

November 7, 2013

MEMORANDUM TO: Gregory Suber, Chief  
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Environmental Protection  
and Performance Assessment Directorate  
Division of Waste Management  
and Environmental Protection

THRU: Christopher A. McKenney, Chief */RA/*  
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FROM: Karen E. Pinkston, Systems Performance Analyst */RA/*  
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SUBJECT: TECHNICAL REVIEW: SOLUBILITY OF TECHNETIUM DIOXIDES IN  
REDUCING CEMENTITIOUS MATERIAL LEACHATES, A  
THERMODYNAMIC CALCULATION, DOCKET NO. PROJ0734

On March 8, 2013, the U.S. Department of Energy (DOE) provided the subject report for review by U.S. Nuclear Regulatory Commission (NRC) pursuant to Section 3116(b) of the National Defense Authorization Act for Fiscal Year 2005. The subject report is available on NRC's Agencywide Documents Access and Management System (ADAMS) at accession number ML13070A135. This report was reviewed in accordance with monitoring activities described in *U.S. Nuclear Regulatory Commission Plan for Monitoring Disposal Actions Taken by the U.S. Department of Energy at the Savannah River Site Saltstone Disposal Facility in Accordance with the National Defense Authorization Act for Fiscal Year 2005, Revision 1* (ML13100A076). This technical review supports Monitoring Factors 5.02 *Chemical Reduction of Tc by Saltstone* and 5.05 *Potential for Short-Term Rinse-Release from Saltstone*.

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The NRC staff's conclusions based on its review of the subject report and associated references include:

- The NRC staff agrees with the approach in Li and Kaplan (2013) of using measured values to support the input parameters used in a performance assessment along with using geochemical modeling to better understand the system and the potential uncertainty.
- The NRC staff agrees with DOE's conclusion that the release of technetium from saltstone under young and moderately aged reducing conditions is more realistically represented as being solubility controlled rather than controlled by sorption ( $K_d$  values).
- The NRC staff agrees with DOE's conclusion that the solubility of technetium (Tc) in the saltstone leachates appears to be controlled by a  $TcO_2 \cdot xH_2O$  phase, which is likely to be  $TcO_2 \cdot 1.6H_2O$ .
- The measured values for Tc solubility show variability between the two different studies (i.e., a two order of magnitude difference) not fully explained by the difference in pH in the two studies.
- The determination of the solubility of Tc in moderately-aged cement based only on the Estes et al. (2012) data without consideration of the Cantrell and Williams (2012) data does not capture the uncertainty in this parameter and may be non-conservative. However, this potential non-conservatism may be counteracted by the use of data from experiments that had a higher pH, and consequently a higher solubility, than is expected for moderately-aged cement.
- It is important for the uncertainty in the solubility of Tc to be captured, especially for moderately-aged cementitious materials since this may be one of the most risk-significant parameters in the model.
- It is only appropriate to exclude the early stage cement from the performance assessment modeling if this assumption does not lead to an underestimation of the dose.
- Neglecting the potential for leaching of the phases responsible for the reducing capacity of blast furnace slag may be non-conservative, based on observations of reduced sulfur species in leachates from saltstone simulant experiments. The slag is likely to contain several different reduced sulfur species that have different solubilities.

Additional information is still needed to close Monitoring Factors 5.02 and 5.05. The NRC staff will continue to monitor information provided by DOE on those factors as it is developed.

For Monitoring Factor 5.02, the additional information needed includes:

- The fraction, if any, of the Tc in saltstone that remains oxidized initially,
- Additional model support on the ability of saltstone to maintain Tc in the reduced form over time,
- An estimate of the potential impact of leaching of reduced sulfur phases on the evolution of saltstone reducing capacity, and a list of the dominant reduced sulfur species expected to be in the slag,
- A performance assessment model that adequately considers the uncertainty in the Tc solubility, or additional experimental data to reduce this uncertainty.

For Monitoring Factor 5.05, the additional information needed includes:

- Experimental measurements of the early rinse-release of Tc and an analysis that this fraction released would not significantly affect the projected dose. Alternately, an analysis based on existing measurements that demonstrates that an early rinse release would not significantly affect projected peak doses. The analysis should consider the fraction, if any, of Tc that is either not fully incorporated into saltstone or not fully reduced by saltstone as well as potential effects of high ionic strength.

The NRC staff expects to receive the Special Analysis (SA) for the Saltstone Disposal Facility (SDF) in the near future. As part of the NRC's review of the SA, the NRC staff will continue to review these areas. The NRC staff will also review any additional that is related to these areas (e.g., information on the form of reduced sulfur in cementitious materials provided as part of the H-Tank Farm review).

