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Long-term Technetium Interactions with Reducing Cementitious Materials

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EXECUTIVE SUMMARY

Technetium is among the key risk drivers at the Saltstone Facility. The way that it is immobilized in this cementitious waste form is by converting its highly mobile Tc(VII) form to a much less mobile Tc(IV) form through reduction by the cement's blast furnace slag. This report includes a review of published data and experimental results dealing with Tc leaching from Portland cement waste forms. The objectives for the literature study were to document previous reports of Tc interactions with slag-containing cementitious materials. The objectives for the laboratory study were to measure Tc-saltstone K_d values under reducing conditions. From the literature it was concluded:

1. Spectroscopic evidence showed that when Tc(IV) in a slag-cement was exposed to an oxidizing environment, it will convert to the more mobile Tc(VII) species within a short time frame, 2.5 years.
2. SRS saltstone will reduce Tc(VII) in the absence of NaS or sodium dithionite in a reducing atmosphere.
3. Only trace concentrations of atmospheric oxygen (30 to 60 ppm O_2 ; Eh 120 mV) at the high pH levels of cementitious systems is required to maintain Tc as Tc(VII).
4. Experimental conditions must be responsible for wide variability of measured K_d values, such that they are either very low, ~ 1 mL/g, or they are very high ~ 1000 mL/g, suggesting that Tc(VII) or Tc(IV) dominate the systems. Much of this variability appears to be the result of experimental conditions, especially direct controls of oxygen contact with the sample.
5. A field study conducted at SRS in the 1980s indicated that a slag-saltstone immobilized Tc for 2.5 years. Below background concentrations of Tc leached out of the slag-containing saltstone, whereas Tc leached out of the slag-free saltstone at the rate of nitrate loss. One possible explanation for the immobilization of Tc in this study was that the slag-saltstone maintained reducing conditions within the core of the 55-gallon sample, whereas in the small-scale lab experiments, where samples were crushed to <1 mm, oxygen diffused through the particles and reoxidize the slag during the contact period.
6. Present site specific reduction capacity value of 820 $\mu\text{eq/g}$ is in the realm of literature values that were either measured or theoretically estimated based on thermodynamic calculations.
7. Almond and Kaplan (2011) measured desorption K_d values from a Vault 4 saltstone core sample. Desorption leaching tests were conducted in a glovebag maintained at 30 to 60 ppm O_2 . A ground olive-colored saltstone sample, as compared to black monolith sample, was used in this study, indicating the sample had been exposed to O_2 , which is likely the cause for the lower than anticipated K_d value measured, 139 mL/g.

Tc adsorption experiments were conducted under reducing conditions (<0.5 ppm $O_{2(g)}$ -585 mV, 2% H_2 , pH 11.66) and obtained K_d values of ~ 1000 mL/g in a saltstone formulated with 45% slag (nominal concentration) and a K_d of 10,000 mL/g when the saltstone contained 95% slag. The K_d values logarithmically increased from 1 day to 56 days, with little sorption generally occurring in the first eight days. Steady state had not been achieved during the initial 56 days. However, the slag -free cement control samples also had K_d values near 1000 mL/g and extremely low redox conditions, due to the 2% H_2 atmosphere.

A key concept that this literature review and the experimental results provide is that Tc immobilization is dependent on experimental conditions, specifically, the available oxygen that

can oxidize technetium in a portland cement or saltstone-like monolith. The shrinking core model used in the saltstone performance assessment describes the existence of an oxidized outer layer of concrete surrounding a shrinking core of reducing intact saltstone. A sharp boundary between the two zones moves slowly inward, resulting in oxidation of Tc(IV). This work largely reinforced our conceptual model of the shrinking core model, but more importantly provided clarity regarding process kinetics, mechanisms, and input values for future detailed modeling. The shrinking core model in itself is devoid of geochemical mechanisms. This study provided more geochemical detail to this conceptual numerical model.

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LIST OF ABBREVIATIONS

BFS	Blast furnace slag
DDI	Distilled deionized water
Eh	Redox potential
ICP-MS	Inductively coupled plasma mass spectrometry
LBNL	Lawrence Berkeley National Laboratory
QA/QC	Quality assurance/Quality control
SHE	Standard hydrogen electrode
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
XAFS	X-ray absorption fine structure spectroscopy

1.0 Introduction

This project consisted of a literature study and a laboratory study from a completed thesis study (Lilley 2010). The objectives for the literature study were to compare relevant research on Tc interactions with cementitious materials. The objectives for the laboratory study were 1) to measure Tc-saltstone K_d values between 1- and 56-day contact periods under reducing conditions, and 2) to conduct long-term (weeks) Eh measurements in saltstone under reducing conditions.

2.0 Literature Review

2.1 Technetium Interactions with Reducing Cementitious Materials

2.1.1 *LBL Spectroscopy Measurements of Tc in SRS Saltstone*

From a project conducted in the late 1990s, Lawrence Berkeley National Laboratory (LBL) issued several reports and manuscripts on the subject of Tc interaction with saltstone (Shuh et al. 1994; Shuh et al. 2000; Allen et al. 1997; Lukens et al. 2005). These studies used X-ray absorption fine structure (XAFS) spectroscopy to determine the speciation of Tc in the solid phase. This is the best means available today to measure oxidation states of solid phase Tc. In these studies, they added TcO_4^- to an SRS saltstone formulation¹ and followed the speciation of Tc over a 25-mo period. The cement was cast in polystyrene cuvettes, which were closed with vinyl tape and sealed inside two concentric, thin-walled polyethylene pages. Importantly, oxygen could diffuse at a slow rate into the cuvette. Oxygen would then have to diffuse into the saltstone material, and this should be a very slow process (shrinking core model), however, they saw appreciable oxidation of Tc in their samples. None of their samples were ground for the XAFS experiments. It is also important to note that alkaline (1.8 M NaOH) Na_2S was added to all the samples at time zero to insure that all the TcO_4^- was initially reduced by the saltstone. Therefore, their experiment was not designed to address the question, “Does saltstone reduce TcO_4^- ?” Instead it was designed to address the questions, “How rapidly does Tc(IV) reoxidize and what species of Tc exists in saltstone over time as it reoxidizes?”

Four saltstone samples (46% type F fly ash, 46% BFS, 8% Portland cement) were created with the same solids compositions, but varying aqueous solution composition, whereby aqueous concentrations of nitrate/nitrite and phosphate were the independent variables in Table 1.

¹ Dry cement consisted of 46% fly ash, 46% BFS, and 8% Portland cement (Langton 1988).

Table 1. Components of aqueous solutions (M) (Shuh et al. 2000).^a

Sample	NO ₃ ⁻	NO ₂ ⁻	PO ₄ ³⁻
Tc-1	2.0	0.62	0.12
Tc-2	none	none	0.12
Tc-3	2.0	0.62	0.2
Tc-4	none	none	0.2

a) In addition, each sample contained 0.35 M NaAl(OH)₄, 0.17 M Na₂CO₃, 0.15M Na₂SO₄, 0.93M NaOH, and 0.22M NaCl

Across the top of Table 2 we see months of exposure to air and within the body of the table we see the percentage of each Tc species. As noted earlier, initially all the Tc was reduced to TcS₂, therefore all the Tc remained reduced in the saltstone either by the slag or by the added alkaline Na₂S (Table 2). Tc^{IV}S₂ is the least soluble form of Tc in Table 2, followed by TcO₂·xH₂O, and TcO₄⁻ is soluble. With the exception of sample Tc-2, ≥25% of the TcS₂ had oxidized to TcO₄⁻. Therefore one important point we can take from this study is that

- Tc(IV) is converted to Tc(VII) as saltstone oxidizes. TcO₂ hydrate appears to be an intermediate phase formed as a result of oxidation. TcO₂ hydrate is also insoluble but further oxidizes to Tc(VII).
- The presence or absence of nitrate/nitrite does not appear to be correlated with the oxidation of Tc(IV).

Table 2. Speciation of Tc in saltstone samples during a 25-mo period. Sample identification is in Table 1. (Shuh et al. 2000).

