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Technetium Sorption by Cementitious Materials Under Reducing Conditions

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EXECUTIVE SUMMARY

The objective of this study was to measure Tc sorption to cementitious materials under reducing conditions to simulate Saltstone Disposal Facility conditions. Earlier studies were conducted and the experimental conditions were found not to simulate those of the facility. Through a five month subcontract with Clemson University, sorption of ^{99}Tc to four cementitious materials was examined within an anaerobic glovebag targeting a 0.1% $\text{H}_2(\text{g})/99.9\% \text{N}_2(\text{g})$ atmosphere. Early experiments based on Tc sorption and Eh indicated that 0.1% $\text{H}_2(\text{g})$ (a reductant) was necessary to preclude experimental impacts from $\text{O}_2(\text{g})$ diffusion into the glovebag. Preliminary data to date (up to 56 days) indicates that sorption of ^{99}Tc to cementitious materials increased with increasing slag content for simulated saltstone samples. This is consistent with the conceptual model that redox active sulfide groups within the reducing slag facilitate reduction of Tc(VII) to Tc(IV).

These experiments differ from previous experiments where a 2% $\text{H}_2(\text{g})$ atmosphere was maintained (Kaplan et al., 2011 (SRNL-STI-2010-00668)). The impact of the 2% $\text{H}_2(\text{g})$ reducing atmosphere on this data was examined and determined to cause the reduction of Tc in experimental samples without slag. In the present ongoing study, after 56 days, Tc sorption by the 50-year old cement samples (no slag) was undetectable, whereas Tc sorption in the cementitious materials containing slag continues to increase with contact time (measured after 1, 4, 8, 19 and 56 days). Sorption was not consistent with spike concentrations and steady state has not been demonstrated after 56 days. The average conditional K_d value for the Vault 2 cementitious material was 873 mL/g (17% slag), for the TR547 Saltstone (45% slag) the conditional K_d was 168 mL/g, and for TR545 (90% slag) the conditional K_d was 1,619 mL/g. It is anticipated that additional samples will be collected until steady state conditions are established to permit measuring more representative K_d and solubility values under these experimental conditions.

The purpose of this revision is to correct K_d values reported in the original document. This document reports results for the first 56 days of a 319 day experiment. After the experiment had finished and all the data were compiled for QA/QC analysis, a mistake in the K_d calculations was found. The K_d values reported in revision 0 of this report were essentially one order of magnitude higher than the actual values. In this revision, the text references to K_d values have been updated along with the data in Figure 2 and Appendix B. Between the time the original document was issued, January 2012, and this document was issued, a final report (Estes et al. 2012; SRNL-STI-2012-00596, Rev. 0) describing all the corrected data for the 319 day experiment was issued. This document does not contain any data that is not already reported in the final report (SRNL-STI-2012-00596, Rev. 0).

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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
SRNL	Savannah River National Laboratory
XAS	X-ray Absorption Spectroscopy

1.0 Introduction

Technetium is among the key risk drivers at the Saltstone Facility. It is immobilized in saltstone by (1) minimizing diffusion within the pore spaces of the cementitious wasteform, and (2) promoting the reduction of the highly mobile Tc(VII) form to a highly immobile Tc(IV) form by blast furnace slag. Kaplan et al. (2011; reporting the thesis work by Lilley (2010)) attempted to measure its equilibrium constant by conducting (ad)sorption TcO_4^- studies in a glovebag. The objective was to measure the distribution coefficient, K_d value, between solid phase saltstone and the aqueous phase. It became apparent that too reducing a condition had been created by the H_2 gas, when experimental results showed the slag-free cementitious controls removed as much Tc from solution as the slag-containing cementitious materials. The objective of this study was to perform the original study with a less reducing condition 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 %.

This is a status report and reflects work completed between May 5 and September 30, 2011. At the time of the last sample, steady state conditions have not been demonstrated. It is anticipated that this work will continue in the following year to permit measurement of steady state solubility and/or K_d values.

