

DETERMINATION OF SORPTION COEFFICIENTS FOR NEPTUNIUM,
PLUTONIUM, IODINE, AND TECHNETIUM IN ENGINEERED AND NATURAL
SYSTEMS UNDER OXIDIZING AND REDUCING CONDITIONS

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ABSTRACT

Plutonium, neptunium, technetium, and iodine present appreciable risks at nuclear waste disposal sites around the world due to their potential mobility. Sorption of each of these radionuclides is profoundly influenced by oxidation/ reduction reactions. Therefore, the mobility of each radionuclide may be greatly influenced by redox conditions of the natural or engineered system. The primary focus of this study was to determine distribution coefficients (K_d) for each radionuclide for engineered concrete and saltstone systems with varying amounts of reducing slag (a cement additive to create a reducing environment), and for iodide/iodate in natural sediments. Saltstones are a mixture of cement, high ionic strength liquid wastes, and reducing slag used to sequester radionuclides. The engineered solids examined in this work are 1) aged cement: an 50 year old aged concrete from which the aggregate has been removed 2) Vault 2 concrete: a concrete formulation containing 17% reducing slag to be used as during vault construction at the SRS, 3) TR547: a saltstone formulation containing 45% reducing slag and 4) TR545: a saltstone formulation containing 90% reducing slag. The natural sediments used are two end member sediments (subsurface clayey and subsurface sandy) as well as a wetland sediment from Four Mile Branch.

Sorption experiments were performed under oxidizing and reducing conditions using Np(V), Pu(IV), Tc(VII), I(VII) and I(I). Neptunium and plutonium both exhibited strong affinity for concrete and saltstones (a cementitious low-level nuclear waste form) under both oxidizing and reducing conditions. Distribution coefficient (K_d) values of $>10^5$ (mL/g) were calculated for all Np and Pu systems under oxidizing and reduction

conditions. Experimental conditions had a far greater effect on Tc sorption. Under oxidizing conditions, Tc showed similar affinity for concrete and saltstone despite the presence of reducing slag, and K_d values remained around 10 (mL/g). However, under reducing conditions, Tc sorption increased relative to the oxidizing conditions, and the K_d values increased with increasing reducing slag concentration in the solid with values ranging from approximately 200 to 15,000 (mL/g). This behavior is consistent with reduction of Tc(VII) to Tc(IV). Similar reduction of Tc(VII) in the presence of saltstone was observed by Lukens *et al.* (2005). The rate of Tc sorption, from which reduction was inferred, increased with increasing reducing slag content. It was determined there is a second order dependence on slag concentration, and steady state is reached around 3 weeks. Under oxidizing conditions, the iodide exhibited similar behavior to Tc, and had K_d values significantly lower than Np and Pu. However, unlike the Tc systems, increased sorption was not observed under reducing conditions thus indicating that the majority of iodine remains as the initially amended iodide in both systems.

Unlike with the highly reducing engineered systems above, when found in natural environments, iodine can exist as either iodate or iodide. Although easily reducible, iodate is known to experience stronger sorption to sediments than the reduced form iodide. This was shown to be true for all three soils under oxidizing conditions with the most sorption to the wetland soil, followed by the clayey, and then the sandy. There was no noticeable change in the iodate clayey soil K_d values under either oxidizing or reducing conditions indicating it remained as iodate. However, under reducing conditions, the wetland soil apparently reduced the iodate to iodide by the 4th day, which

resulted in an 8 fold decrease in sorption. The final iodate equilibrium K_d value under reducing conditions was equal to that of iodide suggesting complete reduction of the iodate.

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Chapter 1 INTRODUCTION

PERFORMANCE ASSESSMENT BACKGROUND

Performance assessments (PA) at the Savannah River Site (SRS) require soil-water distribution coefficients (K_d) to predict the steady state sorption behavior of the potentially mobile radionuclides technetium, iodine, neptunium, and plutonium. The mobility of each of these radionuclides is primarily controlled by redox chemistry due to the differing sorption affinity exhibited by the oxidation state of each radionuclide. This is because these species can exist in multiple oxidation states and as anions, cations, oxyanions, and oxycations, all of which have differing geochemical behavior. Previous work has examined the distribution coefficients, which have been used in risk assessments. However, recent work suggests the systems used to determine the K_d s were not at equilibrium (Kaplan *et al.*, 2008). Therefore, this work will examine the sorption of these radionuclides to engineered solids and natural soils under oxidizing as well as reducing conditions to determine a steady-state K_d for each radionuclide and reevaluate conceptual models of redox active radionuclide sorption. These engineered solids are saltstone formulations, a cementitious material used for radiological waste disposal, with varying concentrations of reducing slag and an aged cement. The natural soils are end member sediments representative of Savannah River Site soils.

BACKGROUND

Geochemical Behavior of Redox Active Radionuclides

This project will examine the radionuclides Tc, I, Np, and Pu because of their potential risk posed by the migration away from waste sites. Each of these radionuclides is subject to oxidation/reduction depending on its surrounding environment and the mobility of each ion is profoundly influenced by its oxidation state. In addition to the oxidation state, the surrounding environment can dictate sorption behavior, which also affects these radionuclides mobility. There is one major distinction that can be made for these elements, and that is Np and Pu are cations in both oxidized and reduced forms (An^{3+} , An^{4+} , AnO_2^+ , and AnO_2^+), while Tc and I predominately exist as the anions pertechnetate (TcO_4^-) and iodate (IO_3^-), in their oxidized states, and a neutral Tc(IV) species ($TcO_2 \cdot nH_2O(s)$ or $TcO(OH)_2(s)$) and iodide (I^-) in their reduced forms.

Neptunium

Neptunium and plutonium are subject to redox chemistry. While Np can exist in the +3, +4, +5, +6, and +7 oxidation states, only Np(IV) and Np(V) are stable in natural environments. Neptunium's geochemical behavior is highly governed by redox speciation. As seen in the E_H -pH diagram below (Figure 1.1), Np is commonly found as mobile Np(V), in the form of the dioxycation, NpO_2^+ under neutral, oxidizing conditions, and as $Np(V)O_2(OH)_2^-$ as conditions become more basic. However, as conditions become reducing, Np(IV)(OH)₄ becomes the predominant species. From the standpoint

of a PA, this Np(IV) species is the least immobile because it is insoluble and has a high sorption affinity and (Silva and Nitsche, 1995).

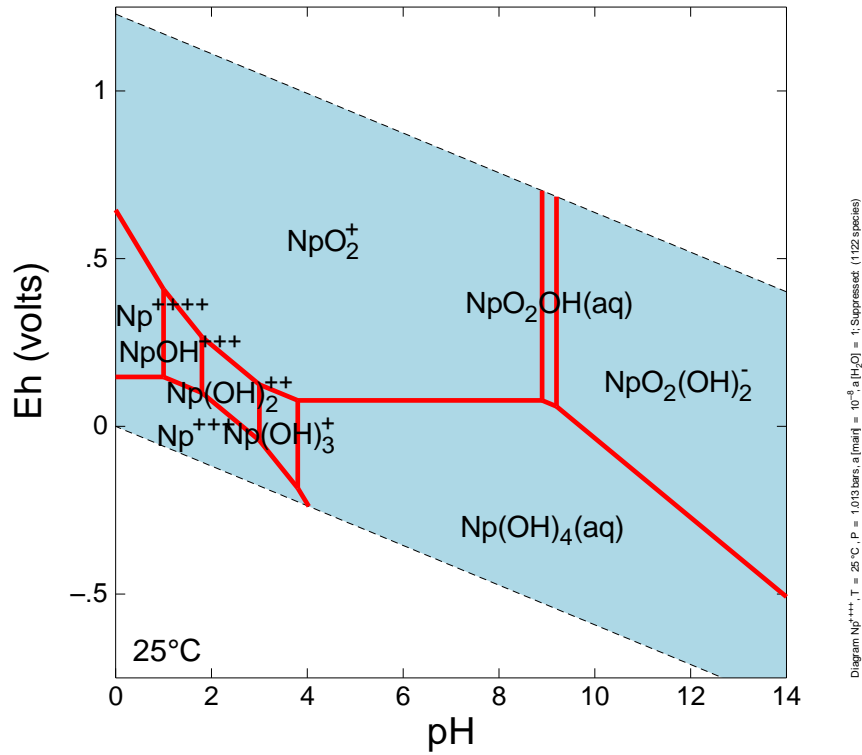


Figure 1.1: Neptunium E_h -pH Diagram. Modeled with Geochemist Workbench, LLNL thermochemical database with precipitation of solids suppressed. Total $\{\text{Np}\} = 1 \times 10^{-8}$ M.

Neptunium is known to undergo surface complexation reactions with mineral phases. It has been shown that mixed ferrous/ferric iron oxides, such as magnetite, are capable of reducing Np(V) to Np(IV), while ferric iron oxides such as hematite cannot (Nakata *et al.*, 2002). While this reduction and sorption occurs under oxidizing conditions, it is two to three times greater under anaerobic conditions (Nakata *et al.*, 2002). These findings build upon those of Lieser and Muhlenweg (1988), which showed Np(V) in the presence of reducing groundwaters was reduced to Np(IV). The K_d values

from these experiments were much higher than occurred under aerobic conditions. In each case, the Np associated with the aqueous phase was the Np(V), while Np(IV) was associated with solid phases.

In addition to mineral surfaces, there have been several studies examining Np interactions with engineered systems, which will be used in the following experiments. Instead of a groundwater, a calcite solution is used to simulate pore water found in cements. One study examining Np(V) sorption to calcite found the highest K_d value of 215 (mL/g) was around a pH of 8. However, as the pH increased to 9.5, the sorption decreased to 0 (mL/g) due to formation of neptunyl carbonate aqueous species (Zavarin *et al.*, 2005). Herberling *et al.* (2008) also examined Np(V) adsorption to calcite, and found maximum adsorption occurred at a pH of 8.3, and decreased as the pH was increased to 9.4. In a recent review Wang *et al.* (2009) reviewed K_d values for actinides and cements. They concluded a majority of the Np sorbed to cement was predominantly Np(IV). Another study examined the sorption of Np(V) to untreated and hydrothermally altered concrete, and found higher sorption values for the unaltered concrete samples. Additionally, EXAFS was used to examine the samples, and confirmed the Np(V) was sorbing to, and then being reduced by the concrete to Np(IV) over a six month period (Zhao *et al.*, 2000).

Plutonium

Similar to neptunium, redox conditions and oxidation states control plutonium's geochemical behavior. In acidic solutions, Pu can simultaneously be found in the +3,+4, +5, and +6 oxidation states, each having similar reduction potentials (Silva and Nitsche,

1995). Figure 1.2 is an E_H -pH diagram showing Pu speciation over a wide range of conditions. It shows that at neutral and basic pH values, Pu(IV)(OH)_4 is the most common Pu species. Pu(V) species do not begin to dominate solutions until the redox potentials are $> +0.5\text{V}$. Under these oxidizing systems Pu(V)O_2^+ is the most common until approximately a pH of 10, when hydrolysis begins and $\text{Pu(V)O}_2\text{OH}$ becomes the dominant species. These oxidized forms of Pu are more mobile, while the hydrolyzed species of Pu(IV) are considered to be relatively immobile due to low solubility and high sorption affinities (Morse and Choppin, 1986).

There have been several studies examining Pu interactions with mineral surfaces. In the case of the synthetic iron oxides hematite and magnetite, it was shown Pu(V)O_2^+ adsorbed onto the mineral surfaces and was then reduced to Pu(IV) over a broad range of pH values. The adsorption of the Pu(V) was the rate limiting step in the reaction with greater adsorption at higher pH's when the mineral surface was more negatively charged. Additionally, after reduction occurred, the Pu(IV) solid phases became more stable over time (Powell *et al.*, 2004; Powell *et al.*, 2005). However, this was not the case with goethite with which Pu(V) adsorbed rapidly (Powell *et al.*, 2005).

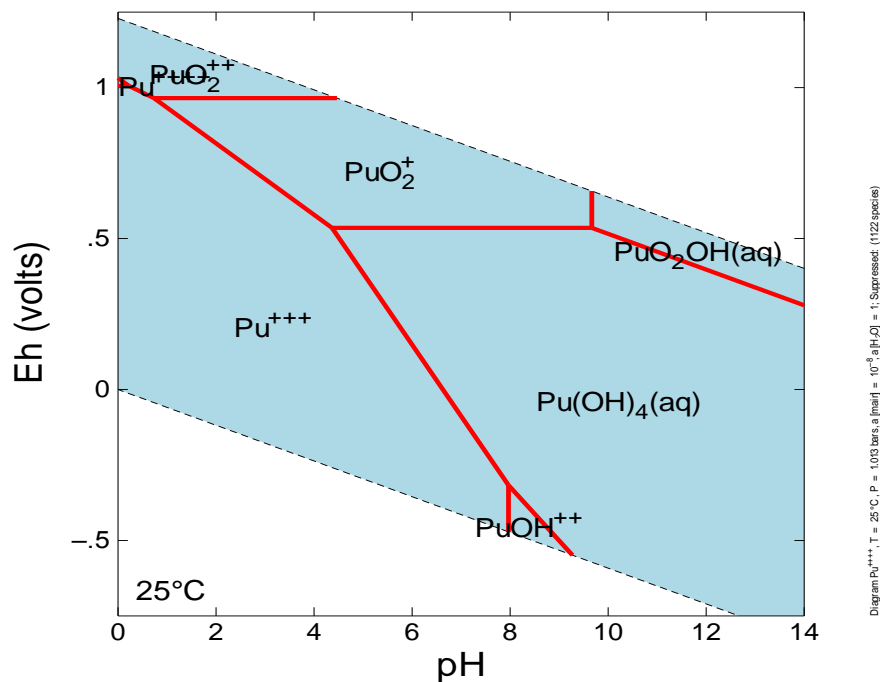
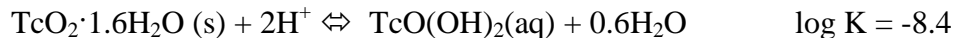


Figure 1.2: Plutonium E_h -pH Diagram. Modeled with Geochemist Workbench, LLNL thermochemical database with precipitation of solids suppressed. Total $\{\text{Pu}\} = 1 \times 10^{-8}$ M.

While the above is true for groundwaters, the pore water associated with engineered solids has a high calcite content. Zavarin *et al.* (2005) showed Pu(IV) experienced a much higher and more stable sorption affinity for calcite than Pu(V). The highest degree of sorption occurred at a pH of 8, where the Pu(IV) K_d was 1100 (mL/g), and it dropped as the pH increased. However, the highest pH tested was 9.5, and approximately 60% of the Pu(IV) was sorbed with a K_d of ~60 (mL/g). This strong potential for Pu sorption to, and co-precipitating into calcite at elevated pH values is important when performing experiments with engineered solids.

Technetium

Technetium can be found in oxidation states from +2 to +7, of which Tc(IV) and Tc(VII) are the most common in the natural environment (Warwick *et al.*, 2007). Figure 1.3 shows a typical Tc E_H -pH diagram, where Tc(VII) is the most oxidized state, and is commonly found as pertechnetate (TcO_4^-). It dominates oxidizing conditions, while Tc(IV) is normally found in reducing/ anaerobic conditions as insoluble TcO_2 (s) or $\text{TcO}(\text{OH})_2$. Pertechnetate has been shown to exhibit little sorption in environments of neutral to basic conditions, making it highly mobile. The reduced Tc(IV) forms a sparingly soluble solid phase, which greatly reduces its mobility. The solubility of this solid was shown to be independent of pH up to 13.5 (Peretyazhko *et al.*, 2008) and can be described as (Guillaumont *et al.*, 2003):



This influence of pH on solubility must be considered when dealing with the cements with reducing slag of engineered systems in which pH values in the pore water can exceed 12.5 (Kaplan and Coates, 2007). Lukens *et al.* (2005) found that in the absence of O_2 , when TcO_4^- is combined with a reducing grout similar to that which will be used in this experiment, the Tc was reduced to a Tc(IV) species. When O_2 (g) was introduced to these samples, the reduced Tc(IV) was quickly reoxidized to Tc(VII), thus indicating that reducing conditions must be maintained in order to keep Tc in a tetravalent state. It is common practice for saltstone formulations to use a reducing slag to maintain reducing conditions. However, it is not known if varying the slag content will increase the sorption rate.

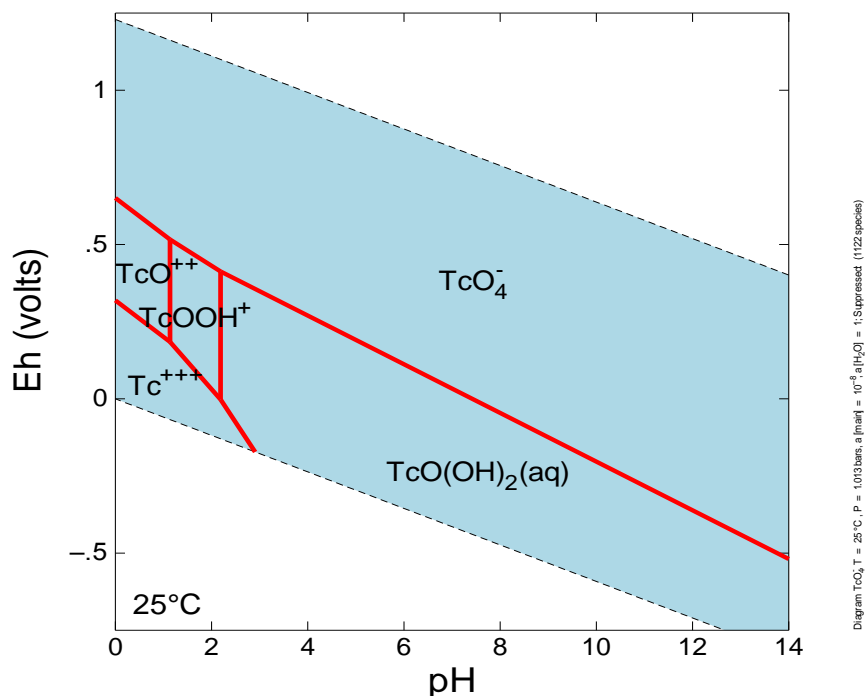


Figure 1.3: Technetium E_H -pH Diagram. Modeled with Geochemist Workbench, LLNL thermochemical database with precipitation of solids suppressed. Total $\{Tc\} = 1 \times 10^{-8}$ M.

Iodine

Like Tc, I is commonly found as an anion in various oxidation states as seen in Figure 1.4. The most common being the reduced iodide (I^-), and the oxidized iodate (IO_3^-). Iodide is the dominate oxidation state under all but the most oxidizing conditions. According to this diagram, at a neutral pH, the redox potential would need to be at least +0.75V for IO_3^- to become the dominate species.

Iodide has been observed to have a lower K_d than IO_3^- , and has been used as a groundwater tracer due to its relatively low affinity for solid phases (Kaplan *et al.*, 2000). Iodate showed stronger sorption to several Chinese soils than the reduced iodide (Dai *et al.*, 2009). When Hu *et al.* (2005) examined IO_3^- and I^- interactions with soils, they found

IO_3^- was easily reduced to I^- , especially at low concentrations. Reduction was speculated to be promoted by Fe(II) found in the clays. Sheppard *et al.* (1995) noted I^- exposed to natural bog water was not readily oxidized to IO_3^- , but in fact remained as the reduced I^- . Kaplan *et al.* (2000) examined the sorption of I^- to certain sediments and illitic minerals. They noted K_d values less than 1 (mL/g) for minerals such as calcite, goethite, montmorillonite, and vermiculite. However, illite had a K_d of 15 (mL/g), which increased to 27 (mL/g) when iron oxides, carbonate, and organic matter were removed.

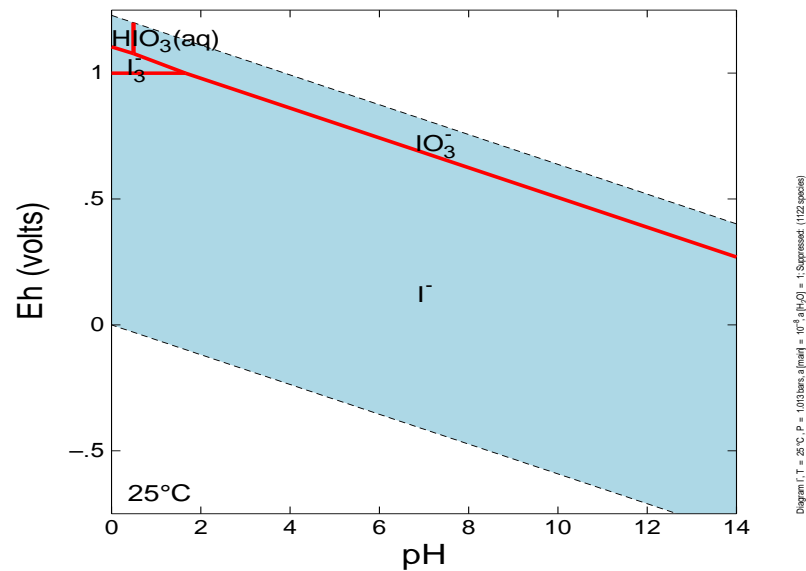


Figure 1.4: Iodine E_h -pH Diagram. Modeled with Geochemist Workbench, LLNL thermochemical database with precipitation of solids suppressed. Total $\{\text{I}\} = 1 \times 10^{-8}$ M.

CONCEPTUAL SUMMARY OF REDOX ACTIVE RADIONUCLIDE BEHAVIOR

Based on the above discussions, it can be summarized that under oxidizing conditions the dominant redox active radionuclide oxidation states will be Pu(V), Np(V), I(VII), and Tc(VII). Under these conditions, Pu(V), Np(V), and Tc(VII) will be mobile and I(VII) will be slightly retarded. In reducing environments or in the presence of

reducing solid phases, the dominant oxidation states will be Pu(IV), Np(IV), Tc(IV), and I(-I). Under these conditions, I(-I) will be relatively mobile while Pu(IV), Np(IV), and Tc(IV) will be immobile due to the strong sorption affinity and low solubility of the tetravalent states. Therefore, based on this conceptual understanding, the redox conditions of the natural and engineered systems to be examined in this work will primarily focus on understanding which oxidation state of each radionuclide is dominant.

PREVIOUS WORK WITH ENGINEERED SYSTEMS

Concretes and saltstones are common materials used to help contain redox active radionuclides like Pu, Np, Tc, and I which pose possible health risks. Saltstones are a mixture of cement, high ionic strength liquid wastes, and reducing slag used to sequester radionuclides. Concretes are a mixture of sand, cement, and aggregate used to make structures such as the vault walls which will ultimately contain the saltstone materials. The reasons for using these engineered solids are to try to sequester the radionuclides of concern and to control the redox chemistry, and maintain a specific oxidation state. In the case of Pu and Np, if it is present as pentavalent Pu(V) or Np(V), it is less likely to undergo sorption, and is more likely to be mobile. However, if it is possible to create a reducing environment, these radionuclides will reduce to Pu/Np(IV), which are insoluble and undergo sorption. Similar to Pu and Np, Tc is commonly found in the oxidized form as pertechnetate (TcO_4^-). It can be reduced down to an immobile Tc(IV), but if exposed to $\text{O}_2(\text{aq})$ it will readily reoxidize. A potential problem with creating a reducing environment is IO_3^- is readily reduced to I^- , which is less likely to undergo sorption.

There have been several studies performed to determine K_d values for Np, Pu, Tc, and I using various engineered solids. In 2008, Kaplan *et al.* set about to determine if the then current K_d values were in fact appropriate. Their findings are listed in Table 1.1. As expected they found Np and Pu exhibited high sorption values of $3,856 \pm 1,415$ (mL/g) and $100,256 \pm 59,584$ (mL/g) to the Vault 2 concrete, and $3,701 \pm 1,198$ (mL/g) and $110,159 \pm 69,152$ (mL/g) to the saltstone under oxidizing conditions. Under reducing conditions, the reducing saltstone produced K_d values of $6,911 \pm 2,478$ (mL/g) and $165,570 \pm 111,515$ (mL/g) for Np and Pu, respectively. In each of the above cases, the values were an order of magnitude greater than the previous numbers for Np, and three orders of magnitude greater for Pu. Additionally, iodine behaved as expected producing K_d values of -0.01 ± 5.89 (mL/g) for the Vault 2 concrete, and 3.94 ± 1.89 (mL/g) for the saltstone under oxidizing conditions. There was not a large change in the amount of sorption under reducing conditions with a K_d of -3.2 ± 4.1 (mL/g). However, they found Tc had K_d values of 0.23 ± 0.02 (mL/g) for Vault 2 concrete, and 0.16 ± 0.14 (mL/g) for the saltstone under oxidizing conditions, which is to be expected with O_2 present. However, this value only increased to 6.5 ± 2.6 (mL/g) under reducing conditions. These numbers were significantly less than the previously accepted values of 5000 (mL/g) for each condition. The explanation offered for the discrepancy was because the researchers believed their system did not reach steady state with respect to the fresh cementitious system.

Table 1.1: Previously reported K_d values (Kaplan *et al.*, 2008)

	Vault 2 concrete- Oxidizing (mL/g)	Reducing Saltstone*- Oxidizing (mL/g)	Reducing Saltstone*- Reducing (mL/g)
Np	$3.86 \times 10^3 \pm 1.42 \times 10^3$	$3.70 \times 10^3 \pm 1.20 \times 10^3$	$6.91 \times 10^3 \pm 2.48 \times 10^3$
Pu	$1.00 \times 10^5 \pm 5.96 \times 10^5$	$1.10 \times 10^5 \pm 6.91 \times 10^5$	$1.66 \times 10^5 \pm 1.11 \times 10^5$
Tc	0.230 ± 0.0200	0.160 ± 0.140	6.50 ± 2.60
I	-0.0100 ± 5.89	-5.29 ± 2.79	-3.20 ± 4.10

*Reducing Saltstone refers a specific saltstone formulation with reducing slag.

CURRENT KNOWLEDGE GAPS

As highlighted above, there have been several studies on Pu, Np, Tc, and I interactions with both engineered and natural systems. However, there are still knowledge gaps, which need to be addressed. It is a currently accepted practice to add reducing slag to engineered solids to induce reduction of radionuclides, but there is little understanding of the influence the slag has on sorption processes. Despite its deceptively simple E_h -pH diagram, iodine has proven to be a very difficult element to work with due to its complex redox behavior (including formation of I_2 (g) under certain conditions) and difficulty in quantifying speciation. This has in turn has left a need for reliable sorption data, especially for natural sediments.

Chapter 2 RESEARCH OBJECTIVES

GOAL

Refine conceptual models of redox active radionuclide behavior in natural and engineered systems to support performance assessments at the SRS.

OBJECTIVES

1. To determine distribution coefficients (K_d) for the redox active radionuclides Np, Pu, and Tc for engineered systems under oxidizing and reducing conditions.
2. To determine distribution coefficients (K_d) for iodide and iodate for both natural and engineered systems under oxidizing and reducing conditions.
3. Use Tc and I distribution coefficients to develop conceptual models describing their behavior in natural and engineered systems.

TASKS AND HYPOTHESES

Task 1: Quantify sorption of Tc, I, Np, and Pu to concrete and saltstones.

Variables to be examined are percent reducing slag in the concrete or saltstone formulation, oxidizing and reducing conditions, and time. Four engineered solids (aged cement, Vault 2 concrete, TR545, and TR547 (each described in the Materials and Methods section)) will be examined. Each of these solids will be provided by SRS collaborators and the reducing slag content will be based on specific formulations provided by the SRS.

The hypotheses for Task 1 are:

- a) Increasing the amount of reducing slag will increase reduction rates and extents of redox active radionuclides.
- b) Neptunium and plutonium will have higher sorption values than Tc or I in the engineered systems due to solubility controlling the system.

Task 2: Quantify I sorption to a variety of natural sediments with varying compositions under oxidizing and reducing conditions.

The hypothesis for Task 2 is:

- a) Due to the influence of ambient pH conditions, expect I to have higher steady state distribution coefficients in the natural systems as compared to the engineered systems.

Chapter 3 MATERIAL AND METHODS

SOLID PHASES USED IN THIS WORK

Engineered Solids

The engineered solids examined in this work are 1) aged cement: an 50 year old aged concrete from which the aggregate has been removed 2) Vault 2 concrete: a concrete formulation containing 17% reducing slag to be used as during vault construction at the SRS, 3) TR547: a saltstone formulation containing 45% reducing slag and 4) TR545: a saltstone formulation containing 90% reducing slag. All engineered solids were provided by SRS collaborators as crushed materials. General characteristics of these solids are seen in Table 3.1

Table 3.1: Characteristics of cement, concrete, and saltstone formulations used in this work.

Sample	Reducing Equivalents ($\mu\text{eq/g}$)*	Percent Reducing Slag (wt-%)
Aged cement	85.5 ± 10.1	0
Vault 2 concrete	$240. \pm 31.1$	17
TR547	NA	45
TR545	NA	90
Blast furnace slag*	832 ± 4.90	100*

*Kaplan *et al.* (2008). This blast furnace slag is the material used to amend the other samples listed.

Natural Sediments

The Savannah River Site provided three different soils for this iodine sorption study. The first is a subsurface yellow sandy sediment, referred to as sandy. This sediment has very little organic material (Table 3.2). The second is a subsurface red clayey sediment, commonly referred to as clayey, has little organic material but a significantly higher clay fraction than the sandy sediment. The third soil, known as

wetland, is a wetland soil from Four Mile Branch. This soil is primarily sand with a high organic matter content. Some additional analyses of these three natural materials are given in Table 3.2.

Table 3.2: Savannah River Site sediment characterizations.

