June 4, 2015

MEMORANDUM TO: Gregory F. Suber, Chief
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                  Division of Decommissioning, Uranium Recovery
                    and Waste Programs
                  Office of Nuclear Material Safety
                    and Safeguards

THRU: Christepher A. McKenney, Chief   **/RA/**
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FROM: A. Christianne Ridge, Sr. Systems Performance Analyst   **/RA/**
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     SUBJECT: TECHNICAL REVIEW: OXIDATION OF REDUCING
                        CEMENTITIOUS WASTE FORMS, DOCKET NO. PROJ0734

The U.S. Nuclear Regulatory Commission (NRC) staff performed this review pursuant to
Section 3116(b) of the National Defense Authorization Act for Fiscal Year (FY) 2005. This
report was performed in accordance with monitoring activities described in *U.S. Nuclear
Regulatory Commission Plan for Monitoring Disposal Actions Taken by the U.S. Department of
Energy at the Savannah River Site Saltstone Disposal Facility in Accordance with the National
Defense Authorization Act for Fiscal Year 2005, Revision 1* (2013 monitoring plan)
(ML13100A076). This technical review is related to Monitoring Factors (MF) 5.01 "Radionuclide
Release from Field-Emplaced Saltstone," MF 5.02 "Chemical Reduction of Tc by Saltstone," MF
5.03, "Reducing Capacity of Saltstone," and MF 5.05 "Potential for Short-Term Rinse-Release
from Saltstone."

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NRC staff made the following conclusions based on this review:

- A significant amount of chemical reduction of technetium (Tc) from Tc(VII) to Tc(IV) appears to occur within the first week of curing and additional chemical reduction may continue for months. However, no study has shown complete reduction of Tc(VII) in saltstone under conditions that are consistent with field-emplaced saltstone.

- Different methods of quantifying reducing capacity yield different measured reducing capacities of saltstone and its components. The cerium (Ce) method (also called the Angus-Glasser method) may overestimate the amount of reducing capacity available to reduce Tc in saltstone.

- It is unclear which components of saltstone dry premix or salt solution are responsible for the measured reducing capacity of saltstone. The identity of the components contributing reducing capacity is important to long-term predictions of the ability of saltstone to chemically reduce contaminants.

- There is evidence for gas-phase transport of oxygen in laboratory samples of a reducing grout exposed to moist soil.

- It is unclear how much reducing capacity is consumed during field-scale mixing, pumping, and pouring. Measurements of reducing capacity or studies designed to evaluate the progress of an oxidizing front in cored samples of field-emplaced saltstone may address this issue.

- Independent experiments suggest Tc oxidation is not well correlated to consumption of reducing capacity in reducing cementitious wasteforms.

- Short-term rinse-release may be a concern if significant saltstone oxidation occurs from gas-phase transport of oxygen into saltstone fractures prior to water infiltration to saltstone. Release of Tc that remains oxidized in saltstone (a "persistent oxidized fraction") also could contribute to this short-term release, if a fraction of Tc remains oxidized.

- There is evidence that once chromium (Cr) is oxidized in saltstone, it is not re-reduced by residual reducing capacity in saltstone if oxygen is present. The applicability of this result to Tc re-reduction is unclear. However, because Tc(IV) appears to be more readily oxidized in saltstone than Cr(IV), the result suggests if low levels of oxygen can keep Cr oxidized in areas of saltstone with residual reducing capacity, low levels of oxygen also could keep Tc oxidized in areas of saltstone with residual reducing capacity.

The NRC staff will continue to monitor information provided by the U.S. Department of Energy (DOE) as it is developed. As described in the NRC 2013 monitoring plan, additional information is needed to close Monitoring Factors (MF) 5.01, 5.02, 5.03, and 5.05. The NRC staff updated those information needs based on the information in this review.

For MF 5.01, "Radionuclide Release from Field-Emplaced Saltstone," the additional information needed includes the following:

- Measurements of radionuclide release from core samples of field-emplaced saltstone; and

- An estimate of the oxidation of Tc in saltstone that could occur if oxygen preferentially reacts with Tc before consuming saltstone reducing capacity. This estimate may be affected by the degree of fracturing expected in field-emplaced saltstone as a function of time.

For MF 5.02, "Chemical Reduction of Tc by Saltstone," the additional information needed includes the following:

- Experimental evidence supporting the degree of re-reduction of oxidized Tc that DOE predicts in mathematical models of Tc transport in saltstone; or

- Further analyses to combine DOE sensitivity analyses showing the effects of non-depleting sources of oxygen and fractions of Tc entering the saturated zone when oxidized (i.e., not undergoing re-reduction).

For MF 5.03, "Reducing Capacity of Saltstone," the additional information needed includes the following:

- Information to support the identity of the components of saltstone dry premix or salt solution that supply the measured reducing capacity in saltstone, the ability of these components to reduce Tc in saltstone under field conditions, and the expected evolution of the reducing capacity over time.

For MF 5.05, "Potential for Short-Term Rinse-Release from Saltstone," the additional information needed includes the following:

- Experimental measurements of rinse-release of risk-significant radionuclides from saltstone and an analysis of the effect of the release on the projected dose; and

- Analyses of the potential effect on dose of the fraction, if any, of Tc that is likely to be (1) rinsed from the surface of saltstone, (2) oxidized before advective flow of water through saltstone begins, or (3) not chemically reduced by saltstone. The analysis should also address potential effects of high ionic strength.

The NRC staff is reviewing the U.S. Department of Energy (DOE) "FY2014 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site" (ML14316A586). As part of the NRC's review, the NRC staff will continue to review these areas.

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

Enclosure:
Technical Review

- An estimate of the oxidation of Tc in saltstone that could occur if oxygen preferentially reacts with Tc before consuming saltstone reducing capacity. This estimate may be affected by the degree of fracturing expected in field-emplaced saltstone as a function of time.

For MF 5.02, "Chemical Reduction of Tc by Saltstone," the additional information needed includes the following:

- Experimental evidence supporting the degree of re-reduction of oxidized Tc that DOE predicts in mathematical models of Tc transport in saltstone; OR

- Further analyses to combine the effects of DOE sensitivity analyses showing the results of non-depleting sources of oxygen and certain fractions of Tc entering the saturated zone when oxidized (i.e., not undergoing re-reduction).

For MF 5.03, "Reducing Capacity of Saltstone," the additional information needed includes the following:

- Information to support the identity of the components of saltstone dry premix or salt solution that supply the measured reducing capacity in saltstone, the ability of these components to reduce Tc in saltstone under field conditions, and the expected evolution of the reducing capacity over time.

For MF 5.05, "Potential for Short-Term Rinse-Release from Saltstone," the additional information needed includes the following:

- Experimental measurements of rinse-release of risk-significant radionuclides from saltstone and an analysis of the effect of the release on the projected dose; and

- Analyses of the potential effect on dose of the fraction, if any, of Tc that is likely to be (1) rinsed from the surface of saltstone, (2) oxidized before advective flow of water through saltstone begins, or (3) not chemically reduced by saltstone. The analysis should also address potential effects of high ionic strength.

The NRC staff is reviewing the U.S. Department of Energy (DOE) "FY2014 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site" (ML14316A586). As part of the NRC's review, the NRC staff will continue to review these areas.

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

Enclosure:
Technical Review

ML15098A031

OFC	DWMEP:TR	DWMEP:LA	DWMEP:PM	DWMEP:BC
NAME	ARidge	TMoon	HFelsher	CMcKenney
DATE	4/20/15	4/29/15	4/30/15	6/4/15

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Technical Review: Oxidation of Technetium in Reducing Cementitious Material

June 2015

Reviewers: A. Ridge, G. Alexander, K. Pinkston, H. Arlt

Documents Reviewed:

Almond, P.M., Stefanko, D.B., and C.A. Langton, *Effect of Oxidation on Chromium Leaching and Redox Capacity of Slag-containing Waste Forms*. Cementitious Barriers Partnership. March, 2013. CBP-TR-2013-02. ML15105A170.

Almond, P.M., and Kaplan, D.I., *Distribution Coefficients (Kd) Generated from a Core Sample Collected from the Saltstone Disposal Facility*. Savannah River National Laboratory. Aiken, SC. April 30, 2011. SRNL-STI-2010-00667. ML113320284.

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

Langton, C.A. and P.M. Almond, *Cast Stone Oxidation Front Evaluation: Preliminary Results for Samples Exposed to Moist Air*. Savannah River National Laboratory. Aiken, SC. November 2013. SRNL-STI-2013-00541. ML15106A902.

Langton, C.A., *Tc Oxidation in Slag-based Sodium Salt Waste Forms Exposed to Water and Moist Hanford Soil*. Cementitious Barriers Partnership. August 2014. CBP-TR-2014-05. ML15105A171.

Kaplan, D.I., M.S. Lilley, P.M. Almond, and B.A. Powell, *Longterm Technetium Interactions with Reducing Cementitious Materials*. Savannah River National Laboratory. Aiken, SC. March 15, 2011. SRNL-STI-2010-00668. ML111290356.

Pabalan, R.T., Alexander, G.W., and D.J. Waiting, *Experimental Study of Contaminant Release from Reducing Grout*. Center for Nuclear Waste Regulatory Analyses, San Antonio, TX. March 29, 2012. ML112089A319.

Painter, S.L., and Pabalan, R.T. Estimated Longevity of Reducing Environments in Grouted Systems for Radioactive Waste Disposal. Center for Nuclear Waste Regulatory Analyses, San Antonio, TX. 2009. ML101160513.