Sample	0	3	9	12	16	25
Tc-1						
TcS ₂	100%	69%	83%	29%	52%	30%
TcO ₂ •xH ₂ O	0%	28%	15%	40%	35%	35%
TcO ₄ ⁻	0%	4%	3%	32%	13%	33%
Tc-2						
TcS ₂	99%	97%	91%	91%	65%	40%
TcO ₂ •xH ₂ O	1%	2%	6%	6%	35%	56%
TcO ₄ ⁻	1%	1%	2%	3%	0%	4%
Tc-3						
TcS ₂	98%	97%	41%	61%	30%	28%
TcO ₂ •xH ₂ O	2%	2%	38%	37%	40%	47%
TcO ₄ ⁻	1%	1%	21%	2%	29%	25%
Tc-4						
TcS ₂	96%	93%	73%	85%	37%	27%
TcO ₂ •xH ₂ O	4%	5%	27%	13%	42%	42%
TcO ₄ ⁻	0%	1%	0%	2%	21%	31%

Shuh et al. (2000) conducted additional experiments where they attempted to reduce the saltstone with alkaline Na₂S solution, however the sulfide solution had partially oxidized therefore did not completely reduce the TcO₄⁻ to TcS₂ at time zero (Table 3 and Table 4). This turned out to be a fortuitous mistake that provided important insight into saltstone reduction properties. The three samples created for this second study are described in Table 3. The cement samples were placed in polystyrene cuvettes, sealed by filling the headspace with liquid epoxy, which formed an airtight seal with the cuvettes. The samples were then sealed in concentric polyethylene bags as in the first set of samples. The implications of potential O₂ gas diffusion through the impermeable polystyrene cuvettes were not discussed.

Table 3. Components of aqueous solution (M) in second study conducted by Shuh et al. 2000)

Sample	Cl ⁻	NO ₃ ⁻	NO ₂ ⁻
Tc-A	4	None	None
Tc-B	None	4	None
Tc-C	None	None	4

In addition, each sample contained 4M NaOH.

The evolution of the Tc speciation for the sealed cement samples is provided in Table 4. These results are in marked contrast with those from the first experiment. In Table 4 only 40% of the Tc exists as TcS₂, but more importantly, the fraction of Tc(IV) steadily increased with time. Since the 0.29 mM Na₂S had been completely oxidized, as evidenced by the presence of the

partially reduced 0.02 mM Tc (the sulfate/sulfide has a lower standard reduction couple than the Tc(IV/VII) couple), the reductant responsible for converting the TcO_4^- to Tc(IV) in these experiments is most likely BFS. The reductant can not be the Na_2S solution because it is obviously oxidized as evidenced by the fact that it did not completely reduce the TcO_4^- during the preparation of the samples. This argument is important to understand. If it had completely reduced the added TcO_4^- , as was observed in Table 2 at month 0, then this assertion could not be made. At time 0 mo, the samples contained between 24 to 27% TcO_4^- (Table 4). Shuh et al. (2000) attributed the air leak to the different ways that the cuvettes were sealed with epoxy.

Table 4. Speciation of Tc in sealed cement samples versus age in months. These samples were initially unsuccessfully reduced by alkaline Na_2S as a result of an experimental artifact (Shuh et al. 2000).

Sample	0	5	9
Tc-A			
TcS ₂	40%	51%	46%
TcO ₂ •xH ₂ O	34%	29%	42%
TcO ₄ ⁻	26%	20%	12%
Tc-B			
TcS ₂	40%	44%	51%
TcO ₂ •xH ₂ O	36%	41%	39%
TcO ₄ ⁻	24%	16%	10%
Tc-C			
TcS ₂	40%	37%	41%
TcO ₂ •xH ₂ O	33%	38%	42%
TcO ₄ ⁻	27%	25%	17%

2.2 Reduction Capacity of SRS Saltstone

SRS saltstone nominally contains 45 wt-% slag. This slag provides a reduction capacity of nominally 820 $\mu\text{eq/g}$ (Roberts and Kaplan 2009; Table 5). This method of measuring reduction capacity came from Angus and Glasser (1985). In going through the literature it is possible to compare the SRS values to those previously reported.

Table 5. Reduction capacity ($\mu\text{eq/g}$) of solids using the Ce(IV)- Fe(II) colorimetric titration method with 0.5 g of solid sample (Roberts and Kaplan 2009).

Sample	% Blast Furnace Slag	Reduction Capacity This Study ($\mu\text{eq/g}$)	Reduction Capacity Kaplan et al. (2008) ($\mu\text{eq/g}$)
Saltstone TR437	45 %	849	NA
Saltstone TR451	45 %	793	NA
Saltstone TR547	45 %	607	NA
Saltstone TR431	45 %	NA	821 ± 5
Saltstone TR545	90 %	681	NA
Portland Cement	0 %	198	NA
Class F Fly Ash	0 %	299	NA
Blast Furnace Slag	100 %	819	832.4 ± 5
Vault 2 Concrete	10 %	178	239 ± 31
Aged (30 yr.) Cement	0 %	NA	86 ± 10

It was established in Roberts and Kaplan (2009) that the value measured reported within their report, 819 $\mu\text{eq/g}$, agreed well with those previously reported:

- 819 $\mu\text{eq/g}$ (Roberts and Kaplan 2009)
- 832 $\mu\text{eq/g}$ (Kaplan et al. 2008), and
- 817 $\mu\text{eq/g}$ (Kaplan et al. 2005).

These values also agree well with a measurement conducted at LBNL using the same SRS slag and the method of Anus and Glasser (1985):

- 820 $\mu\text{eq/g}$ (Lukens et al. 2005).

Angus and Glasser (1985) measured the reduction capacity of two slag-containing cements using the same analytical method as used by Robert and Kaplan (2009) and Lukens et al. (2005), the compositions of the cements were not specified:

- 1140 $\mu\text{eq/g}$ (Ravenscraig slag; Angus and Glasser 1985) and
- 1100 $\mu\text{eq/g}$ (Frodingham slag; Angus and Glasser 1985).

Finally, providing the most independent review of the reduction capacity values, Smith and Walton (1993) conducted thermodynamic calculations to estimate the reduction capacity of an 85% blast furnace slag + 15 % ordinary Portland cement formulation. They based their input in these calculations on the sulfide, thiosulfide, Eh, and pH, data from Angus and Glasser (1985) and their thermodynamic data came from cement phases and Tc species reported primarily from Criscenti and Serne (1990). They reported a reduction capacity of:

- 950 $\mu\text{eq/g}$ (Frodingham slag; Smith and Walton 1993)

Together these values provide a consistent description of the reduction capacity of reducing cement. The present site-specific value of 820 $\mu\text{eq/g}$ appears to be in the realm of literature values that were measured or theoretically estimated.

2.3 Discussion Points from Literature Review in Section 2.1 and 2.2

1. Solid phase Tc(IV) in a slag-cement (Ordinary Portland Cement/Blast Furnace Slag) when exposed to an oxidizing environment will oxidize to the more mobile form Tc(VII) within a short time frame, <2.5 years (Shuh et al. 2000).
2. SRS saltstone will reduce Tc(VII) in the absence of NaS or sodium dithionite in a reducing atmosphere (Shuh et al. 2000).
3. Only trace concentrations of atmospheric oxygen (30 to 60 ppm O₂; Eh 120 mV) at the high pH levels of cementitious systems is required to maintain Tc as Tc(VII) (Almond and Kaplan 2011).
4. Experimental conditions must be responsible for wide variability of measured K_d values, such that they are either very low, ~1 mL/g, or they are very high ~1000 mL/g, suggesting that Tc(VII) or Tc(IV) dominate the systems. Much of this variability appears to be the result of experimental conditions, especially direct controls of oxygen contact with the sample. Experimental conditions (or formulations) are responsible for the uncertainties. As will be discussed in the experimental section (Section 3.0) we believe that much of this variability can be attributed to experimental conditions, especially direct controls of oxygen contact with the sample.
5. A field study conducted at SRS in the 1980s indicated that a slag-saltstone immobilized Tc for at least 2.5 years (Langton 1988). Below background concentrations of Tc leached out of the slag-containing saltstone, whereas Tc leached out of the slag-free saltstone at the rate of nitrate loss. One possible explanation for the immobilization of Tc in this study was that the slag-saltstone maintained reducing conditions within the core of the 55-gallon sample, whereas in the small-scale lab experiments, where samples were crushed to <1mm, oxygen diffused through the particles and reoxidize the slag during the contact period (oxygen travel distance is ~ $D_d \cdot \sqrt{\text{time}}$).
6. SRNL measurements of reducing capacity of 820 $\mu\text{eq/g}$ using the Angus-Glasser method is in the realm of literature values that were either measured or theoretically estimated based on thermodynamic calculations.