PARAMETER	Subsurface Red Clayey	Subsurface Yellow Sandy	Four Mile Branch Wetland
% sand (>53 μm)	57.9	97	85.5
% silt (53 – 2 μm)	40.6	2.9	11.7
% clay (<2 μm)	1.6	0.2	2.8
Textural classification	Silty clay	Sand	
pH	4.55	5.10	4.10
% OM	NA	0	7.9
CEC (cmol/kg)	1.09 \pm 0.31	<0.05	
AEC (cmol/kg)	1.58 \pm 0.61	0.06 \pm 0.19	
BET surface area (m^2/g)	15.3	1.27	3.76
CDB extractable Fe (mg/g)	15.3	7.06	
Al (ppm)	63.6	16.6	
Na (ppm)	42.9	34.7	
Mg (ppm)	144	98.8	
Ca (ppm)	64.4	24.6	
K (ppm)	183	93.0	
Mineralogy	Kaolinite, goethite, hematite	Kaolinite, goethite, muscovite/14A	

PREPARATION OF ICP-MS STANDARDS, STOCK SOLUTIONS, AND WORKING SOLUTIONS

Plutonium

A plutonium stock was needed in order to make standards to calibrate the Thermo Scientific X Series 2 inductively coupled plasma – mass spectrometer (ICP-MS) for quantification of ^{242}Pu , and for sample preparation. 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 . 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% HNO₃. All volume additions were monitored gravimetrically. A representative calibration curve for ²⁴²Pu is shown in Figure 3.1, while Table 3.3 shows the data used to generate this curve. This table highlights the accuracy of this instrument over several orders of magnitude, while showing the linearity between the standards' concentrations and detected counts. The instrument performance was monitored using ²⁰⁹Bi, ²³²Th, and ²³⁸U as internal standards, and 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%).

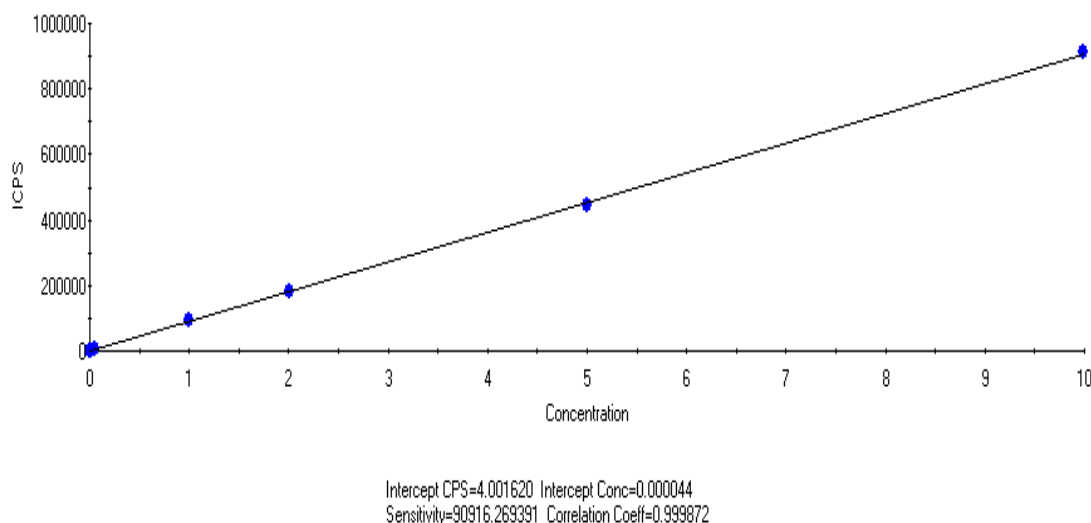


Figure 3.1: Screen Capture of a Typical ²⁴²Pu Calibration Curve using Thermo PlasmaLab Software to Control the Data Collection and Analysis. R²=0.999872, Intercept Conc. (Detection Limit) = 0.000044 ppb. y-axis represents ion counts per second (ICPS) measured by the ICP-MS and x-axis represents concentration of ²⁴²Pu in parts per billion.

Table 3.3: Sample plutonium calibration data.

Sample	Defined Conc. (ppb)	Measured Conc. (ppb)	Counts	Error
Blank	0.000	0.000	0.000	0.000
0.01 ppb	1.00×10^{-2}	1.00×10^{-2}	578	0.000
0.05 ppb	5.00×10^{-2}	4.90×10^{-2}	2.98×10^3	-1.00×10^{-3}
1 ppb	0.999	0.988	5.99×10^4	-1.01×10^{-3}
2 ppb	2.01	2.00	1.21×10^5	-6.00×10^{-3}
5 ppb	5.00	4.98	3.02×10^5	-2.50×10^{-3}
10 ppb	9.99	10.0	6.07×10^5	1.50×10^{-3}

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 the calibrated ICP-MS. 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.

Neptunium

In order to analyze ^{237}Np , a stock solution was needed to prepare standards to calibrate the ICP-MS. A National Institute of Standards and Technology, Standard Reference Material (NIST SRM 4341) was used to prepare a stock ^{237}Np solution using the same preparation techniques as previously described for ^{242}Pu . This stock solution was then used to prepare Np standards for the ICP-MS. A representative calibration curve for ^{237}Np is shown in Figure 3.2, while Table 3.4 shows the data used to generate it. This table highlights the accuracy of this instrument over several orders of magnitude, while showing the linearity in the standards.

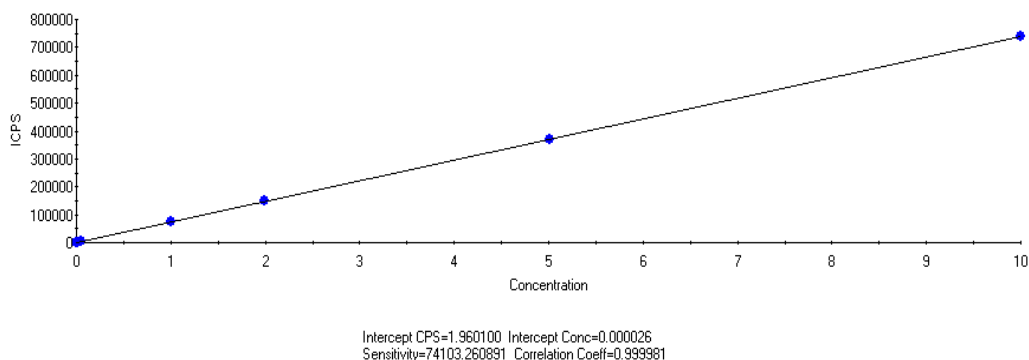


Figure 3.2: Screen Capture of a Typical ^{237}Np Calibration Curve using Thermo PlasmaLab Software to Control the Data Collection and Analysis. $R^2=0.999981$, Intercept Conc. (Detection Limit) = 0.000026 ppb. y-axis represents ion counts per second (ICPS) measured by the ICP-MS and the x-axis represents concentration of ^{237}Np in parts per billion.

Table 3.4: Sample neptunium calibration data.

Sample	Defined Conc (ppb)	Measured Conc (ppb)	Counts	Error
Blank	0.000	0.000	0.000	0.000
0.01 ppb	1.00×10^{-2}	1.00×10^{-2}	458	0.000
0.05 ppb	5.00×10^{-2}	5.00×10^{-2}	2.16×10^3	0.000
1 ppb	1.00	1.02	4.46×10^4	2.00×10^{-2}
2 ppb	1.99	1.99	8.70×10^4	6.00×10^{-3}
5 ppb	5.02	5.026	2.19×10^5	1.10×10^{-2}
10 ppb	10.0	9.99	4.36×10^5	-9.00×10^{-3}

To prepare ^{237}Np working solutions, 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 Plus Detectors). No other alpha

peaks besides ^{237}Np were observed. The approximate concentration was determined using liquid scintillation counting where trace ^{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 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 final concentration of 820 ppb in Working Solution 1.

Technetium

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 data used to generate this curve is shown in Table 3.5. As with Np, and Pu, the ICP-MS is able to accurately measure Tc over many orders of magnitude. 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%).

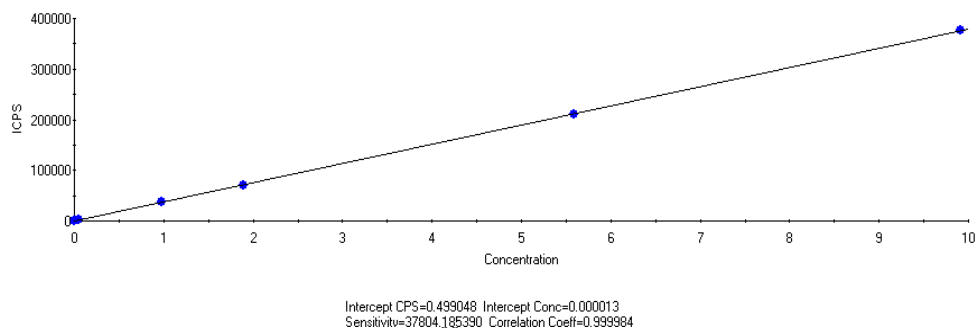


Figure 3.3: Screen Capture of a Typical ^{99}Tc Calibration Curve using Thermo PlasmaLab Software to Control the Data Collection and Analysis. $R^2=0.999984$, Intercept Conc. (Detection Limit) = 0.000013 ppb. y-axis represents ion counts per second (ICPS) measured by the ICP-MS and x-axis represents concentration of ^{99}Tc in parts per billion.

Table 3.5: Sample technetium calibration data.

Sample	Defined Conc (ppb)	Measured Conc (ppb)	Counts	Error
Blank	0.000	0.000	1.00	0.000
0.5 ppb	5.00×10^{-2}	5.10×10^{-2}	1.62×10^3	1.00×10^{-3}
1 ppb	0.977	0.978	3.11×10^4	1.00×10^{-3}
2 ppb	1.90	1.86	5.94×10^4	-3.10×10^{-2}
5 ppb	5.58	5.63	1.79×10^5	4.30×10^{-2}
10 ppb	9.91	9.89	3.15×10^5	-1.80×10^{-2}

Iodine

A 100 µg/mL iodide (I⁻) 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 ¹²⁷I. A screen shot of a representative calibration curve is shown in Figure 3.4. The data used to generate this curve are shown in Table 3.6. Although the background counts are higher for iodine, this data illustrates the ICP-MS is still accurate over many orders of magnitude. 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. Initially there were not any reliable internal standards, so none were used for iodine analysis. This resulted in up to 20% error for QA/QC samples. With such large errors, it was necessary to find suitable internal standards. In house experiments have shown ⁹⁵Mo, ¹¹⁵In, and ¹⁸⁷Re are acceptable internal standards, which was used with

iodine analysis in later experiments. 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.

The 100 µg/mL (ppm) stock iodide solution from High Purity Standards was used as the working solution for iodide experiments.

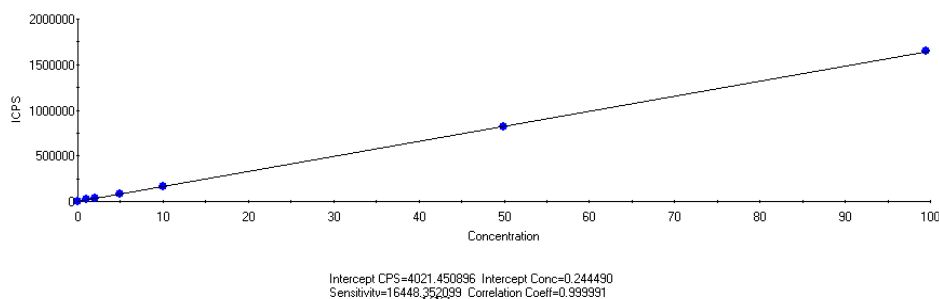


Figure 3.4: Screen Capture of a Typical ^{127}I Calibration Curve using Thermo PlasmaLab Software to Control the Data Collection and Analysis. $R^2=0.999991$, Intercept Conc. (Detection Limit) = 0.24 ppb. y-axis represents ion counts per second (ICPS) measured by the ICP-MS and x-axis represents concentration of ^{127}I in parts per billion.

Table 3.6: Sample iodine calibration data.

Sample	Defined Conc (ppb)	Measured Conc (ppb)	Counts	Error
Blank	0.000	0.000	1.44×10^3	0.000
1 ppb	0.971	1.24	6.61×10^3	0.269
5 ppb	4.90	5.00	2.23×10^4	0.102
10 ppb	9.84	9.88	4.26×10^4	0.083
50 ppb	49.0	50.1	2.10×10^5	1.14
500 ppb	494	494	2.06×10^6	-0.116

An iodate working solution was prepared using standard potassium iodate (KIO_3). Here, 0.0122g KIO_3 was dissolved 100.62g DDI H_2O . This stock solution was then measured using the Thermo Scientific X Series 2 ICP-MS, and the previously prepared

iodide standards. The ICP-MS measured a final concentration of 70,000 μ g/mL ionic iodide.

ICP-MS DETECTION LIMITS

The PlasmaLab software (Thermo Scientific) 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 3.7. 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 below. Therefore, experiments were run with initial iodide and iodate concentrations higher than Tc, Np, and Pu to maintain analytical sensitivity.

Table 3.7: Detection limits for each isotope based on representative calibration curves generated in Plasmalab.

Isotope	Detection Limit (ppb)	Detection Limit (M)
^{99}Tc	1.3×10^{-5}	1.3×10^{-14}
^{127}I	0.24	1.9×10^{-10}
^{237}Np	2.6×10^{-5}	9.7×10^{-15}
^{242}Pu	4.4×10^{-5}	1.8×10^{-14}

EXPERIMENTAL METHODS FOR SALTSTONE EXPERIMENTS

The experimental methods used in this work closely followed those previously described for experiments examining radionuclide sorption to engineered solids (Kaplan

and Coates, 2007; Powell *et al.*, 2002). Brief descriptions of each method are provided below.

Preparation of Calcite Solution for Aerobic Conditions

Using a hot/stirring plate, 1.0 L of 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 at the elevated temperature. The elevated temperature was used as calcite exhibits retrograde solubility. Therefore, the solution will be just below calcite saturation at room temperature and further precipitation of calcite will not occur. After 24 hours the solution was vacuum filtered through a 0.45 μm filter to ensure no solid CaCO_3 remained in solution.

Preparation of Trap Solution

Analysis of iodine required the use of a reducing, basic solution that was capable of reducing iodate to iodine, holding the iodine in solution, and preventing off-gassing of $\text{I}_2(\text{g})$. This minimized the loss of I during sample analysis. A 1 L trap solution was prepared by weighing out 0.0500 g NaHSO_3 (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.

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.

For each of the four solids, aged cement, Vault 2 concrete, TR547, and TR545, 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 ^{99}Tc , ^{237}Np , and ^{242}Pu samples were 1 ppb, 5 ppb, and 10 ppb. Target initial concentrations for the ^{127}I samples were 100 ppb, 500 ppb, and 1000 ppb. A set of samples absent of solids were used as controls with initial concentrations of 1 ppb and 10 ppb for ^{99}Tc , ^{237}Np , and ^{242}Pu and initial concentrations of 100 ppb and 1000 ppb ^{127}I 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 values 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 ^{127}I , ^{237}Np , ^{242}Pu , and ^{99}Tc . It is important to note that all four isotopes were added to the same vial. Assuming a site density of 2.3 sites per nm^2 and an average surface area of $20 \text{ m}^2/\text{g}$, the 25 g/L suspensions used in this experimental design will contain $1.9 \times 10^{-3} \text{ M}$ of sorption sites. This represents a greater than 10^3 molar excess relative to the sum of ^{99}Tc , ^{127}I , ^{237}Np , and ^{242}Pu . Therefore, the amount of solids used provides enough surface sites that competition between the radionuclides should be minimal. 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 ^{99}Tc , ^{237}Np , and ^{242}Pu concentrations of 10 ppb and initial ^{127}I concentration of 100 ppb, a 100 μL aliquot of each radionuclide working solution was added to 3 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 ^{237}Np , ^{242}Pu , and ^{99}Tc and 50 ppb ^{127}I samples were prepared in the same manner but adding 50 μL of the respective spike solutions. The final three tubes with initial ^{237}Np , ^{242}Pu , and ^{99}Tc concentrations of 1 ppb and 10 ppb ^{127}I 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 3.8 below.

Table 3.8: Experimental matrix of sorption experiments under aerobic conditions.

Experiment	Target Initial Concentration ⁹⁹ Tc, ²³⁷ Np, ²⁴² Pu (each isotope)	Target 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

In order to adjust the pH of these systems, 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 3 additional days. On day 4, the above sampling procedure was repeated.

The ^{237}Np , ^{242}Pu , and ^{99}Tc 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 ^{127}I analysis, the ICP-MS must be reconfigured to accommodate the basic, reducing trap solution. The trap solution is used 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 100 $\mu\text{L}/\text{min}$, 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 iodide 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 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.

Experimental Protocol for Sorption Experiments under Anaerobic Conditions

In order to examine the effects of reducing conditions of sorption of each isotope to the various saltstones, a series of sorption experiments were performed in an anerobic glovebox under a 2% $\text{H}_2(\text{g})$ / 98% $\text{N}_2(\text{g})$ atmosphere. Based on the measured pH and E_{H} of these systems as discussed below, these systems were reducing and at equilibrium with

the 2% H₂(g) atmosphere. Therefore, they are expected to represent a lower end of the possible range for reducing conditions expected in the porewater available in engineered solids.

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 above. After filtration, the calcite solution was then transferred from the glove bag into the glove box.

Preparation of Working Solutions under Reducing Conditions

The solutions of calcite and solid 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 3 days. The concentrations of each isotope in the working solutions were measured to determine any change in the concentration due to evaporation while the solutions were equilibrating with the glovebox atmosphere.

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 4.0 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.

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 1 and 4 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. 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 (Powell *et al.*, 2002). This process was performed for both the solid suspension and the no solid controls. The samples were then run on the ICP-MS to determine the concentration of ⁹⁹Tc, ²³⁷Np, and ²⁴²Pu sorbed to the vial walls.

DATA ANALYSIS

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

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

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

C_{ICP-MS} = Aqueous concentration of nuclide from ICP-MS measurement (ppb, $\mu g_{nuclide}/kg_{solution}$)

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

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

$$C_{solid} = \frac{C_{stock} * m_{spike} - C_{ICP-MS} * (m_{spike} + m_{calcite})}{m_{solid}} \quad (\text{Equation 3.2})$$

C_{solid} = calculated solid phase concentration of the nuclide associated with the saltstone (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_{ICP-MS} = aqueous concentration of nuclide determined 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:

$$K_d = \frac{C_{solid}}{C_{ICP-MS}} \quad (\text{Equation 3.3})$$

K_d = saltstone-water partitioning coefficient ($g_{\text{solution}}/g_{\text{solid}}$, assuming density of 1.0 g/mL traditional unit of $mL_{\text{solution}}/g_{\text{solid}}$ 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.*, 2000; Powell *et al.*, 2002).

EXPERIMENTAL METHODS FOR LONG TERM SORPTION EXPERIMENTS

After analyzing the results from the above saltstone experiments, it was apparent ^{99}Tc and ^{127}I had not reached equilibrium after the 4 day sampling event. It was deemed necessary to extend the sampling events over a longer period.

Sample Preparation

Falcon BlueMax 50mL polypropylene vials were labeled, and weighed as previously described. Then approximately 1.25 +/- 0.01 g of a given solid was added and the exact mass was determined gravimetrically.

For each of the four engineered solids, two sets of triplicate samples were prepared. The two sets of samples were used to allow for experiments to be run with varying concentrations of each isotope. Target initial concentrations for ^{99}Tc samples were 5 ppb, and 10 ppb. Target initial concentrations for the ^{127}I samples were 50 ppb, and 100 ppb. A set of no-solids controls at initial concentrations of 5 ppb and 10 ppb for ^{99}Tc and initial concentrations of 50 ppb and 100 ppb ^{127}I 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 45 +/- 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 50 +/- 0.1 mL of calcite solution was added to each tube. The mass 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. They 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 ^{127}I and ^{99}Tc . It is important to note that both 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 ^{99}Tc concentrations of 10 ppb and initial ^{127}I concentration of 100 ppb, a 500 μL aliquot of the ^{99}Tc working solution, and 50 μL of the ^{127}I working solution were added to the first 3 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 ^{99}Tc and 50 ppb ^{127}I samples were prepared in the same manner but adding

250 μL of the ^{99}Tc working solution, and 25 μL of the ^{127}I working solution. These were done for all four saltstones, and a set of no solid controls. For clarity, this experimental matrix is shown in Table 3.9 below.

Table 3.9: Experimental matrix of sorption experiments under aerobic conditions.

Experiment	Initial Concentration ^{99}Tc	Initial Concentration ^{127}I
Solids-Present	5 ppb	50 ppb
Solids-Present	10 ppb	100 ppb
Solids-Free	50 ppb	50 ppb
Solids-Free	100 ppb	100 ppb

This sample preparation was repeated to prepare anaerobic samples for use in the glovebox. The calcite used for these samples was prepared using the procedure previously described for anaerobic conditions.

Long Term Sampling Procedure

Both the aerobic and anaerobic samples were sampled using the method described in the initial saltstone experiments. However, the sampling timeline was much longer for these. Samples were taken at 1, 4, 8, 22, and 56 day intervals.

EXPERIMENTAL METHODS FOR SOIL EXPERIMENTS

Preparation of Trap Solution

As with the saltstone solutions, the iodine analysis involved with these soil experiments required the use of a reducing, basic solution capable of reducing iodate to iodide, and holding it in solution. To allow the same trap solution to be used in all experiments, a 4 liter solution was produced by scaling up the method described above.

Determining Water Content of Wetland Soil

The Four Mile Branch wetland soil is unlike the sandy and clayey soils in that it is saturated with water. Because dehydrating the soil could lead to changes in soil chemistry, it was necessary to determine the water content. This was done by weighing three 15mL Falcon BlueMax 15mL polypropylene vials on a calibrated Sartorius LA 230S scale, and recording the masses. The scale was then zeroed, and 6.0 ± 0.01 g of wetland soil was added. These samples were then placed uncapped in an oven at 100°C overnight. After 24 hours, the vials were reweighed on the Sartorius LA 230S scale, and the dry weight was recorded to within 0.001g. A water/dry soil ratio was then calculated using the initial mass of the “wet” soil and the final dry weight. The resulting water content was 1.044 ± 0.044 g H_2O /g dry soil or 2.044 ± 0.044 g wetland soil/g dry soil.

Preparation of Iodate Stock

In addition to the iodide stock from High Purity Standards (Charleston, SC), soil experiments were also performed using an iodate stock. This stock solution was prepared by weighing 0.0122g potassium iodate (Alfa Aesar) on a calibrated Sartorius LA 230S scale, and diluting with 100mL DDI in an amber bottle. The stock concentration was then checked using the ICP-MS and the iodide standards. The iodine concentration of the stock was determined to be 74,280ppb. This stock concentration was re-checked every time samples were run on the ICP-MS.

EXPERIMENTAL METHODS IN AEROBIC CONDITIONS

Preparation of 0.01M NaCl

Since the soil suspensions in this experiment lack the buffering capacity of the previously used saltstones, a 0.01M NaCl solution was used. This solution was prepped by weighing 1.168g NaCl (EM Science, ACS Grade) on a calibrated Sartorius LA 230S scale, and diluting in 2.0L of DDI water.

Experimental Protocol for Iodide Sorption

For each of the three soils, three sets of triplicate samples were prepared in Falcon BlueMax 15mL polypropylene vials as describe above, but with 0.30 +/- 0.01g of either sandy or clayey soil was added, and the mass recorded to within 0.001g. In the case of the saturated wetland soil, 0.60 +/- 0.01g of soil was added to each tube and the mass recorded to within 0.001g.

As was the case with the saltstone samples, the three sets allow for experiments to be run with varying concentrations of iodide. Target initial ^{127}I concentrations were 1000ppb, 500ppb, and 100ppb. A set of controls containing no solids at 1000ppb and 100ppb ^{127}I were also prepared.

The solids were equilibrated with the 0.01M NaCl solution before spiking with iodide. This was accomplished by adding 12mL 0.01M NaCl to each tube and soil, and recording the mass. The samples were then placed on a Labquake end-over-end shaker at 8 rpm overnight. After 24 hours, the suspensions were spiked with the iodide stock. For the 1000ppb iodide suspensions, a calibrated pipette was used to add a 120 μL aliquot of the iodide stock solution to the first three tubes for each soil. The 500ppb suspensions

were prepared by adding 60 μL of the working solution to the next three tubes for each soil. The final three tubes were used for the initial concentrations of 100ppb. They were prepared by adding 12 μL aliquots of the iodide stock to each tube. A set of solid-free controls (no-solids controls) with ^{127}I concentrations of 100ppb and 1000 ppb were also prepared using this technique.

Table 3.10: Experimental matrix of soil sorption experiments for iodide and iodate under aerobic and reducing conditions.

Experiment	Target Initial Concentration ^{127}I
Solids-Present	1000 ppb
Solids-Present	500 ppb
Solids-Present	100 ppb
Solids-Free	1000 ppb
Solids-Free	100 ppb

After spiking the samples with the iodide stock solution, the pH values of each sample were recorded. The samples were then placed on an end-over-end shaker at approximately 8 rpm. After 24 hours, the samples were removed from the shaker, and the sediment suspensions settled for an hour. The pH was then recorded using an Orion Ross semi-micro glass electrode, which was calibrated against pH 4, 7, and 10 buffers (Thermo). Each sample was then hand shaken to ensure a homogenous mixture. A transfer pipette was then used to pipette approximately 3 mL of each suspension to a 5 mL syringe. The solution was then passed through a 200 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 5 mL trap solution. Each of these steps involved the use of a calibrated pipette. The samples

were then placed back on the shaker to mix until sampling events at 4 and 8 days using the same procedure discussed above.

Experimental Protocol for Iodate Sorption

The same sample preparation and sampling procedure described above, was used to test iodate sorption to these three soil types.

Analyzing Iodide and Iodate Samples

The samples acquired at 1, 4, and 8 day intervals in the above two experiments were analyzed using the same ICP-MS procedure used in the saltstone studies.

EXPERIMENTAL PROCEDURE IN REDUCING CONDITIONS

Preparation of 0.01M NaCl

When preparing the samples in the anaerobic glove box, the 0.01M NaCl needed to be prepared in a manner that insured it was oxygen free. This was accomplished by bringing 2.5L DDI water to a rolling boil for 30 minutes. This was then cooled using an argon gas purge. While cooling, 1.168g NaCl was weighed on a calibrated Sartorius LA 230S scale, and added to a 2L volumetric flask. The cooled DDI water and volumetric flask containing the NaCl were then placed in the glove box. The DDI water was added to the flask, and the remaining water was saved to use as an electrode wash.

Preparation of Iodide Samples

The soil samples used in the glove box were prepared in much the same manner as those under aerobic conditions. The soil was added to the labeled vials under aerobic

conditions, and the masses recorded. The masses were the same used for aerobic conditions. The samples were then transferred to the glove box, where they were left uncapped overnight. The 0.01M NaCl described above was then added to each sample in three 4.0mL aliquots using a calibrated pipette. The samples equilibrated overnight. After 24 hours, the predetermined mass of iodide stock was pipetted into the vials to achieve the desired initial concentrations found in the matrix in Table 3.6. This was done using calibrated pipettes. These samples mixed for approximately 1 hour, and then the pH was recorded.

Preparation of Iodate Samples

The soil samples used for iodate sorption under reducing conditions were prepared using the above method with the only difference being the masses of iodate stock used. The iodide and iodate stocks had different iodine concentrations, so it was important to use the correct masses to insure initial concentrations found in the matrix in Table 3.10.

Sampling of Iodide and Iodate Samples

Both the iodide and iodate samples were collected in the same manner as the previous samples. The sampling events occurred at 1, 4, and 8 day intervals. These samples were then analyzed using the Teflon setup on the ICP-MS. Data Analysis

The K_d calculation for the sediment experiments is slightly different from that used with the engineered solids. These sediments had iodine naturally associated with them, which could not be removed, as was the case with the engineered systems when the radionuclides were removed in the “washing step.” This was accounted for by measuring

the aqueous I for samples without any spiked I. These samples were then averaged, and this average was then subtracted from the ICP-MS measurements for each sample. These average values of aqueous iodine in the ICP-MS samples were 16.5, 68.7, and 7.60 ppb for the sandy, clayey, and wetland sediments, respectively. The concentration on the solid was then calculated using:

$$C_{solid} = \frac{C_{stock} * m_{spike} - C_{[I]measured-[I]native} * (m_{spike} + m_{aq})}{m_{solid}} \quad (\text{Equation 3.4})$$

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

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

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

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

$C_{[I]measured-[I]native}$ = the measured I concentration corrected for the native I leached from the soil during the course of the experiment (ppb)

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

The K_d can be calculated using the equation:

$$K_d = \frac{C_{solid}}{C_{aqueous}} \quad (\text{Equation 3.5})$$

$C_{aqueous}$ = aqueous concentration of iodine determined via ICP-MS

K_d = sediment-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 (3.5) is numerically equivalent to the traditional K_d equation proposed in ASTM D-4646 which has been used in previous experiments (Kaplan *et al.*, 2000; Powell *et al.*, 2002).

Chapter 4 RESULTS AND DISCUSSION

SHORT-TERM RADIONUCLIDE SORPTION EXPERIMENTS

Redox Conditions During Sorption Experiments

As previously described, reducing slag is added to engineered systems as a means of controlling the redox conditions. Therefore, throughout these experiments redox potentials were measured under reducing conditions, and are reported in Table 4.1. There is a noticeable trend in the samples containing reducing slag. As the reducing slag content increases, the conditions become more reducing. Additionally, even the aged cement and no-solids controls experience reducing conditions, despite no reducing slag is present.

Table 4.1: Redox potentials for reducing conditions.

Solids	1 day E_h (mV)	4 day E_h (mV)
Aged cement	-498	-451
Vault 2 concrete	-511	-361
TR547	-585	-498
TR545	-600	-584
No-Solids	-529	-491

Radionuclide Sorption under Oxidizing Conditions

In all cases, Pu strongly sorbed to all engineered solids 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 concentration. This is not expected since 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 1 day and 4 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 appears to be a correlation with the concentration of reducing slag. As more slag is added, the K_d values decrease. This decrease could be a result of Pu higher sorption affinity to cement, and as reducing slag is added, the cement concentration decreases. The Vault 2 concrete samples with 17% reducing slag has a K_d similar to that of the TR547 (45%), while the saltstone with the most reducing slag TR545 (90% slag) has the lowest K_d value.

It was observed that similar aqueous concentrations of Pu were observed regardless of the solid phase present. At the end of the batch experiments, the fraction of Pu in the aqueous phase was <0.001 for each set of samples. Figure 4.2 shows the average aqueous phase concentrations measured after 1 day and 4 days for all solids. As stated above, triplicate samples were prepared for each solid phase and each initial concentration. Therefore, each of the reported aqueous concentrations in Figure 4.2 is an average of nine measurements. This is not a traditional solubility value based on a pure phase, but describes the aqueous Pu concentration in the bulk water of these suspensions. 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).