Um,W., Jung, H.B., Wang, G., Westsik, J.H. Jr., and Peterson, R.A., *Characterization of Technetium Speciation in Cast Stone.* Pacific Northwest National Laboratory. November 2013. PNNL-22977. ML15105A154.

Witmer, M. and Powell, B.A., *Determination of Constituent Concentrations in Field Lysimeter Effluents, FY13 Final Report, Task 2: Lysimeter Leachate Chemistry*. Savannah River Remediation, LLC. Aiken, SC. September 2013. SRR-CWDA-2013-00121. ML15105A159.

Background

Saltstone is made by mixing radioactive liquid salt solution with cement, fly ash, and Blast Furnace Slag (BFS). The BFS is included to create a reducing environment to decrease the mobility of redox sensitive radionuclides, such as technetium (Tc). In the U.S. Department of Energy (DOE) "FY2014 Special Analysis for the Saltstone Disposal Facility at the Savannah River Site" (Fiscal Year (FY) 2014 Special Analysis) (ML14316A586), Tc-99 was the largest contributor to the projected dose within 50,000 years of site closure[1]. In accordance with NUREG-1854, "NRC Staff Guidance for Activities Related to U.S. Department of Energy Waste Determinations", the time for which the 0.25 mSv/yr (25 mrem/yr) dose limit in §61.41 must be met is generally[2] 10,000 years. However, as described in the NRC Request for Additional Information (RAI) regarding the FY 2013 Special Analysis for the Saltstone Facility (NRC, 2014a) (ML14148A153), the U.S. Nuclear Regulatory Commission (NRC) staff questions many of the DOE assumptions regarding the projected timing of the peak dose from Tc-99.

The solubility of Tc and its release from saltstone into the environment is strongly influenced by E_h. Tc is relatively insoluble and immobile in its reduced form (i.e., Tc(IV)) but mobile in its oxidized form (i.e., Tc(VII)). This behavior is key to projecting the long-term ability of saltstone to immobilize Tc, because the E_h of water in contact with saltstone will rise as oxygen consumes the reactive fraction of chemically reducing phases in the saltstone. The solubility of Tc is also pH dependent. Technetium is less soluble at the pH characteristic of middle-aged cementitious material (approximately 10.5) than at the high pH values found in fresh cementitious materials (approximately 12.5) (NRC, 2014b) (ML13304B159).

Different studies have come to different conclusions about how BFS contributes to the reducing capacity of saltstone. Um et al. (2013) (PNNL-22977) concluded both reduced sulfur and reduced iron species likely contribute to the reduction of Tc in samples of a reducing cementitious wasteform. Kaplan et al. (2008) (SRNS-STI-2008-00045) characterized ferrous iron (i.e., Fe(II)) as the most significant reducing agent contributed by BFS and sulfide as a precipitating agent that limits the solubility of several species, including Tc(IV). Arai and Powell (2014) (SRRA042328SR) also suggested that the reducing capacity contributed by BFS is attributable to ferrous iron species because they found that the sulfur in BFS oxidized to sulfate (SO_4^{2-}) within hours of contacting a simulated salt solution. However, Cantrell and Williams (2012) (PNNL-21723) suggest it is unclear whether ferrous iron contributes significantly to the reduction of Tc because ferrous iron has a low solubility at high pH values.

Some authors indicate fly ash should contribute additional reducing capacity to saltstone (Roberts and Kaplan, 2009 [SRNL-STI-2009-00637]). However, the reducing capacity attributable to fly ash depends on whether a Ce-based method[3] or a Cr-based method is used to measure the reducing capacity. The less acidic Cr-based method showed no measureable reducing capacity from fly ash (PNNL-22977).

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[1] I-129 caused the largest projected peak dose within 10,000 years of site closure.
[2] NUREG-1854 also indicates that assessments beyond 10,000 years may be necessary in some cases to demonstrate that the disposal of certain types of waste does not result in high impacts to future generations.
[3] Also referred to as the Angus-Glasser method.

This technical review by the NRC staff is related to Monitoring Factors 5.01 "Radionuclide Release from Field-Emplaced Saltstone," MF 5.02 "Chemical Reduction of Tc by Saltstone," MF 5.03 "Reducing Capacity of Saltstone," and MF 5.05 "Potential for Short-Term Rinse-Release from Saltstone" in the 2013 NRC monitoring plan for the Saltstone Disposal Facility (NRC, 2013) (ML13100A076). In the 2013 monitoring plan, the NRC staff noted that the studies that had been done to demonstrate Tc retention in saltstone included experimental artifacts that made it difficult to interpret the results. As described in the 2013 NRC monitoring plan under Monitoring Factor 5.01, the NRC staff concluded additional information is needed to show radionuclide release rates used in the DOE Performance Assessment (and subsequent Special Analyses) are reliable. Under Monitoring Factor 5.02, the NRC staff concluded that additional information is needed to support the modeled extent of Tc(VII) reduction to Tc(IV) by saltstone and the projected maintenance of Tc as Tc(IV) in saltstone. Under Monitoring Factor 5.03, the NRC staff concluded that additional information is needed to support the initial reducing capacity of saltstone and the expected evolution of redox conditions over time. Under Monitoring Factor 5.05, the NRC staff concluded that additional support was needed to support the assumption that short-term rinse release of radionuclides from saltstone seen in laboratory experiments will not significantly affect projected peak doses from groundwater pathways at the SDF.

The key references reviewed in this report provide additional information both on the chemical reduction of Tc by saltstone and the oxidation of the saltstone waste form.

Summaries of Technical Reports

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

Arai and Powell (2014) (SRRA042328SR)

This study used X-Ray Absorption Spectroscopy (XAS) to evaluate the speciation of Tc, sulfur, and iron in laboratory-prepared simulated saltstone samples. The study also included XAS measurements of speciation of sulfur species in saltstone leachate and BFS, as well as leaching tests of iron and sulfur from laboratory-prepared simulated saltstone samples. Available results include leaching and XAS results of simulated saltstone samples cured for 29 days in the presence of atmospheric oxygen. The study is ongoing and results from simulated saltstone samples cured for longer times are anticipated in the future.

In samples cured for 29 days, the researchers found that Tc existed in significant fractions of both Tc(IV) and Tc(VII). Specifically, using X-ray absorption near edge spectroscopy (XANES) measurements in the layer closest to the exposed surface, researchers found 38 percent Tc(IV) and 62 percent Tc(VII). In a layer further from the surface, researchers found 41 percent Tc(IV) and 59 percent Tc(VII). However, the authors noted that the relative amount of oxidized Tc may have been affected by the high concentrations of Tc used in the study to accommodate the XAS detection limit (i.e., over 200 times the concentration expected in saltstone).

XANES measurements of the oxidation state of sulfur in BFS showed that the sulfur in BFS was oxidized to SO_4^{2-} rapidly (i.e., within hours) after exposure to the simulated salt solution.

Um et al. (2013) (PNNL-22977)

This study evaluated the reducing capacity and oxidation of laboratory-prepared samples of simulated Cast Stone, as well as Tc speciation in and release from Cast Stone under a variety of leaching conditions. Cast Stone is a cementitious waste form made of Portland cement, BFS, and fly ash, with a composition very similar to saltstone. The dry premix for Cast Stone has a cement:slag:fly ash ratio of 8:47:45, whereas Saltstone has a cement:slag:fly ash ratio of 10:45:45.

To evaluate the main contributors to the reducing capacity, the researchers evaluated each dry component of the Cast Stone with two different measurement methods. The cerium (i.e., Ce(IV)) method uses a very acidic solution (i.e. pH of approximately 1 to 2) whereas the chromium (i.e., Cr(VI)) method uses a pH near 7 (i.e., approximately neutral). For the slags and fly ash samples (Table 1), the Ce(IV) method resulted in significantly greater measured reducing capacities than the Cr(VI) method. The authors attributed this difference to the difference in pH between the two measurement methods. Because the Ce(IV) method uses a lower pH, it typically measures larger reducing capacity than the Cr(VI) method because solids dissolve completely. In contrast, the Cr(VI) method typically does not completely dissolve solids and so may measure only the reducing capacity available on surfaces.

In addition, there is evidence that Cr(III) may react with Fe(III) to form a layer of Cr-Fe hydroxides that passivate the iron surfaces and prevent some of the reducing capacity of the ferrous iron from reacting. Despite this general trend, for the Portland cement sample the Cr(VI) method resulted in the greater measured reducing capacity than the Ce(IV) method. The authors suggested that the reducing capacity measured by the Cr(VI) method may have been overestimated because the Cr precipitated as Cr-carbonate phases.

Despite the differences in the reducing capacities of the dry components measured with the two different methods (Table 1), the reducing capacities of Cast Stone samples were similar when measured with the two different methods. In addition, the measured reducing capacities of the simulated Cast Stone samples were higher than would be predicted if the dry components were the only source of reducing capacity in the Cast Stone. The authors suggest both results are explained by reducing capacity contributed by dissolved NO_2^-, which contributes similarly to the reducing capacity measured by either method. However, the authors stated they did not expect the reducing capacity attributable to NO_2^- to effectively reduce Tc in Cast Stone because the reduction potential of the NO_2^-/ NO_3^- redox couple (approximately 0.01 millivolt) at the high pH of a cementitious wasteform is weak compared to the reduction potential of the Tc(IV) / Tc(VII) redox couple at high pH (approximately -0.36 millivolt).