3.0 Laboratory Study: Tc Sorption to Cementitious Materials under Reducing Conditions

These studies were conducted at Clemson University (Lilley 2010) and were designed to address the following objectives:

1. To compare long-term (56-day contact) Tc-saltstone K_d values under reducing conditions, and
2. To conduct long-term (weeks) Eh measurements in saltstone under reducing conditions.

To put these measurements in context, the sorption of Tc to other cementitious materials were also measured. The cementitious materials used in this study were Vault 2, a 50-year-old cement, and a saltstone sample containing 90% slag (TR545) and a sample containing 45% slag (TR547).

These materials will be discussed in more detail below. The sample closest to expected saltstone formulation was designated TR547 (45% slag). The Vault 2 sample is a simulant cementitious material containing 17% slag and contains the formulation of the vault walls used to house the saltstone waste. The Aged Cement sample was a boring from a field pad (15cm to 30 cm depth) that had been exposed to weather conditions for 50 years.

In this section the Materials and Methods will be presented then the Results.

3.1 Materials and Methods

The objectives for the laboratory study were:

1. To measure Tc-saltstone K_d values between 1- and 56-day contact periods under reducing conditions, and
2. To conduct long-term (weeks) Eh measurements in crushed saltstone under reducing conditions.

They are taken from the thesis of Michael Lilley at Clemson University (Lilley 2010). Additional details, such as individual sample results, as opposed to average values, and numerous quality control sample results can be obtained from his thesis.(Lilley 2010) (In the thesis, the reader will also see results for Pu, I, and Np sorption to saltstone and SRS soil.)

3.1.1 *Solution Preparations*

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, Tc(VII) is the expected oxidation state. The reduced Tc(IV) oxidation state would not be soluble under these conditions. The expected concentration of 950 ppb based on the dilution was verified using liquid scintillation counting. The ^{99}Tc working solution was used to make 0.01, 0.05, 1, 2, 5, and 10 ppb standards by dilution using 2% HNO_3 . These standards were used to calibrate the Thermo Scientific X Series 2 inductively coupled plasma mass spectrometer (ICP-MS) for quantification of ^{99}Tc . A screen shot of a representative calibration curve is shown in Figure 1. 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%).

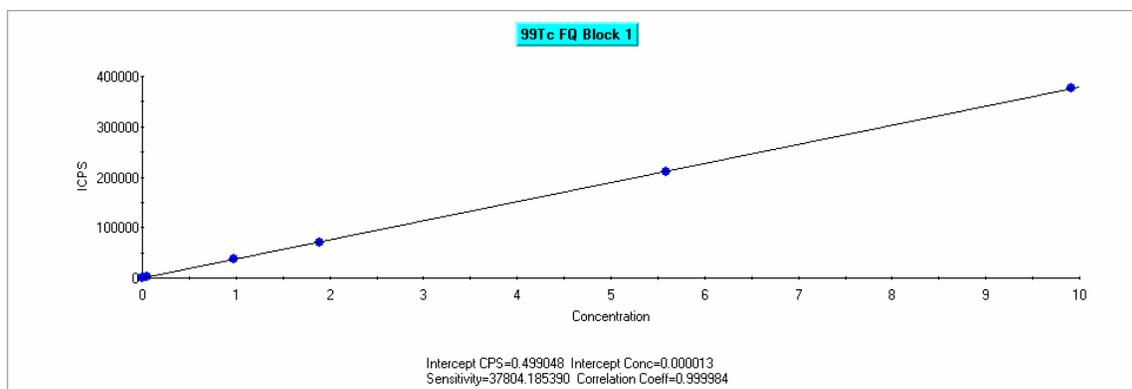


Figure 1. Screen capture of a typical ^{99}Tc calibration curve using Thermo PlasmaLab software to control the data collection and analysis ($R^2=0.999984$, Intercept Concentration (Detection Limit) = 0.000013 ppb).

3.1.2 Cementitious and Saltstone Formulations Selected for Experiments

There were four different cementitious formulations selected for this sorption study (Table 6). The first, referred to as Aged Cement, is a 50 year old sample that does not contain any reducing slag. The Vault 2 formulation is 17% reducing slag. The TR547 and TR545 saltstone formulations contain 45% and 90% reducing slag, respectively.

Table 6. Saltstone reduction capacity and slag content.

Sample	Reducing capacity ($\mu\text{eq/g}$)	Slag (wt-%)
Aged Cement	85.5 ± 10.1	0
Vault 2	239.8 ± 31.1	17
TR547	NA	45
TR545	NA	90
Saltstone DDA stimulant*	821.8 ± 8.1	23*
Blast furnace slag*	832.4 ± 4.9	100*

* First described in Kaplan et al. 2008.

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

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

3.1.3 Sorption Experiments under Anaerobic Conditions

In order to examine the effects of reducing conditions of sorption of each isotope to the various saltstone samples, a series of sorption experiments were performed in an anaerobic glovebox under a 2% H₂(g)/ 98% N₂(g) atmosphere. Based on the measured pH and E_H of these systems as discussed below, these systems were reducing and close to equilibrium with the 2% H₂(g) atmosphere. (Theoretically, a 2% H₂ atmosphere will create a -650 mV atmosphere at equilibrium; based on the simplified 2H⁺ + 2e⁻ ⇌ H₂(g): 2H⁺ + 2e⁻ ⇌ H₂(g). None of the cementitious samples were that low.) Therefore, they are expected to represent a lower end of the possible range for reducing conditions expected in the porewater available in reducing saltstone samples.

Preparation of Calcite for Reducing Conditions: Approximately 3.5 L of DDI water was boiled for 45 minutes. Argon was slowly bubbled through the water as it cooled. Once it cooled to below 50⁰C, approximately 3 g of calcite was added. This solution mixed overnight under a continuous Ar flow. After 12 hours the solution was moved into an oxygen free glove bag for filtration as described above. After filtration, the calcite solution was moved into the glove box.

Preparation of Working Solutions under Reducing Conditions: The calcite and solid solutions were prepared in the glove box. The radionuclide working solutions were transferred to the glovebox and stirred open to the reducing atmosphere for at least 3 days. The concentrations of each isotope in the working solutions were measured to determine any change in the concentration due to evaporation while the solutions were equilibrating with the glovebox atmosphere.

Falcon BlueMax 15mL polypropylene vials were labeled and weighed to within 0.001 g on a calibrated Sartorius LA 230S scale. The scale was then zeroed and 0.25 +/- 0.01 g of a given solid were added to each tube, and the weight was recorded to within 0.001g. For each of the four solids, three sets of triplicate samples were prepared. The three sets of samples were used to allow for experiments to be run with varying concentrations of ⁹⁹Tc. Target initial concentrations for ⁹⁹Tc samples were 1 ppb, 5 ppb, and 10 ppb. A set of no solids controls at initial concentrations of 1 ppb and 10 ppb for ⁹⁹Tc were also prepared by adding the calcite solution to pre-weighed, pre-labeled centrifuge tubes as discussed above.

The solids were equilibrated with the calcite solution before spiking with the radionuclides. This was done by adding 10 +/- 0.1 mL of calcite solution to each tube, and recording the mass. The samples were then placed on a Thermo Scientific shaker overnight. After 24 hours, the solutions were allowed to settle for 1 hour. The pH was then measured and the samples were then centrifuged for 15 minutes at 8000 rpm to further separate the solids. The aqueous phase was then decanted and 10 +/- 0.1 mL of calcite solution was added to each tube. The weight of the tube (labeled tube + solid + calcite solution) was measured to within 0.001g. During this washing process, the pH was monitored and held steady throughout the process. They ranged from 11-12 depending on the particular saltstone used. Details are presented in Lilley (2010).

The suspensions were spiked not only with ⁹⁹Tc, but also with ²³⁷Np, ²⁴²Pu, and ¹²⁷I to final concentrations as shown in Table 7. Results from only the ⁹⁹Tc will be presented in this report. Given their low concentrations, ppb levels, it is anticipated that there will be minimal interactions between the various radionuclides influencing sorption.

