | 0.794777097 | 12.24497 |
| G | 125.7756 | 109.0023 | 11.42 | 0.866640978 | 6.673619 |
| H | 95.15164 | 318.1754 | 11.43 | 3.343877675 | <0.1* |
| I | 81.92283 | 93.33398 | 11.43 | 1.139291501 | <0.1* |

10.3 Data Tables for TR545

Table 10.17: TR545- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 7.591216275 | 0.003211762 | 11.78 | 0.000423089 | 101443.2 |
| B | 7.220544548 | 0.002476226 | 11.81 | 0.000342942 | 136114.3 |
| C | 6.931442863 | 0.002424369 | 11.84 | 0.000349764 | 138212.5 |
| D | 3.679791021 | 0.002216217 | 11.87 | 0.000602267 | 77895.95 |
| E | 3.700656669 | 0.001909447 | 11.84 | 0.000515975 | 88244.83 |
| F | 3.870057311 | 0.001930251 | 11.79 | 0.000498765 | 89308.85 |
| G | 0.733093687 | 0.001371053 | 11.88 | 0.001870229 | 25202.55 |
| H | 0.714539864 | 0.001661534 | 11.87 | 0.002325321 | 19264.46 |
| I | 0.72348416 | 0.001140936 | 11.88 | 0.001577002 | 27910.27 |

Table 10.18: TR545- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 7.591216 | 0.001366 | 11.8 | 0.00017994 | 238578.8 |
| B | 7.220545 | 0.001296 | 11.82 | 0.000179541 | 260034.1 |
| C | 6.931443 | 0.000913 | 11.83 | 0.000131752 | 366993.7 |
| D | 3.679791 | 0.000811 | 11.85 | 0.000220318 | 213020 |
| E | 3.700657 | 0.001047 | 11.86 | 0.000282847 | 161015.5 |
| F | 3.870057 | 0.000474 | 11.83 | 0.000122483 | 363814.7 |
| G | 0.733094 | 0.000602 | 11.87 | 0.000820842 | 57482.56 |
| H | 0.71454 | 0.000498 | 11.85 | 0.000697618 | 64317.62 |
| I | 0.723484 | 0.000479 | 11.84 | 0.000662029 | 66545.2 |

Table 10.19: TR545- neptunium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.407194102 | 0.008139809 | 11.78 | 0.008139809 | 49660.49 |
| B | 8.812043306 | 0.003090249 | 11.81 | 0.003090249 | 133291.1 |
| C | 8.601491692 | 0.002857833 | 11.84 | 0.002857833 | 145718 |
| D | 4.494913172 | 0.002431822 | 11.87 | 0.002431822 | 86780.61 |
| E | 4.357753634 | 0.001442135 | 11.84 | 0.001442135 | 137682.1 |
| F | 4.723671527 | 0.000789191 | 11.79 | 0.000789191 | 266899.6 |
| G | 0.91531421 | 0.000557461 | 11.88 | 0.000557461 | 77501.98 |
| H | 0.912530034 | 0.000387691 | 11.87 | 0.000387691 | 105658.7 |
| I | 0.908158622 | 0.000165863 | 11.88 | 0.000165863 | 241371.5 |

Table 10.20: TR545- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.407194 | 0.000126 | 11.8 | 1.33952E-05 | 3210587 |
| B | 8.812043 | 0.000303 | 11.82 | 3.4346E-05 | 1361380 |
| C | 8.601492 | 0.000156 | 11.83 | 1.81841E-05 | 2663305 |
| D | 4.494913 | 0.000347 | 11.85 | 7.72991E-05 | 607659 |
| E | 4.357754 | 9.06E-05 | 11.86 | 2.07863E-05 | 2192696 |
| F | 4.723672 | 0.000207 | 11.83 | 4.37691E-05 | 1018911 |
| G | 0.915314 | 9.1E-05 | 11.87 | 9.9443E-05 | 474902.3 |
| H | 0.91253 | BDL | 11.85 | NA | NA |
| I | 0.908159 | BDL | 11.84 | NA | NA |