Table 1. Adapted from Um et al (2013) (PNNL-22977). Reducing capacity of dry components of Cast Stone determined with two different measurement

Dry Ingredient	Reducing Capacity	
	Ce(IV) Method (meq/g)	Cr(VI) Method (meq/g)
Northwest Slag	0.793	0.078
Southeast Slag	0.800	0.226
Northwest Fly Ash	0.060	0.007
Southeast Fly Ash	0.288	0.000
Portland Cement (Type I/II)	0.042	0.349

methods.

Almond et al. (2013) (CBP-TR-2013-02)

This study was designed to test a method of analyzing contaminant leaching and redox capacity of reducing grout as a function of the distance from an exposed surface of a chemically reducing cementitious wasteform. The study demonstrates a method of "depth-discrete" sub-sampling, which was used in subsequent studies. The term "depth-discrete" subsampling refers to slicing the sample into disks parallel to the exposed surface, and then studying each slice.

The dry premix consisted of 10 percent Type I/II Portland cement, 45 percent Holcim BFS, and 45 percent Class F fly ash. The dry premix was blended with a simulated salt solution at liquid to dry premix ratio of 0.60. After 21 days of curing in the laboratory, the researchers moved the samples to an enclosure in the field and exposed one surface of the samples to air for either 118 or 302 days.

After the air exposure, the authors took depth-discrete subsamples and crushed each one separately in contact with air. They split each subsample in half to measure leachable Cr in one half and residual reducing capacity in the other. Samples were leached with deionized, de-aired water for either 18 ± 2 hours or 28 days.

The researchers found that the longer leaching time did not change the results. Leachable chromium was detected at greater depths in the sample exposed for 302 days than it was in the sample exposed to air for 118 days (at least 50 millimeters (mm) (2.0 inches) compared to at least 20 mm (0.79 inches)). They also found that the reducing capacity measured with the Ce(IV) method[4] was not a good predictor of the leachable Cr in each section. Once Cr was oxidized to Cr(VI), the authors found that it remained oxidized in regions of the samples where oxygen was present, even if residual reducing capacity was measured in those regions.

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[4] The authors referred to it as the Angus-Glasser method.

Langton (2014a) (CBP-TR-2014-05)

This study examined Tc leaching from two laboratory-prepared chemically reducing grouts exposed to moist soil or deionized water. The grout samples were poured into sealed cylindrical containers with a height of 90 mm (3.5 inches) and a diameter of 35 mm (1.4 inches). The samples were isolated from air in the containers and cured for 113 days[5] at ambient temperature (about 22 C) and 65 percent to 75 percent relative humidity. After curing, the samples were removed from the sealed containers and coated with epoxy to isolate them from oxygen, and a fresh surface was cut to allow exposure from one end of the cylinder. The samples were exposed to either moist soil or deionized water for 154 days. After the exposure period, leaching was evaluated as a function of depth from the surface with depth-discrete subsampling. The subsamples were then each ground before leaching for 48 ± 2 hours in deionized, de-aerated water.

The authors found that soluble Tc was leached from all of the depth-discrete subsamples from both samples (i.e., the sample exposed to deionized water and the sample exposed to moist soil). Although all depths had some fraction of leachable Tc, there was a front that separated areas of relatively more and less leachable Tc (Figure 1). The authors interpreted the
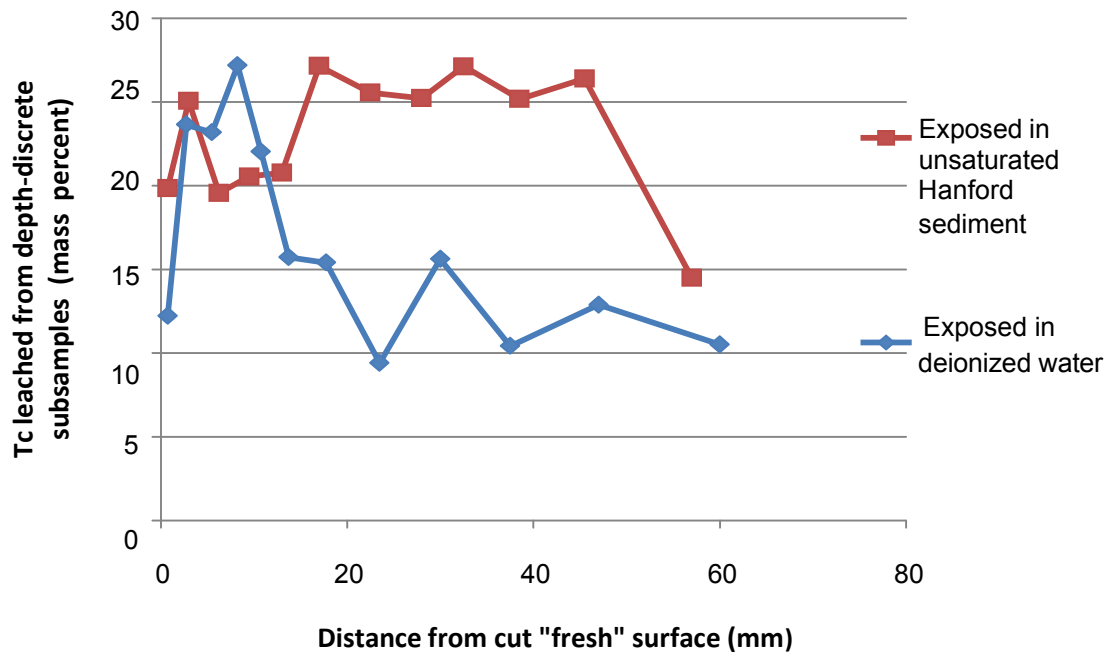

Figure 1. Adapted from Langton (2014a) (CBP-TR-2014-0005). Tc leached from samples of Cast Stone exposed to moist soil and deionized water.

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[5] The text of CBP-TR-2014-05 states samples were cured for 103 days; however Table 5 of CBP-TR-2014-05 states samples were cured for 113 days. The value from the table, 113 days, was used because it is consistent with the total sample age and days of exposure listed in Table 5 of CBP-TR-2014-05.

leachability of Tc along the entire length of the samples to suggest that oxygen had penetrated to parts of the entire length of both samples. The authors acknowledged that the small leachable fraction found throughout the sample could be an experimental artifact, because depth-discrete samples were crushed in contact with air prior to leaching. However, the authors also observed that, based on previous experiments (Langton *et al*., 2012), they would expect less than 5 percent of the Tc to oxidize during sample handling, as compared to more than 10 percent of Tc that could be leached in all of the depth-discrete subsamples.

The authors found that the front of increased Tc leachability extended further into the sample exposed to moist soil than it extended into the sample exposed to deionized water. The authors concluded from this observation that the rate of oxygen migration into the sample exposed to soil was faster than the rate of migration into the sample exposed to water. The authors concluded that this observation was consistent with the more rapid transport of ions through a gas phase as compared to a liquid phase.

Langton and Almond (2013) (SRNL-STI-2013-00541)

This experiment evaluated the oxidation of Cr and Tc in laboratory-prepared samples of Cast Stone, which has a formula similar to saltstone. Three samples are discussed in this summary, all of which were isolated from oxygen in sealed containers during curing at ambient temperatures (i.e., approximately 22 °C (72 °F)). The sealed containers were placed in a secondary container with moist towels to increase humidity (precise humidity values were not given). Of these three samples, one was spiked with Cr and two were spiked with Tc. The Cr spiked sample was cured for 63 days and exposed to moist air and Savannah River Site (SRS) ambient outdoor temperature for 68 days. One Tc-spiked sample was cured for 48 days and then exposed to moist air in a laboratory for 50 days. The other Tc-spiked sample was cured for 10 days and immediately sampled, without intentional air exposure.

For each of the three samples, the researchers cast the samples, and after curing, cut a fresh surface for exposure. The researchers then cut depth-discrete subsamples. In each subsample, they evaluated the leachability of Cr and Tc, as well as the reducing capacity as measured by the Ce(IV) method[6]. Oxidation of Cr and Tc was surmised based on their leachability. The researchers observed that the front of increased Tc leachability extended to a greater depth than the front of increased Cr leachability. In addition, in the area of increased Tc leachability, Tc was more leachable than Cr was. From these results (Table 2), the researchers concluded that Tc was more readily oxidized in the reducing grout samples than Cr was.

One of the key conclusions of the study was that the residual reducing capacity in a depth-discrete subsample was not a good predictor of whether Tc or Cr at that depth was chemically reduced. That is, the authors found a poor correlation between Tc leachability in the depth-discrete subsamples and the residual reducing capacity in the subsamples as measured by the Ce(IV) method. The authors suggested the correlation might be poor because oxygen entering

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[6] The authors referred to it as the Angus-Glasser method.

Table 2. From Langton and Almond (2013) (SRNL-STI-2013-00541). Fraction of constituents leached from depth-discrete samples of Cast Stone as a function of depth.

