

Keywords: *Cement, grout, saltstone, slag, K_d value, distribution coefficient, solubility, Eh, technetium*

Retention: *Permanent*

Technetium Sorption by Cementitious Materials Under Reducing Conditions

**Shanna L. Estes,^a Daniel I. Kaplan,^b and
Brian A. Powell^a**

^a Environmental Engineering and Earth Sciences, Clemson University

^b Savannah River National Laboratory

September 2012

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

Prepared for the U.S. Department of Energy under
contract number DE-AC09-08SR22470.



DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

Prepared for U.S. Department of Energy

REVIEWS AND APPROVALS



Shanna L. Estes, Co-author, Environ. Eng. Earth Sci., Clemson U.

10/1/12

Date



Brian A. Powell, Co-author, Environ. Eng. Earth Sci., Clemson U.

10/1/12

Date



Daniel I. Kaplan, Co-author, Environmental Sciences, SRNL

10/1/2012

Date



Morgana T. Whiteside Technical Reviewer, Environmental Sciences, SRNL

10/1/12

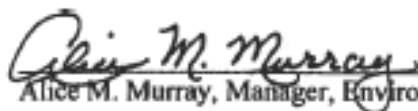
Date



John J. Mayer, Manager, Environmental Sciences, SRNL

10/1/2012

Date



Alice M. Murray, Manager, Environmental Science and Biotechnology, SRNL

October 1, 2012

Date



Kent H. Rosenberger, SRR, Manager, Closure & Disposal Assessment

10/2/2012

Date

EXECUTIVE SUMMARY

The objective of this study was to measure technetium (^{99}Tc) sorption to cementitious materials under reducing conditions to simulate Saltstone Disposal Facility conditions. $^{99}\text{Tc(VII)}$ batch sorption experiments were conducted for 319 days in an inert glovebag with a variety of cementitious materials (aged cement, Vault 2, TR545, and TR547) containing varying amounts of blast furnace slag. Between 154 and 319 days, the ^{99}Tc aqueous concentrations tended to remain constant and samples amended with different initial ^{99}Tc concentrations, tended to merge at about 10^{-9} M for Vault 2 (17% slag) and TR545 (90% slag) and 10^{-8} M for TR547 (45% slag). This data provided strong evidence that solubility, and not adsorption (K_d values), was controlling aqueous ^{99}Tc concentrations. Laboratory data superimposed over thermodynamic speciation diagrams further supported the conclusion that solubility, and not adsorption controlled ^{99}Tc aqueous concentrations. The oxidation state of the aqueous ^{99}Tc at the end of the sorption experiment was determined by solvent extraction to be almost entirely $^{99}\text{Tc(VII)}$. These results are consistent with recent flow-through testing of saltstone similar but not identical in composition to TR547 (Cantrell and Williams, 2012). They reported a solubility of 1.5×10^{-6} M and the aqueous ^{99}Tc concentrations were also determined to be controlled by solubility and not K_d values. Furthermore, they noted that, as the pH of the system decreased from their experimental pH of 13, the ^{99}Tc solubility decreased significantly, approaching the values reported here. The pH of the present system was ~ 11.8 . Most notably, the solid phase identified by Cantrell and Williams (2012) as controlling solubility was $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, which has a very similar solubility as $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$, identified using thermodynamic calculations in this study. Previously proposed solubility controlling phases including Tc-sulfides may be present, but do not appear to control solubility; the solubility of Tc-sulfide phases are more than 10 orders of magnitude lower than either experiment measured.

After the 319 day sorption period, the suspensions were removed from the glovebag and a desorption step under oxic conditions was conducted for 20 days by adding oxic, pH-buffered solutions to the suspensions. ^{99}Tc aqueous concentrations increased by more than an order of magnitude and Eh increased by several hundred millivolts within 24 hours after the introduction of the oxic solutions. These desorption results are consistent with re-oxidation and dissolution/desorption of $^{99}\text{Tc(IV)}$ phases possibly present in the cementitious materials after the anoxic sorption step of the experiment. Aqueous ^{99}Tc concentrations continued to increase slowly until the termination of the desorption experiment after 20 days. Although the cementitious materials investigated demonstrated the ability to strongly sequester aqueous ^{99}Tc under anoxic conditions, the introduction of oxygen resulted in the rapid remobilization of ^{99}Tc . These studies provide experimental support for the use of a solubility based model under reducing saltstone conditions where Tc(IV) is expected to be the dominant species. The existing K_d model would be appropriate for oxidized saltstone conditions (aged saltstone, not directly evaluated in this study) where Tc(VII) is expected to be the dominant species.

TABLE OF CONTENTS

LIST OF TABLES	vi
LIST OF FIGURES	vi
LIST OF ABBREVIATIONS	vii
1.0 Introduction	1
2.0 Materials and Methods	1
2.1 Methods	2
2.1.1 Experimental Conditions and Apparatus.....	2
2.1.2 Sample Preparation and Analysis.....	3
2.1.3 Calculations.....	4
3.0 Results and Discussion from Adsorption Experiments	5
3.1 Results from ⁹⁹ Tc Batch Sorption Experiments.....	5
3.2 Discussion of ⁹⁹ Tc Batch Sorption Experiments.....	11
3.2.1 Solubility versus the Distribution Coefficient Construct	12
4.0 ⁹⁹ Tc Batch Desorption Experiments	15
4.1 Results from Batch Desorption Experiments.....	15
4.2 Discussion of Desorption Experiments.....	15
5.0 Conclusions	20
6.0 References	21
Appendix A: Photos of saltstone samples and radiological inert atmosphere glovebag for Tc sorption experiments	23
Appendix B: Data for ⁹⁹ Tc Concentrations, Fraction Sorbed, and K _d Values as a Function of Time	22

LIST OF TABLES

Table 1. Saltstone reduction capacity and slag content (Lilley et al. 2009).	2
Table 2: Comparison of conditional K_d values under reducing and oxidizing conditions.	20

LIST OF FIGURES

Figure 1. Fraction of ^{99}Tc sorbed as a function of time and cementitious materials (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments).	6
Figure 2. Conditional K_d values (i.e., non-equilibrium) as a function of time measured for ^{99}Tc sorption to cementitious materials (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments).....	7
Figure 3. Aqueous ^{99}Tc concentrations versus time during the sorption step to the cementitious materials. The legend in the lower left corner of each plot notes the specific cementitious material and the initial aqueous ^{99}Tc concentrations.....	8
Figure 4. Aqueous ^{99}Tc concentration versus time in the no solids control reactors. The legend notes the initial aqueous ^{99}Tc concentrations.	9
Figure 5: Oxidation state distribution of aqueous ^{99}Tc measured at 319 days of reaction.	9
Figure 6: pH of cementitious material suspensions measured during ^{99}Tc sorption experiments.	10
Figure 7. Redox potentials (converted to SHE) of cementitious material suspensions measured during ^{99}Tc sorption experiments.	10
Figure 8: Geochemist Workbench Model of Eh-Tc at pH 12 (top) without S present (top) and with 2 mg/L S (bottom). All Tc redox states coupled. Model generated using thermo.com.V8.R6+.dat database. Oval shows approximate E_H and Tc concentrations observed in batch sorption experiments.	13
Figure 9: Geochemist Workbench Model of Eh-Tc concentrations at pH 12. There is no change in speciation when 2 mg/L S is added as done in Figure 8. Only Tc(VII)/Tc(IV) redox couple active. Model generated using thermo.com.V8.R6+.dat database. Oval shows approximate E_H and Tc concentration values observed in batch sorption experiments.	14
Figure 10: pH of cementitious material suspensions measured during the ^{99}Tc desorption experiments (the pH at time 0 is equivalent to the value at 319 days during the anoxic sorption experiment).	16
Figure 11. Eh of cementitious material suspensions measured during the ^{99}Tc desorption experiments (the Eh at time 0 is equivalent to the value at 319 days during the anoxic sorption experiment).	16

- Figure 12. Aqueous ^{99}Tc concentrations versus time during the desorption step to the cementitious materials. The legend in the lower left corner of each plot notes the specific cementitious material and the initial aqueous ^{99}Tc concentrations. The ^{99}Tc aqueous concentration at time zero is equal to the ^{99}Tc aqueous concentration at the end of the 319 day sorption period under anoxic conditions. 17
- Figure 13. Aqueous ^{99}Tc concentrations versus time during the desorption step in the no solids control reactors. The legend in the lower left corner notes the initial aqueous ^{99}Tc concentrations. The ^{99}Tc aqueous concentration at time zero is equal to the ^{99}Tc aqueous concentration at the end of the 319 day sorption period under anoxic conditions. 18
- Figure 14. Fraction ^{99}Tc sorbed as a function of time and cementitious material during the desorption experiment (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments). 18
- Figure 15. Conditional K_d values (i.e., non-equilibrium) as a function of time measured for ^{99}Tc sorption to cementitious materials during the desorption experiment (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments). For reference the K_d determined after 319 days in the sorption step is included. 19
- Figure 16: Radiological inert atmosphere glovebag. Atmosphere maintained at 0.1% $\text{H}_2(\text{g})/99.9\% \text{N}_2(\text{g})$ by mixing pure $\text{N}_2(\text{g})$ with a mixture of 5% $\text{H}_2(\text{g})/95\% \text{N}_2(\text{g})$ 19
- Figure 17: Saltstone suspensions mixing in 50 mL centrifuge tubes (reactors) about their longitudinal axis. Note area outlined in yellow circle shows the oxygen meter reading 0 ppm and the $\text{H}_2(\text{g})$ meter at 0.1%. 20
- Figure 18: On left is the O_2 indicator solution, which turns bright pink in the presence of O_2 . While transferring supplies into the glovebag, a transient $\text{O}_2(\text{g})$ concentration of ~100 ppm would occur and this indicator would go pink then go clear again as the $\text{O}_2(\text{g})$ was scrubbed from the atmosphere. Also shown, are various cementitious samples. 21

LIST OF ABBREVIATIONS

BFS	Blast furnace slag
DDI	Distilled deionized
ICP-MS	Inductive couple plasma-mass spectroscopy
K_d	Distribution coefficient
SHE	Standard Hydrogen Electrode
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
XAS	X-ray Absorption Spectroscopy

1.0 Introduction

Technetium (Tc) is among the key risk drivers at the Saltstone Facility at the Savannah River Site (SRS). By mixing technetium bearing waste with the saltstone, technetium is immobilized by (1) minimizing diffusion within the pore spaces of the cementitious wasteform, and by (2) promoting the reduction of highly mobile $^{99}\text{Tc(VII)}$ to highly immobile $^{99}\text{Tc(IV)}$ by blast furnace slag (BFS). Lilley (2010) attempted to measure the distribution coefficient, K_d , between technetium and solid phase saltstone materials under reducing conditions within an anoxic glovebag. However, it became apparent that the presence of H_2 gas within the glovebag was enhancing technetium reduction, when experimental results showed that the slag-free cementitious controls removed as much ^{99}Tc from solution as the slag-containing cementitious materials. Therefore, the objective of this study was to repeat the original work with minimal H_2 gas (discussed in more detail in the Materials and Methods section), in an effort to experimentally create and control redox conditions that are more representative of the interior saltstone material where oxygen gas levels are calculated to be at or near 0 %. Additionally, it is necessary to understand the long-term ability of saltstone to immobilize ^{99}Tc after oxygen gas has permeated the interior of the material. Therefore, this study also examined ^{99}Tc desorption from equilibrated cementitious materials.

This is a status report and reflects work completed between October 1, 2011 and September 30, 2012, and is an update to the work presented in Kaplan et al. (2011), which presented ^{99}Tc sorption during the first 56 days of the study. This report presents sorption results for the entire 319 day duration of the study. Also presented are the results of a study in which oxidic, pH-buffered water was introduced to the saltstone after the 319 day (ad)sorption study to measure the rate of ^{99}Tc desorption under oxidizing conditions. During the preparation of this report, an issue with how the original K_d data was presented was identified in Kaplan et al. (2011) and corrected in a revision of that report (Kaplan et al. 2012) and in this report. Furthermore, the data which were originally described primarily in terms of the K_d construct, are presented here primarily in terms of solubility, to capture the apparent sorption mechanism identified in this most recent data.