Table 10.21: TR545- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 11.06681063 | 7.191335597 | 11.78 | 0.649811028 | 23.13284 |
| B | 10.42599825 | 7.539402767 | 11.81 | 0.723134858 | 17.87174 |
| C | 10.16670487 | 8.024108456 | 11.84 | 0.789253603 | 12.91 |
| D | 5.33879659 | 2.448368545 | 11.87 | 0.458599331 | 55.40923 |
| E | 5.359438061 | 2.197371376 | 11.84 | 0.41000033 | 65.54461 |
| F | 5.582261683 | 2.335905009 | 11.79 | 0.418451363 | 61.92481 |
| G | 0.935831771 | 0.069557071 | 11.88 | 0.074326469 | 588.0414 |
| H | 1.063230981 | 0.071395625 | 11.87 | 0.067149685 | 623.756 |
| I | 1.087754 | 0.052020649 | 11.88 | 0.04782391 | 877.7157 |

Table 10.22: TR545- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 11.06681 | 0.688024 | 11.8 | 0.062170019 | 647.5252 |
| B | 10.426 | 3.454341 | 11.82 | 0.331319968 | 94.20817 |
| C | 10.1667 | 4.315917 | 11.83 | 0.424514804 | 65.54265 |
| D | 5.338797 | 0.081828 | 11.85 | 0.015326992 | 3015.309 |
| E | 5.359438 | 0.04523 | 11.86 | 0.008439386 | 5351.528 |
| F | 5.582262 | 0.050094 | 11.83 | 0.008973825 | 4920.748 |
| G | 0.935832 | 0.006073 | 11.87 | 0.006489588 | 7228.512 |
| H | 1.063231 | 0.006007 | 11.85 | 0.005649652 | 7902.5 |
| I | 1.087754 | 0.004734 | 11.84 | 0.004352288 | 10084.86 |

Table 10.23: TR545- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 898.113225 | 848.7458671 | 11.78 | 0.945032145 | 2.356428 |
| B | 913.1823285 | 762.1244902 | 11.81 | 0.834580857 | 8.159034 |
| C | 934.7636536 | 745.7911897 | 11.84 | 0.797839311 | 10.50404 |
| D | 457.5756317 | 359.4537413 | 11.87 | 0.785561373 | 11.39171 |
| E | 470.0103984 | 366.0617077 | 11.84 | 0.778837466 | 11.49527 |
| I | 496.493275 | 371.8275456 | 11.79 | 0.748907517 | 5.34887 |
| F | 88.21518816 | 78.05147159 | 11.88 | 0.884784959 | 12.92627 |
| G | 91.04387158 | 68.8000471 | 11.87 | 0.755680156 | 9.609413 |
| H | 91.16507166 | 73.66395982 | 11.88 | 0.808028321 | 13.60264 |

Table 10.24: TR545- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 898.1132 | 837.0881 | 11.8 | 0.932051904 | 2.953447 |
| B | 913.1823 | 7195.504 | 11.82 | 7.879592346 | <0.1* |
| C | 934.7637 | 754.3793 | 11.83 | 0.807026787 | 9.912517 |
| D | 457.5756 | 363.8427 | 11.85 | 0.795153224 | 10.75088 |
| E | 470.0104 | 403.0471 | 11.86 | 0.857527944 | 6.725678 |
| I | 496.4933 | 383.0102 | 11.83 | 0.771430723 | 12.02095 |
| F | 88.21519 | 81.63764 | 11.87 | 0.925437469 | 3.309513 |
| G | 91.04387 | 73.74992 | 11.85 | 0.810048143 | 9.375302 |
| H | 91.16507 | 91.83809 | 11.84 | 1.007382399 | <0.1* |