Cast Stone Sample	Distance from Surface (mm)	Weight Percent Leached			
		Na	NO_3^-	Tc-99	Cr
Cr500-1	0	98	52	--	0.5
	1	111	79	--	0.6
	3	97	84	--	<0.01
Tc2 Cured for 48 days and exposed for 50	0	90	75	40	--
	10	101	84	43	--
	16	94	89	15	--
Tc 4-1 Cured 10 days, No intentional exposure to air	1 - 85	Not measured	Not measured	5	Not measured

the samples reacted preferentially with the Tc and Cr before consuming the residual reducing capacity of the wasteform. In addition, the researchers found that oxidized Tc and Cr co-existed with residual reducing capacity in areas of the samples to which oxygen had penetrated. The researchers suggested that this finding showed that residual reducing capacity is not effective in re-reducing oxidized Cr or Tc if oxygen is present.

The authors also observed that in the sample cured for 10 days and not intentionally exposed to air, no Tc oxidation front was observed, but 5 percent of the Tc could be leached at each depth (Figure 2). The researchers concluded from this observation that 5 percent of the Tc remained oxidized after 10 days of curing, and suggested that additional testing at longer curing times would be needed to determine whether 100 percent of the Tc(VII) in Cast Stone could be reduced with longer curing times. However, the authors acknowledged that the oxidized fraction could be an experimental artifact because each depth-discrete subsample was crushed in contact with air prior to leaching.

Painter and Pabalan (2009)

This study used a numerical model to estimate oxidation front movement by aqueous diffusion in near-surface slag-bearing grouted systems. The researchers did not include movement of dissolved oxygen by water advection through the intact matrix in the mathematical model; however, they did consider dissolved oxygen in water entering fractures. They also considered gas-phase oxygen entering unsaturated fractures in the grout. The researchers evaluated grout oxidation for a range of hydrological conditions, fracturing scenarios, and grout parameter values, including reducing capacity. The numerical model is based on the assumption that there is no damage to the grout matrix (i.e., no change in parameters affecting oxygen diffusion) behind the oxidation front.
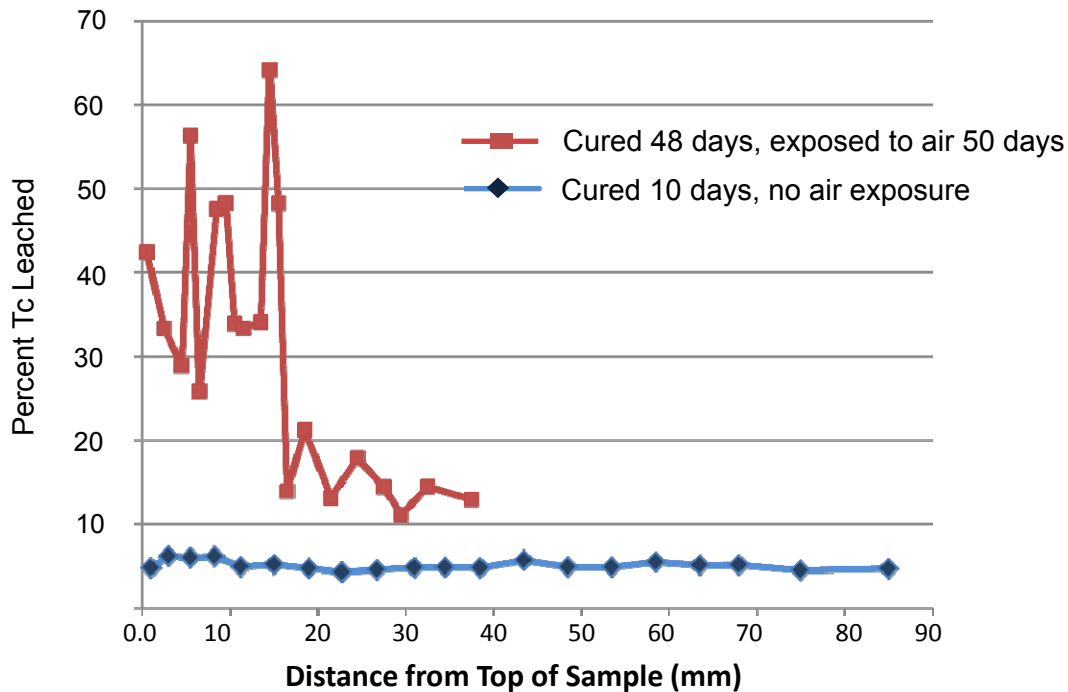
Figure 2. Adapted from Langton and Almond (2013) (SRNL-STI-2013-00541). Comparison of Tc-99 fraction leached as a function of distance from the top surface for a 10 day old and a 98 day old (exposed to air) Cast Stone sample.

The researchers also evaluated the effects of fracture saturation. As shown in Figure 3, certain assumed fracture characteristics allowed slight depletion of oxygen along the length of the fracture. The authors determined this effect was caused when the amount of water in the fracture, in combination with the size of the fracture aperture, was sufficient to limit diffusion of oxygen from the gas phase, but not sufficient to comparably increase advection of water through the fracture. However, the authors noted that in each case, the oxygen concentrations in the fractures returned to, or very close to, the steady-state concentration in the surrounding soil. The authors concluded this result occurs because oxygen transport in the fracture is fast compared to the diffusive loss of oxygen to the porous grout matrix. One of the central conclusions of the paper is that for a range of fracture characteristics, grout oxidation is limited by the diffusion rate in the grout. In addition, based on the approach to steady-state conditions shown in Figure 3, the authors observed that for the long time frames of interest in performance assessment, gas-phase diffusion and liquid-phase advection in the fractures can resupply the fractures with oxygen from the surrounding soil.

The authors also suggested that because diffusion in the pore space of intact grout material is expected to be the rate-limiting process for grout oxidation, detailed process-level models coupling fracture transport processes with matrix diffusion and chemical reactions are not needed to adequately project grout oxidation. Instead, fractures can represent internal
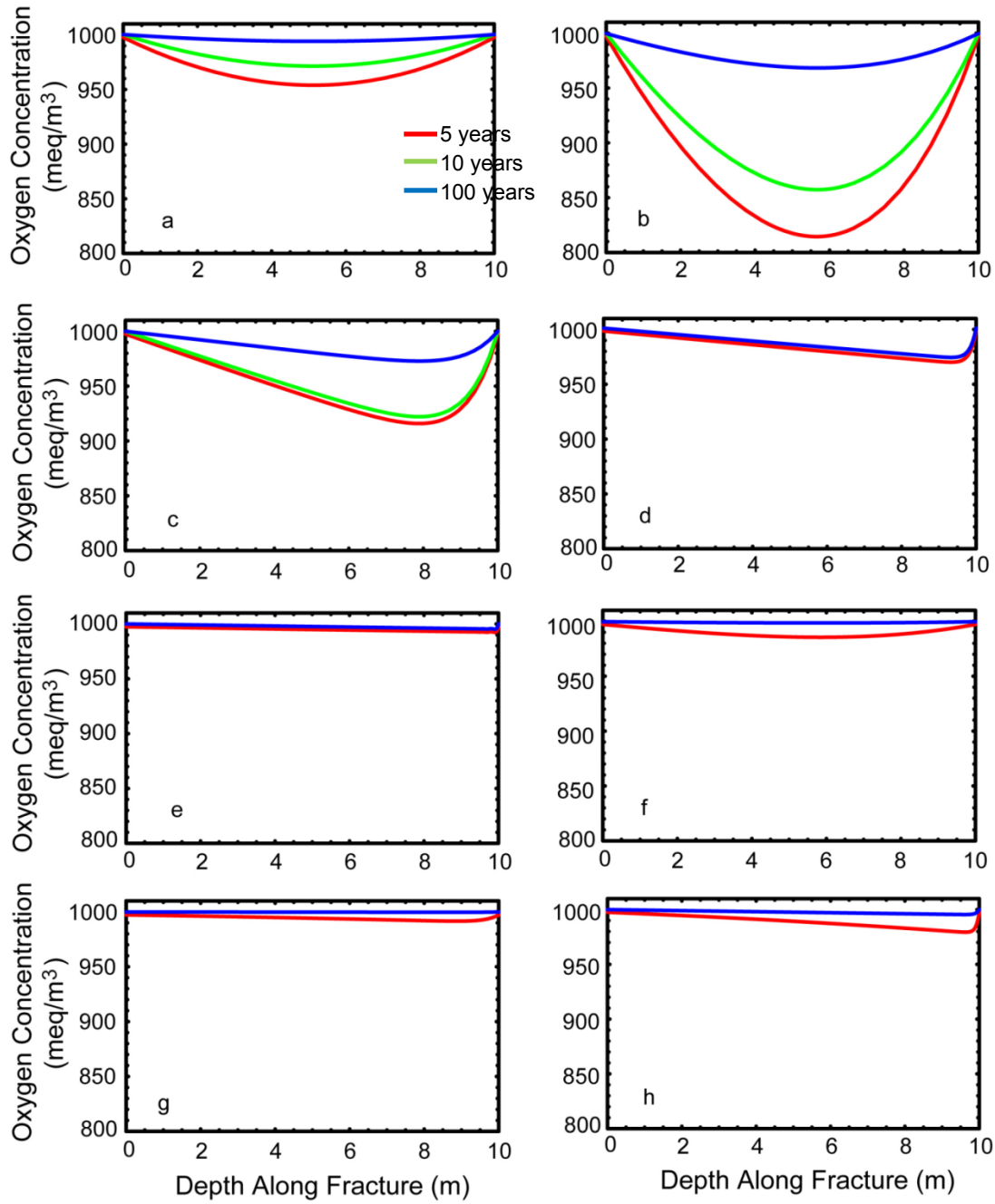
Figure 3 Adapted from Painter and Pabalan (2009). Fracture aperture, saturation, and porosity are as follows for each case: (a) 0.3 mm, 1.0, 0.15; (b) 0.1 mm, 1.0, 0.28; (c) 0.1 mm, 1.0, 0.43; (d) 0.1 mm, 1.0, 0.57; (e) 0.1 mm, 1.0, 0.87; (f) 10 mm, 0.25, 0.31; (g) 10 mm, 0.25, 0.58, (h) 10 mm, 0.25, 0.80.

boundary conditions with specified oxygen concentrations in simpler models that couple oxygen diffusion and grout oxidation reactions.