2.0 Materials and Methods

There were four different cementitious formulations selected for this sorption study (Table 1). The first, referred to as Aged Cement, is a 50-year old sample that was recovered from an outdoor slab used to support a large non-radiological tank located in P-Area on the SRS; it was a rebar-reinforced concrete sample. Its original composition is not known. Before the sample was used in this study, the aggregate was removed. The simulant Vault 2 formulation contains 17% reducing slag. The simulant TR547 and TR545 saltstone formulations contain 45% and 90% reducing slag, respectively. TR547 consists of a similar percentage of slag, portland cement, and fly ash as presently used to make actual SRS saltstone. TR545 simulated saltstone has 90% slag, permitting evaluation of elevated slag percentages on Tc removal from the aqueous phase. The ingredients for the dry mix used for TR547 and TR545 were similar, but may differ from those of Vault 2 and the Aged Cement. In the case of the Vault 2 sample, effort was made to remove the larger aggregate prior to analysis, but the sand remained with the cement, slag, and fly ash. No precautions were made to store the cementitious samples, including the reducing-cementitious samples, in an inert environment since fabrication four years ago, so it is anticipated that oxidation of these samples occurred. At the start of the study, the ground saltstone samples were primarily gray and not dark olive, with the exception of TR545, which was light yellow/beige. A noteworthy observation was that all six TR545 samples turned an olive green color during the

sorption experiment under a 0.1% H₂(g)/ 99.9% N₂(g) atmosphere. Five out of six reactors then returned to their original yellow/beige color after 1 day of exposure to oxidizing conditions and the sixth also changed back after 4 days. It is suspected that the color change is indicative of reducing capacity of the solid. These results will be discussed in detail below.

Table 1. Saltstone reduction capacity and slag content (Lilley et al. 2009).

Sample	Percent Reducing Slag (dry wt-%) ^(c)	Percent Portland Cement (dry wt-%) ^(c)	Percent Fly Ash (dry wt-%) ^(c)	Percent Aggregate/sand (dry wt-%) ^(c)	Reducing Equivalents (μeq/g)
Aged Cement	NA	NA	NA	NA	85.5 ± 10.1 ^(a)
Vault 2 Cement ^(d)	17	13	10	58	178 ^(b)
TR547	45	10	45	0	607 ^(b)
TR545	90	10	0	0	681 ^(b)
Blast Furnace Slag	100	0	0	0	819 ^(b)
Blast Furnace Slag	100	0	0	0	832 ^(a)
Portland Cement	0	100	0	0	198 ^(b)
Fly Ash	0	0	100	0	299 ^(b)

^(a) Kaplan et al. (2008)

^(b) Roberts and Kaplan (2009)

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

^(d) Based on Table 8 in Dixon et al. (2008; SRNL-STI-2008-00421), which shows the following quantity (lbs/cu yd) for saltstone Vault 2 Mix 1 concrete formulation: 201 cement (12.71 wt-%), 268 slag (16.95 wt-%), 44.7 silica fume (2.83 wt-%), 156.3 fly ash (9.89 wt-%), 911 fine sand /aggregate (57.62 wt-%). The large aggregate was removed before the sorption tests were conducted. The large aggregate accounted for 75 wt-% of the original field sample, not the sample used in these tests, before water was added to the mix. By not including the inert sand fraction in the calculated ingredient compositions was 30% cement, 40% slag, and 23% fly ash (and silica fume 7%).

2.1 Methods

2.1.1 Experimental Conditions and Apparatus

All batch sorption experiments were performed in an anoxic glovebag with approximately 0.1% H₂(g)/99.9% N₂(g). This was found to be an optimal H₂(g) concentration to maintain the desired reducing conditions described below. Initial experiments performed with 100% N₂(g) atmosphere within the glovebag were unsuccessful, as determined from elevated aqueous Eh, elevated O₂-gas concentrations (60 ppm O₂) in the glovebag, and minimal ⁹⁹Tc sorption to saltstone (Almond and Kaplan, 2011). The K_d values were similar to those measured under oxidizing conditions with samples having oxidizing Eh values >100 mV (Lilley et al., 2009, SRNL-STI-2009-00636). Therefore, to reach mildly reducing conditions, the 0.1% H₂(g) atmosphere was maintained. A palladium catalyst was used within the glovebag in order to maintain anoxic conditions. The catalyst converts O₂(g) to water via reaction with H₂(g). Therefore, the small amount of H₂(g) is necessary to counter O₂(g) diffusion into the bag.

The oxidation/reduction potential was measured with a Pt redox combination electrode with a Ag/AgCl reference in 4M KCl. Ag/AgCl redox potentials were converted to Eh (Standard Hydrogen Electrode, SHE) values by adding 200 mV to the value measured with the Ag/AgCl reference. Aqueous pH was measured with a Thermo PerpHecT sure-flow electrode.

2.1.2 Sample Preparation and Analysis

A ^{99}Tc working solution was prepared by diluting a stock solution of $^{99}\text{Tc(VII)}$ (Isotope Products, Valencia, CA) in distilled-deionized water (DDI; water resistivity $>18\text{ M}\Omega\cdot\text{cm}$). The oxidation state of ^{99}Tc in the stock solution was not measured. However, based on the aqueous concentration in the DDI water solution, it is reasonable to assume that the Tc existed as Tc(VII). Reduced technetium, $^{99}\text{Tc(IV)}$, would have a very low solubility under these conditions. The expected concentration of 950 ppb ^{99}Tc based on the dilution was verified using liquid scintillation counting. The ^{99}Tc working solution was used to make 0.01, 0.05, 0.5, 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 inductively coupled plasma mass spectrometer (ICP-MS) for quantification of ^{99}Tc . 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 quality assurance/quality control (QA/QC) protocols for the instrument (between 80% and 120%).

For each of the four solids, two sets of triplicate samples were prepared with $^{99}\text{Tc(VII)}$ concentrations of 2.5 ppb and 10 ppb. A set of no solids controls at initial concentrations of 2.5 ppb and 10 ppb ^{99}Tc were also prepared in triplicate. Samples were prepared in Falcon BlueMax 50 mL polypropylene vials. A 1.0 g aliquot of solid was added to the tube followed by 40 mL of calcite-saturated solution. The resulting solutions were then spiked with $^{99}\text{Tc(VII)}$ to either 2.5 ppb or 10 ppb and shaken end-over-end. The moment at which the $^{99}\text{Tc(VII)}$ amendment was added to the cementitious solids was considered time zero. These spike concentrations were selected because they were easy to detect (they would provide sufficient range to permit detecting ^{99}Tc several orders of magnitude lower than the spike concentration). Equally important, these spike concentrations are close to concentrations measured in actual samples recovered from the Saltstone Facility. Almond et al. (2011) recovered samples with ^{99}Tc concentrations of $5.35 \times 10^{-11}\text{ Ci/g}$ in the solid phase, and when leached under oxidizing conditions to measure K_d values ($K_d = 12\text{ mL/g}$), the aqueous phase had $2.82 \times 10^{-12}\text{ Ci/mL}$ or 0.16 ppb ^{99}Tc . Most of the aqueous phase ^{99}Tc values measured in contact with saltstone in these studies were equal to or below this concentration because they were measured under reducing conditions that promote adsorption and precipitation. Also, the spike concentrations are well below the solubility of $^{99}\text{Tc(VII)}$ phases.

At 1, 4, 8, 19, 56, 154, and 319 days after spiking with ^{99}Tc , approximately 2 mL of each suspension was recovered. Care was taken to remove a homogenous sample of the saltstone suspension to prevent changing the aqueous/solid ratio in the sample. This was accomplished by pipetting the 2 mL aliquot while the saltstone suspension was being mixed. The 2 mL aliquot was passed through a 200 nm PTFE filter and the first milliliter was discarded. A 1.0 mL aliquot of the filtrate was then diluted with 9 mL 2% HNO_3 , and the soluble ^{99}Tc concentration was determined using ICP-MS as discussed above. The Eh and pH of the remaining suspensions were measured and recorded at each sampling interval.

At 319 days of reaction, the oxidation state of ^{99}Tc within the aqueous phase of each reactor was measured using a method adapted from Boggs et al. (2010). Briefly, 0.4 mL of the aqueous filtrate from each reactor was mixed with 0.6 mL of an acetate buffer at pH 4.5 and 0.5 mL of 0.1 M Bis-(2-ethylhexyl) phosphoric acid (HDEHP) in cyclohexane. The mixture was shaken vigorously for three minutes, and then centrifuged to separate the organic and aqueous phases. Under these conditions, $^{99}\text{Tc(IV)}$ partitions within the organic phase and $^{99}\text{Tc(VII)}$ remains in the aqueous phase. The organic and aqueous phases were decanted separately, diluted with 2% HNO_3 , and analyzed using ICP-MS, as above.

After the sorption step, the samples were removed from the glovebag and immediately diluted with a saturated calcite solution that had been pre-equilibrated with the respective cementitious material. These diluents were prepared by suspending each of the respective cementitious materials at 25 g/L in a saturated calcite solution, initially prepared in DDI water. The solids were removed by filtration using a 0.45 μm nylon syringe filter, and the supernatant was used as the diluent. This was done to buffer the aqueous phase pH of the diluent to the expected pH of the suspension, as the saltstone has a strong pH buffering capacity and will change the pH of DDI water or saturated calcite. This pre-equilibration step prevented the large pH shift that could impact the sorption behavior. All preparation was done on the bench top under oxic conditions. After all sampling events during the sorption step there was approximately 15 mL remaining in each reactor. Therefore, 20 mL of the pre-equilibrated solution for each solid was added to reach a total volume of approximately 35 mL in each reactor. This was necessary to have sufficient volume for the desorption step. During the desorption period, samples were removed after 1, 7, and 20 days and the aqueous ^{99}Tc concentration was determined as discussed above.

2.1.3 Calculations

The calculations of the reported K_d values and fraction sorbed were performed as follows. For the sorption experiments,

$$K_d = \frac{C_s}{C_t} = \frac{(C_0 - C_t) \cdot m_{\text{calcite}}}{m_s \cdot C_t} \quad (1)$$

$$f_{\text{sorbed}} = 1 - \frac{C_t}{C_0} \quad (2)$$

where C_s is the ^{99}Tc concentration in the solid phase at time t , C_t is the ^{99}Tc concentration in the aqueous phase at time t , C_0 is the initial ^{99}Tc concentration in the aqueous phase, m_{calcite} is the initial total mass of the aqueous phase, and m_s is the initial mass of cement.

For the desorption experiments,

$$K_d = \frac{C_s}{C_t} = \frac{\left(\frac{f_R \cdot m_{Tc,0}}{(f_R \cdot m_{\text{calcite}}) + m_d} - C_t \right) ((f_R \cdot m_{\text{calcite}}) + m_d)}{f_R \cdot m_s \cdot C_t} \quad (3)$$

$$f_{\text{sorbed}} = 1 - \frac{C_t \cdot ((f_R \cdot m_{\text{calcite}}) + m_d)}{f_R \cdot m_{Tc,0}} \quad (4)$$

$$f_R = \frac{m_R}{m_T} \quad (5)$$

where f_R is the fraction of mass remaining in the reactor at the start of the desorption experiment, m_d is the mass of added calcite solution, $m_{Tc,0}$ is the initial mass of ^{99}Tc in each reactor, m_R is the total mass remaining in the reactor at the start of the desorption experiment, and m_T is the initial total mass of each reactor.

3.0 Results and Discussion from Adsorption Experiments

3.1 Results from ^{99}Tc Batch Sorption Experiments

The partitioning of ^{99}Tc during the sorption step is shown in Figures 1-3. Again, TR547 is the formulation closest to that presently used at the SRS Saltstone Facility. The figures are derived from the same dataset, but are plotted in three different ways to highlight different aspects about the dataset. Figure 1 shows the fraction of sorbed ^{99}Tc in the four cementitious solid suspensions as well as the no solids controls. Figure 2 shows the same data plotted as conditional K_d values; they are referred to as “conditional” K_d values because they are not at equilibrium, as assumed in the theory underscoring the construct. Figure 3 shows the ^{99}Tc molar aqueous concentrations versus time. The data in tabular format is presented in Appendix B. Attempts were made to fit the observed experimental data to zero order, first order, and second order rate laws, but none of these numerical representations could accurately describe the data. For comparison with Figure 3, the data in Figure 4 show the measured aqueous concentration of ^{99}Tc at two concentrations versus time when no solids were present. Both the fraction sorbed data of the no solids controls in Figure 1, and the aqueous concentration data in Figure 4 demonstrate that ^{99}Tc remained soluble over the course of the experiments and that homogeneous reductive precipitation did not occur as a result of contact with the glovebag’s inert environment. This is consistent with the aqueous phase oxidation state analysis data in Figure 5, which shows that Tc(VII) was the dominant aqueous phase oxidation state in all systems.

The measured E_h and pH values for each reactor are shown in Figures 6 and 7. There was relatively little change in these values during the 319-day sorption period, with the exception of at 56 day, when some reactor E_h values increased. Overall, high pH and reducing conditions were maintained in all reactors. The cementitious solids used in these experiments had been ground to a powder and stored in the laboratory under atmospheric conditions. All solids initially had a gray appearance similar to that of cement, except for TR545, which was light yellow/beige. However, during the sorption experiment, after 154 days, all six reactors containing TR545 turned an olive green similar to the color of the saltstone materials when they are first formed. Therefore, it is possible that over the course of the experiment, TR545 had returned to the initial conditions. However, it is noteworthy that there was no clear change in the E_h values of the suspension when this transition occurred.

