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May 22, 2018

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Office of Nuclear Materials Safety
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SUBJECT: TECHNICAL REVIEW: UPDATE ON PROJECTED TECHNETIUM RELEASE FROM SALTSTONE

The U.S. Nuclear Regulatory Commission (NRC) staff performed a technical review to update the NRC position on the projected technetium release from saltstone as part of the NRC monitoring of the U.S. Department of Energy (DOE) disposal actions to determine compliance with the performance objectives (POs) set forth in Subpart C of Title 10, Part 61, of the *Code of Federal Regulations* (10 CFR Part 61) at the Savannah River Site (SRS) Saltstone Disposal Facility (SDF) pursuant to Section 3116(b) of the Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005 (NDAA).

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The NRC review was performed in accordance with monitoring activities described in the NRC 2013 SDF Monitoring Plan, available in the NRC's Agencywide Documents Access and Management System (ADAMS) at Accession No. ML13100A076. The 2013 SDF Monitoring Plan contains monitoring areas and each monitoring area contains one or more monitoring factors. This NRC technical review report (TRR) is related to Monitoring Area (MA) 5 (Waste Form Chemical Performance), MA 6 (Disposal Structure Performance), and MA 10 (Performance Assessment Model Revisions). Within those three monitoring areas, this TRR addresses Monitoring Factor (MF) 5.01 (Radionuclide Release from Field-Emplaced Saltstone), MF 5.02 (Chemical Reduction of [Technetium] by Saltstone), MF 5.03 (Reducing Capacity of Saltstone), MF 5.05 (Potential for Short-Term Rinse-Release from Saltstone), MF 6.02 ([Technetium] Sorption in Disposal Structure Concrete), and MF 10.02 (Defensibility of Conceptual Models).

In the NRC 2012 SDF Technical Evaluation Report and the subsequent TRRs on Technetium (Tc) Solubility and Oxidation of Reducing Waste Forms, the NRC identified several potential concerns related to the projected performance of the saltstone waste form and disposal structures as chemical barriers to Tc release. This TRR updates many of the issues raised in those TRRs in the context of new research results based on cores of field-emplaced saltstone from Saltstone Disposal Structure (SDS) 2A and new modeling analyses conducted by the DOE. The table below summarizes the status and priority of monitoring factors described in this TRR, including any changes recommended by the NRC staff.

Summary of status and priority of monitoring factors described in this TRR under both §61.41 and §61.42 Performance Objectives

Monitoring Factor Number and Title	Status	Priority
5.01, “Radionuclide Release from Field-Emplaced Saltstone”	No change (open)	No change (high)
5.02, “Chemical Reduction of Tc by Saltstone”	No change (open)	Recommended change from high to medium
5.03, “Reducing Capacity of Saltstone”	No change (open)	Recommended change from medium to low
5.05, “Potential for Short-Term Rinse-Release from Saltstone"	Recommended closure	Not applicable because of recommended closure (was medium)
6.02, “Tc Sorption in Disposal Structure Concrete”	Recommended closure	Not applicable because of recommended closure (was high)
10.02, “Defensibility of Conceptual Models”	No change* (open)	No change* (high)

* This TRR describes a change in the NRC staff conceptual model of projected Tc release from saltstone at the SDF. Although no change to the status or priority of MF 10.02 was recommended, the recommended changes in status and priority of other monitoring factors described in this TRR reflect that change in the NRC staff conceptual model.

Enclosure:
Technical Review: Update on Projected Technetium Release from Saltstone

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Technical Review: Update on Technetium-99 Release from Saltstone

Date

May 22, 2018

Reviewers

A. Christianne Ridge, Sr. Risk Analyst, U.S. Nuclear Regulatory Commission (NRC)
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Purpose

The purpose of this NRC staff Technical Review Report (TRR) is to update the NRC technical position on Technetium (Tc) release from Saltstone at the U.S. Department of Energy (DOE) Savannah River Site (SRS) Saltstone Disposal Facility (SDF). The NRC staff technical position on Tc release had previously been described in two TRRs:

- "Technical Review: Solubility of Technetium Dioxides in Reducing Cementitious Material Leachates, a Thermodynamic Calculation," which is available in the NRC's Agencywide Documents Access and Management System (ADAMS) at Accession No. ML13304B159; and
- "Technical Review: Oxidation of Reducing Cementitious Waste Forms," (Accession No. ML15098A031).

This TRR updates many of the issues raised in those TRRs based on recent DOE research on cores of field-emplaced Saltstone and changes to the DOE models of Tc release from the SDF.

Background

Tc [1] release from saltstone was identified as a key issue in both the NRC 2005 Technical Evaluation Report (TER) for the SDF (Accession No. ML053010225) and the NRC 2012 SDF TER (Accession No. ML121170309), which was based on the DOE 2009 SDF Performance Assessment (PA) (SRR-CWDA-2009-00017). The DOE later supplemented the DOE 2009 SDF PA with the DOE document "Fiscal Year 2013 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site" (SRR-CWDA-2013-00062, Rev. 2) (FY 2013 SDF Special Analysis Document). The DOE later supplemented the DOE 2009 SDF PA and the DOE FY 2013 SDF Special Analysis Document with the DOE document "Fiscal Year 2014 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site" (SRR-CWDA-2014-00006, Rev. 2) (FY 2014 SDF Special Analysis Document). In this TRR, the phrase "the 2014 Evaluation Case" is used to mean the Evaluation Case model that the DOE used to support the FY 2014 SDF Special Analysis Document and the phrase "the 2013 Evaluation Case" is used to mean the Evaluation Case model that the DOE used to support the FY 2013 SDF Special Analysis Document. In addition, in this TRR, the phrase "the DOE Evaluation Cases" is used to mean: (1) the Base Case[2] model that the DOE used to support the 2009 PA; (2) the Evaluation

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[1] The isotope of Tc of concern for the SDF is Tc-99. However, because release, sorption, and solubility are chemical properties that are the same for all isotopes of Tc, the more general elemental designation Tc is used throughout this TRR rather than the specific radionuclide designation Tc-99.

[2] In the DOE 2009 PA, the DOE referred to Case A as the Base Case, which was described as the scenario that the DOE most expected for the duration of the performance period. In the DOE SDF FY

Case model that the DOE used to support the FY 2013 SDF Special Analysis Document; and (3) the Evaluation Case model that the DOE used to support the FY 2014 SDF Special Analysis Document.

Two previous NRC TRRs[3] evaluated technical topics related to Tc release from saltstone. The first was entitled “Technical Review: Solubility of Technetium Dioxides in Reducing Cementitious Material Leachates, a Thermodynamic Calculation,” and is referred to in this TRR as the “Tc Solubility TRR” (Accession No. ML13304B159). The second was entitled “Technical Review: Oxidation of Reducing Cementitious Waste Forms,” (Accession No. ML15098A031) and is referred to as the “Oxidation TRR” in this TRR. This TRR updates many of the issues raised in those TRRs in the context of new DOE research on cores of field-emplaced saltstone from Saltstone Disposal Structure (SDS) 2A and new modeling analyses that were issued by the DOE since those TRRs were issued.

The Tc Solubility TRR documented the NRC staff review of measurements of Tc solubility in samples of laboratory-made, simulated saltstone. It also provided the NRC evaluation of the solubility values that the DOE recommended to represent different chemical conditions in PA models of the SDF (SRNL-STI-2012-00769). Those chemical conditions included both oxidizing and reducing redox conditions as well as pH conditions representative of young, middle, and old cementitious material. A subset of the solubility values proposed in that DOE document were subsequently used in the 2013 and 2014 Special Analysis Evaluation Cases and sensitivity analyses. In the Solubility TRR, the NRC staff concluded that the DOE use of the recommended solubility of Tc in middle-age cementitious material to represent Tc release at early times appeared to be non-conservative because the high pH and higher ionic strength conditions in young saltstone could lead to higher-than-predicted releases of Tc at early times.

The Oxidation TRR addressed the following issues related to the chemical reduction of Tc in saltstone:

- the ability of saltstone to chemically reduce Tc(VII) to Tc(IV);
- the ability of saltstone to maintain Tc(IV) in a chemically reduced form;
- the applicability of different methods of measuring reducing capacity to Tc reduction in saltstone;
- the correlation of residual reducing capacity with Tc retention in saltstone; and
- the potential for early releases of Tc from saltstone if a fraction of Tc remains oxidized or becomes oxidized prior to contact with infiltrating water.

2013 and FY 2014 Special Analysis documents, the DOE did not use the term “Base Case”, but instead developed an “Evaluation Case” by selecting parameter values that the DOE considered to be most probable and defensible. The DOE also ran a variety of sensitivity analysis cases with “Best Estimate” values. Although there were slight differences in how the DOE described the Base Case and Evaluation Case, the DOE used the Base Case and Evaluation Case results for comparison to the 10 CFR Part 61 performance objectives. Therefore, the NRC regards the DOE Base Case and the DOE Evaluation Case as serving the same purpose.

[3] One of these, the “Technical Review: Solubility of Technetium Dioxides in Reducing Cementitious Material Leachates, a Thermodynamic Calculation,” (Accession No. ML13304B159) used the older name of “Technical Review Memo,” which is the same as a TRR.

The NRC questioned the ability of saltstone to fully reduce Tc (VII) to Tc (IV) and to maintain Tc in a reduced form because of experiments that appeared to show either evidence of mobile Tc or spectroscopic evidence of Tc (VII) in simulated reducing cementitious waste forms. As described in the Oxidation TRR, both types of studies raised concerns about a “persistent oxidized fraction” of Tc in saltstone. However, as described below, the results of those studies were inconclusive.

One of the studies that provided spectroscopic evidence of Tc (VII) in saltstone (Lukens et al., 2005) measured approximately three percent (%) of Tc as Tc (VII) after 30 months of curing in low-permeability cuvettes, which the authors referred to as “impermeable.” Although the thickness of the “impermeable” cuvette walls was not given, for reasonable assumptions of the thickness of the cuvette walls (e.g., 1 millimeter (mm)) and at the oxygen diffusion coefficient the researchers provided for the impermeable cuvette walls, (i.e., diffusion coefficient of oxygen of 2.3×10^{-9} (square centimeters per second (cm^2/s)), the oxidized Tc (VII) can be explained by oxygen diffusion through the cuvette wall. Thus, it was unclear to the NRC staff whether the observed oxidized fraction of Tc in that study represented a small fraction of Tc that could remain oxidized in field-emplaced saltstone or if it was due to an experimental artifact.

The Oxidation TRR cited another study that showed spectroscopic evidence of Tc (VII) in samples aged for 29 days (SRRA042328SR). However, when that study was continued and waste forms were aged for 453 to 458 days, the authors did not find any evidence of Tc (VII) in the waste form (SRRA042328-0004). That result could imply that Tc (VII) was reduced to Tc (IV) by saltstone as the sample aged. However, there is uncertainty in that interpretation because a significant fraction of the Tc initially added to the waste form (i.e., from 46% to 62%) was lost in bleed water in that study (SRRA042328-0004). Therefore, it is not clear if the lack of Tc (VII) observed in the solid samples was attributable to the ability of saltstone to reduce Tc (VII) to Tc (IV) or simply due to all of the Tc (VII) having migrated out of the sample.

A study conducted by the Cementitious Barriers Partnership (CBP) (CBP-TR-2014-05) provided evidence of mobile Tc in chemically reducing parts of samples of Cast Stone, which is a reducing cementitious waste form very similar to saltstone. However, the lack of spectroscopic evidence in that study meant the authors could not determine whether the observed Tc mobility was due to the presence of Tc (VII) or unanticipated mobility of Tc (IV). That distinction would change the modeled Tc release from the SDF because, in the current DOE models, Tc mobility depends on its oxidation state and the grout pH.

In the 2013 and 2014 Evaluation Cases and sensitivity analyses, the oxidation state of Tc in a modeled finite element of saltstone was governed by the modeled reducing capacity in that finite element. In those models that reducing capacity was projected to be consumed by oxygen in infiltrating water. The Oxidation TRR questioned three fundamental aspects of those models:

- whether Tc mobility should be represented as being governed only by the oxidation state of the surrounding saltstone grout;
- whether the value of the reducing capacity the DOE used was appropriate; and
- whether the DOE model of oxygen ingress was adequate.

The NRC staff questioned the relationship between Tc mobility and oxidation state because of the results of the research described in CBP-TR-2014-05, which had appeared[4] to show the presence of oxidized Tc in areas where saltstone had measured reducing capacity.

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[4] That apparent result has been reevaluated by the NRC staff later in this TRR.

As described in the Oxidation TRR, the NRC staff also determined that the cerium (Ce) method (i.e., the Angus-Glasser method) used by the DOE to measure reducing capacity in saltstone may overestimate the amount of reducing capacity available to reduce Tc. In the Oxidation TRR the NRC staff reiterated its concern that the DOE should include gas-phase transport of oxygen in its SDF models (i.e., in addition to oxygen in infiltrating water) and the NRC staff questioned whether air exposure during mixing, pumping, and emplacement, as well as exposure to entrained air, was adequately represented in the DOE models.

The DOE has addressed many of those sources of uncertainty with recent research on saltstone cores from SDS 2A. Additional studies that were conducted with simulated reducing cementitious waste forms also have provided new information about Tc release.

Recent Research

In April and May 2015, the DOE used a wet drilling technique to collect cores from three locations in SDS 2A (SRR-CWDA-2015-00066). The initial DOE plan was to collect two separate cores from each of three camera ports. However, complications encountered in the first drilling attempt resulted in only one core being collected from camera Port B. Therefore, cores were collected from five drill holes. Upper and lower sections of the cores were transported and stored separately and given separate sample designations. Because only one sample section could be retrieved from Port B, a total of nine designated samples were collected:

- upper and lower sections from two drill holes in Port A (i.e., four samples);
- upper and lower sections from two drill holes in Port C (i.e., four samples); and
- lower section from one drill hole in Port B (i.e., one sample).

After the cores were collected, they were immediately transferred to core holders and the atmosphere in the holders was made chemically inert in the field with 99.99% pure nitrogen gas for transportation back to the laboratory. The DOE subsequently used those cores in physical property measurements (SRNL-STI-2016-00106[5]) and in leaching experiments (SRNL-STI-2016-00106; SREL DOC No. R-16-0003; SREL DOC No. R-17-0005). This TRR addresses the results of those three DOE leaching studies. The initial physical and hydraulic properties of those core samples were reviewed in an NRC TRR on saltstone hydraulic properties (ADAMS Accession No. ML17018A137).

The DOE leaching studies evaluated the release of several radionuclides and non-radioactive constituents from the cores using three different experimental techniques:

- seven (7)-day batch leaching procedure
- semi-dynamic test based on U.S. Environmental Protection Agency (EPA) Method 1315; and
- dynamic leaching method (DLM).

In the DOE leaching study described in SRNL-STI-2016-00106, subsamples were taken from the interiors of six saltstone cores, crushed to powder, and leached with a 7-day batch leaching procedure. Both anoxic and oxic leaches were conducted. Samples representing oxic conditions were crushed under normal atmospheric conditions, mixed with leachate, and

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[5] Measurements reported in SRNL-STI-2016-00106 were subsequently reported again in comparison to measurements of laboratory-made samples in the DOE report SRR-CWDA-2016-00051. This TRR references the original study (SRNL-STI-2016-00106), except where it refers explicitly to analyses or discussions that were included only in SRR-CWDA-2016-00051.

tumbled end-over-end in the laboratory for seven days. Samples representing anoxic conditions were crushed in a glove box with an inert atmosphere (i.e., purged with 99.99% pure nitrogen gas), added to bottles in the glove box with deoxygenated leachate, and tumbled end-over-end for seven days in the glove box. The pH and Eh of the leachate were measured before and after leaching and the expected high pH and intended oxic and anoxic conditions were verified. For both types of leaching, leaches were conducted in triplicate for each core sampled (i.e., total of 18 subsamples). For each leaching measurement, approximately 1 gram (g) of powdered core sample was mixed with 10 g of leachate. The leachate was approximately 1,000 times more concentrated than SDF groundwater and was less concentrated, and in different salt proportions, than pore water in fresh saltstone. Dissolved Tc concentrations measured after seven days of leaching (SRNL-STI-2016-00106) are provided in Table 1.

Table 1. Tc release from SDS 2A cores under oxic and anoxic conditions representing lower bounds of Tc solubility using a batch leaching method. Adapted from SRNL-STI-2016-00106 Table 3-12 and Table 3-13

Sample ID (Sample Set 9)	Anoxic Leachate		Oxic Leachate	
	Leachate Concentration (mol/L)	Percent Leached[a]	Leachate Concentration (mol/L)	Percent Leached[a]
SDU2A-0931-A-1-L-3	< $1.16\text{x}10^{-8}$	10	$2.62\text{x}10^{-8}$	24
SDU2A-0931-A-2-L-2	$3.95\text{x}10^{-8}$	42	$2.52\text{x}10^{-8}$	27
SDU2A-0931-C-1-L-2	$3.32\text{x}10^{-8}$	42	$2.27\text{x}10^{-8}$	29
SDU2A-0931-B-1-L-2	$1.87\text{x}10^{-8}$	22	$2.03\text{x}10^{-8}$	24
SDU2A-0931-C-2-L-5	$7.02\text{x}10^{-9}$	9	$2.42\text{x}10^{-8}$	29
SDU2A-0931-C-2-L-2	$2.41\text{x}10^{-8}$	31	$2.16\text{x}10^{-8}$	28
Average[a] (Standard Deviation)	$2.14\text{x}10^{-8}$ [b] ($1.25\text{x}10^{-8}$)[b]	26 (15)	$2.34\text{x}10^{-8}$	27 (2.3)

[a] Values of averages, standard deviations, and percents leached reflect the NRC staff calculations based on data in SRNL-STI-2016-00106 Tables 3-12 and 3-13.

[b] Average concentration and standard deviations were based on including the value for SDU2A-0931-A-1-L-3 at one half the detection limit. Excluding the value for SDU2A-0931-A-1-L-3 yielded an average concentration of $2.45\text{x}10^{-8}$ mol/L and a standard deviation of $1.24\text{x}10^{-8}$ mol/L.

Based on those data, the DOE concluded that contrary to the DOE expectations, the Tc release was insensitive to the leaching atmosphere. The authors of the study also indicated that, "[s]ince it is not certain that equilibrium was attained during the 7-day leach experiments, desorption distribution ratios presented in this study should be regarded as upper bounds, and solubility's interpreted from leachate concentrations should be regarded as lower bounds."

A similar insensitivity to leaching atmosphere was observed in another study of simulated saltstone samples conducted by the DOE (SREL DOC No. R-15-0003)[6]. In that study, laboratory-made simulated saltstone samples were leached with a method similar to EPA Method 1315 to measure diffusive release and simulated saltstone samples were leached with artificial groundwater (AGW) solutions equilibrated with one of three different test atmospheres: oxic, anoxic, and reducing. Oxic conditions were implemented by placing the samples in leaching solutions that were in contact with the ambient laboratory atmosphere. Anoxic conditions were implemented by placing the samples in leaching solutions in an atmosphere purged with ultra-high purity nitrogen (99.999%). Reducing conditions were implemented by placing the samples in leaching solutions in an atmosphere purged with 98% nitrogen and 2% hydrogen. Aqueous Tc concentrations after leaching under oxic and reducing atmospheres are shown in Figure 1.

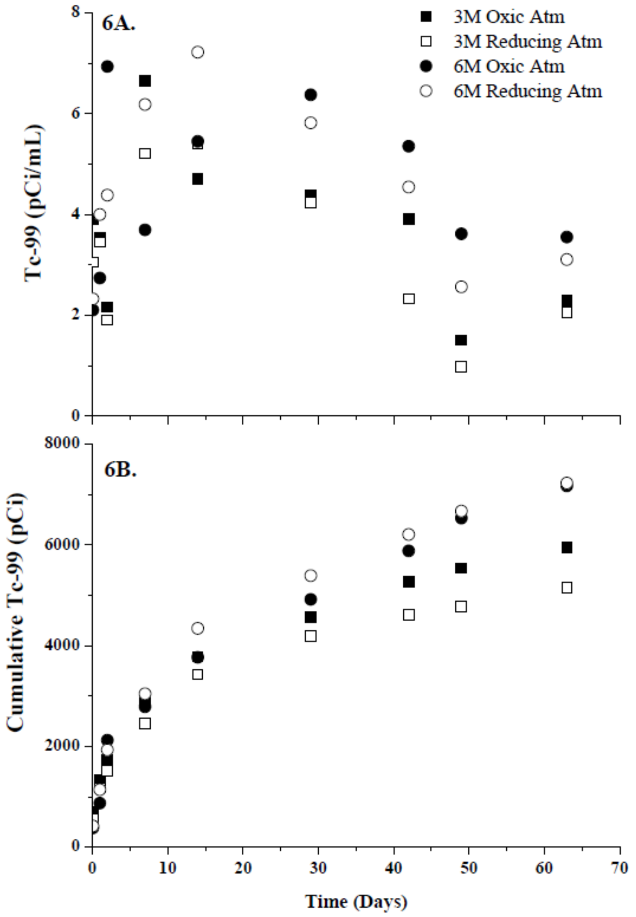

Figure 1. Tc concentrations (at top) and cumulative activity (at bottom) leached from simulated saltstone samples in a semi-dynamic leaching procedure under different atmospheres and curing times of 3 months (3M) or 6 months (6M) (from SREL DOC. No. R-15-0003 Figure 6)

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[6] The NRC staff previously reviewed nitrate diffusivity results reported in SREL DOC No. R-15-0003 in a TRR related to the hydraulic properties of saltstone (Accession No. ML17018A137). In that TRR, the NRC staff concluded that the effective diffusion coefficient that the DOE used in both the 2013 and 2104 Evaluation Cases was well supported.

The Tc fluxes from the anoxic tests (not shown) were similar to the fluxes from the oxic and reducing tests. The semi-dynamic leaching procedure used with simulated saltstone samples documented in SREL DOC No. R-15-0003 was repeated with cores of emplaced saltstone from SDS 2A and additional simulated saltstone samples, as documented in SREL DOC No. R-16-0003. Because of the insensitivity to leaching atmosphere observed in SREL DOC No. R-15-0003, the semi-dynamic tests used in SREL DOC No. R-16-0003 were conducted in contact with the laboratory atmosphere. The latter study made two different comparisons: (1) SDS 2A core samples versus simulated samples; and (2) simulated samples made with Blast Furnace Slag (BFS) from two different vendors. Figure 2 shows that the cumulative amount of Tc released from the SDS 2A samples per unit of exposed surface area was within the range of releases observed from the simulated samples. The authors of the study noted that the SDS 2A samples, which all contained Holcim BFS, all had lower leached Tc concentrations than the simulated samples that also contained Holcim BFS. The authors attributed the difference to the longer curing time available to the SDS 2A samples as compared to the simulated samples (i.e., approximately two years versus 90 days). In contrast, the SDS 2A core samples all had higher Tc diffusive release concentrations than the simulated sample made with Lehigh BFS, despite the longer curing time available to the SDS 2A cores. The authors attributed that difference to the higher reducing capacity of the Lehigh BFS as compared to the Holcim BFS as measured using the Ce method (i.e., 1.6 milliequivalents of electrons per gram (meq e^- / g), 0.713 meq e^- / g, respectively).