Table 7. Experimental matrix of sorption experiments under aerobic conditions

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

After spiking the radionuclides, a precalculated amount of 10M NaOH was added to each sample to counter the acidity of the ²³⁷Np and ²⁴²Pu spike solutions and the pH of one of the triplicate samples was measured to ensure the proper pH range was reached. The samples were then placed on an end-over-end shaker to mix at approximately 8 rpm. After 24 hours, the samples were removed from the shaker and the pH of each sample was measured using an Orion Ross semi-micro glass electrode calibrated against pH 4, 7, and 10 buffers (Thermo). The samples were then shaken and a transfer pipette was used to transfer 3.5 mL of a homogenous suspension to a 5 mL syringe. The solution was then passed through a 100 nm nylon syringe filter. The first 0.25-0.50 mL of filtrate was discarded and the remaining filtrate was collected in a clean polyethylene vial. After the 24 hour sampling event, the samples were put back on the shaker to mix for 3 additional days. On day 4, the above sampling procedure was repeated. The ⁹⁹Tc samples were analyzed on the Thermo Scientific ICP-MS using the standard setup and procedure which included a standard flow glass nebulizer and bulb spray chamber.

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

Once the 1 and 4 days samples were collected and run on the ICP-MS, it was necessary to determine the degree each radionuclide was sorbing to the vial walls. The remaining suspensions and controls were emptied into a waste container. Then 5 mL of the calcite solution was added to each vial using a calibrated pipette. The vials were sonicated for approximately one minute, and then emptied into the waste container. Another 5 mL of calcite solution was added for the second wash, and then discarded into the waste container. This procedure was expected to remove any soluble radionuclide from the system or radionuclide associated with colloidal particles. After each vial was washed, 10 mL of 2% HNO₃ was added using a calibrated pipette. The acid solution is expected to remove any Tc associated with the vial walls. This procedure has been shown to complete mass balances of Pu in similar sorption experiments using Pu (Powell et al. 2002). This process was performed for both the solid suspension and the no solids controls. The samples were then run on the ICP-MS to determine the concentration of ⁹⁹Tc sorbed to the vial walls.

3.1.5 Data Analysis

The solubilities of ⁹⁹Tc was calculated by using the formula:

$$C_{sol} = \frac{C_{ICP-MS} * 10^{-6} \left(\frac{g_{nuclide}}{\mu g_{nuclide}} \right)}{M_{nuclide}} \quad (4)$$

C_{sol} = observed nuclide/compound solubility ($\text{mol}_{\text{nuclide}}/\text{kg}_{\text{solution}}$)
 C_{ICP-MS} = Aqueous concentration of nuclide from ICP-MS measurement (ppb, $\mu\text{g}_{\text{nuclide}}/\text{kg}_{\text{solution}}$)
 M_{nuclide} = molecular mass of nuclide ($\text{g}_{\text{nuclide}}/\text{mol}_{\text{nuclide}}$)

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

$$C_{\text{solid}} = \frac{\left[\frac{(C_{\text{stock}} * m_{\text{spike}})}{(m_{\text{calcite}} + m_{\text{spike}})} - C_{\text{aq}} \right] * (m_{\text{spike}} + m_{\text{calcite}})}{m_{\text{solid}}} \quad (5)$$

C_{solid} = calculated solid phase concentration of the nuclide associated with the saltstone (ppb)
 C_{stock} = concentration of the nuclide stock solution (ppb)
 m_{spike} = mass of nuclide spiked into the saltstone suspension (g)
 m_{calcite} = total mass of calcite solution used in the saltstone suspension (g)
 C_{aq} = aqueous concentration of nuclide from ICP-MS measurement (ppb)
 m_{solid} = mass of the saltstone used in the suspension (g)

The K_d can be calculated using the equation:

$$K_d = \frac{C_{\text{solid}}}{C_{\text{aq}}} \quad (6)$$

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

3.1.6 Experimental Methods for Long Term Saltstone Experiments

After analyzing the results from the above saltstone experiments, it was apparent ^{99}Tc had not reached equilibrium after the 4 day sampling event (to be discussed in Section 3.2.1). It was deemed necessary to extend the sampling events over a longer period.

Falcon BlueMax 50mL polypropylene vials were labeled and weighed to within 0.001 g on a calibrated Sartorius LA 230S scale. The scale was then zeroed and 1.25 +/- 0.01 g of a given solid was added to each tube, and the weight was recorded to within 0.001g. For each of the four solids, two sets of triplicate samples were prepared. The two sets of samples were used to allow for experiments to be run with varying concentrations of each isotope. Target initial concentrations for ^{99}Tc samples were 5 ppb, and 10 ppb. A set of no solids controls at initial concentrations of 5 ppb and 10 ppb ^{99}Tc were prepared by adding the calcite solution to pre-weighed, pre-labeled centrifuge tubes as discussed above.

The solids were equilibrated with the calcite solution before spiking with the radionuclides. This was done by adding 45 +/- 0.1 mL of calcite solution to each tube, and recording the mass. The samples were then placed on a Thermo Scientific shaker overnight. After 24 hours, the solutions were allowed to settle for 1 hour. The pH was then measured and the samples were

then centrifuged for 15 minutes at 8000 rpm to further separate the solids. The aqueous phase was then decanted and 50 +/- 0.1 mL of calcite solution was added to each tube. The weight of the tube (labeled tube + solid + calcite solution) was measured to within 0.001g. During this washing process, the pH was monitored and held steady throughout the process. They ranged from 11-12 depending on the particular saltstone used.

The resulting suspensions were then spiked with ⁹⁹Tc (and ¹²⁷I, but the ¹²⁷I results are not reported here; see Lilley 2010). It is important to note that both isotopes were added to the same vial (see Table 8).

Table 8. Experimental matrix of sorption experiments under aerobic conditions

Experiment	Initial Concentration ⁹⁹ Tc	Initial Concentration ¹²⁷ I ^(a)
Solids-Present	5 ppb	50 ppb
Solids-Present	10 ppb	100 ppb
Solids-Free	50 ppb	50 ppb
Solids-Free	100 ppb	100 ppb

^(a) Iodine data is not reported here. Iodine spike information is presented to inform reader that it was present in experiment.

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

3.1.7 Long Term Sampling Procedure

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

3.2 Experimental Results

Redox potential (Eh) and pH were measured in the test suspension 1 and 4 days after preparing the suspension in the anaerobic glovebox (Table 9). The conditions within the glovebox are highly reducing, not changing very much from 1 day to 4 days. The Eh also generally decreased in a consistent trend with the amount of slag added. An important point to note here is that the No-Solids Control also had a very low redox, comparable to those with reducing cement. The fact that Eh decreases in a systematic manner with increasing amount of slag suggests that slag likely controlled Eh in the reducing cementitious materials, whereas the H₂/N₂ gases controlled the Eh in the Aged Cement (0% slag) and the Solids-Free Control. Significant ($p \leq 0.01$, $n = 4$) inverse correlations, existed between slag content and Eh with cementitious materials ($r = -0.93$, 1 day data, $P \leq 0.01$; and $r = -0.88$ for 4 day data, $P \leq 0.05$; Table 9). Had the H₂/N₂ gases been controlling the Eh, then there would not have been any correlation between slag content and Eh.

The Solids-Free Control therefore provides a test of whether the aqueous phase alone can promote the conversion of Tc(VII) to Tc(IV), sans solids to catalyze or promote the reduction reaction. Finally, by day 4, there was a near perfect inverse correlation between Eh and pH, as

thermodynamic theory would predict: $r = -0.995$ for $n = 4$, $P \leq 0.01$. This indicated that these two independent measurements were varying in a well behaved manner.

Table 9. Redox potentials (Eh) for reducing conditions.