The staff's technical review summary is enclosed for your use.

Enclosure:

Technical Review: Solubility of Technetium  
Dioxides in Reducing Cementitious Material  
Leachates, a Thermodynamic Calculation

For Monitoring Factor 5.02, the additional information needed includes:

- The fraction, if any, of the Tc in saltstone that remains oxidized initially,
- Additional model support on the ability of saltstone to maintain Tc in the reduced form over time,
- An estimate of the potential impact of leaching of reduced sulfur phases on the evolution of saltstone reducing capacity, and a list of the dominant reduced sulfur species expected to be in the slag,
- A performance assessment model that adequately considers the uncertainty in the Tc solubility, or additional experimental data to reduce this uncertainty.

For Monitoring Factor 5.05, the additional information needed includes:

- Experimental measurements of the early rinse-release of Tc and an analysis that this fraction released would not significantly affect the projected dose. Alternately, an analysis based on existing measurements that demonstrates that an early rinse release would not significantly affect projected peak doses. The analysis should consider the fraction, if any, of Tc that is either not fully incorporated into saltstone or not fully reduced by saltstone as well as potential effects of high ionic strength.

The NRC staff expects to receive the Special Analysis (SA) for the Saltstone Disposal Facility (SDF) in the near future. As part of the NRC's review of the SA, the NRC staff will continue to review these areas. The NRC staff will also review any additional that is related to these areas (e.g., information on the form of reduced sulfur in cementitious materials provided as part of the H-Tank Farm review).

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Technical Review: Solubility of Technetium  
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Leachates, a Thermodynamic Calculation

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## Technical Review: Solubility of Technetium Dioxides in Reducing Cementitious Material Leachates, a Thermodynamic Calculation

November 2013

**Reviewers:** K. Pinkston, A. Ridge, and G. Alexander

**Document:** SRNL-STI-2012-00769, Rev. 1, D. Li and D.I. Kaplan, *Solubility of Technetium Dioxides in Reducing Cementitious Material Leachates: A Thermodynamic Calculation*. Savannah River National Laboratory. February 1, 2013. ML13070A135.

**Other Key References:** SRNL-STI-2012-00596, Rev. 0, S.L. Estes, D.I. Kaplan, and B.A. Powell, *Technetium Sorption by Cementitious Materials Under Reducing Conditions*. Savannah River National Laboratory. September 2012. ML12345A134.

PNNL-21723, K.J. Cantrell and B.D. Williams, *Equilibrium Solubility Model for Technetium Release from Saltstone Based on Anoxic Single-Pass Flow through Experiments*. Pacific Northwest National Laboratory. September 2012. ML12345A267.

### **Background**

Saltstone is made by mixing liquid salt solution with cement, fly ash, and blast furnace slag. The blast furnace slag is included to create a reducing environment in order to decrease the mobility of redox sensitive radionuclides, such as technetium (Tc). Sulfide and ferrous iron provide most of the reducing capacity in the slag, but the water in contact with saltstone will be influenced mainly by the sulfur chemistry because iron has a low solubility at high pH values (Kaplan, 2008 [SRNS-STI-2008-00045]). The fly ash and Portland cement add additional reducing capacity (Roberts and Kaplan, 2009 [SRNL-STI-2009-00637]), which could contribute to the reduction and retention of Tc. The initial pH of saltstone is high (~12.5 to 13), though as water leaches through the saltstone, the pH value will decrease. Similarly, as water leaches through the saltstone and the saltstone is exposed to oxygen, the saltstone will become more oxidized and the  $E_h$  will increase.

In the U.S. Department of Energy (DOE) 2009 Saltstone Performance Assessment (PA) (SRR-CWDA-2009-00017), Tc-99 was the largest contributor to the predicted dose. The solubility of Tc and its release from the saltstone wastefrom into the environment is strongly influenced by  $E_h$ . Tc is relatively insoluble and immobile under chemically reducing conditions, but is mobile under oxidizing conditions. The solubility of Tc is also pH dependent. Technetium is less soluble at more neutral pH values than at the high pH values found in fresh cementitious materials.