10.4 Data Tables for TR547

Table 10.25: TR547- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 7.331081035 | 0.001713462 | 11.55 | 0.000233726 | 205208.6 |
| B | 7.328043805 | 0.000872426 | 11.6 | 0.000119053 | 397817.2 |
| C | 7.071427186 | 0.000766705 | 11.62 | 0.000108423 | 443366 |
| D | 3.635696803 | 0.000569848 | 11.65 | 0.000156737 | 292607.2 |
| E | 3.652534842 | 0.000393375 | 11.66 | 0.000107699 | 427111.1 |
| F | 3.684343628 | 0.000302746 | 11.63 | 8.21708E-05 | 549298.4 |
| G | 0.743960581 | 0.000514945 | 11.64 | 0.000692167 | 67527.87 |
| H | 0.777698097 | 0.000252938 | 11.64 | 0.000325239 | 141399.9 |
| I | 0.723194348 | 0.000177006 | 11.62 | 0.000244756 | 195850.5 |

Table 10.26: TR547- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 7.331081 | 0.000518 | 11.61 | 7.07249E-05 | 678263.9 |
| B | 7.328044 | 0.000412 | 11.64 | 5.62039E-05 | 842722.2 |
| C | 7.071427 | 0.000332 | 11.68 | 4.69813E-05 | 1023256 |
| D | 3.635697 | 0.000201 | 11.71 | 5.53737E-05 | 828316.4 |
| E | 3.652535 | 0.000192 | 11.70 | 5.24331E-05 | 877345.9 |
| F | 3.684344 | 0.000272 | 11.72 | 7.38169E-05 | 611467.6 |
| G | 0.743961 | 9.6E-05 | 11.73 | 0.000129031 | 362447.9 |
| H | 0.777698 | 0.000121 | 11.70 | 0.000155632 | 295546.9 |
| I | 0.723194 | 0.000187 | 11.73 | 0.000258316 | 185567.3 |

Table 10.27: TR547- neptunium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 8.913321113 | 0.000398128 | 11.55 | 4.46666E-05 | 1073986 |
| B | 8.957071854 | 0.00032779 | 11.6 | 3.65957E-05 | 1294283 |
| C | 8.627854248 | 0.000337955 | 11.62 | 3.91703E-05 | 1227315 |
| D | 4.445064053 | 0.000242059 | 11.65 | 5.44558E-05 | 842279.8 |
| E | 4.490502056 | 0.000292509 | 11.66 | 6.51396E-05 | 706197.5 |
| F | 4.459268715 | 0.000676132 | 11.63 | 0.000151624 | 297665.5 |
| G | 0.900219568 | 4.54363E-05 | 11.64 | 5.04725E-05 | 926653.3 |
| H | 0.946539946 | 0.000171998 | 11.64 | 0.000181712 | 253122.2 |
| I | 0.912956209 | 6.06879E-05 | 11.62 | 6.6474E-05 | 721246.3 |

Table 10.28: TR547- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 8.913321 | 0.000242 | 11.61 | 2.71084E-05 | 1769639 |
| B | 8.957072 | 0.000116 | 11.64 | 1.28974E-05 | 3672542 |
| C | 8.627854 | 0.000116 | 11.68 | 1.34188E-05 | 3582700 |
| D | 4.445064 | BDL | 11.71 | NA | NA |
| E | 4.490502 | 6.05E-05 | 11.70 | 1.3468E-05 | 3415784 |
| F | 4.459269 | 8.06E-05 | 11.72 | 1.80709E-05 | 2497898 |
| G | 0.90022 | 1.52E-05 | 11.73 | 1.68369E-05 | 2777954 |
| H | 0.94654 | 6.05E-05 | 11.70 | 6.39353E-05 | 719488.7 |
| I | 0.912956 | BDL | 11.73 | NA | NA |

Table 10.29: TR547- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.779962734 | 10.60834347 | 11.55 | 1.08470183 | 0.910195 |
| B | 9.835835051 | 10.50945992 | 11.6 | 1.0684868 | 1.638845 |
| C | 9.507654819 | 10.27484967 | 11.62 | 1.080692333 | 0.941248 |
| D | 4.824820947 | 5.07820462 | 11.65 | 1.0525167 | 1.843339 |
| E | 4.872457168 | 5.239952738 | 11.66 | 1.075423048 | 0.880238 |
| F | 4.913611454 | 5.328321311 | 11.63 | 1.084400214 | 0.509761 |
| G | 0.962090763 | 1.0672488 | 11.64 | 1.109301577 | <0.1* |
| H | 1.00515912 | 1.062338104 | 11.64 | 1.056885505 | 1.452343 |
| I | 0.887794331 | 0.990729562 | 11.62 | 1.115944907 | <0.1* |