Solids ^a	Slag (%-wt)	1 day		4 day	
		Eh (mV)	pH	Eh (mV)	pH
Aged cement	0	-498	11.56	-451	11.55
Vault 2 concrete	10	-511	11.28	-361	11.31
TR547	45	-585	11.66	-498	11.70
TR545	95	-600	11.84	-584	11.86
No-Solids Control	0	-529	11.75	-491	11.71

^a Suspensions were mixed in an anaerobic glovebox under a $N_2(g)/H_2(g)$ mixture. The $H_2(g)$ fraction averaged 1.5% over the course of the experiment. An oxygen gas monitor continuously read units of 0 ppm. Redox potentials were corrected to SHE. The aqueous phase was $Ca(OH)_2$ -saturated solution (a surrogate for cement leachate).

3.2.1 ⁹⁹Tc Sorption to Cementitious Materials under Reducing Conditions

A plot of the Tc K_d values for the cementitious material under reducing conditions is shown in Figure 2 (log y-axis). Sorption data after 1 day of equilibration for the Aged Cement and Vault 2 Cement are not shown because there was minimal sorption. This figure generally shows a steady increase in K_d values for each cement and saltstone during the 56 days this study was conducted. Even after 56 days, almost 2 months, it is not clear that the experiments came to steady state. There is no evidence that this system has obtained steady state. It is possible that additional Tc removal from the aqueous phase would occur had the experiment been permitted to run longer.

The results in Figure 2 are consistent with Atkins and Glasser (1992) who demonstrate that the creation of a reducing environment in slag-containing grout (and therefore Tc removal from the aqueous environment) occurs over a period of months. They showed that the rate reducing grout creates a reducing environment depends on the amount of slag in the formula. They showed that a grout containing 85%, and 70%, and 50% would require about <1 mo, 3 mo, and >18 mo to create reducing conditions (Figure 3; Atkins and Glasser 1992). They attributed the rate limiting process to the hydration of the slag, which when hydrated releases S^{2-} into the aqueous phase, which in turn creates the reducing environment.

TR547 is most closely formulated to the saltstone presently being used at the Saltstone facility. Its Tc K_d was ~1000 mL/g, whereas the controls had comparable values. Two points can be made from this observation. The first is that we can not be entirely sure what is promoting the reduction of Tc(VII) in the saltstone samples: is it the slag in the saltstone or the reducing conditions in the glovebox? The Eh data in Table 9 suggests that not only the N_2 and H_2 gases are controlling the redox of the suspension because the Eh values of the cementitious suspension are not the same as those of the control. In fact, as noted above, the Eh values decrease with increasing slag content, thereby demonstrating the impact of slag on controlling the system's Eh values. There is more than one chemical couple (e.g., Fe^{2+}/Fe^{3+}) controlling Eh in the

cementitious systems we studied. Finally, it is possible, if not likely, that there is one process (N_2/H_2 gases) in the No-solids Control sample and separate ones in the four other cementitious materials.

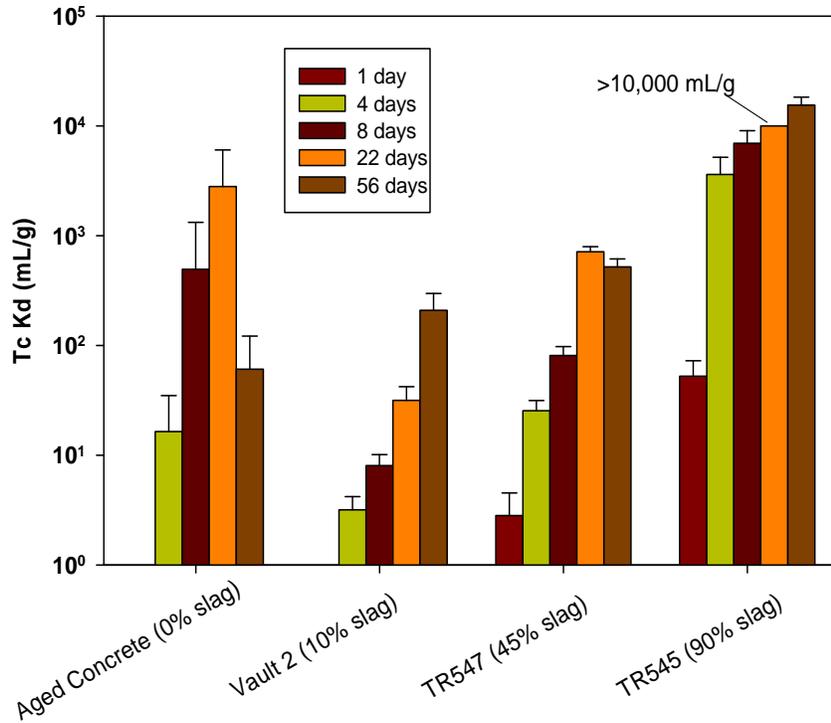


Figure 2. Tc K_d values (mL/g) under reducing conditions. Tc K_d values for various saltstone and concrete formulations measured after one, four, eight, twenty-two, and fifty-six day equilibration under reducing conditions. Total Tc concentrations in each system were 10 ppb and 5 ppb with each concentration set up in triplicate. The values expressed are averages of all six samples with the error bars representing the standard deviation.

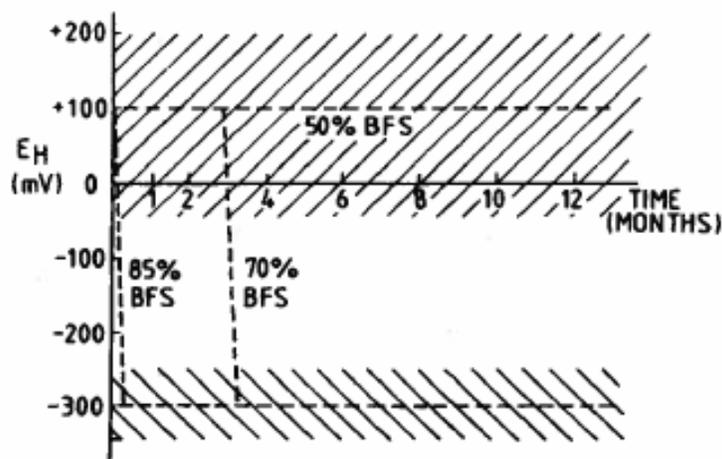


Figure 3. Eh evolution with time as a function of blast furnace slag in cement (water/solid ratio = 0.5, cured at 25° C. Cross hatching indicates variation in measured values (Atkins and Glasser 1992).

The 1-day data presented in Figure 2 for the TR547 and TR545 saltstone samples were in general agreement with those from an initial short-term study conducted by Lilley (2010) (Table 10). By the 4-day sampling event, there was agreement between measured K_d values between both experiments: the initial short-term trial and the long-term experiment. We present these data to provide confidence in the experimental approach and to show that the data are reproducible.

Table 10. Comparison of 1 and 4 Day TR547 and TR545 K_d Values under reducing conditions from Initial and Long Term Experiments (Lilley 2010).

	Initial Experiment ^c		Long Term Experiment ^c	
	1 Day K_d	4 Day K_d	1 Day K_d	4 Day K_d
TR547	-3.45 ± 0.89^a	24.89 ± 17.03	2.82 ± 1.71	25.43 ± 6.03
TR545	39.47 ± 23.9^b	4367.9 ± 3658.5	52.6 ± 19.94	3490 ± 1526.1

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

^b $n = 6$; no 1 ppb samples were used in average calculations due to large number of below detection values.

^c The Initial Experiment was conducted for 8 days and the Long Term Experiment was conducted for 56 days, of which some of the data is presented in Figure 2.

3.2.2 Technetium Sorption to Vial Walls under Reducing Conditions

A plot of the technetium (and iodine as part of another study not discussed here) in the aqueous fraction near 1.0 of each sample under reducing conditions is found in Figure 4, demonstrating near 100% recovery. At the 1 day sampling event, there were unexplained inconsistencies with both the Tc and I, which resulted in large standard deviations for each. Also, when analyzing the 22 day iodine samples, there was a problem with the Teflon nebulizer for

both the No-Solids Control samples (as well as the saltstone and cement samples). Those data were lost and are not reported here. However, at the 4, 8, and 56 day sampling events, there was 100% mass recovery for both the Tc and I. This was also the case for the 22 day Tc samples. This shows there is not any significant sorption to the vial walls, so any loss of mass when solids are present is due to sorption to that particular solid phase.