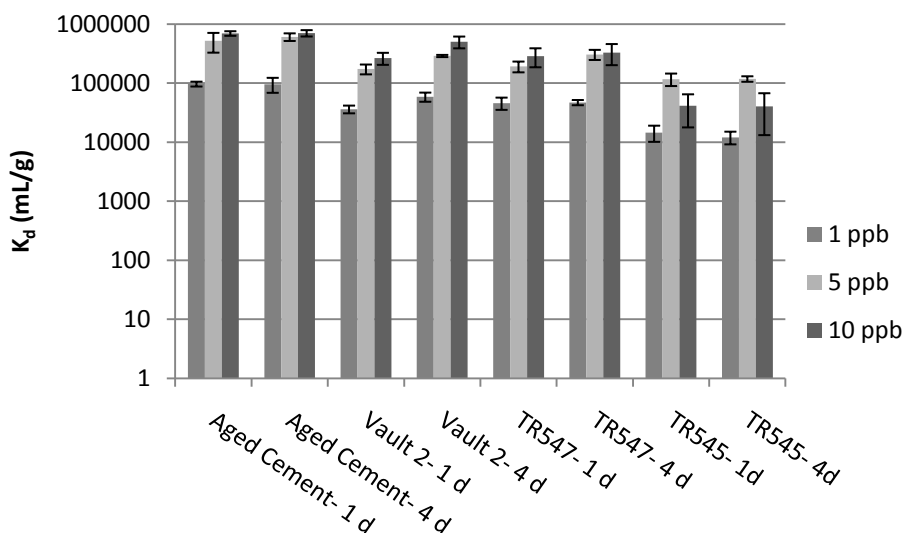


Figure 4.1: Plutonium K_d Values under Oxidizing Conditions. Plutonium K_d values for engineered solids measured after one day equilibration (1d) and four day equilibration (4d under oxidizing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Sample prepared in triplicate except as follows: Value for dataset TR547-4d 10 ppb, is reported based on duplicate samples. Error bars represent the standard deviation of samples. Plutonium was added as Pu(IV).

Overall, the K_d values for Np range from 10^5 to $>10^6$ (mL/g) with only a few outliers. The most significant outlier is the 1 ppb solution in the TR545 sample after 4 days. It drops two orders of magnitude, while the 5 and 10 ppb solutions remain constant. However, this is most likely an analytical artifact from working at the detection limits of the ICP-MS. In the day 1 sample, only one of the triplicates, had detectable Np (Sample E in Table 6.25, see Appendix), while in the day 4 samples, again only one sample had detectable amounts present (Sample F in Table 6.26, see Appendix). The

graph also shows that despite the 5 ppb sample in the aged cement, Np sorption to TR545 (90% slag) and TR547 (45% slag) have K_d s approximately one order of magnitude over the aged cement (no slag) and Vault 2 concrete (17% slag) samples.

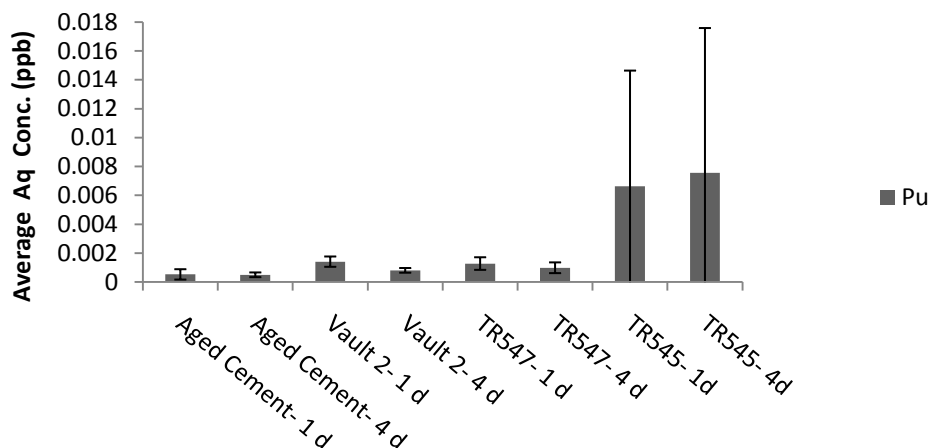


Figure 4.2: Plutonium Aqueous Concentrations for Engineered Solids. Aqueous concentrations measured after one day equilibration (1d) and four day equilibration (4d) under oxidizing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Samples prepared in triplicate, and an average of all samples (9) was used to determine average aqueous concentration. The error bars represent standard deviation of 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 1 day and 4 days for all solids. As stated above, triplicate samples were prepared for each solid phase and each initial concentration. Therefore, each of the reported aqueous concentrations in Figure 4.4 is an average of nine measurements 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 Np in the pore water associated with the saltstone formulations will be approximately 2×10^{-11} mol/L.

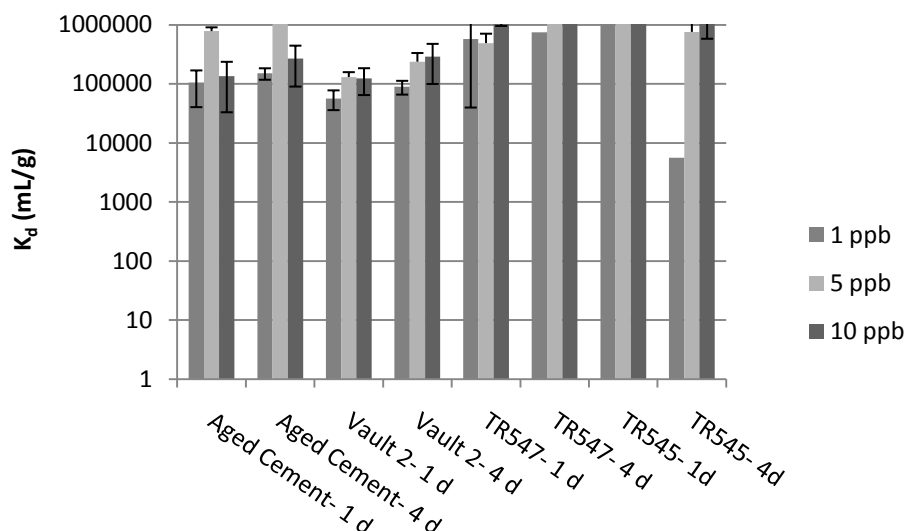


Figure 4.3: Neptunium K_d Values under Oxidizing Conditions. Neptunium K_d values for various engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under oxidizing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Sample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

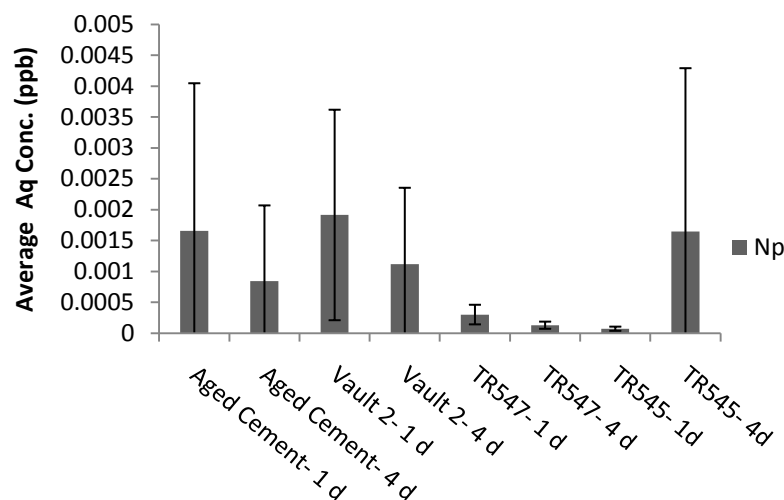


Figure 4.4: Average Aqueous Concentrations of Neptunium under Oxidizing Conditions. Neptunium aqueous concentration for various engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under oxidizing conditions. Total Np concentrations in each system were 1ppb, 5 ppb,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

The K_d values for ^{99}Tc are significantly lower than that of Pu or Np. As a whole, the values are comparable. The values for the 1 day and 4 day solutions in the Vault 2 (17% slag) and TR545 (90% slag) remained constant within reasonable error with just a slight increase from 1 day to 4 day. However, the aged cement (no slag) and TR547 (45% slag) appeared to show a noticeable decrease from day 1 to day 4.

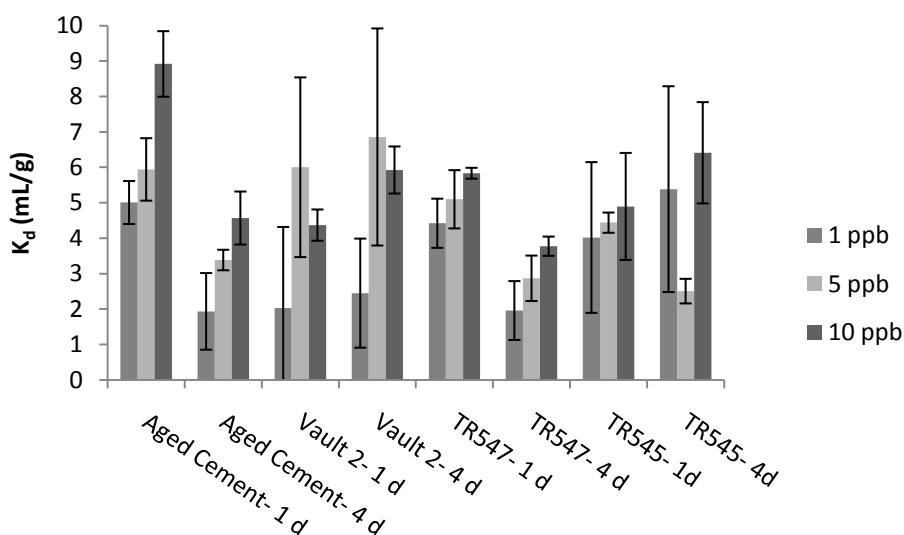


Figure 4.5: Technetium K_d Values under Oxidizing Conditions. Technetium K_d values for various engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under oxidizing conditions. Total Tc concentrations in each system were 1 ppb, 5 ppb, and 10 ppb as noted above.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

Unlike the ^{242}Pu , ^{237}Np , and ^{99}Tc , there were no internal standards available to track the ^{127}I during these experiments. Although QA/QC samples were included, there was approximately 20% error associated with them. Therefore, the ^{127}I data will not be shown for these experiments. This problem was resolved for the “Long Term Sorption Experiments” discussed in a later section.

Radionuclide Sorption to Vial Walls under Oxidizing Conditions

Figure 4.6 shows the aqueous fractions found in the solid free controls to examine the solubility of each radionuclide as well as examine the fraction of each radionuclide sorbed to the vial walls. After 1 day, only 25% of the Pu remained in solution and the concentration decreased even more after 4 days. The loss of Pu in 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 4.7 below). Additional experiments are planned in future studies to examine the solubility of the Pu in high pH, calcite saturated solutions. For Np after 1 day, about 80% remained in solution. However, the aqueous concentration in the initially 10 ppb solution was significantly reduced after 4 days. Approximately 60% of the neptunium 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 1 day ranged from about 88% to about 95%, and by day 4, virtually 100% remained in the aqueous phase.. These values are consistent with internal standards used to monitor ^{99}Tc detection performance on the ICP-MS. As will be discussed below, it is possible to differentiate between sorption to the vial walls and the solid phase by washing the vial walls after the experiment has concluded. This was monitored for Np and Pu, and neither radionuclide was recovered in the washing procedure.

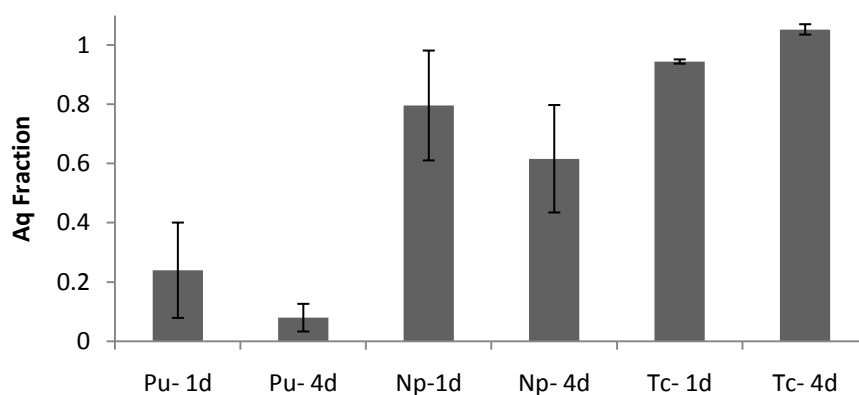


Figure 4.6: Fraction of Aqueous Plutonium, Neptunium, and Technetium . Fraction of Pu, Np, and Tc remaining in the aqueous phase for the no-solids controls after a one day equilibration (1d) and four day equilibration (4d) under oxidizing conditions. The total concentration for each radionuclide 10 ppb as noted above. Samples were prepared in triplicate and the error bars represent the standard deviation of the samples.

As discussed above, the loss of Np and Pu from solid free control (Figure 4.6) 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 above. The data in Figure 4.7 indicate that significant sorption of Np and Pu to the vial walls may occur. When combining the mass of Np represented in Figure 4.6 and 4.7, 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, since 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 4.6 represents solid free control samples where there was no solid phase present for Np or Pu to sorb to besides the vial walls. However, when a solid phase is present in the sample, there will be competition between the vial walls and the solid 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 saltstones, it is assumed that the solids will outcompete the vial walls for sorption sites. This 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 above. Figure 4.8 and 4.9 show that although some of the Pu and Np sorbed to the vial walls of the samples, this 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 solid free experiments and experiments with saltstone 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.

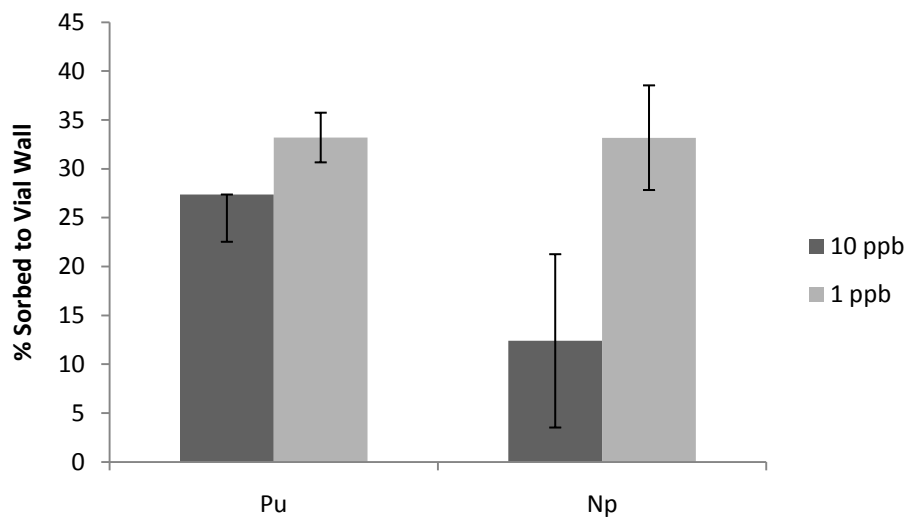


Figure 4.7: Percent Pu and Np Sorbed to Vial Walls of the No-Solids Controls. Measured after the aqueous phases were discarded and the vials were washed. Both the 10 ppb and 1 ppb data sets were prepared in triplicate, and the error bars show the standard deviation.

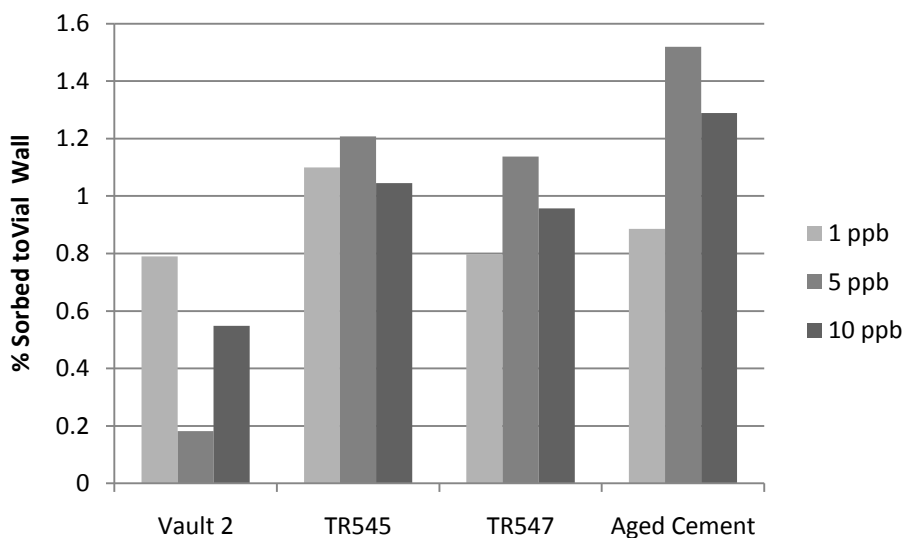


Figure 4.8: Percent Pu Sorbed to Vial Walls. Measured after the solids and aqueous phases were removed and the vials were washed. The graph illustrates one sample from each of the 1 ppb, 5 ppb, and 10 ppb systems. Therefore, no error bars are present.

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 is consistent with the ~100% mass balance on Np achieved with 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 solid free 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).

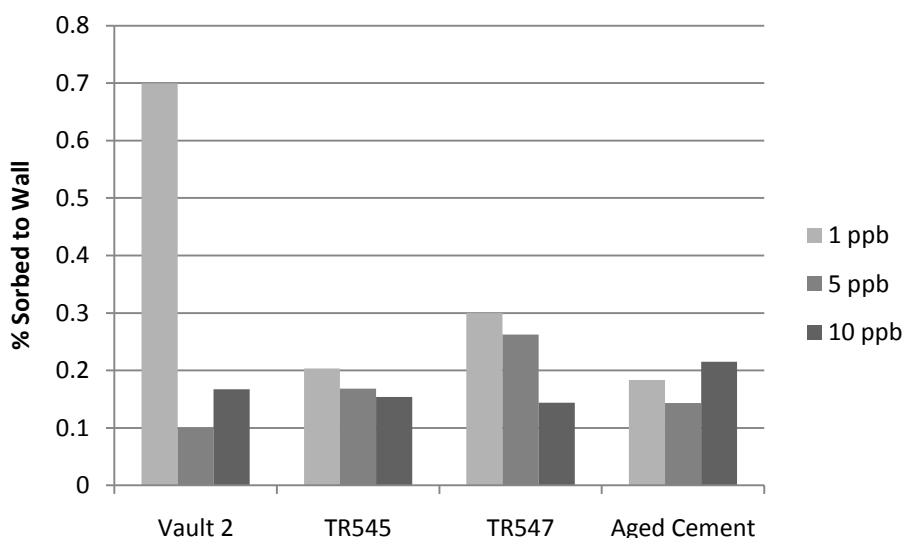


Figure 4.9: Percent Np Sorbed to Vial Walls. Measured after the solids and aqueous phases were removed, and the vials were washed. The graph illustrates one sample from each of the 1 ppb, 5 ppb, and 10 ppb systems. Therefore, no error bars are present.

Radionuclide Sorption under Reducing Conditions

Similar to the Pu K_d values under oxidizing conditions, Pu K_d values ranged from 10^4 to $>10^5$ (mL/g) under reducing conditions (Figure 4.10). Also similar to the results under oxidizing conditions, the K_d increases with increasing initial Pu concentration. Again, this 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 is evident because the K_d values between 1 day and 4 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.

It was observed that similar aqueous concentrations of Pu were present regardless of the solid phase present. Figure 4.11 shows the average aqueous phase concentrations measured after 1 day and 4 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 4.11 is an average of up to nine measurements. 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 saltstone formulations will be approximately 2×10^{-11} mol/L (calculated from equation 3.1). This is on the same order as the solubility of Pu hydrous oxide solid phases (Yamaguchi *et al.*, 2006).

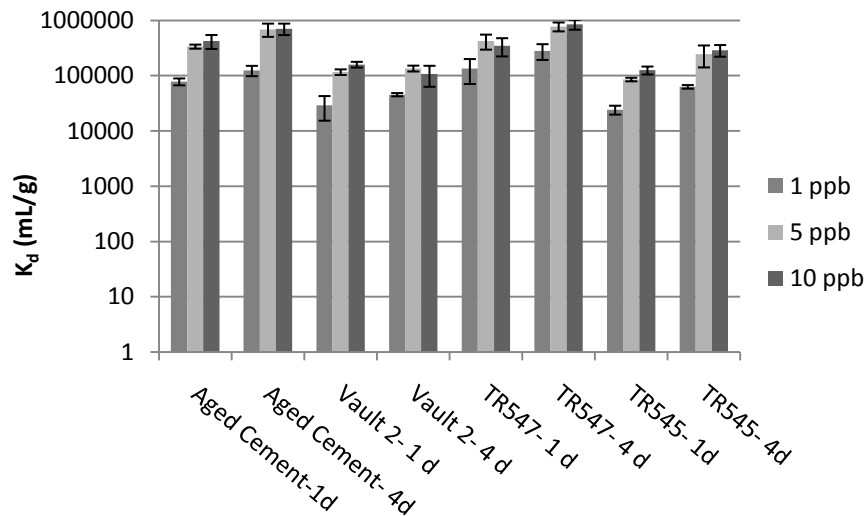


Figure 4.10: Plutonium K_d Values under Reducing Conditions. Plutonium K_d values for engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under reducing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Sample prepared in triplicate and error bars represent standard deviation of samples.

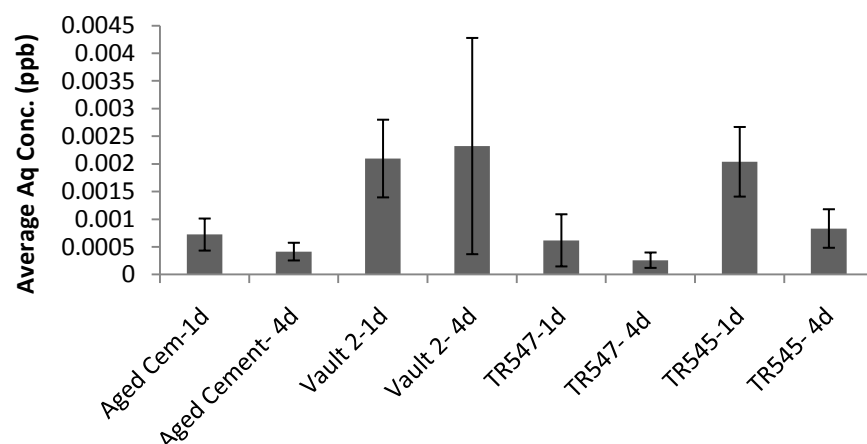


Figure 4.11: Average Aqueous Concentration of Plutonium under Reducing Conditions. Plutonium aqueous concentration for engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under reducing conditions. Total plutonium concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Samples prepared in triplicate, and an average of all samples (9) was used to determine average aqueous concentration. The error bars represent standard deviation of samples.

The Np K_d values reported in Figure 4.12 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 is evident because the K_d values between 1 day and 4 days are very similar. As was the case with Pu, the amount of reducing grout present in each solid does not seem to have a significant effect on the K_d values. Again, the aged cement with no grout has as high a K_d as the TR545 with 90% reducing grout.

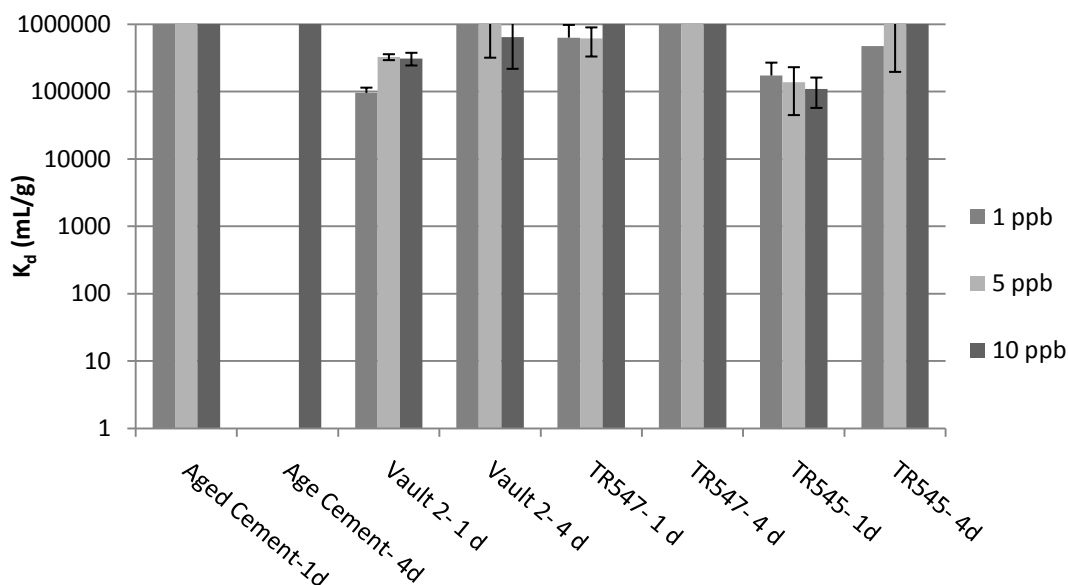


Figure 4.12: Neptunium K_d Values under Reducing Conditions. Neptunium K_d values for engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under reducing conditions Total Np concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Samples were prepared in triplicate, and the error bars represent standard deviation of samples. TR545-4d 1 ppb data set consisted of 1 sample, aged cement-1d 1 ppb, TR547- 4d 5 ppb, 1 ppb data sets consisted of duplicate samples. Aged cement- 4d 5 ppb, 1 ppb data sets no results were obtained. K_d values limited to $>10^6$ were at instrumental background. Y-axis on log scale.

It was observed that similar aqueous concentrations of Np were present regardless of the solid phase present. Figure 4.13 shows the average aqueous phase concentrations measured after 1 day and 4 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 4.13 is an average of up to nine measurements. Using the highest reported value 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 saltstone formulations will be approximately 2×10^{-11} mol/L.

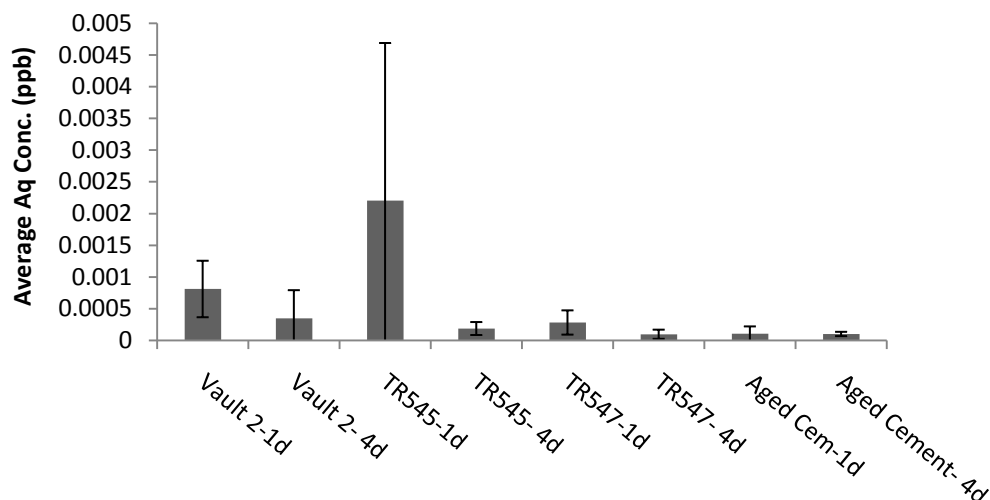


Figure 4.13: Average Aqueous Concentration of Neptunium under Reducing Conditions. Neptunium aqueous concentration for various engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under reducing conditions. Total plutonium concentrations in each system were 1ppb,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

A plot of the Tc K_d values for each engineered solid under reducing conditions is shown in Figure 4.14 (log y-axis) and Figure 4.15 (reduced scale linear y-axis). The K_d values for each of the initial Tc concentrations are relatively similar. This is consistent with the K_d expression. However, the increasing K_d values from 1 day to 4 days for each solid indicate that steady state was not reached within 1 day and it is unclear whether steady state was reached after 4 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 is highly speculative and a significant amount of future work is required to test this hypothesis. It is proposed that this future work should focus

on understanding reactivity of the solid phases and the kinetics of possible redox reactions. As for the solid phases themselves, there is a noticeable increase in the K_d values as the amount of reducing grout in the formulation increases. TR547 (45% slag) is visibly higher than the aged cement and Vault 2 concrete, while the most reducing TR545 (90% slag) is significantly higher than the others.

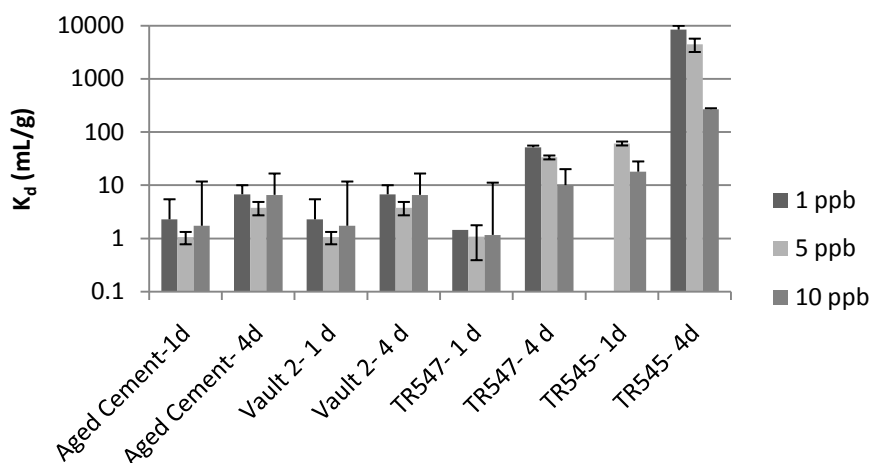


Figure 4.14: Technetium K_d Values under Reducing Conditions. Technetium K_d values for various engineered solids measured after one day equilibration (1d) and four day equilibration (4d) under reducing conditions. Total Tc concentrations in each system were 1ppb, 5 ppb, and 10 ppb as noted. Sample prepared in triplicate except as follows: TR547-1d 1 ppb is based on a single data set. Data sets Vault 2-1d 5ppb, Vault 2- 4d 1ppb, aged cement-1d 5ppb, and aged cement-4d 1ppb are duplicates. The 1ppb TR545-1d data were omitted due to sampling error. The error bars represent the standard deviations of the samples.