For the base case, the study assumed a lower reducing capacity than DOE used to model saltstone in the FY 2014 Special Analysis (i.e., 0.0498 milliequivalents electrons (meq e⁻) / g grout in the Painter and Pabalan study as compared to 0.607 meq e⁻ / g saltstone). The grout modeled in the Painter and Pabalan study also had a lower porosity than saltstone (i.e., 0.46 as compared to 0.60 in saltstone). Therefore, the progress of the oxidation front predicted with the numerical model is not directly applicable to saltstone. However, the authors concluded that, for a range of parameters relevant to saltstone waste disposal, the complex numerical model could be adequately represented with the following analytical equation:

$$\xi(t) = \sqrt{2 \frac{D_e \Phi C_0 t}{R_0 \rho_{grout}}}$$

where

$\xi(t)$ = position of the oxidation front measured from the fracture wall (m)
D_e = effective oxygen diffusion coefficient in the matrix (m^2 / yr)
Φ = matrix porosity (dimensionless)
C_0 = oxidant (oxygen) concentration at interface of fracture and matrix (meq e⁻ / g grout)
R_0 = initial reducing capacity of the grout (meq e⁻ / g grout)
ρ_{grout} = bulk density of grout (g / m^3)

Thus, although Painter and Pabalan used assumptions about the grout properties that differ from saltstone, using this equation, their results can be adjusted for different parameter values, as discussed further as part of the NRC evaluation.

Pabalan et al. (2012)

The study included two types of experiments, column tests performed with samples of crushed simulated saltstone, and static leaching experiments performed with intact laboratory-formed simulated saltstone samples. In the column experiments, the researchers studied the release of Tc, selenium, neptunium, uranium, nitrite, and nitrate with oxygen-bearing simulated SRS groundwater under atmospheric conditions. The researchers also studied the evolution of pH and Eh of the eluent.

The column experiments were characterized by a pronounced initial Tc release for the first several pore volumes (10 in column 1, 14 in column 2), followed by a more gradual release (to 51 pore volumes in column 1 and 26 in column 2), finally ending with increased releases. The researchers concluded that the Tc that was released in the first several pore volumes was likely to be attributable to Tc that was not effectively immobilized in the reducing grout or Tc that was reoxidized during the crushing and sieving of the grout material. The researchers concluded that the increased release rate after 26 or 51 pore volumes was most likely to be due to Tc oxidation, because it followed a significant increase in the E$_h$ in the eluent. The researchers attributed the delay between the E$_h$ increase and the increase in the rate of Tc release to slow oxidation of Tc at depth within the grout particles, which in turn is likely controlled by oxygen

diffusion into the particles. The authors noted that the behavior also could be explained by the formation of a low solubility metastable Tc(IV) phase that is resistant to oxidative remobilization.

Almond and Kaplan (2011) (SRNL-STI-2010-00667)

This study examined sorption coefficients (K_d) of several elements, including Tc, in a saltstone sample cored from field-emplaced saltstone (Saltstone Disposal Structure (SDS) 4 Cell E). Although the researchers reported K_d values, they were based on measurements of release of Tc that was initially present in the field-emplaced samples, and therefore likely reflected mechanisms other than sorption to surface sites alone.

The authors ground the sample in a sub-oxic glove bag filled with nitrogen and leached radionuclides from the sample with deionized water equilibrated with portlandite. Samples were leached for 20 days. Both oxic and anoxic tests were run. In the anoxic tests, the leach solution was purged with nitrogen. The authors noted that the samples were olive green when freshly cored, but that they had a grey outer layer after storage, before the leaching tests began. The authors concluded this color change indicated that some oxidation had occurred during storage, although the PVC tubes the samples were stored in had been filled with nitrogen. The glovebag maintained a reduced oxygen environment of 30-60 parts per million (ppm) oxygen during the course of the experiment. The authors concluded that the measured K_d value of 139 mL/g likely reflected some oxidation of the sample. If the dissolved Tc was interpreted as a solubility limit instead of a K_d value, the measured solubility would be 2×10^{-10} moles / liter. A sample exposed to a solution continuously bubbled with air had a measured solubility of approximately 2×10^{-9} moles / liter. These values differed from the results of other authors, as discussed in the evaluation section.

Witmer and Powell (2013) (SRR-CWDA-2013-00121)

Witmer and Powell (SRR-CWDA-2013-00121) studied 3.2-cm (1.25-inch) diameter, 1.3-cm thick (0.5 inch-thick) pucks of laboratory-made simulated saltstone. Sample construction is discussed by Roberts et al. (2012) (SRNL-STI-2012-00603). The samples were placed in field lysimeters exposed to natural precipitation at SRS. The pucks were placed in the lysimeters approximately 2 months before precipitation was allowed into the lysimeters. Four samples were exposed: two that contained Tc but no BFS, and two that contained Tc and BFS. After the first three quarters, the lysimeters containing Tc and no slag released approximately 50 to 60 percent of the Tc-99. For the two lysimeters containing Tc and slag, one released 27 percent within the first three quarters and the second released approximately 11 percent within the first two quarters.

Cantrell and Williams (2012) (PNNL-21723)

Cantrell and Williams (2012) measured Tc leaching from simulated saltstone using a single-pass flow-through system under anoxic conditions. The E_h, pH, and the concentrations of sulfide and other ions were also measured. The researchers used heavy-walled Teflon reactors operated in a low-oxygen atmosphere to minimize oxygen contamination without using hydrogen gas, which appeared to reduce Tc in other experiments (Kaplan et al., 2011

(SRNL-STI-2010-00668)). They also used a large saltstone-to-leachant ratio to minimize the impact of trace amounts of oxygen. The simulated saltstone was cured for 30 days before being crushed and sieved. The samples were exposed to oxygen while being crushed and sieved, so this step was done quickly to minimize oxidation.

The concentration of Tc measured in the leachate began at approximately 300 µg/L (3×10^{-6} moles / liter) and decreased with time. The E_h conditions were reducing over the course of the experiments and the pH was in the range of 12.5-13. The results of leaching experiments were compared to thermodynamic modeling performed using the Geochemist's Workbench software to evaluate the potential solubility controlling phases. The authors concluded that the Tc released under anoxic conditions was controlled by an oxide of the form $TcO_2 \cdot xH_2O$, which the authors expected was likely to be $TcO_2 \cdot 1.6H_2O$.

Two reactors were sparged with pure oxygen after 84 days. Reactor 3 was exposed for 30 minutes on one day, while Reactor 2 was exposed for 30 minutes on 3 consecutive days. Exposure to pure oxygen resulted in increased Tc release in both cases. The sample that was exposed to oxygen three times showed a much greater release of Tc than the reactor that was only exposed to oxygen once. That is, the Tc release from Reactor 2 increased from 17 micrograms / liter to 112 micrograms / liter less than a day after the three exposures. The Tc release from Reactor 3 increased from 15.2 micrograms / liter to 24.3 micrograms / liter after the single oxygen exposure.

The researchers did not sample Reactor 2 after the 112 micrograms / liter Tc release was observed. However, the release from Reactor 3 decreased gradually in the subsequent weeks without oxygen exposure (i.e., from 24.3 micrograms / liter shortly after oxygen exposure to 13.6 micrograms / liter within 15 days without oxygen exposure). Based on this result, the researchers concluded that the reducing capacity of saltstone could overcome an exposure that occurred over a short time by reducing the Tc back to $TcO_2 \cdot xH_2O$.

Kaplan et al., 2011 (SRNL-STI-2010-00668)

This study includes a literature review as well as original experiments. The most significant papers from the literature review of Kaplan et al. are included in this review. The results of the original experiments are ambiguous because the experiments were conducted in a controlled anoxic atmosphere containing 2 percent hydrogen gas. The researchers found that Tc(VII) was reduced to Tc(IV) even in control samples that did not contain BFS and concluded the Tc was chemically reduced by the hydrogen gas.

Even with the reducing atmosphere (i.e., <0.5 ppm oxygen, E_h of -585 millivolt, 2 percent hydrogen gas, pH 11.66), however, sorption was not immediate. Sorption coefficients increased logarithmically until the measurements were stopped at 56 days, with little sorption occurring in the first eight days. Steady state had not yet been achieved when the measurements were stopped.

NRC Evaluation

Tc in salt waste, before incorporation into a saltstone waste form, is oxidized (i.e., Tc(VII)). The DOE conceptual model of the oxidation state of Tc in saltstone is as follows:

1. Tc begins to be chemically reduced to Tc(IV) as saltstone is produced, and the fraction of Tc(IV) gradually increases as saltstone cures;
2. Tc oxidizes and becomes mobile when oxygen in infiltrating water consumes the saltstone's reducing capacity; and
3. Tc(VII) is re-reduced to Tc(IV) if it moves to an area in saltstone that still has reducing capacity.