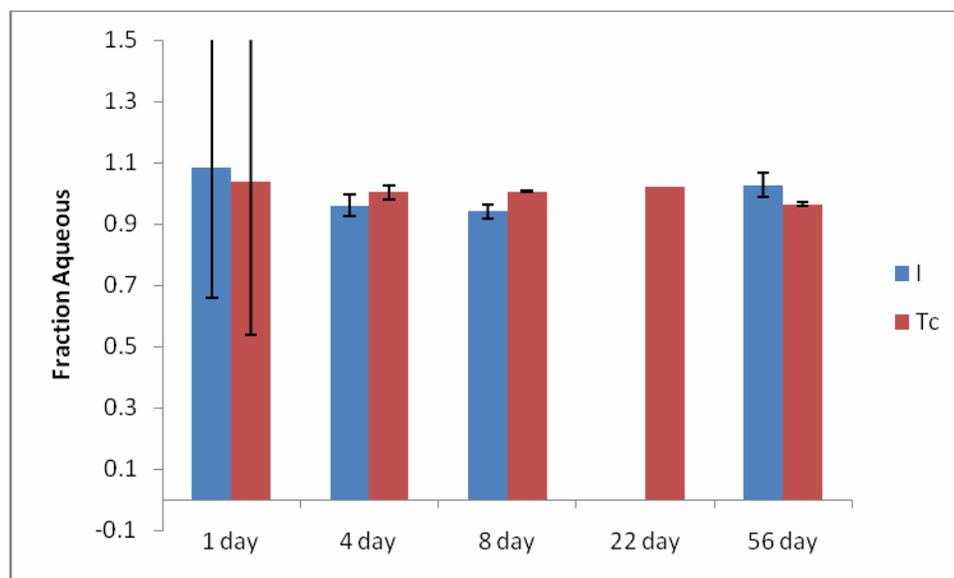


Figure 4. Fraction of aqueous Tc and I under reducing conditions in No-Solid Control samples (The iodine data is not of interest to this discussion).

4.0 Discussion

4.1 Tc Leaching Studies for Cementitious Waste Forms

There were a few studies involving Tc and slag-cementitious materials (Serne et al (1992), Langton 1988, Kaplan and Coates 2007, Kaplan et al. 2009; Brodda 1988; Tallent et al. 1988) (Table 12). Studies by Serne et al. (1992), Langton (1988), Brodda (1988) and Tallent et al. (1988) measured effective diffusion, D_e , (or its negative logarithm, leachability index) from monoliths of reducing grout using a standardized method, ANSI/ANS-16.1. As such they did not measure K_d values. But in all cases they also calculated the D_e of nitrate per ANSI/ANS-16.1. As a first approximation it is possible to estimate Tc K_d values from D_e values when nitrate D_e values are also measured by assuming that nitrate does not sorb to sediments, i.e., it has a $K_d = 0$ mL/g.

$$D_e = D/R_f \quad (1)$$

where D (cm^2/s) is diffusion in water (without cement) and R_f is retardation factor ($\text{cm}/s_{\text{water}} / \text{cm}/s_{\text{contaminant}}$), which is related to K_d (mL/g) by:

$$R_f = 1 + (\rho_b/n)K_d \quad (2)$$

where ρ_b is the bulk density (g/cm^3), n = the effective porosity ($\text{cm}^3_{\text{pores}}/\text{cm}^3_{\text{total}}$). For this calculation, it is assumed that R_f of nitrate in cement equal 1 (and a $K_d = 0 \text{ mL/g}$), meaning that nitrate moves, more specifically diffuses, at the same rate as water. Again, this is an approximation to help convert D_e values to K_d values and to permit comparing D_e values with K_d values, but technically the two values may be measuring two different phenomena.

$$D_e(\text{Tc}) / D_e(\text{NO}_3^-) = R_f(\text{NO}_3^-) / R_f(\text{Tc}) = K_d(\text{NO}_3^-) / K_d(\text{Tc}) \quad (3)$$

Another important caveat with regards to K_d values is that it is generally reserved for reversible adsorption reactions (Krupka et al. 1999). As such it should not be used for describing solubility conditions, which may exist in systems when estimated or calculated K_d values were high, e.g. $>1000 \text{ mL/g}$. None of the studies in Table 12 conducted spectroscopy studies to confirm the oxidation state of Tc or to confirm whether sorption or precipitation occurred. For simplicity of presentation and ease for comparison, all the data in Table 12 was converted to K_d values, but it is not meant to suggest a sorption mechanism.

Using the D_e (or the leachability indexes) of the Tc and NO_3^- data presented in Table 12 and Equation 3, it is possible to estimate order-of-magnitude K_d values. What we observe from Serne et al. (1992) is that Tc(VII) when added to Hanford reducing grout had relatively high (fast) D_e values ($10^{-8} \text{ cm}^2/\text{s}$; or using equation 3, low K_d values), whereas under identical experimental conditions (ANSI/ANS-16.1-1986) Langton (1988) reported low (slow) D_e values using SRS saltstone ($10^{-12} \text{ cm}^2/\text{s}$). In Serne et al. (1992), the Tc(VII) was added to two cement formulations (T106-AN 47.5% slag and DSSF 47% slag). They added Tc(VII) to the portland type I/II cement monoliths, then conducted leaching experiments, measuring the amount of Tc that leached into replaced volumes of Hanford groundwater or distilled water. There was little to no difference between the D_e value of NO_3^- and Tc, consequently Tc had low estimated K_d values. No precautions were taken to exclude air from these experiments. Brodda (1988) and Tallent et al. (1988) also did D_e measurements of slag-cements and reported that nitrate (indicative of a conservative tracer or of how fast water moves) leached about 100 times faster than Tc.

Langton (1988) measured D_e for three NUCEM slag concentrations in SRS saltstone, 0%, 15% and 26%; the D_e values were 10^{-9} , 10^{-12} and 10^{-12} , respectively. The NO_3^- D_e values for the 0%, 15% and 26% slag concentrations were 10^{-9} , 10^{-7} and 10^{-9} , respectively. These Tc D_e values permit estimating K_d values in the order of 1000 to 100,000 mL/g . These values suggest the presence of Tc(IV). No precautions were taken to exclude air from these experiments; they were conducted on the lab bench.

Gilliam et al. (1988) tested six different cementitious materials containing 20% slag and reported similar Tc and nitrate leachability indices (determined from D_e values) as Langton (1988) (leachability indexes are approximately equal to the $-\log$ of the D_e) (Table 12). They measured strongly reducing conditions of approximately -250 mV for the reducing cement and approximately 450 mV for fly ash and the cement. The average ^{99}Tc leachability value was 10.50 ± 0.5 for the six reduction cementitious materials. The average comparable nitrate leachability value was 7.30 ± 0.10 . Therefore by subtracting the $-\log$ of these values it can be concluded that in the order of 100 to 1000 times more nitrate than Tc leached from these BFS-grout samples.

Kaplan and Coates (2007) and Kaplan et al. (2008) conducted (ad)sorption experiments with Tc and SRS saltstone. K_d values can be measured by either adsorption or desorption measurements (Krupka et al. 1999). But desorption tests tend to yield larger K_d values due to

hysteresis effects (Krupka et al. 1999). Their experiments were performed on the lab benchtop exposed to air. They added Tc(VII) to saltstone (45% slag), vault concrete (10% slag), or 50-year-old aged cement (0% slag). The measured Tc K_d values ranged from 0.8 to 91 mL/g.

Langton (1988) conducted a field study with 55-gal slag saltstone sample containing Tc and nitrate (Figure 5 and Figure 6). Langton (1988) measured Tc and nitrate leachate for 2.5 years that came from slag-cement (Mix 3) and a slag-free cement (Mix 1) lysimeters (Table 11). By normalizing the data to nitrate concentration, Langton (1988) simplified a number of interpretations for the reader (Figure 6). If as above, it is assumed that nitrate moves as a conservative tracer, then it can be seen that without slag, nitrate and Tc were released at equal amounts from the slag-free cement lysimeter. When slag was present, the nitrate continued to be released, however only detection limit Tc concentrations were released from the lysimeters (Figure 6).

Table 11. Formulations for saltstone waste forms used by Langton (1988).