The technical review of "Solubility of Technetium Dioxides in Reducing Cementitious Material Leachates, a Thermodynamic Calculation" (Li and Kaplan, 2013) and associated references by the U.S. Nuclear Regulatory Commission (NRC) staff supports Monitoring Factors 5.02 "Chemical Reduction of Tc by Saltstone" and 5.05 "Potential for Short-Term Rinse-Release from Saltstone" in the 2013 NRC monitoring plan for the Saltstone Disposal Facility (NRC, 2013d). In the 2013 monitoring plan, the NRC staff noted that the studies that had been done to

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demonstrate Tc retention in saltstone included experimental artifacts that made it difficult to interpret the results. As described under Monitoring Factor 5.02, the NRC staff concluded that the NRC needed to determine that DOE has robust model support for the chemical reduction of Tc(VII) to Tc(IV) and that this reduced state is maintained under field conditions. Additionally, under Monitoring Factor 5.05, the NRC staff concluded that additional support was needed to demonstrate that the short-term rinse-release from saltstone during the first few pore volumes will not significantly affect peak doses. The subject report and its associated references provide additional information both on the chemical reduction of Tc by saltstone and the release of Tc, including the initial release of Tc during the first few pore volumes.

### **Summaries of Technical Reports**

Summaries of the key documents reviewed by the NRC staff are provided in the following sections.

#### **Li and Kaplan 2013 (SRNL-STI-2012-00769)**

The objective of the subject report was to generate best estimates for technetium geochemical input values to support transport modeling by comparing thermodynamic modeling results and recent laboratory measurements. The thermodynamic modeling was performed using the Geochemist's Workbench React module (Bethke, 2010). In this modeling, the authors calculated the speciation and solubility of  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ ,  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{TcO}_2(\text{c})$  in reducing saltstone leachates, and Portland cement leachates with the presence of pyrrhotite. The pyrrhotite was included as a surrogate to simulate the reductant present in blast furnace slag. The results of these calculations were compared to similar calculations performed using different databases (i.e., Denham and Millings 2012 [SRNL-STI-2012-00404], Wang et al 2009, and Cantrell and Williams 2012). The solubility values calculated using the databases from Li and Kaplan (2013) were similar to those calculated using the databases described in Denham and Millings (2012) and Wang et al. (2009). The values calculated in Cantrell and Williams (2012) were higher by a factor of 2 to 5. Overall, the calculated solubility of each  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$  species varied by less than an order of magnitude (for a given pH value) regardless of which database was used.

Based on the research described in this paper, the authors concluded that the solubility of  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ , likely  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ , controlled the Tc concentration in saltstone leachates as long as the  $E_h$  was less than -0.38 V. As the  $E_h$  increased above -0.35,  $\text{TcO}_4^-$  became the dominant species and the solubility of Tc increased significantly. As part of this research, the authors developed guidelines for the selection of parameters related to the release of Tc from saltstone for use in PA modeling (Table 1).

**Table 1: DOE Guidelines for Selection of Parameters in PA Modeling of Saltstone and Saltstone Disposal Structures\***

	<b>Parameter Value Selected</b>	<b>Basis</b>
<b>Reduced</b>		
Young Cement 1 <sup>st</sup> Stage (pH~12)	$6 \times 10^{-7}$ mol/L solubility	Average of experimentally derived values in Cantrell and Williams (2012) and Estes et al. (2012)
Moderately-Aged Cement 2 <sup>nd</sup> Stage (pH~10.5)	$1 \times 10^{-8}$ mol/L solubility	Experimentally derived value in Estes et al (2012)
Aged Cement 3 <sup>rd</sup> Stage (pH~5.5)	0.5 mL/g $K_d$	Based on the assumption that the aged cement becomes oxidized
<b>Oxidized</b>		
Young Cement 1 <sup>st</sup> Stage (pH~12)	0.8 mL/g $K_d$	Kaplan (2010) [SRNL-STI-2009-00473]
Moderately-Aged Cement 2 <sup>nd</sup> Stage (pH~10.5)	0.8 mL/g $K_d$	Kaplan (2010)
Aged Cement 3 <sup>rd</sup> Stage (pH~5.5)	0.5 mL/g $K_d$	Kaplan (2010)

\* Based on information in Table 11 in Li and Kaplan [2013]

Prior to the subject article being published, it was reviewed by an expert panel and was revised to address the reviewers' comments. The panel recommended that the authors check the validity of Geochemist's Workbench modeling for saltstone leachates with high ionic strength and check the consistency between the report and previous reports on this topic. The reviewers also requested additional guidance for modelers on how to account for uncertainty associated with the recommended solubility and  $K_d$  values. The authors addressed the topic of high initial ionic strength by stating that the high ionic strength environment will last for only a very short period, so it is expected that the error associated with activity coefficients during this time will have little effect on predicted long-term geochemistry. The subject report indicated that DOE should model uncertainty in the cement geochemistry constants with the equations provided by Almond et al (2012, SRNL-STI-2011-00672) (i.e., a lognormal distribution with a range of  $0.25 * K_d$  to  $1.75 * K_d$ ).