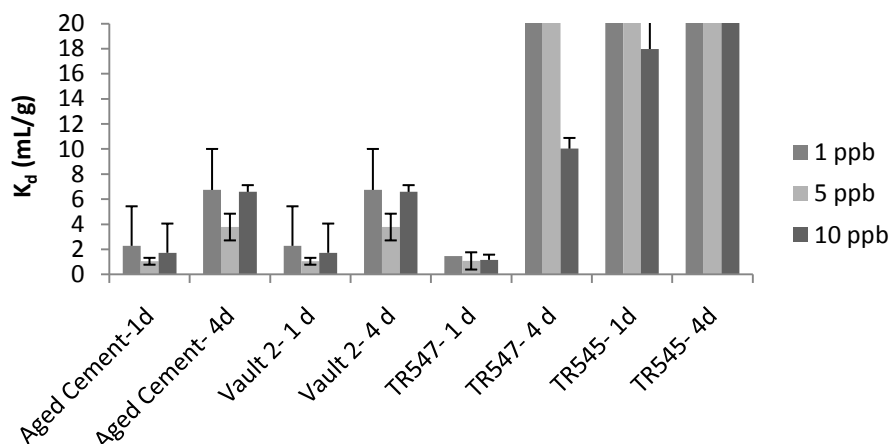


Figure 4.15: Technetium K_d Values under Reducing Conditions. Data from Figure 4.14 replotted on a reduced linear scale for easier viewing. Each sample was prepared in triplicate except as follows: TR547-1d 1 ppb is based on a single data set. Data sets Vault 2-1d 5ppb, Vault 2- 4d 1ppb, aged cement-1d 5ppb, and aged cement-4d 1ppb are duplicates. Error bars represent the standard deviation of the samples.

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 4.16. The results are similar to those presented for experiments performed under oxidizing conditions above. The 1 ppb Pu aqueous fraction is approximately 3 times greater than the 10 ppb fraction at day 1. This fraction decreases over time, and by day 4 they are approximately equal when taking error into account. This is similar to the aqueous fraction under oxidizing conditions. The 1ppb Np aqueous fraction is significantly higher on both day one and four than the 10 ppb samples. However, each of the samples remained constant from day one to day four. The data for the 10 ppb aqueous fraction is twice as low as under oxidizing conditions, which suggests either higher sorption to the vial walls, or more Pu is possibly lost to precipitation under the reducing conditions. Like Pu and Np, Tc shows a decrease from day one to day four,

especially for the 1ppb samples. The decrease in the 10 ppb sample is minimal, and the aqueous fraction remains around 0.9. This 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 4.17. However, this 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. This unaccounted Pu was likely lost due to precipitation, and further solubility tests should be performed to provide additional insight. Np follows the same trend as Pu, while less than 0.05% of the Tc sorbed to the wall.

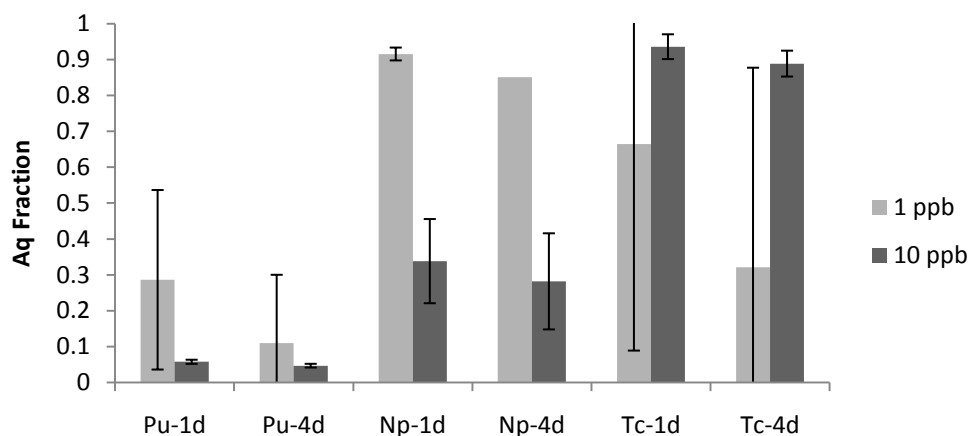


Figure 4.16: Fraction of Aqueous Plutonium, Neptunium, and Technetium in No-Solids Samples under Reducing Conditions. Aqueous Pu, Np, and Tc fractions of no-solids controls after a one day equilibration (1d) and four day equilibration (4d) under reducing conditions. The total concentration for each radionuclide was 1 ppb and 10 ppb as noted above. Samples were prepared in triplicate and the error bars represent the standard deviation of the samples.

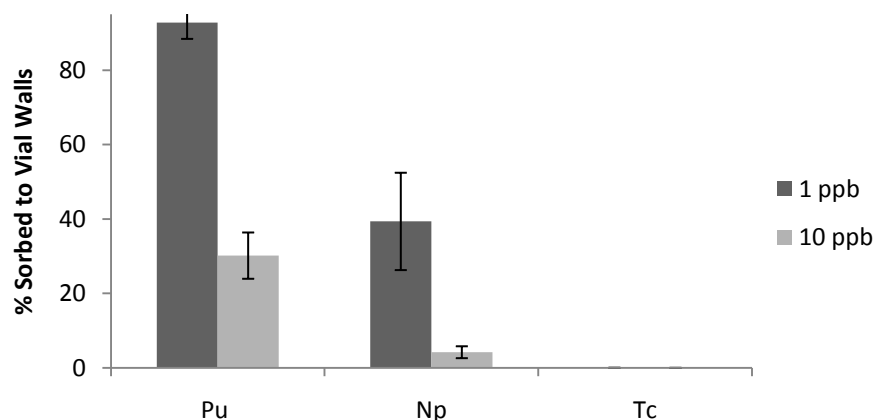


Figure 4.17: Percent of Pu, Np, and Tc Sorbed to the Vial Walls of the No-Solids Control Samples under Reducing Conditions. Each of the 1 ppb and 10 ppb samples were prepared in triplicate, and the error bars represent the standard deviations of triplicate samples.

Comparison of Radionuclide Sorption under Oxidizing and Reducing Conditions

In the following figures (4.18 through 4.21), the data shown above has been replotted to allow comparison between the oxidizing and reducing conditions for each engineered solid. General observations based on these data follow.

Vault 2 concrete observations (Figure 4.18):

- Pu K_d s are greater than 10^4 (mL/g) 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 greater than 10^4 (mL/g) 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 and Pu were observed in all samples. This 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 4 days under oxidizing conditions. This does not appear to be the case under reducing conditions. After 4 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.

- For all isotopes examined, the sorption behavior to each of the solid phases is very similar.

TR545 and TR547 observations (Figure 4.19 and 4.20):

- Similar to the discussion above with respect to Vault 2 concrete, 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 (mL/g) 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 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, yet it appears that in the base case, TR547, that the Tc was reduced, and its sorption controlled by solubility
- For all isotopes examined, the sorption behavior to each of the solid phases is very similar.

Aged cement observations (Figure 4.21):

- Pu appears to be close to steady state for each solid by day one with similar K_d values reached between day one and four.
- Np has a higher K_d under reducing conditions than oxidizing (10^5 (mL/g) under oxidizing conditions and $>10^5$ (mL/g) 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_{ds} decrease from day one to four under oxidizing conditions, but increase under reducing conditions.
- 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 iodine redox behavior in addition to any reactivity expected in the solid phases.

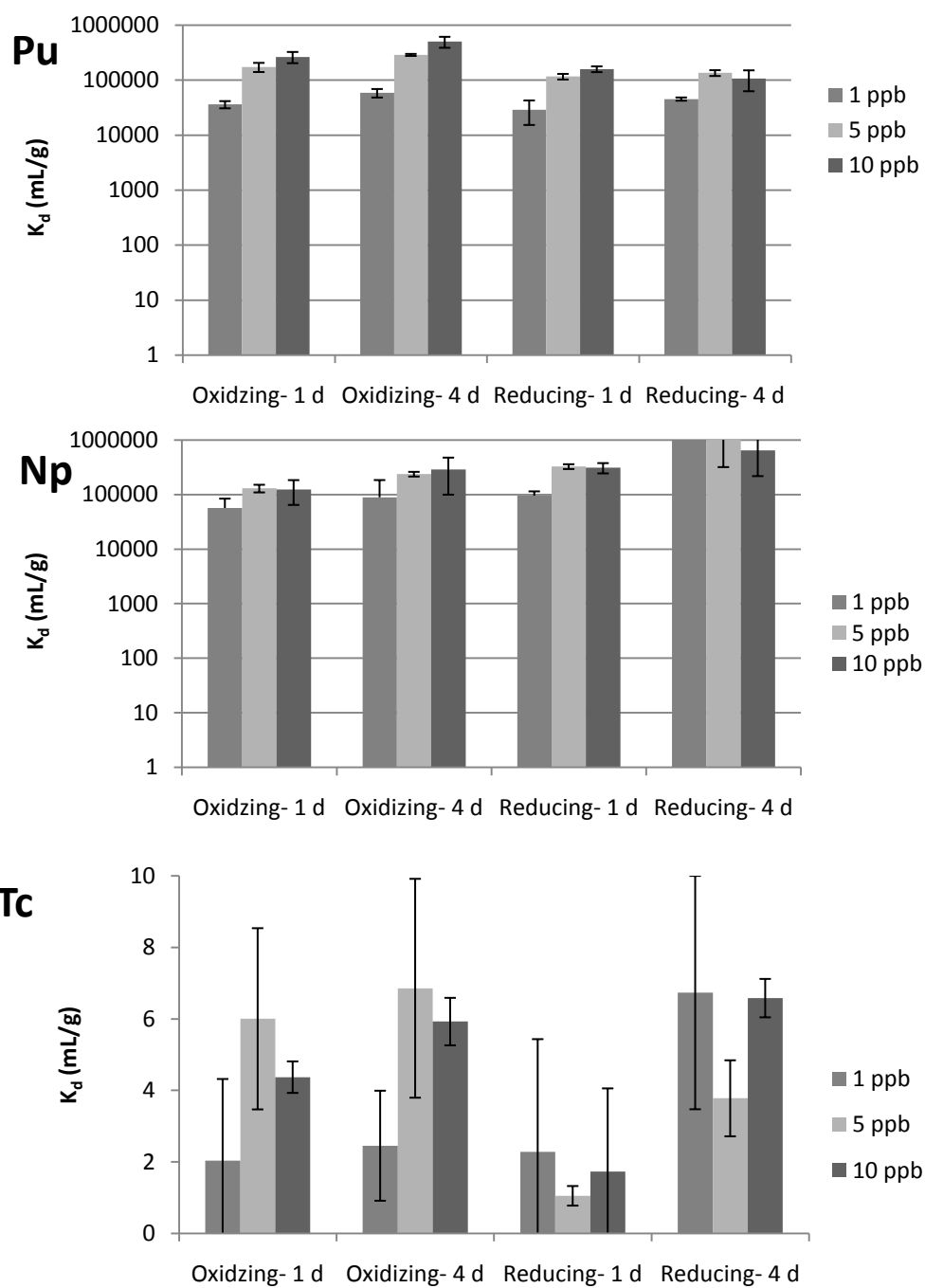


Figure 4.18: Comparison of Tc, Np, and Pu Sorption to Vault 2 Concrete under Oxidizing and Reducing Conditions.

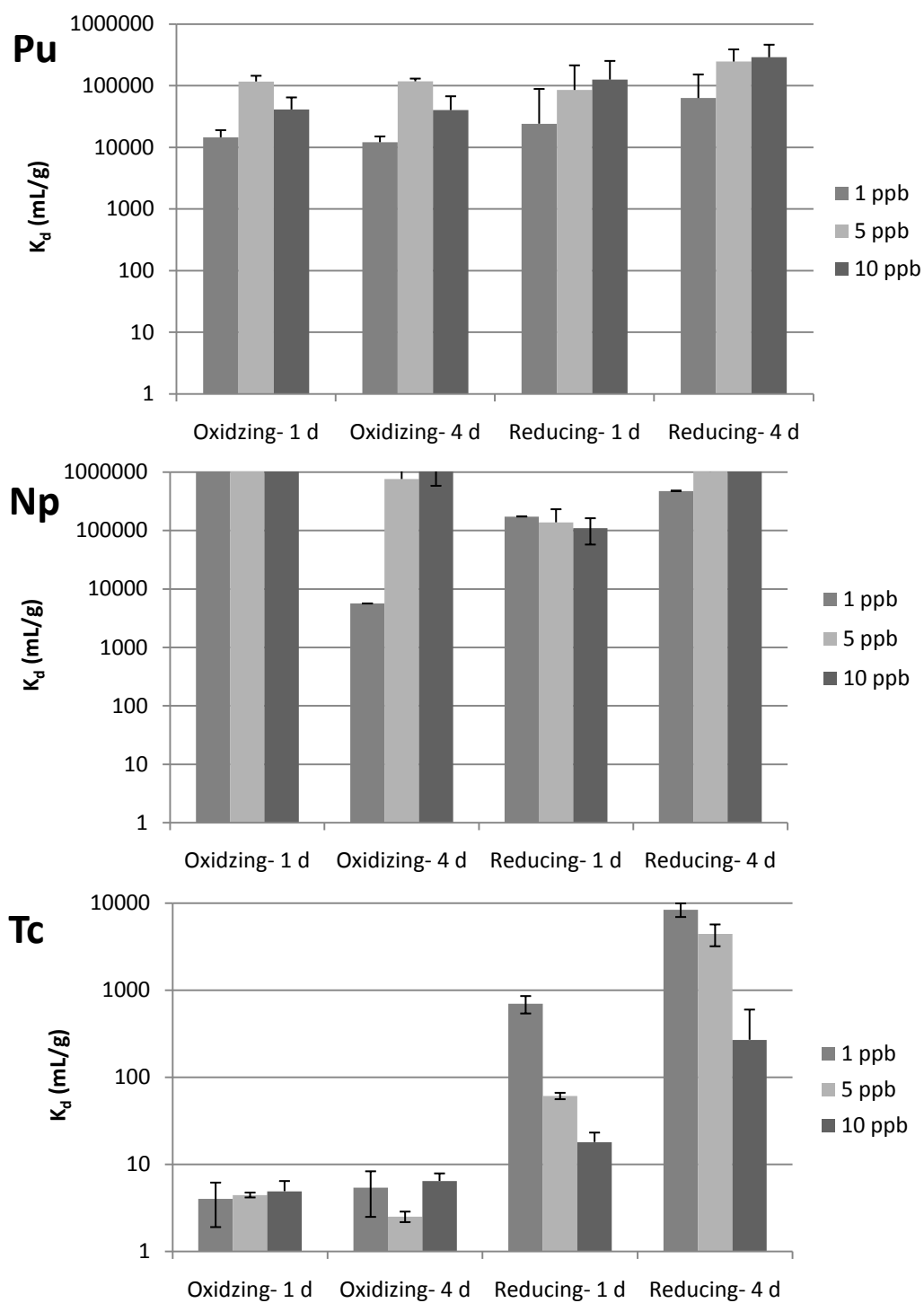


Figure 4.19: Comparison of Tc, Np, and Pu Sorption to TR 545 Saltstone under Oxidizing and Reducing Conditions.

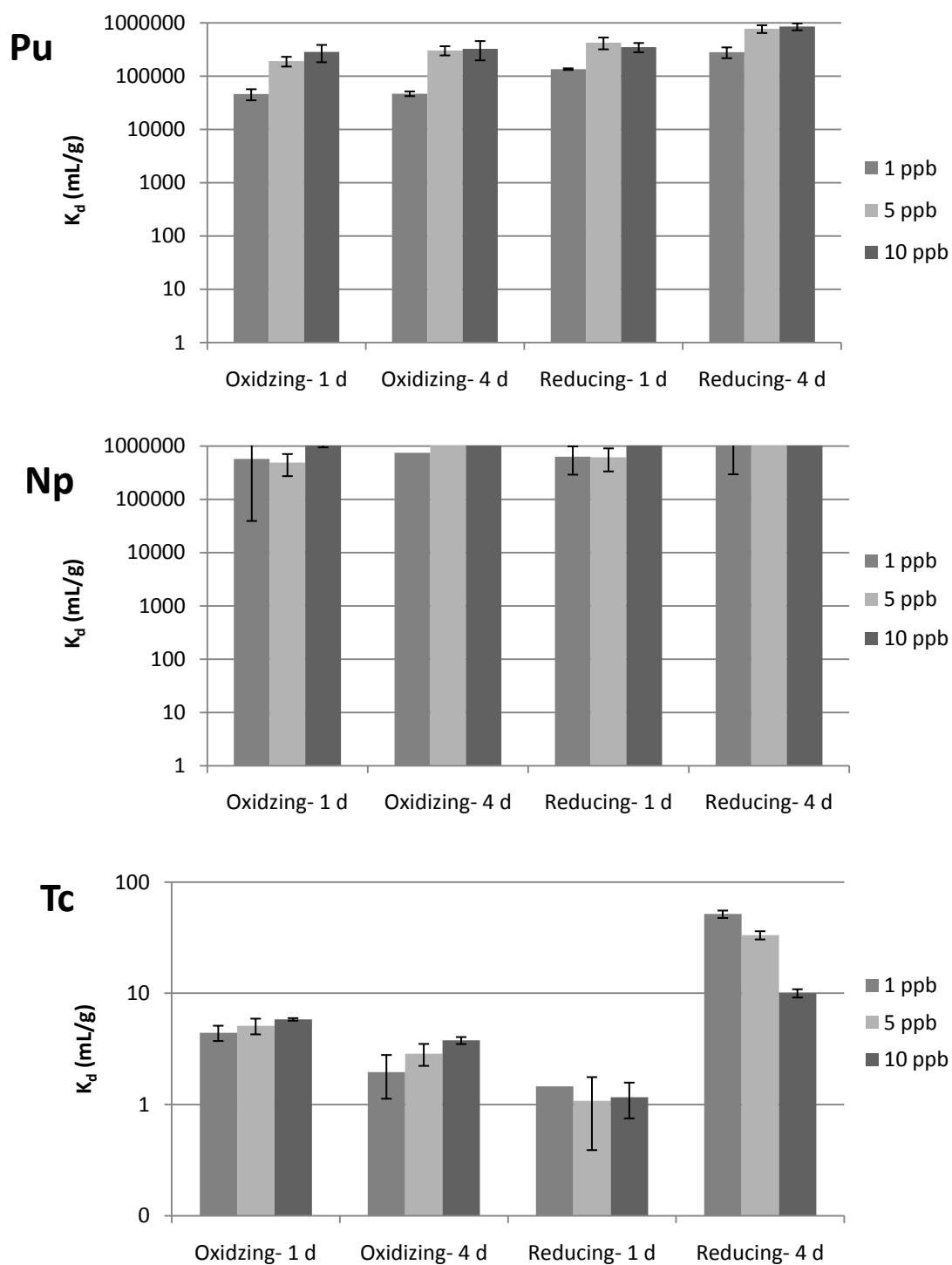


Figure 4.20: Comparison of Tc, Np, and Pu sorption to TR 547 Saltstone under Oxidizing and Reducing Conditions.

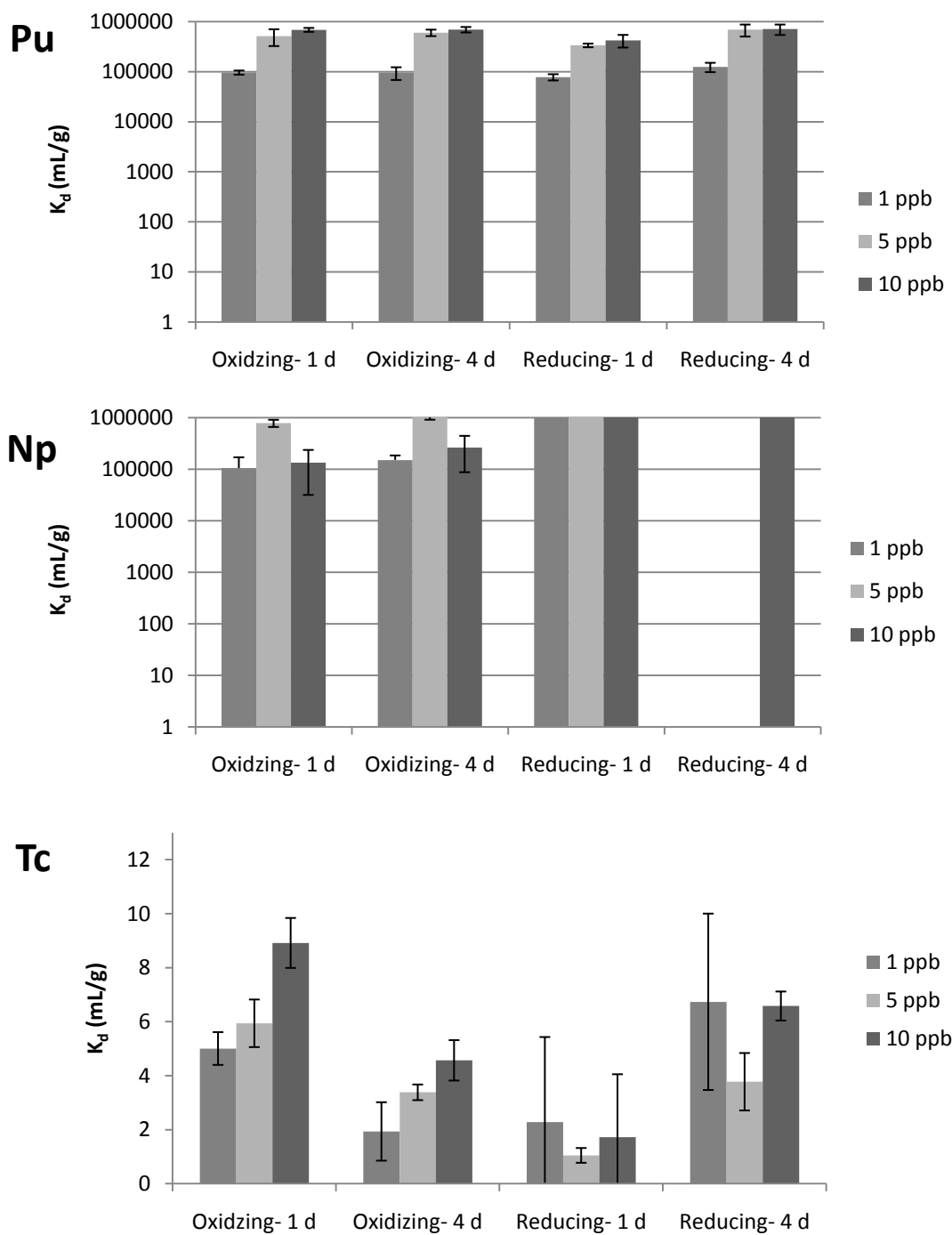


Figure 4.21: Comparison of Tc, Np, and Pu Sorption to Aged Cement under Oxidizing and Reducing Conditions.

In an effort to summarize all of the available data, the following tables are provided which report either the average solubility (for Np and Pu) or average K_d (for Tc)

determined under both oxidizing and reducing conditions for each engineered solid. 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 4.2. Under oxidizing conditions, the solubilities associated with the aged cement (0% slag), Vault 2 concrete (17% slag), and TR547 (45% 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% 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 solubilities are slightly lower than under oxidizing conditions. In this set of samples, the Vault 2 concrete with 17% reducing slag had the highest solubility, but once again when considering the standard deviation, the values are similar.

Table 4.2: Comparison of plutonium solubilities under oxidizing and reducing conditions.

Solid	Oxidizing Aqueous Concentrati on (M)	Std. Dev	# of Replicates	Reducing Aqueous Concentrati on (M)	Std. Dev	# of Replicates
Aged cement	2.08×10^{-12}	5.65×10^{-13}	9	1.71×10^{-12}	6.61×10^{-13}	9
Vault 2 concrete	3.35×10^{-12}	6.71×10^{-13}	9	9.60×10^{-12}	8.08×10^{-12}	9
TR547	4.09×10^{-12}	1.54×10^{-12}	8	1.07×10^{-12}	5.75×10^{-13}	9
TR545	3.12×10^{-11}	4.14×10^{-11}	9	3.44×10^{-12}	1.44×10^{-12}	9

Table 4.3 lists the solubilities of Np in the presence of each engineered solid under both oxidizing and reducing conditions. Under oxidizing conditions, the saltstone

formulation does not appear to have a dramatic effect on the solubility. The solubilities are similar to those of Pu under similar conditions, except their 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 4.3: Comparison of neptunium solubilities under oxidizing and reducing conditions.

Solid	Oxidizing Aqueous Concentration (M)	Std. Dev	# of Rep- licates	Reducing Aqueous Concentration (M)	Std. Dev	# of Rep- licates
Aged cement	3.49×10^{-12}	5.06×10^{-12}	9	4.24×10^{-13}	1.39×10^{-13}	3
Vault 2 concrete	4.62×10^{-12}	5.10×10^{-12}	9	1.43×10^{-12}	1.84×10^{-12}	9
TR547	5.34×10^{-13}	2.40×10^{-13}	6	4.07×10^{-13}	2.98×10^{-13}	7
TR545	6.80×10^{-12}	1.09×10^{-11}	6	7.80×10^{-13}	4.22×10^{-13}	7

Unlike the solubilities of Pu and Np, the aqueous/atmospheric conditions and saltstone formulation seem to have an effect on the Tc K_d values as seen in Table 4.4. Under oxidizing conditions, there is not a discernible difference between the different engineered solids, 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 solids with the least amount of reducing slag (aged cement and Vault 2 concrete) had K_d values which were similar to those observed under oxidizing conditions. However, the TR547 (45% slag) increased by almost an order of magnitude, while the TR545 (90% slag) increased by about 3 orders of magnitude.

Although the respective standard deviations are large, the higher K_d values do appear to be significant.

Table 4.4: Comparison of technetium K_d values under oxidizing and reducing conditions.

<u>Solid</u>	Oxidizing K_d (mL/g)	Std. Dev	#of Replicates	Reducing K_d (mL/g)	Std. Dev	# of Replicates
Aged cement	3.30	1.33	9	5.57	2.03	8
Vault 2 concrete	5.08	2.66	9	5.569	2.03	8
TR547	2.75	0.948	8	3.16×10^1	1.82×10^1	9
TR545	4.77	2.39	9	4.37×10^3	3.66×10^3	9

Summary of Short-Term Sorption Studies

The increased sensitivity of the ICP-MS over conventional low-energy gamma spectroscopy or liquid scintillation counting (LSC) analysis allowed for determination of K_d values and solubilities at significantly lower concentrations 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). For example, a ^{237}Np sample with 1 cpm/mL approximately represents a 6.40×10^{-1} ppb detection limit, which is significantly higher than that of the ICP-MS. Therefore, the reported K_d values based on LSC may only be reliably reported up for a K_d of 10^3 to 10^4 (mL/g). This is believed to be the difference between the observed K_d values for ^{237}Np of $> 10^5$ (mL/g) observed in this work when compared with the K_d values between 3,000 (mL/g) and

4,000 (mL/g) reported by Kaplan *et al.*, (2008). A similar observation was made for Pu since ^{242}Pu was used for ICP-MS analysis and ^{238}Pu was used in the work of Kaplan *et al.* (2008). This may account for the different K_d value of $>10,000$ (mL/g) reported in Kaplan *et al.* (2008) compared with the value of $>10^4$ (mL/g) 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 concrete 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. Kaplan *et al.*, (2008) also suggest some formulations have a Tc K_d of around 5000 (mL/g), which is significantly higher than those observed in this work (even with TR545 under reducing conditions). It is important to note that although similar engineered solids were used in Kaplan *et al.* (2008), only the Vault 2 concrete formulation was the exact same as in the above experiments.

Based on the above results, sorption of Np and Pu appear to reach a steady state within the 4 day equilibration which was previously used as the standard method (Kaplan *et al.*, 2008). However, the Tc data indicate that steady state sorption was not reached. Therefore, additional studies were undertaken to examine sorption of Tc under extended time periods.

TECHNETIUM AND IODINE LONG TERM SORPTION EXPERIMENTS

Technetium and Iodine Long Term Sorption under Oxidizing Conditions

After performing the initial studies above, it was obvious a few problems needed to be addressed. The first being, that while ^{237}Np and ^{242}Pu appeared to reach equilibrium

within the first 24 hours in both oxidizing and reducing conditions, this was not the case for ^{99}Tc , especially under reducing conditions. In reducing conditions, the TR547 (45% slag) and TR545 (90%) showed a dramatic increase in K_d s from 24 hours to 4 days. The second problem, which was addressed above, was the fact there was not a set of reliable internal standards for use with the ^{127}I samples. Therefore, it was necessary to perform a new experiment that would allow the K_d s to be monitored over a longer sampling period. As stated above, samples were taken at 1, 4, 8, 22, and 56 days.

A plot of the Tc K_d values for each engineered solid over the extended sampling period under oxidizing conditions is shown in Figure 4.22. These K_d values were calculated using triplicate samples with initial aqueous Tc concentrations of 5 and 10 ppb. As expected, there is little to no sorption. The negative K_d values shown in the figure are a result of slightly greater than 100% recovery of the aqueous Tc concentration measured in the samples. It would have been possible to correct this data in a scientifically accepted fashion based on the similar >100% recovery for the no-solid control data (shown below). However, stock solutions were measured throughout these experiments, so the known stock solution concentration was used and the data were not corrected based on the no solid controls, thus providing the negative bias. Also, as previously shown, there is no correlation between the slag content and K_d values. However, the K_d values are all even lower than those shown in the previous experiment (Figure 4.5), where they ranged from 3-9 (mL/g). The reason for this discrepancy between these experiments is not known. However, the 4 day K_d values shown in figure 4.22 resemble those reported by Kaplan *et al.* (2008). They reported a K_d of 0.17 ± 0.01

(mL/g) for ^{99}Tc and the Vault 2 cement, while this experiment produced a K_d of -1.49 ± 0.77 (mL/g) after the same 4 day equilibration time. If the K_d s of the 4, 8, 22, and 56 are averaged, the resulting equilibrium K_d is -0.62 ± 0.85 (mL/g) (24 samples). This further highlights the similarity in the two K_d values, and illustrates there is virtually no sorption in either study. Additionally, the reducing saltstone used by Kaplan *et al.* (2008) which based on reducing equivalents is similar to the TR545 used here, had a K_d of 0.16 ± 0.14 (mL/g). This mirrors the TR545 K_d value of 0.16 ± 0.52 (mL/g). When an average of the 4, 8, 22, and 56 day K_d s are taken, the resulting K_d is 2.8 ± 0.71 (mL/g), once again showing minimal sorption under oxidizing conditions. It is important to note each sampling event in Figure 4.22 illustrates the average K_d of 6 samples (unless otherwise noted) at varying concentrations, where as Kaplan *et al.* (2008) used 2 samples. Kaplan *et al.*, (2008) also used liquid scintillation counting (LSC) as opposed to the ICP-MS used in this experiment.