Table 10.30: TR547- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.779963 | 8.774052 | 11.61 | 0.897145797 | 10.8521 |
| B | 9.835835 | 9.081111 | 11.64 | 0.923267955 | 9.140247 |
| C | 9.507655 | 8.622742 | 11.68 | 0.906926233 | 10.08659 |
| D | 4.824821 | 3.174345 | 11.71 | 0.657919842 | 30.08172 |
| E | 4.872457 | 3.023902 | 11.70 | 0.620611305 | 34.77241 |
| F | 4.913611 | 3.011782 | 11.72 | 0.612946765 | 35.13874 |
| G | 0.962091 | 0.511292 | 11.73 | 0.531438732 | 48.85935 |
| H | 1.005159 | 0.493115 | 11.70 | 0.490584261 | 56.07747 |
| I | 0.887794 | 0.473141 | 11.73 | 0.532939428 | 49.65678 |

Table 10.31: TR547- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 852.6222244 | 759.657507 | 11.55 | 0.89096611 | 5.070018 |
| B | 845.7478089 | 783.1245583 | 11.6 | 0.925955173 | 3.298918 |
| C | 845.4964361 | 748.7755693 | 11.62 | 0.885604643 | 5.222873 |
| D | 426.3831311 | 362.1172193 | 11.65 | 0.849276608 | 7.01438 |
| E | 426.0937738 | 362.895009 | 11.66 | 0.851678741 | 6.966757 |
| F | 429.4940694 | 359.5565556 | 11.63 | 0.837163028 | 7.672974 |
| G | 85.54929637 | 76.23627363 | 11.64 | 0.891138523 | 4.941109 |
| H | 88.19365709 | 77.33611311 | 11.64 | 0.876889741 | 5.728039 |
| I | 83.00395228 | 73.52643249 | 11.62 | 0.885818452 | 5.240798 |

Table 10.32: TR547- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 852.6222 | 777.5594 | 11.61 | 0.911962405 | 3.999451 |
| B | 845.7478 | 9568.055 | 11.64 | 11.3131301 | <0.1* |
| C | 845.4964 | 819.1721 | 11.68 | 0.968865194 | 1.299343 |
| D | 426.3831 | 371.6515 | 11.71 | 0.87163741 | 5.820501 |
| E | 426.0938 | 629.9986 | 11.70 | 1.478544594 | <0.1* |
| F | 429.4941 | 366.7886 | 11.72 | 0.854001563 | 6.743887 |
| G | 85.5493 | 82.68725 | 11.73 | 0.966545113 | 1.400015 |
| H | 88.19366 | 95.58545 | 11.70 | 1.083813162 | <0.1* |
| I | 83.00395 | 79.43227 | 11.73 | 0.956969779 | 1.828191 |

10.5 Data Tables for Aged Cement

Table 10.33: Aged cement- plutonium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.079224621 | 0.001409021 | 11.50 | 0.000155192 | 287217.3 |
| B | 8.613004882 | 0.0008076 | 11.55 | 9.37652E-05 | 513144.7 |
| C | 8.541919589 | 0.000863136 | 11.53 | 0.000101047 | 468296 |
| D | 4.538279014 | 0.000687826 | 11.56 | 0.000151561 | 305169.7 |
| E | 4.358905759 | 0.000552396 | 11.58 | 0.000126728 | 361610.9 |
| F | 4.450334725 | 0.000623348 | 11.58 | 0.000140068 | 339957.7 |
| G | 0.840653709 | 0.000516994 | 11.60 | 0.000614991 | 74433.06 |
| H | 0.897570902 | 0.000450005 | 11.60 | 0.000501358 | 90197.31 |
| I | 0.921814908 | 0.000594538 | 11.62 | 0.000644965 | 68794.45 |