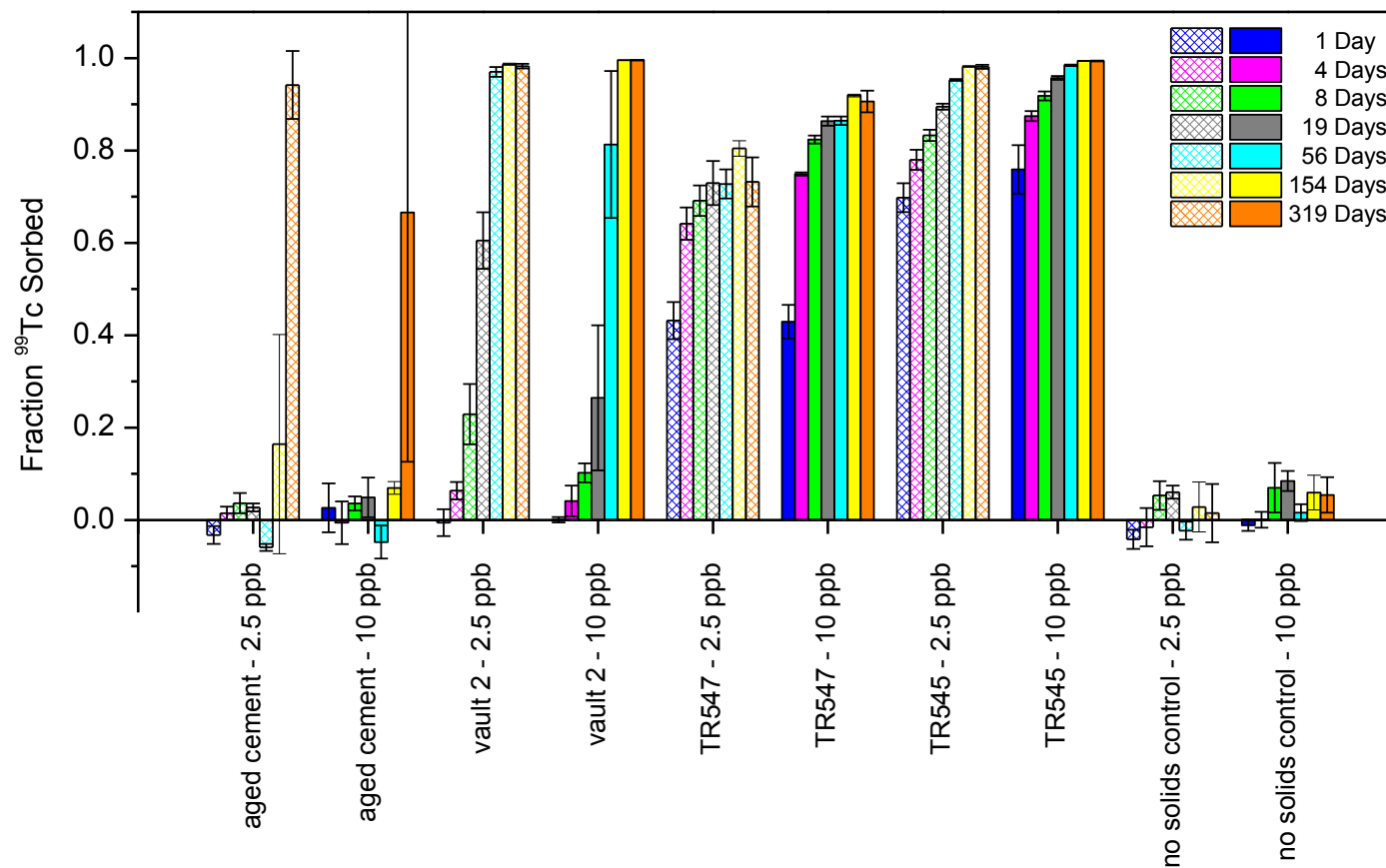


Figure 1. Fraction of ^{99}Tc sorbed as a function of time and cementitious materials (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments).

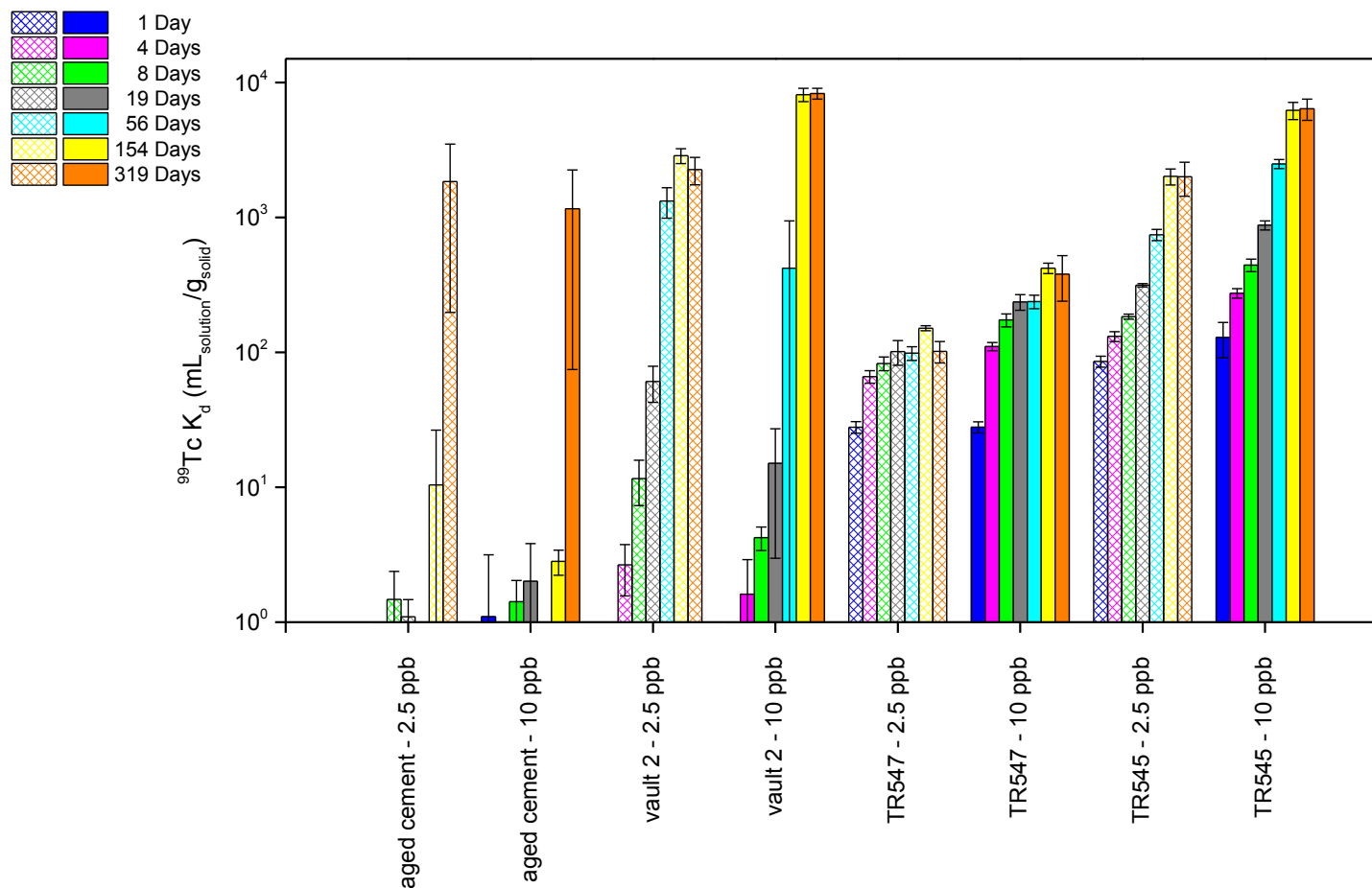


Figure 2. Conditional K_d values (i.e., non-equilibrium) as a function of time measured for ^{99}Tc sorption to cementitious materials (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments).

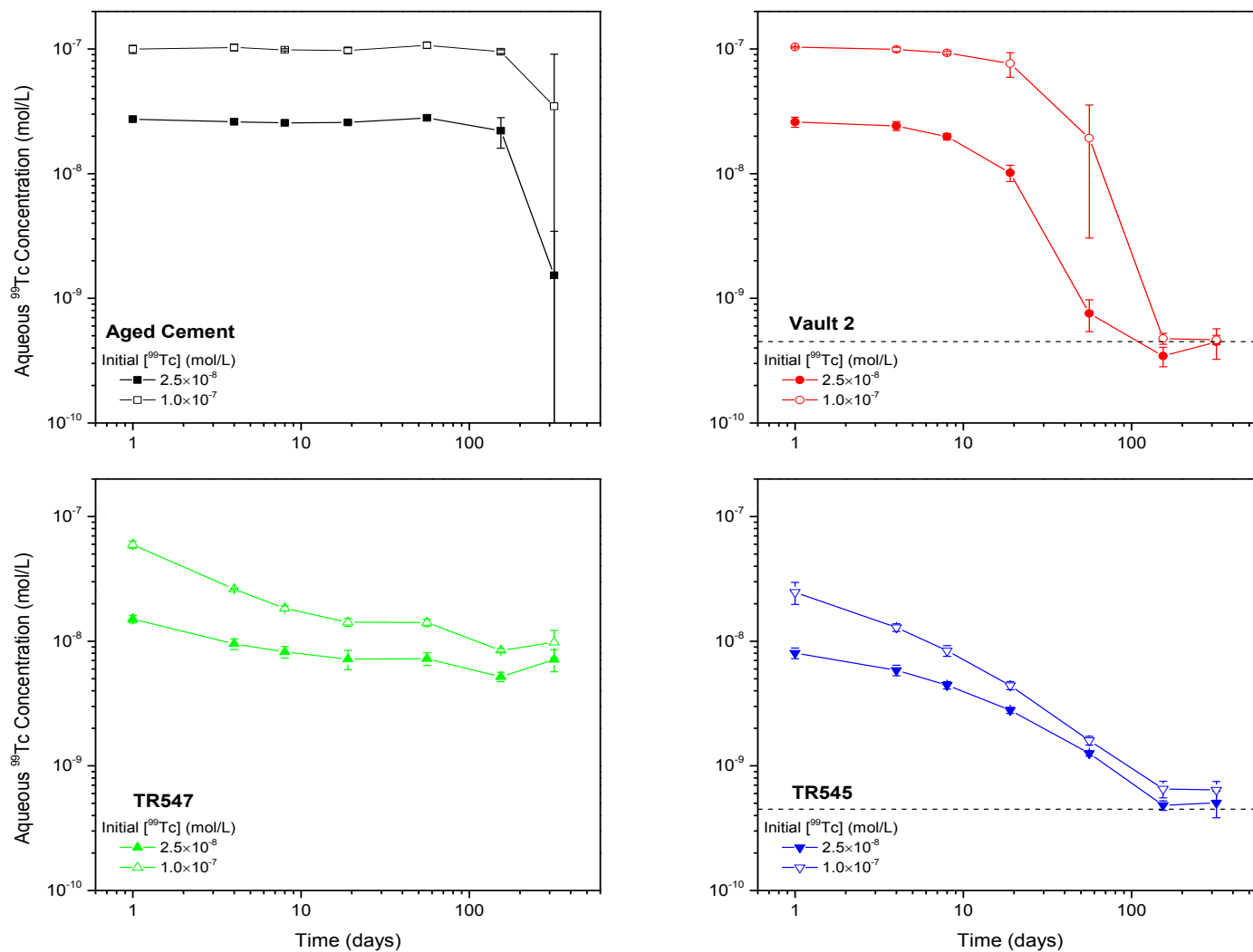


Figure 3. Aqueous ^{99}Tc concentrations versus time during the sorption step to the cementitious materials. The legend in the lower left corner of each plot notes the specific cementitious material and the initial aqueous ^{99}Tc concentrations.