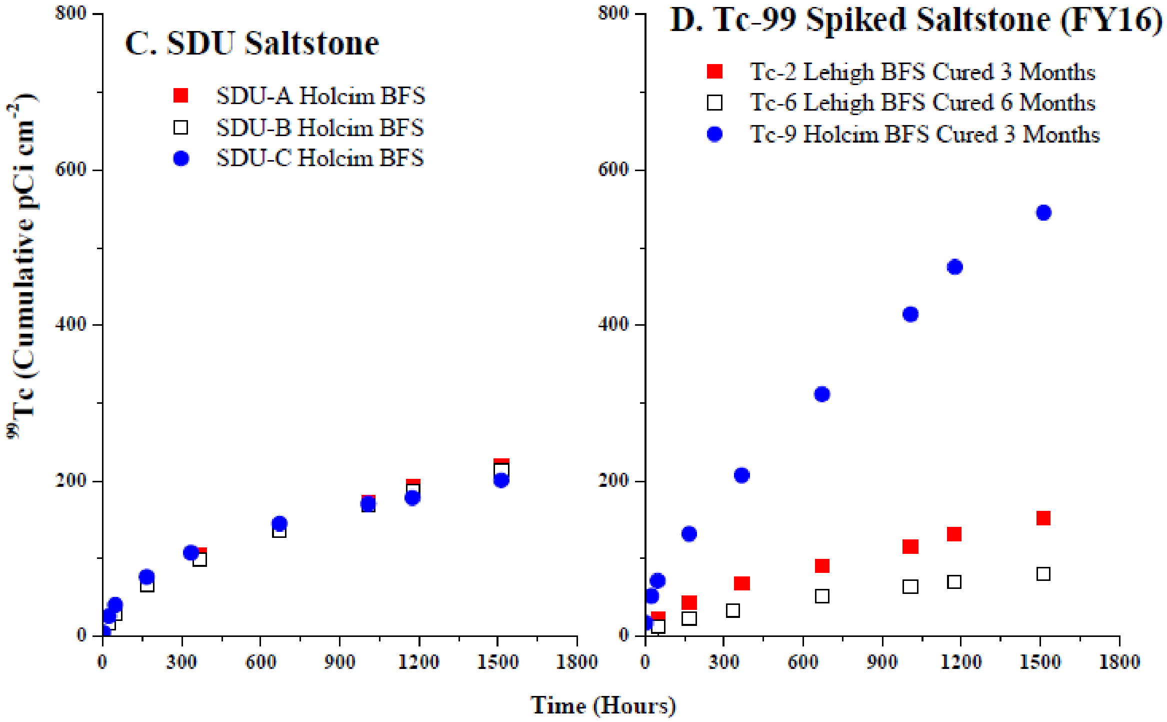

Figure 2. Cumulative Tc released per unit of exposed surface area from SDS 2A cores (left) and simulated saltstone samples (right) (from SREL DOC No. R-16-0003 Figure 3)

In addition to measuring diffusive release, in the study documented in SREL DOC No. R-16-0003, the DOE also used a dynamic leaching procedure based on ASTM D5084-10 (ASTM,

2010) to measure the advective release of certain radionuclides and chemical constituents from saltstone. In the dynamic leaching method, a permeant representing SRS groundwater was forced through samples in a permeameter using pressures of approximately 83 kiloPascals (kPa) (i.e., 12 pounds per square inch (psi)) and Tc was measured in the effluent. Three samples were used in that test: two samples of SDS 2A cores ("SDU-A" and "SDU-B" in Figure 2 and Figure 3) and one Tc-99-spiked simulated saltstone sample. The simulated saltstone sample used in that test was made in 2015 (SREL DOC No. R-15-0003) using the same procedure and recipe as for the diffusive release test sample with Holcim slag. The permeant was first either equilibrated with lab air or was degassed with ultra high-purity nitrogen to remove dissolved oxygen. The degassed permeant was used for both the laboratory-made, Tc-spiked sample (i.e., "Tc-Spiked" in Figure 3) and one of the core samples (i.e., "SDU-B" in Figure 3). The permeant equilibrated with laboratory air was used with the other core sample (i.e., "SDU-A" in Figure 3). Dynamic leaching of those three samples (SDU-A, SDU-B, and the Tc-spiked sample) was continued in FY 2017 (SREL DOC No. R-17-0005). Results from those dynamic leaching tests are shown in Figure 3.

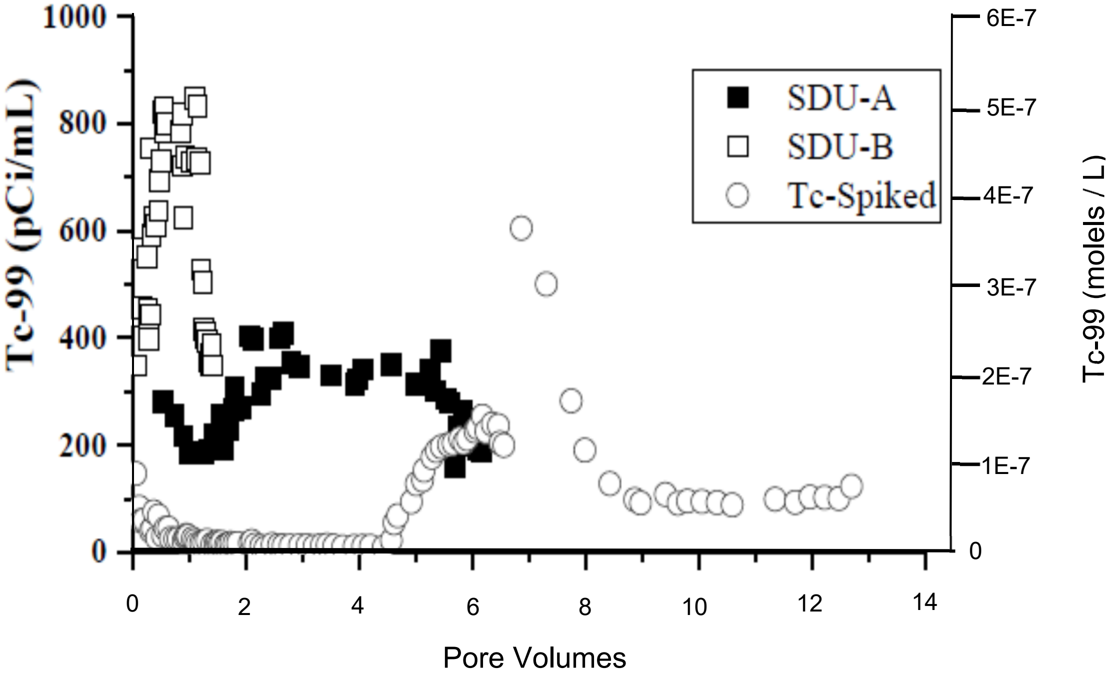

Figure 3. Tc-99 releases from two cores of field-emplaced saltstone ("SDU-A" and "SDU-B") and one laboratory-made Tc-spiked simulated saltstone sample ("Tc-99 Spiked") leached with a dynamic leaching procedure (from SREL DOC No. R-17-005 Figure 8, adapted by the NRC staff by adding the y-axis on the right)

NRC Evaluation

The NRC staff determined that the measured Tc releases from samples of field-emplaced saltstone were the best data available to evaluate model assumptions about the release of Tc from saltstone. Comparison of measured release rates from SDS 2A core samples with releases from samples of laboratory-made simulated saltstone also provided information about how well data from laboratory-made samples can represent releases from cores of field-emplaced saltstone. Varying conditions in laboratory samples also provided insight into variables that affect Tc release (e.g., BFS origin, leaching atmosphere). That information helped address the NRC staff concerns previously identified in the Tc Solubility TRR and the Saltstone Oxidation TRR. In this TRR, the NRC staff observations in the Tc Solubility TRR and Saltstone Oxidation TRR are described in the context of MF 5.01, MF 5.02, MF 5.03, MF 5.05, MF 6.02, and MF 10.02 from the 2013 SDF Monitoring Plan.

Monitoring Factor 5.01, "Radionuclide Release from Field-Emplaced Saltstone"

As described in the NRC 2013 SDF Monitoring Plan, the main NRC staff concern in MF 5.01 is that factors related to field-emplacement of saltstone are adequately represented in the DOE models of SDF performance. For example, the technical discussion of MF 5.01 indicated that it is important to have measurements of leaching from field-emplaced saltstone in order to understand the effects of the admixtures as well as potential variability in the formulation and curing conditions in the field. The collection of the cores from SDS 2A, described in the DOE document SRR-CWDA-2015-00066, was designed to limit mechanical disruption and environmental exposure of the cores as much as possible. Therefore, the NRC staff expects the cores to provide the current best available evidence of the initial condition of field-emplaced saltstone. Furthermore, the NRC staff expects that measurements of radionuclide release from those cores are directly relevant to MF 5.01.

Because MF 5.01 is focused on the effects of field emplacement and the DOE has collected cores of field-emplaced saltstone, the NRC staff evaluation of MF 5.01 focuses on whether data from those core samples support the values used in the model that supports the FY 2014 Special Analysis Document. The scope of MF 5.01 includes all radionuclide releases from field-emplaced saltstone. However, this TRR only discusses the aspect of MF 5.01 related to Tc release. In the 2014 Evaluation Case, the DOE used a K_d of 0.5 mL/g to represent Tc release from chemically oxidized saltstone and a solubility of 1×10^{-8} mol/L to represent Tc release from chemically reduced saltstone. The NRC staff evaluation of the DOE support for each of those values follows.

Sorption Coefficient (K_d)

In the DOE Evaluation Cases, the DOE used K_d values less than 1 mL/g to represent the release of Tc from oxidized saltstone. In the 2009 PA, the DOE used a value of 0.8 mL/g and in both the FY 2013 and FY 2014 Special Analysis Documents, the DOE used a value of 0.5 mL/g. The FY 2014 Special Analysis Document cites the DOE document SRNL-STI-2009-00473 as a reference for the K_d for Tc in oxidized cementitious materials. The recommended sorption coefficient for Tc in Revision 0 of that document was 0.8 mL/g in moderately-aged oxidizing cementitious material. The DOE did not provide an explanation for using a value of 0.5 mL/g instead of 0.8 mL/g for the sorption coefficient for Tc in moderately-aged saltstone. The NRC staff expects that using 0.5 mL/g instead of 0.8 mL/g would increase the projected dose because it would speed the projected release of Tc from oxidized cementitious material.

All of the values that the DOE used for the sorption coefficient for Tc in oxidized cementitious material represent values for "middle-age" (i.e., "moderately-aged") material. The threshold pH values that the DOE used to identify "young," "middle-age," and "old" cementitious material varied slightly between the DOE Evaluation Cases. However, in general, the DOE used the following thresholds:

- pH greater than 12 for young cementitious material;
- pH between 10.5 and 12 for middle-age cementitious material; and
- pH less than 10.5 for old cementitious material.

The sorption values for Tc in young oxidizing saltstone were not used because the DOE projected that the transition from oxidizing to reducing conditions in saltstone would occur during the middle-age period (i.e., young oxidizing conditions would not occur). The sorption values for Tc in old saltstone were not used because the DOE projected the transition from middle-age to old conditions to take place more than 100,000 years after site closure.

Studies based on field-emplaced cores from SDS 4 and SDS 2A have measured higher values of partitioning coefficients for Tc under oxidizing leaching atmospheres. Prior to the DOE development of the models used to support both the FY 2013 and FY 2014 Special Analysis Documents, a study of cores of field-emplaced saltstone collected from SDS 4 and leached under oxidizing conditions measured a K_d value of 12 mL/g for Tc (SRNL-STI-2010-00667). In general, the NRC staff gives more consideration to studies of field-emplaced saltstone than studies of laboratory-made simulated saltstone. However, as described in the 2013 Monitoring Plan, leaching in an oxidizing atmosphere is not sufficient to show that the measurement truly reflects partitioning of Tc in oxidized saltstone because the saltstone may have residual reducing capacity even if the atmosphere of the experiment is oxidizing. That explanation is also consistent with the observations of more recent research (SREL DOC No. R-15-0003), in which diffusive releases of Tc from submerged samples of simulated saltstone were insensitive to the leaching atmosphere. For that reason and in consideration of the recent research results in SREL DOC No. R-15-0003, the NRC staff supports the use of a K_d value less than one rather than the empirical partitioning coefficients measured in SRNL-STI-2010-00667.

More recently, a study of ground samples of cores taken from SDS 2A (SRNL-STI-2016-00106) reported a K_d for Tc under oxidizing conditions of 28 mL/g[7]. However, the authors of that study noted that: “Since it is not certain that equilibrium was attained during the 7-day leach experiments, desorption distribution ratios presented in this study should be regarded as upper bounds …“ The concern that equilibrium may not have been reached would not necessarily make that data inapplicable to the field system if the contact time in the laboratory system approximated the contact time in the field system. However, in that study, the contact time used in the laboratory system (i.e., seven days) is orders of magnitude shorter than the contact time expected in the field system. Therefore, because the authors of that study regarded the values as upper bounds, the NRC staff does not conclude that SRNL-STI-2016-00106 supports the use of a K_d value greater than 1, even though the study used samples of field-emplaced saltstone.

Tc Solubility in Chemically Reduced Saltstone

In the DOE Evaluation Cases, the DOE used different methods to represent the release of Tc from reduced saltstone. In the 2009 PA, the DOE used a “pseudo-K_d” of 1,000 mL/g to represent Tc release from reduced saltstone. In the 2009 PA, the DOE described that it chose the value of 1,000 mL/g to implement the conceptual model that Tc is relatively immobile in reduced saltstone. The DOE further described that it determined that 1,000 mL/g was a conservative choice when compared to the value of 5,000 mL/g recommended for Stage I and Stage II cementitious materials recommended by Bradbury and Sarott (1995). However, in the 2012 SDF TER, the NRC staff compared the chosen value (i.e., 1,000 mL/g) to measured

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[7] The K_d result reported in both SRR-CWDA-2016-00051 and SRR-CWDA-2016-00053 is based on the same measurements.

values in reduced saltstone and concluded that the value that the DOE used in the PA was not adequately justified and that the NRC staff would monitor the development of additional information regarding Tc sorption in reduced saltstone.

In the 2013 Evaluation Case and 2014 Evaluation Case, the DOE implemented a solubility limit to model Tc release from reduced saltstone. The DOE documented the solubility values that the DOE planned to use to represent different chemical conditions in SRNL-STI-2012-00769. In the Tc Solubility TRR, the NRC staff reviewed several studies of Tc solubility and the NRC staff evaluated the support for the values that the DOE proposed to use in SDF models. During the June 2013 Onsite Observation Visit, the DOE indicated that it would evaluate the effects of increasing Tc solubility up to 1×10^{-7} mol/L in sensitivity analyses. In the Tc Solubility TRR, the NRC staff concluded that, because the range of measured values extended from 1×10^{-8} mol/L to 1×10^{-6} mol/L, considering the range from 1×10^{-9} mol/L to 1×10^{-7} mol/L in sensitivity analyses might not be adequate to capture the uncertainty in the solubility of Tc in reduced saltstone. However, in deterministic sensitivity analyses reported in Section 5.6.6.1 of the FY 2014 Special Analysis Document, the DOE only varied the modeled solubility from 1×10^{-9} mol/L to 1×10^{-7} mol/L.

In a probabilistic analysis called the “Probabilistic Tc-Ox Model” provided with the DOE response to the NRC Request for Additional Information (RAI) Questions on the FY 2014 Special Analysis Document (SRR-CWDA-2016-00004), the DOE varied Tc solubility with a log-normal distribution from approximately 3.0×10^{-10} mol/L to 3.0×10^{-7} mol/L, which the DOE referred to as an “unrealistically wide range”. That sensitivity analysis is discussed in detail in the context of MF 5.02 because it addresses the effects of assumptions about saltstone reducing capacity and re-reduction. In the context of MF 5.01, the relevant result from that analysis is that the solubility of Tc in reduced saltstone appeared to have a significant effect on the flux of Tc from the modeled disposal structure (i.e., not yet constructed SDS 9) over a wide range of modeled saltstone reducing capacities, whereas the reducing capacity had a clear effect on the timing of the peak of Tc flux from the disposal structure. The DOE did not present the results of that sensitivity analysis in terms of dose.

As shown in Figure 3, measured Tc concentrations from dynamically-leached samples of SDS 2A cores exceeded 1×10^{-7} mol/L for both core samples and exceeded 3×10^{-7} mol/L for one core sample, reaching approximately 5×10^{-7} mol/L. Furthermore, it is unclear to the NRC staff whether the Tc permeate concentrations shown in Figure 3 bound the concentrations that would occur in the field. The authors of study documented in SREL DOC No. R-16-0003 suggested that the greater Tc concentrations in permeate from the two cores of field-emplaced saltstone as compared to the permeate from the laboratory-made Tc-spiked sample could be attributable to the slower flow rate through the cores of field-emplaced saltstone. That phenomenon, referred to as a “residence time effect,” has been observed in a study of crushed saltstone (Pabalan et al., 2012) as well as a study of an intact sample of laboratory-made simulated saltstone leached with the DLM process (Accession No. ML17221A038). In both of those studies, a period of stopped flow (i.e., longer residence time) was associated with a marked increase in Tc concentrations in the permeant when the flow was resumed.

A residence time effect could occur if the diffusion of a constituent (e.g., Tc) from inactive pores to active pores is slow compared to the advective flow through the porous medium. In that case, the concentration in the active pores would not be in equilibrium with the concentration in the inactive pores. A longer residence time, equating to a slower advective flow rate, would allow more of the constituent to diffuse into the active pores as the fluid flowed through the active pores. Another possible mechanism for a residence time effect could be that Tc dissolution and desorption are kinetically limited, and faster flow maintains the Tc concentration below equilibrium concentrations.

The authors of the study documented in SREL DOC No. R-17-0005, which was a continuation of the study documented in SREL DOC No. R-16-0003, suggested that a physical mechanism, such as relatively slow diffusion from inactive to active pores, could be at least in part responsible because highly-soluble and non-sorbing constituents, such as nitrate, showed the same release pattern in time as Tc, as shown in Figure 4. The authors of SREL DOC No. R-17-0005 indicated additional work should be done to study whether a residence time effect is affecting Tc release from saltstone samples and described planned tests to compare Tc release from samples subject to different flow rates.

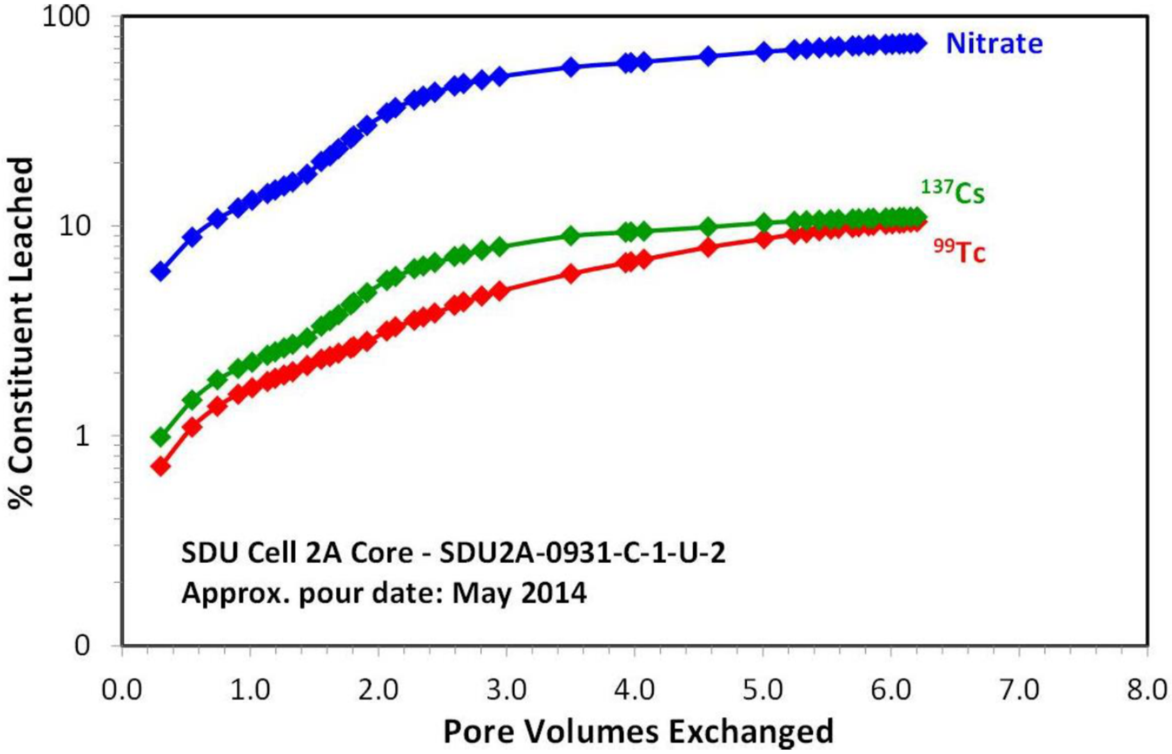

Figure 4. Cumulative fractions of nitrate, cesium, and Tc-99 leached from a core of field-emplaced saltstone with a dynamic leaching procedure (from SREL DOC No. R-17-0005 Figure 9)

Comparison of dynamic leaching procedure results with previous measurements raises questions about how Tc concentration measurements from previous studies should be interpreted. Values labeled as solubility limits for Tc in reducing saltstone based on measurements from cores from SDS 2A under reducing conditions were reported in SRNL-STI-2016-00106. The Tc concentration at the end of the 7-day batch tests was 38±21 picocuries per milliliter (pCi/mL) or $2.3\times10^{-8}\pm1.3\times10^{-8}$ mol/L. In contrast, as shown in Figure 3, leachate from the dynamic leaching procedure had effluent concentrations exceeding 2×10^{-7} mol/L (SREL DOC No. R-17-0005).

The reason for the order of magnitude difference between the Tc concentrations from the 7-day batch test with crushed samples (SRNL-STI-2016-00106) and Tc concentrations in eluant from the dynamic leaching procedure (SREL DOC No. R-17-0005) is not known. Both sets of samples were taken from field-emplaced saltstone. Furthermore, although the core samples used in these two studies were from different elevations in SDS 2A and, therefore, had different pour dates (i.e., third quarter Calendar Year (CY) 2013 versus second quarter CY 2014), both pour dates had the same estimated Tc concentration based on Tank 50 salt waste concentrations, as reported in quarterly permit reports that the DOE submits to the South Carolina Department of Health and Environmental Control (i.e., 1.2×10^4 pCi of Tc per mL of grout). Therefore, a difference in Tc concentration in the grout is not expected to explain the difference in aqueous Tc concentrations. However, the authors of study documented in SRNL-STI-2016-00106 noted that the measured concentrations of Tc in the solid grout sample were only approximately 25% of the projected values based on Tank 50 concentrations. Therefore, it is possible that differences in saltstone core sample concentrations between samples used in SRNL-STI-2016-00106 and SREL DOC No. R016-0003 is responsible or partly responsible for the observed difference in leachate concentrations.

Another potential source of differences in the results of the batch and flow-through tests is the liquid-to-solid ratio used in the batch test, and the resulting physical averaging of releases that may occur in the first few pore volumes. As previously described, releases from the first few pore volumes cannot be neglected because the DOE projects the first few pore volumes of flow through saltstone will take place over several thousand years after site closure (see Figure 5). The batch test in SRNL-STI-2016-00106, which also used cores from SDS 2A, used 1 g grout and 10 mL fluid. For comparison, based on a porosity of 0.6 and a dry bulk density of saltstone of 1.01 (SRR-CWDA-2014-00006), the liquid-to-solid ratio in 1 pore volume of saltstone is 1.5 mL fluid/g grout. Based on that value, the liquid-to-solid ratio used in STI-2016-00106 represents the same liquid-to-solid ratio as approximately 6.7 pore volumes of fluid flowing through an intact grout sample. Therefore, increases and decreases in Tc concentration that happen over fewer pore volumes (e.g., the factor of two increase and decrease that occurred within the first two pore volumes for sample SDU-A, as shown in Figure 3) will not be observable in the results of batch testing. In general, physical averaging should be accounted for when comparing the results of a batch test and studies based on a dynamic leaching procedure. However, in the specific case of the dynamic leaching results reported in SREL DOC No. R-17-0005 and the batch results reported in SRNL-STI-2016-000106, averaging does not explain the order of magnitude difference between the Tc concentration in the batch test (i.e., 2×10^{-8} mol/L) and the average of the first six pore volumes in the dynamic leaching procedure (i.e., approximately 2×10^{-7} mol/L) (see Figure 3).