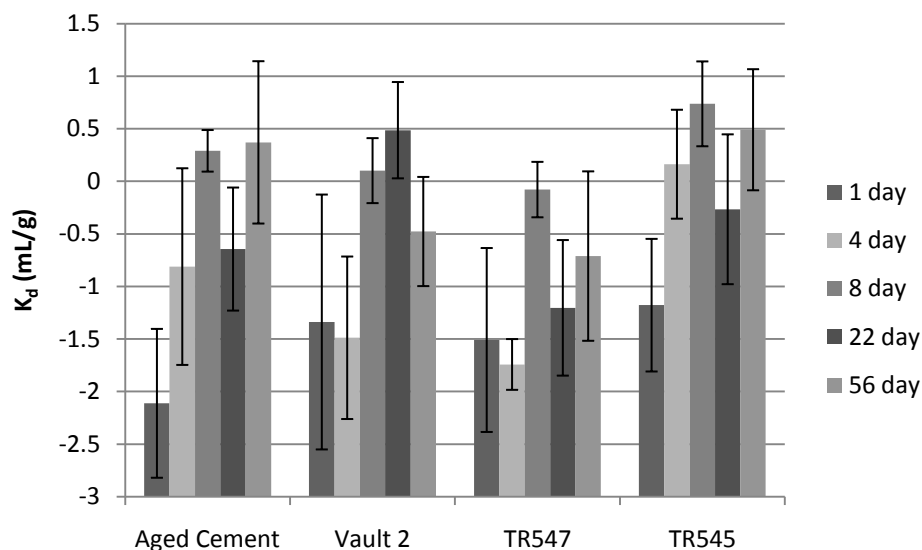


Figure 4.22: Technetium K_d Values under Oxidizing Conditions. Technetium K_d values for various engineered solids measured after one, four, eight, twenty-two, and fifty-six day equilibration under oxidizing conditions. Total technetium concentrations in each system were 10 ppb and 5 ppb with each concentration set up in triplicate. The values expressed are averages of all six samples with the error bars representing the standard deviation, except for the aged cement where $n=5$.

Because there is little to no sorption in these experiments, the K_d values appear to have a negative bias, and appear to have large standard deviations. These negative values represent a slightly greater than 100% mass recovery (less than 105%). An alternate approach is to report the fraction of the Tc remaining in the aqueous phase. These aqueous fractions are reported in Table 4.5. It is important to note the relationship between the Tc fractions in the aqueous phase for the solids and the controls. The controls experience the same increase as the samples, which resulted in the earlier negative K_d values. This table better illustrates the similarity of the K_d values for each saltstone at each sampling period. Looking at Figure 4.22, it appears there is a significant difference between the K_d values for each solid at each sampling event. However, examining the fraction of Tc in the aqueous phases for each, there is only a maximum

difference (including standard deviations) of 2.87 %, 5.04%, 1.61%, 1.73%, and 3.49% for the 1, 4, 8, 22, and 56 day sampling periods respectively. This table also shows there is less than a 5% change for each solid over the entire experiment. Based on these observations, it can be concluded that there is virtually no sorption of Tc to cement, concrete, or saltstone under oxidizing conditions.

Table 4.5: Aqueous fractions of technetium under oxidizing conditions.

	1 Day	4 Day	8 Day	22 Day	56 Day
Aged cement*	1.05 ± 0.0200	1.02 ± 0.0200	0.99 ± 0.0100	1.02 ± 0.0100	0.990 ± 0.0200
Vault 2 concrete	1.03 ± 0.0300	1.04 ± 0.0200	1.00 ± 0.0100	1.02 ± 0.0200	1.01 ± 0.0100
TR547	1.04 ± 0.0200	1.04 ± 0.0100	1.00 ± 0.0100	1.03 ± 0.0200	1.02 ± 0.0200
TR545	1.03 ± 0.0200	0.996 ± 0.0100	0.980 ± 0.0100	1.01 ± 0.0200	0.990 ± 0.0100
Controls	1.05 ± 0.0200	1.03 ± 0.0100	1.00 ± 0.0100	1.02 ± 0.0200	0.990 ± 0.0100

Averages and standard deviations of 6 samples per data set are shown above.

*n=5 for each data set for the solid

Experiments were also setup to monitor the long-term sorption of iodine under similar conditions to the Tc studies above. After analyzing the initial short-term ¹²⁷I data without using any internal standards during ICP-MS analysis, the concentrations of the QA/QC samples were varying up to 20%. However, after some experimentation it was determined that ⁹⁵Mo, ¹¹⁵In, and ¹⁸⁷Re are all suitable internal standards, and were used for this, along with all subsequent ¹²⁷I experiments. Table 4.6 shows a comparison of QA/QC analyses over the course of the engineered and natural solids experiments chosen at random. There is never more than a 10% difference in the QA/QC samples and the standard values, which shows these internal standards are accurate internal standards.

Table 4.6: Comparison of a random selection of QA/QC samples for iodine.

Known Standard Concentration (ppb)	Measured Concentration (ppb)	% difference
100.*	100.	0.000
9.86*	9.44	4.26
494**	513	3.71
4.91**	5.02	2.19
9.83***	9.02	8.24
494***	475	3.84

*Samples from 11/06/2009

**Samples from 4/19/2010

***Samples from 5/11/2010

A plot of the long term I values for each engineered solid under oxidizing conditions is shown in Figure 4.23. These K_d values were calculated using triplicate samples with initial aqueous I concentrations of 50 and 100 ppb. The aged cement shows the highest K_d values with an equilibrium K_d of between 7-9 (mL/g), which is reached around the 4 day sampling period. It appears that for each solid, steady state is reached by the four day mark. Also, as was the case with Tc, there is not a strong correlation between slag content and K_d for the Vault 2 (17% slag) and the TR547 (45% slag). However, there does seem to be an increase in sorption to saltstone TR545 (90%), but the resulting K_d values at equilibrium are still lower than those of the aged cement (0% slag). Also, it does not appear there is a significant change in solids with reducing slag between day 1 and day 8, which suggests they are quickly reaching equilibrium. However, there is an unexplained drop at the 56 day mark.

As was the case with Tc under oxidizing conditions, a table of the fraction of I in the aqueous phase offers another means of showing sorption in these systems. Table 4.7 shows the average fraction of I remaining each system at the given equilibration time. The greatest differences in K_d values from Figure 4.23 is in the aged cement. Table 4.7

shows the greatest difference in K_d values is represented by a drop in I of approximately 20% in the aqueous phase. Also, after the 4 day sampling event, the I fraction in the aqueous phase does not change by more than maximum of 5%, which is another indication that the system is at equilibrium.

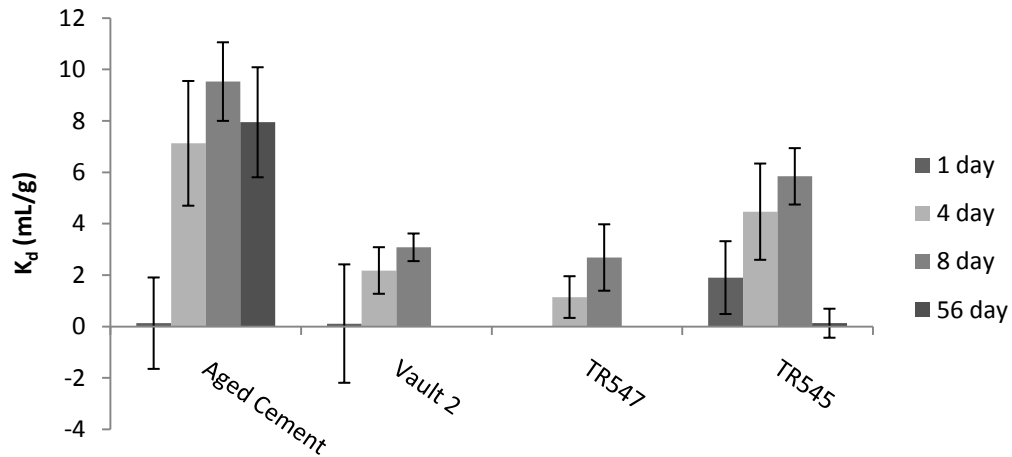


Figure 4.23: Iodide K_d Values under Oxidizing Conditions. Average I K_d values for various engineered systems measured after one, four, eight, and fifty-six day equilibration. Averages based on six total samples with three 100 ppb and three 50 ppb initial concentrations. The error bars represent the total standard deviation in all six samples, except for Vault 2 56 day where $n=5$.

Table 4.7: Aqueous fractions of I under oxidizing conditions.

Solid	1 Day	4 Day	8 Day	56 Day
Aged cement	0.998 ± 0.0423	0.855 ± 0.0433	0.814 ± 0.0248	0.841 ± 0.0381
Vault 2 concrete	1.00 ± 0.0539	0.950 ± 0.0201	0.931 ± 0.0113	$1.05 \pm 0.0200^*$
TR547	1.01 ± 0.0444	0.974 ± 0.0183	0.941 ± 0.0276	1.07 ± 0.0356
TR545	0.958 ± 0.0304	0.906 ± 0.0364	0.874 ± 0.0168	0.997 ± 0.0131

Averages and standard deviations of 6 samples per data set are shown above.

* $n=5$ for the data set

Iodide and Technetium Sorption to Vial Walls under Oxidizing Conditions

During these experiments, control samples containing no solids were also used to track mass recovery. Figure 4.24 shows nearly 100% mass recovery for both ^{127}I and ^{99}Tc throughout the experiment. This means there was virtually no sorption of I or Tc to the vial walls throughout the entire experiment. Therefore, there is little or no competition for sorption between the vial walls and the solids. This is in agreement with the findings of the initial saltstone reports.

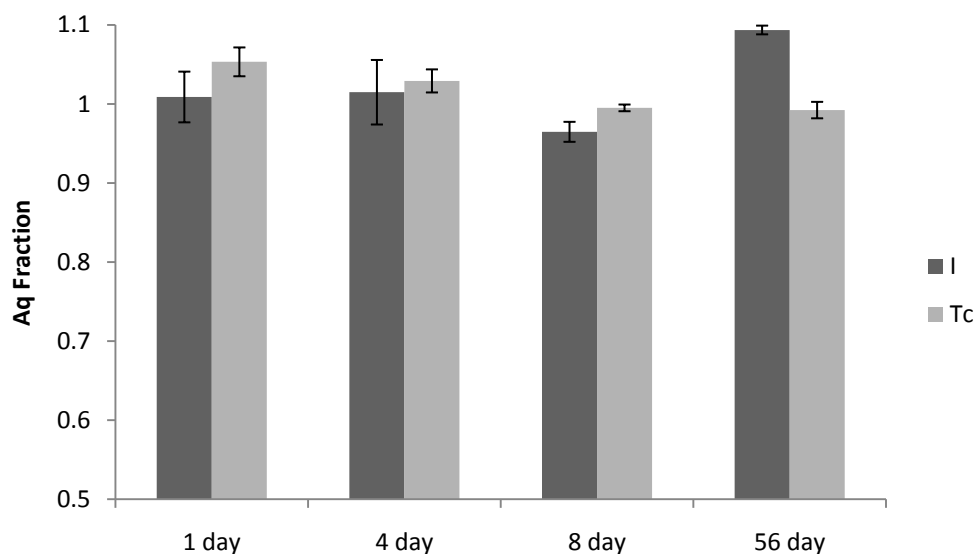


Figure 4.24: Fraction of Iodine and Technetium Remaining in the Aqueous Phase when No Solid Phases Are Present. Each bar represents the average of six samples with varying concentrations. The iodine concentrations are 100 ppb and 50 ppb, and the technetium concentrations are 10 ppb and 5 ppb. The error bars show the standard deviation.

Technetium and Iodine Long Term Sorption under Reducing Conditions

A plot of the Tc K_d values for each engineered solid under reducing conditions is shown in Figure 4.25 (log y-axis). Sorption data after 1 day of equilibration for the aged

cement and Vault 2 concrete are not shown because there was minimal sorption. In the initial study (Figure 4.14) there was also minimal sorption with average K_d values around 1 (mL/g). The 1 day data presented for the TR547 and TR545 saltstones here is also in agreement with those from the initial study as seen in Table 4.8. By the 4 day sampling event, there is agreement between engineered solid with the values found in Figure 4.14. This figure shows a steady increase in K_d values for each solid as was predicted in the initial experiments. Using figure 4.25, it is possible to get an approximate time for K_d values for each engineered solid to reach equilibrium. The values for the aged cement had large ranges for each sampling event, which led to a large standard deviation. Therefore, it is difficult to determine when equilibrium is reached. As for the Vault 2 concrete, a steady increase in K_d values throughout the experimental time frame suggests equilibrium had not been reached by the end of the experiment. There was a significant increase from the 22 day to the 56 day sampling event, which was not seen with the aged cement and saltstones. The TR547 showed steady increases until the 22 day sampling event, where it appears they reach equilibrium. However, for the TR545, there was a large spike in the K_d values at the 22 day mark. When examining the actual ICP-MS data, it shows that the amount of aqueous Tc being measured was around background at the 22 day, so there is more potential for deviation in the measurements. Therefore, this data was not included in Figure 4.25. Also, when calculating the concentration of Tc associated with the TR545 solid phase, there is no significant change from the 8 day to the 56 day sampling event, even for the excluded 22 day data. Therefore, it is most likely reaching equilibrium between the 8 and 22 day marks. Unlike under oxidizing

conditions, the amount of reducing slag has a direct correlation to the amount of Tc sorption. This will be examined in a later section.

Table 4.8: Comparison of 1 and 4 Day TR547 and TR545 K_d values (mL/g) under reducing conditions from initial and long term experiments.

	Initial Experiment		Long Term Experiment	
	Avg 1 Day K_d	Avg. 4 Day K_d	Avg 1 Day K_d	Avg. 4 Day K_d
TR547	-3.45 ± 0.890	24.9 ± 17.0	2.82 ± 1.71	25.4 ± 6.03
TR545	$39.5 \pm 23.9^*$	$4.37 \times 10^3 \pm 3.6 \times 10^3$	52.6 ± 19.9	$3.49 \times 10^3 \pm 1.52 \times 10^3$

Averages are of 9 samples with concentrations of 1, 5, and 10 ppb.

*n=6, no 1 ppb samples were used

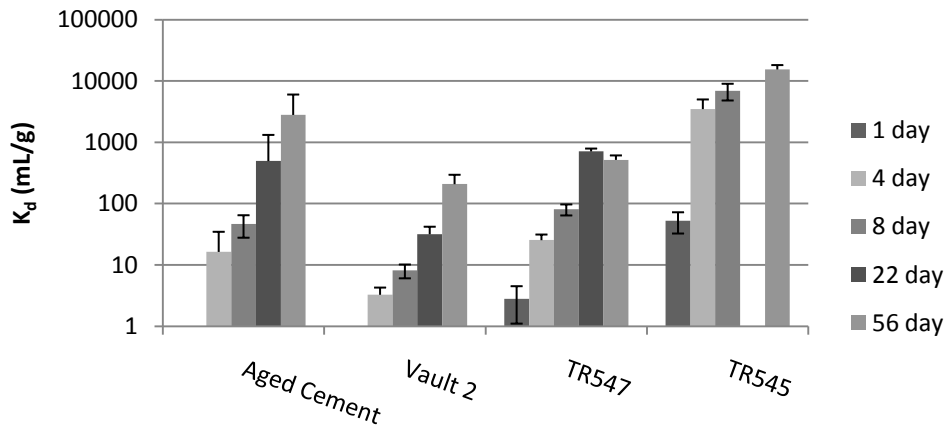


Figure 4.25: Technetium K_d Values under Reducing Conditions. Technetium K_d values for engineered solids measured after one, four, eight, twenty-two, and fifty-six day equilibration under reducing conditions. Total technetium concentrations in each system were 10 ppb and 5 ppb with each concentration set up in triplicate. The values expressed are averages of all six samples with the error bars representing the standard deviation.

Unlike the ^{99}Tc data above, the reducing conditions did not have a noticeable effect on ^{127}I sorption to the engineered solids. Figure 4.26 illustrates the K_d values for each solid at the different sampling events. It shows K_d values less than 5 (mL/g) for each of the solids in the experiment, each with large standard deviations. These large

standard deviations are slightly misleading, and clearer approach to these systems with little sorption is by examining the fraction of iodide remaining in the aqueous phase, as shown in Table 4.9.

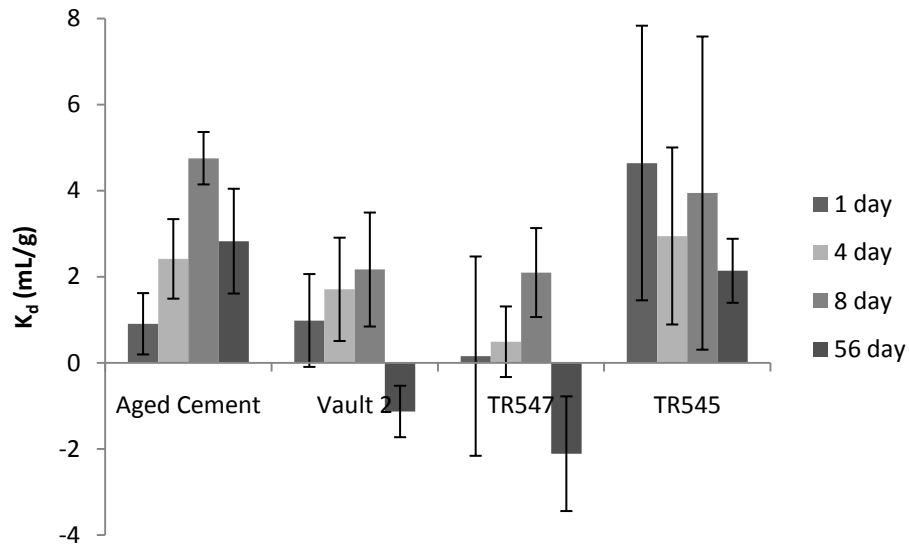


Figure 4.26: Iodide K_d Values under Reducing Conditions. Iodine K_d values for engineered solids measured after one, four, eight, twenty-two, and fifty-six day equilibration under reducing conditions. Total iodide concentrations in each system were 100 ppb and 50 ppb with each concentration set up in triplicate. The values expressed are averages of all samples with the error bars representing the standard deviation. Note $n=6$ except TR547 8 and 56 day where $n=3$, and Vault 2 56 day, TR547 1 and 4 day, and TR545 1 and 56 day where $n=4$, and $n=5$ for Vault 2 4 day.

Table 4.9: Aqueous fraction of iodine under reducing conditions.

	1 Day	4 Day	8 Day	56 Day
Aged cement	0.979 ± 0.0160	0.946 ± 0.0197	0.899 ± 0.0117	0.938 ± 0.0586
Vault 2 concrete	0.978 ± 0.0239	0.962 ± 0.0257	0.952 ± 0.0289	$1.03 \pm 0.0446^{**}$
TR547	$0.998 \pm 0.0522^{**}$	$0.989 \pm 0.0191^{**}$	$0.954 \pm 0.0219^{*}$	$1.05 \pm 0.0754^{*}$
TR545	$0.903 \pm 0.0304^{**}$	0.936 ± 0.0364	0.919 ± 0.0361	$0.952 \pm 0.0152^{*}$

Averages and standard deviations of 6 samples per data set are shown above.

*n=3 for the data set

**n=4 for the data set

Iodine and Technetium Sorption to Vial Walls under Reducing Conditions

A plot of the iodine and technetium in the aqueous fraction of each sample under reducing conditions is found in Figure 4.27. At the 1 day sampling event, there were unexplained inconsistencies with both the Tc and I, which resulted in large standard deviations for each. Also, when analyzing the 22 day iodine samples, there was a problem with the Teflon nebulizer for both the solid free control samples as well as the saltstone and cement samples. Those data were lost and are not reported here. However, at the 4, 8, and 56 day sampling events, there was 100% mass recovery for both the Tc and I. This was also the case for the 22 day Tc samples. This shows there is not any significant sorption to the vial walls, so any loss of mass when solids are present is due to sorption to that particular solid phase.

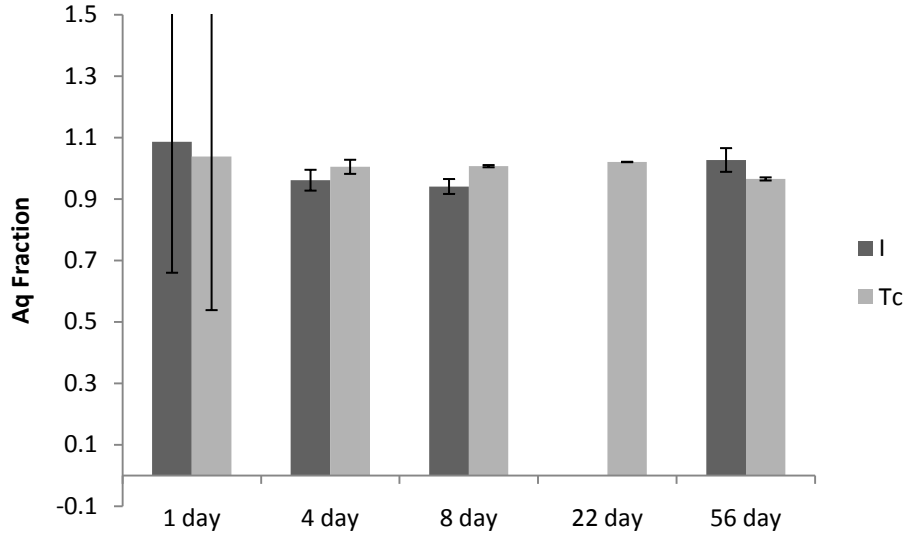


Figure 4.27: Fraction of Tc and I in Aqueous Phase under Reducing Conditions.

Correlation between Slag Content and Sorption of Technetium

As seen in Figure 4.25, there is a correlation between the slag content and the amount of Tc reduction. This correlation was quantified by rearranging the following equation to solve for k' .

$$C(t) = C_0 e^{-k'_{\text{sorption}} t}$$

(equation 4.1)

$C(t)$ = measured concentration

C_0 = initial concentration

k'_{sorption} = pseudo first-order rate constant

Using this equation, k'_{sorption} was calculated for each solid by plotting $\ln(C(t)/C_0)$ vs. time. Then the k'_{sorption} values were used for determine the overall rate constant and reaction order relative to the slag content using:

$$k'_{\text{sorption}} = k_{\text{overall}} * (\% \text{ slag})^n \quad (\text{equation 4.2})$$

A plot of $\log(\% \text{ slag})$ vs. $\log(k')$ is shown in Figure 4.28. Based on equation 4.2 the slope of the line represents the reaction order with respect to slag content and the intercept represents the overall sorption rate constant. This plot confirms the observation that slag content effects the reduction of Tc. The plot shows two significant correlations. The y intercept of -4.2 theoretically represents the sorption rate with zero percent slag. Therefore the addition of slag helps to increase the reaction rate by 4 orders of magnitude. Additionally, the slope of the equation represents n in Equation 4.2 indicating there is approximately a 2nd order dependence on the slag content.

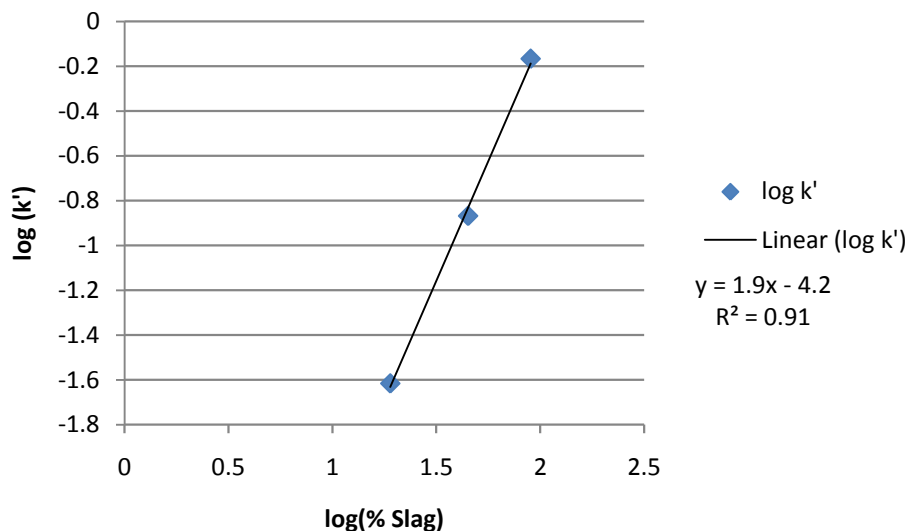


Figure 4.28: Plot of $\log(k')$ vs. $\log(\% \text{ Slag})$

IODIDE AND IODINE SORPTION TO NATURAL SEDIMENTS

The data discussed above for the engineered solids fills knowledge gaps with regard to Pu, Np, Tc, and I behavior in engineered systems. There are still existing knowledge gaps with regard to iodine/iodate behavior in natural systems at the SRS. Therefore iodine and iodate sorption to three representative SRS sediments were studied.

Where the engineered systems were highly buffered with pH's >10, the soils were less buffered, and had more neutral pH's. Two other important differences in these systems are the soils were not initially washed, and a 0.01M NaCl solution was used to add buffering capacity instead of the CaCO₃ solution used for the cements and saltstones.

Redox Conditions for the Natural Sediments

The soil experiments below focus on iodide and iodate sorption to natural sediments. As mentioned above, iodide is expected to experience less sorption than iodate. Therefore, it is important to know what the redox conditions will be like for each soil. Table 4.10 shows the redox conditions for the sediments under oxidizing conditions for single suspensions prepared under similar conditions as the samples used for sorption studies. Under oxidizing conditions, the sandy soil is only slightly more oxidizing than the control. The wetland soil is more oxidizing than the sandy, but less than the clayey.

Table 4.10: E_h measurements for soil sediments under oxidizing conditions.

Sample	1 Day E _h (mV)	4 Day E _h (mV)	8 Day E _h (mV)
Control	219	235	250
Sandy	185	269	276
Clayey	251	294	355
Wetland	267	297	320

However, under anaerobic conditions, this order varies slightly (Table 4.11). The wetland soils become the most reducing. The control and the sandy sediment are a little

more oxidizing, but still have a negative potential. The clayey sediment remains the most oxidizing, and is the only sediment to have a positive potential.

Table 4.11: E_h measurements for soil sediments under reducing conditions.

Sample	1 Day E_h (mV)	4 Day E_h (mV)	8 Day E_h (mV)
Control	78.1	44.2	-39.0
Sandy	102	114	-34.7
Clayey	101	113	44.2
Wetland	105	82.4	-47.6

Sorption of Iodide to Natural Sediments under Oxidizing Conditions

A plot of the K_d values for iodide in natural soils is present in Figure 4.29 (note y-axis is on log scale). The data is then replotted in Figure 4.30 with a standard y-axis configuration. As expected, the sandy soil experienced the least amount of sorption, followed by the clayey, and the wetland had the most sorption. However, what is surprising is at equilibrium, there is not a significant difference in the K_d values between the sandy and clayey soils, especially when taking into account the standard deviations. What is apparent is the sandy soil takes longer to reach equilibrium than either the clayey or wetland, which appear to reach it around the 1st day, while the sandy soil takes 4 days.

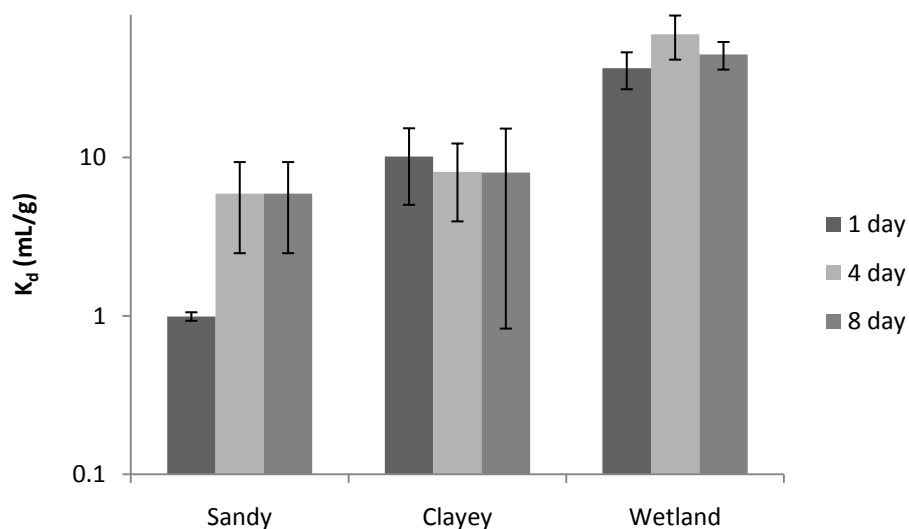


Figure 4.29: Iodide K_d Values for Natural Soils under Oxidizing Conditions. Iodide K_d values measured after 1, 4, and 8 day equilibration times. Represents average K_d values of 6 samples with varying concentrations, except for the 1, and 4 day wetland where $n=5$. The error bars represent the standard deviations. Note the y-axis is on a log scale.