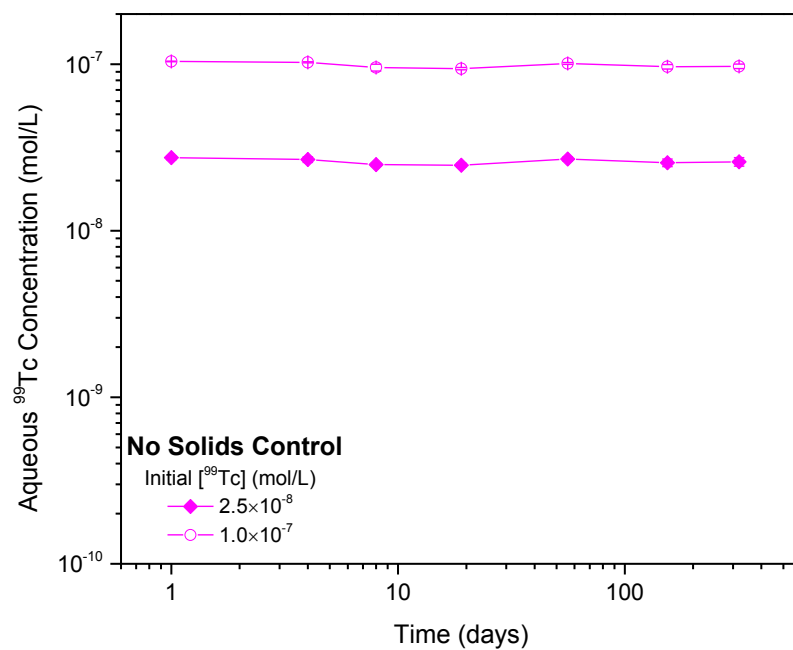


Figure 4. Aqueous ^{99}Tc concentration versus time in the no solids control reactors. The legend notes the initial aqueous ^{99}Tc concentrations.

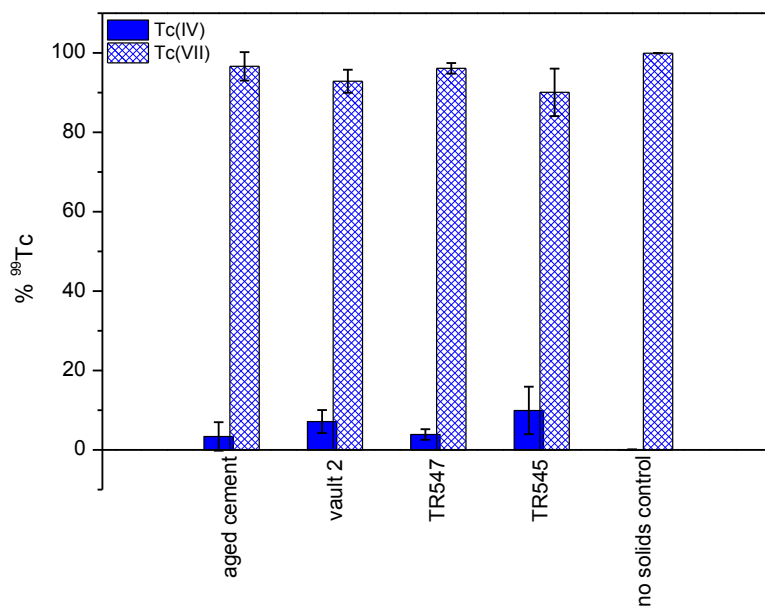


Figure 5: Oxidation state distribution of aqueous ^{99}Tc measured at 319 days of reaction.

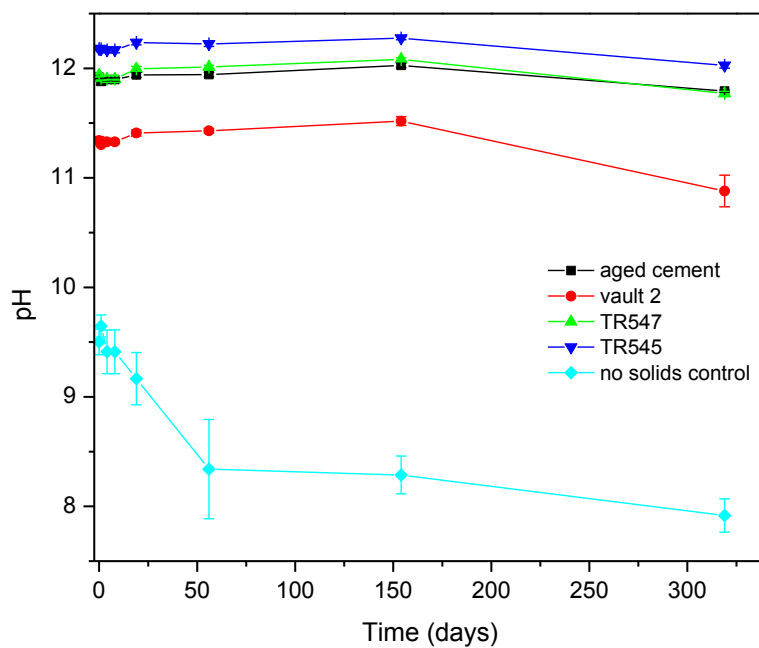


Figure 6: pH of cementitious material suspensions measured during ^{99}Tc sorption experiments.

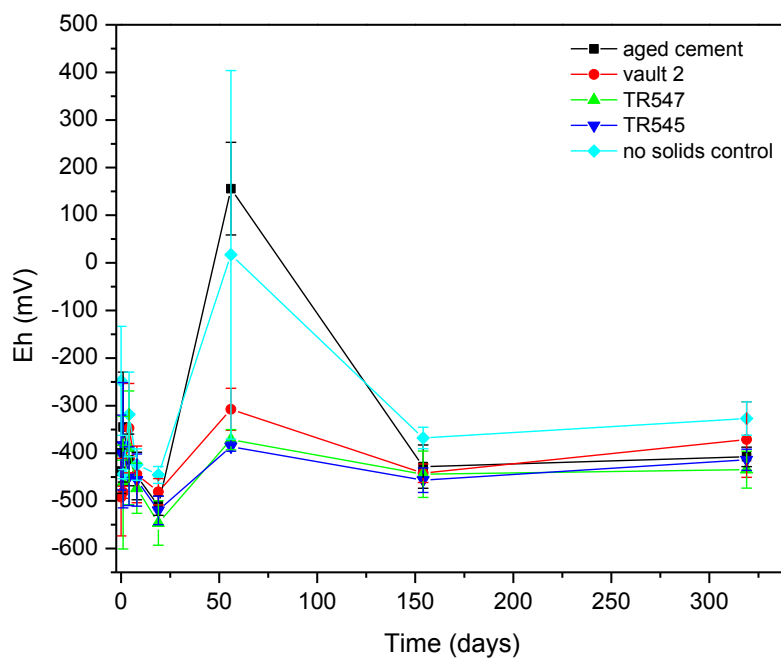


Figure 7. Redox potentials (converted to SHE) of cementitious material suspensions measured during ^{99}Tc sorption experiments.

3.2 Discussion of ^{99}Tc Batch Sorption Experiments

As shown in Figure 1, there is little or no loss of ^{99}Tc in the no-solids control sample and ^{99}Tc was maintained as $^{99}\text{Tc(VII)}$ (Figure 5). Therefore, the reducing conditions maintained as shown in Figure 7 were not sufficient to facilitate aqueous reduction of $^{99}\text{Tc(VII)}$ to $^{99}\text{Tc(IV)}$ in the absence of solids. The amount of ^{99}Tc sorbed to the Aged Cement remains low through the 154 day sampling event. Then, there is a marked decrease in the aqueous ^{99}Tc concentration at the 319 day sampling event. This increase was not accompanied by any change in E_h or pH in the system, and there was no visible change in the appearance of the suspension. The ≤ 56 day data are consistent with the conceptual model that the aged cement has little to no reducing capacity, and therefore will not sorb significant amounts of ^{99}Tc . However, the last data point at 319 days does not support that conceptual model. One possible explanation of the observed behavior is that the Aged Cement required a significant amount of “equilibration” time with the low redox aqueous phase to promote the reduction of sulfate and iron(II) in the cement and/or fly ash. Based on SRS saltstone feed materials, sulfate concentration of fly ash is 0.2%, of Portland cement is 3.3%, and of slag is 1.8% (Harbour et al. 2006). This hypothesis is supported by observations by Atkins and Glasser (1992), who observed that creation of reducing conditions in slag-containing grouts occurs at a rate proportional to the amount of slag in the cement. Atkins and Glasser (1992) showed that it can take >18 months to create maximum reducing conditions in cement containing 50% slag. Therefore, the slow kinetics and eventual removal of $^{99}\text{Tc(VII)}$ from the aqueous phase may be due to the low amount of reduction potential expected in the aged concrete. This proposed reduction of the solid phase is likely responsible for the color change of the TR545 solids as discussed above. Furthermore, it suggests that non-slag components may increase their reduction potential when in low E_h environments, similar to that expected in the Saltstone Facility, that can promote aqueous ^{99}Tc removal. Roberts and Kaplan (2006) measured a small amount of reduction potential in this Aged Cement (86 $\mu\text{eq/g}$). Similarly, they measured reduction capacity in portland cement (198 $\mu\text{eq/g}$) and fly ash (299 $\mu\text{eq/g}$). Although these are smaller amounts of reduction capacity than saltstone (consistently ~ 820 $\mu\text{eq/g}$), it is reasonable to assume that a slag-free cementitious materials would have some capacity to create a reducing environment.

Vault 2 solids may have exhibited similar aging behavior and development of reduction capacity as proposed for the aged cement above. The early data up to 19 days exhibited little to no sorption of ^{99}Tc . At ≥ 56 days of contact, the sorption of ^{99}Tc increased markedly and the shape of the sorption curves for the 2.5 and 10 ppb amended samples were similar (Figure 3). Therefore, similar processes of sequestering ^{99}Tc may be occurring, despite the difference in aqueous concentration. It is noteworthy that lower K_d values were determined for 2.5 ppb initial ^{99}Tc solution concentrations as compared with the system with an initial ^{99}Tc concentration of 10 ppb. The use of a K_d term has an inherent assumption that sorption is linear and should not change with concentration. Therefore, there should be no difference in K_d values between the reactors initially prepared at 2.5 ppb and at 10 ppb ^{99}Tc . Generally, the 10 ppb ^{99}Tc suspension had a higher fraction sorbed (Figure 1) and higher K_d value (Figure 2) than the 2.5 ppb suspension, especially for the longer contact times for the Vault 2 and the two saltstone samples. After the 56 day sampling event, the aqueous ^{99}Tc concentrations were essentially at background (Figure 3). Thus, the Vault 2 solid was exhibiting a higher K_d than TR547 at extended periods. This is unexpected due to the higher BFS content in TR547 (90% slag). It is unclear what is causing the increase in ^{99}Tc partitioning after the 56 day sampling event in the Vault 2 suspensions. However, development of reducing conditions, as noted for the aged cement and TR545 above, is a possibility. Another possibility is that the 58% sand added to the Vault 2 dry mix, may be inert. It is possible that in estimating the “effective” reducing capacity of Vault 2 solids, one should

consider only the potentially reactive components; such that the calculated ingredient compositions, negating the sand's contribution, would be 30% cement, 40% slag, and 23% fly ash (and silica fume 7%) (Table 1).

3.2.1 Solubility versus the Distribution Coefficient Construct

For the Vault 2, TR547, and TR545 solids, it appears that a relatively constant ^{99}Tc concentration was obtained between the 154 and 319 day sampling events, suggesting equilibrium with respect to ^{99}Tc partitioning had been reached. As shown in Figure 3, the aqueous ^{99}Tc concentrations of these cementitious materials appears to level off and the samples receiving 2.5 and 10.0 ppb total ^{99}Tc also appear to be converging on single concentrations: Vault 2 and TR545 are converging on 10^{-9} M, and TR547 is converging on 10^{-8} M.

Based on the observations of different K_d values (Figure 2) and similar aqueous phase concentrations (Figure 3) for similar cementitious solids, it is hypothesized that the aqueous phase concentrations of ^{99}Tc in the Vault 2, TR545, and TR547 suspensions were controlled by solubility of a $^{99}\text{Tc(IV)}$ bearing phase. Previous research with SRS saltstone by Allen et al., (1997) and Lukens et al., (2005) identified ^{99}Tc bearing solids. Lukens et al., (2005) used X-ray absorption spectroscopy (XAS) to identify both Tc-S bearing solids as well as $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$.