The observed difference is consistent with a residence time effect. Based on the reported flow rate of 0.5 mL/day to 1.0 mL/day through a 2.5-cm (1-inch) long, 5.0-cm (2-inch) diameter sample with a porosity of 0.6, the residence time would be between 30 days and 60 days. In contrast, the lower-concentration leachates resulted from the experiment that used a 7-day leach time (SRNL-STI-2016-00106). Furthermore, as described above, the authors of the study documented in SRNL-STI-2016-00106 indicated that the solubility values reported in that document should be regarded as lower bounds because there was no evidence that equilibrium had been attained.

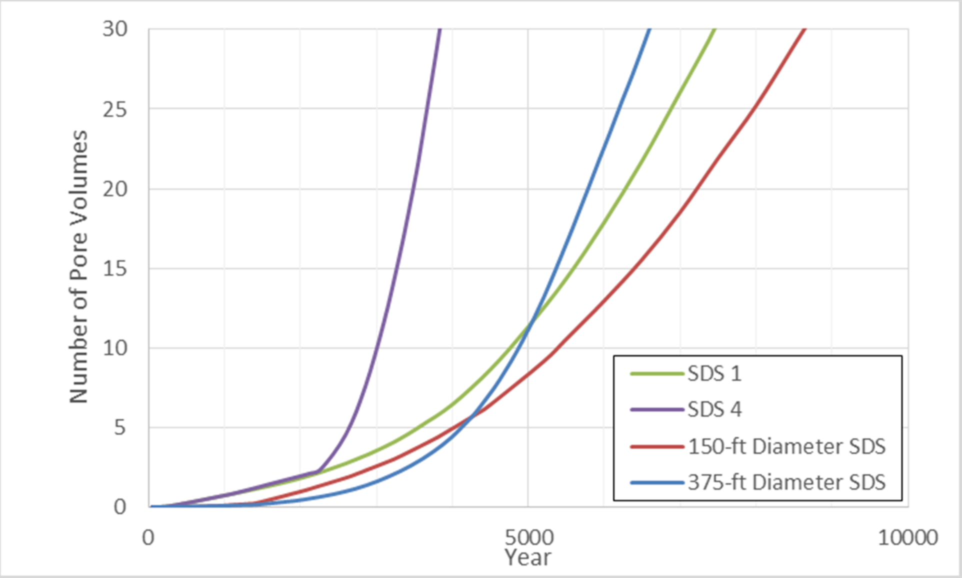

Figure 5. Number of pore volumes projected to migrate through saltstone grout for each disposal structure (based on data from the DOE PORFLOW model files).

Studies based on cores of field-emplaced saltstone, rather than simulants, eliminate many potential sources of uncertainty (e.g., effects of field exposure to oxygen during mixing and emplacement, effects of admixtures not included in laboratory samples). For that reason, the NRC staff expects that data from field-emplaced cores will provide the best-available evidence of Tc releases from field-emplaced saltstone. Studies based on intact samples also would appear to more closely mimic field conditions than studies based on crushed samples. However, the DLM conditions differ from expected field conditions because the permeant is forced through the sample under pressure, and consequently travels through the samples faster than DOE projects liquid will travel through saltstone in the field. To address both of those related issues, it might be important to identify whether there are unidentified artifacts caused by forcing liquid through the DLM samples under pressure (e.g., activating inactive pore space by deforming the sample) and whether the speed of liquid flow through the samples influences leaching. For example, additional research might be needed to determine if a residence time effect explains the difference between the measurements interpreted as solubility values in SRNL-STI-2016-00106 and the observed leachate concentrations from the DLM experiments in SREL DOC No. R-17-0005.

If a residence time effect is occurring and Tc concentrations released are greater for slower flow rates, concentrations released from field-emplaced saltstone could be greater than the measured concentrations in SREL DOC No. R-17-0005 (i.e., 5×10^{-7} mol/L). In response to an NRC RAI Question about the projected dose consequences of increased Tc release concentrations, the DOE provided additional sensitivity analyses (SRR-CWDA-2016-00134). Those sensitivity analyses showed that, at a solubility limit of 5×10^{-7} mol/L, peak Tc releases within 10,000 years of closure could be limited to approximately the 10 CFR 10.41 dose limit (i.e., 25 mrem/yr) if the DOE used its Best Estimate degradation rate instead of the Nominal degradation rate used in the 2014 Evaluation Case. The NRC staff concerns about the DOE Best Estimate degradation rate will be described in a future TRR on Saltstone Degradation. The supplemental sensitivity analyses provided by the DOE (SRR-CWDA-2016-00134) do not alleviate the NRC staff concerns about the dose implications of the measured Tc release concentrations from cores of field-emplaced saltstone because the NRC staff still questions whether the DOE Best Estimate degradation rate is adequately supported and the available data from cores of field-emplaced saltstone indicate Tc may be released at concentrations greater than 5×10^{-7} mol/L.

One other set of Tc concentrations from leaching of field-emplaced saltstone is available for comparison to recent research. In 2008, the DOE used a dry-drilling technique to extract nine core samples from SDS 4. One of those cores was used in batch leaching experiments to evaluate radionuclide release under oxic and sub-oxic conditions (i.e., 30 parts per million (ppm) to 60 ppm oxygen) (SRNL-STI-2010-00667). The NRC staff described the Tc concentration measurements from that study in the Oxidation TRR. This section of this TRR updates that TRR by comparing the results of SRNL-STI-2010-00667 with recent research results. In addition, in this TRR the description of the difference between the oxic and sub-oxic leaching test results in SRNL-STI-2010-00667 is updated in the context of MF 5.02.

In SRNL-STI-2010-00667, the core used for leaching studies was initially stored in a stainless steel tube that was evacuated of air before being sealed to limit oxidation (SRNL-STI-2009-00804). However, seven months later when the core was transferred to the laboratory, the authors of the study documented in SRNL-STI-2010-00667 interpreted the pale color of the exterior of the sample as compared to the olive green interior to mean some oxidation had taken place during storage. In the laboratory, the core was transferred to a polyvinyl chloride (PVC) tube and back-filled with nitrogen to limit further oxidation. The core was divided into a part that would be kept under sub-oxic conditions and a part that was exposed to normal atmospheric levels of oxygen. The part to be kept under sub-oxic conditions was transferred to a glove box that was maintained at 30 ppm to 60 ppm oxygen, except for a brief excursion to 1,000 ppm oxygen. Both parts of the sample were ground with a mortar and pestle prior to leaching. Ground samples were then mixed with deionized water equilibrated with portlandite for 20 days at a 1 g to 70 mL solid-to-liquid ratio (i.e., 30 g of sample were leached with 210 mL of solution). In the measurement made under sub-oxic conditions, the leach solution was purged with nitrogen. In the measurement made under oxic conditions, the leachate was bubbled with laboratory air. One oxic sample and one sub-oxic sample were mixed with the corresponding solutions for 20 days and then filtered with a 45 micron filter before the Tc was measured. The Tc concentration in the oxic leachate was 2×10^{-9} mol/L and the Tc concentration in the sub-oxic leachate was 2×10^{-10} mol/L.

To describe the difference in leachate concentrations observed in the study documented in SRNL-STI-2010-00667 and the study documented in SREL DOC No. R-16-0003, the NRC staff evaluated differences between the two studies. Both the leaching procedures used and the Tc concentrations in the cores differed significantly between the two studies. In SRNL-STI-2010-00667, a batch method was used with ground samples. In the dynamic leaching procedure used in SREL DOC No. R-16-0003 and SREL DOC No. R-17-0005, water was forced under pressure (i.e., approximately 1.4×10^{5} Pascals [20 pounds per square inch]) through intact core samples. Further research may be necessary to determine whether forcing water through the core under pressure caused experimental artifacts that increased leachate concentrations (e.g., if the pressure opened normally inactive pores).

The Tc concentrations in the cores used in the two studies also differed significantly. The cores used in SRNL-STI-2010-00667 were from SDS 4, Cell E. Those cores were from saltstone made with salt waste from the Deliquification, Dissolution, and Adjustment (DDA) process, which has a significantly lower Tc concentration than most of the saltstone in the SDF. Specifically, the cores used in SRNL-STI-2010-00667 had a Tc concentration of approximately 50 pCi/g grout. That concentration must be converted to a volumetric basis (i.e., pCi/mL) to be compared to the Tc concentrations in saltstone that are reported in the quarterly permit reports. The DOE study documented in SRNL-STI-2010-00667 did not report the saturated density of the core samples. However, a DOE report of core samples taken from SDS 2A (SRR-CWDA-2016-00053) reported the saturated density of field-emplaced saltstone as 1.73 g/mL. Adjusting the concentration of 50 pCi/g grout to a volumetric basis using the saturated density of 1.73 g/mL yields a concentration of approximately 90 pCi/mL. That value is significantly less than the concentration of approximately 30,000 pCi/mL grout in the saltstone in SDS 2A reported in the quarterly permit report for the quarters when those samples were poured (i.e., third quarter CY 2013 and second quarter CY 2014). That factor of almost three orders of magnitude corresponds to the difference between the leachate concentrations in the two studies (i.e., 2×10^{-10} mol/L compared to 5×10^{-7} mol/L). If interpreted as a K_d value instead of a solubility constraint, the results of SREL DOC No. R-16-0003 are in good agreement with the results of SRNL-STI-2010-00667, which reported a K_d value of 137 mL/g for Tc in reduced grout. That K_d value, if applied to a core with a Tc concentration of 30,000 pCi/mL grout, would result in an equilibrium aqueous Tc concentration of 1×10^{-7} mol/L Tc, which is similar to the values observed in the effluent of the dynamic leaching tests that were documented in SREL DOC No. R-17-0005 (see Figure 3).

That correspondence does not necessarily indicate that sorption was responsible for the observed Tc concentrations in SRNL-STI-2010-00667. There are other potential mechanisms that could cause different releases between the two studies. One potential mechanism is that there could be chemical differences between the DDA waste emplaced in SDS 4 and the Actinide Removal Process/Modular Caustic Side Solvent Extraction (ARP/MCU) process waste that affected removal. Another potential mechanism is that more soluble solid phases could be readily depleted in a less concentrated sample, which would cause a lower observed solubility value when only lower-solubility phases were left. That mechanism would require that there is a kinetic constraint preventing the system from reaching equilibrium because, in an equilibrated system, only the most thermodynamically stable solid phase would exist and control aqueous concentrations. However, that type of equilibrium could take significantly longer than the 20-day batch test used in SRNL-STI-2010-00667 to be achieved.

In the Oxidation TRR, the NRC staff observed that the data from SRNL-STI-2010-00667 would provide good model support for projections of adequate SDF performance with respect to Tc if the measured Tc concentrations were confirmed to be solubility limits. The NRC staff gave significant weight to the results from that study because that study was based on cores of field-emplaced saltstone rather than laboratory-made simulants. However, recent research results from SREL DOC No. R-16-0003 also represent releases from field-emplaced cores and the releases from those cores do not support the interpretation of the leachate concentrations observed in SRNL-STI-2010-00667 as solubility limits applicable to all of the saltstone in the SDF. Because both studies were based on cores of field-emplaced samples, those studies would appear to have similar applicability. However, the Tc concentrations in the cores from SDS 4, Cell E (i.e., 50 pCi per gram of grout or 90 pCi per mL grout), which were measured in the study documented in SRNL-STI-2010-00667, were much less concentrated than the remaining cells in SDS 4, which range from 280 pCi of Tc per mL of grout to 2.4×10^4 pCi of Tc per mL of grout or the concentration projected for the remainder of the SDF (i.e., 3×10^4 pCi/mL grout). For that reason, the NRC staff determined that the results from SREL DOC No. R-16-0003 may be more representative of releases from most of the SDF than the results of SRNL-STI-2010-00667, which appear to apply only to saltstone made from DDA waste.

Releases from Young Saltstone

As described in the Tc Solubility TRR, the DOE proposed in a Pacific Northwest National Laboratory (PNNL) Report (PNNL-21723) that the solubility of Tc in chemically reducing saltstone was controlled by the solubility of the Tc oxide TcO_2 $1.6H_2O$. Results documented in PNNL-21723 of thermodynamic modeling and laboratory measurements suggested that the solubility of that mineral is highly pH dependent, with higher solubilities measured at pH values around 12.5, which is typical of young cementitious material, than at pH values around 10, which is typical of middle-age cementitious material. As shown in Table 2, based on that information, as well as information from another research study (SRNL-STI-2012-00596), the DOE developed proposed solubility values for use in saltstone modeling. However, in the 2014 Evaluation Case, the DOE chose not to use that proposed solubility for young cementitious materials (i.e., $6x10^{-7}$ mol/L), and instead chose to represent Tc solubility with a constant value of $1x10^{-8}$ mol/L.

Table 2. Recommended and implemented values of solubility limits for saltstone for the DOE 2014 Evaluation Case

	Recommendations from SRNL-STI-2012-00769		**2014 Evaluation Case**
	Basis	**Value**	
Reduced Young Cement 1st Stage (pH~12)	Average of experimentally derived values in PNNL-21723 and SRNL-STI-2012-00596	$6x10^{-7}$ mol/L solubility	Not Used (condition not modeled)
Reduced Moderately-Aged Cement 2nd Stage (pH~10.5)	Experimentally derived value in SRNL-STI-2012-00596	$1x10^{-8}$ mol/L solubility	$1x10^{-8}$ mol/L solubility
Aged Cement 3rd Stage (pH~5.5)	Based on the assumption that the aged cement becomes oxidized	0.5 mL/g K_d	Not Used (condition not projected to be reached)

In the NRC RAI Questions on the FY 2014 Special Analysis Document, the NRC staff questioned that choice. In response, the DOE considered a sensitivity case with an initial Tc solubility in chemically reduced saltstone of $4.2x10^{-8}$ mol/L. However, that value was more than an order of magnitude lower than the value of $6x10^{-7}$ mol/L recommended to represent young cementitious material in DOE document SRNL-STI-2012-00769. The DOE chose the value of $4.2x10^{-8}$ based on a modeled relationship between Tc solubility and pH and geochemical modeling that suggested that water infiltration through saltstone would drop to a pH of 11 between 10 to 50 pore volumes (SRR-CWDA-2016-00004). Similarly, in the DOE document SRNL-STI-2009-00473, the DOE characterized young cement conditions as “not important” and “extremely short lived” because those conditions were expected to persist “on the order of 30 pore volumes.” However, as shown in Figure 5, in the 2014 Evaluation Case, infiltration of the first 10 pore volumes is projected to take between approximately 3,000 to 5,000 years, depending on the disposal structure, after disposal. Thus, the higher-pH first few pore volumes appear to be applicable to a significant fraction of the projected dose within 10,000 years of site closure.

As shown in Figure 6, pH values greater than 10.5, which correspond to “young” cementitious material, are expected to have Tc solubilities greater than $1x10^{-7}$ mol/L. Although the authors of the study documented in SREL DOC No. R-17-0005 expressed concern about the reliability of pH measurements of the permeant from cores of emplaced saltstone because of the small sample volumes used, the measured Tc concentrations of approximately 1×10^{-7} mol/L to 6×10^{-7} mol/L (see Figure 3) were consistent with the projected Tc solubility limits in young cementitious material (see Figure 6). Thus, it appears that recent research results are consistent with thermodynamic projections of the solubility of $TcO_2\cdot1.6H_2O$ or $TcO_2\cdot2H_2O$ under the expected conditions of young cementitious material. If the conditions of young cementitious material last for between 10 to 50 pore volumes, as the DOE previously projected (SRR-CWDA-2016-00004), and if it takes between 3,000 to 5,000 years after site closure for 10 pore volumes to pass through saltstone, as the DOE projects in the 2014 Evaluation Case, then the Tc concentrations released from cores of field-emplaced saltstone would be relevant to projections of Tc release for several thousand years after site closure.

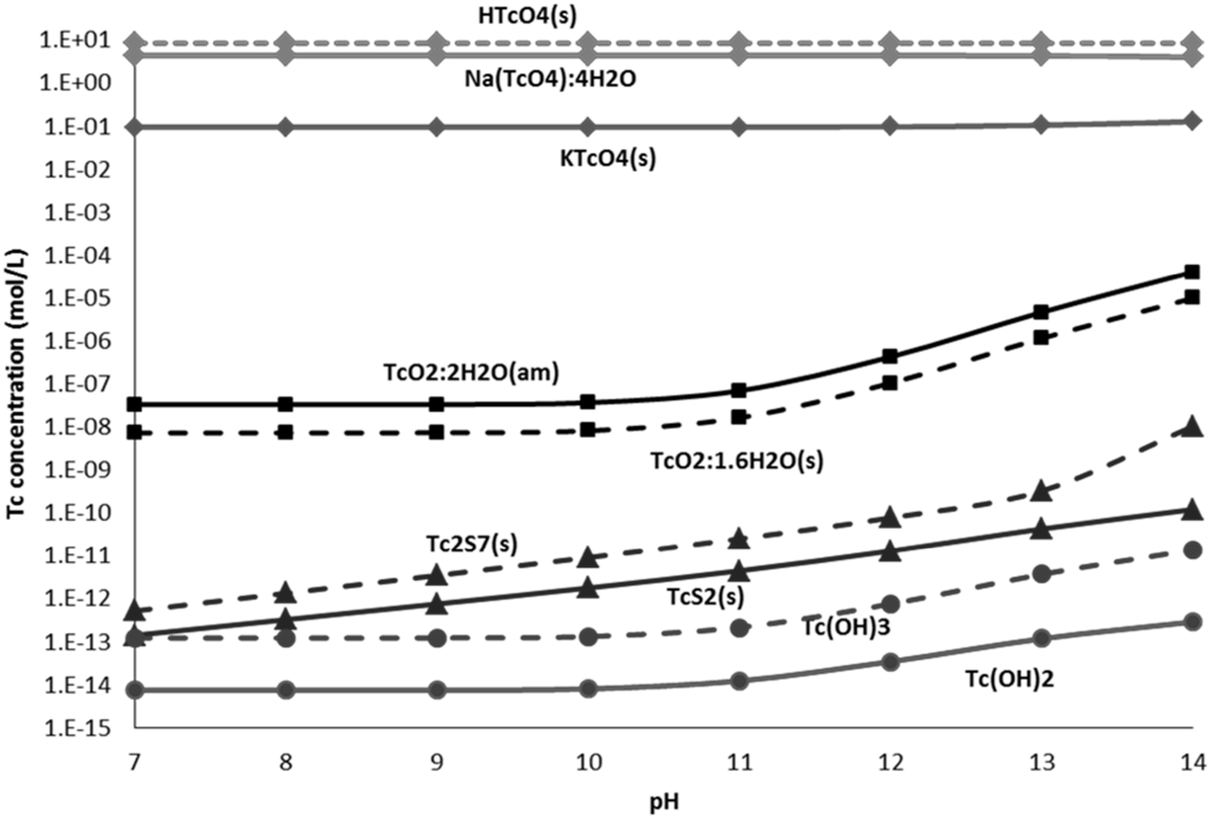

Figure 6. Relationship between Tc solubility and pH for several Tc solid phases (from SREL DOC No. R-17-005 Figure 1)

Summary for MF 5.01

The NRC 2013 SDF Monitoring Plan indicates that the NRC staff expects to close MF 5.01 under both §61.41 and §61.42 POs after the NRC determines that measurements of radionuclide release rates from field-emplaced saltstone used in the PA are reliable.

The NRC staff recommends that MF 5.01 remain open under both §61.41 and §61.42 POs because the Tc solubility limits that the DOE used to model Tc release from chemically reduced saltstone in the 2014 Evaluation Case are not supported by recent data from dynamic leaching of cores of field-emplaced saltstone. The NRC staff recommends that MF 5.01 remain prioritized as high priority under both §61.41 and §61.42 POs because of the risk-significance of the rate of Tc release from saltstone. To fulfil the condition for the NRC staff to close MF 5.01, the NRC staff expects that the DOE would address how Tc concentration data from cores of field-emplaced saltstone from SDS 2A are reflected in the Evaluation Case model of SDF performance. The NRC staff expects that the DOE would adequately incorporate the information from recent research with cores from SDS 2A, including providing a technical justification for the projected duration of the conditions associated with young cementitious material. Alternatively, the DOE could provide an explanation for why the measurements of Tc releases from cores of saltstone from SDS 2A are not applicable to projections of SDF performance.

MF 5.02, "Chemical Reduction of Tc by Saltstone"

It was unclear to the NRC staff whether saltstone could reduce all of the Tc in salt waste and maintain it in a reduced state when the NRC 2013 SDF Monitoring Plan was written. Although reduced Tc (i.e., Tc(IV)) had been directly observed with spectroscopic methods used on laboratory-produced samples (Lukens, 2005), it was unclear to the NRC staff whether that Tc(IV) was entirely attributable to reduction by saltstone or if it could be partially attributed to sodium thiosulfate or $H_{2(g)}$ that was used in the experiments. In addition, the NRC staff was concerned that exposure to oxygen during saltstone mixing, pumping, and pouring, as well as exposure to any air entrapped in saltstone, could result in incomplete conversion of Tc(VII) to Tc(IV) or re-oxidation of Tc(IV) to Tc(VII). Uncertainty in the extent to which saltstone could reduce Tc and maintain it in a reduced form has a significant impact on projected Tc release (and, therefore, dose) in the conceptual model used in the DOE Evaluation Cases. The NRC developed MF 5.02, "Chemical Reduction of Tc by Saltstone," in response to that uncertainty.

The assumption that Tc is essentially immobile when chemically reduced and relatively mobile when chemically oxidized has been fundamental to the DOE conceptual model of Tc release from saltstone since at least the 2005 SDF PA. However, as described in the previous section, Tc releases from chemically reduced saltstone may be greater than the DOE had previously projected. In addition, Tc release from saltstone may not be as sensitive to trace quantities of oxygen as implied by three key studies that will be described further in this section. Taken together, those two observations provide support for a conceptual model in which releases from reduced saltstone may be as important, or more important, to SDF performance as saltstone oxidation. That conceptual model is consistent with the results of sensitivity analyses performed by the DOE and documented in both the FY 2014 Special Analysis Document and the DOE response to the NRC RAI Questions about that document. Those DOE sensitivity analyses showed only a moderate sensitivity of Tc release to sources of oxygen in saltstone and to the reducing capacity of saltstone. The comparison of releases from reduced and oxidized saltstone is discussed in this section because it affects the priority of MF 5.02.

Sensitivity of Tc Oxidation State to Trace Quantities of Oxygen: Reinterpretation of SRNL-STI-2010-00667, SRNL-STI-2013-00541, and CBP-TR-2014-005

The DOE study SRNL-STI-2010-00667, which was described in the previous section in the context of MF 5.01, was a key factor that prompted the NRC staff to develop MF 5.02. The authors of that study concluded that the retention of Tc in reduced saltstone, which the authors expressed as a sorption coefficient, was less than expected because the saltstone had been oxidized by being stored with 30 to 60 ppm oxygen. As stated in that study, "[a] concern is that the slightest amount of O_2 oxidizes the Tc(IV) to Tc(VII)." Sharing that concern, the NRC staff cited that study as a basis for requesting additional information about potential sources of oxygen in the SDF and the potential effects of oxygen exposure on SDF performance.