Table 10.34: Aged cement- plutonium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 9.079225 | 0.000712 | 11.45 | 0.000155192 | 568215.1 |
| B | 8.613005 | 0.000626 | 11.46 | 9.37652E-05 | 661726.3 |
| C | 8.54192 | 0.000454 | 11.46 | 0.000101047 | 890459.8 |
| D | 4.538279 | 0.000394 | 11.55 | 0.000151561 | 533244.6 |
| E | 4.358906 | 0.000314 | 11.56 | 0.000126728 | 636801.4 |
| F | 4.450335 | 0.000237 | 11.55 | 0.000140068 | 892832.7 |
| G | 0.840654 | 0.00038 | 11.65 | 0.000614991 | 101411.9 |
| H | 0.897571 | 0.000344 | 11.62 | 0.000501358 | 117954.3 |
| I | 0.921815 | 0.000268 | 11.64 | 0.000644965 | 152706.5 |

Table 10.35: Aged cement- neptunium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|---------|
| A | 8.849444124 | 0.000306309 | 11.50 | 3.46133E-05 | 1289533 |
| B | 8.447823057 | 0.000150131 | 11.55 | 1.77715E-05 | 2711019 |
| C | 8.590597085 | 0.000199185 | 11.53 | 2.31864E-05 | 2044057 |
| D | 4.491250244 | 5.17162E-05 | 11.56 | 1.15149E-05 | 4020064 |
| E | 4.391894479 | 2.04591E-05 | 11.58 | 4.65838E-06 | 9846089 |
| F | 4.210703646 | 2.04376E-05 | 11.58 | 4.85374E-06 | 9816203 |
| G | 0.86381524 | 5.22216E-06 | 11.60 | 6.04546E-06 | 7577764 |
| H | 0.870501884 | BDL | 11.60 | NA | NA |
| I | 0.861953838 | BDL | 11.62 | NA | NA |

Table 10.36: Aged cement- neptunium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|---------|
| A | 8.849444 | 0.000131 | 11.45 | 1.48418E-05 | 3007445 |
| B | 8.447823 | 0.000111 | 11.46 | 1.31529E-05 | 3662996 |
| C | 8.590597 | 6.56E-05 | 11.46 | 7.6328E-06 | 6209405 |
| D | 4.49125 | BDL | 11.55 | NA | NA |
| E | 4.391894 | BDL | 11.56 | NA | NA |
| F | 4.210704 | BDL | 11.55 | NA | NA |
| G | 0.863815 | BDL | 11.65 | NA | NA |
| H | 0.870502 | BDL | 11.62 | NA | NA |
| I | 0.861954 | BDL | 11.64 | NA | NA |

Table 10.37: Aged cement- technetium after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 8.426518355 | 8.33290075 | 11.50 | 0.98889012 | 0.476492 |
| B | 8.638001423 | 7.823321167 | 11.55 | 0.905686487 | 4.413063 |
| C | 9.323317745 | 9.25927516 | 11.53 | 0.993130923 | 0.294664 |
| D | 4.42651005 | 4.300859603 | 11.56 | 0.971614106 | 1.242837 |
| E | 4.426849405 | 4.336992073 | 11.58 | 0.979701742 | 0.855315 |
| F | 3.929483125 | 3.938204338 | 11.58 | 1.00221943 | <0.1* |
| G | 0.817864386 | 0.81693181 | 11.60 | 0.998859743 | 0.049487 |
| H | 0.878958929 | 0.792412508 | 11.60 | 0.901535306 | 4.510199 |
| I | 0.772205665 | 0.871436364 | 11.62 | 1.128502941 | <0.1* |

Table 10.38: Aged cement- technetium after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 8.426518 | 7.387328 | 11.45 | 0.876676186 | 5.966258 |
| B | 8.638001 | 7.419385 | 11.46 | 0.858923768 | 6.960547 |
| C | 9.323318 | 8.036996 | 11.46 | 0.862031802 | 6.818523 |
| D | 4.42651 | 3.962629 | 11.55 | 0.895203859 | 4.979995 |
| E | 4.426849 | 4.090424 | 11.56 | 0.92400338 | 3.395329 |
| F | 3.929483 | 3.698764 | 11.55 | 0.941285083 | 2.958172 |
| G | 0.817864 | 0.742066 | 11.65 | 0.907321016 | 4.428077 |
| H | 0.878959 | 0.720997 | 11.62 | 0.820285656 | 9.047228 |
| I | 0.772206 | 0.788286 | 11.64 | 1.020823931 | <0.1* |