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 does not contain any reducing slag. The Vault 2 formulation contains 17% reducing slag. The TR547 and TR545 saltstone formulations contain 45% and 90% reducing slag, respectively. 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. The composition of the Aged Cement is not known. No precautions were made to store the reducing-cementitious samples in an inert environment since fabrication four years ago, so it is anticipated that some oxidation of these samples occurred. At the start of the study the ground saltstone samples were primarily greenish gray.

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 ($\mu\text{eq/g}$)
Aged Cement	NA	NA	NA	NA	85.5 \pm 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	832 ^(a) / 819 ^(b) / 817 ^(d) / 820 ^(e)
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. Based on Table 8 in Dixon et al. (2008; SRNL-STI-2008-00421), which shows the following quantity (lbs/cu yd) for saltstone Vault 2 Mix 1 concrete formulation: 201 cement (12.71 wt-%), 268 slag (16.95 wt-%), 44.7 silica fume (2.83 wt-%), 156.3 fly ash (9.89 wt-%), 911 fine sand (57.62 wt-%). The large aggregate, which accounted for 75 dry-wt % of the original field sample, was removed before the sorption tests were conducted.
^(d) Kaplan et al. (2005)
^(e) Lukens et al. (2005)

2.1 Methods

2.1.1 Experimental Conditions and Apparatus

All experiments were performed in an anaerobic 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. A first set of experiments performed with 100% N₂(g) atmosphere within the glovebag were unsuccessful. Most likely, oxygen diffusion into the bag resulted in oxidizing conditions within the samples and therefore minimal sorption of ⁹⁹Tc(VII) was observed. 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. In order for the glovebag to maintain anaerobic conditions, a palladium catalyst is used inside the bag. 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. All pH and Eh data are reported below.

2.1.2 Sample Preparation and Analysis

A ^{99}Tc working solution was prepared by diluting a stock solution of ^{99}Tc (Isotope Products, Valencia, CA) in distilled-deionized water (distilled deionized (DDI) water 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, it is reasonable to assume that the Tc existed in as Tc(VII). The reduced Tc(IV) oxidation state would have a very low solubility 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, 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 saturated calcite 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 point at which the $^{99}\text{Tc(VII)}$ amendment was made 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 actual concentration measured in actual samples recovered from the Saltstone Facility. Almond et al. (2011) recovered samples with Tc concentrations of $5.35\text{e-}11\text{ Ci/g}$ in the solid phase and when leached under oxidized conditions to measured K_d values ($K_d = 12\text{ mL/g}$) the aqueous phase had $2.82\text{e-}12\text{ Ci/mL}$ 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.

At 1, 4, 8, 19, and 56 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. 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.

3.0 Results and Discussion

3.1.1 ⁹⁹Tc Batch Sorption Experiments

The fraction of aqueous ⁹⁹Tc in the four cementitious solid suspensions as well as the no solids blanks are plotted in Figure 1. The data are also presented with K_d on the y-axis in Figure 2. As expected based on the high solubility and low sorption affinity of ⁹⁹Tc(VII), there was little loss of ⁹⁹Tc to the container walls in the no solids control samples presented in Figure 1. (It is not necessary to have to assume a speciation for Tc, but due to the high concentrations in the no solids controls, and the lack of sorption to the slag-free Aged cement, it is likely that the original spike was TcO_4^- .) The data in tabular format is presented in Appendix B. At the end of the study, aqueous suspensions will be analyzed the ratio of $\text{Tc(VII/IV)}_{\text{aq}}$ in the aqueous phase to confirm experimental results.

In samples containing cementitious solids, sorption generally increased with increasing slag content in the solid. There is little sorption of ⁹⁹Tc to the aged cement sample. The high amount of ⁹⁹Tc sorption to the Vault 2 solid (17% slag) at 56 days was somewhat unexpected due to the low slag content, with respect to TR547 (45% slag). However, at early sampling points, there is clearly greater sorption of ⁹⁹Tc to TR545 and TR547. It is unclear what is causing the relatively strong sorption to the Vault 2 sediment at extended times. It is noteworthy that similar elevated ⁹⁹Tc uptake compared to TR545, containing a higher concentration of slag, was also observed under more reducing conditions (Lilley et al., 2009, SRNL-STI-2009-00636).