However, recent research suggests an alternative interpretation of the results from SRNL-STI-2010-00667. Although the authors of the study determined that the release of Tc from the sample kept in sub-oxic conditions was greater than they expected and suggested exposure to trace quantities of oxygen as a reason, the Tc release may have instead been characteristic of normal releases from chemically reduced saltstone. Rather than being greater than expected, as the authors suggested, the releases from SRNL-STI-2010-00667 were less than would be predicted by the solubility of TcO_2 $1.6H_2O$ at the measured pH (i.e., 12.05) (see Figure 6). One reason could be that a less soluble phase controlled Tc solubility in SRNL-STI-2010-00667 because the samples used in that study were significantly more dilute than the samples used in SREL DOC No. R-17-0005. That interpretation of SRNL-STI-2010-00667 is consistent with recent research results, and provides an alternative explanation of the observed releases other than a sensitivity of saltstone to trace quantities of oxygen.

Similarly, an alternative interpretation can be made of the results documented in CBP-TR-2014-05, which also had caused the NRC staff concern about the ability of saltstone to maintain Tc in a reduced state. The authors of that study stated, “[s]oluble Tc was leached from all of the depth-discrete subsamples from both Tc2-9 and Tc2-10 which strongly suggests that oxygen was present in the entire length of both samples.” That conclusion appeared to be based on the assumption that any release of Tc indicated the Tc had been oxidized. However, the leachate concentrations measured in that study (i.e., 2.6×10^{-7} mol/L to 1.1×10^{-6} mol/L), were consistent with recent measurements of the Tc released from cores of chemically reduced field-emplaced grout (see Figure 3). Rather than suggesting that there was an oxidized fraction of Tc throughout the sample, as the authors of the study documented in CBP-TR-2014-005 concluded, it now appears more likely to the NRC staff that the releases measured CBP-TR-2014-005 were releases of chemically reduced Tc and that those releases did not indicate that oxygen had permeated the sample.

Finally, the DOE study documented in SRNL-STI-2013-00541 also appeared to show that Tc was very sensitive to oxygen ingress. The authors of that study concluded that the results showed that Tc could be preferentially oxidized in areas of the sample that still had residual reducing capacity. That conclusion caused the NRC staff concern because it implied that Tc release could be sensitive to relatively small inflows of oxygen, even if the chemical barrier against oxidation (i.e., reducing capacity of the grout) was not depleted. That NRC staff concern is related to MF 5.02 because it increased the uncertainty that saltstone could maintain Tc in a reduced state. However, as described later in this TRR in the context of MF 10.02, the apparent front of mobile Tc at a greater depth than reducing capacity was depleted in that study appears to have been an experimental artifact. Thus the conclusion of that study that Tc could be readily oxidized at sample depths that still have residual reducing capacity is now of less concern to the NRC staff.

Sensitivity of Tc Oxidation State to Trace Quantities of Oxygen: Recent Research

Recent research provides model support for the conceptual model that Tc release from field-emplaced saltstone is not insensitive to trace quantities of oxygen. One line of support for that conceptual model is the similarity of the releases from the two cores of field-emplaced saltstone (see Figure 3) despite one being leached with deaerated liquid and the other being leached with liquid equilibrated with laboratory air for more than one pore volume (i.e., two pore volumes for one sample and six pore volumes for the other sample). As shown in Figure 5, the DOE projected that number of pore volume replacements in field-emplaced saltstone would take thousands of years after site closure. Therefore, the NRC staff determined that the observed behavior is relevant, at a minimum, to a significant fraction of the 10,000-year period after site closure. The similarity of those releases supports a model in which minor exposures to oxygen do not cause significant Tc release, in contrast with the conclusions of the prior studies that were reinterpreted earlier in this section of this TRR.

There are several potential interpretations of the comparable Tc releases from the two cores of field-emplaced saltstone shown in Figure 3. In a subsequent work that continued to evaluate the data shown in Figure 3, in addition to new data from the same core samples (SRR-CWDA-2017-00085), the authors showed that the measured Eh of the permeant solution would suggest that the Tc should be in the oxidized state (see Figure 7).

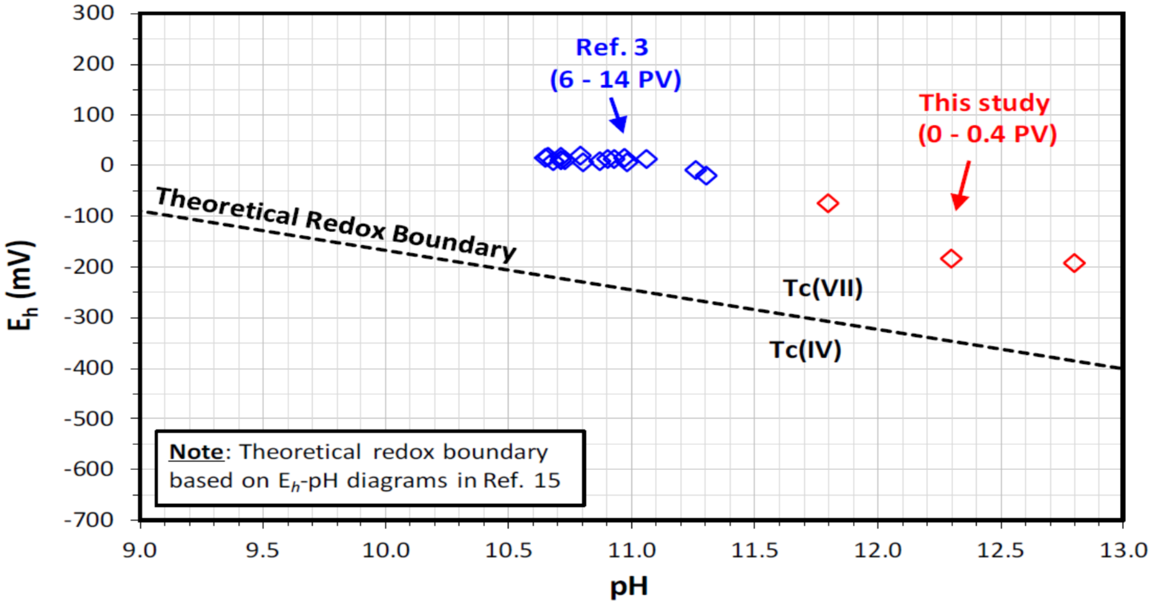

Figure 7. Eh and pH of permeant passed through cores of field-emplaced saltstone with a dynamic leaching procedure relative to expected boundary between oxidized and reduced Tc (from SRR-CWDA-2017-00085 Figure 12)

Note: “Ref 3” refers to Simner et al. (2017)
Note: “Ref. 15” refers to the National Geological Survey of Japan (2005)
Note: “This study” refers to SRR-CWDA-2017-00085

The authors indicated that that result was unexpected, especially given the consistency between the observed Tc concentrations in the permeant with the projected solubility of the reduced-Tc solid phase $TcO_2 \cdot 2H_2O$ (see Figure 8). The authors of the study that was documented in SRR-CWDA-2017-00085 questioned whether the measured Eh of the permeant accurately reflected the Eh experienced by Tc in the pore solutions throughout the samples. The NRC staff agrees that the question is significant to understanding Tc behavior in the saltstone system.

Additional sources of uncertainty might also include uncertainty in the Eh measurements, which, because of the nature of the experiment, were constrained to be performed with very small sample sizes. In addition, it appears that there may be some uncertainty in the theoretical redox boundary show in Figure 7 because all of the potential phases of Tc in cementitious material may not be known. In any case, the observed Tc releases at concentrations consistent with solid phases of reduced Tc, even with measured Eh values suggesting Tc should be oxidized, provide further support for the conceptual model that Tc in saltstone is not sensitive to minor sources of oxygen.

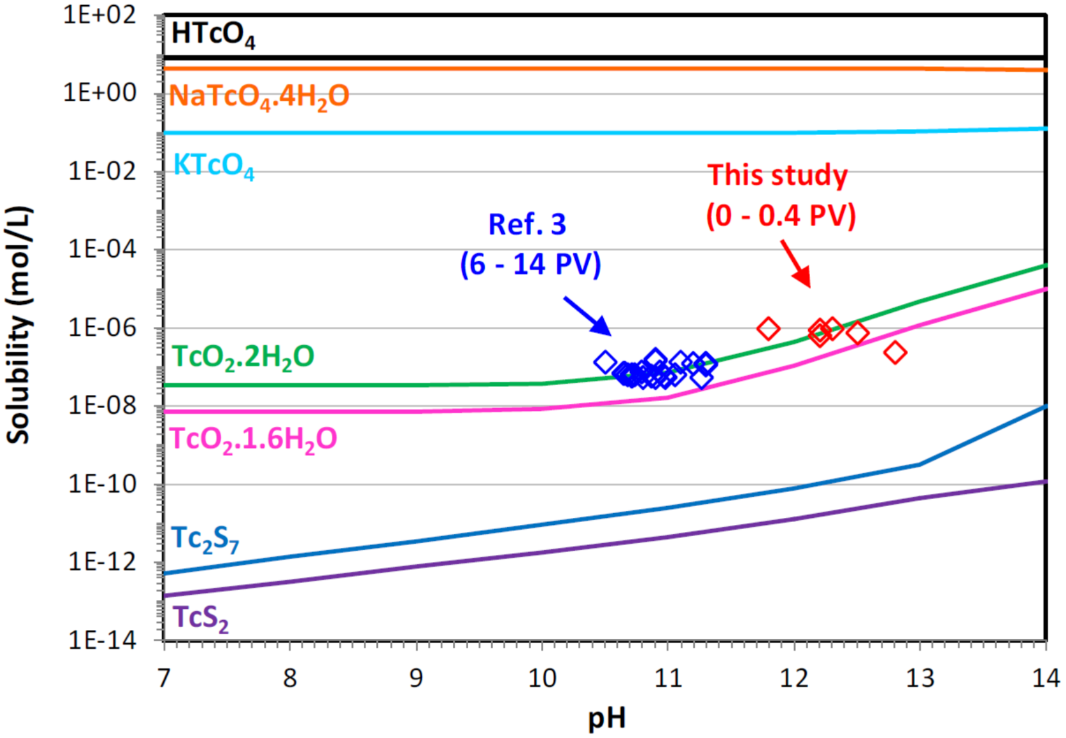

Figure 8. Observed Tc concentrations and calculated solubility as a function of pH (from SRR-CWDA-2017-00085 Figure 11)

Note: “Ref 3” refers to Simner et al. (2017)
Note: “Ref. 15” refers to the National Geological Survey of Japan (2005)
Note: “This study” refers to SRR-CWDA-2017-00085

Sensitivity and Uncertainty Analyses Regarding Saltstone Oxidation, Reducing Capacity, and Tc Re-Reduction

The NRC staff was concerned that gas-phase transport of oxygen into saltstone fractures could lead to greater Tc oxidation than the DOE had predicted along fractures because of studies that appeared to show sensitivity of Tc releases to trace quantities of oxygen. The NRC staff also was concerned that fractures could subsequently become fast pathways for water transport and Tc release. A conceptual model in which Tc oxidation is sensitive to fracturing could cause large uncertainty in dose projections because the extent of fracturing that will occur in saltstone as it ages is highly uncertain. As described in the previous section of this TRR, the reinterpretation by the NRC staff of three key studies supporting a conceptual model in which Tc was highly sensitive to trace concentrations of oxygen reduces that concern to some extent. In addition, the DOE has performed sensitivity and uncertainty analyses that evaluate the effects of alternative assumptions about the ability of saltstone to reduce Tc and maintain it in a reduced state on projected SDF performance.

In Section 5.6.6.2 of the FY 2014 Special Analysis Document, the DOE described a sensitivity analysis that tested the sensitivity of projected SDF performance to assumptions about Tc re-reduction in saltstone and disposal structure concrete. In that alternative conceptual model, referred to as the "bypass" model in this TRR, a new parameter was introduced that had the effect of allowing a certain fraction of the Tc in an oxidized modeling cell to bypass additional transport through the waste form and disposal structure and to be modeled as moving to the unsaturated zone immediately when the modeling cell became oxidized. As shown in Table 3, increases in the fraction of Tc that was transferred immediately into the unsaturated zone when oxidized increased the peak Tc flux from the 150-foot and 375-foot disposal structures within 10,000 years of site closure and decreased the peak Tc flux within 50,000 years of site closure. For the assumption of 100% bypass, the projected peak Tc flux within 10,000 years increased by a factor of nine for the 150-foot disposal structures and by a factor of five for the 375-foot disposal structures.

Table 3. Effects of Tc bypass fraction on projected Tc peak flux from SDS 9 (using data from SRR-CWDA-2014-00006)

Bypass Fraction	Peak Flux within 10,000 years of closure (g/yr)	Peak Flux within 50,000 years of closure (g/yr)
150-foot Disposal Structures		
0	0.054	72
0.25	0.11	57
0.50	0.18	20
0.75	0.27	31
1.0	0.50	4.9
375-foot Disposal Structures		
0	1.1	190
0.25	2.1	160
0.50	3.1	110
0.75	4.0	64
1.0	5.9	12

The Evaluation Case model that the DOE used to support the DOE 2009 PA corresponds to 0% bypass, which corresponds to re-reduction of all oxidized Tc that flows through an area of saltstone or disposal structure concrete with residual reducing capacity. The Oxidation TRR indicated that more model support was needed for Tc re-reduction before MF 5.02 could be closed because of the importance of assumptions about Tc re-reduction to the projected performance of the SDF in the DOE 2009 PA. Although there is not yet experimental evidence for the assumption that oxidized Tc would be reduced if it flowed through chemically reduced saltstone, the bypass sensitivity analysis performed by the DOE does provide information about the importance of assumptions about Tc re-reduction to projections of Tc release. Model support does not yet exist to support a choice of what fraction of bypass best represents expected SDF field conditions. However, the DOE analysis summarized in Table 3 bounds the effects by providing values for 100% bypass. Therefore, incomplete re-reduction is projected to cause less than a factor of nine increase in peak Tc fluxes from the 150-foot disposal units and less than a factor of five increase in peak Tc fluxes from the 375-foot disposal structures, as compared to the 2014 Evaluation Case results. As shown in Table 3, longer term peak Tc fluxes are projected to decrease if Tc re-reduction is incomplete. That result occurs because increased Tc flux at earlier times is projected to remove some of the Tc from saltstone before Tc oxidation is projected to accelerate at later times.

In response to an NRC RAI question about the risk associated with gas-phase transport of oxygen into unsaturated fractures, the DOE provided an uncertainty analysis based on the bypass sensitivity analysis model described above. The DOE referred to that uncertainty analysis as the "Tc-Ox" uncertainty analysis. It is discussed in this section because it affects the priority of MF 5.02. It also indirectly addresses a conceptual model of Tc release in which Tc is oxidized along fractures in saltstone that subsequently become fast pathways for water and Tc release. Although the amount of Tc that is oxidized in that model is based on the progress of an oxidation front through intact saltstone and not on fractures in saltstone, because the oxidized Tc bypasses additional transport through the waste form, the location of the Tc at the time of oxidation becomes moot.

The DOE Tc-Ox uncertainty analysis began with the bypass sensitivity analysis model described above and then it varied four parameters:

- reducing capacity of saltstone;
- reducing capacity of disposal structure concrete;
- amount of Tc that bypassed re-reduction and was transferred to the unsaturated zone immediately when oxidized; and
- Tc solubility in reduced saltstone and disposal structure concrete.

The reducing capacity of saltstone and disposal structure concrete were both varied with triangular distributions. The minimum of those distributions was equal to 0 meq e^-/g, the mode was set to the 2014 Evaluation Case value, and the maximum was set to a value of double the 2014 Evaluation Case value (i.e., 0 meq e^-/g, 0.607 meq e^-/g, and 1.216 meq e^-/g for saltstone; 0 meq e^-/g, 0.178 meq e^-/g, and 0.356 meq e^-/g for disposal structure concrete). The bypass fraction was varied between 1% and 99% with a uniform distribution. The solubility of Tc in reduced concrete was varied from 3×10^{-9} mol/L to 3×10^{-7} mol/L with a logarithmic distribution (i.e., cumulative probability increased linearly with the logarithm of the solubility, from 0 at 3×10^{-9} mol/L to 1.0 to 3×10^{-7} mol/L).

In the evaluation of model outputs for that uncertainty analysis, the DOE determined that different types of behavior in different ranges of Tc solubility. Figure 9 shows the uncertainty analysis results segregated into different ranges of Tc solubility. In the Tc-Ox model, the DOE implemented the increase in Tc solubility with a "solubility multiplier" applied to the 2014 Evaluation Case value of 1×10^{-8} mol/L. Therefore, in Figure 9, concentrations similar to those observed in recent research on cores of field-emplaced saltstone (see Figure 3) correspond to a "solubility multiplier" of 20 or more (i.e., blue dots in Figure 9). The NRC staff considers the modeling results corresponding to lower values of the solubility multiplier to be less likely because those values are not consistent with recent results from cores of field-emplaced saltstone. Based on the results of the Tc-Ox uncertainty analysis, the DOE concluded that the Tc solubility in reduced cementitious material could cause higher Tc fluxes within 10,000 years of site closure when it was greater than 7×10^{-8} mol/L, even if the reducing capacity of saltstone was equal to or greater than the nominal value (i.e., 0.607 meq e^-/g). Conceptually, that effect indicates that, for modeled Tc solubility in reducing saltstone above a value of 7×10^{-8} mol/L, releases from the reduced saltstone contribute enough to the overall projected Tc releases that a greater modeled residual reducing capacity, which would slow down the projected rate of saltstone oxidation, is not as important to Tc release because the releases are primarily coming from chemically reduced saltstone.

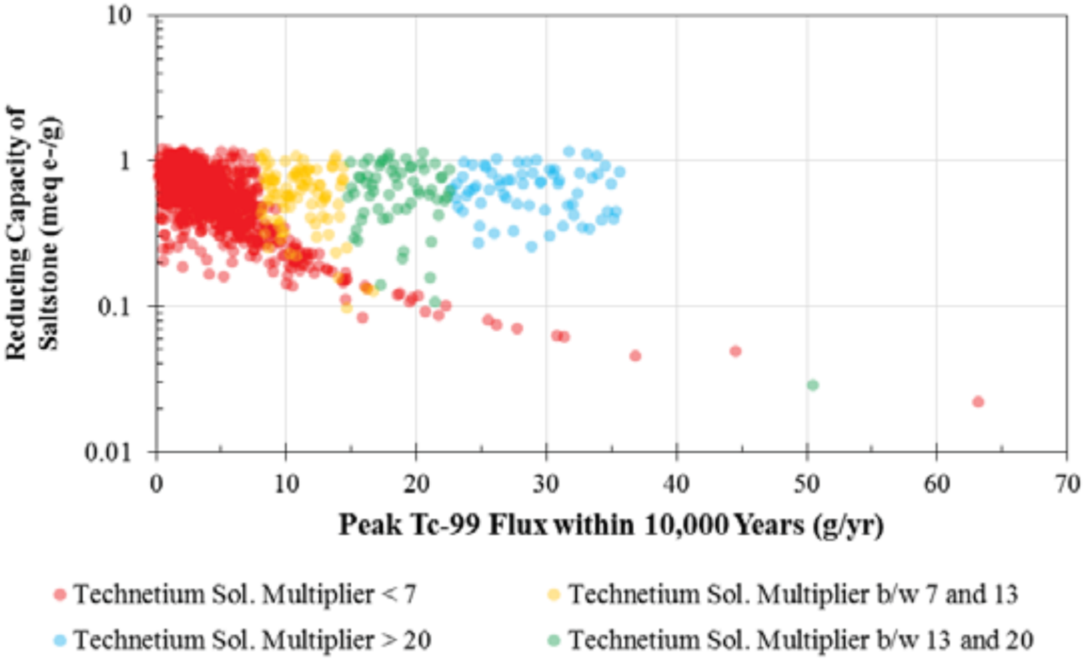

Figure 9. Projected Tc flux from future SDS 9 as a function of assumed saltstone reducing capacity and Tc solubility in reduced saltstone (from SRR-CWDA-2016-00004, Rev. 1 Figure SP-2.9)

As illustrated by the distinct bands of color in Figure 9, the modeled solubility of Tc in reduced saltstone has a clear effect on the model outputs in the Tc-Ox uncertainty analysis. The effect of saltstone reducing capacity is only evident where it is lower than approximately 0.2 meq e^-/g grout. That result makes sense to the NRC staff because the reducing capacity of saltstone controls how much saltstone is oxidized by a given influx of oxygen. Therefore, below some value of residual reducing capacity, saltstone is projected to be oxidized fast enough that Tc releases from the fraction of saltstone oxidized each year contribute most significantly to the overall projected Tc release. In contrast, above some value of the reducing capacity, the amount of saltstone oxidized in a year is simply too small for releases from the oxidized fraction to be significant compared to releases from the larger volume of reduced saltstone, even though Tc is projected to be released more rapidly from oxidized saltstone than it is from an equal volume of reduced saltstone.

The specific values of Tc solubility and residual reducing capacity at which the overall projected Tc release changes from being dominated by releases from reduced saltstone to being dominated by releases from oxidized saltstone also depend on other factors that influence saltstone oxidation, such as the projected rate of inflow of oxygen. Therefore, the specific values at which release behaviors appeared to change in the Tc-Ox sensitivity analysis (i.e., 7×10^{-8} mol/L solubility; 0.2 meq e^-/g residual reducing capacity) are influenced by the 2014 Evaluation Case assumptions and the NRC staff expects that those values would be different for different sets of assumptions. However, based on what is known about the solubility of Tc from cores of field-emplaced saltstone and the reducing capacity of saltstone, the NRC staff expects that releases from chemically reduced saltstone will be an important part of the conceptual model of SDF performance.

Barrier Analysis for the Chemical Reduction of Tc in Saltstone

This section compares recent information on the concentration of Tc released from chemically reduced saltstone to the pore volume Tc concentration that would be projected if saltstone were completely oxidized. The NRC staff does not expect saltstone to be completely oxidized in one year. Rather, this comparison was made to quantify the importance of the chemical reduction of Tc as a barrier to Tc release by comparing the annual Tc release from completely reduced saltstone to the hypothetical release from completely oxidized saltstone.