Estes et al. 2012 (SRNL-STI-2012-00596)

The objective of the study described in Estes et al. (2012) was to measure Tc-99 sorption to cementitious materials under reducing conditions. In this study, the sorption of Tc onto four different cementitious materials was measured over 319 days. The four cementitious materials were a 50 year old aged cement sample, simulated Vault 2 concrete, simulated saltstone, and a material containing 90% slag and 10% Portland cement. The sorption experiments were conducted under an atmosphere of 0.1%  $H_2(g)$ /99.9%  $N_2(g)$  with a palladium catalyst to maintain anoxic conditions. Prior to the experiment, the samples were not stored in an inert environment, so some amount of oxidation might have occurred during that time. After the 319-day sorption step, oxic conditions were introduced and desorption was measured for a period of 20 days.

The aqueous Tc concentration, calculated  $K_d$  value, and  $E_h$  and pH values were reported over the time of the sorption experiment. The pH values were high and reducing conditions were observed over the time of the sorption experiment for the simulated saltstone sample. Little or no loss of Tc was observed in the no solids control, so the reducing atmosphere did not appear to be contributing to Tc precipitation or sorption due to the chemical reduction of Tc.

The aqueous concentrations of Tc were similar for the simulated saltstone samples independent of the amount of Tc added to the system, so the aqueous Tc concentrations appeared to be controlled by solubility rather than sorption. The aqueous concentration of Tc converged at a value of  $10^{-8}$  M, and the aqueous Tc measured at end of the sorption experiment was found to be almost all Tc(VII). Geochemical modeling was performed using Geochemist Workbench to simulate the experimental conditions in this study. The modeled solubility values are comparable to the measured values, which also supported the aqueous concentrations of Tc being controlled by solubility, not sorption.

During the desorption experiments, the introduction of oxygen resulted in the  $E_h$  value increasing and the remobilization of the Tc. The authors concluded that the  $K_d$  model would be appropriate for modeling oxidized systems where Tc(VII) is expected to be the dominant form of Tc.

#### Cantrell and Williams 2012 (PNNL-21723)

The goal of the research described in Cantrell and Williams (2012) was to develop a mechanistically-based conceptual model for the release of technetium from saltstone. An additional goal was to establish the impact of oxidation on the leachability of technetium from saltstone.

In this research, the authors measured the leaching from simulated saltstone using a single-pass flow-through system under anoxic conditions. In the experimental set-up, the researchers wanted to minimize oxygen contamination without using hydrogen because it could act as a reductant. To accomplish this, a large saltstone-to-leachant ratio was used to minimize the impact of trace amounts of oxygen in the system. They also used heavy walled Teflon reactors and placed the reactors in a controlled atmospheric environment maintained at low oxygen concentrations to minimize oxygen contamination. The simulated saltstone was cured for 30 days before being crushed and sieved. The saltstone was crushed and sieved in an environment that was exposed to air, so this step was done quickly to minimize oxidation.

The concentration of Tc measured in the leaching experiments was initially approximately 300  $\mu\text{g/L}$ , and this concentration decreased with time. The  $E_h$ , pH, and the concentrations of sulfide and other anions and cations were also measured. The  $E_h$  conditions were reducing over the course of the experiments and the pH was in the range of 12.5-13. The results of leaching experiments were compared to thermodynamic modeling performed using the Geochemist's Workbench software to evaluate the potential solubility controlling phases. The authors concluded based on the geochemical modeling that the Tc release from saltstone under anoxic conditions is controlled by  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ . They also concluded that the likely  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$  species is  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ .

The reactors were sparged with pure oxygen after 84 days. One of the reactors was exposed for 30 minutes on one day, while the other reactor was exposed for 30 minutes on 3 consecutive days. The exposure of the saltstone to multiple large amounts of oxygen resulted in the formation of soluble  $\text{TcO}_4^-$  and its subsequent release. The researchers also concluded that the reducing capacity of saltstone could overcome an exposure that occurred over a short time by reducing the Tc back to  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ .

### **Technical Exchanges**

On April 30, 2013, NRC staff held a teleconference with DOE to discuss the Li and Kaplan (2013) report (NRC 2013b). DOE staff provided additional information on the basis for the recommended solubility and  $K_d$  values for Tc, the reasons for modeling the reducing capacity as pyrrhotite, the uncertainty in measured  $E_h$  values, and the basis for differences between solubility measurements in Estes et al. (2012) and Cantrell and Williams (2012).

During this teleconference, DOE described the basis for the values recommended in Table 11 of Li and Kaplan (2013) for the use in PA modeling. They explained that the values selected were based on experimental values. The geochemical modeling was performed to support their conclusions, but was not directly used in generating the recommended solubility and  $K_d$  values.