To examine further this possibility, Geochemist Workbench[®] was used to simulate the experimental conditions in this study. Figure 8 shows a simulation of varying E_h and varying ^{99}Tc concentrations at a constant pH of 12. In the presence and absence of sulfate (Figures 8A and 8B, respectively), several reduced Tc phases were thermodynamically calculated to form, but all of them are saturated with respect to the Tc concentrations measured in these experiments. That is to say, the experimentally measured aqueous Tc concentrations (identified by the ovals drawn in Figures 8A & 8B) were less than is theoretically estimated to be supported by these phases (Tc_3O_4 , TcS_2 , and Tc(OH)_2) and therefore it is not expected that these phases would control the ^{99}Tc solubility. Furthermore, some of these reduced Tc phases have not been observed using in-situ techniques, such as XAS. Therefore, in an attempt to model the system in a way believed to be more consistent with the experimental conditions, only $^{99}\text{Tc(IV)}$ and $^{99}\text{Tc(VII)}$ oxidation states were allowed and the model was run a second time (Figure 9). The revised model output shows TcO_4^- , $\text{TcO(OH)}_2(\text{aq})$ as the dominant aqueous species and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ as the dominant solid phase (Figure 9). The range of E_h and aqueous ^{99}Tc concentration values in the batch experiments falls within the region between aqueous $\text{TcO(OH)}_2(\text{aq})$ and solid $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$. Therefore, based on this model it is entirely feasible that precipitation of $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ could occur as well as precipitation of a number of other thermodynamically favored reduced Tc-oxides and Tc-sulfides.

Recent flow-through testing of saltstone similar but not identical in composition to TR547 were found to have a solubility of 1.5×10^{-6} M and the aqueous ^{99}Tc concentrations were determined to be controlled by solubility and not K_d values (Cantrell and Williams, 2012). The solid phase controlling solubility was $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$. Furthermore, they noted that as the pH of the system decreased from their experimental pH of 13 the ^{99}Tc solubility decreased significantly. The pH of this system was ~ 11.8 (Figure 6). Given the fact that Cantrell and Williams (2012) tended to dilute their aqueous phase by introducing more pH-buffered solution each time they sampled, the batch test results reported in Figure 3 are certainly consistent. Most notably, the solid phase identified in this study, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, has only a slightly different solubility than $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$, identified by Cantrell and Williams (2012). Sulfide-Tc phases may be present, but do not appear

to control solubility; the solubility of Tc-sulfide phases are several orders of magnitude lower than either experiment measured.

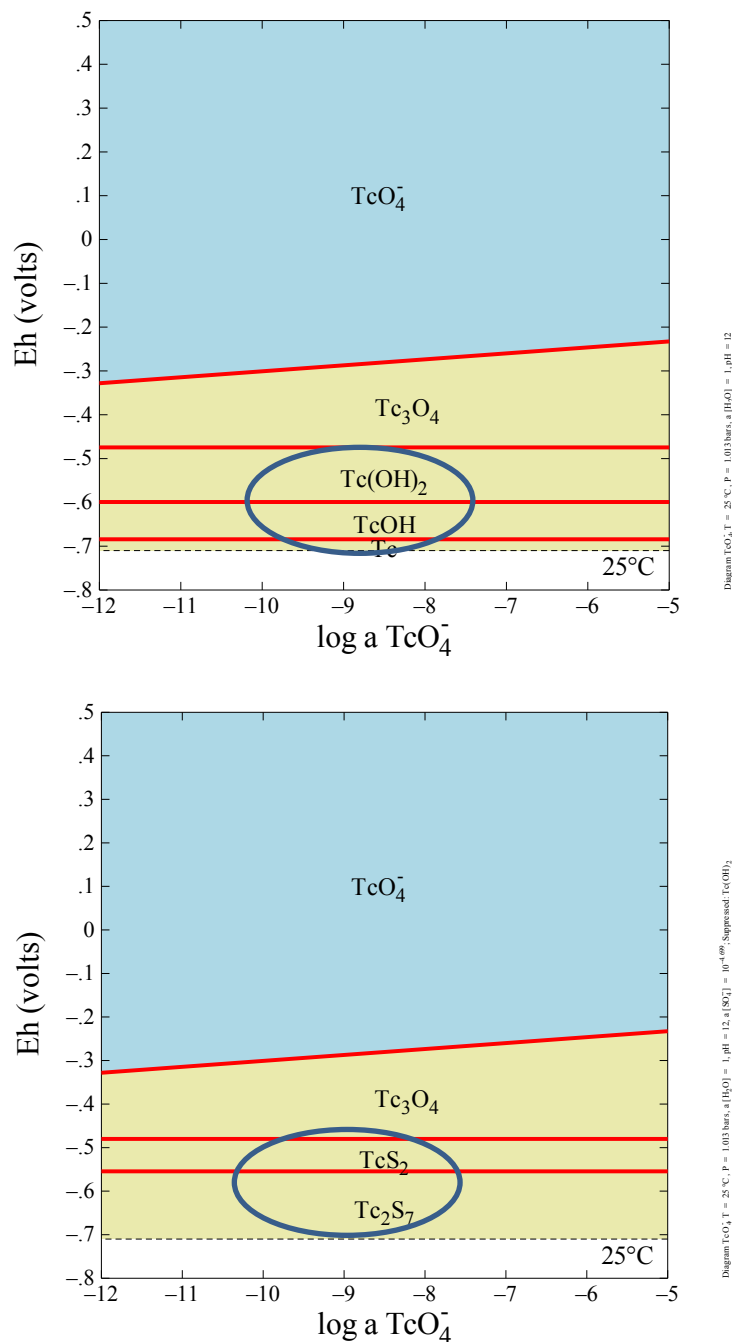


Figure 8: Geochemist Workbench Model of Eh-Tc at pH 12 (top) without S present (top) and with 2 mg/L S (bottom). All Tc redox states coupled. Model generated using thermo.com.V8.R6+.dat database. Oval shows approximate E_H and Tc concentrations observed in batch sorption experiments.

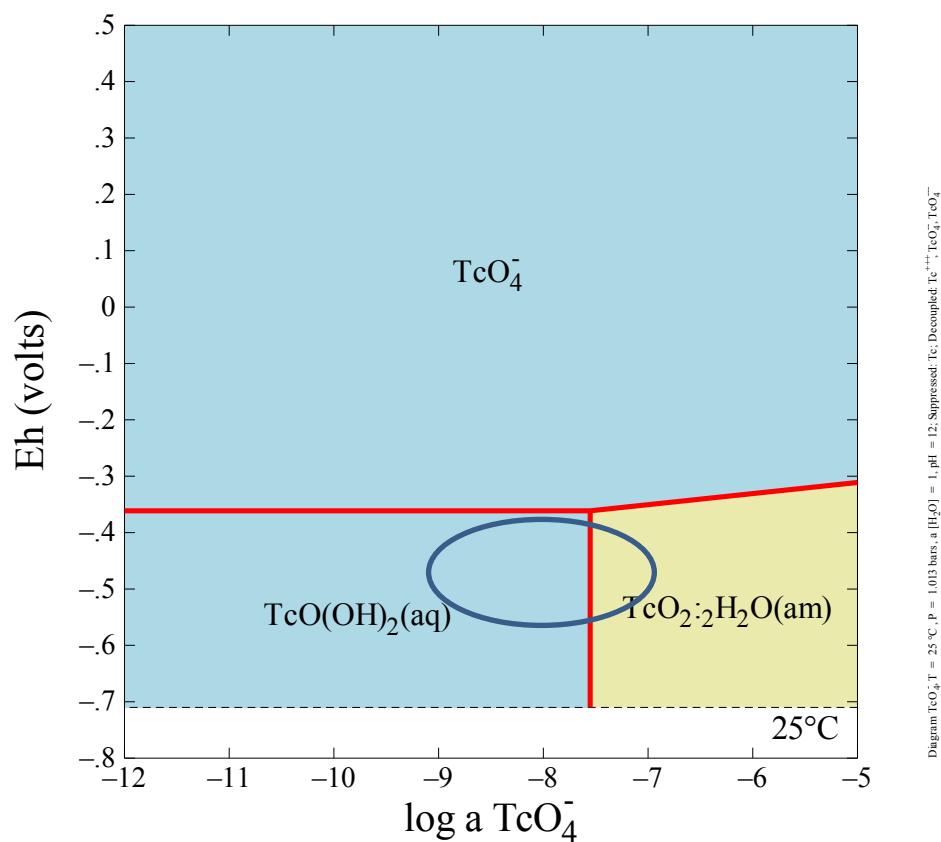


Figure 9: Geochemist Workbench Model of Eh-Tc concentrations at pH 12. There is no change in speciation when 2 mg/L S is added as done in Figure 8. Only Tc(VII)/Tc(IV) redox couple active. Model generated using thermo.com.V8.R6+.dat database. Oval shows approximate E_H and Tc concentration values observed in batch sorption experiments.

4.0 ⁹⁹Tc Batch Desorption Experiments

4.1 Results from Batch Desorption Experiments

The pH of each cementitious suspension as a function of time after starting the desorption experiments is shown in Figure 10. The pH values remained stable. Thus, running the desorption step with solids which had been pre-equilibrated with each respective cementitious material prevented any drastic pH changes at the start of the desorption step. However, the changes in E_h (Figure 11) were much greater than those for pH. At the end of the sorption step, after over 300 days of equilibration in the 0.1% $H_2(g)$ atmosphere, the E_h values for all suspensions was between -350 and -450 mV. After adding the pH equilibrated, oxic solutions, the E_h values increased to over 100 mV in each suspension within the first 24 hours. The E_h of each solution continued to slightly rise until the experiment was terminated after 20 days. It should also be noted that five out of six TR545 reactors, which turned an olive green during the sorption experiment, returned to their original yellow/beige color after 1 day. The sixth TR545 reactor also returned to the yellow/beige color after 4 days.

The measured aqueous phase concentrations of ⁹⁹Tc as a function of time are shown in Figures 12 and 13. The data show that ⁹⁹Tc is rapidly released from the saltstone upon exposure to oxidizing conditions. The aqueous ⁹⁹Tc concentrations increase by more than an order of magnitude for all suspensions. For comparison, the data are also plotted as fraction sorbed (Figure 14), and as conditional K_d values (“conditional” is used to indicate that the samples are clearly not at steady state; Figure 15). The oxidation state of ⁹⁹Tc in the aqueous phase was not determined, but based upon the previous measurements (Figure 5), under anoxic conditions and using the E_h -⁹⁹Tc concentration diagram in Figure 9, it can be reasonably assumed that the oxidation state of the aqueous ⁹⁹Tc is ⁹⁹Tc(VII).

4.2 Discussion of Desorption Experiments

The desorption experiments show that while cementitious materials can effectively sequester ⁹⁹Tc under reducing conditions, exposure to oxidizing conditions causes a rapid release of ⁹⁹Tc. The conditional K_d values under oxidizing conditions decrease significantly as shown in Table 2. While direct oxidation state analysis was not performed in this portion of the work, this desorption phenomena is likely due to oxidation of surface bound or precipitated ⁹⁹Tc(IV) to aqueous ⁹⁹Tc(VII).

The data in Figure 12 indicate that ⁹⁹Tc release undergoes a fast then a slow desorption step characteristic of most metal desorption. The desorption experiments could not continue beyond 20 days due to sample volume limitations. Therefore, the 20 day values must be considered to be conditional K_d values, which may not have reached equilibrium.

TR545 and TR547 maintain the highest K_d values under oxidizing conditions, but it is noteworthy that those suspensions also have the greatest change in aqueous ⁹⁹Tc over time, and appear to be the least likely suspensions to have reached equilibrium. Therefore, the release of ⁹⁹Tc may be rate limited and dependent on either ⁹⁹Tc(IV) reoxidation and/or dissolution kinetics. It is also noteworthy that the aged cement maintains relatively high K_d values. As noted above during the discussion of the sorption data, it is unclear how ⁹⁹Tc is interacting with the aged cement. Based on similar partitioning behavior, reduction of ⁹⁹Tc(VII) followed by precipitation seems to be a likely mechanism, but the source of reducing capacity is unclear based on this existing data. The

aged cement and Vault 2 samples appear to have relatively higher variability than TR545 and TR547. This could be due to sample heterogeneity or differences in kinetics. However, the complete removal of ^{99}Tc from Vault 2 during the desorption step may imply a different sequestration mechanism from the other three cementitious solids.

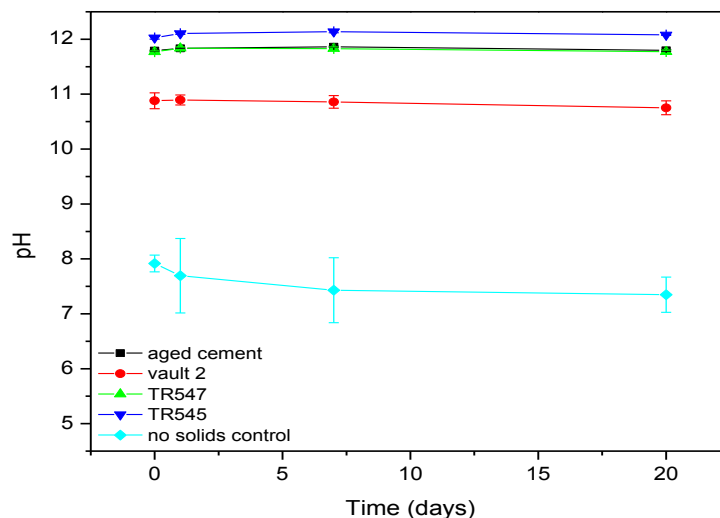


Figure 10: pH of cementitious material suspensions measured during the ^{99}Tc desorption experiments (the pH at time 0 is equivalent to the value at 319 days during the anoxic sorption experiment).