In the 2014 Evaluation Case, the DOE assumed there was no solubility limit of Tc in oxidized saltstone and that Tc in oxidized saltstone would be partitioned into the solid phase with a sorption coefficient, or K_d value, as defined in Equation 1:

$$K_{d_{Tc}} \equiv \frac{C_{Tc_{solid}}}{C_{Tc_{aq}}} \qquad \text{(Equation 1)}$$

where:

$C_{Tc_{solid}} = Concentration\ of\ Tc\ in\ the\ solid\ phase\ (i.e., excluding\ pore\ space)$

$C_{Tc_{aq}} = Concentration\ of\ Tc\ in\ the\ liquid\ phase$

Because both $C_{Tc_{solid}}$and $C_{Tc_{aq}}$ are unknown, an additional equation is needed to relate these parameters to the concentration of Tc per volume of grout (i.e., $C_{Tc_{grout}}$), which is available in quarterly permit reports that the DOE submits to the South Carolina Department of Health and Environmental Control. That relationship is given by the following mass balance:

$$M_{Tc_{grout}} = M_{Tc_{aq}} + M_{Tc_{solid}} \qquad \text{(Equation 2)}$$

where:

$M_{Tc_{grout}} = mass\ of\ Tc\ in\ a\ unit\ volume\ of\ grout\ (i.e., both\ the\ liquid\ and\ solid\ phases)$

$M_{Tc_{aq}} = mass\ of\ Tc\ in\ the\ pore\ liquid\ in\ a\ unit\ volume\ of\ grout$

$M_{Tc_{solid}} = mass\ of\ Tc\ in\ the\ solid\ phase\ in\ a\ unit\ volume\ of grout$

The mass in each phase is related to the concentration in each phase and the volume of each phase by the following relationships:

$$M_{Tc_{grout}} = V_{bulk} \cdot C_{Tc_{grout}}$$

$$M_{Tc_{aq}} = V_{aq} \cdot C_{Tc_{aq}}$$

$$M_{Tc_{solid}} = M_{solid} \cdot C_{Tc_{solid}} = V_{solid} \cdot \rho_{solid} \cdot C_{Tc_{solid}}$$

where:

$V_{bulk} = volume\ of\ grout\ (i.e., both\ liquid\ and\ solid\ phases)$

$V_{aq} = volume\ of\ liquid\ phase$

$V_{solid} = volume\ of\ solid\ phase\ (i.e., grout\ volume\ excluding\ pore\ space)$

$\rho_{solid} = density\ of\ solid\ phase\ (i.e., solid\ material\ density\ excluding\ pore\ space)$

Substituting those relationships into Equation 2 yields:

$$V_{bulk} \cdot C_{Tc_{grout}} = V_{aq} \cdot C_{Tc_{aq}} + V_{solid} \cdot \rho_{solid} \cdot C_{Tc_{solid}} \qquad \text{(Equation 3)}$$

Solving Equation (1) for $C_{Tc_{solid}}$and substituting the result into Equation (3) yields:

$$V_{bulk} \cdot C_{Tc_{grout}} = V_{aq} \cdot C_{Tc_{aq}} + V_{solid} \cdot \rho_{solid} \cdot K_{d_{Tc}} \cdot C_{Tc_{aq}}$$

And solving for $C_{Tc_{grout}}$

$$V_{bulk} \cdot C_{Tc_{grout}} = C_{Tc_{aq}}\left(V_{aq} + V_{solid} \cdot \rho_{solid} \cdot K_{d_{Tc}}\right)$$

Dividing both sides by V_{bulk} yields

$$C_{Tc_{grout}} = C_{Tc_{aq}}\left(\frac{V_{aq}}{V_{bulk}} + \frac{V_{solid}}{V_{bulk}} \cdot \rho_{solid} \cdot K_{d_{Tc}}\right) \qquad \text{(Equation 4)}$$

The DOE FY 2017 Second Quarter Permit Report for saltstone gives $C_{Tc_{grout}}$ as 3x10^4 picocurie (pCi) Tc per mL grout, which is consistent with the projected Tc concentration in saltstone in the 375-foot disposal structures provided in the FY 2014 Special Analysis Document. The volume of liquid in a unit volume of saltstone, $\frac{V_{aq}}{V_{bulk}}$, is given by the water content, θ. The DOE assumption was that saltstone will remain fully saturated, and, therefore, the water content, θ, is equal to the porosity (n). Based on recent research, the best estimate for the porosity of field-emplaced saltstone is 0.66 (SRR-CWDA-2016-00051). The fraction of a unit volume of grout that is solid is the remaining space, or 0.34 $\frac{mL\ solid}{mL\ grout}$, because the saltstone is assumed to be saturated. In the 2014 Evaluation Case, the DOE represented Tc release from oxidized saltstone with a K_d of 0.5 mL/g. The remaining value in Equation 4 is the density of the solid phase itself, ρ_{solid}, (i.e., density of the solid material only, excluding the pores). The DOE document SRNL-STI-2008-00421 lists the density of the solid phase of cured saltstone as 2.42 g solid / mL solid. Substituting those values into Equation 4 yields:

$$C_{Tc_{grout}} = C_{Tc_{aq}}\left(0.66\frac{mL\ liquid}{mL\ grout} + 0.34\frac{mL\ solid}{mL\ grout}2.42\frac{g\ solid}{mL\ solid} \cdot 0.5\,\frac{mL\ liquid}{g\ solid}\right)$$

$$\frac{3 \cdot 10^4\ {}^{pCi}\!/_{mL\ grout}}{\left(0.66\,\frac{mL\ liquid}{mL\ grout} + 0.34\frac{mL\ solid}{mL\ grout} \cdot 2.42\frac{g\ solid}{mL\ solid} \cdot 0.5\,\frac{mL\ liquid}{g\ solid}\right)} = C_{Tc_{aq}} = 2.8 \cdot 10^4\,\frac{pCi}{mL\ liquid}$$

Converting units:

$$C_{Tc_a} = 2.8 \cdot 10^4\,\frac{pCi}{mL\ liquid} \cdot \frac{1000\frac{mL}{L}}{1 \cdot 10^{12}\frac{pCi}{Ci}} \cdot \frac{1\ g\ Tc}{1.69 \cdot 10^{-2}\ Ci\ Tc} \cdot \frac{mole\ Tc99}{99\ g\ Tc99} = 1.7 \cdot 10^{-5}\frac{moles\ Tc99}{L\ liquid}$$

In contrast, the concentration of Tc released from field-emplaced saltstone that the DOE attempted to maintain in a chemically reduced state is approximated at 5x10^{-7} mol/L (see Figure 3).

The comparison between the release from totally oxidized saltstone and reduced saltstone indicates that, at a saltstone Tc concentration of $3x10^4$ pCi/g grout and a K_d for oxidized Tc of 0.5 mL/g, chemical reduction could reduce Tc release by approximately a factor of 30 (i.e., $1.7x10^{-5}$ mol/L divided by $5x10^{-7}$ mol/L equals 34). The reliance on that chemical barrier would increase with increasing Tc concentration in the solid phase because increasing the solid-phase Tc concentration would increase the Tc concentration in the pore water of oxidized Tc without increasing the concentration of Tc released from reduced saltstone if the release of Tc from reduced saltstone is solubility-limited and the release from oxidized Tc is best modeled with a sorption coefficient. However, the FY 2014 Special Analysis Document projects an expected average Tc concentration in saltstone grout of slightly less than $3x10^4$ pCi/g, as used in this calculation, for the remainder of the SDF. Although deviations from this average are expected in individual disposal structures, the average value is sufficient to determine an approximate benchmark of the importance of chemical reduction as a barrier to Tc release.

That comparison indicates the importance of chemical reduction of Tc by saltstone by comparing completely oxidized saltstone to completely reduced saltstone. In essence, it bounds the magnitude of the barrier function by modeling complete failure of the chemical barrier in a single year. However, neither the DOE nor the NRC staff expects saltstone to oxidize completely in one year. Instead, the NRC staff expects that: (1) saltstone will oxidize behind fronts that move from surfaces exposed to soil gas or infiltrating water into intact areas of the waste form; (2) complete oxidation will take hundreds to thousands of years; and (3) Tc would be released from both oxidized and reduced saltstone during that time. Therefore, to evaluate the expected magnitude of the chemical barrier function of saltstone, it is more realistic to compare the amount of Tc that could be released from oxidized saltstone versus reduced saltstone as saltstone is oxidized, rather than after complete oxidation has occurred. However, that comparison relies on both the rate of saltstone oxidation and the spatial distribution of water flow through the oxidized and reduced areas.

The spatial component of the comparison between Tc releases from oxidized versus reduced saltstone is not directly modeled in the FY 2014 Evaluation Case or sensitivity analyses because fracturing is not explicitly modeled in those analyses. Fractures are of particular importance to the projected Tc released from reduced and oxidized areas of saltstone because fractures could divert water away from intact chemically reduced areas of saltstone, increasing the relative importance of releases from oxidized areas. In addition, fractures could cause increased water flow in areas where Tc had been oxidized by oxygen diffusing into saltstone from the gas phase, which would cause an increase in the release of oxidized Tc for a time until any Tc that had been oxidized by diffusion of gas-phase oxygen was depleted. Thus it is difficult to project the relative fraction of Tc that could be released from oxidized and reduced areas of saltstone without additional understanding of the rate and extent of saltstone fracturing with time and explicit modeling of that fracturing

However, it is useful to evaluate the contribution of Tc releases from oxidized saltstone in the absence of fractures to understand the importance of oxidation under different conceptual models. If fractures are neglected and water is assumed to flow through oxidized and reduced saltstone in the same way, it is possible to calculate the maximum fractional contribution of Tc released from oxidized saltstone by considering the rate of oxidation compared to the rate of water flow through saltstone. In saturated, intact saltstone, Tc oxidation is expected to be controlled by dissolved oxygen in infiltrating water and release of reduced Tc is expected to be controlled by the rate of water flow and Tc solubility. Because both of those processes are linearly dependent on water flow, the ratio between them is fixed even as water flow through the saltstone matrix changes with time. If it is assumed that oxidized Tc is released instead of being re-reduced, the relative magnitude of releases of oxidized and reduced Tc can be quantified by considering that ratio. Figure 10 depicts infiltrating water entering a unit volume of intact saltstone grout and contrasts the volume of saltstone that would be oxidized by dissolved oxygen in water that infiltrates into intact saltstone in a fixed time with the volume of saltstone that the water would flow through in that time.

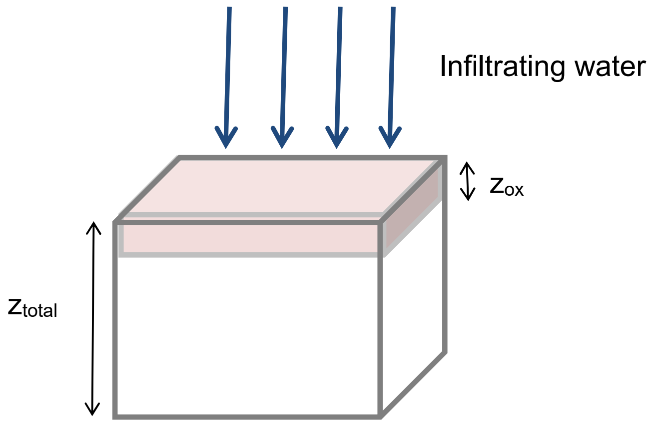

Figure 10. Conceptual diagram of saltstone volume oxidized in a fixed time by dissolved oxygen in infiltrating water as compared to the volume of saltstone that the water would flow through in that time (not to scale)

In a fixed time Δt, the volume of grout oxidized by the infiltrating water can be defined with Equation 5:

$$V_{ox} = A \cdot \Delta \mathrm{z}_{\mathrm{ox}} \qquad \text{(Equation 5)}$$

where where V_{ox} is the oxidized volume, A is the cross sectional area of the unit volume, and $\Delta \mathrm{z}_{\mathrm{ox}}$ is the progress of the oxidation front in time Δt. The volume of saltstone grout that water flows through in the same time (Δt) is given by:

$$V_{total} = A \cdot \Delta \mathrm{z}_{\mathrm{total}}$$

where V_{total} is the volume of grout that water flows through in time Δt and $\Delta\, z_{total}$ is the distance water flows through intact saltstone in time Δt (i.e. the total depth of the unit volume).

Under saturated conditions, progress of an oxidation front, shown as Δz_{ox} in Figure 10, can be determined by setting the equivalents of oxidizing capacity in the water equal to the equivalents of reducing capacity in the saltstone:

$$C_{ox} \cdot V_{water} = C_{red} \cdot V_{ox}$$

where $C_{ox}$is the concentration of equivalents of oxidizing capacity in water, V_{water} is the amount of water flows through the unit volume in time Δt, C_{red} is the reducing capacity of saltstone grout, and V_{ox} is as defined in Equation 5. Dividing by C_{ox}:

$$V_{water} = \frac{C_{red}}{C_{ox}} \cdot V_{ox} \qquad \text{(Equation 6)}$$

The term V_{water} can be related to V_{total} by the porosity, n, as follows:

$$V_{total} = \frac{V_{water}}{n}$$

Substituting that result into Equation 6:

$$V_{total} \cdot n = \frac{C_{red}}{C_{ox}} \cdot V_{ox}$$

The dissolved oxygen concentration in the water projected to infiltrate into saltstone, C_{ox}, is uncertain. Biological and chemical processes can affect the concentration of oxygen in soil gas and the resulting dissolved oxygen concentration in groundwater. To estimate C_{ox}, the NRC staff used the average of measurements of dissolved oxygen in water-table aquifers at the SRS, (i.e., 8.1 mg O_2 / L water) (WSRC-RP-92-0450)[8]. That oxygen content can be converted to equivalents of oxidizing capacity as follows:

$$C_{ox} = 8.1 \frac{mg\ O_2}{L} \cdot \frac{mole\ O_2}{3.2 \cdot 10^4\ mg\ O_2} \cdot \frac{4\ eq\ e^-}{mole\ O_2} = 1.01 \cdot 10^{-3} \frac{eq}{L\ water}$$

In the 2014 Evaluation Case, the reducing capacity of saltstone, C_{red}, is assumed to be 0.607 meq/g saltstone. Given the density of saltstone grout reported in the FY 2014 Special Analysis Document of 1.01 g saltstone per mL saltstone,

$$C_{red} = 6.07 \cdot 10^{-4} \frac{eq\ e^-}{g\ saltstone} \cdot \frac{1.01\ g\ saltstone}{mL\ saltstone} \cdot \frac{1000\ mL}{L} = 0.613 \frac{eq}{L\ saltstone}$$

Substituting in to Equation 6:

$$\frac{V_{ox}}{V_{total}} = \frac{1.01 \cdot 10^{-3}\ eq}{L\ water} \cdot \frac{L\ saltstone}{0.613\ eq} \cdot \frac{0.66\ L\ water}{L\ saltstone} = 1.1 \cdot 10^{-3} \qquad \text{(Equation 7)}$$

This result indicates that in a time Δt, the volume of intact saltstone oxidized by oxygenated infiltrating water is $1.1\text{x}10^{-3}$ of the volume of saltstone that that water flows through. That result is similar to a result show in in the DOE document SRNL-STI-2014-00083, Rev. 1, which determined that, under advection-dominated conditions, the speed of an oxidation front in saltstone would be approximately three orders of magnitude slower than the rate of water flow through saltstone.

Relative releases of oxidized and reduced Tc from the unit volume of saltstone shown in Figure 10 can be calculated based on the result of Equation 7 if it is assumed that oxidized Tc is released from saltstone instead of being re-reduced. Because of the relatively large volume of water flowing through the unit cell (i.e., compared to the volume of the oxidized area) and the relatively low sorption coefficient for Tc in oxidized saltstone (i.e., 0.5 mL/g), the amount of Tc released from the oxidized fraction can be assumed to be the Tc inventory in that volume:

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[8] That average value excludes measurements from one well with anomalous values, as discussed in the NRC Technical Evaluation Report for the H-Area Tank Farm Facility (ML14094A514).

$$Tc_{ox} = V_{ox} \cdot \frac{3 \cdot 10^4 pCi}{g\ grout} \cdot \frac{1.01\ g\ grout}{mL\ grout} \cdot \frac{1\ mol\ Tc}{99\ g\ Tc} \cdot \frac{1\ g\ Tc}{1.69 \cdot 10^{-2} Ci} \cdot \frac{1\ Ci}{10^{12}\ pCi}$$

$$Tc_{ox} = V_{ox} \cdot 1.8 \cdot 10^{-8} \frac{mol\ Tc}{mL\ grout}$$

where Tc_{ox} is the Tc in the unit cell that is oxidized by the infiltrating water. The release of reduced Tc can be calculated from the amount of water that passed through the remaining volume (i.e., $V_{total} - V_{ox}$) multiplied by the solubility limit of Tc. Because of the small ratio of V_{ox} to V_{total}, the difference $V_{total} - V_{ox}$ can be approximated by V_{total}. The amount of water that corresponds to the pore volume of V_{total} is given by $V_{total} \cdot n$. Therefore,

$$Tc_{red} \approx V_{total} \cdot \frac{0.66\ mL\ water}{mL\ grout} \cdot \frac{5 \cdot 10^{-7} mol}{L\ water}$$

To compare the relative releases of reduced and oxidized Tc,

$$\frac{Tc_{ox}}{Tc_{red}} = \frac{V_{ox}}{V_{total}} \cdot 1.8 \cdot 10^{-8} \frac{mol\ Tc}{mL\ grout} \cdot \frac{mL\ grout}{0.66\ mL\ water} \cdot \frac{L\ water}{5 \cdot 10^{-7} mol\ Tc} \cdot \frac{1000\ mL\ water}{L\ water}$$

Substituting in the result of Equation 7 for the term $\frac{V_{ox}}{V_{total}}$ yields:

$$\frac{Tc_{ox}}{Tc_{red}} = 1.1 \cdot 10^{-3} \cdot \frac{1.8 \cdot 10^{-8} mol\ Tc}{mL\ grout} \cdot \frac{mL\ grout}{0.66\ mL\ water} \cdot \frac{L\ water}{5 \cdot 10^{-7} mol\ Tc} \cdot \frac{1000\ mL\ water}{L\ water} = 0.059$$

and

$$\frac{Tc_{red}}{Tc_{ox}} = \frac{1}{0.059} = 17$$

Therefore, under the following conditions:

- water has uniform flow through oxidized and reduced areas of saltstone;
- concentration of Tc in saltstone grout is 3x10^4 pCi/g grout;
- release from the oxidized fraction of saltstone is governed by a K_d of 0.5 mL/g; and
- release from the reduced fraction of saltstone is governed by a solubility limit of 5x10^{-7} mol/L;

the NRC staff expects that releases of Tc from chemically reduced saltstone will be more significant to the total Tc flux from saltstone than releases from chemically oxidized saltstone (i.e., by approximately a factor of 17). That conclusion would not necessarily be valid during time periods when Tc that has previously oxidized without water flow (e.g., from gas-phase transport of oxygen in unsaturated fractures) is contacted by water and stored oxidized Tc is released, depending on how much Tc was oxidized before being contacted with water. That conclusion also would not necessarily be valid if there were significant channelization of flow in oxidized areas of saltstone that diverted water from chemically reduced areas of saltstone.

Summary for MF 5.02

The NRC 2013 SDF Monitoring Plan indicates that the NRC staff expects to close MF 5.02 under both §61.41 and §61.42 POs after the NRC determines that: (1) model support for the chemical reduction of Tc(VII) to Tc(IV) is robust; and (2) a reduced state is maintained under field conditions. The NRC expects that the DOE will inform the NRC what the ranges of those conditions are expected to be during the performance period.

The Oxidation TRR identified that more information about Tc re-reduction by reducing areas of saltstone or disposal structure concrete was needed before MF 5.02 could be closed. The DOE has not yet provided physical evidence of re-reduction of oxidized Tc in reduced saltstone or disposal structure concrete. In addition, experimental support for the projected duration of Tc releases consistent with releases from chemically-reduced Tc is not yet available. For those reasons, the NRC staff recommends keeping MF 5.02 open under both §61.41 and §61.42 POs. To close MF 5.02, the NRC staff expects that it would need: (1) data from ongoing experiments conducted with cores of field-emplaced saltstone to provide additional information about the projected duration of Tc releases consistent with releases from chemically-reduced Tc; and (2) physical evidence of Tc re-reduction in reduced cementitious material.
Although the NRC staff recommends keeping MF 5.02 open, several factors support reducing the priority of MF 5.02. First, the research results that originally prompted the NRC staff to develop MF 5.02 have been reinterpreted by the NRC staff based on more recent research results and the concern that the redox state of Tc is sensitive to trace quantities of oxygen has been reduced. Second, data from experiments conducted by the DOE with cores of field-emplaced saltstone showed that both cores leached with deareated liquid and cores leached with liquid equilibrated with laboratory air released similar concentrations of Tc and those concentrations were consistent with releases from reduced Tc solid phases. Third, based on the current knowledge of the inventory, solubility, and sorption of Tc in saltstone, Tc mobilization in reduced saltstone is expected by the NRC staff to be as or more important to performance than Tc mobilization in oxidized saltstone unless there is significant saltstone oxidation prior to contact with water (e.g., from oxygen transport in unsaturated fractures) or significant channelization of flow in oxidized areas of saltstone. Thus, the extent and timing of fracturing relative to the timing of water flow through saltstone is a significant source of uncertainty in projecting Tc release. Finally, although the Oxidation TRR indicated that model support for re-reduction of Tc in saltstone or disposal structure concrete was needed before MF 5.02 could be closed and that model support has not yet been provided, the bypass sensitivity analysis provided by the DOE in the FY 2014 Special Analysis Document bounds the effects in a range that is consistent with how the NRC staff decides that a monitoring factor is medium priority. For those four reasons, the NRC staff recommends reducing the priority of MF 5.02 from high to medium.

Monitoring Factor 5.03, "Reducing Capacity of Saltstone"

MF 5.03 addresses the reducing capacity of saltstone. In the Oxidation TRR, the NRC staff indicated that to close MF 5.03, the NRC staff needed additional information in the following three areas: (1) the identity of the components of saltstone dry premix or salt solution that supply the measured reducing capacity in saltstone, (2) the ability of these components to reduce Tc in saltstone under field conditions, and (3) the expected evolution of the reducing capacity over time.

In the NRC RAI Comments on the DOE FY 2013 Special Analysis Document, the NRC staff expressed concern that sulfur species could be more easily leached from saltstone than iron species and that this loss mechanism was not reflected in the DOE model of SDF performance. In the DOE Response to the RAI Comments (SRR-CWDA-2014-00099, Rev. 1), the DOE addressed that concern by indicating that ferrous iron may be more responsible for the measured reducing capacity of saltstone than sulfide species. That DOE hypothesis was based on a study (SRRA042328SR) that showed some oxidation of sulfur species at early times (i.e., within several hours of sample preparation). However, when those simulated saltstone samples were permitted to age in a continuation of the original study (SRRA042328-0004), the authors determined that a fraction of the sulfur persisted in reduced forms in the simulated samples for the 458-day aging period. In that updated study (SRRA042328-0004), the authors concluded:

> "XAS analysis of iron speciation indicated that ferrous iron which was initially present as a component of the BFS was fully oxidized to ferric iron after 117 days. Similar analysis of the sulfur speciation indicated that a small but measureable amount of sulfur was present as sulfide or elemental sulfur which persisted for up to 458 days. Thus, it appears that the reduction capacity of the saltstone is predominantly provided by reduced sulfur species rather than ferrous iron."

In the DOE Response to the NRC RAI Comments, the DOE indicated that future research might address the NRC staff concern that the components of saltstone that supply the measured reducing capacity may not be able to reduce Tc in a cementitious matrix. The NRC staff concern was based on both a Cementous Barriers Partnership (CBP) report (CBP-RP-2010-013-01) and a Pacific Northwest National Laboratory (PNNL) study (PNNL-22957) that indicated that nitrite was a major contributor to the measured reduction capacity. However, as described in the PNNL report, the reduction potential of nitrite is not sufficient to reduce Tc(VII) to Tc(IV). Accordingly, it may not be appropriate to base the assumed reducing capacity of saltstone on those measurements because nitrite was part of the measured reducing capacity without being able to reduce Tc.

The PNNL report also demonstrated that the use of the Ce(IV) titration method, which included sulfuric acid, may overestimate the reducing capacity available in saltstone. The PNNL report indicated that the method measured nearly all of the reducing capacity of the solid sample because most of the solids dissolved in the strong acid. The PNNL report indicated that with the Cr(VI) method, which used neutral or alkaline conditions, only the reducing capacity of the solid surface and any internal surface that oxygen can reach in the available contact time was likely to be measured. The formation of a passivation layer on the blast furnace slag was indicated as potentially contributing to the decreased reactivity under the Cr(VI) method. It is not clear to the NRC staff that the DOE use of the Ce(IV) method was appropriate for determining the reducing capacity of saltstone because the conditions for the Cr(VI) method were more consistent with the expected alkaline conditions of saltstone.

In the DOE Response to the NRC RAI Questions on the FY 2014 Special Analysis Document (SRR CWDA-2016-00004, Rev. 1), the DOE supplied deterministic and probabilistic analyses that addressed the sensitivity of projected SDF performance to assumptions about the reducing capacity of saltstone. One of those analyses was the Tc-Ox probabilistic sensitivity analysis discussed in this TRR in the context of MF 5.02. As shown in Figure 9, the peak projected flux of Tc from a 375-foot disposal structure was more sensitive to Tc solubility in reduced saltstone than it was to the measured reducing capacity, unless the reducing capacity was less than approximately 0.2 meq e^- per gram saltstone grout, which is less than one-third the value the DOE assumed in saltstone grout (i.e., 0.607 meq e^- per gram grout) in the 2014 Evaluation Case.