DOE also provided additional details on the way that  $E_h$  was modeled in the geochemical modeling and the basis for using pyrrhotite to represent the reducing capacity provided by sulfur species in the saltstone. It was discussed that blast furnace slag is likely to contain several different reduced sulfur species. DOE stated that the use of pyrrhotite in their geochemical model is a proxy to account for the reducing capacity.

The DOE and NRC staffs also discussed the uncertainty around the measured  $E_h$  value and the sensitivity of the form of Tc to the  $E_h$ . NRC staff noted that the measured  $E_h$  values reported for saltstone are similar to the value reported by Li and Kaplan at which the solubility of Tc increases dramatically (-0.35 V). DOE described the difficulties in measuring  $E_h$  and stated that an experimental measurement of -0.35 V is not meaningfully different than one of -0.38 (i.e., the value assumed in Li and Kaplan). However, DOE also stated that there is experimental evidence (e.g., Cantrell and Williams, 2012) that shows that saltstone contains a sufficiently reducing environment for Tc to be in its reduced and less mobile form.

DOE also provided their hypothesis on the basis for the difference between the solubility measurements reported in Estes et al. (2012) and Cantrell and Williams (2012) (i.e.,  $9 \times 10^{-9}$  M at pH 11.9 in Estes et al and  $1.5 \times 10^{-6}$  M at pH 12.66 in Cantrell and Williams). The environment used in the Estes et al. experiments contained 0.1%  $\text{H}_2(\text{g})$  and was more reducing. Additionally, the contact time was longer in the Estes et al. experiments than in the Cantrell and Williams experiments.

A follow up conversation was held during the June 2013 onsite observation (NRC, 2013d). During this discussion, DOE provided additional information on the basis for the solubility value recommended for Tc for moderately-aged reduced cementitious materials, the potential effect of the initial high ionic strength in the saltstone pore solution on Tc solubility, the basis for which species is expected to control solubility, and how DOE intends to use the information in Li and Kaplan (2013) to support a PA.

The DOE staff stated that the recommended value for Tc for moderately-aged reduced cementitious materials was based on an experimental value provided in Estes et al. (2012) which was measured at a pH value comparable to the pH of moderately-aged reduced cementitious materials.

The DOE staff described the conditions under which the Debye-Hückel equation used in the thermodynamic modeling to calculate activity coefficients based on the ionic strength is applicable. The DOE staff stated that this equation is valid for ionic strengths up to 1 M. The ionic strength of the pore solution in saltstone is expected to exceed this molarity during the first few pore volumes. The DOE staff also noted that the leaching experiments performed included the early time when the ionic strength is high, so these experiments provide information on the potential for a higher solubility at that time.

The DOE staff explained that the sulfur was modeled as one species (pyrrhotite), but in reality there is an assemblage of sulfur-bearing species. Additionally, over time as water passes through saltstone, the sulfur will become pyrite, which is a more soluble species than pyrrhotite.

DOE is developing a new Special Analysis (SA) that incorporates recently available technical data and modeling lessons learned from other activities to resolve uncertainties and address issues identified in the NRC TER (NRC, 2012). The DOE staff described the proposed SA approach for modeling the release of Tc. They stated that the saltstone was initially modeled as being reduced and moderately-aged (2<sup>nd</sup> stage) and having a Tc solubility limit of  $1 \times 10^{-8}$  mol/L. At later times, the Tc was modeled as having a  $K_d$  value of 0.5 mL/g, which represents oxidized aged cement (3<sup>rd</sup> stage). Oxidized moderately-aged saltstone was not explicitly included in the model because the  $K_d$  value for this (0.8 mL/g) is similar to the  $K_d$  value for oxidized aged cement and the use of the lower  $K_d$  value for oxidized aged saltstone is conservative. The NRC staff stated that it is only appropriate to exclude the young cement (1<sup>st</sup> stage) from the model if the properties of the young and moderately-aged saltstone are similar and if this simplification does not lead to an underestimation of the dose.

The NRC staff asked if the model used in the SA accounted for the possibility that the reduced sulfur is present in a more soluble form and is leached out. The DOE staff stated that in the model, the reductant is only consumed by oxygen and the model does not include any leaching of the sulfur reductant.

In response to an NRC question, the DOE staff stated that the Tc solubility limit would not be modeled probabilistically in the new SA, but sensitivity cases were run in which the solubility limit was increased and decreased by an order of magnitude.