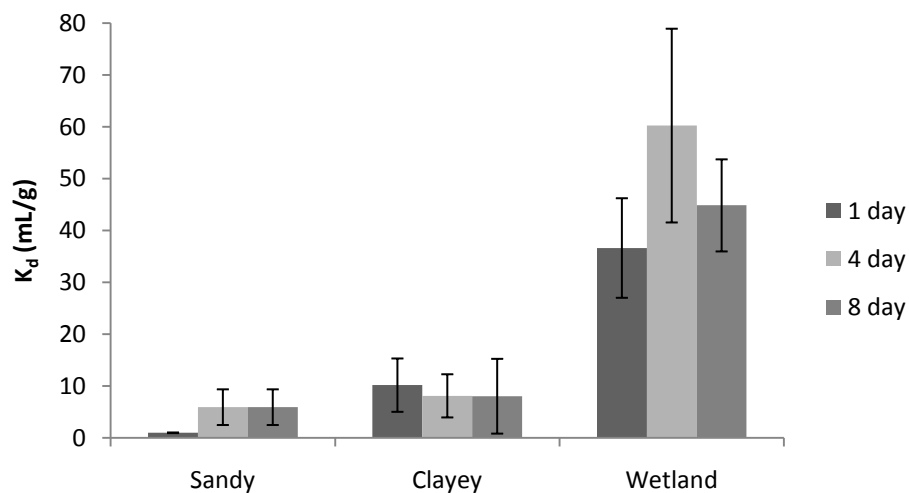


Figure 4.30: Iodide K_d Values for Natural Soils under Oxidizing Conditions. Iodide K_d values measured after 1, 4, and 8 day equilibration times. Represents average K_d values of 6 samples with varying concentrations, except for the 1, and 4 day wetland where $n=5$. The error bars represent the standard deviations.

Iodide Sorption to Vial Walls under Oxidizing Conditions

A set of control samples containing no solids was used to monitor iodide sorption to the vial walls. This data is plotted in Figure 4.31. After 24 hours the average iodide fraction aqueous for 1000ppb triplicate samples is 0.97, suggesting minimal sorption to the vial wall. However, by day 4, the fraction of iodide in the aqueous phase drops to approximately 0.90 with an 8% standard deviation. If this drop is attributable to iodide sorption to the vial wall, it is minimal sorption. It is also reversible as seen by the slightly greater than 100% recovery by day 8. When considering the standard deviations in each set of samples, there is overlap, suggesting the observed changes are likely from natural fluctuations in the data.

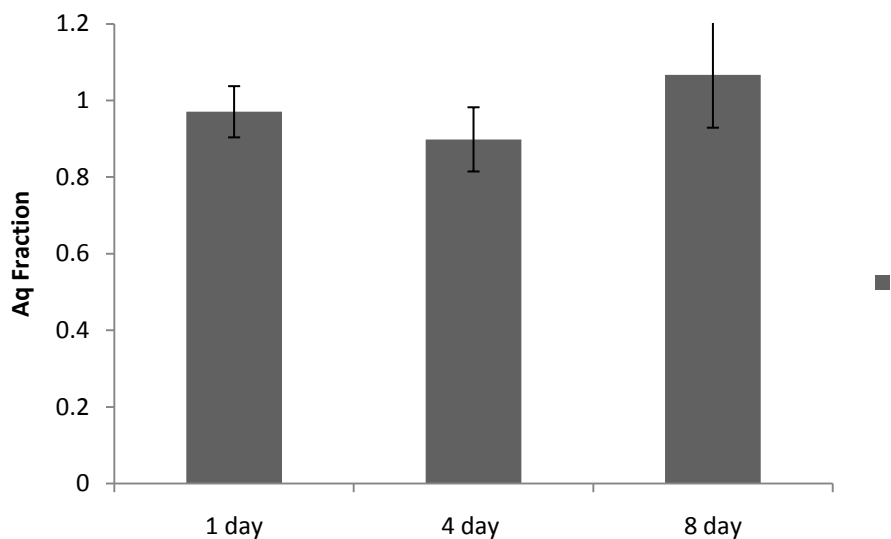


Figure 4.31: Aqueous Fraction of Iodine. Bars represent averages of triplicate 1000ppb samples with the error bars representing the standard deviations.

Iodide Sorption to Natural Sediments under Reducing Conditions

The average iodide K_d values for three natural soils under reducing conditions are plotted below in Figure 4.32. As was the case under oxidizing conditions, there was no sorption to the sandy soil after the 1st day, but equilibrium was reached by day 4 with a $K_d < 10$ (mL/g). There is some initial sorption to the clayey soil, which increases from day 1 to day 4, but drops by the 8 day sampling. As for the wetland soil, there is strong sorption at day 1 with an average K_d value of approximately 20 (mL/g). It appears to have reached equilibrium by day 4, but like the clayey, the K_d values drop on day 8. The seemingly elevated 4 day K_d values correspond with loss of iodine in solid free control sample (presumably due to sorption to vial walls, or an experimental artifact as discussed below and therefore may represent an artificial K_d increase). The drop in the 8 day K_d values could be due to native iodine being released from the soils adding to the aqueous concentration. In an attempt to correct for this, triplicate unamended samples were used to monitor the release of native iodide from the sediments. The resulting average iodide concentrations were 12 ± 1.8 , 24 ± 0.9 , and 34 ± 3.3 ppb at 1, 4, and 8 days respectively. These concentrations were then subtracted out of the measured aqueous concentrations to minimize any effect the native iodine might have. This would have the most significant effect on the 100ppb samples, in which it accounts for up to a third of the spike iodide concentration. It appears the average equilibrium K_d values for each soil coincide with each other when taking into account the standard deviations. Additionally, Table 4.12 shows the equilibrium K_d values for the sandy and clayey soil samples under oxidizing conditions are comparable, especially when taking their respective standard deviations

into account. However, there is a difference between the oxidizing and reducing wetland sediment equilibrium K_d values. Those under oxidizing conditions are approximately 4-5 times greater than the equilibrium K_d s under reducing conditions. These data do not provide any indication as to what mechanism may be responsible for the difference in iodide sorption to the wetland sediment under oxidizing and reducing conditions.

Oxidation of iodide to iodate in the SRS subsurface is actively being studied, and it has been found that under ambient wetland conditions, natural microbes can promote this speciation change (Li *et al.*, 2010). It should be added that these oxidizing microbes are not especially common.

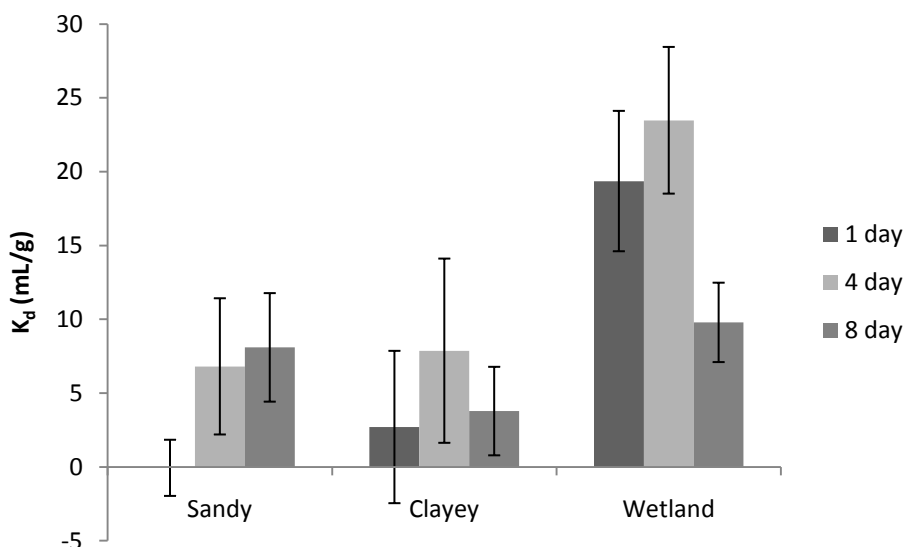


Figure 4.32: Iodide K_d Values for Natural Soils under Reducing Conditions. Iodide K_d values measured after 1, 4, and 8 day equilibration times. Represents average K_d values of 9 samples with varying concentrations, except for the 1 and 4 day clayey, and 1 day wetland where $n=8$, 1 day clayey where $n=7$, and 4 and 8 day sandy, and 4 day wetland where $n=6$. The error bars represent the standard deviations.

Table 4.12: Iodide steady state K_d values determined after 8 days of equilibration.

Soil	Oxidizing	Reducing
Sandy	5.93 ± 3.44	8.09 ± 3.68
Clayey	8.04 ± 7.21	3.78 ± 3.00
Wetland	44.8 ± 8.88	9.79 ± 2.69

As for a comparison with other sediment data, it is difficult to find studies using analogous soils. Kaplan *et al.* (2000) used sediments with the closest composition to the sandy in this study, but their sorption experiments were at a pH slightly above 8, where as these pH's were around 5. They observed K_d values of approximately 1-2 (mL/g) after 7 days, which is lower than observed for the 8 day sandy soil. This is likely due to the differences in pH. At a pH of 5 there should be more positively charged binding sites for the anionic I^- than at a pH of 8. Although K_d values were not calculated, Yamaguchi *et al.* (2006) monitored concentrations of extracted I^- over time. They noted retardation of the spiked I^- with some fraction I^- being more strongly associated with the soils. This conclusion was based on the findings that NO_3^- was able to leach some I^- off the soils, but a retreatment of SO_4^{2-} was able to recover additional I^- .

Iodide Sorption to Vial Walls under Reducing Conditions

A plot of the aqueous iodide fractions for the no-solids controls under reducing conditions is shown in Figure 4.33. There is approximately 100% recovery for the 1 day samples, and over 95% recovery for the 8 day samples. This shows iodide was not sorbing to the vial walls. There is a dip in the recovery of the 4 day samples with only 85% being recovered. This drop could be due to sorption to the vial walls. However, it

appears to be easily reversible as the iodide recovery is 95% for the 8 day samples. It is noteworthy that the drop in aqueous iodide after 4 days is consistent with an increase in the sorption K_d at 4 days. Therefore, there is also a possibility of analytical error but none can be found in these datasets. Based on the good mass balance (95%) in the solid free controls after 8 days, these values are assumed to represent the most realistic K_d values.

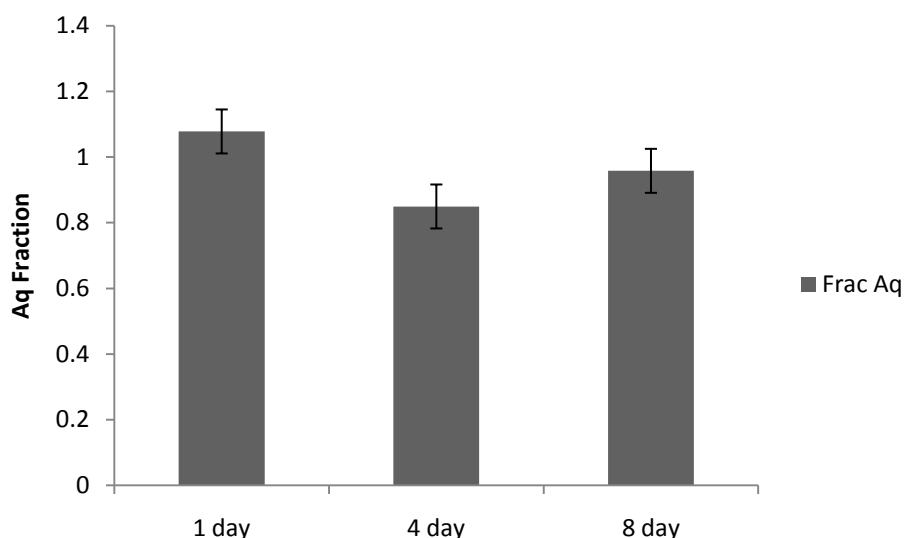


Figure 4.33: Aqueous Fractions of No-Solids Controls under Reducing Conditions. Iodine aqueous fractions above are averages of 6 samples, except for 1 day where $n=3$. The error bars represent the standard deviation in the samples.

Iodate Sorption to Natural Sediments under Oxidizing Conditions

The previous soil experiments were repeated using the oxidized iodate (IO_3^-) instead of iodide (I^-). The results are plotted in Figure 4.34. Under oxidizing conditions, iodate is expected to have a higher degree of sorption to soil sediments than its reduced form iodide (Fox *et al.*, 2010). There was some sorption to the sandy with an equilibrium K_d value of around 5 (mL/g). This was reached by the 1 day sampling event. This value is similar to that of iodide under oxidizing conditions. There was however a noticeable

increase for the clayey and wetland soils. There was a dramatic increase in the amount of sorption to the clayey soil as compared to the sandy. The equilibrium K_d value is just over 40 (mL/g), and like the sandy, steady-state sorption was quickly reached. As was the case when iodide was used, the wetland soil showed the most iodate sorption. However, it took the longest to reach equilibrium with steady increases between each sampling event. It seemed to still be increasing by the 8 day sampling, so there is not a definite equilibrium K_d . At the 8 day event, the average K_d value is around 80 (mL/g) with a large standard deviation.

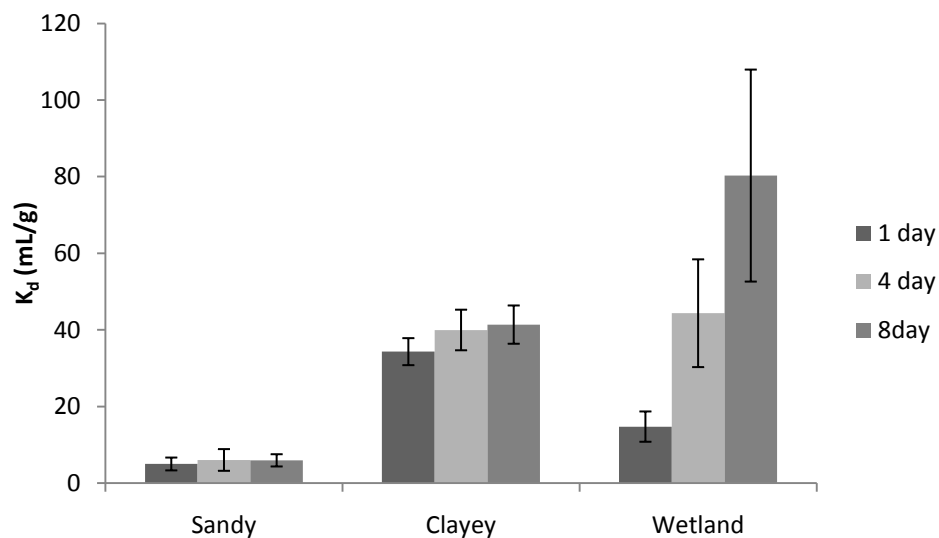


Figure 4.34: Iodate K_d Values for Natural Sediments under Oxidizing Conditions. Iodate K_d values measured after 1, 4, and 8 day equilibration times. The bars represent the average of 9 samples of varying concentrations, except for the following: sandy 4 and 8 day $n=8$, clayey 1,4, and 8 day and the wetland 1 and 4 day $n=6$, and the wetland 4 day $n=5$. The error bars represent the respective standard deviations.

Although the standard deviations seen in Figure 4.34 are small for the sandy and clayey soils, they are large for the wetland soils. This is in large part to the method of calculating K_d values, which can lead to misleadingly large deviations. Another approach

is to report the fraction of the initial iodate remaining in the aqueous phase as reported in Table 4.13. This shows that the large standard deviation in the wetland soil K_d value actually represents about an 11% standard deviation in the fraction of the initial iodate remaining in the aqueous phase. Also the relatively small change in the aqueous fractions for the sandy and clayey soils from the 1 and 8 day sampling events is further evidence equilibrium is reached by the 1 day mark. However, there is a significant and steady decrease in the wetland soil from the 1 to 8 day events, which suggests equilibrium has not been reached by the 4 day sampling event.

Table 4.13: Aqueous fraction of iodate for natural soils under oxidizing conditions.

Soil	1 Day	4 Day	8 Day
Sandy	0.891 ± 0.033	$0.872 \pm 0.051^*$	$0.872 \pm 0.032^*$
Clayey	$0.540 \pm 0.025^{**}$	$0.503 \pm 0.034^{**}$	$0.494 \pm 0.029^{**}$
Wetland	$0.707 \pm 0.098^{**}$	$0.496 \pm 0.078^{***}$	$0.326 \pm 0.113^{**}$

Averages and standard deviations of 9 samples

*n=8 for the data set

**n=6 for the data set

***n=5 for the data set

Iodate Sorption to Natural Sediments under Reducing Conditions

Iodate sorption to the clayey and wetland soils was also examined under reducing conditions using an anaerobic glove box (98% $N_2(g)$ and 2% $H_2(g)$ atmosphere). The resulting average K_d values are plotted in Figure 4.35. There are small increases from the 1 to 8 day, but when considering the standard deviations, there does not appear to be a significant difference. Therefore, steady state appears to be reached by the day 1 sampling event. The resulting K_d values agree with those found under oxidizing

conditions (Figure 4.34), which suggests iodate is not being reduced to iodide. If iodate was being reduced to iodide, the resulting K_d values would be similar to the equilibrium K_d s for iodide in reducing conditions. As for the wetland soil K_d values, there is significant sorption for the 1 day sorption followed by a significant decrease in sorption for the 4 and 8 day samples. This suggests the iodate in the system is being reduced to iodide by day 4. It appears equilibrium is reached around the 4 day mark, and the resulting average equilibrium K_d value at day 8 is in agreement with the equilibrium K_d value of iodide and the wetland soil under reducing conditions seen in Figure 4.32, further supporting the idea of iodate being reduced.

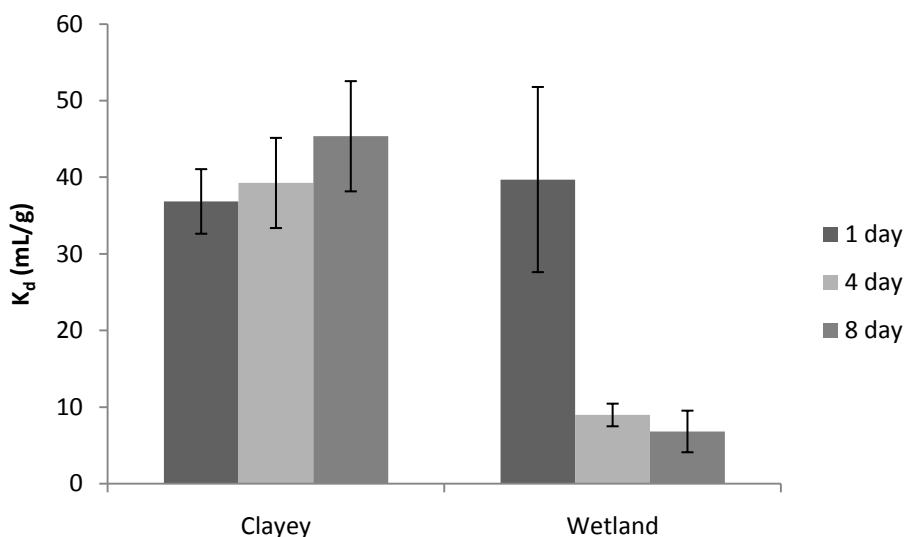


Figure 4.35: Iodate K_d Values for Natural Sediments under Reducing Conditions. Iodate K_d values measured after 1, 4, and 8 day equilibration times. The bars represent the averages of 6 samples except for the wetland 4 and 8 day samples where $n=5$. The error bars represent the standard deviations.

As was the case with many of the iodine experiments, the standard deviations associated with the K_d values of iodate under reducing conditions are large. The aqueous fractions better represent the agreement of the samples, and are found below in Table

4.14. In the case of the clayey soil, there is a decrease of 5% in the iodine fraction from day 1 to day 8, suggesting equilibrium is reached around day 1. However, for the wetland soil, there is an increase in the fraction of aqueous iodine of 35% from day 1 to day 8. This suggests the iodate is being reduced to iodide causing it to desorb. This increase is most significant from day 1 to day 4. From day 4 to day 8 there is an increase of <5% indicating may have reached steady state. It is also important to note that the largest standard deviation is the wetland 1 day of 8.4%, while all the others was <5%.

Table 4.14: Aqueous fraction of iodate for natural soils under reducing conditions.

Soil	1 Day	4 Day	8 Day
Clayey	0.526 ± 0.031	0.511 ± 0.0400	0.476 ± 0.0420
Wetland	0.513 ± 0.084	$0.825 \pm 0.0230^*$	$0.862 \pm 0.0480^*$

Averages and standard deviations of 6 samples

*n=5 for the data set

The iodate equilibrium K_d values for the clayey and wetland sediments under both oxidizing and reducing conditions are shown below in Table 4.15. There is not a discernible difference between the two sets of clayey data. However this is not the case for the wetland soil. These data indicate that the relatively high K_d values observed for the wetland soil under oxidizing conditions may not persist under reducing conditions. This finding has large implications regarding development of conceptual models of iodine biogeochemical behavior.

Table 4.15: Iodate steady-state K_d values (mL/g) after 8 day equilibration.

Soil	Oxidizing	Reducing
Clayey	41.4 ± 4.99	45.3 ± 7.19
Wetland	80.3 ± 27.7	6.82 ± 2.72

Additionally, Table 4.16 shows a comparison of the equilibrium K_d values for iodide and iodate under oxidizing and reducing conditions. For the sandy soil, the oxidation state of iodine nor the redox conditions had any effect on sorption. The oxidation state seems to control the extent of sorption for the clayey soils, with significantly more sorption occurring when iodate is used as opposed to iodide. The wetland sediments appear to be effected by both the redox conditions and oxidation state. Under oxidizing conditions there is twice as much sorption for iodate compared to iodide. However, under reducing conditions, there is a dramatic decrease in sorption. For the iodate samples, it appears under reducing conditions, the iodate is being reduced to iodide with a steady state K_d value of 7 to 10 (mL/g) being reached.

Table 4.16: Iodide and iodate equilibrium K_d values (mL/g).

Soil	Iodide		Iodate	
	Oxidizing	Reducing	Oxidizing	Reducing
Sandy	5.93 ± 3.44	8.09 ± 3.68	5.95 ± 1.60	NA
Clayey	8.04 ± 7.21	3.78 ± 3.00	41.4 ± 4.99	45.3 ± 7.19
Wetland	44.8 ± 8.88	9.79 ± 2.69	80.3 ± 27.7	6.82 ± 2.72

Equilibrium K_d values represent averages and standard deviations of 9 samples after 8 days.

Chapter 5 CONCLUSIONS AND FUTURE WORK

RADIONUCLIDE BEHAVIOR IN ENGINEERED SYSTEMS

The results of the studies with engineered solids (cement, concrete, and saltstone) confirmed the behavior of Np and Pu seen in prior sorption experiments. However, the lower detection limits of the ICP-MS over LSC allowed for more accurate sorption coefficients to be calculated, resulting in accepted K_d values two orders of magnitude greater than those found by Kaplan et al. (2008). The data suggest that even aged cement without any reducing slag, and exposed to the atmosphere appeared to reduce Np(V) to Np(IV), resulting in K_d values of $>10^5$ (mL/g). Similar to Np, Pu had K_d values of $>10^4$ (mL/g), which suggests these engineered solids were able to keep the spiked Pu(IV) in this reduced state, even when exposed to the atmosphere. These observations are consistent with those of Zhao et al. (2000) and Wang et al. (2009) who observed Np(V) reduction to Np(IV) and Pu(V) reduction to Pu(IV) using X-ray Absorption Spectroscopy. The K_d values under oxidizing and reducing conditions were similar indicating the reactions are likely driven by the surface and the aqueous redox conditions have little impact on the degree of sorption. Under each condition, these high K_d values were reached within after 24 hours, and remained constant suggesting each system quickly reached equilibrium. Also, with these high sorption values for both Np and Pu to cement and all three saltstones, it was not possible to determine how much effect the reducing slag had on sorption. The observation of a constant aqueous concentration of both Np and Pu in all systems indicates that these are likely solubility controlled and should be treated as such in performance assessments.

Iodine did not experience high sorption values like Pu and Np, nor did it reach equilibrium quickly. Under oxidizing conditions, it took approximately 8 days for each sample to reach equilibrium. Under oxidizing conditions, iodide had equilibrium K_d values ranging from 2-10 (mL/g), and between 2-5 (mL/g) for reducing conditions. There was no direct correlation between these K_d values and the amount of reducing slag. However, in each case the engineered solids appeared to maintain iodine in the reduced iodide state.

Both redox conditions and reducing slag content effected Tc sorption. Under oxidizing conditions the Tc appeared to remain as TcO_4^- , resulting in little sorption for any of the solids. However, under reducing conditions, the Tc(VII) was reduced to Tc(IV) , and showed a higher sorption affinity for the solid phases. K_d values ranged from 100 to 10,000 (mL/g). Additionally, there was a noticeable trend in the amount of reducing slag, and degree of sorption. It was determined reducing slag increased the reaction rate by 4 orders of magnitude, and there is a 2nd order dependence on the slag content.

IODINE BEHAVIOR IN NATURAL SYSTEMS

K_d values for both iodide and iodate were determined for natural end member sediments from the Savannah River Site. Under oxidizing conditions, iodide exhibited minimal sorption to both sandy and clayey soils. Equilibrium was reached by day 1 for the clayey soil, and day 4 for the sandy. In each case, the equilibrium K_d was approximately 10 (mL/g). When iodide was spiked in with the wetland soil under oxidizing conditions, it experienced much greater sorption than for either the sandy or

clayey. It had an equilibrium K_d of approximately 50 (mL/g), which is 5 times that of either the sandy or clayey.

When these experiments were repeated under reducing conditions, similar results were seen for the sandy and clayey soils. They each reached equilibrium by the 8 day sampling period, and each had a K_d value of around 8 (mL/g). This is similar to the K_d values of 10 (mL/g) each had under oxidizing conditions. However, the wetland soil showed a different behavior. There was a high degree of initial sorption with K_d values of 20 and 25 (mL/g) at the 1 day and 4 day sampling events, respectively. By the 8th day, the K_d values dropped to 10 (mL/g), which is equal to those of the sandy and clayey soils. It appears the reducing conditions altered the wetland soil in some way that hindered the iodide's ability to sorb to the soil.

Spiking iodate into these soil samples produced significantly different results than iodide. Under oxidizing conditions, there was little difference in the sandy soil. It reached equilibrium by the 1st day, and had a K_d of approximately 10 (mL/g). When the clayey soil was used, there was a dramatic jump in K_d values. Steady state was approached at day 1, but not actually reached until day 4 with a K_d of about 50 (mL/g). Again, the wetland soil had the highest equilibrium K_d values of any soil under oxidizing conditions. The K_d values steadily increased until day 8, where they reached 80 (mL/g). Because there was a noticeable increase between each sampling period, it is not possible to confirm this was the equilibrium K_d value.

Only the clayey and wetland soils were examined for iodate sorption under reducing conditions. The iodate in the clayey systems behaved similarly under the reducing conditions as it did under oxidizing conditions. The measured K_d after 8 days was approximately 45 (mL/g), which is close to the 50 (mL/g) from oxidizing conditions. However, there was a dramatic change with the wetland soil. Like iodide under reducing conditions, there was a high degree of initial sorption with a 1 day K_d of 40 (mL/g), but this quickly reduced down until an equilibrium K_d of about 8 (mL/g) reached at the 8 day sampling event. This suggests the iodate was reduced to iodide in the wetland soil. Therefore, regardless of the initial oxidation state of iodine in reducing wetland soil, an equilibrium K_d of 8-10 (mL/g) can be expected.

FUTURE WORK

This project was designed to examine knowledge gaps in the understanding of redox active radionuclides to support performance assessments at the SRS. Therefore, the work was necessarily broad reaching. Due to the breadth of knowledge required to fully understand redox active radionuclide geochemical behavior, there remain knowledge gaps should be addressed by future work. As was alluded to earlier in this document, experiments should be performed examining Pu solubility in calcite in this high pH range. It would also be beneficial to determine the aqueous and solid phase speciation of both the Pu and Np found in the aqueous phases of these systems.

Additionally, in the experiments examining Pu sorption to engineered solids, Pu(IV) was used as the initial oxidation state. This reduced form is expected to show

strong sorption affinity for these solids. It would be beneficial to use Pu(V), and monitor the K_d values over time. Although unlikely, it might reveal a correlation similar to that seen with Tc, where the amount of reducing slag affects the reaction rate. Some X-ray Absorption Spectroscopy (XAS) measurements should also be performed that could possibly confirm Np(V) reduction to Np(IV) sorption and reduction on engineered solids. This method should also be used to examine the reduction of Tc(VII) to Tc(IV) by these same engineered solids. These measurements will also yield vital information regarding the local chemical environment at the solid-water interface.

As for the studies of iodine sorption to natural sediments, it would be beneficial to develop a better understanding of the specific mechanisms involved between iodine and iodate and the sediments, especially the wetland soil. More work should be done examining the change in the wetland soil chemistry between oxidizing and reducing conditions. Because the wetland soil is high in both organic and inorganic matter, spectroscopy should be used to understand iodine binding with either inorganic or organic components of the wetland soil. It would also be beneficial to determine if the reoxidation of I^- to IO_3^- is possible by transferring the wetland soil from reducing conditions to highly oxidizing ones. If reoxidation does occur, a reaction mechanism could be determined.