Table 10.39: Aged cement- iodine after one day

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 841.8563537 | 737.977259 | 11.50 | 0.876607103 | 6.272787 |
| B | 797.1671977 | 685.3215035 | 11.55 | 0.859696066 | 7.850152 |
| C | 804.9572051 | 705.537908 | 11.53 | 0.876491202 | 6.667104 |
| D | 414.5684267 | 298.0931093 | 11.56 | 0.719044409 | 18.07023 |
| E | 411.1069758 | 310.676185 | 11.58 | 0.75570643 | 14.81422 |
| F | 408.6431184 | 322.6673231 | 11.58 | 0.789606648 | 12.68657 |
| G | 78.86778865 | 66.17517673 | 11.60 | 0.839064691 | 8.785091 |
| H | 82.59334117 | 69.70070149 | 11.60 | 0.84390219 | 8.368448 |
| I | 83.9926338 | 66.4029369 | 11.62 | 0.790580482 | 11.76026 |

Table 10.40: Aged cement- iodine after four days

| Sample ID | Initial Aq Conc (ppb) | Equil. Aq. Conc. (ppb) | pH | Fraction Aq | Kd |
|-----------|-----------------------|------------------------|-------|-------------|----------|
| A | 841.8564 | 768.77 | 11.45 | 0.913184256 | 4.23658 |
| B | 797.1672 | 992.224 | 11.46 | 1.244687434 | <0.1* |
| C | 804.9572 | 729.9231 | 11.46 | 0.906784993 | 4.863719 |
| D | 414.5684 | 311.6002 | 11.55 | 0.751625609 | 15.28223 |
| E | 411.107 | 351.634 | 11.56 | 0.855334565 | 7.750838 |
| F | 408.6431 | 329.3867 | 11.55 | 0.806049742 | 11.45648 |
| G | 78.86779 | 77.59404 | 11.65 | 0.983849604 | 0.751874 |
| H | 82.59334 | 88.239 | 11.62 | 1.068354932 | <0.1* |
| I | 83.99263 | 71.1941 | 11.64 | 0.847623085 | 7.981093 |

10.6 Data Tables for Sorption to Vial Walls

Table 10.41: % Plutonium sorbed to vial wall in no solids control

| Sample ID | Initial Conc. (ppb) | Conc. In Wash of Vial (ppb) | % Sorbed to Walls |
|-----------|---------------------|-----------------------------|-------------------|
| NS-A | 8.197769521 | 0.082513388 | 1.00653462 |
| NS-B | 8.221312733 | 0.0787687 | 0.95810368 |
| NS-C | 8.126405694 | 0.074648839 | 0.91859602 |
| NS-E | 0.892430451 | 0.003210839 | 0.35978593 |
| NS-F | 0.851281521 | 0.002677402 | 0.31451429 |
| NS-G | 0.867134776 | 0.002050021 | 0.23641316 |

Table 10.42: % Neptunium sorbed to vial wall in no solids control

| Sample ID | Initial Conc (ppb) | Conc. In Wash of Vial | % Sorbed to Walls |
|-----------|--------------------|-----------------------|-------------------|
| NS-A | 10.01822029 | 0.056017 | 0.559151 |
| NS-B | 10.00816271 | 0.036572 | 0.365421 |
| NS-C | 9.982091832 | 0.029872 | 0.299253 |
| NS-E | 1.005570326 | 0.000511 | 0.050771 |
| NS-F | 1.074652687 | 0.00057 | 0.053056 |
| NS-G | 1.030704749 | 0.000249 | 0.024193 |