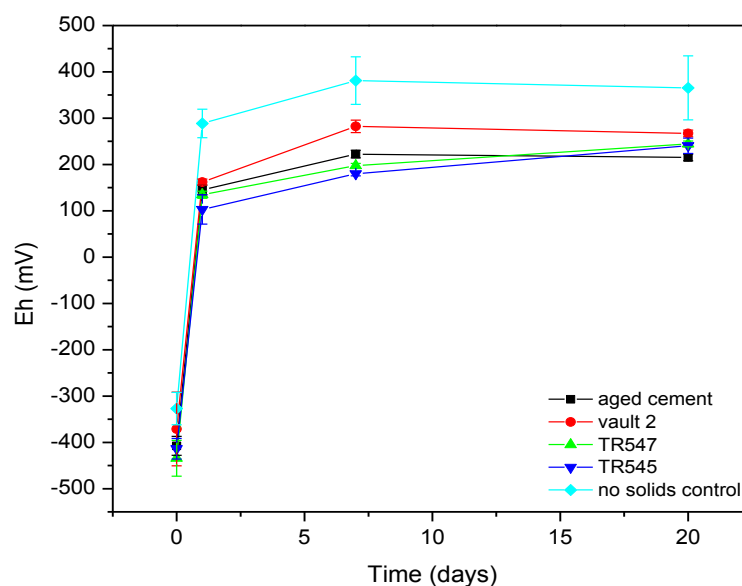


Figure 11. Eh of cementitious material suspensions measured during the ^{99}Tc desorption experiments (the Eh at time 0 is equivalent to the value at 319 days during the anoxic sorption experiment).

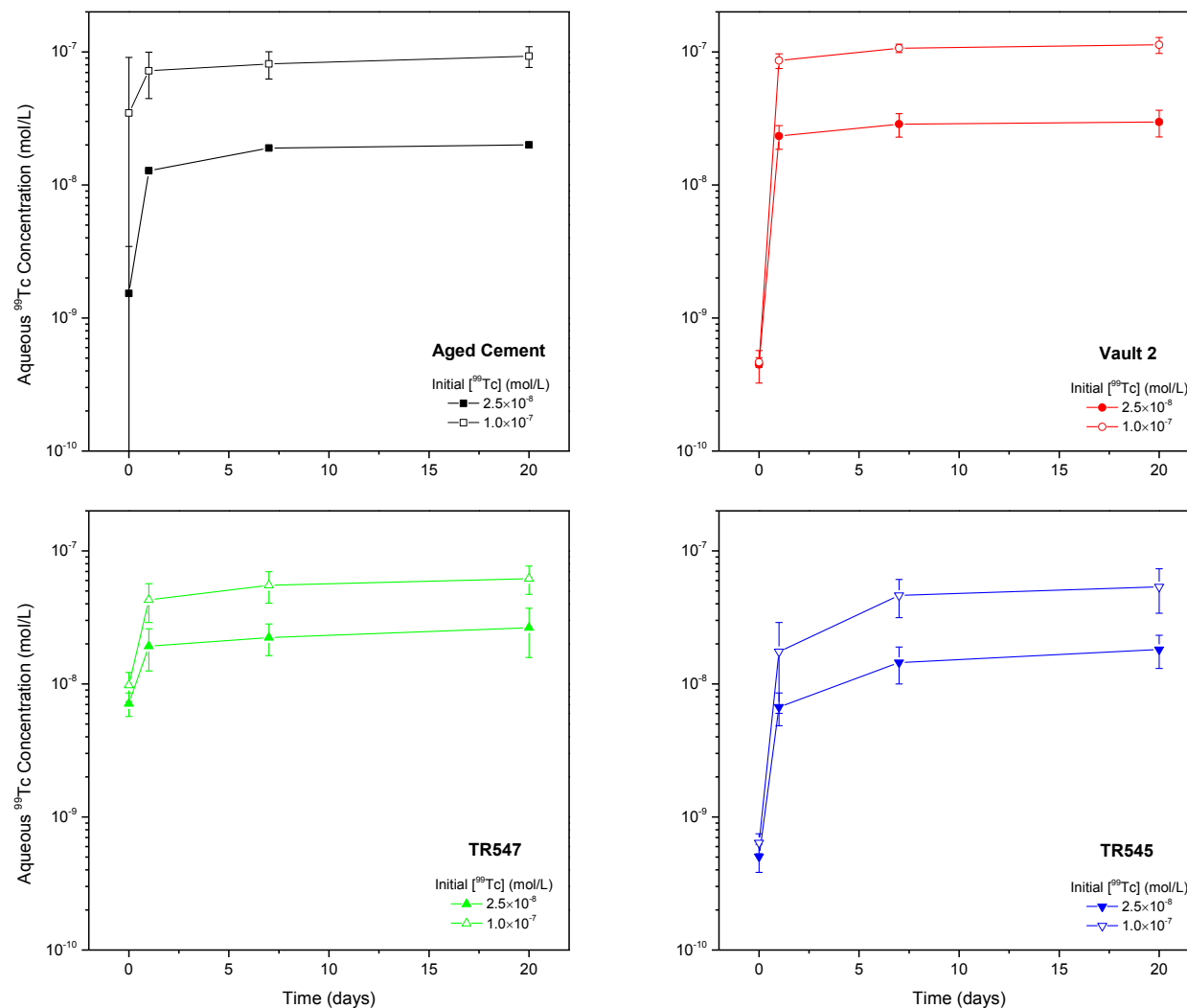


Figure 12. Aqueous ^{99}Tc concentrations versus time during the desorption step to the cementitious materials. The legend in the lower left corner of each plot notes the specific cementitious material and the initial aqueous ^{99}Tc concentrations. The ^{99}Tc aqueous concentration at time zero is equal to the ^{99}Tc aqueous concentration at the end of the 319 day sorption period under anoxic conditions.

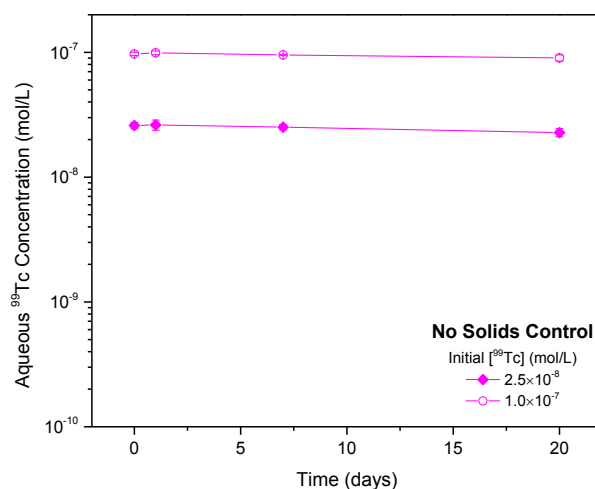


Figure 13. Aqueous ^{99}Tc concentrations versus time during the desorption step in the no solids control reactors. The legend in the lower left corner notes the initial aqueous ^{99}Tc concentrations. The ^{99}Tc aqueous concentration at time zero is equal to the ^{99}Tc aqueous concentration at the end of the 319 day sorption period under anoxic conditions.

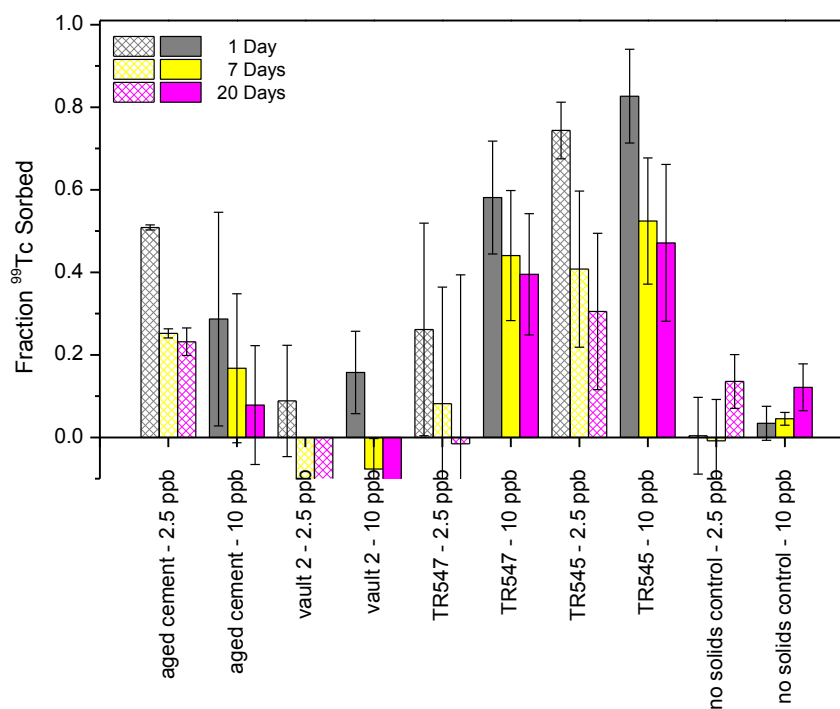


Figure 14. Fraction ^{99}Tc sorbed as a function of time and cementitious material during the desorption experiment (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments).

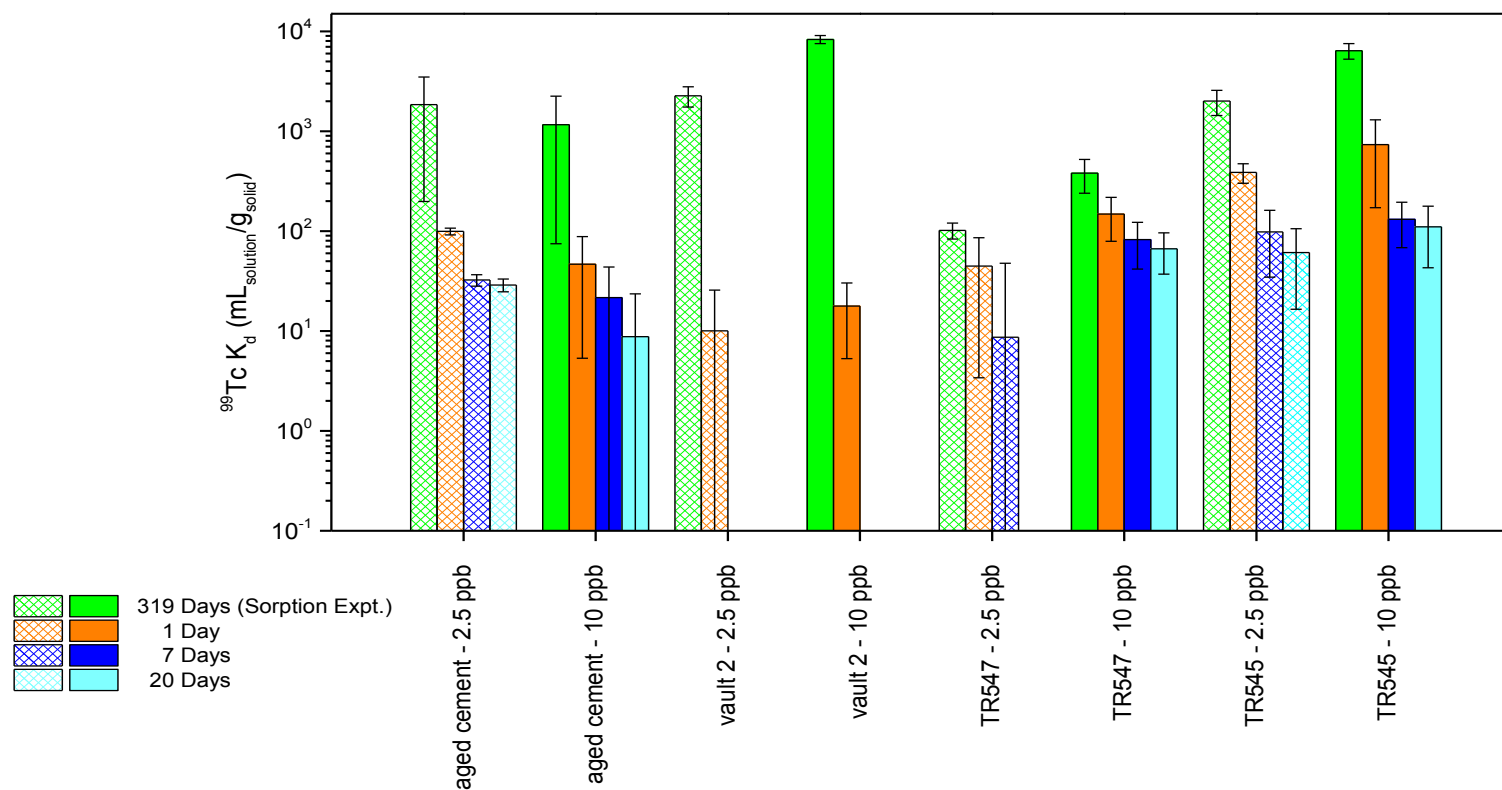


Figure 15. Conditional K_d values (i.e., non-equilibrium) as a function of time measured for ^{99}Tc sorption to cementitious materials during the desorption experiment (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration; hatched bars are for 2.5 ppb ^{99}Tc treatments and solid bars are for 10 ppb ^{99}Tc treatments). For reference the K_d determined after 319 days in the sorption step is included.