In another sensitivity analysis, which was supplied in response to another NRC RAI Question, the DOE used the 2014 Evaluation Case as a starting point and independently varied the saltstone and disposal structure reducing capacities to five values between 0.0812 meq e^- per gram grout and 0.822 meq e^- per gram grout (i.e., using twenty five combinations). Those results were consistent with the results of the Tc-Ox analysis in that they projected very little (i.e., less than 1 mrem/yr) sensitivity of the projected dose from the SDF within 10,000 years to saltstone reducing capacity when the saltstone reducing capacity was greater than 0.178 meq e^- per gram grout, even when the reducing capacity of the disposal structure concrete was at its lowest value. When the saltstone reducing capacity was reduced to 0.0855 meq e^- per gram grout from 0.812 meq e- per gram grout, the projected peak dose within 10,000 years increased by less than a factor of two, even when the reducing capacity of the disposal structure concrete was at its lowest value.

Summary for MF 5.03

The NRC 2013 SDF Monitoring Plan indicates the NRC staff expects to close MF 5.03 under both §61.41 and §61.42 POs after the NRC determines that information for the initial reducing capacity of saltstone and the expected evolution of redox conditions over time is adequate.

The NRC staff recommends keeping MF 5.03 open under both §61.41 and §61.42 POs because the DOE has not directly addressed the implications of potential sulfur dissolution and release on the projected evolution of saltstone reducing capacity or the applicability of the Ce (i.e., Angus-Glasser) method of measuring reducing capacity to the species that reduce Tc in saltstone, However, based on the sensitivity analyses described in this section, which the DOE presented in response to the NRC RAI Questions on the DOE FY 2014 Special Analysis Document (SRR-CWDA-2016-00004, Rev.1), the NRC staff recommends reducing the priority of MF 5.03 under both §61.41 and §61.42 POs from medium to low.

Monitoring Factor 5.05, “Potential for Short-Term Rinse-Release from Saltstone”

As described in the NRC 2013 SDF Monitoring Plan, some studies of simulated chemically reducing cementitious waste forms have shown an initial release of Tc that is rapid compared to subsequent releases. The description in this TRR distinguishes between a surficial “rinse-release” mechanism and volumetric processes that can lead to elevated release rates in the first one or two pore volumes, such as an initial “flush” of a poorly-incorporated contaminant from the waste form pores. That distinction is made because different types of data are relevant to each type of process. In particular, data from recent studies with cores from field-emplaced saltstone are directly relevant to volumetric processes because they measured Tc release in the initial flush of saltstone pores. Those cores do not reflect surficial processes directly because they were taken from the interior of the monolith. Therefore, in this TRR, true surficial rinse-release is evaluated by scaling the effects seen in a laboratory experiment that identified surficial rinse-release based on the relative surface area to volume ratios of the laboratory samples and field monoliths.

Regarding volumetric processes, in the NRC 2013 SDF Monitoring Plan, the NRC described the potential for a contaminant to be initially “poorly encapsulated” in the waste form. For Tc, it specifically noted the potential for Tc that was not initially reduced by saltstone to be present in greater than expected concentrations in the pore volumes and to result in an initially high Tc release. That type of volumetric process could also occur if a certain fraction of a contaminant is more easily removed from the solid phase and that fraction is preferentially removed. For example, the Oxidation TRR described the potential concern that there is a “persistent oxidized fraction" of Tc in saltstone and that this fraction of Tc could be released with the first pore volume of water that infiltrated through saltstone. The NRC 2013 SDF Monitoring Plan cited two studies demonstrating rinse-release in reducing cementitious waste forms: (1) Tallent *et al*. (1987); and (2) Pabalan *et al*. (2012). This TRR section describes the results of those two studies and compares them to the DOE results of recent data from experiments on the SDS 2A core samples.

The study by Tallent *et al.* tested diffusive release from intact simulated cementitious waste forms with a standard test procedure from the American Nuclear Society (ANS) (i.e., Standard ANS 16.1). In that procedure, a waste form is submerged in a leaching solution that is periodically sampled and replaced with fresh solution. One of the 11 different grout blends used in that study (i.e., Blend No. 19) was very similar to saltstone grout (i.e., 47.5% BFS, 47.5% fly ash, and 5% lime in Blend No. 19 compared to 47% BFS, 47% fly ash, and 6% lime or Portland cement in saltstone). However, the authors provided release data only for the blend composed of 100% BFS (i.e., Blend No. 14). For Blend No. 14, the authors provided cumulative release data as a function of the square root of time, which is a standard way of evaluating whether a release is well-fit by a diffusion-dominated release model. The cumulative release data showed a significant non-linearity with the square root of time, with faster-than-expected releases occurring during the first five days of the 90-day experiment. The authors reported that those results were "typical" of the results from the other blends and did not provide releases as a function of time for the other blends.

The authors also reported the results only as fractional cumulative releases (i.e., releases represented as a fraction of the constituent originally in the sample) rather than as cumulative activities, masses, or moles released. The authors did not indicate how much Tc was included in the solid samples or the concentration, total volume, or total activity of the Tc spike. Therefore, it is not known if the concentration of Tc used is relevant to saltstone. Furthermore, because concentration data was not provided for any of the samples, it is difficult to evaluate the data in terms of more recent results (e.g., to determine if solubility limits were reached during the measurements).

The test procedure used by Tallent et al. (i.e., ANS 16.1) is similar to the EPA Method 1315 diffusive release test procedure used with cores of field emplaced saltstone in SREL DOC No. R-2016-0003. In both standard tests (i.e., ANS 16.1 and EPA Method 1315), the cumulative amount of the contaminant leached is graphed as a function of the square root of total time elapsed, and linearity is interpreted as evidence of diffusion-controlled release. It is not clear to the NRC staff why the data from Tallent et al. show a non-linear pattern with the square root of time, with faster releases in the first five days and slower releases measured through 90 days. It is not possible for the NRC staff to understand the releases further by re-examining the release data because the authors of that study did not provide the concentration data. Data from samples of cores of field-emplaced saltstone are more relevant to projecting SDF performance. Of three samples of field-emplaced cores tested with EPA Method 1315, all three showed linearity of cumulative releases with the square root of time (see Figure 11) and none showed the non-linearity of diffusion data that Tallent et al. identified as evidence of a rinse-release phenomenon. Tallent *et al.* described the observed initial release as a "surface-related or wash-off problem" and did not further characterize the mechanism of release.

The NRC staff concerns about rinse-release that were based on the study by Pabalan et al. were based on results from crushed simulated saltstone samples. However, tests of intact samples conducted in the same study also did not show evidence of a surface-wash off effect because releases were well-fit by a diffusive release model (see Figure 12).

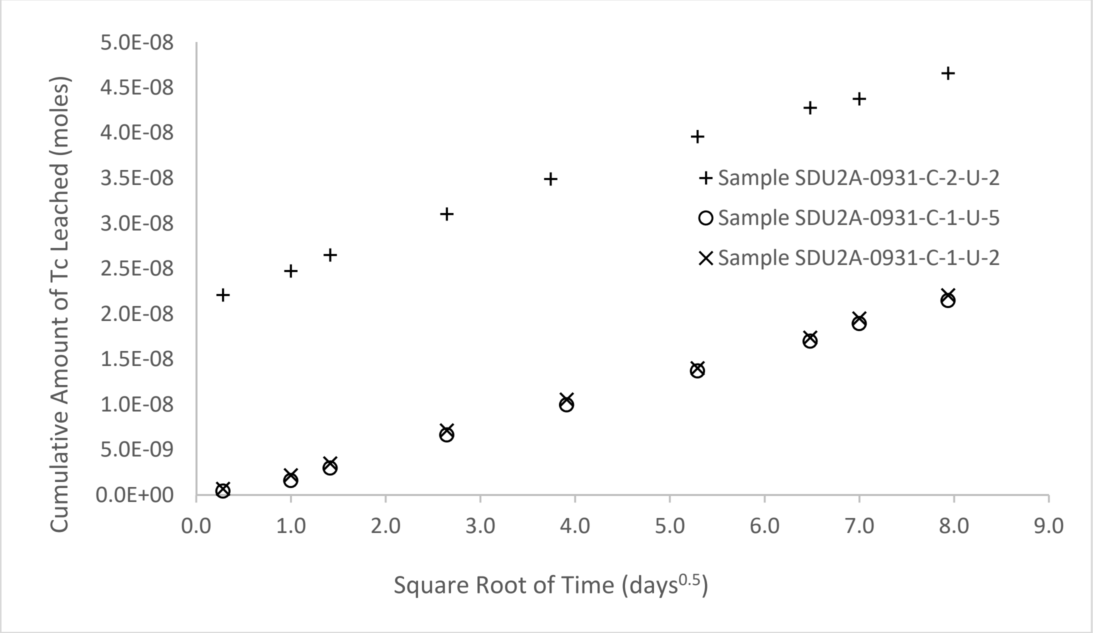

Figure 11. Cumulative amounts of Tc leached from three samples of cores of field-emplaced saltstone with EPA Method 1315 (from data provided in SREL DOC No. R-2013-0003)

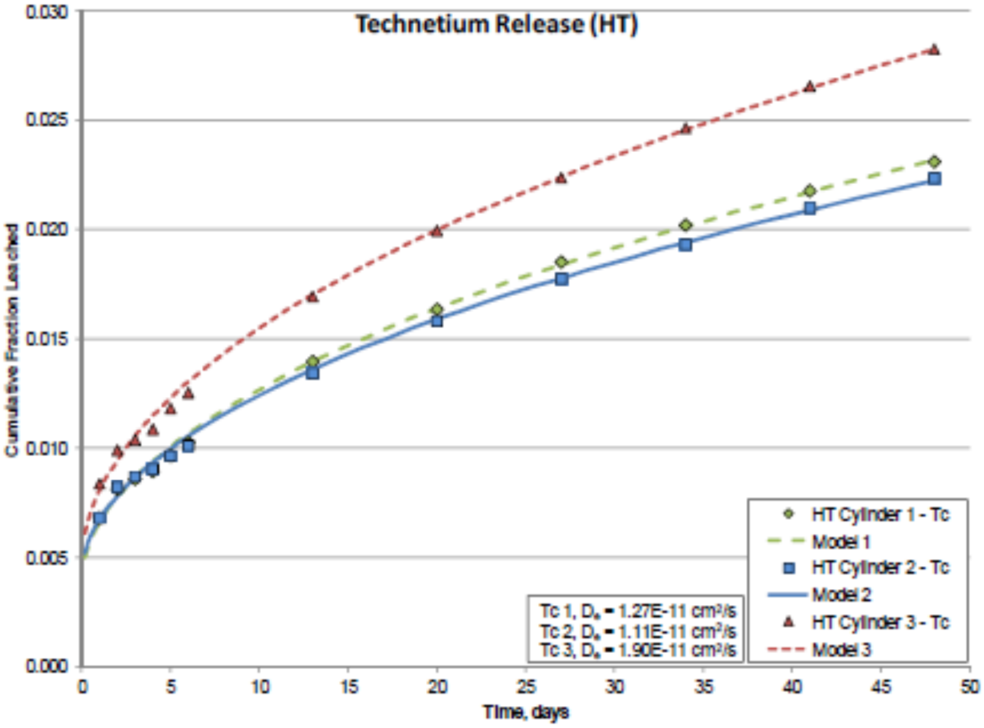

Figure 12. Diffusive release of Tc from intact cylinders of simulated saltstone in a semi-batch, deionized water, oxic leach test (from Pabalan et al. (2012) Figure 3-26)

Pabalan *et al.* hypothesized that Tc was not fully encapsulated in saltstone and that the early high concentrations represented flushing of concentrated pore fluid. Pabalan *et al.* also hypothesized that Tc may not initially be completely chemically reduced in the saltstone and the high initial concentrations represented flushing of an oxidized, mobile fraction of Tc initially present in the waste form. However, the authors acknowledged that the early Tc release could be due to an experimental artifact related to grinding the simulated saltstone samples under atmospheric conditions containing oxygen.

Dynamic leaching of cores of field-emplaced saltstone (see Figure 3) provides model support for assumptions about releases from saltstone pores (i.e., volumetric as opposed to surface releases) at very early times (i.e., the first few pore volumes). Although the data shown in Figure 3 do not address the existence of a persistent oxidized fraction of Tc in saltstone with direct spectroscopic evidence, those data do provide information about Tc mobility in intact portions of field-emplaced saltstone. Figure 3 provides support for the determination that, whether or not there is a “persistent oxidized fraction” of Tc initially present in saltstone, it does not appear to lead to elevated Tc concentrations in the first pore volume of liquid to be transported through saltstone, as hypothesized in both the NRC 2013 SDF Monitoring Plan technical notes supporting MF 5.05 and the Oxidation TRR. As shown in Figure 3, one of the samples tested did not show elevated concentrations in the first few pore volumes, and the other sample showed releases elevated by approximately a factor of two between the first and second pore volume. However, the authors of the data shown in Figure 3 subsequently analyzed it as a function of pH (SRR-CWDA-2017-00085) and determined that the releases were consistent with the DOE conceptual model that Tc release from reduced saltstone is governed by the solubility of $TcO_2 \cdot 1.6\ H_2O$ or $TcO_2 \cdot 2\ H_2O$ (see Figure 8) and therefore, do not appear to indicate releases from a “persistent oxidized fraction” of Tc. The importance of including the relevant chemical conditions of Tc release, including pH and Eh, is described in the Solubility TRR and is reviewed in this TRR in the context of MF 5.01.

Similarly, the data from cores of field-emplaced saltstone address the NRC staff concern that exposure to oxygen during mixing, pumping, and pouring, or to entrained air during curing, would lead to an initial flush of oxidized Tc in the first pore volume of water to infiltrate through saltstone because those cores of field-emplaced saltstone were subject to field mixing, pumping, and pouring and did not show evidence of oxidized Tc release. Therefore, the NRC staff has determined that those mechanisms are no longer of significant concern and are not a basis to keep this MF open.

Because the data shown in Figure 3 were taken from intact cores, they do not provide information about potential oxidation of Tc due to exposure to air in unsaturated fractures. As described in the NRC 2013 SDF Monitoring Plan and in this TRR in the context of MF 10.02, if the closure cap is successful in diverting a significant fraction of water away from saltstone for hundreds of years after closure, oxidation could proceed from unsaturated fractures before a significant amount of water contacts saltstone. Although it would happen long after closure, this phenomenon would represent the initial release (i.e., the first pore volume) and could be significant, if sufficient oxidation of saltstone occurs before the first pore volume of water infiltrates through saltstone. However, the mechanism of that release is related to the oxidation of Tc in saltstone by infiltrating oxygen, which is covered by MF 5.02.

Regarding surficial process, a study performed at PNNL (PNNL-24297) reported evidence of rinse-release from intact samples of simulated Cast Stone tested with a semi-batch leaching procedure similar to EPA Method 1315 with additional time intervals. The authors of that report observed that the observed releases from the first four leaching intervals (i.e., 0.08, 1, 2, and 7 days) showed releases indicative of a greater diffusion coefficient than releases from subsequent intervals. The authors commented on those results as follows:

> "We don't generally recommend using the 0.08 to 7 day data because when leach testing small monoliths the "surface wash off" and release from "surface pores" that directly intercept the monolith outer surface dominate the early release data. The wash off effect is believed to be caused by salts that evaporate on the monolith surface during curing."

The mechanism of rinse-release suggested by the authors of PNNL-24297 is consistent with the lack of significant rinse-release from the cores of field-emplaced saltstone (see Figure 3), because the cores featured in Figure 3 were internal to the saltstone monolith during curing and would not have experienced the same surface accumulation of evaporation salts that samples cured in a laboratory would have. Therefore, although the results from cores of field-emplaced saltstone (see Figure 3) provide strong model support regarding the flush of the first pore volume though saltstone, those results do not directly address surface rinse-release because those cores were taken from inside the saltstone monolith.

To assess the significance of the surface rinse-release phenomenon observed in PNNL-24297 to SDF performance, it is useful to compare the surface area to volume ratios in the PNNL laboratory samples and field-emplaced saltstone monoliths. The PNNL study (PNNL-24297) used samples that were 5.1 cm (2.0 inches) and 10.2 cm (4 inches) long, yielding a surface area to volume ratio of 0.94 cm^{-1}. For comparison, a 150-foot and a 375-foot saltstone disposal structure have a surface area to volume ratio of $8.8x10^{-4}$ cm^{-1} and $3.5x10^{-4}$ cm^{-1}, respectively. Therefore, the relative importance of surficial rinse-release is expected to be less significant for field-emplaced saltstone than it was for the PNNL laboratory samples. For example, the samples used in PNNL-24297 leached, on average, 1.3% of their Tc inventory during the first four batch replacements (i.e., during the interval during which the authors indicated there was evidence of rinse-release). Scaling that release by the surface area to volume ratios of the field emplaced saltstone relative to the laboratory experiments yields anticipated fractional releases in the first four rinses of $1x10^{-5}$ and $5x10^{-6}$ for a 150-foot and a 375-foot disposal structure, respectively. Performing a similar calculation for the first rinse only, the average fractional release from the PNNL-24297 was 0.31% and scaling by the relative surface area to volume ratios in the field and laboratory as in the previous calculation yields projected fractional releases in a single rinse of $3x10^{-6}$ and $1x10^{-6}$ for a 150-foot and a 375-foot disposal structure, respectively. In comparison, the peak annual fractional release rate for Tc within 20,000 years of site closure projected in the 2014 Evaluation Case[9] is $1x10^{-5}$ for both the 150-foot and 375-foot disposal structures. That fractional release led to a projected dose from Tc of 4 mrem/yr. Thus, even if the first rinse of an entire disposal structure occurred in one year, the result would contribute on the order of 1 mrem/yr. However, the NRC staff does not expect that the first rinse will occur in a single year due to the low flow rates that the DOE projects to occur at early times. One possibility that could cause the contact of a large fraction of the surface area of a saltstone waste form with water would be if: (1) a shrinkage gap develops between the waste form and the wall of the disposal structure; and (2) the cover is severely compromised while the disposal structure remains intact, such that a "bathtub" effect could develop. However, the NRC staff does not expect the disposal structures to maintain enough physical integrity to cause such a bathtub effect to occur. Another possibility for a significant fraction of the surface area to

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[9] Fractional release calculated from flux rates provided in the FY 2014 Special Analysis Document Table 5.6.2-3 and Table 5.6.2-4, divided by disposal unit inventory.

contact water could occur if the water table rises significantly (i.e., approximately 15 meters (50 feet)) in a single year. The potential for a sudden rise in the water table in a single year is not consistent with the expected evolution of the SDF and is addressed in MF 10.14, “Scenario Uncertainty.” Therefore, the NRC staff does not expect a surface rinse-release process to significantly affect SDF performance.

Summary for MF 5.05

The NRC 2013 SDF Monitoring Plan indicates the NRC staff expects to close MF 5.05 under both §61.41 and §61.42 POs after the NRC determines that model support for the exclusion of rinse-release phenomenon from the conceptual model assumed in the DOE 2009 PA is adequate. Alternatively, MF 5.05 may be closed after the NRC determines that the phenomenon is well-understood and the effect on the projected dose is well supported.

The NRC staff developed MF 5.05 because of previous studies that showed releases of Tc in the first few pore volumes that were elevated compared to subsequent releases. However, the studies cited in the NRC 2013 SDF Monitoring Plan used simulants not representative of saltstone, did not report concentration results necessary to interpret the applicability of the results, or used samples crushed in air. When data from a study of intact laboratory samples that indicated that rinse-release was observed was scaled to the surface area to volume ratio of field-emplaced saltstone monoliths at the SDF, the projected peak fractional releases were small (i.e., less than 1 mrem/yr) even if a rinse of the entire surface area of the saltstone in a disposal structure occurred in one year, which is not expected by the NRC staff because of the limited amount of water infiltration projected at early times. Furthermore, core samples of field-emplaced saltstone showed releases consistent with the DOE conceptual model that Tc release from reduced saltstone is governed by the solubility of $TcO_2 \cdot 1.6\ H_2O$ or $TcO_2 \cdot 2\ H_2O$. Therefore, it does not appear that any additional volumetric release mechanisms, such as elevated releases from a “first flush” of the saltstone pore volume, releases from a “persistent oxidized fraction” of saltstone, or other unidentified volumetric release mechanism are needed to represent Tc release from field-emplaced saltstone. The importance of chemical conditions to Tc release is well understood and documented by the DOE and the NRC staff and will be monitored under both MF 5.01, “Releases from Field-Emplaced Saltstone” and MF 10.01 “Conceptual Model Implementation.” The NRC staff recommends closing MF 5.05 under both §61.41 and §61.42 POs because additional release mechanisms do not appear to be necessary to explain Tc release from field-emplace saltstone.

MF 6.02, “Tc Sorption in Disposal Structure Concrete”

The NRC staff developed MF 6.02 because of concerns about how the DOE modeled Tc retention in disposal structure concrete in an important alternative case in the DOE 2009 SDF PA. Specifically, the concern was based on the modeled re-reduction (and resulting retention and re-concentration) of previously-oxidized Tc in disposal structure concrete in Case K1,[10] which the DOE supplied in response to the NRC RAI Questions on the 2009 PA. As described in the NRC 2012 SDF TER, the NRC TER conclusions were heavily based on the DOE Case K, Case K1, and Case K2 because of concerns with the DOE Base Case in the 2009 PA. The NRC identified MF 6.02 as high-priority in the NRC 2013 SDF Monitoring Plan because the

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[10] As described in the NRC 2012 SDF TER, the NRC staff did not find Case A of the 2009 PA to be an appropriate compliance case and relied heavily on Case K1 in its review and conclusions of the 2012 TER because Case K1 resolved many of the concerns the NRC staff had about using Case A as a compliance case.

NRC staff determined that the projected Tc retention in disposal structure concrete in Case K1 significantly contributed to a reduction and delay in the projected peak dose, was not adequately supported, and appeared to be unrealistic. The NRC staff determined that the modeled re-reduction and re-concentration of Tc in disposal structure concrete was not adequately supported because there was no experimental evidence that Tc could be reduced by flowing through a reduced cementitious material, or that it could then be re-concentrated to concentrations over ten times the original concentration in the waste form, as modeled in Case K1. The NRC staff determined that the projected re-reduction of Tc in the disposal structure concrete was unrealistic for the following three reasons:

- disposal structure concrete was expected to have about 40% of the specific reducing capacity of saltstone due to its lower blast furnace slag concentration and, therefore, was not expected to retain Tc more effectively than saltstone;
- disposal structure floors and walls were designed to be more exposed to environmental conditions than saltstone and therefore, appeared to be more likely to fracture than saltstone; and
- fractures in disposal structure concrete, or joints between disposal structure floors and walls, were expected to be oxidized by inflowing water and therefore, it was not expected that those conduits would effectively reduce and retain Tc that had been oxidized in the waste form.

Recent research has not changed those previous NRC staff reasons for finding the re-reduction and re-concentration of Tc projected in Case K1 to be unrealistic. However, changes that the DOE made in both the 2013 and 2014 Evaluation Cases, including replacing the average-K_d approach used in Case K1[11], significantly reduced the modeled retention of Tc in disposal structure concrete. The reduced risk-significance of Tc retention in disposal structure concrete was demonstrated in the FY 2013 Special Analysis Document. In sensitivity analyses that the DOE used to support that document, the DOE altered the 2013 Evaluation Case and a number of alternative cases to test the effects of modeling those cases with oxidized disposal structure concrete. Figure 13 shows the results of a sensitivity case conducted for a 150-foot disposal structure to test the effects of assuming different solubility values for Tc in reduced saltstone, and, for each solubility, alternatively assuming the disposal structure concrete is oxidized or reduced. As shown in Figure 13, assuming the disposal structure concrete is either chemically reduced or oxidizing had little to no effect on the projected flux of Tc from the disposal structure. The same modeling tests run for SDS 4 yielded similar results. Similar sensitivity analyses were not conducted for a 375-foot disposal structure because that disposal structure design was not included in the FY 2013 Special Analysis Document. However, because of similarities in the designs of a 150-foot and a 375-foot disposal structure, the NRC staff expects that the results for a 375-foot disposal structure would be similar to the results for a 150-foot disposal structure.