Data in Figure 2 show that there are no consistent differences in the K_d values between the 2.5 ppb and 10 ppb ⁹⁹Tc loadings for the same solid. This is somewhat unexpected because the K_d values should be independent of total analyte concentration. However, these are the initial data points and the systems have clearly not reached equilibrium. Therefore, the observed difference in K_d values may be a manifestation of ⁹⁹Tc concentration dependence on the sorption kinetics. It is noteworthy that the relatively large K_d variations in Figure 2 are the result of relatively small differences in fraction sorbed (Figure 1; Appendix B). Additionally, there is not a consistent trend, whereby one spike concentration produces a greater or lower relative K_d value. The average conditional K_d values for both spike concentrations (average of 6 values):

- Aged Cement $K_d = -2$ mL/g,
- Vault 2 $K_d = 873$ mL/g,
- TR547 Saltstone (45% slag) = 168 mL/g
- TR545 Saltstone (90% slag) = 1619 mL/g

The pH and redox potentials measured at each sampling interval are provided in Figure 3 and Figure 4, respectively. As expected, the pH values of the four cementitious materials were between 11.25 and 12.25 (Figure 3). They did not vary as a function of time. The no solids control did change during the course of the study, likely as a result of changes in the redox status (Figure 4). Generally, as Eh increases, pH in aqueous systems decreases.

The Eh of all five systems, regardless of whether they contained slag or not, during the first 19 days of the study, had Eh values of about -400 (Figure 4). By the time the next measurement was taken, day 56, the Eh of the two slag-free systems (no solids controls and the aged cement) increased substantially to above zero mV. The cause for this is not known but it is possible that

the reductant (perhaps H_2 originating from the glovebag atmosphere) was eventually dissipated or consumed and the system returned to its anticipated redox state. The slag containing systems, the Vault 2 and the two saltstone samples, remained at very low Eh values. There is essentially no ^{99}Tc sorption to these slag-free systems, so it is not surprising that ^{99}Tc sorption to these two systems did not change significantly at day 56.

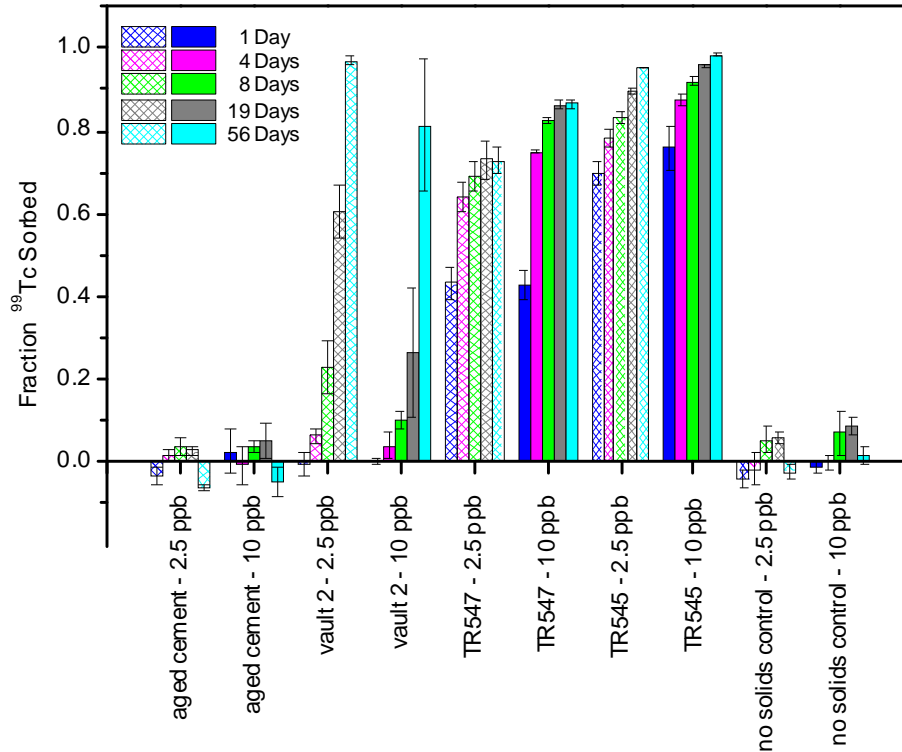


Figure 1. Fraction of ^{99}Tc sorbed as a function of time and cementitious materials (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration).