Chapter 6 APPENDICES

APPENDIX A: DATA TABLES FOR ENGINEERED SYSTEMS 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 saltstone 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

Data Tables for No-Solids Controls

Table 6.1: Plutonium 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	10.981	0.589	12.060	0.054
B	10.985	3.624	11.680	0.330
C	10.956	3.667	11.710	0.335
D	1.084	0.224	11.960	0.207
E	1.063	0.218	11.840	0.205
F	1.073	0.187	11.850	0.174
G	10.476	0.245	11.520	0.023
H	0.989	0.054	11.540	0.054

Table 6.2: Plutonium 4 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	10.981	0.278	12.020	0.025
B	10.985	1.180	11.700	0.107
C	10.956	1.149	11.740	0.105
D	1.084	0.062	11.860	0.057
E	1.063	0.052	11.860	0.049
F	1.073	0.045	11.850	0.042
G	10.476	0.272	11.500	0.026
H	0.989	0.056	11.480	0.275

Table 6.3: Neptunium 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	9.690	5.636	12.060	0.582
B	9.847	8.816	11.680	0.895
C	9.749	8.872	11.710	0.910
D	1.154	1.140	11.960	0.987
E	0.998	0.716	11.840	0.717
F	0.973	0.599	11.850	0.615
G	9.761	0.376	11.520	0.039
H	0.983	0.019	11.540	0.019

Table 6.4: Neptunium 4 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	9.690	4.815	12.020	0.497
B	9.847	8.120	11.700	0.825
C	9.749	5.125	11.740	0.526
D	1.154	0.065	11.860	0.056
E	0.998	0.007	11.860	0.007
F	0.973	0.013	11.850	0.013
G	9.761	0.397	11.500	0.041
H	0.983	0.038	11.480	0.039

Table 6.5: Technetium 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	9.970	8.758	12.060	0.878
B	10.358	9.223	11.680	0.890
C	9.756	8.681	11.710	0.890
D	0.991	0.957	11.960	0.966
E	1.001	0.959	11.840	0.958
F	1.000	0.954	11.850	0.954
G	10.157	0.867	11.520	0.085
H	1.001	0.917	11.540	0.916

Table 6.6: Technetium 4 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	9.970	9.681	12.020	0.971
B	10.358	10.397	11.700	1.004
C	9.756	9.652	11.740	0.989
D	0.991	1.048	11.860	1.058
E	1.001	1.047	11.860	1.046
F	1.000	1.027	11.850	1.027
G	10.157	9.612	11.500	0.946
H	1.001	1.001	11.480	0.999

Table 6.7: Iodine 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	1033.097	518.501	12.060	0.502
B	1033.466	727.693	11.680	0.704
C	1035.728	860.014	11.710	0.830
D	99.819	8.483	11.960	0.085
E	98.800	5.447	11.840	0.055
F	99.736	9.041	11.850	0.091
G	1003.615	435.361	11.520	0.434
H	94.863	5.684	11.540	0.060

Table 6.8: Iodine 4 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq
A	1033.10	325.51	12.02	0.32
B	1033.47	652.06	11.70	0.63
C	1035.73	763.73	11.74	0.74
D	99.82	BDL	11.86	NA
E	98.80	BDL	11.86	NA
F	99.74	BDL	11.85	NA
G	1003.62	343.82	11.50	0.34
H	94.86	2.53	11.48	0.03

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Table 6.9: Plutonium 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq	K _d
A	10.6237	0.0017	11.0100	0.0002	257380.6152
B	10.6561	0.0021	11.0500	0.0002	206799.6449
C	10.1480	0.0013	11.0100	0.0001	327843.2967
D	1.0357	0.0014	11.3400	0.0013	30344.2599
E	1.1326	0.0011	11.3500	0.0010	41080.9124
F	1.0055	0.0011	11.4000	0.0011	36860.4488
G	5.3642	0.0012	11.2000	0.0002	178141.9647
H	5.3704	0.0011	11.2300	0.0002	202974.0957
I	5.4943	0.0017	11.2500	0.0003	137974.2851

Table 6.10: Plutonium 4 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq	K _d
A	10.624	0.001	11.090	0.000	381237.316
B	10.656	0.001	11.110	0.000	512147.437
C	10.148	0.001	11.090	0.000	605548.441
D	1.036	0.001	11.260	0.001	53245.049
E	1.133	0.001	11.220	0.001	51934.162
F	1.006	0.001	11.300	0.001	70450.163
G	5.364	0.001	11.190	0.000	301136.734
H	5.370	0.001	11.230	0.000	282939.572
I	5.494	0.001	11.280	0.000	277947.754

Table 6.11: Neptunium 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	pH	Fraction Aq	K _d
A	9.21692635	0.005957077	11.01	0.000646319	65041.88498
B	9.170432784	0.00306662	11.05	0.000334403	123477.5756
C	9.096163751	0.002111663	11.01	0.000232149	184471.9408
D	0.968314926	0.000867507	11.34	0.000895894	45223.52496
E	0.994314793	0.000898163	11.35	0.000903298	44178.52495
F	0.969777681	0.000484972	11.4	0.000500086	80796.95937
G	3.929661216	0.001578688	11.2	0.000401736	98671.71664
H	3.911007939	0.001115352	11.23	0.000285183	145101.4431
I	4.054091025	0.001146601	11.25	0.000282826	147323.3255

Table 6.12: Neptunium 4 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	89862.7263
B	9.1704328	0.0012261	11.11	0.0001337	308879.287
C	9.0961638	0.0008395	11.09	9.229E-05	464093.334
D	0.9683149	0.000481	11.26	0.0004967	81594.7683
E	0.9943148	0.0005631	11.22	0.0005664	70485.8657
F	0.9697777	0.0003397	11.3	0.0003503	115357.04
G	3.9296612	0.000686	11.19	0.0001746	227125.084
H	3.9110079	0.0004796	11.23	0.0001226	337488.396
I	4.054091	0.0011432	11.28	0.000282	147761.077

Table 6.13: Technetium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.413679	9.310939	0.989086	0.458602
B	9.347881	9.573665	1.024154	-0.9818
C	9.238518	9.348823	1.01194	-0.49674
D	4.7291	4.956542	1.048094	-1.89303
E	4.709347	5.021844	1.066357	-2.57745
F	4.847115	5.168154	1.066233	-2.53813

Table 6.14: Technetium 4 days

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.413679	9.643207	1.024382	-0.98924
B	9.347881	9.857623	1.05453	-2.15272
C	9.238518	9.345439	1.011573	-0.48167
D	4.7291	4.870803	1.029964	-1.20018
E	4.709347	5.022484	1.066493	-2.5824
F	4.847115	5.03477	1.038715	-1.52291

Table 6.15: Technetium 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.413679	9.363471	0.994666	0.222859
B	9.347881	9.39899	1.005467	-0.22637
C	9.238518	9.136458	0.988953	0.470293
D	4.7291	4.690584	0.991856	0.338748
E	4.709347	4.743963	1.007351	-0.30224
F	4.847115	4.834511	0.9974	0.106518

Table 6.16: Technetium 22 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.413679	9.68567	1.028893	-1.16711
B	9.347881	9.311572	0.996116	0.162328
C	9.238518	9.417143	1.019335	-0.79857
D	4.7291	4.638026	0.980742	0.810082
E	4.709347	4.87945	1.03612	-1.44394
F	4.847115	5.016617	1.03497	-1.38056

Table 6.17: Technetium 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.413679	9.409122	0.999516	0.020129
B	9.347881	9.582012	1.025047	-1.01722
C	9.238518	9.271839	1.003607	-0.1513
D	4.7291	4.828375	1.020992	-0.84822
E	4.709347	4.82159	1.023834	-0.96422
F	4.847115	4.835824	0.997671	0.0954

Table 6.18: Iodine 1 day

Sample	Initial Conc. (ppb)	Aqueous Conc. (ppb)	Frac. Aq.	K _d
A	101.954113	102.8912	1.009192	-0.37854
B	101.221857	105.3267	1.040553	-1.62244
C	100.197479	103.2204	1.03017	-1.23299
D	50.2974507	52.88655	1.051476	-2.01962
E	50.0840955	46.14485	0.921347	3.535873
F	50.9212015	48.10559	0.944706	2.391497

Table 6.19: Iodine 4 days

Sample	Initial Conc. (ppb)	Aqueous Conc. (ppb)	Frac. Aq.	K _d
A	101.954113	98.50015	0.966122	1.457368
B	101.221857	98.70229	0.975108	1.062692
C	100.197479	96.27147	0.960817	1.716898
D	50.2974507	47.15573	0.937537	2.748526
E	50.0840955	47.08287	0.940076	2.640235
F	50.9212015	46.96707	0.922348	3.439934

Table 6.20: Iodine 8 day

Sample	Initial Conc. (ppb)	Aqueous Conc. (ppb)	Frac. Aq.	K _d
A	101.954113	94.24608	0.924397	3.399138
B	101.221857	93.22185	0.920966	3.572577
C	100.197479	92.99955	0.928163	3.258501
D	50.2974507	47.36221	0.941642	2.556696
E	50.0840955	47.49201	0.948245	2.260667
F	50.9212015	46.97958	0.922594	3.428138

Table 6.21: Iodine 56 day

Sample	Initial Conc. (ppb)	Aqueous Conc. (ppb)	Frac. Aq.	K _d
A	101.954113	108.1067	1.060347	-9.39763
B	101.221857	105.1025	1.038338	-6.14508
C	100.197479	102.6851	1.024828	-4.05783
D	50.2974507	53.6287	1.066231	-10.2025
E	50.0840955	53.6983	1.072163	-11.1135
F	50.9212015	64.86916	1.273913	-34.985

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Table 6.22: Plutonium 1 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	17022.62855
B	10.4436762	0.010478566	11.83	0.001003341	42594.87423
C	10.49080459	0.006700641	11.8	0.000638716	63660.24765
D	1.13124665	0.004242148	12	0.003749977	10734.92351
E	1.174037402	0.003429046	11.99	0.00292073	13453.71126
F	1.101694915	0.002227889	11.98	0.002022238	19403.59276
G	5.448687281	0.002419858	11.86	0.000444118	93896.51471
H	5.342234695	0.001490989	11.88	0.000279095	147892.788
I	5.388454776	0.002074015	11.89	0.0003849	108704.1753

Table 6.23: Plutonium 4 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	39119.2414
C	10.490805	0.0062925	11.85	0.0005998	67791.6115
D	1.1312466	0.0044912	11.97	0.0039702	10137.3384
E	1.1740374	0.0029871	12	0.0025443	15449.7797
F	1.1016949	0.0040505	12.06	0.0036766	10655.0053
G	5.4486873	0.0020968	11.96	0.0003848	108370.37
H	5.3422347	0.0019612	11.96	0.0003671	112422.505
I	5.3884548	0.0017107	11.94	0.0003175	131795.525

Table 6.24: Neptunium 1 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	9980816.931
B	9.352537276	0.000110618	11.83	1.18276E-05	3616812.684
C	9.363541597	7.05331E-05	11.8	7.53273E-06	5401185.78
D	0.993110568	BDL	12	NA	NA
E	0.977247222	3.00794E-05	11.99	3.07797E-05	1280331.438
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	2380003.157
I	4.116819691	0.000110748	11.89	2.69014E-05	1555863.747

Table 6.25: Neptunium 4 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	2067198.95
C	9.3635416	4.119E-05	11.85	4.4E-06	9247818.45
D	0.9931106	BDL	11.97	NA	NA
E	0.9772472	BDL	12	NA	NA
F	0.9624413	0.0066817	12.06	0.0069424	5624.21017
G	4.0591285	0.0003289	11.96	8.103E-05	514827.426
H	4.0651615	0.0025316	11.96	0.0006228	66257.374
I	4.1168197	0.0001018	11.94	2.474E-05	1692126.48

Table 6.26: Technetium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	107.6978	9.479483	1.031597	-1.2944
B	107.0124	9.188399	1.001608	-0.06848
C	107.0898	9.57004	1.036071	-1.47574
D	56.83627	4.787252	1.034542	-1.40656
E	74.1562	4.714151	1.021986	-0.9149
F	980	4.698887	1.046117	-1.90875

Table 6.27: Technetium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	107.6978	9.101694	0.990485	0.405985
B	107.0124	9.252313	1.008575	-0.36278
C	107.0898	9.246482	1.001042	-0.04413
D	56.83627	4.615776	0.997485	0.106198
E	74.1562	4.634784	1.00478	-0.2023
F	980	4.38318	0.975831	1.072405

Table 6.28: Technetium 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	107.6978	8.872037	0.965492	1.510419
B	107.0124	9.071386	0.988852	0.481052
C	107.0898	9.088841	0.983976	0.690295
D	56.83627	4.545458	0.982289	0.759547
E	74.1562	4.572287	0.991231	0.376238
F	980	4.429948	0.986243	0.603972

Table 6.29: Technetium 22 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	107.6978	9.4439	1.027725	-1.14005
B	107.0124	8.933013	0.973768	1.149481
C	107.0898	9.110868	0.98636	0.586148
D	56.83627	4.74019	1.024372	-1.00228
E	74.1562	4.710322	1.021156	-0.88108
F	980	4.519498	1.006179	-0.26591

Table 6.30: Technetium 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	107.6978	9.158601	0.996677	0.140878
B	107.0124	9.196866	1.00253	-0.10771
C	107.0898	8.962506	0.970298	1.297522
D	56.83627	4.624475	0.999365	0.026762
E	74.1562	4.555132	0.987512	0.537828
F	980	4.385661	0.976383	1.047301

Table 6.31: Iodine 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	98.9433125	97.11759	0.981548	0.794451
B	98.4588366	98.68486	1.002296	-0.09773
C	99.357396	95.6425	0.962611	1.6464
D	49.8560101	47.26532	0.948036	2.309051
E	50.2782238	46.9299	0.933404	3.034305
F	48.667993	44.82071	0.920948	3.716601

Table 6.32: Iodine 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	98.9433125	95.45023	0.964696	1.546545
B	98.4588366	89.77737	0.911826	4.126298
C	99.357396	92.23848	0.92835	3.271455
D	49.8560101	44.37285	0.89002	5.205631
E	50.2782238	43.64845	0.868138	6.459686
F	48.667993	42.58672	0.875046	6.182876

Table 6.33: Iodine 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	98.9433125	89.67523	0.906329	4.367657
B	98.4588366	88.73149	0.901204	4.677901
C	99.357396	87.34478	0.879097	5.829618
D	49.8560101	42.79363	0.858345	6.952349
E	50.2782238	43.69571	0.869078	6.406698
F	48.667993	42.05405	0.864101	6.809618

Table 6.34: Iodine 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	98.9433125	99.60453	1.006683	-0.28054
B	98.4588366	99.90146	1.014652	-0.61619
C	99.357396	98.60887	0.992466	0.321759
D	49.8560101	49.5771	0.994406	0.236998
E	50.2782238	49.0864	0.976295	1.032601
F	48.667993	48.59426	0.998485	0.065696

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Table 6.35: Plutonium 1 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	211228.1195
B	10.39943573	0.001770549	11.57	0.000170254	246048.7004
C	10.84651695	0.001127533	11.53	0.000103953	401491.8013
D	1.088686867	0.001201087	11.72	0.001103244	35645.24436
E	1.119673887	0.000783288	11.77	0.000699568	57098.97168
F	1.045722787	0.000914861	11.81	0.00087486	44953.2415
G	5.387981131	0.001444832	11.69	0.000268158	149471.4715
H	5.412748988	0.001143483	11.69	0.000211257	196574.9358
I	5.373948758	0.0010003	11.64	0.000186139	228047.2281

Table 6.36: Plutonium 4 day

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	238313.167
C	10.846517	0.0010788	11.64	9.946E-05	419615.909
D	1.0886869	0.0009131	11.84	0.0008388	46897.7787
E	1.1196739	0.0010624	11.89	0.0009488	42089.2778
F	1.0457228	0.0007967	11.91	0.0007619	51625.8022
G	5.3879811	0.0007915	11.73	0.0001469	272899.276
H	5.412749	0.0008355	11.75	0.0001544	269064.069
I	5.3739488	0.0006103	11.74	0.0001136	373789.244

Table 6.37: Neptunium 1 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	911633.5442
B	9.293228768	0.000260081	11.57	2.7986E-05	1499475.4
C	10.08725504	0.000302018	11.53	2.99405E-05	1397124.908
D	0.952173007	0.00019177	11.72	0.000201403	195460.3297
E	0.992224074	BDL		NA	NA
F	0.967815522	4.02137E-05	11.81	4.1551E-05	947469.8744
G	4.068405786	0.000222282	11.69	5.46361E-05	733698.5891
H	4.09543171	0.000531619	11.69	0.000129808	319915.1761
I	4.017406611	0.000410123	11.64	0.000102086	415780.7192

Table 6.38: Neptunium 4 day

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	1818463.02
C	10.087255	0.0001628	11.64	1.614E-05	2591215.23
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	746037.482
G	4.0684058	0.0001336	11.73	3.284E-05	1220543.97
H	4.0954317	8.151E-05	11.75	1.99E-05	2086795.32
I	4.0174066	0.0001322	11.74	3.292E-05	1289604.84

Table 6.39: Technetium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.2967561	9.74372	1.048077	-1.94912
B	9.2909416	9.613902	1.034761	-1.40604
C	9.3736727	9.426285	1.005613	-0.23392
D	4.737981	4.829725	1.019364	-0.79689
E	4.6151974	4.915264	1.065017	-2.58426
F	4.7100796	4.957526	1.052536	-2.08605

Table 6.40: Technetium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.2967561	9.709913	1.044441	-1.80797
B	9.2909416	9.642097	1.037795	-1.52431
C	9.3736727	9.730805	1.038099	-1.53815
D	4.737981	4.927697	1.040042	-1.61511
E	4.6151974	4.820354	1.044452	-1.80166
F	4.7100796	4.96733	1.054617	-2.16442

Table 6.41: Technetium 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.2967561	9.347268	1.005433	-0.22961
B	9.2909416	9.270959	0.997849	0.090216
C	9.3736727	9.340553	0.996467	0.148604
D	4.737981	4.715428	0.99524	0.200643
E	4.6151974	4.666082	1.011026	-0.46164

Table 6.42: Technetium 22 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.2967561	9.450051	1.016489	-0.68926
B	9.2909416	9.453411	1.017487	-0.71933
C	9.3736727	9.550784	1.018895	-0.77718
D	4.737981	5.010747	1.05757	-2.28365
E	4.6151974	4.804668	1.041054	-1.66933
F	4.7100796	4.835256	1.026576	-1.08196

Table 6.43: Technetium 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.2967561	9.41512	1.012732	-0.53417
B	9.2909416	9.429654	1.01493	-0.6157
C	9.3736727	9.38821	1.001551	-0.06489
D	4.737981	4.965316	1.047981	-1.92071
E	4.6151974	4.76918	1.033364	-1.36676
F	4.7100796	4.683738	0.994407	0.235049

Table 6.44: Iodine 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	100.7259	104.7992	1.040439	-1.6515
B	100.58434	103.292	1.026919	-1.09715
C	102.21106	97.99861	0.958787	1.801495
D	51.251966	50.55584	0.986418	0.577641
E	48.534853	52.35323	1.078673	-3.08746
F	51.744965	50.82861	0.982291	0.753469

Table 6.45: Iodine 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	100.7259	98.17062	0.974631	1.105984
B	100.58434	100.4322	0.998488	0.063386
C	102.21106	100.2982	0.981285	0.7993
D	51.251966	50.38681	0.98312	0.720311
E	48.534853	46.41176	0.956256	1.93645
F	51.744965	49.11602	0.949194	2.237005

Table 6.46: Iodine 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	100.7259	94.80803	0.941248	2.652231
B	100.58434	96.05624	0.954982	1.973043
C	102.21106	94.01491	0.919812	3.653686
D	51.251966	48.02691	0.937075	2.817048
E	48.534853	47.79601	0.984777	0.654375
F	51.744965	46.87116	0.905811	4.345819

Table 6.47: Iodine 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	100.7259	105.8781	1.051151	-2.06765
B	100.58434	107.1094	1.064872	-2.54979
C	102.21106	106.5964	1.042905	-1.72417
D	51.251966	55.51785	1.083234	-3.22343
E	48.534853	55.0445	1.134123	-5.00621
F	51.744965	53.77036	1.039142	-1.57425

Data Tables for Aged Cement

Table 6.48: Plutonium after 1 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	757083.2793
B	10.44676116	0.000712674	11.54	6.82196E-05	634071.0439
C	10.40494422	0.000659215	11.63	6.33559E-05	685779.4584
D	1.069574815	0.000501161	11.81	0.000468561	87438.05867
E	1.119884926	0.000459622	11.82	0.000410419	96118.08152
F	1.132798521	0.000428241	11.84	0.000378038	105626.3913
G	5.494249954	0.000427061	11.7	7.77287E-05	528785.3983
H	5.407466468	0.000325564	11.69	6.02064E-05	699373.561
I	5.3502419	0.000692442	11.7	0.000129423	321010.1874

Table 6.49: Plutonium after 4 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	602873.492
B	10.446761	0.0005881	11.61	5.629E-05	768392.363
C	10.404944	0.0006194	11.61	5.953E-05	729854.938
D	1.0695748	0.0005383	11.84	0.0005033	81398.477
E	1.1198849	0.0005656	11.87	0.000505	78106.958
F	1.1327985	0.0003573	11.88	0.0003154	126606.278
G	5.49425	0.0003353	11.77	6.103E-05	673465.67
H	5.4074665	0.0003576	11.76	6.612E-05	636796.474
I	5.3502419	0.0004411	11.76	8.244E-05	503954.079

Table 6.50: Neptunium after 1 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	54392.87814
B	9.320139831	0.004011335	11.54	0.000430394	100629.7188
C	9.508541493	0.00166325	11.63	0.000174922	248827.9826
D	0.97028876	0.000726172	11.81	0.000748408	54737.49798
E	1.081890779	0.000520905	11.82	0.000481476	81948.95343
F	0.994472941	0.000224317	11.84	0.000225563	177080.3075
G	4.062063373	0.000183026	11.7	4.50574E-05	912048.5958
H	4.091295968	0.000223825	11.69	5.47076E-05	769603.6161
I	4.079362752	0.000254574	11.7	6.24054E-05	665753.7455

Table 6.51: Neptunium after 4 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	101304.158
B	9.3201398	0.0016426	11.61	0.0001762	245800.939
C	9.5085415	0.0009139	11.61	9.611E-05	452897.951
D	0.9702888	0.0002133	11.84	0.0002198	186450.392
E	1.0818908	0.0002982	11.87	0.0002756	143179.339
F	0.9944729	0.0003267	11.88	0.0003285	121583.016
G	4.0620634	0.0001016	11.77	2.501E-05	1642829.78
H	4.091296	0.0001998	11.76	4.884E-05	862107.802
I	4.0793628	8.206E-05	11.76	2.012E-05	2065348.46

Table 6.52: Technetium after 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.231065	9.508229	1.030025	-1.23153
B	9.345782	10.09246	1.079894	-3.07057
C	9.430754	14.14366	1.499738	-13.8422
D	4.75804	5.037843	1.058806	-2.30154
E	4.721899	5.002827	1.059495	-2.3227
F	4.710657	4.904716	1.041196	-1.63248

Table 6.53: Technetium after 4 days

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.231065	9.155713	0.991837	0.347704
B	9.345782	9.471905	1.013495	-0.55264
C	9.430754	13.91791	1.475801	-13.3929
D	4.75804	4.891833	1.028119	-1.13337
E	4.721899	4.782767	1.012891	-0.52641
F	4.710657	4.974894	1.056094	-2.19149

Table 6.54: Technetium after 8 days

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.231065	9.107756	0.986642	0.571996
B	9.345782	9.293403	0.994395	0.233919
C	9.430754	13.76088	1.45915	-13.0717
D	4.75804	4.714967	0.990947	0.37856
E	4.721899	4.696603	0.994643	0.222778
F	4.710657	4.705861	0.998982	0.042048

Table 6.55: Technetium after 22 days

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.231065	9.295252	1.006953	-0.29174
B	9.345782	9.489578	1.015386	-0.62891
C	9.430754	13.77898	1.461069	-13.1091
D	4.75804	4.745366	0.997336	0.110674
E	4.721899	4.846055	1.026294	-1.05972
F	4.710657	4.87038	1.033907	-1.35311

Table 6.56: Technetium after 56 days

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.231065	9.292932	1.006702	-0.28126
B	9.345782	9.112307	0.975018	1.063399
C	9.430754	13.56806	1.438703	-12.6671
D	4.75804	4.618362	0.970644	1.253288
E	4.721899	4.69039	0.993327	0.277867
F	4.710657	4.763941	1.011311	-0.46149

Table 6.57: Iodine after 1 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	46.01017526
B	955.1280827	19.17864389	11.54	0.020079657	2112.282243
C	983.6817804	28.50427319	11.63	0.028977128	1457.908793
D	99.43520802	53.54401206	11.81	0.53848142	35.30200937
E	99.2014285	3.303880468	11.82	0.033304767	1145.599417
F	100.4016064	4.562722289	11.84	0.045444714	839.1728604
G	485.6028999	298.1077404	11.7	0.61389201	26.66130381
H	487.1988025	24.55078723	11.69	0.050391723	794.196478
I	487.7095245	173.01515	11.7	0.354750402	76.38667915

Table 6.58: Iodine after 4 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	51.4894323
B	955.12808	681.3704	11.61	0.7133812	19.1139167
C	983.68178	277.08852	11.61	0.2816851	112.581725
D	99.435208	71.523103	11.84	0.7192935	16.1675784
E	99.201429	67.909668	11.87	0.6845634	18.3571224
F	100.40161	65.826354	11.88	0.6556305	21.1506139
G	485.6029	274.20191	11.77	0.5646628	32.4971254
H	487.1988	185.38966	11.76	0.3805216	69.3719517
I	487.70952	138.93489	11.76	0.2848722	105.113549

APPENDIX B: DATA TABLES FOR ENGINEERED SYSTEMS UNDER REDUCING CONDITIONS

Data Tables for No Solids Controls

Table 6.59: Plutonium 1 day

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

Table 6.60: Plutonium 4 day

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

Table 6.61: Neptunium 1 day

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

Table 6.62: Neptunium 4 day

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

Table 6.63: Technetium 1 day

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

Table 6.64: Technetium 4 day

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

Table 6.65: Iodine 1 day

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

Table 6.66: Iodine 4 day

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

Data Tables for Vault 2

Table 6.67: Plutonium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.4058918	0.002841681	0.000302117	140393.6
B	9.602498	0.002282224	0.00023767	178325.2
C	9.630618675	0.002608744	0.00027088	157169.7
D	4.945396384	0.002082692	0.000421137	100991.1
E	4.964945192	0.001703548	0.000343115	120299.9
F	4.441601383	0.00165649	0.000372949	127140
G	1.079602045	0.001250199	0.001158019	37399.33
H	1.031512133	0.003222175	0.003123739	13179.61
I	0.939293925	0.001224667	0.001303816	36320.54

Table 6.68: Plutonium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.405892	0.007019	0.000746258	56812.06
B	9.602498	0.003294	0.000342992	123554
C	9.630619	0.002936	0.000304893	139631.8
D	4.945396	0.001795	0.000363011	117168.8
E	4.964945	0.001373	0.000276484	149301.5
F	4.441601	0.001516	0.000341219	138967.4
G	1.079602	0.001109	0.001027508	42155.19
H	1.031512	0.000883	0.000855983	48205.76
I	0.939294	0.000978	0.001040992	45502.55

Table 6.69: Neptunium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.425042625	0.001709054	0.000181331	234315.5
B	9.611386476	0.001184125	0.0001232	344614
C	9.579553607	0.001155517	0.000120623	353557
D	4.974000414	0.000672325	0.000135168	315013.7
E	4.916731623	0.000675371	0.000137362	300789.1
F	4.373142817	0.000570681	0.000130497	363682.4
G	0.943366414	0.000389738	0.000413136	104910.4
H	1.011745587	0.000565648	0.000559081	73838.3
I	0.865252712	0.000379545	0.000438653	108057.1

Table 6.70: Neptunium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.425043	0.001341	0.000142314	298567.4
B	9.611386	0.000792	8.23889E-05	515339.4
C	9.579554	0.000363	3.79197E-05	1124764
D	4.974	6.56E-05	1.31798E-05	3231076
E	4.916732	0.000212	4.3111E-05	958475.6
F	4.373143	0.000252	5.75681E-05	824464
G	0.943366	3.55E-05	3.75857E-05	1153591
H	1.011746	3.53E-05	3.49083E-05	1183195
I	0.865253	2.02E-05	2.33004E-05	2035123

Table 6.71: Technetium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.162195	9.086618	0.991751	0.352389
B	9.297909	9.576969	1.030013	-1.22868
C	9.012832	9.306671	1.032602	-1.36454
D	4.502874	4.613602	1.024591	-1.03461
E	4.672443	4.824176	1.032474	-1.31632
F	4.587317	4.671073	1.018258	-0.766

Table 6.72: Technetium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.162195	8.661554	0.945358	2.448878
B	9.297909	8.569827	0.921694	3.582437
C	9.012832	8.145426	0.903759	4.602362
D	4.502874	4.122276	0.915477	3.980045
E	4.672443	4.43415	0.949	2.249079
F	4.587317	4.360596	0.950576	2.221133

Table 6.73: Technetium 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.162195	7.840967	0.855796	7.139124
B	9.297909	7.628733	0.820478	9.226138
C	9.012832	7.24821	0.80421	10.52187
D	4.502874	3.690571	0.819603	9.488192
E	4.672443	4.176449	0.893847	4.970191
F	4.587317	3.950372	0.861151	6.88799

Table 6.74: Technetium 22 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.162195	5.886684	0.642497	23.57464
B	9.297909	4.857892	0.522471	38.53959
C	9.012832	4.323403	0.479694	46.87769
D	4.502874	2.524795	0.560707	33.77354
E	4.672443	3.263597	0.698478	18.06638
F	4.587317	2.737278	0.596706	28.87286

Table 6.75: Technetium 56 Day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.162195	2.425756	0.264757	117.6577
B	9.297909	2.150694	0.231309	140.1292
C	9.012832	0.964628	0.107028	360.588
D	4.502874	0.715814	0.158968	228.0664
E	4.672443	0.701066	0.150043	237.0751
F	4.587317	0.938875	0.204668	166.0075

Data Tables for TR545

Table 6.76: Plutonium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	7.591216275	0.003211762	0.000423089	101443.2
B	7.220544548	0.002476226	0.000342942	136114.3
C	6.931442863	0.002424369	0.000349764	138212.5
D	3.679791021	0.002216217	0.000602267	77895.95
E	3.700656669	0.001909447	0.000515975	88244.83
F	3.870057311	0.001930251	0.000498765	89308.85
G	0.733093687	0.001371053	0.001870229	25202.55
H	0.714539864	0.001661534	0.002325321	19264.46
I	0.72348416	0.001140936	0.001577002	27910.27

Table 6.77: Plutonium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	7.591216	0.001366	0.00017994	238578.8
B	7.220545	0.001296	0.000179541	260034.1
C	6.931443	0.000913	0.000131752	366993.7
D	3.679791	0.000811	0.000220318	213020
E	3.700657	0.001047	0.000282847	161015.5
F	3.870057	0.000474	0.000122483	363814.7
G	0.733094	0.000602	0.000820842	57482.56
H	0.71454	0.000498	0.000697618	64317.62
I	0.723484	0.000479	0.000662029	66545.2

Table 6.78: Neptunium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.407194102	0.008139809	0.008139809	49660.49
B	8.812043306	0.003090249	0.003090249	133291.1
C	8.601491692	0.002857833	0.002857833	145718
D	4.494913172	0.002431822	0.002431822	86780.61
E	4.357753634	0.001442135	0.001442135	137682.1
F	4.723671527	0.000789191	0.000789191	266899.6
G	0.91531421	0.000557461	0.000557461	77501.98
H	0.912530034	0.000387691	0.000387691	105658.7
I	0.908158622	0.000165863	0.000165863	241371.5