In addition to those sensitivity analyses, the DOE also evaluated the effect of assuming disposal structure concrete was oxidized in sensitivity analyses that modeled non-depleting sources of oxygen in saltstone. For those analyses, the effect of assuming oxidized disposal structure concrete had a greater effect for a 150-foot disposal structure than it did for SDS 4. For SDS 4, the effect of assuming oxidized disposal structure concrete was minimal (see Figure 14).

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[11] In the 2009 PA, the DOE referred to this approach as a "single-porosity" approach. To avoid confusion with the use of the term "single-porosity" in fracture flow modeling, the NRC staff refers to the Case K1 Tc release model as an "average-K_d" approach.

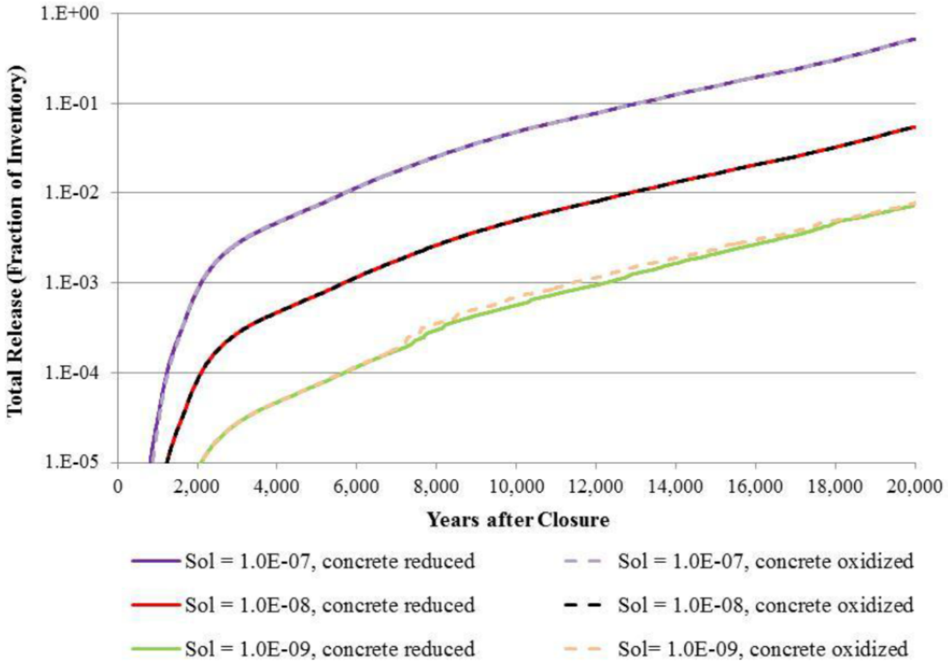

Figure 13. Projected Tc release from a 150-foot disposal structure for three different Tc solubilities in reduced saltstone, with disposal structure concrete either initially completely oxidized or initially completely reduced (from SRR-CWDA-2013-00062 Figure 5.6-81)

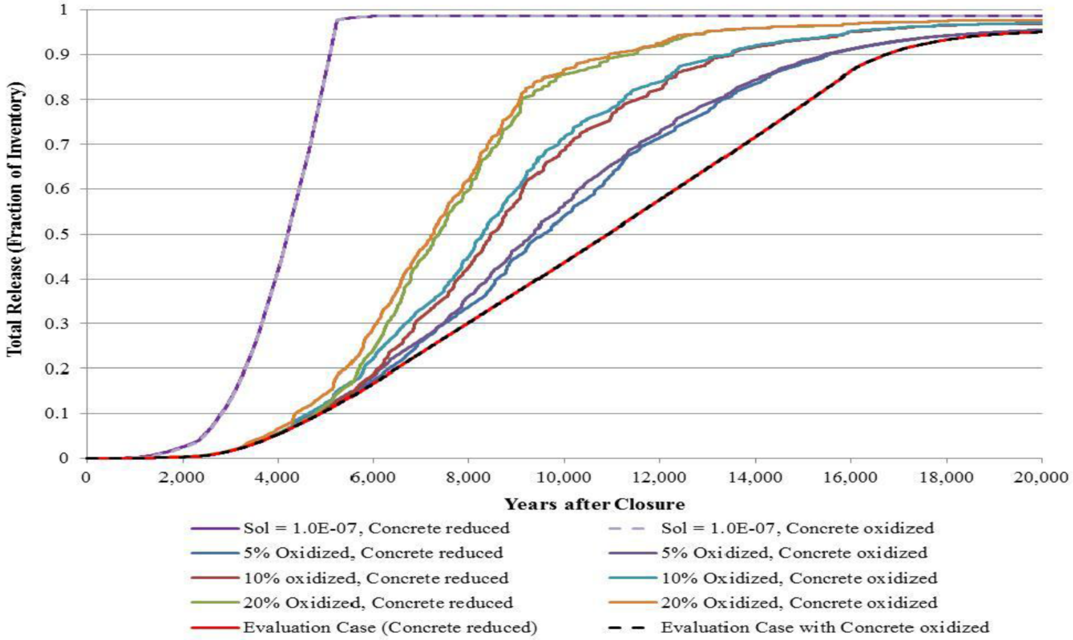

Figure 14. Projected Tc release from SDS 4 with 0%, 5%, 10%, and 20% of saltstone occupied by non-depleting sources of oxygen, with disposal structure concrete either initially completely oxidized or initially completely reduced (from SRR-CWDA-2013-00062 Figure 5.6-82)

For a 150-foot disposal structure, the effect of assuming initially oxidized disposal structure concrete was more pronounced than it was for SDS 4; however, the effect was much less significant than it was for Case K1 in the 2009 PA (see Figure 15). The largest effect of assuming oxidizing disposal structure concrete was for a case modeling a 150-foot disposal structure with 20% of saltstone occupied by non-depleting sources of oxygen. In that case, the assumption about the initial chemical state of the disposal structure concrete caused a maximum of approximately a factor of three difference in Tc release. That factor of three difference occurred at approximately 7,000 years after site closure (note the logarithmic scale). The difference at other times, including 1,000 years and 10,000 years after site closure, was much smaller. Therefore, the effect of assuming the disposal structure concrete was initially oxidized primarily resulted in a change to the timing, and not the magnitude of the projected flux. The maximum differences for assuming different disposal structure concrete oxidation states if there were 5% and 10% non-depleting sources of oxygen in saltstone also were smaller.

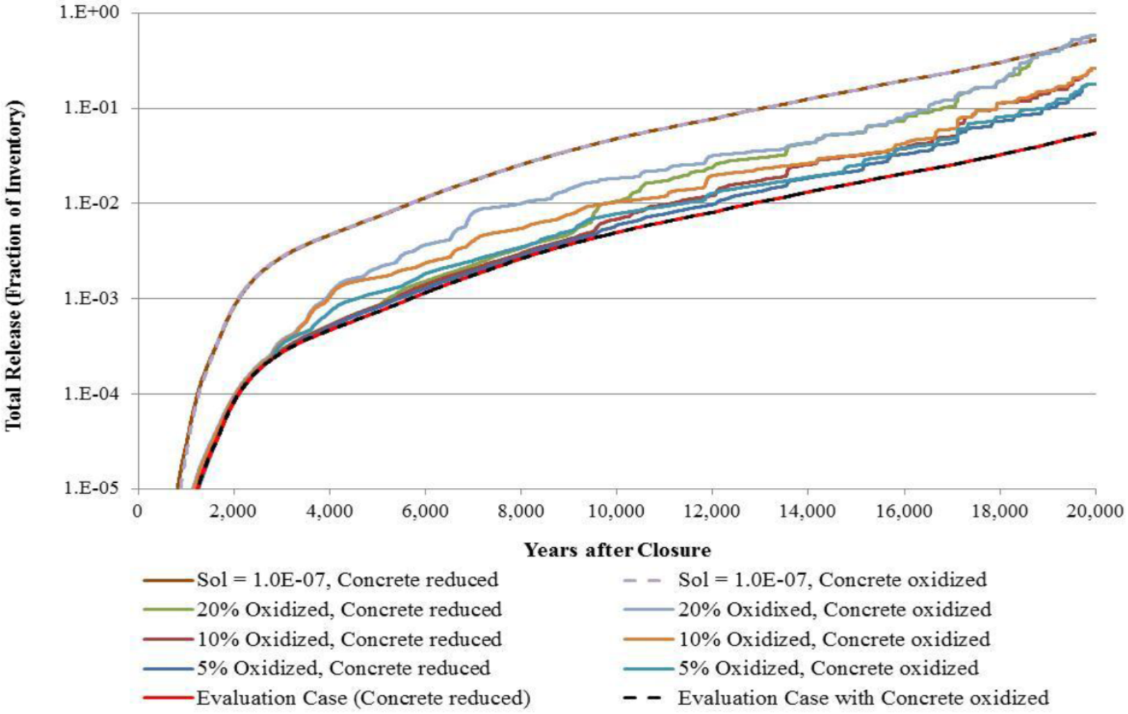

Figure 15. Projected Tc release from a 150-foot disposal structure with 0%, 5%, 10%, and 20% of saltstone occupied by non-depleting sources of oxygen, with disposal structure concrete either initially completely oxidized or initially completely reduced (from SRR-CWDA-2013-00062 Figure 5.6-83)

As shown in Figure 13, Figure 14, and Figure 15, the reduction in the Tc release rate attributable to retention in the disposal structure concrete is negligible in the 2013 Evaluation Case and minimal or limited in the relevant sensitivity analyses. Although the DOE did not repeat those sensitivity analyses with the models that the DOE used to support the FY 2014 Special Analysis Document, the NRC staff expects the results would be similar because Tc release model for 2014 Evaluation Case is very similar to the Tc release model for the 2013 Evaluation Case. Specifically, both models represent Tc release from chemically reduced saltstone with the same solubility (i.e., 1×10^{-8} moles/L) and both models represent Tc release from chemically oxidized saltstone with a K_d of 0.5 mL/g. Most importantly, neither model uses the average-K_d approach that was used in Case K1 of the 2009 PA, which caused significant retention and re-concentration of Tc in disposal structure concrete that was unsupported by experimental evidence. There is a slight difference in how Tc release is modeled in the 2013 Evaluation Case versus the 2014 Evaluation Case. In the 2014 Evaluation Case, Tc is projected to be released gradually from a finite element as the modeled reducing capacity in that element is consumed. In the 2013 Evaluation Case, the release is switched from being solubility limited to being sorption-controlled with a K_d of 0.5 mL/g only when all of the residual reducing capacity is consumed, resulting in a more sudden projected release. However, that change primarily affects the “spiky” nature of releases projected by the 2013 Evaluation Case, which the DOE and the NRC staff understood to be a modeling artifact. That model change is not expected to affect the modeled effect of assuming the disposal structure concrete is initially reduced or oxidized.

MF 6.02 was developed because of specific concerns about the average-K_d approach used in Case K1 of the 2009 PA and for specific reasons that Tc retention was thought to be over-estimated in the 2009 PA. In both the 2013 and 2014 Evaluation Cases, the DOE replaced the average-K_d approach used to represent Tc retention in disposal structure concrete in Case K1 of the 2009 PA. In addition, both the 2013 and 2014 Evaluation Cases include explicit modeling of construction joints in the disposal structure floors, which directly addresses one of the reasons that the NRC staff developed MF 6.02.

Summary for MF 6.02

The NRC 2013 SDF Monitoring Plan indicates the NRC staff expects to close MF 6.02 under both §61.41 and §61.42 POs after the NRC determines that K_d values for Tc in reduced and oxidized disposal structure concrete are well-supported. Alternatively, if the DOE dose projection changes, then the NRC could determine that the potential dose from Tc is appropriate without Tc sorption in disposal structure concrete.

The NRC staff recommends closing MF 6.02 under both §61.41 and §61.42 POs because the NRC staff concerns that led its development have been resolved and the DOE has demonstrated that Tc sorption in the disposal structure concrete is not risk-significant in the model that the DOE used to support the FY 2014 Special Analysis Document. The NRC staff determines that the sorption coefficient for Tc in oxidized cementitious material that the DOE used in the 2014 Evaluation Case to be acceptable. In addition, the NRC staff determines that the DOE addressed the NRC staff concerns underlying the development of MF 6.02 by using an appropriate K_d value, discontinuing the average-K_d approach, and modeling fast pathways in disposal structure floors. Furthermore, in the FY 2013 Special Analysis Document, the DOE demonstrated the low risk significance of projected Tc transport through disposal structure concrete as it is implemented in the models that the DOE used to support the FY 2013 Special Analysis Document. That demonstration was not repeated in the FY 2014 Special Analysis Document; however, the NRC staff expects those results to be applicable to the models that the DOE used to support the FY 2014 Special Analysis Document because of close similarities in the modeling approaches used and the relevant features of the 150-foot and 375-foot disposal structures.

The DOE FY 2017 PA Maintenance Plan indicated that the DOE is reviewing the assumed degradation of disposal structure concrete. If the performance of disposal structure concrete is revised in future analyses and the concrete provides a significant delay or reduction in peak dose, then the NRC staff would expect an appropriate level of model support. The NRC staff expects the barrier performance of disposal structure concrete to be significantly less than that of saltstone for the same reasons as above, which are summarized below:

- lower reducing capacity of concrete relative to saltstone;
- exposure of the disposal structure concrete to environmental conditions, which would tend to increase its susceptibility to fracturing; and
- limited ability of fractured concrete as well as concrete with joints to reduce and retain Tc.

<u>MF 10.02, “Defensibility of Conceptual Models”</u>

MF 10.02 covers hydraulic as well as chemical performance of the SDF. This TRR addresses the part of the MF 10.02 related to Tc release.

Since the 2009 PA, the DOE modeled Tc release as dependent on the oxidation sate of the surrounding saltstone grout. In the Oxidation TRR, the NRC staff questioned that conceptual model, primarily because of the results of a study of simulated Cast Stone samples in contact with moist air (SRNL-STI-2013-00541). In that study, two simulated Cast Stone samples spiked with Tc-99 were created and designated Tc2 and Tc-4-1. Sample Tc2 was cured for 48 days in a sealed cylindrical mold and then exposed to air on one circular face for 50 days. Sample Tc-4-1 was cured for 10 days in a sealed container and was not intentionally exposed to air.

Each of the two samples was cut perpendicular to the long axis into circular sub-samples, which were referred to “depth-discrete sub-samples” because each had a different average depth from the exposed surface (see Figure 16).

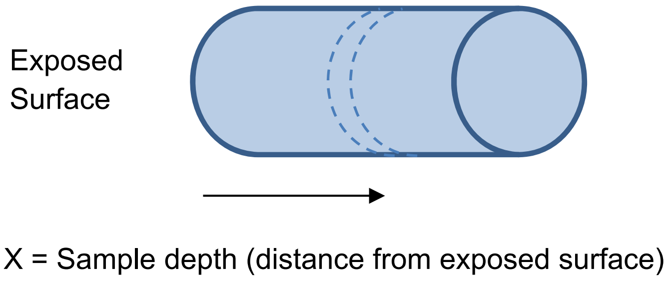

Figure 16. Diagram of a Depth-Discrete Sub-Sample of Simulated Sample of a Reducing Cementitious Waste Form

The sub-samples were then crushed in contact with air prior to leaching and chemical testing. The authors indicated they did not expect significant oxidation to take place during the crushing step because crushing took a relatively short amount of time (i.e., approximately 5 minutes). For Sample Tc2, part of each sub-sample was then leached in deareated, deionized water for 48 hours and part was used for a measurement of residual reducing capacity with the cerium (Ce) method (also called the Angus-Glasser method). For Sample Tc-4-1, only leaching was conducted. The authors of the study interpreted the amount of the Tc leached from each sub-sample to represent the amount of Tc that had been oxidized in that sub-sample, although no direct spectroscopic measurements of oxidation state were made.

The main conclusion of that study (SRNL-STI-2013-00541) was that the residual reducing capacity in a depth-discrete subsample was not a good predictor of whether Tc at that depth was mobile. That conclusion directly contradicted a fundamental assumption of the DOE Tc release conceptual and mathematical models. The authors based that conclusion, in large part, on a comparison of the Tc leaching data shown in Figure 17 with a profile of residual reducing capacity in sample Tc2 shown in Figure 18.

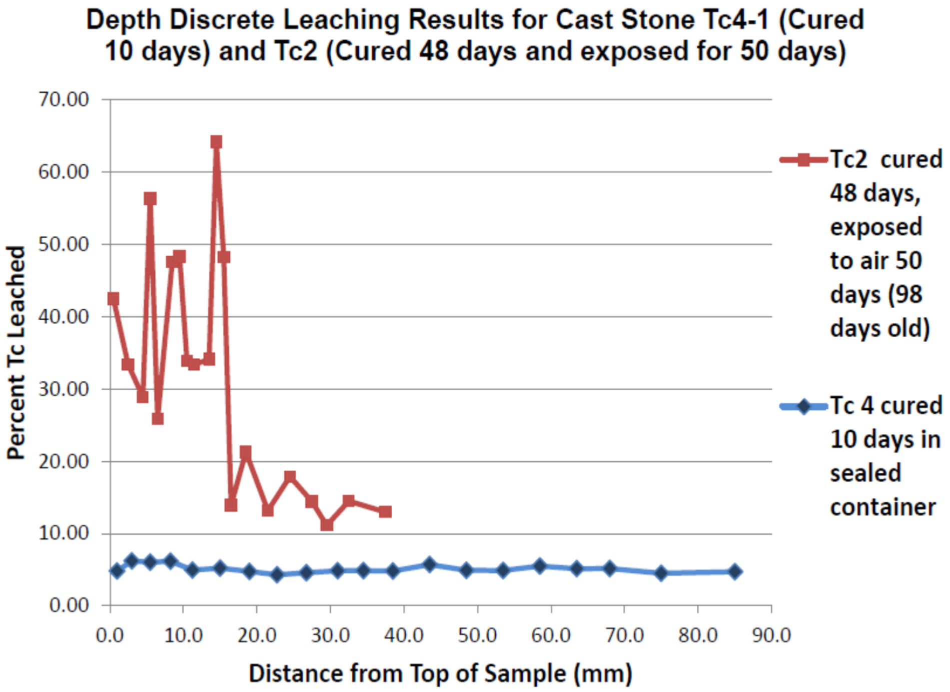

Figure 17. Percent of Tc released from depth-discrete sub-samples of a simulated cast stone sample exposed to atmospheric oxygen at one surface (0 mm) (from SRNL-STI-2013-00541 Figure 3-3)

Figure 18 appears to show a depletion of reducing capacity in approximately the first 5 mm of the sample, as measured from the exposed surface. The authors compared that result to Figure 17, which shows elevated fractional releases extended approximately 17 mm from the exposed surface. Based on that comparison, the authors drew the conclusions that residual reducing capacity was not a good predictor of Tc mobility and Tc could be mobile in areas of the sample that still had residual reducing capacity. The authors still attributed the increased Tc mobility to Tc oxidation from Tc(IV) to Tc(VII). To explain the difference between the measured depth of the depletion of residual reducing capacity versus the “Tc-specific oxidation front,” as measured by fractional Tc releases, the authors hypothesized that oxygen preferentially reacted with Tc to oxidize it before consuming the reducing capacity in the area.

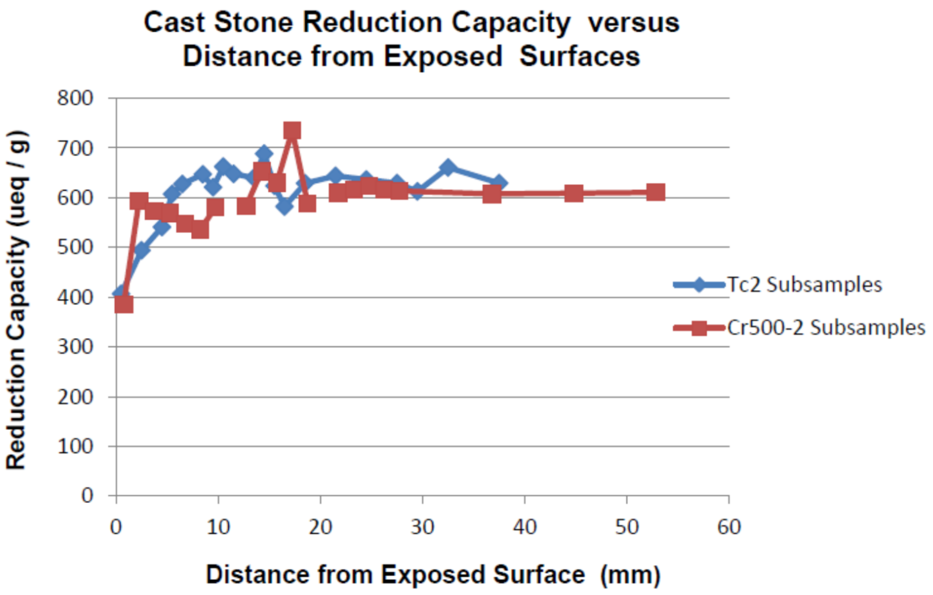

Figure 18. Residual reducing capacity in two samples of simulated Cast Stone as a function of depth from a surface exposed to air for 50 days (sample Tc2) or 68 days (Sample labeled "Cr500-2") (from SRNL-STI-2013-00541 Figure 3-4)
Note: Although the graph legend in the original paper refers to "Cr500-2," the figure caption and all the data provided in the report refer to "Cr500-1"

The authors further supported their conclusion about the sensitivity of Tc mobility to oxygen exposure by comparing the results from sample Tc2 and Sample Tc-4-1. The authors pointed out that the fractional release of Tc-99 from the Tc-4-1, which had not been intentionally exposed to oxygen, had a fractional release of Tc approximately eight times less than the fractional release of Tc from the top 16 mm of Sample Tc2 and approximately three times less than the fraction release from the rest of sample Tc2 (see Figure 17). However, those ratios of eight times and three times the amount of Tc leached in one sample as compared to another are only true based on fractional releases. Another interpretation of the same data is that the concentrations of Tc in the leachate from all the subsamples of both samples were fairly consistent.

Figure 19 shows the aqueous concentrations of Tc in the leachate from the two Tc-spiked simulated Cast Stone samples. The data is from a table in the DOE document SRNL-STI-2013-00541. Those samples do not show the same pattern as the fractional releases of Tc that appears in Figure 17. Instead, the pattern in Figure 17 appears to be an artifact of the author's chosen thickness of the depth-discrete sub-samples. The authors explained that "The thickness of the subsamples ranged from less than 1 mm to several mm depending on the location along the cylinder and the desired resolution of the sample location versus the fraction leached." However, choosing different sub-samples masses and reporting the values as the percent leached caused similar release concentrations (see Figure 19) to appear to have a pattern as a function of depth because the authors chose to use larger sub-samples for the deeper samples. In general, fractional Tc release was inversely correlated to the sub-sample mass (see Figure 20). That is the pattern that would be expected if the leachate concentrations were fairly consistent (e.g., because of a solubility limit) and were represented as fractional releases of different sub-sample masses. Indeed, the leachate concentrations observed in SRNL-STI-

2013-00541 were similar to the leachate concentrations observed in recent dynamic leach testing (see Figure 3).