<u>MIX 1</u> <u>Cement-Based (WT%)</u>		<u>MIX 2</u> <u>Slag+Cement-Based (WT%)</u>		<u>MIX 3</u> <u>Slag-Based (WT%)</u>	
H Cement	11.5	NUCEM Slag	15	NUCEM Slag	26
C Fly Ash	46	D-Area Ash (ESP)	20	D-Area Ash (ESP)	26
Salt Solution (29% Salt)	42.5	Type II Cement	7.5	Ca(OH) ₂	3
		Salt Solution (29% Salt)	57.5	Salt Solution (29% Salt)	45
Water to Cementitious Solids Ratio	0.525	Water to Cementitious Solids Ratio	2.68	Water to Cementitious Solids Ratio	1.16

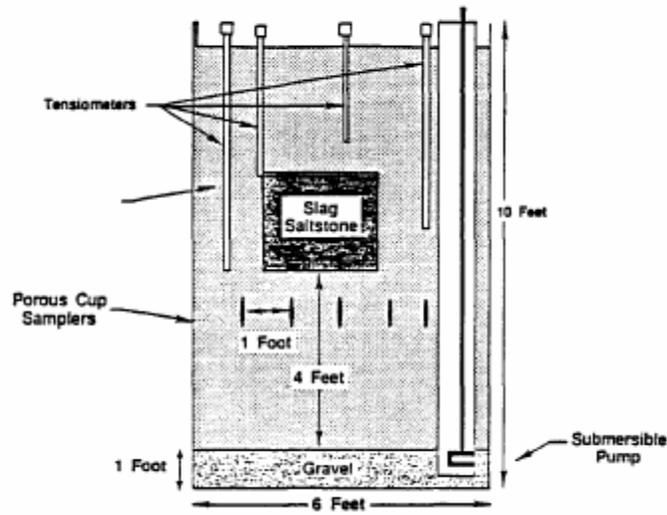


Figure 5. Schematic diagram of slag saltstone lysimeter (Langton 1988).

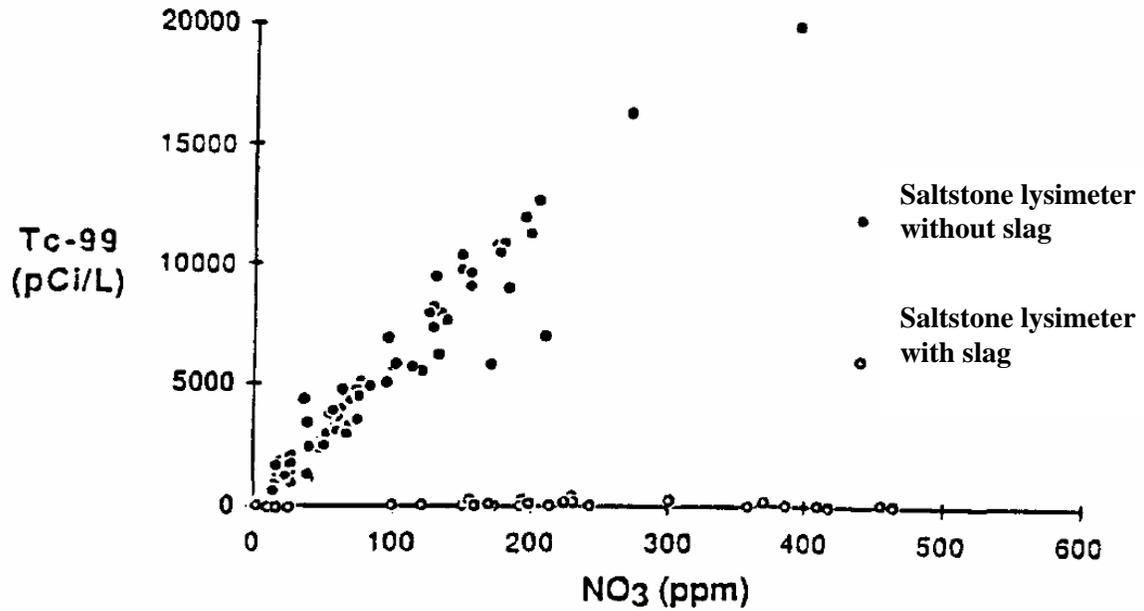


Figure 6. Tc versus nitrate concentrations for slag- and cement-based saltstone lysimeters after 2.5 years in the field (Langton 1988).

4.2 Tc Desorption K_d Value from a Saltstone Core and other Cementitious Materials

Almond and Kaplan (2011) measured desorption K_d values from a Vault 4 saltstone sample that was collected September 2008. The grout was poured into the vault in December 2007 and the saltstone was comprised of BFS (45%), OPC 10%, Deliquification, Dissolution, and Adjustment (DDA) Batch 2 radioactive salt solution; 0.6 water: premix ratio, fly ash 45%. The samples were cored/sampled, maintained in nitrogen, and received in olive green color with an external thin layer of light gray, indicating that a vast majority of the sample was still reduced, but that the exterior had been oxidized. Desorption leaching tests were conducted in a glovebag maintained at 30 to 60 ppm O_2 . In a glovebag, 30 g of ground olive green saltstone was placed in 210 mL of saturated $Ca(OH)_2$ solution placed on a platform shaker for 20 days. They conducted an identical desorption test outside the glovebag with air sparged into the bottom of the suspension, maintaining the aqueous system at ~ 8 ppm O_2 . Reduced suspension pH was 12.05, and the Eh was 140 to 400 mV. Oxidized suspension pH was 11.46 and the Eh was +160 mV.

The Tc K_d under the oxidizing experiment was 12 mL/g and under reducing conditions the K_d value was 139 mL/g. In the reducing experiment, the Tc K_d value does not suggest that it is being controlled by a Tc-sulfide phase solubility, as has been used in defense of using low solubility values. The glovebag had very low atmospheric O_2 concentrations of between 30 to 60 ppm, but the Eh of the suspensions were between 140 and 400 mV, which are in the category of suboxic. This demonstrates that only a small concentration of O_2 needs to be present for oxidation of Tc(IV) to occur at the high pH levels of these systems. Another important point to make is that these samples were not fully reduced. A fully reduced sample would be dark black, not olive green. As such, the solid sample and the aqueous system was slightly oxidized. As such, it is not surprising that greater aqueous Tc concentrations than TcS_x -solubility were detected in these experiments.

The results from the desorption experiments with the Tc-amended cementitious materials by Lilley (2010), as discussed in Section 3.0, are also included in Table 12 for comparison. Tc K_d values increased with slag content. As discussed, Lilley (2010) did not establish steady state in these studies and it appears that the amount of Tc sorption would have increased with contact time; this is more apparent for the saltstone with 10% and 45% slag content and less apparent for the saltstone with 95% slag content.

Table 12. Sorption and diffusion measurements and calculated sorption coefficients for Tc(IV) and Tc(VII) with cementitious materials.

	Reference	Cementitious Materials	Experimental Conditions	pH	Eh (mV)	Effective Diffusion (D_e , cm^2/s)	K_d^d (mL/g)
1	Bayliss et al. (1992)	Ordinary Portland Cement	1g: 50 mL; Added Tc(IV); Nitrogen and hydrogen glovebox; non-saline aqueous Sodium dithionite added	13.1	-228		6000 Tc(IV)
2	Bayliss et al. (1992)	Ordinary Portland Cement	1g: 50 mL; Added Tc(IV); Nitrogen and hydrogen glovebox; saline aqueous Sodium dithionite added	12.6	-264		1000 Tc(IV)
3	ANDRA (2005)	CEM I/V and CSH		9.9-12.1			760-3,700 Tc(IV)
4	Gilliam et al. (1988)	Tested 6 different types of slags: (20% slag, 20 % fly ash,, 20% OPC, 40% HMS filter)	ANSI 16.1; Calculated K_d based on Leachability Index (which is $\approx -\log$ of D_e).		Ave = -250		Cleveland ~1000 Japan = ~100 Japan-a ~1000 Cleveland-b ~1000 Cleveland = 1000 Sparrow Pt ~ 1000 Avg of 6 ~ 1000
5	Serne et al (1992)	T-106 AN ^a (47.5% slag)	ANSI/ANS 16.1; oxidizing conditions, D_e nitrate = 10^{-8} cm^2/s			10^{-8}	$\sim 1^b$
6	Serne et al (1992)	DSSF (47% slag)	ANSI/ANS 16.1; oxidizing conditions, D_e nitrate = 10^{-8} cm^2/s			10^{-8}	$\sim 1^b$
7	Langton (1988)	Saltstone Mix 2 (25% slag) ^a	ANSI/ANS 16.1; oxidizing conditions, D_e nitrate = 10^{-9} cm^2/s			10^{-12}	$\sim 1000^b$
8	Langton (1988)	Saltstone Mix 2 (25% slag) ^a	ANSI/ANS 16.1; oxidizing conditions, D_e nitrate = 10^{-7} cm^2/s			10^{-12}	$\sim 100,000^b$
9	Langton (1988)	Saltstone without slag	ANSI/ANS 16.1 ; oxidizing conditions, D_e nitrate = 10^{-9} cm^2/s			10^{-9}	$\sim 1^b$
10	Brodda (1988)	Portland, aluminous cement blast furnace cement	ANSI/ANS 16.1 ; Cl leached by a factor of >100 faster than Tc				~ 100
11	Tallent et al. (1988)	70% slag/25% cement	ANSI/ANS 16.1; leachability index (LI) $\approx -\log$ of D_e : Tc LI = 9.3 & NO ₃ LI = 7.8				~ 100