## **NRC Evaluation**

The subject report (Li and Kaplan, 2013) and associated references provide useful information to support NRC monitoring regarding Monitoring Factors 5.02 “Chemical Reduction of Tc by Saltstone” and 5.05 “Potential for Short-Term Rinse-Release from Saltstone” (NRC, 2013d). In particular, these reports provide useful information on the ability of saltstone to reduce Tc initially and the potential for a higher initial release from saltstone. These reports also provide useful model support for parameters used to model the release of Tc from the saltstone wastefrom in a performance assessment of the Saltstone Disposal Facility (SDF).

The NRC staff finds that the use of geochemical modeling to better understand the system and the potential uncertainty is also useful. The NRC staff agrees with DOE’s use of measured values to support the development of input parameters, especially given the considerable uncertainty in the geochemical modeling and the thermodynamic data. It is important for the experimental measurements to be done in an environment that is representative of the real conditions. In Estes et al. (2012), a small amount of H<sub>2</sub>(g) was used along with a palladium catalyst to remove oxygen from the system, which is not consistent with the actual system. Although a no-solids control in the Estes et al. (2012) experiments did not show reduction of Tc, indicating the H<sub>2</sub>(g) was not causing Tc reduction, the NRC staff has previously expressed concern that other DOE reports (Kaplan et al., 2011 [SRNL-STI-2010-00668]) have shown that even trace quantities of oxygen (e.g., 30 to 60 ppm) can cause measurable Tc oxidation in saltstone samples (NRC, 2013d). In response to the concern that the methods used by Estes et al. (2012) do not adequately represent field-emplaced conditions, which may include trace quantities of oxygen, DOE responded that the complete lack of oxygen in the system used by Estes et al. is expected to be representative of the conditions inside a block of saltstone, where DOE expects that even trace quantities of oxygen would be scavenged by the reducing capacity of the saltstone wastefrom.

Another aspect of adequately representing field conditions is to mimic the chemical composition of the as-emplaced saltstone. As-emplaced saltstone contains admixtures which could affect the release of key radionuclides. The experiments that have been conducted to support the solubility of technetium do not include all of the chemicals that have been used in the production of saltstone. Waste release experiments conducted on actual saltstone samples would provide important additional insight. As a follow-up action of the June 2013 onsite observation visit, the NRC staff requested information on all admixtures that are currently in use at the SDF (NRC, 2013c).

Research by Lukens et al. (2005, PIT-MISC-0117) showed that a fraction of the Tc in saltstone simulant samples remained oxidized even under reducing conditions. Although it does not appear to the NRC staff that this persistent oxidized fraction of Tc will be modeled explicitly in DOE’s waste release model in the SA, the potential release of this more mobile Tc fraction may be captured implicitly. The solubility study conducted by Cantrell and Williams (2012) is based on saltstone simulant samples that would include this persistent oxidized fraction of Tc. The observed release of Tc under reducing conditions would include at least a portion of the oxidized technetium and would therefore be included in DOE’s waste release models. However, the Tc that was released in the Cantrell and Williams (2012) experiments may not include the entire oxidized fraction because in these experiments the leachate flowed around particles of crushed saltstone. In the real system, there may be flow through the saltstone

matrix itself that could result in the water contacting and releasing a higher fraction of the oxidized Tc.

The NRC staff agrees with the conclusion that the release of Tc is likely to be controlled by solubility rather than sorption under reducing conditions. Understanding the solubility of Tc in saltstone and the factors that influence its solubility is important to understanding the potential dose from saltstone because the measured  $E_h$  values are very similar to those at which oxidation and mobilization of Tc is observed to occur. The leaching experiments described in the subject report and its references provide some evidence that the saltstone contains conditions that are sufficiently reducing to reduce Tc and decrease its mobility. Additional information is still needed regarding: (i) what fraction, if any, of the Tc in saltstone remains oxidized and (ii) the ability of saltstone to maintain the Tc in reduced and less mobile form.

The NRC staff understands the modeling approach of using pyrrhotite as a surrogate in geochemical modeling to represent the reducing capacity of saltstone. However, it is important to understand the particular form that the sulfur is in to understand the potential for saltstone to maintain a reducing environment for a long period of time. If the sulfur is in a more soluble form, the sulfur may be leached out of the saltstone, which would decrease the amount of reducing capacity remaining in the saltstone. Recent research by Cantrell and Williams (2012) indicates that the use of pyrrhotite may non-conservatively underrepresent the solubility of the reduced sulfur phase(s) present in blast furnace slag. The authors observed reduced sulfur species present in the leachates from saltstone simulant experiments. DOE indicated that in its current special analysis, DOE assumes that the consumption of the reducing capacity is due only to the reaction with oxygen. If the reduced sulfur phase or phases in the blast furnace slag are sufficiently soluble that leaching of the reducing agent could remove reducing capacity at a rate that is significant compared to the rate at which the reducing capacity is removed through oxidation, DOE's geochemical modeling of saltstone would overestimate the longevity of reducing conditions. Additional support is needed for the assumption that the reducing capacity of saltstone is not significantly affected by leaching of the reducing phases.