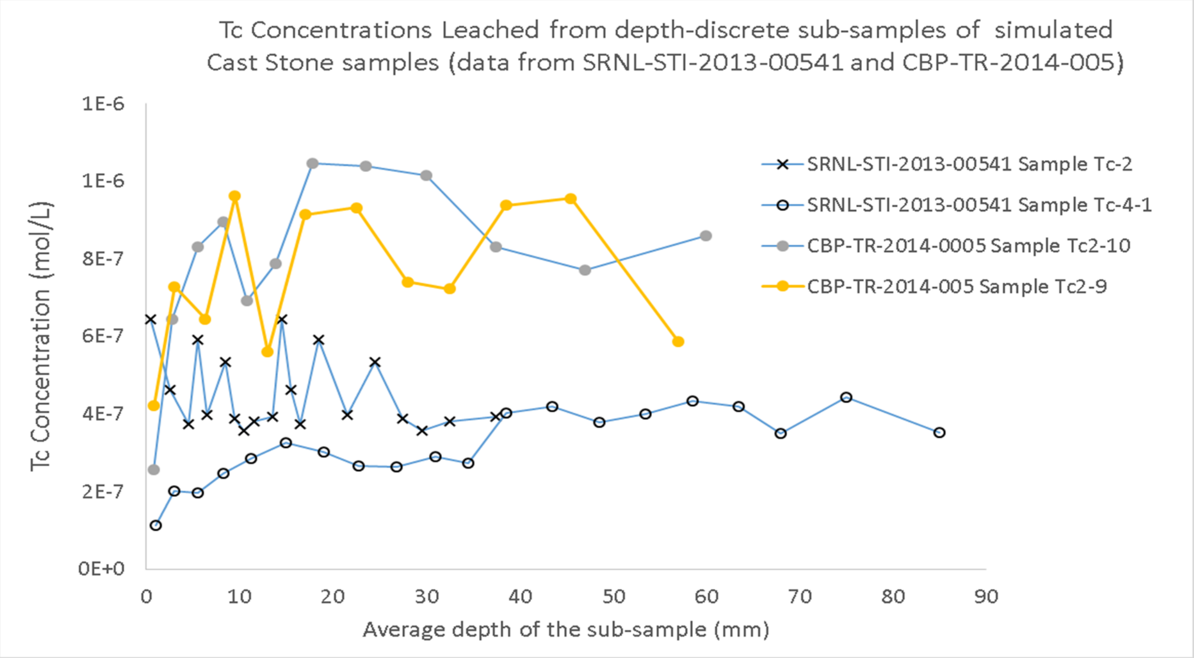

Figure 19. Concentrations of Tc leached from depth-discrete subsamples of simulated Cast Stone samples (created from data in SRNL-STI-2013-00541 and CBP-TR-2014-005)

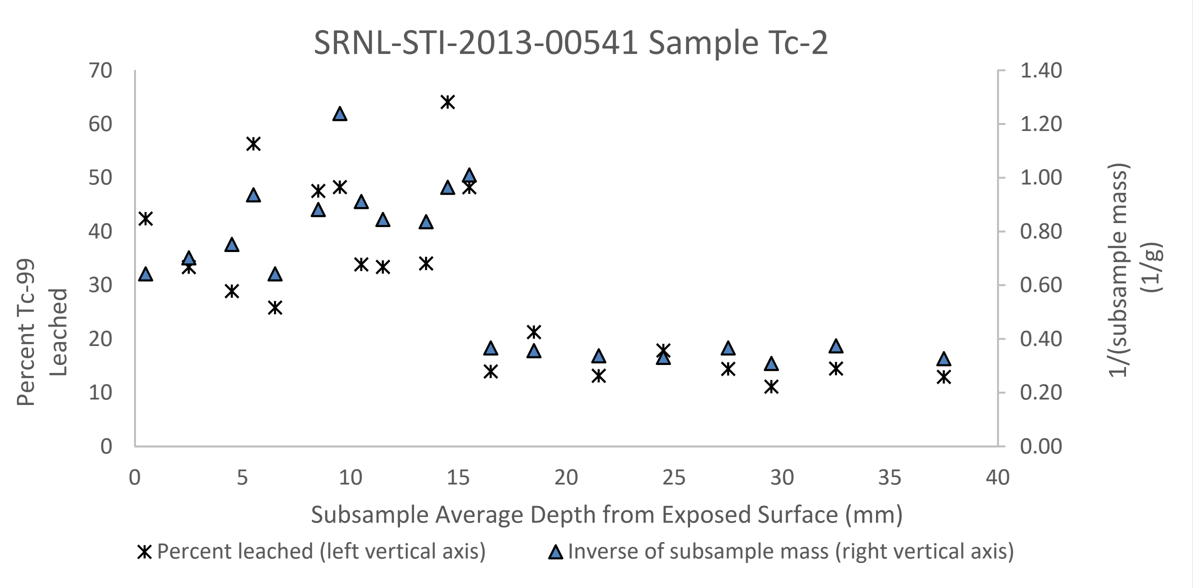

Figure 20. The left axis corresponds to the fractional release data from Figure 17 (ж) and the right axis corresponds to the inverse of the sub-sample thickness chosen for the given sub-sample depth (▲) (created from data in SRNL-STI-2013-00541)

A similar study of intact samples of simulated Cast Stone (PNNL-25578) did not find the clear evidence of a Tc-specific oxidation front implied by the data in Figure 17. In that PNNL study, samples of simulated Cast Stone were fully submerged in water that was open to the atmosphere (i.e., oxic conditions). As in SREL-STI-2010-00541, the leachate was initially replaced on a schedule prescribed by EPA Method 1315. However, unlike SREL-STI-2010-00541, after the replacement schedule dictated by EPA Method 1315, the samples remained submerged in water open to the atmosphere for a total of between 569 days[12] and 590 days, broken into two sampling intervals (with leachate replacement). After that initial leaching period, the samples were then stored in their final leachate in closed containers from between 319 and 393 additional days. Despite the longer exposure time than was used in SRNL-STI-00541, the PNNL study did not find a trend of greater Tc mobility closer to the exposed surfaces of the sample. Instead, the study found lower fractional releases overall, with a slight trend toward increasing releases further from the exposed surfaces (see Figure 21). The authors of PNNL-25578 described their results as showing "little oxygen ingress into the monolith."

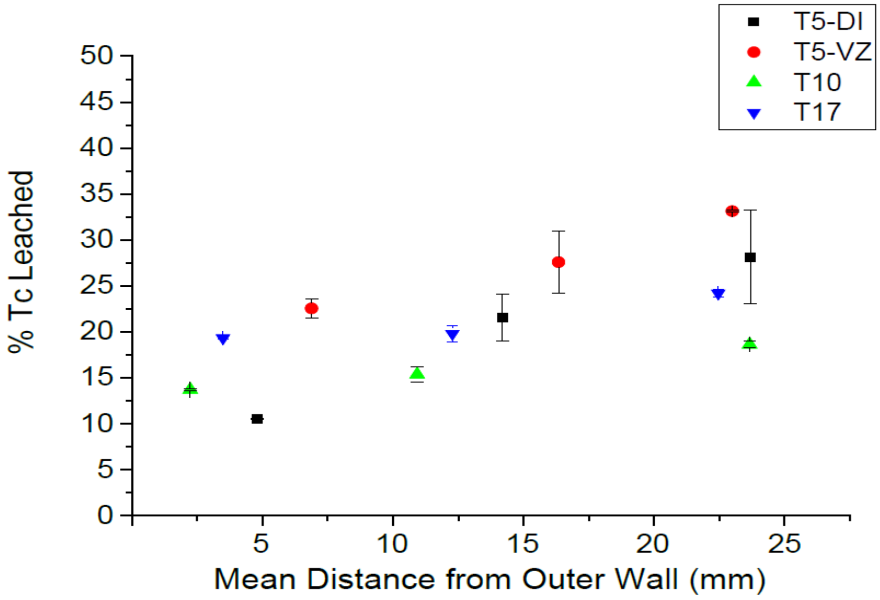

Figure 21. Percent Tc released from four simulated Cast Stone samples as a function of the distance from an outer sample wall exposed to oxic leachate for 569 to 590 days and stored in a closed container for an additional 319 to 393 days (from PNNL-25578 Figure 3-5)

Because the authors of PNNL-25578 used uniform sizes for the majority of sub-samples, the trends in Figure 21 are not correlated with the inverse of sub-sample size as the apparent "Tc-specific oxidation front" is in SRNL-STI-2010-00541 (see Figure 20). The authors of PNNL-25578 compared their results to the results of SRNL-STI-2010-00541 and noted there was, in general, a lower fraction of Tc release in their study, and that the trend of increasing Tc mobility toward the center of their simulated Cast Stone samples was opposite the apparent trend shown in Figure 17. The authors of PNNL-25578 attributed the difference between their results

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[12] Conflicting information was given for the initial leaching times of Samples 5T-DI and 5-VZ, which are reported as 570 days on page 2.1 of PNNL-25578 and 569 days on page 3.1 of the same document. The remaining four samples were initially leached for 590 days.

and those in SRNL-STI-2010-00541 to the gas-phase transport of oxygen in the SRNL study, in which the samples were exposed to moist air, instead of being submerged, as they were in the PNNL study. Another major difference between the two studies was the extended sample time used in the PNNL study (i.e., years) as compared to the 63-day leaching time used in the SRNL study. However, it seems likely that the results of PNNL-25578 did not reproduce the trend the authors of SRNL-STI-2013-00541 identified in Figure 17 because that trend was spurious. Aside from the saturated conditions used in the PNNL study and the unsaturated conditions used in the SRNL study, and the longer exposure time used in the PNNL study, the two studies were similar. For example, mobility was assessed with the same deionized water leaching procedure after depth-discrete or radially-discrete sampling. In addition, both studies used similar Tc concentrations in the simulated Cast Stone samples. Those concentrations were within an order of magnitude of the Tc concentrations in saltstone that the DOE projected for most of the SDF (see Table 4).

Table 4. Comparison of Tc concentrations in saltstone and simulated waste forms

Reference (Study or Model)	Grout Type	Tc Concentration (pCi Tc / g grout)
SREL DOC No. R-17-0005	Field-emplaced saltstone (value based on Tank 50 analysis)	6.4×10^{3} (a)
FY 2014 Special Analysis Document (SRR-CWDA-2014-00006, Rev. 2)	Projected value for saltstone in SDS 3A, SDS 3B, SDS 5A, and SDS 5B	2.9×10^{4} (b)
FY 2014 Special Analysis Document (SRR-CWDA-2014-00006, Rev. 2)	Projected value for saltstone in 375-foot disposal structures	1.6×10^{4} (b)
SRNL-STI-2013-00541	Simulated Cast Stone Sample Tc2	6.9×10^{4} to 7.8×10^{4} (c)
PNNL-25578	Simulated Cast Stone	1.3×10^{5} to 1.8×10^{5} (d)

[a] Concentration given in Table 2 of SREL DOC No. R-17-0005 based on Tank 50 sample analysis.

[b] Concentrations calculated by the NRC staff based on total inventory given in Table 3.4-1 of the FY 2014 Special Analysis Document and the dimensions of the 150-foot and 375-foot disposal structures. Concentrations converted from a volume basis to a mass basis assuming a saturated grout density of 1.73 g/mL, which is the average of the saturated density of six samples of field-emplaced saltstone given in Table 3-4 of SRNL-STI-2016-00106.

[c] Concentrations given in Table 3-4 and Table 3-8 of SRNL-STI-2010-00541.

[d] Concentrations calculated by NRC staff based on spike concentrations given in Table 2-1 of PNNL-25578 and a liquid to premix ratio of 0.60. That liquid to premix ratio was given in two separate studies (i.e., PNNL-22747, PNNL-24297) that were precursors to PNNL-25578.

The PNNL study documented in PNNL-25578 used both a simulated Hanford vadose zone pore water (VZPW) and deionized water (DIW) in the long-term leaching experiments. For the Cast Stone samples submerged in VZPW, the authors observed an evenly distributed, white precipitate with a thickness of approximately 5 mm on the surface of the Cast Stone samples. The authors noted that a similar precipitate from an earlier study had previously been characterized and determined to be predominantly aragonite (i.e., a calcium carbonate polymorph). Two Cast Stone samples were submerged in DIW. One had an incomplete layer of a white precipitate and the other had several surface cracks infilled with white precipitate. Although the groundwater at SRS is more dilute than at Hanford, which would be expected to lead to less calcium carbonate precipitation at SRS, the DIW water used in the Cast Stone study would bound (i.e., is more dilute than) SRS groundwater. Therefore, it is significant that the Cast Stone samples leached in DIW also showed evidence of calcium carbonate precipitation.

Results from that PNNL study (PNNL-25578) and recent research from the CNWRA (ADAMS Accession No. ML17221A038) could indicate that calcium carbonate precipitate affects constituent release. Figure 22 shows that Tc was more concentrated closer to the exterior of the samples, where calcium carbonate precipitates were found. Greater concentrations of Tc at the exterior of the samples and a decreased mobility relative to the interior of the samples are both consistent with the formation of a secondary mineral phase affecting release behavior. Tc could be diffusing out of the sample and precipitating within the calcium carbonate phase. The resultant Tc in the calcium carbonate phase could be less mobile than the Tc in the interior of the samples. Alternatively, the observed greater mobility of Tc in the interior of the sample also could also be due to more mobile Tc diffusing from the interior of the sample, leaving less mobile Tc in the interior of the sample.

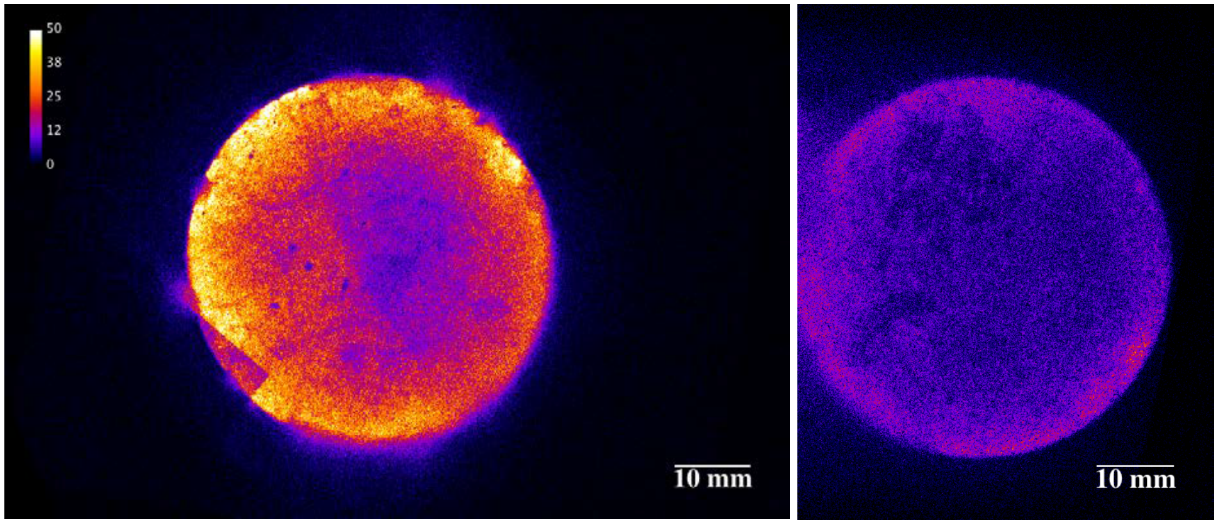

Figure 22. Beta autoradiography of two samples of simulated Cast Stone leached in deionized water (on the left) and simulated Hanford vadose zone water (on the right) Showing Tc concentrated near the edges of the samples (from PNNL-25578 Figure 3-13)

In addition, correlations between the releases of various constituents from samples of simulated saltstone in recent CNWRA research (ADAMS Accession No. ML17221A038) that used a dynamic leaching procedure are also consistent with the formation of a secondary mineral phase that could be affecting constituent release. Tc and Ca concentrations in the first two pore volumes did not correlate well (i.e., correlation coefficients of -0.090 for Sample SS2 and -0.729 for Sample SS3A). However, the release of Tc from simulated saltstone was strongly correlated with Ca after the first two pore volumes (i.e., correlation coefficients of 0.962 for Sample SS2 and 0.999 for Sample SS3A). Soluble species, such as potassium, sodium, nitrate, nitrite, and sulfate, also correlated strongly with Ca after the first two pore volumes. For Sample SS2 and Sample SS3A, the average correlation for those species with Ca was 0.951 and 0.991, respectively. The lag time between the leachant, which is in equilibrium with atmospheric CO_2, migrating through the samples and Tc correlating with Ca, is consistent with the conceptual model of a calcium carbonate phase precipitating and then affecting constituent release.

More research is needed to determine if a calcium carbonate phase is affecting the release of constituents, such as Tc. Both the DOE and the CNWRA are continuing research efforts to better understand constituent release from saltstone. As part of that research, the DOE is planning to conduct mineralogical analyses of the samples before and after leaching (SRR-CWDA-2017-00085). Coupling solid and liquid-phase analyses with geochemical modeling could provide important insights for modeling future constituent release from saltstone. The NRC staff will continue to monitor information about the potential effects of secondary minerals on Tc release under MF 10.02 and MF 5.01.

Summary for MF 10.02

The NRC 2013 SDF Monitoring Plan indicates the NRC staff expects to close MF 10.02 under both §61.41 and §61.42 POs after the DOE updates the PA and the NRC determines that the conceptual models are appropriate.

The conceptual models for the SDF include a range of hydraulic and chemical phenomena that are beyond the scope of this TRR. Therefore, the NRC staff does not recommend any change to the status or priority of MF 10.02. However; the NRC staff concerns about the conceptual model that Tc release can be modeled based on projected residual reducing capacity have been alleviated.

Although PAB staff does not recommend a change in status (i.e., open or closed) or priority of MF 10.02 at this time, taken together, the information described in this TRR provides a basis for a change in the NRC staff conceptual model of Tc release. Previously, the NRC staff conceptual model had been that Tc oxidation was the dominant factor influencing Tc release. That conceptual model was based on references to “immobile” reduced Tc and “mobile” oxidized Tc and previous DOE studies that appeared to show the sensitivity of Tc to trace quantities of oxygen. That conceptual model also appeared to be pervasive in experiments with Tc, with one author even commenting that: “Soluble Tc was leached from all of the depth-discrete subsamples… which strongly suggests that oxygen was present in the entire length of both samples.” In this TRR, the NRC staff compared the results from that study with results of recent research conducted by the DOE and determined that the results were consistent with an alternative conceptual model in which the releases did not indicate pervasive oxidation of the samples and instead indicated normal releases from reduced Tc. This TRR describes the lines of evidence for a conceptual model, supported by the results of both modeling analyses and recent research conducted by the DOE, in which Tc is not very sensitive to trace quantities of oxygen and projected SDF performance is governed equally, if not more, by releases from reduced Tc as it is by Tc oxidation. In addition, preliminary evidence indicated the potential importance of secondary mineral formation to Tc release. The NRC staff will monitor information about that process under MF 10.02 and MF 5.01.

Follow-up Actions

There are no Follow-up Actions related to this TRR.

Open Issues

There are no Open Issues related to this TRR.

Conclusions

In the NRC 2012 SDF TER and the subsequent TRRs on Tc Solubility and Oxidation of Reducing Waste Forms, the NRC identified several potential concerns related to the projected performance of the saltstone waste form and disposal structures as chemical barriers to Tc release. This TRR addressed and updated many of the issues raised in those TRRs in the context of new research results based on cores of field-emplaced saltstone from SDS 2A and new modeling analyses conducted by the DOE. Table 5 summarizes the status and priority of monitoring factors described in this TRR, including any changes recommended by the NRC staff.

Table 5. Summary of status and priority of monitoring factors described in this TRR under both §61.41 and §61.42 Performance Objectives

Monitoring Factor Number and Title	Status	Priority
5.01, “Radionuclide Release from Field-Emplaced Saltstone”	No change (open)	No change (high)
5.02, “Chemical Reduction of Tc by Saltstone”	No change (open)	Recommended change from high to medium
5.03, “Reducing Capacity of Saltstone”	No change (open)	Recommended change from medium to low
5.05, “Potential for Short-Term Rinse-Release from Saltstone"	Recommended closure	Not applicable because of recommended closure (was medium)
6.02, “Tc Sorption in Disposal Structure Concrete”	Recommended closure	Not applicable because of recommended closure (was high)
10.02, “Defensibility of Conceptual Models”	No change* (open)	No change* (high)

* This TRR describes a change in the NRC staff conceptual model of projected Tc release from saltstone at the SDF. Although no change to the status or priority of MF 10.02 was recommended, the recommended changes in status and priority of other monitoring factors described in this TRR reflect that change in the NRC staff conceptual model

The recent DOE research on cores of field-emplaced saltstone provided strong model support for the projected release of Tc from saltstone. Those results showed Tc releases greater than those assumed in the 2014 Evaluation Case. However, those releases were consistent with the DOE conceptual model that the release of reduced Tc is governed by the solubility of $TcO_2 \cdot 1.6\ H_2O$ or $TcO_2 \cdot 2\ H_2O$. The difference between the Tc solubility assumed in the 2014 Evaluation Case and the calculated $TcO_2 \cdot 1.6\ H_2O$ or $TcO_2 \cdot 2\ H_2O$ solubility appears to have occurred because the chemical conditions of early releases were not adequately accounted for in the 2014 Evaluation Case. As described in both the Solubility TRR and the 2012 TER, the NRC staff previously expressed concern about the DOE modeling of chemical conditions for the first few pore volumes of water to flow through saltstone. In 2014 Evaluation Case, the DOE projects that it will take thousands of years for the first few pore volumes of liquid to move through saltstone. Therefore, the chemical conditions of those releases cannot be discounted as a short-term transient event.

The results discussed in this TRR provide a basis for a change in the NRC staff conceptual model of Tc release. Previously, the NRC staff conceptual model had been that Tc oxidation was the dominant factor influencing Tc release. This TRR describes the lines of evidence for a conceptual model in which the projected SDF performance is governed equally, if not more, by releases from reduced Tc as it is by Tc oxidation. In this TRR, that shift in the conceptual model is supported by the following lines of evidence:

- consistency of releases of Tc from cores of field-emplaced saltstone with releases from $TcO_2 \cdot 1.6\ H_2O$ or $TcO_2 \cdot 2\ H_2O$ at pH values of “young” cementitious material (i.e., around pH 12) in research conducted by the DOE;

- re-evaluation by the NRC staff of previous studies that had had appeared to show the sensitivity of Tc to trace quantities of oxygen, resulting in a demonstration that the prior results were generally consistent with the projected release from chemically reduced Tc and that some were apparently due to experimental artifacts;

- results from studies conducted by the DOE with cores of field-emplaced saltstone that showed comparable releases from core samples leached with deareated liquid and liquid equilibrated with laboratory air;

- an independent analysis by NRC staff that showed greater projected releases from reduced as compared to oxidized saltstone under conditions of uniform flow in intact saltstone with a Tc concentration and Tc sorption as assumed in the 2014 Evaluation Case and Tc release from reduced saltstone consistent with recent results from studies that the DOE conducted with cores of field-emplaced saltstone.

Taken together, those four lines of evidence provide a basis for a conceptual model in which the projected SDF performance is not as sensitive to hypothesized sources of oxidation as it is to:

- initial chemical conditions;
- persistence of those conditions; and
- solubility of reduced Tc under those conditions.

In addition, this shift in conceptual model is consistent with the results of sensitivity and uncertainty analyses conducted by the DOE that showed the large relative risk-significance of assumptions about Tc solubility in reduced saltstone, as compared with assumptions about saltstone reducing capacity. The shift in conceptual model for Tc release discussed in this TRR has resulted in recommended changes in the status or priority of several monitoring factors (see Table 5). In general, monitoring factors developed to address potential Tc oxidation have been recommended to be lowered in priority, and monitoring factors related to releases from reduced Tc have remained high priority. The NRC staff concerns about accurately capturing the conditions of saltstone in the first few pore volumes, as described in both the Solubility TRR and the 2012 SDF TER, are further supported by the results of recent research conducted by the DOE as described in the context of MF 5.01 in this TRR.

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