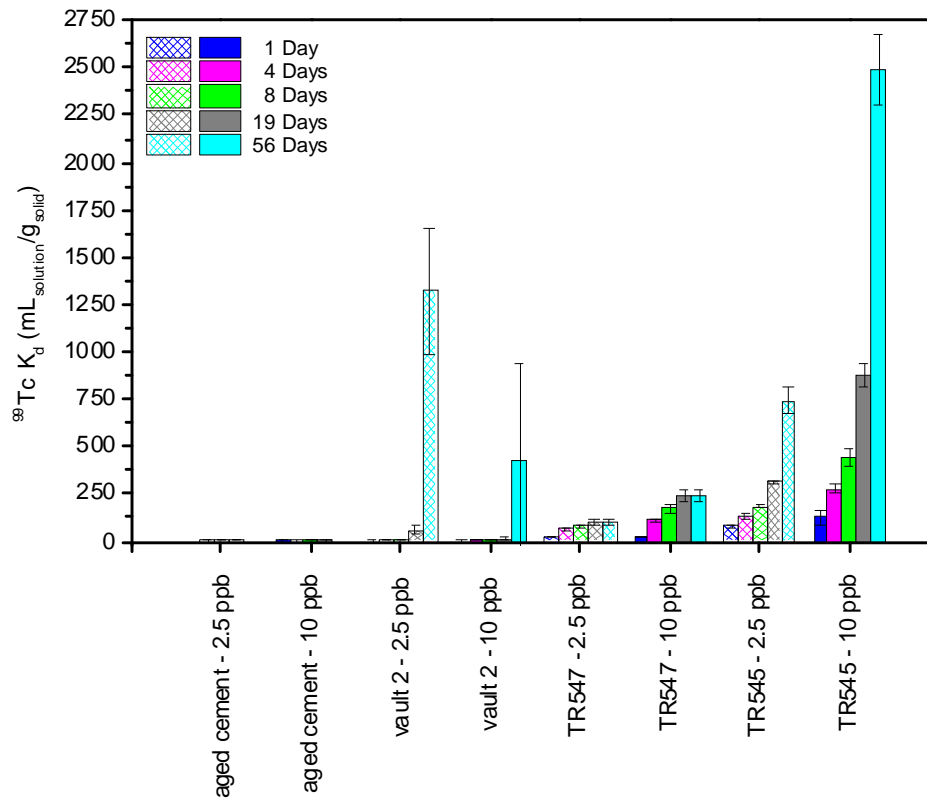


Figure 2. Conditional K_d values (i.e., non-equilibrium) as a function of time measured for ^{99}Tc sorption to cementitious materials (X-axis labels note which cementitious material was used and the total ^{99}Tc concentration).