The NRC staff has Monitoring Factors related to each step of that conceptual model. Specifically, NRC staff has the following questions:

1. Is Tc ever completely reduced in saltstone, or does a fraction remain oxidized?
2. Does the Ce(IV) method of measuring reducing capacity of saltstone provide an appropriate measurement of the capacity of saltstone to reduce Tc(VII) to Tc(IV)?
   a. What components of saltstone supply the measured reducing capacity, and are these components capable of chemically reducing Tc(VII) to Tc(IV) under field conditions?
   b. Is there an unreactive fraction of saltstone reducing capacity (e.g., passivated minerals that do not contribute to effective reducing capacity in field-emplaced saltstone)?
3. Have all of the relevant mechanisms of oxygen ingress into saltstone been identified?
   a. Is water infiltration the only relevant mechanism for oxygen infiltration into saltstone, or is oxygen in soil gas migrating into unsaturated fractures also important to saltstone oxidation?
   b. How much of the saltstone reducing capacity is consumed by contact with and entrainment of air during mixing, pumping, and pouring of saltstone under field conditions?
4. Does oxygen entering saltstone react preferentially with Tc before consuming the reducing capacity of saltstone?
5. How effectively can Tc(VII) be re-reduced if it moves into an area of saltstone with residual reducing capacity?

Each of these issues is discussed below.

Question 1 – Is Tc ever completely reduced in saltstone, or does a fraction remain oxidized?

NRC staff has not found sufficient evidence to make a conclusion about whether Tc is completely reduced by saltstone. An ongoing DOE experiment (SRRA042328SR) showed that a significant fraction of Tc remained oxidized in simulated saltstone samples after 29 days of curing; however, (1) additional chemical reduction may take place with longer curing times and (2) the high concentrations of Tc used in the experiment make the applicability to emplaced saltstone uncertain. Langton and Almond (2013) (SRNL-STI-2013-00541) observed that 95 percent of the Tc in Cast Stone, a cementitious waste form similar to saltstone, was reduced after 10 days of curing, but suggested that longer curing times should be tested to determine whether complete reduction is achieved. Pabalan et al. (2013) noted one possible explanation for the initial pulse release of Tc observed in their column experiment was that Tc was not completely reduced by the simulated saltstone sample. However, the research teams of

Langton and Almond (2013) and Pabalan et al. (2013) both acknowledged that the observation of oxidized Tc may have been an experimental artifact, because both teams prepared samples for measurement in contact with air.

Sample preparation in air was avoided by Lukens et al. (2005), who cured grout samples in cuvettes analyzed with x-ray absorption fine structure (EXAFS) spectroscopy and XANES. The researchers used EXAFS to study the structure of precipitated Tc in a reducing grout and XANES to study the oxidation state of Tc. The researchers measured approximately 3 percent of Tc as Tc(VII) after 30 months of curing in low-permeability cuvettes, which the researchers 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 mm) and at the oxygen diffusion coefficient the researchers provided for the impermeable cuvette walls, (i.e., diffusion coefficient of oxygen = 2.3×10^{-9} cm^2/s), the oxidized Tc(VII) can be explained by oxygen diffusion through the cuvette wall. Thus in each of these studies it is unclear if the observed oxidized fraction of Tc represented a small fraction of Tc that could remain oxidized in field-emplaced saltstone or if it was due to an experimental artifact.

Almond and Kaplan (2011) (SRNL-STI-2010-00667) observed Tc solubility from an SDS 4 core sample under suboxic and oxic (i.e., atmospheric) conditions. The suboxic sample was kept in a glove bag with oxygen concentrations of 30 to 60 ppm, and had a measured solubility of approximately 2×10^{-10} mole / liter. The sample measured under oxic conditions was exposed to a solution continuously bubbled with air, and had a measured solubility of approximately 2×10^{-9} mole / liter. If these results are representative of as-emplaced saltstone, the study would provide additional confidence in the ability of saltstone to reduce Tc.

As discussed in the February 2015 Onsite Observation Report (ML15041A562), DOE characterized this sample as a high quality sample because it was cored from field-emplaced saltstone. However, the values reported by Almond and Kaplan (2011) were unexpected. The relatively small (i.e., single order of magnitude) difference in Tc solubility between reducing and oxidizing conditions is not consistent with the current understanding of the redox sensitivity of Tc solubility. Furthermore, Estes et al., (2012) and Lilley (2010) both observed Tc solubilities of approximately 1×10^{-8} mole / liter under reducing conditions, which were higher than the solubility value reported by Almond and Kaplan (2011) for oxidizing conditions. Additionally, both Estes et al., (2012) and Lilley (2010) used hydrogen gas to eliminate oxygen in their reducing experiments, so their results should reflect a best-case-scenario for reducing conditions.

The reasons for the unexpected results are not clear. One possibility is that there is a difference between field-emplaced and laboratory-prepared samples that is not yet understood, and is not characterized by the redox conditions alone. Another possibility is that there was an unexplained experimental artifact in the solubility study of Almond and Kaplan (2011). For example, Almond and Kaplan (2010) observed the formation of calcium carbonate in an oxidizing sample. Presumably, calcium carbonate could have precipitated without observation in the reducing sample. For any samples that included calcium carbonate precipitation, the release of Tc into solution may have been limited. It is not clear if this mechanism is representative of field conditions, or whether it is responsible for the differences between Tc solubility values observed by Almond and Kaplan (2011) and those observed by other authors.

The Almond and Kaplan (2011) solubility measurements could significantly affect long-term projections of doses from the SDF. Additional information (e.g., confirmatory testing on future core samples) would provide additional confidence in the ability of saltstone to completely reduce Tc.

The question of whether Tc is completely reduced by saltstone grout is relevant to MF 5.05, "Potential for Short-Term Rinse-Release from Saltstone," because any oxidized Tc present when water initially infiltrates to the saltstone waste form could be released more rapidly than Tc release limited by the annual oxidation of saltstone (e.g., as seen in the early pulse release observed by Pabalan et al. (2012)).

Question 2 – Does the Ce(IV) method of measuring reducing capacity of saltstone provide an appropriate measurement of the capacity of saltstone to reduce Tc(VII) to Tc(IV)?

The uncertainty in the chemical species that contribute reducing capacity to saltstone is related to safety in three ways:

1. The identity of the species that supply the chemical reducing capacity affects the persistence of the reducing capacity because different chemical species leach from saltstone at different rates;

2. The identity of the species that contribute reducing capacity is needed to correctly interpret the measured reducing capacity with different measurement methods, which yield different results; and

3. The identity of the species that contribute reducing capacity is needed to determine what fraction of the measured reducing capacity will be able to reduce Tc(VII) to Tc(IV) under the conditions of emplace saltstone.

The relative importance of reduced sulfur and iron species to the measured reducing capacity is unclear. While a recent DOE study (SRRA042328SR) supports the conclusion that Fe(II) in BFS contributes more to the reducing capacity of saltstone than reduced sulfur species, another study (PNNL-21723) questions the contribution of Fe(II) to the reducing capacity of emplaced saltstone. Additional studies (PNNL-22977; CBP-RP-2010-013-01) support the conclusion that one of the primary contributors to the measured reducing capacity is not in the dry premix, but in the decontaminated salt waste itself. Specifically, the studies suggest that one of the main contributors to the measured reducing capacity by either the Ce or Cr method is nitrate in the treated liquid salt waste. However, as previously discussed, because of the relative Eh values of the NO_2^-/ NO_3^- and Tc(IV) / Tc(VII) redox couples, the reducing capacity attributable to nitrate is not expected to effectively reduce Tc(VII) to Tc(IV).

In a Request for Additional Information (RAI) for the FY 2013 Special Analysis (ML14148A153), the NRC staff expressed concern that if the reducing capacity is primarily attributable to reduced sulfur species, sulfur leaching should be represented in DOE's evaluation case because it would represent a mechanism for the loss of reducing capacity from saltstone independent of oxygen ingress. In the reply to the RAI (ML15020A655), DOE cited recent research results (SRRA042328SR) that indicate that Fe(II) may contribute more to the reducing capacity of

saltstone than reduced sulfur species. However, the ability of Fe(II) species to reduce Tc(VII) to Tc(IV) under the conditions of field-emplaced saltstone are unclear because saltstone pore water has a higher pH than either of the methods used to measure reducing capacity, and Fe(II) has a low solubility at high pH.

In addition, in the same RAI (ML14148A153), the NRC staff expressed concern that the Ce(IV) method, which is performed at a low pH (i.e., pH 1 to 2) with sulfuric acid, may overestimate the reducing capacity. As discussed in PNNL-22977, the Ce(IV) method measures nearly all of the reducing capacity of the solid sample because most of the solids dissolve in the strong acid. The NRC staff expressed concern that reducing capacity measured with this method may not be applicable to saltstone pore solutions, which have a much higher pH (e.g., 10.5 to 12.5). Specifically, the NRC staff expressed concern that if a passivation layer forms on the BFS, some of the reducing capacity measured with the Ce(IV) method would not be available to reduce Tc(VII) in saltstone pore water.

Given these sources of uncertainty, it is unclear to the NRC staff whether the reducing capacity of saltstone measured by the Ce(IV) method, which DOE uses as a parameter in the FY 2014 Special Analysis, is a good representation of the capacity of saltstone to chemically reduce Tc(VII) to Tc(IV).

Question 3 – Have all of the relevant mechanisms for oxygen ingress into saltstone been identified?