Table 2: Comparison of conditional K_d values under reducing and oxidizing conditions.

Cementitious material	319 Days Sorption (reducing conditions)		20 Days Desorption (oxidizing conditions)	
	K_d (n=3) (mL _{soln} /g _{solid})	K_d standard deviation	K_d (n=3) (mL _{soln} /g _{solid})	K_d standard deviation
aged cement - 2.5 ppb	1846	1648	29	4
aged cement - 10 ppb	1161	1087	9	15
vault 2 - 2.5 ppb	2265	519	-12	16
vault 2 - 10 ppb	8302	766	-8	11
TR547 - 2.5 ppb	102	18	-4	54
TR547 - 10 ppb	380	141	67	30
TR545 - 2.5 ppb	2001	564	61	45
TR545 - 10 ppb	6388	1135	110	67

5.0 Conclusions

^{99}Tc sorption experiments to cementitious materials in an anaerobic glovebag were conducted to provide input for the performance assessment of ^{99}Tc in saltstone. Between 154 and 319 days, the ^{99}Tc aqueous concentrations tended to remain constant and samples amended with different initial ^{99}Tc concentrations, tended to merge at about 10^{-9} M for Vault 2 (17% slag) and TR545 (90% slag) and 10^{-8} M for TR547 (45% slag). This data provided strong evidence that solubility, and not adsorption (K_d values), was controlling aqueous Tc concentrations. Laboratory data superimposed over thermodynamic speciation diagrams further supported the notion that solubility, and not adsorption, controlled ^{99}Tc aqueous concentrations. The oxidation state of the aqueous ^{99}Tc at the end of the sorption experiment was determined by solvent extraction to be almost entirely $^{99}\text{Tc(VII)}$. These results are consistent with recent flow-through testing of saltstone similar but not identical in composition to TR547 (Cantrell and Williams, 2012). They reported a solubility of 1.5×10^{-6} M and the aqueous ^{99}Tc concentrations were also determined to be controlled by solubility and not K_d values. Furthermore, they noted that, as the pH of the system decreased from their experimental pH of 13, the ^{99}Tc solubility decreased significantly. The pH of the present system was ~ 11.8 . Most notably, the solid phase identified by Cantrell and Williams (2012) as controlling solubility was $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, which has a very similar solubility to $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$, identified using thermodynamic calculations in this study. Previously proposed solubility controlling phases including Tc-sulfides may be present, but do not appear to control solubility; the solubility of Tc-sulfide phases are more than 10 orders of magnitude lower than either experiment measured.

After the 319 day sorption period, the suspensions were removed from the glovebag and a desorption step under oxic conditions was conducted for 20 days by adding oxic, pH-buffered solutions to the suspensions. ^{99}Tc aqueous concentrations increased by more than an order of magnitude and Eh increased by several hundred millivolts within 24 hours after the introduction of the oxic solutions. These results are consistent with re-oxidation and dissolution/desorption of $^{99}\text{Tc(IV)}$ phases possibly present in the cementitious materials after the anoxic sorption step of the experiment. Aqueous ^{99}Tc concentrations continued to increase slowly until the termination of the desorption experiment after 20 days. Although the cementitious materials investigated demonstrated the ability to strongly sequester aqueous ^{99}Tc under anoxic conditions, the introduction of oxygen resulted in the rapid remobilization of ^{99}Tc . These studies

provide experimental support for the use of a solubility based model under reducing saltstone conditions where Tc(IV) is expected to be the dominant species. The existing K_d model would be appropriate for oxidized saltstone conditions (aged saltstone, not directly evaluated in this study) where Tc(VII) is expected to be the dominant species.

6.0 References

- Allen, P. G., G. S. Siemering, D. K. Shuh, J. J. Bucher, N. M. Edelstein, C. A. Langton, S. B. Clark, T. Teich, and M. A. Denecke. 1997. Technetium Speciation in Cement Waste Forms Determined by X-ray Absorption Fine Structure Spectroscopy. *Radiochimica Acta* 76:77–86.
- Almond, P. M., and D. I. Kaplan. 2011. Distribution Coefficients (K_d) Generated from a Core Sample Collected from the Saltstone Disposal Facility. SRNL-STI-2010-00667. Savannah River National Laboratory, Aiken, SC.
- Atkins M., and F. P. Glasser. 1992. Application of Portland Cement-Based Materials to Radioactive Waste Immobilization. *Waste Management* 12:105–131.
- Boggs, M. A., W. Dong, B. Du, and N. A. Wall. Complexation of Tc(IV) with Acetate at Varying Ionic Strengths. *Radiochimica Acta*, 2010, **98**, 583-587.
- Cantrell, K. J., and B. D. Williams. 2012. Equilibrium Solubility Model for Technetium Release from Saltstone Based on Anoxic Single-pass Flow Through Experiments. PNNL-21723. Pacific Northwest National Laboratory, Richland, WA.
- Dixon, K., J. Harbour, and M. Phifer. Hydraulic and Physical Properties of Saltstone Grouts and Vault Concretes. SRNL-STI-2008-00421. Savannah River National Laboratory, Aiken, SC.
- Estes, S. L., Y. Arai, D. I. Kaplan, and B. A. Powell. 2011. Technetium Sorption by Cementitious Materials under Reducing Conditions. SRNL-STI-2011-00716. Savannah River National Laboratory, Aiken, SC.
- Harbour, J. R., E. K. Hansen, T. B. Edwards, V. J. Williams, R. E. Eibling, D. R. Best, and D. M. Missimer. Characterization of Slag, Fly Ash, and Portland Cement for Saltstone. WSRC-TR-2006-00067. Savannah River National Laboratory, Aiken, SC.
- Kaplan, D. I., J. M. Coates, M. Siegfried, K. Roberts, K., and S. Serkiz. 2008. Saltstone and Radionuclide Interactions: Technetium Sorption and Desorption, Saltstone Reduction Capacity, and Radionuclide Sorption (K_d) Value. SRNS-STI-2008-00045. Savannah River National Laboratory, Aiken, SC.
- Kaplan, D. I., M. S. Lilley, P. M. Almond, and B. A. Powell. 2011. Long-term Technetium Interactions with Reducing Cementitious Materials. SRNL-STI-2010-00668, Revision 0. Savannah River National Laboratory, Aiken, SC.
- Kaplan, D. I., M. S. Lilley, P. M. Almond, and B. A. Powell. 2012. Long-term Technetium Interactions with Reducing Cementitious Materials. SRNL-STI-2010-00668, Revision 1. Savannah River National Laboratory, Aiken, SC (in preparation).

- Lilley, M. S. 2010. Determination of Sorption Coefficients for Neptunium, Plutonium, Iodine, and Technetium in Engineered and Natural Systems under Oxidizing and Reducing Conditions. M.S. Thesis, Clemson University, Clemson, SC.
- Lilley, M. S., B. A. Powell, and D. I. Kaplan. 2009. Iodine, Neptunium, Plutonium, and Technetium Sorption to Saltstone Under Oxidizing and Reducing Conditions. SRNL-STI-2009-00636. Rev.0, Savannah River National Laboratory, Aiken, SC.
- Lukens, W. W., J. J. Bucher, D. K. Shuh, and N. M. Edelstein. 2005. Evolution of Technetium Speciation in Reducing Grout. *Environmental Science & Technology* 39(20):8064–8070.
- Roberts, K. A., and D. I. Kaplan. 2009. Reduction Capacity of Saltstone and Saltstone Components. SRNL-STI-2009-00637. Savannah River National Laboratory, Aiken, SC.

**Appendix A: Photos of saltstone samples and radiological inert atmosphere
glovebag for Tc sorption experiments**



Figure 16: Radiological inert atmosphere glovebag. Atmosphere maintained at 0.1% $\text{H}_2(\text{g})$ /99.9% $\text{N}_2(\text{g})$ by mixing pure $\text{N}_2(\text{g})$ with a mixture of 5% $\text{H}_2(\text{g})$ /95% $\text{N}_2(\text{g})$.



Figure 17: Saltstone suspensions mixing in 50 mL centrifuge tubes (reactors) about their longitudinal axis. Note area outlined in yellow circle shows the oxygen meter reading 0 ppm and the H₂(g) meter at 0.1%.

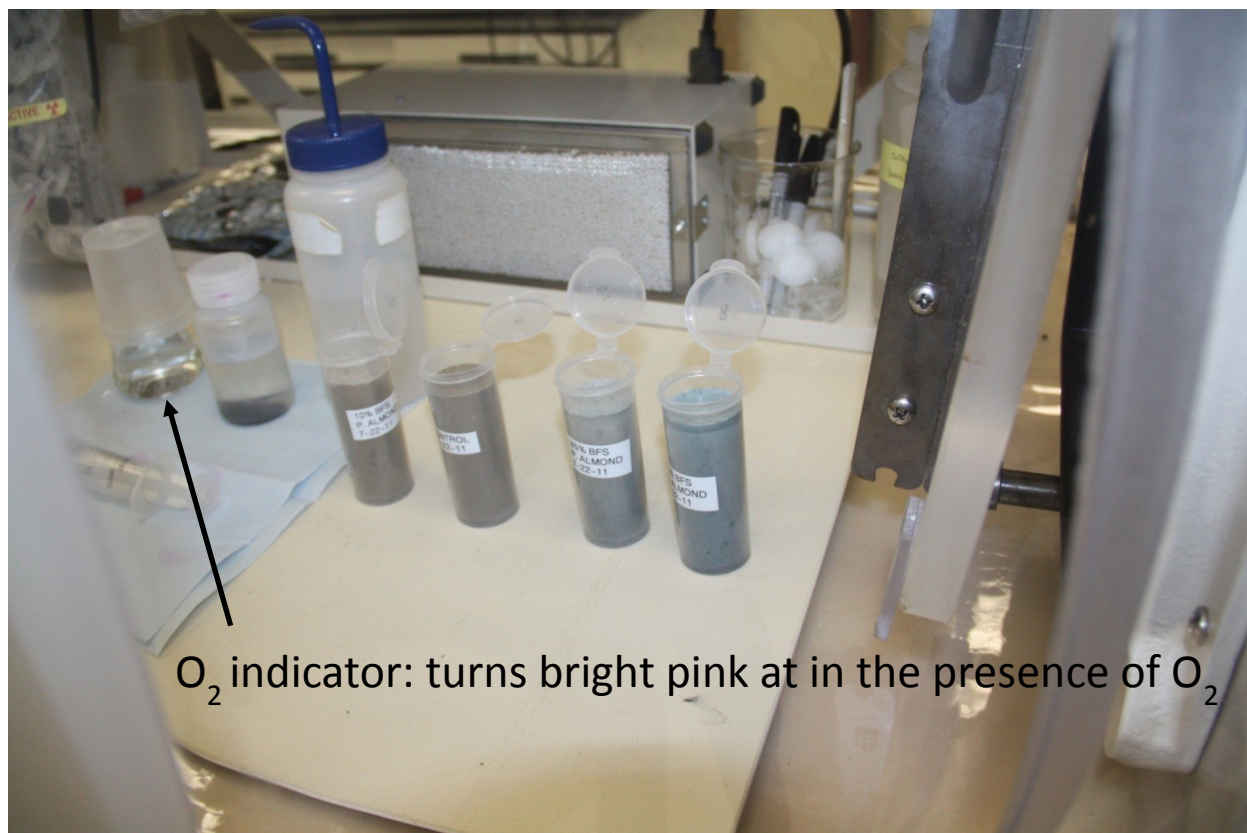


Figure 18: On left is the O_2 indicator solution, which turns bright pink in the presence of O_2 . While transferring supplies into the glovebag, a transient $O_2(g)$ concentration of ~100 ppm would occur and this indicator would go pink then go clear again as the $O_2(g)$ was scrubbed from the atmosphere. Also shown, are various cementitious samples.