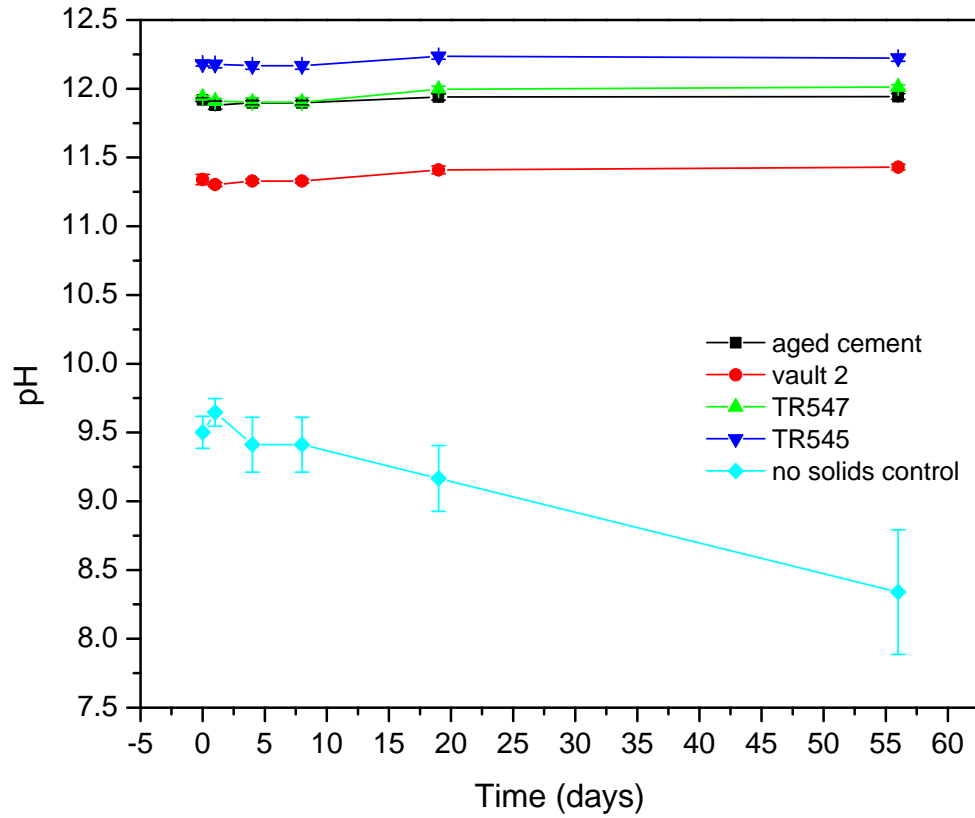


Figure 3. pH of cementitious material suspensions measured during ^{99}Tc sorption experiments.

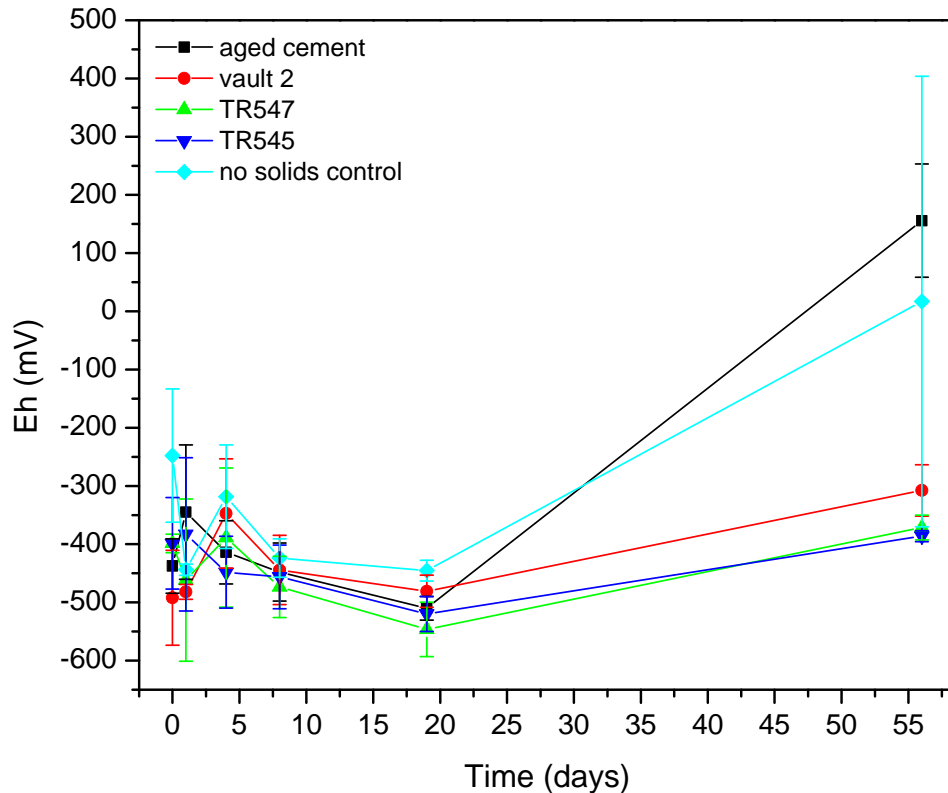


Figure 4. Redox potentials (converted to SHE) of cementitious material suspensions measured during ^{99}Tc sorption experiments.