Table 10.43: % Technetium sorbed to vial wall in no solids control

| Sample ID | Initial Conc (ppb) | Conc. In Wash of Vial | % Sorbed to Walls |
|-----------|--------------------|-----------------------|-------------------|
| NS-A | 11.79928939 | 5.55806E-05 | 0.00047105 |
| NS-B | 12.253209 | 7.74746E-05 | 0.00063228 |
| NS-C | 11.5498292 | 4.85721E-05 | 0.00042054 |
| NS-E | 1.206356364 | 4.90926E-06 | 0.00040695 |
| NS-F | 1.218363059 | 3.99779E-06 | 0.00032813 |
| NS-G | 1.217636322 | 3.81518E-06 | 0.00031333 |

**11.0 Appendix C: Dixon et al. (2009). FY09 PA/CA Maintenance Program:
Additional Saltstone Property Testing. SRNL L3100-2009-00019, Rev. 0**



SRNL L3100-2009-00019, Rev. 0

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L. B. Romanowski
Waste Determinations

From: K. L. Dixon, M. A. Phifer and J. R. Harbour

FY09 PA/CA Maintenance Program: Additional Saltstone Property Testing

BACKGROUND

Additional tests have been identified for measurement of important hydraulic and physical properties of saltstone. The initial phase of this work [1] was completed last year and the results were detailed in an internal report [2]. The proposed testing for FY09 includes measurement of saturated hydraulic conductivity, porosity, bulk density, particle density, water retention and Young's modulus of simulated Saltstone grouts. For completeness, the bleed volumes and gel times for each mix will also be measured.

The testing will be based on a projected salt solution composition for the ARP/MCU stream that will be fed to the Saltstone Production Facility over the next few years. The scope for FY09 will include testing to determine the impact of (1) admixtures, (2) organics, (3) w/cm ratio, (4) aluminate concentration, and (5) temperature of curing on the hydraulic properties of saltstone mixes. Samples of selected batches prepared as part of this task will be provided to Dan Kaplan for measurement of K_d through leaching tests. The eleven mixes that will be batched and tested are detailed in Table 1.

Table 1 The Eleven Mixes That will be Batched and Tested

| Mix # | Simulant | Descriptor | w/cm | Aluminate | BFS* | FA* | PC* |
|-------|----------|---|-------|-----------|------|------|------|
| | Type | | ratio | molarity | wt % | wt % | wt % |
| 1 | ARP/MCU | Control - BFS/PC | 0.60 | 0.054 | 90 | 0 | 10 |
| 2 | ARP/MCU | Baseline | 0.60 | 0.054 | 45 | 45 | 10 |
| 3 | ARP/MCU | Baseline with Admixtures | 0.60 | 0.054 | 45 | 45 | 10 |
| 4 | ARP/MCU | Baseline with Organics | 0.60 | 0.054 | 45 | 45 | 10 |
| 5 | ARP/MCU | Baseline Combo -Organics and Admixtures | 0.60 | 0.054 | 45 | 45 | 10 |
| 6 | ARP/MCU | w/cm ratio impact | 0.55 | 0.054 | 45 | 45 | 10 |
| 7 | ARP/MCU | w/cm ratio impact | 0.65 | 0.054 | 45 | 45 | 10 |
| 8 | ARP/MCU | Impact of Aluminate | 0.55 | 0.280 | 45 | 45 | 10 |
| 9 | ARP/MCU | Impact of Aluminate | 0.65 | 0.280 | 45 | 45 | 10 |
| 10 | ARP/MCU | Baseline Combo and Aluminate | 0.60 | 0.280 | 45 | 45 | 10 |
| 11 | ARP/MCU | Baseline Combo at 60 oC Cure Temp. | 0.60 | 0.054 | 45 | 45 | 10 |

* BFS is Blast Furnace Slag, FA is Fly Ash and PC is Portland Cement

TEST DETAILS

Test 1 Control (Mix 1)

A control mix will be based on the baseline mix modified by exclusion of the Class F fly ash. Consequently, the cementitious materials premix will be a mixture of 90 % blast furnace slag and 10 % portland cement. The degree of reaction will be much greater than with the normal premix and therefore should result in a lower porosity and a lower permeability. This bounding test at 0.60 w/cm ratio is expected to yield a hydraulic conductivity at or below the detection limit for the Mactec permeameter measurement system. Therefore, this test should demonstrate the lowest level of detection of the Mactec system as well as show a resolvable difference between measurements of the control mix and the control mix with the normal premix composition.