Appendix B: Data for ^{99}Tc Concentrations, Fraction Sorbed, and K_d Values as a Function of Time

⁹⁹Tc sorption data from 1-day

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			1 DAY			
aged cement - 2.5 ppb	2.73E-08	2.73E-10	0.015	0.015	-1.2	0.7
aged cement - 10 ppb	9.96E-08	7.59E-09	-0.006	0.046	1.1	2.1
vault 2 - 2.5 ppb	2.59E-08	2.37E-09	0.064	0.019	-0.1	1.2
vault 2 - 10 ppb	1.04E-07	1.52E-09	0.041	0.033	0.0	0.2
TR547 - 2.5 ppb	1.51E-08	1.08E-09	0.642	0.035	27.9	2.8
TR547 - 10 ppb	5.95E-08	3.98E-09	0.749	0.003	27.9	2.6
TR545 - 2.5 ppb	8.03E-09	7.95E-10	0.780	0.022	85.7	8.0
TR545 - 10 ppb	2.47E-08	4.96E-09	0.875	0.011	128.8	37.9
no solids control - 2.5 ppb	2.74E-08	7.15E-10	-0.016	0.041		
no solids control - 10 ppb	1.04E-07	4.05E-10	0.001	0.017		

⁹⁹Tc sorption data from 4-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			4 DAYS			
aged cement - 2.5 ppb	2.61E-08	6.94E-10	0.015	0.015	0.6	0.6
aged cement - 10 ppb	1.03E-07	6.24E-09	-0.006	0.046	-0.2	1.7
vault 2 - 2.5 ppb	2.41E-08	1.96E-09	0.064	0.019	2.7	1.1
vault 2 - 10 ppb	9.94E-08	3.90E-09	0.041	0.033	1.6	1.3
TR547 - 2.5 ppb	9.51E-09	9.35E-10	0.642	0.035	66.0	7.0
TR547 - 10 ppb	2.62E-08	2.68E-10	0.749	0.003	110.5	7.9
TR545 - 2.5 ppb	5.85E-09	5.61E-10	0.780	0.022	131.5	11.0
TR545 - 10 ppb	1.29E-08	9.07E-10	0.875	0.011	274.2	22.1
no solids control - 2.5 ppb	2.67E-08	1.03E-09	-0.016	0.041		
no solids control - 10 ppb	1.03E-07	7.63E-10	0.001	0.017		

⁹⁹Tc sorption data from 8-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			8 DAYS			
aged cement - 2.5 ppb	2.55E-08	6.02E-10	0.037	0.022	1.5	0.9
aged cement - 10 ppb	9.85E-08	1.86E-09	0.036	0.015	1.4	0.6
vault 2 - 2.5 ppb	1.98E-08	1.16E-09	0.229	0.065	11.6	4.3
vault 2 - 10 ppb	9.30E-08	2.25E-09	0.102	0.020	4.2	0.8
TR547 - 2.5 ppb	8.20E-09	8.79E-10	0.691	0.033	82.7	9.6
TR547 - 10 ppb	1.84E-08	8.49E-10	0.824	0.009	173.7	19.1
TR545 - 2.5 ppb	4.44E-09	3.04E-10	0.833	0.012	184.1	8.0
TR545 - 10 ppb	8.40E-09	8.31E-10	0.918	0.010	443.3	46.9
no solids control - 2.5 ppb	2.49E-08	5.49E-10	0.053	0.031		
no solids control - 10 ppb	9.54E-08	4.51E-09	0.070	0.054		

⁹⁹Tc sorption data from 19-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			19 DAYS			
aged cement - 2.5 ppb	2.57E-08	5.28E-10	0.027	0.009	1.1	0.4
aged cement - 10 ppb	9.72E-08	5.25E-09	0.049	0.043	2.0	1.8
vault 2 - 2.5 ppb	1.01E-08	1.52E-09	0.605	0.061	60.8	18.2
vault 2 - 10 ppb	7.63E-08	1.70E-08	0.264	0.157	15.1	12.1
TR547 - 2.5 ppb	7.18E-09	1.27E-09	0.730	0.048	101.2	20.9
TR547 - 10 ppb	1.42E-08	9.89E-10	0.864	0.010	236.3	31.3
TR545 - 2.5 ppb	2.79E-09	1.57E-10	0.895	0.007	314.4	9.1
TR545 - 10 ppb	4.42E-09	3.32E-10	0.957	0.004	875.8	67.2
no solids control - 2.5 ppb	2.47E-08	6.54E-10	0.060	0.014		
no solids control - 10 ppb	9.40E-08	1.48E-09	0.085	0.022		

⁹⁹Tc sorption data from 56-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			56 DAYS			
aged cement - 2.5 ppb	2.80E-08	4.42E-10	-0.059	0.008	-2.1	0.3
aged cement - 10 ppb	1.07E-07	6.05E-09	-0.048	0.036	-1.7	1.2
vault 2 - 2.5 ppb	7.57E-10	2.16E-10	0.970	0.011	1324.2	335.5
vault 2 - 10 ppb	1.93E-08	1.62E-08	0.813	0.159	421.0	521.8
TR547 - 2.5 ppb	7.23E-09	8.42E-10	0.728	0.032	98.7	11.5
TR547 - 10 ppb	1.41E-08	9.13E-10	0.865	0.009	237.6	27.1
TR545 - 2.5 ppb	1.26E-09	6.31E-11	0.953	0.002	744.8	70.1
TR545 - 10 ppb	1.60E-09	1.29E-10	0.984	0.002	2494.0	189.1
no solids control - 2.5 ppb	2.69E-08	8.26E-10	-0.023	0.019		
no solids control - 10 ppb	1.01E-07	1.37E-09	0.016	0.018		

⁹⁹Tc sorption data from 154-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			154 DAYS			
aged cement - 2.5 ppb	2.21E-08	6.06E-09	0.165	0.237	10.4	16.1
aged cement - 10 ppb	9.51E-08	3.34E-09	0.070	0.014	2.8	0.6
vault 2 - 2.5 ppb	3.44E-10	6.12E-11	0.987	0.002	2871.8	364.0
vault 2 - 10 ppb	4.75E-10	4.78E-11	0.995	0.001	8139.6	913.1
TR547 - 2.5 ppb	5.19E-09	4.49E-10	0.805	0.017	151.2	6.3
TR547 - 10 ppb	8.44E-09	2.55E-10	0.919	0.003	420.5	37.3
TR545 - 2.5 ppb	4.82E-10	4.22E-11	0.982	0.001	2015.0	275.2
TR545 - 10 ppb	6.53E-10	9.97E-11	0.994	0.001	6217.2	899.4
no solids control - 2.5 ppb	2.56E-08	1.34E-09	0.028	0.054		
no solids control - 10 ppb	9.65E-08	3.01E-09	0.060	0.037		

⁹⁹Tc sorption data from 319-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			319 DAYS			
aged cement - 2.5 ppb	1.53E-09	1.92E-09	0.942	0.073	1846.2	1648.2
aged cement - 10 ppb	3.47E-08	5.62E-08	0.666	0.540	1161.4	1086.8
vault 2 - 2.5 ppb	4.47E-10	1.22E-10	0.983	0.005	2264.9	518.5
vault 2 - 10 ppb	4.65E-10	3.93E-11	0.996	0.000	8302.5	765.7
TR547 - 2.5 ppb	7.12E-09	1.42E-09	0.732	0.053	101.8	18.4
TR547 - 10 ppb	9.79E-09	2.42E-09	0.906	0.023	380.3	140.6
TR545 - 2.5 ppb	5.04E-10	1.21E-10	0.981	0.004	2001.4	563.6
TR545 - 10 ppb	6.39E-10	1.10E-10	0.994	0.001	6387.7	1135.2
no solids control - 2.5 ppb	2.59E-08	1.54E-09	0.015	0.063		
no solids control - 10 ppb	9.70E-08	3.00E-09	0.054	0.039		

⁹⁹Tc desorption data from 1-day

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			1 DAY Desorption			
aged cement - 2.5 ppb	1.28E-08	1.59E-10	0.509	0.006	99.3	7.8
aged cement - 10 ppb	7.21E-08	2.74E-08	0.287	0.259	46.7	41.3
vault 2 - 2.5 ppb	2.33E-08	4.70E-09	0.088	0.135	10.0	15.6
vault 2 - 10 ppb	8.60E-08	1.09E-08	0.157	0.100	17.7	12.5
TR547 - 2.5 ppb	1.92E-08	6.71E-09	0.262	0.258	44.7	41.3
TR547 - 10 ppb	4.29E-08	1.39E-08	0.581	0.137	148.2	69.1
TR545 - 2.5 ppb	6.69E-09	1.85E-09	0.744	0.069	386.7	85.9
TR545 - 10 ppb	1.75E-08	1.15E-08	0.827	0.114	735.8	564.2
no solids control - 2.5 ppb	2.62E-08	2.47E-09	0.004	0.093		
no solids control - 10 ppb	9.91E-08	3.35E-09	0.034	0.041		

⁹⁹Tc desorption data from 7-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			7 DAYS Desorption			
aged cement - 2.5 ppb	1.89E-08	4.50E-10	0.252	0.011	32.4	4.2
aged cement - 10 ppb	8.14E-08	1.89E-08	0.168	0.181	21.6	22.1
vault 2 - 2.5 ppb	2.86E-08	5.71E-09	-0.160	0.182	-12.5	14.7
vault 2 - 10 ppb	1.07E-07	7.61E-09	-0.077	0.074	-6.4	5.9
TR547 - 2.5 ppb	2.23E-08	5.94E-09	0.082	0.282	8.6	39.1
TR547 - 10 ppb	5.51E-08	1.47E-08	0.440	0.158	82.1	40.4
TR545 - 2.5 ppb	1.45E-08	4.47E-09	0.408	0.189	98.0	63.4
TR545 - 10 ppb	4.62E-08	1.47E-08	0.524	0.153	131.5	63.1
no solids control - 2.5 ppb	2.51E-08	1.24E-09	-0.008	0.100		
no solids control - 10 ppb	9.52E-08	1.11E-09	0.045	0.016		

⁹⁹Tc desorption data from 20-days

description	Aqueous ⁹⁹ Tc concentration	Stdev in Concentration	Fraction Tc99 Sorbed	Stdev in Fraction Sorbed	Kd	Kd error
	M	M			mL _{soln} /g _{solid}	
			20 DAYS Desorption			
aged cement - 2.5 ppb	2.00E-08	8.34E-10	0.232	0.033	28.9	4.3
aged cement - 10 ppb	9.29E-08	1.65E-08	0.078	0.144	8.8	14.7
vault 2 - 2.5 ppb	2.97E-08	6.76E-09	-0.163	0.205	-12.3	16.2
vault 2 - 10 ppb	1.13E-07	1.56E-08	-0.106	0.148	-8.0	10.6
TR547 - 2.5 ppb	2.65E-08	1.07E-08	-0.015	0.409	-3.5	54.4
TR547 - 10 ppb	6.20E-08	1.49E-08	0.395	0.147	66.6	29.5
TR545 - 2.5 ppb	1.81E-08	5.07E-09	0.305	0.189	61.0	44.5
TR545 - 10 ppb	5.37E-08	1.97E-08	0.471	0.190	110.2	67.2
no solids control - 2.5 ppb	2.28E-08	1.69E-09	0.135	0.065		
no solids control - 10 ppb	9.02E-08	5.09E-09	0.121	0.057		

Distribution:

P. M. Almond, 773-43A – Rm. 227
H. H. Burns, 773-41A – Rm. 214
B. T. Butcher, 773-43A – Rm. 212
A. D. Cozzi, 999-W – Rm. 337
D. A. Crowley, 773-43A – Rm. 216
S. D. Fink, 773-A – Rm. 112
G. P. Flach, 773-42A – Rm. 211
K. M. Fox, 999-W – Rm. 336
J. C. Griffin, 773-A – Rm. A-202
C. C. Herman, 999-W – Rm. 344
G. K. Humphries, 705-3C – Rm. 206
P. R. Jackson, 703-46A – Rm. 223
D. I. Kaplan, 773-43A – Rm. 215
C. A. Langton, 777-42A – Rm. 219
D. Li, 999-W – Rm. 336
S. L. Marra, 773-A – Rm. A-230
J. J. Mayer, 773-42A – Rm. 242
A. M. Murray, 773-A – Rm. A-229
F. M. Pennebaker, 773-42A – Rm. 146
M. A. Phifer, 773-42A – Rm. 252
M. M. Reigel, 999-W – Rm. 404
K. A. Roberts, 773-43A – Rm. 225
K. H. Rosenberger, 705-1C – Rm. 33b
K. H. Subramanian, 766-H – Rm. 2204

(1 file copy & 1 electronic copy), 773-43A – Rm.213