3.1.2 Submission of Proposal for XAS Beamline Time

A proposal for beamline time to examine the redox state of Fe, S, and Cr (non-rad) to understand the measure oxidation rate and understand chemistry/mineralogy responsible redox chemistry was conditionally approved for the end of January 2012. A copy of the submitted proposal is provided in Appendix A. A follow up proposal in the coming year will be written to examine the Tc redox state.

4.0 Conclusions

Tc sorption experiments to cementitious materials in an anaerobic glovebag were conducted to provide input for the performance assessment of Tc in saltstone. Many controls and ancillary measurements were included in the study. Among the more important observations were that Tc did not sorb to the no-solid control glassware and slag-free cementitious material Tc sorption tended to increase with increasing slag content in the cementitious material formulation (with one notable exception). After 56 days of contact, it had been demonstrated that pH had obtained a steady state in the saltstone samples, but it was not demonstrated that Tc had obtained a steady state, evidenced by increasing K_d values. Different Tc K_d values between the two spike concentrations were observed, for some solids the more dilute spike yielded a higher K_d value and for other solids, the opposite was true. Therefore, the observed difference in K_d values may be a manifestation of ^{99}Tc concentration dependence on the sorption kinetics. It is noteworthy that the

relatively large K_d variations in Figure 2 are the result of relatively small differences in fraction sorbed (Figure 1).

5.0 References

- Almond, P. M., 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.
- Dixon, K., J. Harbour, M. Phifer. 2008. Hydraulic and Physical Properties of Saltstone Grouts and Vault Concretes. SRNL-STI-2008-00421. Savannah River National Laboratory, Aiken, SC.
- Estes, S. L., D. I. Kaplan, and B. A. Powell. 2012. Technetium Sorption by Cementitious Materials under Reducing Conditions. SRNL-STI-2012-00596, Rev. 0. Savannah River National Laboratory, Aiken, SC.
- Kaplan, D. I., T. Hang, S. E. Aleman, 2005. Estimated Duration of the Reduction Capacity within a High-Level Waste Tank. WSRC-RP-2005-01674, Rev. 0. Westinghouse Savannah River Company, Aiken, SC
- Kaplan, D. I., J. M. Coates, M. Siegfried, K. Roberts, 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. Savannah River National Laboratory, Aiken, SC.
- Lilley, M. 2010. Determination of Sorption Coefficients for Neptunium, Plutonium, Iodine, and Technetium in Engineered and Natural Systems under Oxidizing and Reducing Conditions. Masters Degree 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, N. M. Edelstein. 2005. Evolution of Technetium Speciation in Reducing Grout. Environ. Sci. Technol. 44:237-241.
- Roberts, K. A. and D. I. Kaplan. 2008. Reduction Capacity of Saltstone and Saltstone Components. SRNS-STI-2008-00637. Savannah River National Laboratory, Aiken, SC.

Appendix A. Submitted X-ray Absorption Spectroscopy Proposal

SSRL LETTER OF INTENT PROPOSAL FORM

For User Admin Use Only	
Proposal No.	_____
Date Received	_____
Date Expires	_____

1. BRIEFLY STATE WHY YOU ARE SUBMITTING A LETTER OF INTENT (LOI)

PROPOSAL RATHER THAN A STANDARD PROPOSAL (Note: LOIs may be requested under a

limited set of conditions. In general, the LOI is used to test feasibility of a "risky" experiment; however, it can be used for novel ideas requiring only a small amount of beam time and which have been conceived too late for the normal review cycle. LOIs do not go through the full review process, but may receive assignment of beam time (usually ~6-12 shifts) at the discretion of the SSRL Director or on the advice of the PRP. Staff members review LOIs to identify and address any technical or safety issues. In general, rated proposals take priority over LOIs in the scheduling process.):

We are interested in studying redox chemistry of ^{99}Tc in cementitious materials. Due to the super redox sensitive nature of reduced Tc, we would like to test feasibility of our redox transport chamber from SC to CA using non-rad samples before we formally submit a full proposal to SSRL. In this rapid access proposal, redox sensitive field simulated saltstone-slag samples will be used to conduct bulk Fe, S and Cr K-edge XANES measurements at BL4-1/4-3.