The value recommended for the solubility of Tc in young reduced cement was based on the averaging of experimentally determined values from Cantrell and Williams, 2012 ( $1.5 \times 10^{-6}$  M) and Estes et al., 2012 ( $9 \times 10^{-9}$  M). The pH in the Cantrell and Williams (2012) experiments were in the pH range of 12.6 to 12.9 and did not show a trend with time. The pH in the Estes et al. (2012) experiments also did not show a trend with time and remained at a value of approximately 11.9. Based on the results of the thermodynamic calculations, the solubility of Tc is expected to decrease with pH, so it is expected that the solubility would be higher in the Cantrell and Williams (2012) experiments than in the Estes et al. (2012) experiments. However, the results of these experiments differs over two orders of magnitude, which is a larger difference than the models predict. For example, in Table 7 in Li and Kaplan (2013), there is approximately one order of magnitude difference between the solubility at pH 11.8 and pH 12.66. In addition to the pH and the hypotheses provided by DOE (i.e., the presence of hydrogen gas and the longer contact time in the experiments by Estes et al. led to lower measured solubility), the difference in observed solubility values in the Cantrell and Williams (2012) and Estes et al. (2012) reports may also be due to sample preparation (i.e., grinding under atmospheric conditions) in the Cantrell and Williams (2012) study. Although the differences in the solubility values between these two studies may be due to the aforementioned experimental artifacts, there is insufficient information in these reports for NRC staff to conclude

that the observed value of  $1 \times 10^{-6}$  mol/L in the Cantrell and Williams (2012) study is not representative of field conditions. Because of the large difference between the solubility measurements, there is significant uncertainty in the solubility value.

Additionally, it appears that the very early releases observed by Cantrell and Williams (2012, Figure 3.1) and in Estes et al. (2012, Figure 3) were higher than the values on which the recommended value was based (i.e., the measured values at early times were a factor of approximately 2-4 times higher than the values used as the basis for the recommended values). The exclusion of the very early release measurements adds to the uncertainty in the recommended value.

During the onsite observation, DOE indicated the value used for the solubility of Tc in moderately-aged cement was based on an experimental value in Estes et al. (2012) measured at a pH value that was comparable to the pH value in moderately-aged cement (i.e., ~10.5). However, according to the data for TR547 (i.e., the simulated saltstone sample that had a formulation comparable to that used for actual saltstone) in Figure 6 in Estes et al. (2012), the pH remained much higher (i.e., in the range of 11.5-12) than the pH of moderately-aged cement for the duration of that experiment. Based on this difference in pH values, it is not clear to the NRC staff that this data is applicable for moderately-aged conditions. However, geochemical modeling suggests that the use of solubility data taken at pH 11.5-12 would conservatively overrepresent the Tc solubility limit at pH 10.5. It would be useful for this measurement to be made under conditions which are comparable to those seen for moderately-aged cements to verify the results of the geochemical modeling. Additionally, the pH value in the Estes et al (2012) experiments is not significantly different than the pH value in the Cantrell and Williams (2012) experiments, so it is not clear why the data from Cantrell and Williams (2012) is not being considered in determining the solubility of Tc in moderately-aged cementitious materials. Because the Cantrell and Williams (2012) data were approximately two orders of magnitude higher than the data from Estes et al. (2012), not considering the data from Cantrell and Williams (2012) seems to underestimate the uncertainty in the solubility and may be non-conservative.

It is difficult to evaluate the appropriateness of particular parameter values and method used to model the release of Tc from the saltstone wastefrom without the context of the complete SA model. However, the assumption that the increased solubility observed for the young cement (1<sup>st</sup> stage) can be ignored and that the solubility can be modeled using the lower (2<sup>nd</sup> stage) value appears to be non-conservative. In the DOE 2009 PA (SRR-CWDA-2009-00017), a similar modeling assumption was made. However, in that PA, the  $K_d$  values for the 2<sup>nd</sup> stage cement were generally the same as the 1<sup>st</sup> stage or were lower (i.e., the moderate-age conditions would result in more Tc release). It is only appropriate to exclude the young cement (1<sup>st</sup> stage) from the model if the properties of the young and moderately-aged saltstone are similar or if this simplification does not lead to an underestimation of the dose.