In the DOE conceptual model, the only source of oxygen modeled as contacting saltstone is oxygen dissolved in groundwater. DOE excludes soil gas infiltrating into saltstone as a potential source of oxygen in its base-case analysis because DOE has concluded the saltstone matrix will remain saturated. In the NRC RAI on the DOE FY 2013 Special Analysis, the NRC staff questioned this conclusion, explaining that if saltstone contains unsaturated fractures, oxygen could be introduced into those fractures in the gas phase. The additional source of oxygen is relevant to safety for two reasons:

1. The amount of oxygen infiltrating into saltstone is related to projected Tc release in DOE's mathematical model; and

2. Short-term rinse release, as covered in MF 5.05, could occur if grout oxidation occurs prior to infiltrating water contacting saltstone, which can only occur if there is another source of oxygen in addition to infiltrating water.

If significant oxidation occurs prior to water interacting with saltstone, there is the potential for a short-term pulse release in the first pore volume released, when the Tc that has oxidized prior to water infiltrating to saltstone is released. This potential for short-term release is not captured in the DOE evaluation case, because the model does not include a mechanism for saltstone to oxidize prior to advective flow of water through saltstone.

The NRC staff has previously expressed concern about the possibility of the ingress of oxygen in soil gas into fractures in saltstone in review documents (NRC, 2010a; NRC 2012b; NRC 2012). Although fractures were not specifically mentioned in a recent study by Langton (2014a)

(CBP-TR-2014-05), the study found that the rate of oxygen migration into samples of Cast Stone exposed to soil was faster than the rate of migration into the sample exposed to water. The authors concluded that this observation was consistent with the more rapid transport of ions through a gas phase as compared to a liquid phase.

Similarly, the results of the numerical model developed by Painter and Pabalan (2009) demonstrate the importance of gas-phase transport of oxygen in saltstone fractures. As previously discussed, the authors modeled a cementitious material with a significantly lower reducing capacity than saltstone, in addition to differences in density, porosity, and diffusivity. Updating Equation (1), taken from the Painter and Pabalan (2009) study, with parameters more characteristic of saltstone, the equation shows slightly slower oxidation than predicted by Painter and Pabalan (Figure 4). However, the oxidation rates were similar enough that the main conclusion of the Painter and Pabalan study that oxygen from soil gas in unsaturated fractures is a non-negligible source of oxidation is expected to be relevant. Figure 4 is intended to show the relationship between the projections of Painter and Pabalan (2009) and what the projections would be if updated with parameters more relevant to saltstone. NRC staff does not regard Figure 4 as a likely projection of saltstone oxidation because there are several complexities the analytical equation developed by Painter and Pabalan (2009) does not address. These complexities include the following issues:

1. There was assumed to be no damage to the wasteform behind the oxidation front, which is likely not realistic. Assuming damage behind the front would cause an increase in the projected extent of oxidation (i.e., the square root of time relationship would be closer to linear).
2. Using the value of 0.607 meq e⁻ / g for the reducing capacity of saltstone assumes all of the measured reducing capacity in saltstone is capable of reducing Tc (i.e., it is due to chemical components that will not be easily leached and have a redox couple Eh below that of Tc(IV) / Tc(VII)).
3. Using the value of 0.607 meq e⁻ / g saltstone for the reducing capacity of saltstone assumes all of the measured reducing capacity in saltstone is in a physical form available to reduce Tc (i.e., not obstructed with a passivating layer).
4. Using the value of 0.607 meq e⁻ / g saltstone assumes the amount of oxidation that occurs in the field during field-scale mixing, pumping, and pouring of saltstone in contact with air is adequately represented by the amount of oxidation that occurred during laboratory-scale mixing and pouring of saltstone samples.
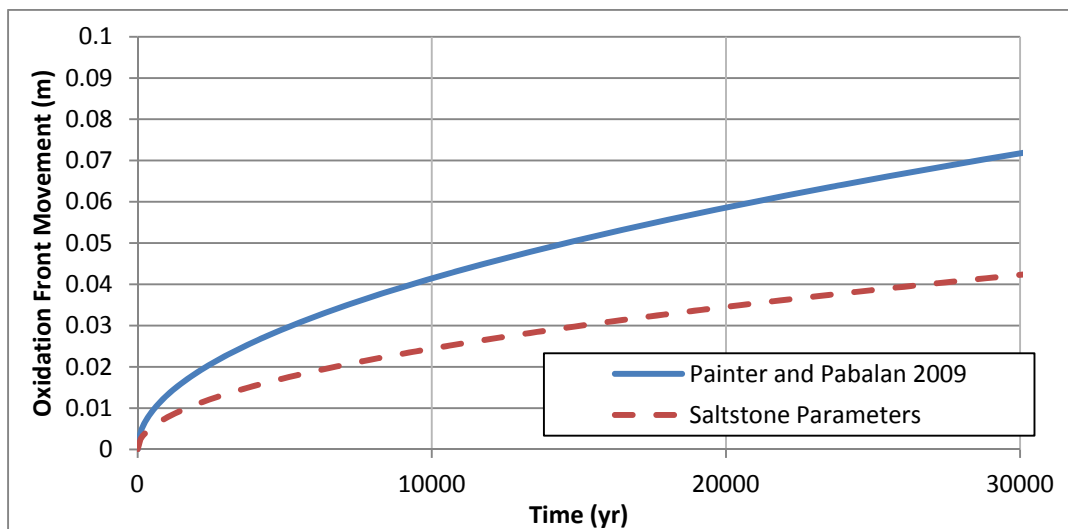
Figure 4. Oxidation projections based on the model of Painter and Pabalan (2009) and predictions modified for saltstone parameters, including a reducing capacity of 0.607 meq e⁻ / g saltstone, porosity of 0.58, density of 1010 kg per m^3, and effective diffusion coefficient of 3.15×10^{-5} m^2 / year.

The NRC staff is not aware of studies specifically designed to quantify oxidation that occurs as saltstone is mixed, pumped, and poured in contact with air. DOE has plans to measure Tc leaching from cored samples of field-emplaced saltstone. Comparing leaching from field-emplaced saltstone and laboratory-created samples may capture some effects of oxidation during field emplacement if the cores are partially oxidized. However, reducing capacity is more likely to affect the duration of reducing conditions than it is to affect Tc leaching from areas that remain reducing. Because the oxidation state of a redox couple depends on the Eh of solution, and not the reducing capacity, Tc leaching is not necessarily a good indication of whether some, but not all, of the reducing capacity in a region of saltstone has been consumed. Thus it is not clear whether measurements of Tc leaching from reduced regions of saltstone will adequately support conclusions about how much reducing capacity is consumed by mixing, pumping, and pouring saltstone in contact with air. Because the reducing capacity is a chemical barrier to oxygen ingress, studies that evaluate the progress of an oxidation front could provide information about the effective reducing capacity of field-emplaced samples. Measurements of reducing capacity also could be useful, if they address the uncertainties related to reducing capacity discussed in this review.

In addition to the limitations of the projections of Painter and Pabalan (2009) discussed above, a more fundamental limitation exists if Tc leaching is not well correlated to residual reducing capacity. This question is discussed further in the evaluation of Question 4.

In the FY 2014 Special Analysis, DOE addressed the possibility of additional sources of oxygen in saltstone with a sensitivity analysis that modeled non-depleting sources of oxygen comprising 5, 10, 15, and 20 percent of the saltstone volume. Unlike fractures, the sources of oxygen were placed randomly in the saltstone and were disconnected from each other by reduced regions of saltstone until approximately 10,000 years after closure, when oxygen diffusion from the

randomly-placed sources began to form connected pathways for oxidized Tc out of saltstone. Although DOE addressed the possibility of oxidized Tc not being re-reduced in saltstone with an additional sensitivity analysis that modeled Tc exiting saltstone as soon as it is oxidized, that sensitivity analysis did not include the possible effects of oxygen in fractures as was captured by the sensitivity analysis with non-depleting oxygen sources. NRC staff is evaluating the meaning of the results of the two separate sensitivity analyses as informed by one another.

Question 4 – Does oxygen entering saltstone react preferentially with Tc before consuming the reducing capacity of saltstone?

It is not clear that oxygen migrating into the saltstone grout will preferentially consume the reducing capacity of saltstone before oxidizing Tc-99. Research from both the Savannah River National Laboratory (SRNL) (SRNL-STI-2013-00541) and the Cementitious Barriers Partnership (CBP) (CBP-TR-2013-002) indicated that residual reducing capacity was not correlated to Tc mobility in chemically reducing cementitious wasteforms. One explanation for the lack of correlation could be that oxygen preferentially reacts with the Tc wherever the oxygen can ingress into saltstone, even in the presence of residual reducing capacity.

In February 2013, NRC and DOE staffs had a technical exchange (ML14057A578) to discuss those studies, among other topics. DOE questioned whether research done on a static system (in CBP-TR-2013-002), rather than flow-through system, would accurately predict behavior in the saltstone system. NRC staff questioned whether the flow through saltstone was expected to be slow enough that the difference between the static system used in the CBP experiment and the slow flow expected in field-emplaced saltstone is significant.