2. TITLE: Kinetics and Mechanistic of Technetium Redox Chemistry in Reducing Cementitious Materials

3. SPOKESPERSON and COLLABORATORS: (list spokesperson first)

<u>Full Name</u>	<u>Full Institution & Address</u>	<u>Work Phone</u>	<u>Fax Number</u>	<u>E-mail Address</u>	<u>Degree</u>
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Daniel Kaplan	Savannah River National Laboratory Aiken, SC 29808	803-725-2363		daniel.kaplan@srnl.doe.gov	Ph.D

4. BRIEFLY DESCRIBE THE PROBLEM TO BE STUDIED: (Please limit to 300 words/2000 characters):

Cementitious materials (CMs) are an important component of the strategy to stabilize nuclear waste resulting from plutonium production by DOE. In particular, ^{99}Tc is one of major risk drivers at the Saltstone Facility at DOE Savannah River Site (SRS). Because of high solubility of Tc(VII) in aerobic environments, the conversion of Tc(VII) to Tc(IV) is required to immobilize Tc in the CMs. The recent shrinking core computer model showed the existence of a sharp boundary that consisted of oxidized outer layer of concrete surrounding a shrinking core of reducing intact saltstone. The slow movement of the boundary seems to be the key to predict the re-mobilization of Tc in the CMs. Unfortunately the current shrinking core model is devoid of geochemical mechanisms. Detail kinetics, mechanisms, and input values are needed to reduce uncertainties in future detailed modeling. The objective of this study is to clarify regarding the process and mechanisms of redox reactions via XAS analysis to improve the Tc stabilization technology in CMs. In our recent laboratory investigation, it was found that Tc(IV) instantaneously oxidized in field simulated slag-containing saltstone (<1mm fraction) with only trace concentrations of atmospheric oxygen (~30 ppm O_2 ; Eh 120 mV) at the high pH, suggesting the super redox sensitive nature of Tc(IV). Prior to the preparation of Tc samples with waste simulant using beta-emitter ^{99}Tc , we are first interested in testing our redox sample transport chamber from Dr. Kaplan's SR National laboratory, Aiken, SC to SSRL, Menlo Park, CA. It consists of five layers of polycarb/glass jar barriers with oxygen scrubbers and sensor strips in each layer. In this rapid access proposal, we will test feasibility of the chamber using field simulated non-rad saltstone-slag samples. As redox indicators, we will conduct bulk XANES measurements at Fe, S and Cr K-edge at BL4-1/4-3.

5. TIME FRAME DESIRED:

Nov-Feb Cycle

6. EXPERIMENTAL STATIONS DESIRED:
(If two stations required, list both under first choice.)

First Choice(s)	Alternates
4-3	
4-1	

7. ESTIMATED BEAM TIME REQUIRED IN 8-HOUR SHIFTS:

5 shifts

8. REQUIRED CRYSTAL SET AND ORIENTATION:

Si(111) Phi=0

9. SSRL EQUIPMENT OR MATERIALS REQUESTED:

Standard XAS configuration, Lytle, GE13, Cryo-set up
For S k-edge XAS, He purged chamber

10. POTENTIAL SAFETY CONCERNS OR HAZARDS

X No hazardous substances, equipment, or procedure will be brought to SSRL as part of this proposed experiment.

IF YES, please complete safety questions below. Additionally, provide detailed safety procedures in proposal text.

Chemical Use () NO (X)Yes

Substance: a mixture of Al2O2, Fe2O3, SiO2

Common Name: Slag containing saltstone with cement

NANOSCALE MATERIALS USE? (X)No ()Yes

- If yes, will there be open manipulation of nanoscale material samples at SSRL? (X)No ()Yes
- If no, how are the samples contained? Sealed with kapton/myler tape
- If yes, a safety plan must be submitted to the SSRL Safety Office for approval. See CDC/NIOSH website for guidance.
<http://www.cdc.gov/niosh/topics/nanotech/safenano/>

BIOHAZARDOUS MATERIALS USE? (X)No ()Yes

- If yes, what type _____ & what is the materials NIH classification _____

HUMAN OR ANIMAL SUBJECT USE? (X)No ()Yes

- If yes, what type _____. *Please contact SSRL Safety Office for further guidance.