The NRC staff does not find the method proposed in Li and Kaplan (2013) to model uncertainty in the geochemical parameters in the cementitious materials to be appropriate. The recommended uncertainty distribution was based on uncertainty in subsurface  $K_d$  values and is not relevant to the uncertainty in solubility and sorption in the wastefrom. The uncertainty in the subsurface  $K_d$  values stems from variability in subsurface soils, while the uncertainty in the wastefrom is likely to be due to variability in the grout formulation and the curing conditions, as

well as variability in the grout components. During the technical exchanges, the DOE staff stated that sensitivity cases would be run in which the solubility ( $1 \times 10^{-8}$  mol/L) is increased and decreased by an order of magnitude. Given that the range of measured values for the solubility is over two orders of magnitude (i.e.,  $1 \times 10^{-8}$  to  $1 \times 10^{-6}$  mol/L), increasing and decreasing the solubility by an order of magnitude (i.e.,  $1 \times 10^{-9}$  to  $1 \times 10^{-7}$ ) may not be adequate to capture the uncertainty in this parameter.

### **Follow-Up Actions**

No new follow up actions were identified during this review. The NRC staff will continue monitoring these monitoring factors as described in the NRC monitoring plan (NRC, 2013d).

### **Open Issues**

No open issues were identified during this review.

### **Conclusions**

The NRC staff's conclusions based on its review of Li and Kaplan (2013) and associated references include:

- The NRC staff agrees with the approach in Li and Kaplan (2013) of using measured values to support the input parameters used in a performance assessment along with using geochemical modeling to better understand the system and the potential uncertainty.
- The NRC staff agrees with DOE's conclusion that the release of technetium from saltstone under young and moderately aged reducing conditions is more realistically represented as being solubility controlled rather than controlled by sorption ( $K_d$  values).
- The NRC staff agrees with DOE's conclusion that the solubility of technetium in the saltstone leachates appears to be controlled by a  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$  phase, which is likely to be  $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}$ .
- The measured values for Tc solubility show variability between the two different studies (i.e., a two order of magnitude difference) that is not fully explained by the difference in pH in the two studies.
- The determination of the solubility of Tc in moderately-aged cement based only on the Estes et al. (2012) data without consideration of the Cantrell and Williams (2012) data does not capture the uncertainty in this parameter and may be non-conservative. However, this potential non-conservatism may be counteracted by the use of data from experiments that had a higher pH, and consequently a higher solubility, than is expected for moderately-aged cement.
- It is important for the uncertainty in the solubility of Tc to be captured, especially for moderately-aged cementitious materials since this may be one of the most risk-significant parameters in the model.

- It is only appropriate to exclude the early stage cement from the performance assessment modeling if this assumption does not lead to an underestimation of the dose.
- Neglecting the potential for leaching of the phases responsible for the reducing capacity of blast furnace slag may be non-conservative, based on observations of reduced sulfur species in leachates from saltstone simulant experiments. The slag is likely to contain several different reduced sulfur species that have different solubilities.

The research described in Li and Kaplan (2013) and associated references provides useful information to support NRC monitoring regarding Monitoring Factors 5.02 “Chemical Reduction of Tc by Saltstone” and 5.05 “Potential for Short-Term Rinse-Release from Saltstone”. Additional information is still needed to close Monitoring Factors 5.02 and 5.05. The NRC staff will continue to monitor information provided by DOE on those factors as it is developed.

For Monitoring Factor 5.02, the additional information needed includes:

- The fraction, if any, of the Tc in saltstone that remains oxidized initially,
- Additional model support on the ability of saltstone to maintain Tc in the reduced form over time,
- An estimate of the potential impact of leaching of reduced sulfur phases on the evolution of saltstone reducing capacity, and a list of the dominant reduced sulfur species expected to be in the slag,
- A performance assessment model that adequately considers the uncertainty in the Tc solubility, or additional experimental data to reduce this uncertainty.

For Monitoring Factor 5.05, the additional information needed includes:

- Experimental measurements of the early rinse-release of Tc and an analysis that this fraction released would not significantly affect the projected dose. Alternately, an analysis based on existing measurements that demonstrates that an early rinse release would not significantly affect projected peak doses. The analysis should consider the fraction, if any, of Tc that is either not fully incorporated into saltstone or not fully reduced by saltstone as well as potential effects of high ionic strength.

The NRC staff expects to receive the SA for the SDF in the near future. As part of the NRC’s review of the SA, the NRC staff will continue to review these areas. The NRC staff will also review any additional that is related to these areas (e.g., information on the form of reduced sulfur in cementitious materials provided as part of the H-Tank Farm review).

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