Table 6.79: Neptunium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.407194	0.000126	1.33952E-05	3210587
B	8.812043	0.000303	3.4346E-05	1361380
C	8.601492	0.000156	1.81841E-05	2663305
D	4.494913	0.000347	7.72991E-05	607659
E	4.357754	9.06E-05	2.07863E-05	2192696
F	4.723672	0.000207	4.37691E-05	1018911
G	0.915314	9.1E-05	9.9443E-05	474902.3
H	0.91253	BDL	NA	NA
I	0.908159	BDL	NA	NA

Table 6.80: Technetium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.118713	4.519415	0.49562	43.42018
B	9.19847	5.072658	0.551468	34.33779
C	9.190857	4.657739	0.50678	41.62341
D	4.633238	4.579926	0.988494	0.49117
E	4.702229	1.964165	0.417709	58.17986
F	4.726198	1.556302	0.329293	84.44846

Table 6.81: Technetium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.118713	0.267848	0.029373	4049.186
B	9.19847	0.779506	0.084743	1339.684
C	9.190857	0.282394	0.030725	3995.815
D	4.633238	0.07231	0.015607	5188.937
E	4.702229	0.07754	0.01649	4971.515
F	4.726198	0.183833	0.038897	2048.319

Table 6.82: Technetium 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.118713	0.03788	0.004154	10228.26
B	9.19847	0.105277	0.011445	3646.541
C	9.190857	0.057597	0.006267	6781.795
D	4.633238	0.030104	0.006497	6451.963
E	4.702229	0.026448	0.005625	7378.475
F	4.726198	0.027698	0.00586	7033.268

Table 6.83: Technetium 22 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.118713	0.003863	0.000424	100662.2
B	9.19847	0.008568	0.000931	45281.83
C	9.190857	0.013616	0.001482	28825.05
D	4.633238	0.00122	0.000263	160253.2
E	4.702229	-0.00372	-0.00079	-52748.3
F	4.726198	-0.00318	-0.00067	-61599.9

Table 6.84: Technetium 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.118713	0.020159	0.002211	19256.4
C	9.190857	0.025206	0.002743	15551.5
D	4.633238	0.017104	0.003692	11387.91
E	4.702229	0.013004	0.002766	15049.28
F	4.726198	0.012228	0.002587	15983.8

Data Tables for TR547

Table 6.85: Plutonium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	7.331081035	0.001713462	0.000233726	205208.6
B	7.328043805	0.000872426	0.000119053	397817.2
C	7.071427186	0.000766705	0.000108423	443366
D	3.635696803	0.000569848	0.000156737	292607.2
E	3.652534842	0.000393375	0.000107699	427111.1
F	3.684343628	0.000302746	8.21708E-05	549298.4
G	0.743960581	0.000514945	0.000692167	67527.87
H	0.777698097	0.000252938	0.000325239	141399.9
I	0.723194348	0.000177006	0.000244756	195850.5

Table 6.86: Plutonium 4 day

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

Table 6.87: Neptunium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	8.913321113	0.000398128	4.46666E-05	1073986
B	8.957071854	0.00032779	3.65957E-05	1294283
C	8.627854248	0.000337955	3.91703E-05	1227315
D	4.445064053	0.000242059	5.44558E-05	842279.8
E	4.490502056	0.000292509	6.51396E-05	706197.5
F	4.459268715	0.000676132	0.000151624	297665.5
G	0.900219568	4.54363E-05	5.04725E-05	926653.3
H	0.946539946	0.000171998	0.000181712	253122.2
I	0.912956209	6.06879E-05	6.6474E-05	721246.3

Table 6.88: Neptunium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	8.913321	0.000242	2.71084E-05	1769639
B	8.957072	0.000116	1.28974E-05	3672542
C	8.627854	0.000116	1.34188E-05	3582700
D	4.445064	BDL	NA	NA
E	4.490502	6.05E-05	1.3468E-05	3415784
F	4.459269	8.06E-05	1.80709E-05	2497898
G	0.90022	1.52E-05	1.68369E-05	2777954
H	0.94654	6.05E-05	6.39353E-05	719488.7
I	0.912956	BDL	NA	NA

Table 6.89: Technetium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.146366	8.756023	0.957323	1.910938
C	8.952657	8.663511	0.967703	1.465116
D	4.676797	8.823233	1.886597	-19.8465
E	4.702203	4.171611	0.887161	5.274274
F	4.717823	4.441745	0.941482	2.612797

Table 6.90: Technetium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.146366	6.114834	0.668553	21.25126
B	9.079452	6.174735	0.680078	20.431
C	8.952657	3.024322	0.337813	86.05076
D	4.676797	2.87361	0.61444	26.50017
E	4.702203	2.600262	0.552988	33.5204

Table 6.91: Technetium 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.146366	3.326765	0.363725	74.98564
B	9.079452	3.803055	0.418864	60.2572
C	8.952657	1.578151	0.176277	205.1325
D	4.676797	1.435229	0.306883	95.38275
E	4.702203	1.449927	0.308351	93.01372

Table 6.92: Technetium 22 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.146366	0.615178	0.067259	594.451
B	9.079452	0.489882	0.053955	761.5252
C	8.952657	0.373865	0.04176	1007.305
D	4.676797	0.259721	0.055534	718.2297
E	4.702203	0.239313	0.050894	773.313

Table 6.93: Technetium 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.146366	0.815567	0.089168	437.8588
B	9.079452	0.642279	0.07074	570.5289
C	8.952657	0.492876	0.055054	753.4795
D	4.676797	0.410794	0.087837	438.5634
E	4.702203	0.292057	0.062111	626.168

Data Tables for Aged Cement

Table 6.94: Plutonium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.079224621	0.001409021	0.000155192	287217.3
B	8.613004882	0.0008076	9.37652E-05	513144.7
C	8.541919589	0.000863136	0.000101047	468296
D	4.538279014	0.000687826	0.000151561	305169.7
E	4.358905759	0.000552396	0.000126728	361610.9
F	4.450334725	0.000623348	0.000140068	339957.7
G	0.840653709	0.000516994	0.000614991	74433.06
H	0.897570902	0.000450005	0.000501358	90197.31
I	0.921814908	0.000594538	0.000644965	68794.45

Table 6.95: Plutonium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.079225	0.000712	0.000155192	568215.1
B	8.613005	0.000626	9.37652E-05	661726.3
C	8.54192	0.000454	0.000101047	890459.8
D	4.538279	0.000394	0.000151561	533244.6
E	4.358906	0.000314	0.000126728	636801.4
F	4.450335	0.000237	0.000140068	892832.7
G	0.840654	0.00038	0.000614991	101411.9
H	0.897571	0.000344	0.000501358	117954.3
I	0.921815	0.000268	0.000644965	152706.5

Table 6.96: Neptunium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	8.849444124	0.000306309	3.46133E-05	1289533
B	8.447823057	0.000150131	1.77715E-05	2711019
C	8.590597085	0.000199185	2.31864E-05	2044057
D	4.491250244	5.17162E-05	1.15149E-05	4020064
E	4.391894479	2.04591E-05	4.65838E-06	9846089
F	4.210703646	2.04376E-05	4.85374E-06	9816203
G	0.86381524	5.22216E-06	6.04546E-06	7577764
H	0.870501884	BDL	NA	NA
I	0.861953838	BDL	NA	NA

Table 6.97: Neptunium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	8.849444	0.000131	1.48418E-05	3007445
B	8.447823	0.000111	1.31529E-05	3662996
C	8.590597	6.56E-05	7.6328E-06	6209405
D	4.49125	BDL	NA	NA
E	4.391894	BDL	NA	NA
F	4.210704	BDL	NA	NA
G	0.863815	BDL	NA	NA
H	0.870502	BDL	NA	NA
I	0.861954	BDL	NA	NA

Table 6.98: Technetium 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.303697	9.782443	1.051458	-2.05403
B	9.234548	9.754179	1.05627	-2.24439
C	9.262234	9.700336	1.0473	-1.89638
D	9.117056	9.370456	1.027794	-1.15858
E	9.115045	9.941135	1.090629	-3.56298
F	9.180328	9.329044	1.016199	-0.67634

Table 6.99: Technetium 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.303697	4.426438	0.475772	46.24553
B	9.234548	2.545083	0.275605	110.7345
C	9.262234	7.928266	0.855978	7.064873
D	9.117056	8.595493	0.942793	2.599643
E	9.115045	5.995404	0.657748	22.3104
F	9.180328	8.448054	0.920234	3.677551

Table 6.100: Technetium 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.303697	0.505858	0.054372	729.9543
B	9.234548	0.183063	0.019824	2083.11
C	9.262234	7.704433	0.831812	8.490016
D	9.117056	8.366001	0.917621	3.8462
E	9.115045	2.248901	0.246724	130.9074
F	9.180328	7.888982	0.859336	6.944855

Table 6.101: Technetium 22 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.303697	0.068766	0.007391	5636.501
B	9.234548	0.053862	0.005833	7180.972
C	9.262234	6.90808	0.745833	14.30919
D	9.117056	7.973611	0.874582	6.143824
E	9.115045	0.098126	0.010765	3939.979
F	9.180328	7.704491	0.839239	8.127109

Table 6.102: Technetium 56 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	9.303697	3.208575	0.344871	79.72941
B	9.234548	1.903778	0.206158	162.2284
C	9.262234	6.718707	0.725387	15.896
D	9.117056	7.669411	0.841216	8.086831
E	9.115045	3.020248	0.331348	86.52428
F	9.180328	7.374047	0.803244	10.39253

APPENDIX C: DATA TABLES FOR IODINE SORPTION TO NATURAL
SEDIMENTS UNDER OXIDIZING CONDITIONS

Data Tables for Sandy Sediment

Table 6.103: Iodide 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	989.43	882.20	0.89	5.04
B	989.43	744.32	0.75	13.00
C	989.43	725.22	0.73	15.17
D	495.02	448.88	0.91	4.20
E	495.02	369.90	0.75	13.48
F	495.02	539.32	1.09	-3.34
G	94.55	87.27	0.92	3.27
H	94.55	92.64	0.98	0.82
I	94.55	72.13	0.76	12.75
No Spike A	8.57	NA	NA	NA
No Spike B	9.81	NA	NA	NA
No Spike C	10.01	NA	NA	NA

Table 6.104: Iodide 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	989.43	733.92	0.74	14.44
B	989.43	879.90	0.89	4.92
C	989.43	898.33	0.91	4.22
D	495.02	399.00	0.81	9.84
E	495.02	419.55	0.85	7.17
F	495.02	532.44	1.08	-2.85
G	94.55	9.85	0.10	336.91
H	94.55	90.87	0.96	1.61
I	94.55	79.68	0.84	7.66
No Spike A	5.38	NA	NA	NA
No Spike B	5.09	NA	NA	NA
No Spike C	7.33	NA	NA	NA

Table 6.105: Iodide 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	989.43	803.45	0.81	9.60
B	989.43	952.30	0.96	1.54
C	989.43	891.22	0.90	4.59
D	495.02	333.23	0.67	19.86
E	495.02	443.54	0.90	4.63
F	495.02	616.19	1.24	-7.99
G	94.55	1.30	0.01	2808.71
H	94.55	113.82	1.20	-6.74
I	94.55	90.16	0.95	2.00
No Spike A	6.28	NA	NA	NA
No Spike B	26.47	NA	NA	NA
No Spike C	-1.79	NA	NA	NA

Table 6.106: Iodate 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	976.2634	912.7058	0.934897	2.886027
B	978.5878	869.4016	0.888425	5.05035
C	982.0745	882.5475	0.898656	4.672555
D	481.1584	444.7884	0.924412	3.208962
E	481.1584	424.4509	0.882144	5.255035
F	479.4151	438.4474	0.914547	3.870304
G	98.20745	86.13671	0.877089	5.59664
H	95.3019	78.55848	0.824312	8.449937
I	98.78856	86.21404	0.872713	6.012749
No Spike A		17.09743	NA	NA
No Spike B		10.07596	NA	NA
No Spike C		32.47042	NA	NA

Table 6.107: Iodate 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	976.2634	881.149	0.902573	4.473637
B	978.5878	869.0302	0.888045	5.069696
C	982.0745	906.9015	0.923455	3.434421
D	481.1584	425.2543	0.883814	5.159045
E	481.1584	412.984	0.858312	6.493074
F	479.4151	441.236	0.920363	3.584064
G	98.20745	56.53933	0.575713	29.43305
H	95.3019	73.35418	0.769703	11.86224
I	98.78856	82.21607	0.832243	8.309807
No Spike A		16.72397	NA	NA
No Spike B		8.945201	NA	NA
No Spike C		43.98373	NA	NA

Table 6.108: Iodate 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	976.2634	854.9915	0.87578	5.87844
B	978.5878	846.5002	0.865022	6.274933
C	982.0745	861.939	0.877672	5.774928
D	481.1584	417.6883	0.868089	5.963364
E	481.1584	406.1864	0.844184	7.259988
F	479.4151	442.7763	0.923576	3.427502
G	98.20745	62.13334	0.632674	23.18744
H	95.3019	78.26686	0.821252	8.629139
I	98.78856	89.30558	0.904007	4.377496
No Spike A		20.77287	NA	NA
No Spike B		12.28154	NA	NA
No Spike C		NA	NA	NA

Data Tables for Clayey Sediment

Table 6.109: Iodide 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	989.43	882.20	0.89	5.04
B	989.43	744.32	0.75	13.00
C	989.43	725.22	0.73	15.17
D	495.02	448.88	0.91	4.20
E	495.02	369.90	0.75	13.48
F	495.02	539.32	1.09	-3.34
G	94.55	87.27	0.92	3.27
H	94.55	92.64	0.98	0.82
I	94.55	72.13	0.76	12.75
No Spike A		8.57	NA	NA
No Spike B		9.81	NA	NA
No Spike C		10.01	NA	NA

Table 6.110: Iodide 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	989.43	733.92	0.74	14.43881
B	989.43	879.90	0.89	4.9154
C	989.43	898.33	0.91	4.221467
D	495.02	399.00	0.81	9.842039
E	495.02	419.55	0.85	7.170036
F	495.02	532.44	1.08	-2.85414
G	94.55	9.85	0.10	336.9098
H	94.55	90.87	0.96	1.609739
I	94.55	79.68	0.84	7.661719
No Spike A		5.38	NA	NA
No Spike B		5.09	NA	NA
No Spike C		7.33	NA	NA

Table 6.111: Iodide 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	989.43	803.45	0.81	9.60
B	989.43	952.30	0.96	1.54
C	989.43	891.22	0.90	4.59
D	495.02	333.23	0.67	19.86
E	495.02	443.54	0.90	4.63
F	495.02	616.19	1.24	-7.99
G	94.55	1.30	0.01	2808.71
H	94.55	113.82	1.20	-6.74
I	94.55	90.16	0.95	2.00
No Spike A		6.28	NA	NA
No Spike B		26.47	NA	NA
No Spike C		-1.79	NA	NA

Table 6.112: Iodate 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	982.0745	530.1518	0.539828	33.79046
B	983.8178	551.1853	0.560251	31.99989
C	979.1689	553.3505	0.565123	30.8541
D	479.4151	243.5707	0.508058	39.67223
E	481.1584	268.084	0.557164	32.01223
F	480.5773	245.9679	0.511818	37.55343
G	97.62634	15.38073	0.157547	209.1124
H	92.39636	20.70096	0.224045	139.5125
I	96.46412	32.61735	0.338129	7.970924
No Spike A		42.15201	NA	NA
No Spike B		16.20041	NA	NA
No Spike C		45.10597	NA	NA

Table 6.113: Iodate 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	982.0745	511.2966	0.520629	36.49835
B	983.8178	525.2333	0.533872	35.59541
C	979.1689	531.6714	0.542982	33.74707
D	479.4151	227.2619	0.47404	45.45943
E	481.1584	232.7153	0.483656	42.99889
F	480.5773	222.8688	0.463752	45.52628
G	97.62634	9.145919	0.093683	378.3239
H	92.39636	64.79401	0.701261	17.16024
I	96.46412	23.71879	0.245882	12.48909
No Spike A		50.73997	NA	NA
No Spike B		28.72917	NA	NA
No Spike C		48.1117	NA	NA

Table 6.114: Iodate 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	982.0745	502.0471	0.511211	37.90108
B	983.8178	507.6823	0.516033	38.23538
C	979.1689	516.5596	0.527549	35.9073
D	479.4151	217.5106	0.4537	49.33428
E	481.1584	233.6441	0.485587	42.66788
F	480.5773	226.465	0.471235	44.17811
G	97.62634	17.60932	0.180375	177.6985
H	92.39636	27.76803	0.300532	93.75404
I	96.46412	43.12961	0.447105	5.035599
No Spike A		80.5132	NA	NA
No Spike B			NA	NA
No Spike C		56.98451	NA	NA

Data Tables for Wetland Sediment

Table 6.115: Iodide 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	952.26	585.97	0.62	26.46
B	952.24	487.27	0.51	40.35
C	952.29	527.41	0.55	34.14
D	488.26	215.28	0.44	53.93
E	488.21	272.46	0.56	33.55
F	488.23	280.93	0.58	31.30
G	97.85	38.31	0.39	64.39
H	97.92	43.54	0.44	53.03
I	97.89	12.66	0.13	282.81
No Spike A		6.843498	NA	NA
No Spike B		12.11982	NA	NA
No Spike C		15.67949	NA	NA

Table 6.116: Iodide 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	952.26	463.72	0.49	44.59
B	952.24	421.39	0.44	53.27
C	952.29	487.73	0.51	40.36
D	488.26	208.74	0.43	56.96
E	488.21	166.18	0.34	82.09
F	488.23	163.71	0.34	84.08
G	97.85	17.92	0.18	184.78
H	97.92	27.46	0.28	108.94
I	97.89	28.80	0.29	100.81
No Spike A		10.59795	NA	NA
No Spike B		10.62104	NA	NA
No Spike C		58.31568	NA	NA

Table 6.117: Iodide 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	952.26	407.10	0.43	56.68
B	952.24	434.06	0.46	50.48
C	952.29	521.44	0.55	35.01
D	488.26	153.98	0.32	92.34
E	488.21	257.14	0.53	38.07
F	488.23	239.76	0.49	43.96
G	97.85	99.61	1.02	-0.73
H	97.92	100.99	1.03	-1.29
I	97.89	100.68	1.03	-1.16
No Spike A		120.19	NA	NA
No Spike B		84.71	NA	NA
No Spike C		-2.29	NA	NA

Table 6.118: Iodate 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1147.632	773.2083	0.673742	20.4967
B	1147.811	525.5291	0.457853	50.4305
C	1147.42	580.5031	0.50592	41.0368
D	543.0128	280.998	0.51748	38.88809
E	543.0981	238.9247	0.439929	53.42176
F	543.0622	262.8321	0.483982	44.62422
No Spike A		11.9349	NA	NA
No Spike B		10.47097	NA	NA
No Spike C		14.12309	NA	NA

Table 6.119: Iodate 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1147.632	1667.059	1.452607	-13.1883
B	1147.811	954.6366	0.831702	8.618165
C	1147.42	900.9985	0.785238	11.49247
D	543.0128	447.4822	0.824073	8.903505
E	543.0981	458.3814	0.844012	7.755328
F	543.0622	455.0511	0.837936	8.094903
No Spike A		25.40584	NA	NA
No Spike B		24.11284	NA	NA
No Spike C		102.9779	NA	NA

Table 6.120: Iodate 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1147.632	1786.242	1.556459	-15.1325
B	1147.811	1033.811	0.90068	4.696421
C	1147.42	920.4051	0.802152	10.36417
D	543.0128	451.6583	0.831764	8.435561
E	543.0981	466.2475	0.858496	6.916542
F	543.0622	499.0634	0.91898	3.689942
No Spike A		37.53084	NA	NA
No Spike B		32.4315	NA	NA
No Spike C		31.94767	NA	NA

Data Tables for No-Solids Controls

Table 6.121: Iodate 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	Fraction Aq
A	981.4456	975.3759	0.993816
B	982.6225	981.5382	0.998897
C	980.3578	1012.35	1.032633
D	97.5239	101.8619	1.044482
E	96.11832	95.4685	0.993239
F	98.4629	99.62809	1.011834
No Spike A		7.772271	NA
No Spike B		4.83976	NA
No Spike C		7.636699	NA

Table 6.122: Iodate 4 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	Fraction Aq
A	981.4456	982.9123	1.0014944
B	982.6225	984.4555	1.0018654
C	980.3578	940.4741	0.9593172
D	97.5239	93.1772	0.9554294
E	96.11832	90.09079	0.9372905
F	98.4629	97.18953	0.9870675
No Spike A		8.15584	NA
No Spike B		4.70369	NA
No Spike C		8.302445	NA

Table 6.123: Iodate 8 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	Fraction Aq
A	981.4456	1005.094	1.024096
B	982.6225	1006.585	1.024386
C	980.3578	1008.81	1.029022
D	97.5239	99.73406	1.022663
E	96.11832	94.43032	0.982438
F	98.4629	98.83888	1.003818
No Spike A		10.44137	NA
No Spike B		8.120995	NA
No Spike C		14.18115	NA

APPENDIX D: DATA TABLES FOR NATURAL SEDIMENTS UNDER REDUCING CONDITIONS

Data Tables for Sandy Sediments

Table 6.124: Iodide 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1082.96	1065.68	0.98	0.64
B	1082.96	1110.69	1.03	-1.01
C	1082.96	1042.48	0.96	1.60
D	543.97	562.81	1.03	-1.36
E	543.97	535.39	0.98	0.64
F	543.97	551.35	1.01	-0.53
G	107.12	97.97	0.91	3.64
H	107.12	111.61	1.04	-1.60
I	107.12	114.49	1.07	-2.58
No Spike A		124.73	NA	NA
No Spike B		125.93	NA	NA
No Spike C		123.47	NA	NA

Table 6.125: Iodide 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1082.96	992.91	0.92	3.59
B	1082.96	1027.39	0.95	2.19
C	1082.96	1011.91	0.93	2.89
D	543.97	443.88	0.82	9.18
E	543.97	440.64	0.81	9.30
F	543.97	403.69	0.74	13.71
G	107.12	-21.32	-0.20	-234.52
H	107.12	-16.89	-0.16	-292.16
I	107.12	-14.57	-0.14	-334.29
No Spike A		-0.57	NA	NA
No Spike B		-1.16	NA	NA
No Spike C		621.38	NA	NA

Table 6.126: Iodide 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1082.96	958.04	0.88	5.17
B	1082.96	972.04	0.90	4.63
C	1082.96	976.24	0.90	4.49
D	543.97	425.70	0.78	11.31
E	543.97	417.15	0.77	12.06
F	543.97	426.05	0.78	10.92
G	107.12	-15.39	-0.14	-310.01
H	107.12	-15.53	-0.14	-314.34
I	107.12	-15.67	-0.15	-313.67
No Spike A		0.36	NA	NA
No Spike B		-0.07	NA	NA
No Spike C		-1.19	NA	NA

Data Tables for Clayey Sediment

Table 6.127: Iodide 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1008.01	1105.24	1.10	-3.62
B	1008.01	886.74	0.88	5.49
C	1008.01	793.40	0.79	11.06
D	504.32	871.18	1.73	-16.94
E	504.32	539.05	1.07	-2.62
F	504.32	469.33	0.93	3.05
G	96.32	96.69	1.00	-0.15
H	96.32	97.82	1.02	-0.62
I	96.32	106.80	1.11	-3.87
No Spike A		8.20	NA	NA
No Spike B		8.90	NA	NA
No Spike C		8.29	NA	NA

Table 6.128: Iodide 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1008.01	704.68	0.70	17.73215
B	1008.01	772.00	0.77	12.26273
C	1008.01	833.66	0.83	8.554869
D	504.32	886.81	1.76	-17.3521
E	504.32	482.23	0.96	1.864089
F	504.32	388.54	0.77	12.20718
G	96.32	90.26	0.94	2.704267
H	96.32	98.06	1.02	-0.71445
I	96.32	79.49	0.83	8.346071
No Spike A		10.24	NA	NA
No Spike B		9.37	NA	NA
No Spike C		9.37	NA	NA

Table 6.129: Iodide 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1008.01	0.94	2332.38	2.45
B	1008.01	0.93	2721.78	2.90
C	1008.01	0.90	4297.72	4.76
D	504.32	2.40	-28437.76	-23.48
E	504.32	0.89	2173.31	4.82
F	504.32	0.96	890.77	1.85
G	96.32	0.94	220.22	2.42
H	96.32	0.80	793.82	10.35
I	96.32	0.98	66.09	0.70
No Spike A		34.36	NA	NA
No Spike B		21.44	NA	NA
No Spike C		30.57	NA	NA

Table 6.130: Iodate 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1193.2	664.7293	0.557098	31.97579
B	1193.2	659.2334	0.552492	33.36228
C	1193.2	657.3759	0.550935	33.82536
D	560.6345	282.1416	0.503254	40.35747
E	560.6345	274.6436	0.48988	41.45062
F	560.6345	281.7404	0.502538	40.05198
No Spike A		8.202494	NA	NA
No Spike B		8.895463	NA	NA
No Spike C		8.287347	NA	NA

Table 6.131: Iodate 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1193.2	661.8256	0.554664	32.29255
B	1193.2	630.8946	0.528742	36.71101
C	1193.2	663.1401	0.555766	33.17062
D	560.6345	269.8751	0.481374	44.05018
E	560.6345	265.2083	0.47305	44.34149
F	560.6345	265.6607	0.473857	44.92517
No Spike A		10.24026	NA	NA
No Spike B		9.368601	NA	NA
No Spike C		9.368601	NA	NA

Table 6.132: Iodate 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1193.2	637.6626	0.534414	35.04028
B	1193.2	608.4773	0.509954	39.58096
C	1193.2	585.3439	0.490567	43.09468
D	560.6345	249.2877	0.444653	51.06465
E	560.6345	246.7233	0.440079	50.64598
F	560.6345	243.6284	0.434558	52.64698
No Spike A		34.35532	NA	NA
No Spike B		21.43609	NA	NA
No Spike C		30.57083	NA	NA

Data Tables for Wetland Sediment

Table 6.133: Iodide 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	967.00	673.02	0.70	18.50
B	967.22	740.67	0.77	13.08
C	967.11	1022.59	1.06	-2.31
D	495.68	316.75	0.64	23.77
E	495.56	357.66	0.72	16.08
F	495.63	368.37	0.74	14.48
G	99.43	60.97	0.61	26.75
H	99.42	67.65	0.68	19.83
I	99.40	64.81	0.65	22.37
No Spike A		11.93	NA	NA
No Spike B		10.47	NA	NA
No Spike C		14.12	NA	NA

Table 6.134: Iodide 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	967.00	692.55	0.72	16.79
B	967.22	638.90	0.66	21.97
C	967.11	650.99	0.67	20.66
D	495.68	321.27	0.65	22.85
E	495.56	NA	NA	NA
F	495.63	657.68	1.33	-10.33
G	99.43	58.52	0.59	29.64
H	99.42	58.98	0.59	28.95
I	99.40	143.33	1.44	-12.85
No Spike A		25.41	NA	NA
No Spike B		24.11	NA	NA
No Spike C		102.98	NA	NA

Table 6.135: Iodide 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	967.00	777.01	0.80	10.36
B	967.22	770.10	0.80	10.94
C	967.11	790.83	0.82	9.48
D	495.68	400.70	0.81	9.98
E	495.56	422.59	0.85	7.20
F	495.63	359.54	0.73	15.86
G	99.43	84.99	0.85	7.20
H	99.42	84.61	0.85	7.39
I	99.40	80.77	0.81	9.67
No Spike A		37.53	NA	NA
No Spike B		32.43	NA	NA
No Spike C		31.95	NA	NA

Table 6.136: Iodate 1 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1147.632	773.2083	0.673742	20.4967
B	1147.811	525.5291	0.457853	50.4305
C	1147.42	580.5031	0.50592	41.0368
D	543.0128	280.998	0.51748	38.88809
E	543.0981	238.9247	0.439929	53.42176
F	543.0622	262.8321	0.483982	44.62422
No Spike A		11.9349	NA	NA
No Spike B		10.47097	NA	NA
No Spike C		14.12309	NA	NA

Table 6.137: Iodate 4 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc. (ppb)	Frac. Aq.	K _d
A	1147.632	1667.059	1.452607	-13.1883
B	1147.811	954.6366	0.831702	8.618165
C	1147.42	900.9985	0.785238	11.49247
D	543.0128	447.4822	0.824073	8.903505
E	543.0981	458.3814	0.844012	7.755328
F	543.0622	455.0511	0.837936	8.094903
No Spike A		25.40584	NA	NA
No Spike B		24.11284	NA	NA
No Spike C		102.9779	NA	NA

Table 6.138: Iodate 8 day

Sample	Initial Conc. (ppb)	Equil. Aq. Conc (ppb)	Frac. Aq.	K _d
A	1147.632	1786.242	1.556459	-15.1325
B	1147.811	1033.811	0.90068	4.696421
C	1147.42	920.4051	0.802152	10.36417
D	543.0128	451.6583	0.831764	8.435561
E	543.0981	466.2475	0.858496	6.916542
F	543.0622	499.0634	0.91898	3.689942
No Spike A		37.53084	NA	NA
No Spike B		32.4315	NA	NA
No Spike C		31.94767	NA	NA

Data Tables for No-Solids Controls

Table 6.139: Iodate 1 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	Fraction Aq
A	1048.541	1005.102	0.958572
B	1048.541	995.1827	0.949112
C	1048.541	946.7963	0.902965
D	524.4306	499.8426	0.953115
E	524.4306	488.7721	0.932005
F	524.4306	457.8073	0.872961
No Spike A		57.29749	NA
No Spike B		59.48766	NA
No Spike C		NA	NA

Table 6.140: Iodate 4 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	Fraction Aq
A	1048.541	1008.182	0.9615096
B	1048.541	990.4855	0.9446321
C	1048.541	982.8139	0.9373157
D	524.4306	478.2518	0.9119448
E	524.4306	486.7246	0.928101
F	524.4306	447.2751	0.8528775
No Spike A		57.58494	NA
No Spike B		57.22211	NA
No Spike C		NA	NA

Table 6.141: Iodate 8 day

Sample ID	Initial Aq. Conc. (ppb)	Equil. Aq. Conc. (ppb)	Fraction Aq
A	1048.541	972.7033	0.927673
B	1048.541	961.6051	0.917089
C	1048.541	961.6818	0.917162
D	524.4306	465.8763	0.888347
E	524.4306	471.916	0.899863
F	524.4306	433.7992	0.827181
No Spike A		57.10949	NA
No Spike B		57.15117	NA
No Spike C		NA	NA

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