RADIOACTIVE MATERIALS USE? (X)No ()Yes*

- If yes, what is the materials specific activity _____

*Radioactive substances may not be brought directly to SSRL. They first must be shipped or taken to Operational Health Physics, Bldg. 24, MS 84, 2575 Sand Hill Rd., Menlo Park, CA 94025, or contact Ray Russ at 650-926-4768.

LASER USE? (X)No ()Yes

- If yes, ANSI classification: _____ Wavelength: _____ Total power: _____
Laser hazards controls you will apply:

HAZARDOUS EQUIPMENT/ELECTRICAL EQUIPMENT? ()No ()Yes

- If yes, describe hazardous/electrical equipment you will be bringing to SSRL. Indicate if it is a commercial product, certified, and if it has been altered in any way.

11. WILL THESE EXPERIMENTS INVOLVE TISSUE FROM HUMAN SUBJECTS OR LABORATORY ANIMALS?

(X)No Yes, provide details.

12. **WILL PRIVATE SECTOR RESEARCH BE PERFORMED?** No Yes
 (Note that private sector research is subject to specific terms and conditions, and SSRL must be reimbursed at full cost recovery. Please complete the Supplemental Use Agreement for Private Sector Research.)

13. **REQUIRED FOR DOE REPORTING PURPOSES:**

RESEARCH AREA (check all that apply)			
Materials Science	Polymers	Earth Sciences	Engineering
Physics	Medical Applications	Environmental Sciences	Instrumentation or Other Development
Chemistry	Biological and Life Sciences	Optics	Purchase of Specialty Services or Materials
Other: (specify)			
FUNDING AGENCY (check all that apply)			
DOE/BES	DVA	NSF	Fdn/Research Inst.
DOE/BER	NASA	USDA	State/County/City
DOE Other: (specify)	X NIH	Other US Gov't: (specify)	Prof/Voluntary Assoc.
DoD: (specify)	NIST	Industry	Foreign: (specify)
Other: (specify) 2011 South Carolina Universities Research and Education Foundation.			

14. **HAS A PROPOSAL COVERING THIS RESEARCH** been submitted to other synchrotron radiation facilities? If so, which? Are there particular capabilities of SSRL that are required for portions of this research?

15. **HAVE YOU RECEIVED BEAM TIME AT SSRL IN THE PAST?** YES NO

16. **IF YOU HAVE PREVIOUSLY RECEIVED BEAM TIME AT SSRL, HAVE YOU NOTIFIED SSRL OF ALL OF YOUR SSRL RELATED PUBLICATIONS, PATENTS AND/OR AWARDS?** YES NO If not previously reported, list below or append to this proposal information on publications, patents, and awards that resulted from your prior beam time at SSRL (refer to lists at www-ssrl.slac.stanford.edu/pubs/):

17. **IF YOU PUBLISHED RESULTS RELATED TO YOUR SSRL BEAM TIME, DID YOU ACKNOWLEDGE SSRL AND FUNDING SOURCES IN THESE PUBLICATIONS?** YES NO (If not already done, please refer to instructions and sample acknowledgements at www-ssrl.slac.stanford.edu/pubs/)

18. **DO YOU HAVE ANY SUGGESTIONS OR CONCERNS WHICH YOU WOULD LIKE TO SHARE WITH SSRL, THE PROPOSAL REVIEW PANEL, OR THE SSRL USERS' ORGANIZATION EXECUTIVE COMMITTEE?**

This research is deemed to be of interest to the DOE and falls within the scope of the BES mission.	
Chi Chang Kao, SSRL Director	Date:

Appendix B. Data for Tc-99 Fraction Sorbed and K_d Values

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/g	
			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/g	
			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/g	
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/g	
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/g	
			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		

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