	Reference	Cementitious Materials	Experimental Conditions	pH	Eh (mV)	Effective Diffusion (D_e , cm^2/s)	K_d^d (mL/g)
12	Tallent et al. (1988)	100% slag	ANSI/ANS 16.1; leachability index (LI) $\approx -\log$ of D_e : Tc LI = 9.8 & NO_3 LI = 8.3				~100
13	Tallent et al. (1988)	47.5% slag/47.5% fly ash/5%lime	ANSI/ANS 16.1; leachability index (LI) $\approx -\log$ of D_e : Tc LI = 9.3 & NO_3 LI = 8.5				~10
14	Kaplan and Coates (2007)	Saltstone (25% slag) $\text{Ca}(\text{OH})_2$ -sat. and CaCO_3 -sat. solution	Adsorption Tc(VII)	11.16 to 12.00	Reducing Grout : 36 Aged Red. Grout: 110		0.8 to 5.08
15	Kaplan et al. (2008)	Saltstone (25%) $\text{Ca}(\text{OH})_2$ -sat. and CaCO_3 -sat. solution	Adsorption Tc(VII), oxidized conditions	10.5 to 12.1			6 to 91
16	Almond et al. (2011)	Saltstone Disposal Facility Vault 4 Sample	Oxidizing Conditions	11.46	160		12
17	Almond et al. (2011)	Saltstone Disposal Facility Vault 4 Sample	Reducing Conditions	12.05	140-400		139
18	Lilly (2010)	TR547 Saltstone (45% slag)	Batch, not steady state yet, Section 3 in this report; H_2/N_2 reducing conditions	11.70	-498		518 \pm 95 (after 56 days) 711 \pm 81 (after 22 day)
19	Lilly (2010)	TR547 Saltstone (90% slag)	Batch, not steady state yet, Section 3 in this report; H_2/N_2 reducing conditions	11.86	-584		15,000 \pm 2800 (after 56 days)
20	Lilly (2010)	Vault 2 Concrete (10% slag)	Batch, not steady state yet, Section 3 in this report; H_2/N_2 reducing conditions	11.31	-361		208 \pm 88 (after 56 days)

^a PSW = Portland type I/II cement, fly ash, attapulgite clay Illite

^b K_d estimated based on $D_e = D/R_f$; where D is diffusion in water (without cement) and R_f is retardation factor, which is related to K_d by $R_f = 1 + (\rho_b/n)K_d$; where ρ_b is the bulk density, n = the effective porosity. It is assumed that R_f of nitrate in cement equal 1 mL/g. It's an approximation to help convert D_e values to K_d values.

^c Frodingham Blast Furnace slag, mixed with $\text{Ca}(\text{OH})_2$ in the ratio 10:1.

^d For simplicity in presentation of data, K_d values are being used in this table to describe both adsorption and solubility processes. Solubility likely controls most of the systems with high K_d values or high effective diffusion values, whereas adsorption likely controls those systems with low K_d values.

5.0 Conclusions

Research and a literature study were completed to investigate the behavior of Tc within cementations materials. From a combination of these studies, it is apparent that Tc can be reduced by BFS under laboratory and field conditions. These results point to the ability of saltstone containing BFS under anaerobic conditions to generate a reducing environment and to effectively immobilizing Tc as TcS_x or $TcO_2 \cdot xH_2O$.

This work largely reinforced our conceptual model of the shrinking core but more importantly provided some clarity regarding process kinetics, mechanisms, and input values for future detailed modeling. The shrinking core model in itself is devoid of geochemical mechanisms, this study permitted us to add more geochemical detail to this model. The shrinking core model describes the existence of an oxidized outer layer of concrete surrounding a shrinking core of reducing intact saltstone. A sharp boundary between the two zones moves slowly inward, resulting in oxidation of Tc(IV). Tc(IV) initially exists as $Tc_2S_{7(s)}$ in the wasteform, then in the presence of O_2 it relatively quickly converts to $TcO_2 \cdot xH_2O_{(s)}$, (Shuh et al. 2000) before in turn rapidly oxidizing to $TcO_4^-_{(aq)}$, the specie that enters the aqueous phase. As $TcO_4^-_{(aq)}$, it diffuses through the solution in the pores and micro cracks in the cementitious material. The solubility of $TcO_2 \cdot xH_2O_{(s)}$ (at pH 12.5 at -400 mV) is 10^{-7} M, which exceeds the maximum contamination limit (MCL) for ^{99}Tc set at 900 pCi/L or 5×10^{-10} M. Therefore, once the O_2 front initially arrives, the conversion from $Tc_2S_{7(s)}$, not the reduction, to $TcO_2 \cdot xH_2O_{(s)}$ will promote Tc concentrations to exceed the MCL by three orders of magnitude (i.e., the solubility of the latter exceeds the MCL by three orders of magnitude). As the Eh continues to increase from -400 to -200 mV at pH 12.5, the solubility of $TcO_2 \cdot xH_2O_{(s)}$ will increase to $>10^{-1}$ M Tc.

Atkins and Glasser (1992) report that under natural and experimental conditions it takes several months to obtain steady state reducing conditions within a cementitious material. This long duration is a result of slow reaction kinetics associated with various chemical and mineralogical transformations that take place within cement, but also because of the need for slag particles to undergo hydrolysis and to release S^{2-} , a reducing agent, into the aqueous phase. Recent batch sorption experiments (Lilley 2010) with slag formulations approaching that of the Saltstone facility, TR547 (45% slag), were in contact with Tc for approximately two months, short of the predicted greater than 18 months required to obtain steady state (Atkins and Glasser 1992). The greatest K_d value measured with the TR547 saltstone was 711 ± 81 mL/g, but presumably the K_d would have continued to increase as the slag had more time to hydrolyze, releasing aqueous S^{2-} . Similarly, the TR545 (90% slag) saltstone, which had a maximum K_d of $14,445 \pm 2,800$ mL/g, also appeared not to have reached steady state (Figure 2)

A sharp boundary will likely form between the oxidized and reduced zones because the kinetics of the oxidation reaction are rapid (Shuh et al. 2000; Lukens et al. 2005). Finally, site specific measurements support assigning K_d values at three points in this field:

- Oxidized zone, where the primary sorption mechanism is by anion exchange: (measured Eh = 450, pH 11.5) $K_d = 0.8$ mL/g (primary data support is in Kaplan 2010)
- Reduced zone, where the primary sorption mechanism is Tc(IV) phase solubility: (measured Eh = -585, 11.7), $K_d = 1000$ mL/g (primarily data supported is in Kaplan 2010, also Figure 2 and Table 12)

- Furthermore, it is possible to assign a third K_d value just ahead of the O_2 front, but within the reducing zone: (measured Eh = 250, pH 12.1), $K_d = 139$ (Almond and Kaplan 2011).

As the boundary moves into the saltstone over time, appreciable oxidation of Tc(IV) species to Tc(VII) will occur in this region facilitating the solubility of Tc into the pore solution where it is released into the aqueous phase.

6.0 Reference

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