In Witmer and Powell (2013) (SRR-CWDA-2013-00121), comparison of laboratory-prepared simulated saltstone samples made with and without BFS and exposed to the atmosphere in field lysimeters showed the presence of slag reduced Tc-99 release by only a factor of 2 to 4. This field result is inconsistent with the results of a previous DOE study conducted with field lysimeters using larger samples (i.e., 55-gallon wasteforms) (Langton, 1988). That study demonstrated a much larger difference between the Tc retention in cementitious wasteforms with and without slag. Specifically, no Tc leaching was detectable in the slag-containing saltstone for the duration of the experiment (i.e., 2.5 years), whereas Tc leached out of the slag-free saltstone at the rate of nitrate loss.

One possible explanation for the difference in the results between the two studies was that Tc release from the smaller samples was dominated by surface defects, whereas the larger sample maintained reducing conditions in a greater fraction of the sample because of its much smaller surface-area to volume ratio. In the more recent study (SRR-CWDA-2013-00121), the two lysimeters with Tc and slag released approximately 27 percent in 9 months and approximately 11 percent in six months. If Tc is only released from the oxidized layer (i.e., neglecting solubility-controlled release from the reduced saltstone) an 11 percent release represents Tc

release from a 0.4 mm deep layer around the sample [7]. A 28 percent release represents Tc release from a layer 1 mm deep. For comparison, the analytical approximation developed by Painter and Pabalan (Equation 1), when updated with parameters DOE uses for saltstone, would predict approximately 0.2 mm of oxidation in 0.75 years. One explanation for the apparent release of Tc from depths to which an oxidation front was not expected to penetrate is that the results may have been dominated by 1 mm of surface flaws. Surface effects on the leaching of non-redox sensitive species were detected up to 16 mm from the surface by Almond and Langton (2013) (SRNL-STI-2013-00541). Another possible explanation for the observed Tc release is that oxygen preferentially oxidized Tc in some areas before completely consuming reducing capacity in those areas.

The DOE conceptual and mathematical models for Tc release assume Tc oxidation is governed by the progress of an oxidation front that consumes saltstone reducing capacity. Based on the studies described in this section, NRC staff questions the validity of the assumption that Tc oxidation is adequately predicted by the progress of this type of oxidation front. DOE has performed a sensitivity analysis related to non-depleting oxygen sources in saltstone that may provide insight into the potential effects of Tc oxidation in areas of saltstone with residual reducing capacity. That analysis was provided originally in the FY 2013 Special Analysis (ML14002A069) and discussed further in Section 5.6.7.4 of the FY 2014 Special Analysis. Although that sensitivity analysis bases Tc oxidation on the consumption of reducing capacity in saltstone, it is relevant to NRC questions about the correlation between Tc oxidation and progress of an oxidizing front because the non-depleting oxygen sources could be interpreted (non-mechanistically) as areas in which Tc is oxidized prior to being reached by an oxidation front moving through saltstone.

In the NRC RAI on the FY 2013 Special Analysis, NRC staff commented that the results of the sensitivity analysis with non-depleting oxygen sources were difficult to interpret because Tc-99 released from areas near the non-depleting oxygen sources was immediately re-reduced by surrounding material and the NRC staff does not find the assumed re-reduction to be adequately supported. As discussed in the following section, DOE has addressed NRC questions about the support for Tc re-reduction in saltstone with a sensitivity analysis. Thus one way to address NRC concerns about Tc oxidation in the presence of residual reducing capacity would be to combine DOE sensitivity analyses showing the effects of non-depleting sources of oxygen and fractions of Tc entering the saturated zone when oxidized (i.e., not undergoing re-reduction).

Question 5 – How effectively can Tc(VII) be re-reduced if it moves into an area of saltstone with residual reducing capacity?

In the final part of DOE's near-field conceptual model, Tc(VII) that is oxidized at one location in saltstone is reduced and immobilized if it is transported into another part of the saltstone waste form that has remaining reducing capacity. The NRC staff does not have sufficient information

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[7] In a 3.2-cm diameter 1.3-cm high (1.25 inch-diameter by 0.25 inch high) sample, a 0.4 mm layer around the cylinder is 11 percent of the sample volume (sample dimensions from Roberts et al. (2012) (SRNL-STI-2012-00603)).

to conclude that this aspect of DOE's conceptual model is adequately supported. As evidence for re-reduction, DOE relies on the results of Cantrell and Williams (2012) (PNNL-21723). Specifically, DOE cites the decrease in Tc releases from Reactor 3 from 24.3 microgram / liter shortly after oxygen exposure to 13.6 microgram / liter within 15 days without oxygen exposure. However, the decrease in Tc release by approximately 50 percent does not seem to support the complete re-reduction of Tc entering a reduced zone of saltstone as assumed in the FY 2014 Special Analysis.

In the FY 2014 Special Analysis, DOE addressed reconcentration with a sensitivity analysis in which a fraction of the oxidized Tc was moved directly from the wasteform to the saturated zone when it was oxidized. This sensitivity analysis showed that when Tc was assumed to be released from saltstone as soon as it is oxidized (i.e., it does not re-reduce), doses increased before 10,000 years but did not exceed 25 mrem / year. This value could change based on changes in assumptions (e.g., the rate of water infiltration through saltstone and Tc solubility). However, this sensitivity analysis is an effective way to address the effects of the assumed re-reduction in the DOE evaluation case. Thus while the NRC staff does not find that DOE's assumption about complete re-reduction of Tc entering a reduced zone of saltstone is adequately supported, the potential effects of the assumption could potentially be addressed through sensitivity analyses.

Follow-Up Actions

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

Open Issues

No open issues were identified during this review.

Conclusions

NRC staff made the following conclusions based on this review:

- A significant amount of chemical reduction of technetium (Tc) from Tc(VII) to Tc(IV) appears to occur within the first week of curing and additional chemical reduction may continue for months. However, no study has shown complete reduction of Tc(VII) in saltstone under conditions that are consistent with field-emplaced saltstone.

- Different methods of quantifying reducing capacity yield different measured reducing capacities of saltstone and its components. The Ce method (also called the Angus-Glasser method) may overestimate the amount of reducing capacity available to reduce Tc in saltstone.

- It is unclear which components of saltstone dry premix or salt solution are responsible for the measured reducing capacity of saltstone. The identity of the components contributing reducing capacity is important to long-term predictions of the ability of saltstone to chemically reduce contaminants.

- There is evidence for gas-phase transport of oxygen in laboratory samples of a reducing grout exposed to moist soil.

- It is unclear how much reducing capacity is consumed during field-scale mixing, pumping, and pouring. Measurements of reducing capacity or studies designed to evaluate the progress of an oxidizing front in cored samples of field-emplaced saltstone may address this issue.

- Independent experiments suggest Tc oxidation is not well correlated to consumption of reducing capacity in reducing cementitious wasteforms.

- Short-term rinse-release may be a concern if significant saltstone oxidation occurs from gas-phase transport of oxygen into saltstone fractures prior to water infiltration to saltstone. Release of Tc that remains oxidized in saltstone (a "persistent oxidized fraction") also could contribute to this short-term release, if a fraction of Tc remains oxidized.

- There is evidence that once Cr is oxidized in saltstone, it is not re-reduced by residual reducing capacity in saltstone if oxygen is present. The applicability of this result to Tc re-reduction is unclear. However, because Tc(IV) appears to be more readily oxidized in saltstone than Cr(IV), the result suggests if low levels of oxygen can keep Cr oxidized in areas of saltstone with residual reducing capacity, low levels of oxygen also could keep Tc oxidized in areas of saltstone with residual reducing capacity.

The NRC staff will continue to monitor information provided by the U.S. Department of Energy (DOE) as it is developed. As described in the NRC 2013 monitoring plan, additional information is needed to close Monitoring Factors (MF) 5.01, 5.02, 5.03, and 5.05. The NRC staff updated those information needs based on the information in this review.

For MF 5.01, "Radionuclide Release from Field-Emplaced Saltstone," the additional information needed includes the following:

- Measurements of radionuclide release from core samples of field-emplaced saltstone; and

- An estimate of the oxidation of Tc in saltstone that could occur if oxygen preferentially reacts with Tc before consuming saltstone reducing capacity. This estimate may be affected by the degree of fracturing expected in field-emplaced saltstone as a function of time.

For MF 5.02, "Chemical Reduction of Tc by Saltstone," the additional information needed includes the following:

- Experimental evidence supporting the degree of re-reduction of oxidized Tc that DOE predicts in mathematical models of Tc transport in saltstone; or

- Further analyses to combine DOE sensitivity analyses showing the effects of non-depleting sources of oxygen and fractions of Tc entering the saturated zone when oxidized (i.e., not undergoing re-reduction).

For MF 5.03, "Reducing Capacity of Saltstone," the additional information needed includes the following:

- Information to support the identity of the components of saltstone dry premix or salt solution that supply the measured reducing capacity in saltstone, the ability of these components to reduce Tc in saltstone under field conditions, and the expected evolution of the reducing capacity over time.

For MF 5.05, "Potential for Short-Term Rinse-Release from Saltstone," the additional information needed includes the following:

- Experimental measurements of rinse-release of risk-significant radionuclides from saltstone and an analysis of the effect of the release on the projected dose; and

- Analyses of the potential effect on dose of the fraction, if any, of Tc that is likely to be (1) rinsed from the surface of saltstone, (2) oxidized before advective flow of water through saltstone begins, or (3) not chemically reduced by saltstone. The analysis should also address potential effects of high ionic strength.

The NRC staff is reviewing the FY 2014 Special Analysis for the Saltstone Disposal Facility (ML15097A366). As part of the NRC's review, the NRC staff will continue to review these areas.

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