Test 2 –Impact of Admixtures (Mixes 2 and 3)

Recent saltstone batches have required both a set retarder (Daratard 17) and an antifoam agent (Q2) for processing of the saltstone. Therefore, the baseline mix will be prepared with and without nominal levels of these two admixtures to determine whether these admixtures appreciably affect the hydraulic and physical properties of saltstone at these nominal concentrations.

Test 3–Impact of Organics (Mixes 2 and 4)

The solvent extraction process is expected to result in some carryover of organics [3].

Consequently, a test will be performed on the impact of Caustic Side Solvent Extraction (CSSX) organics at 100 microliters per 1600 gram batch. The CSSX solvent consists of 0.75 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB) and 0.003 M tri-n-octylamine (TOA) in an Isopar® L diluent.

Test 4—Impact of Combination of Admixtures and Organics (Mixes 2, 5, 10 and 11)

This test will determine the impact of a combination of admixtures (Test 2) and organics (Test 3) together in the mix vs. the baseline case without admixtures and organics.

Test 5— Impact of w/cm Ratio (Mixes 2, 6 and 7)

It is well known that decreasing the w/cm ratio in a mix will improve permeability in normal portland cement water mixes. This test will measure the variation in permeability for the case of the MCU salt solution at three different w/cm ratios. The initial selection of w/cm ratios is 0.55, 0.60 and 0.65. However, if the mix at an as-batched 0.65 w/cm ratio has significant bleed water and the resulting actual w/cm ratio is close to 0.60, then the three ratios will be adjusted to provide a more evenly spaced set of values. However, the baseline mix at 0.60 will be included as one of the three mixes.

Test 6 – Impact of Aluminate Concentration (Mixes 8, 9 and 10)

The DWPF has modified its process flowsheet to include a caustic washing of HLW sludge to remove some of the aluminum from the HLW prior to vitrification. The resulting aluminate stream will then be blended with tank 50 material and fed to the SPF. This increased aluminate concentration in the salt solution has significant impact on heat of hydration and set times and consequently, it is likely that it will also impact permeability. Therefore a set of three samples will be made at w/cm ratios of 0.55, 0.60 and 0.65 (as in Test 3) with a higher level of aluminate (0.28 M) for testing.

Test 7 – Impact of Increased Curing Temperature (Mix 11)

In an ongoing task, there is evidence that Young's modulus (a performance indicator) [4] is reduced by increasing the curing temperature of the mix. Since the vault temperature increases during curing as a result of the exothermic hydration reactions, one of the baseline mixes with a combination of admixtures and organics will be cured at 60 °C rather than the normal 22 °C to determine the impact of curing temperature on the permeability.

SCHEDULE

The schedule for the task of batching and testing of the samples is provided in Table 2. This schedule is based on the fact that the cementitious materials will be available for the testing as needed.

Table 2 Additional Saltstone Hydraulic and Physical Property Tests


| Item | Schedule |
|--|-----------------|
| Start Work | 12/1/08 |
| Test Plan Complete | 1/5/09 |
| Preparation of 1 st set of Samples Complete | 1/19/09 |
| 90-Day Cure Period for 1 st set of Samples Complete | 4/20/09 |

| | |
|---|----------|
| 1 st set of Samples to Subcontract Laboratory | 4/27/09 |
| Testing of 11 th set of Samples by Subcontract Laboratory Complete | 10/26/09 |
| Draft Report Issued | 12/18/09 |

REFERENCES

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- [2] *Hydraulic and Physical Properties of Saltstone Grouts and Vault Concretes*, K. L. Dixon, J. R. Harbour and M. A. Phifer SRNL-STI-2008-00421, Rev. 0, 2008
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- [4] *Saltstone Performance Indicator - Dynamic Young's Modulus*, J. R. Harbour and V. J. Williams, SRNL-STI-2008-00488, Rev. 0, 2008


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