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MEMORANDUM TO: Richard Chang, Acting Chief
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                        Division of Decommissioning, Uranium Recovery,
                          and Waste Programs

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SUBJECT: TECHNICAL REVIEW OF REAL WASTE RELEASE TESTING
                        RESULTS FOR TANK 18F AND ASSOCIATED PERFORMANCE
                        ASSESSMENT DOCUMENTATION FOR F-AREA AND H-AREA
                        TANK FARM FACILITIES AT SAVANNAH RIVER SITE, AIKEN,
                        SOUTH CAROLINA (DOCKET NO. PROJ0734)

The U.S. Nuclear Regulatory Commission (NRC) staff has performed a technical review of
documents prepared by the U.S. Department of Energy (DOE) that detail results of experiments
designed to study the release behavior of residual wastes stored in high-level waste tanks at the
Savannah River Site (SRS), South Carolina, and supporting performance assessment
documentation that studies the impact of the real waste release testing results on the
performance assessments. This technical review supports Monitoring Factors 1.1, "Final
Inventory and Risk Estimates," 2.1, "Solubility-Limiting Phases/Limits and Validation," 2.2,
"Chemical Transition Times," 3.2, "Groundwater Conditioning Via Reducing Grout," and 6.3,
"Tank Farm Performance Assessment Revisions," detailed in NRC staff's plan for monitoring the
SRS Tank Farm Facilities (Agencywide Documents Access and Management System
Accession No. ML15238A761).

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As a result of the review of several DOE documents related to the real waste release testing and associated impacts on the performance assessments, NRC staff needs additional information to make a determination that the performance objectives in Title 10 of the *Code of Federal Regulations* (10 CFR) Part 61, Subpart C can be met. Additional conclusions and findings are discussed below.

In conclusion, DOE performed waste release testing from actual high-level-waste samples collected from Tank 18F to inform waste release modeling results and performance assessment (PA) assumptions. The results of the analysis greatly improve understanding of the waste and tank grout as a chemical barrier to mitigate releases from the tank farm facilities after closure. The results of the experiments were used to evaluate whether the F-Area Tank Farm Facility (FTF) and H-Area Tank Farm Facility (HTF) PA results were under-predicted. Results of the analyses are informative to the NRC staff in assessing the ability of the disposal facilities to meet performance objectives in 10 CFR Part 61, Subpart C.

The waste release testing results demonstrate the importance of the experiments, which were recommended by NRC staff in its TER (ML112371715) and monitoring plan (ML15238A761), as well as an independent peer review group under contract with the DOE (LA–UR–2012–00079). The experiments were recommended to validate the waste release modeling used in the FTF and HTF PAs. In many cases, the results of the waste release experiments demonstrate the difficulty in projecting solubility of key radionuclides for these unique tank wastes, notwithstanding use of the best thermodynamic data available in the literature for the geochemical modeling. Therefore, additional waste release testing and updated geochemical modeling are needed for NRC staff to have confidence in the PA results. The NRC staff offer the following additional conclusions and comments related to waste release testing and PA modeling.

Conclusions and Comments for Future Waste Release Testing and Modeling

- Although DOE only used a single sample (FTF-1) for the Tank 18F waste release testing, their rationale (e.g., good characterization, and high concentrations of key radionuclides) is reasonable. In future waste release testing, if testing of multiple samples is impractical, DOE should consider compositing samples to get representative results for the entire tank contents rather than just a small portion of the waste.
- DOE should consider the impact of waste treatment methods, grout additives, and other chemical constituents that may increase radionuclide solubility (e.g., oxalates and carbonates) in designing and evaluating the results of future experiments.
- In future testing, DOE should consider water rinses with synthetic SRS ground water in addition to grout conditioned ground water to study the impact of grout bypass on waste release results. DOE should also consider evaluating the change in concentration over time for the rinse solutions.
- DOE should continue to conduct solid phase analysis of residual waste to inform waste release assumptions for other tanks.
- As recommended by an independent peer review group (LA-UR-2012-00079), DOE should consider conducting spectroscopic analyses [e.g., Extended X-Ray Absorption Fine Structure or (EXAFS)] of plutonium (Pu) and other metals such as iron (Fe) in waste residues.
- DOE should analyze all major ions, alkalinity, and appropriate trace components (e.g., Pu, Fe, and sulfide).

- DOE should consider the following: (1) comparison of the experimental conditions against those for which the Nuclear Energy Agency's (NEA's) thermodynamic database is based to better understand differences in the modeled and experimental results, and (2) updating the assumed phases and geochemical modeling as warranted.
- DOE should consider performing updated geochemical modeling using information gained from characterization of the tanks, and knowledge gained from comparisons of the experimental to previously modeled results.

Conclusions and Comments Related to Performance Assessment Modeling

- DOE should consider a larger range of uncertainty in key radionuclide solubility due to experimental limitations (e.g., substantial metal losses of uranium during leach testing which compromised the utility of the uranium data collected from the experiments and apparent lack of ability to achieve equilibrium conditions particularly for Pu and Tc).
- DOE should perform probabilistic or multi-variate sensitivity analysis considering uncertainty in performance of multiple barriers including scenarios that evaluate basemat bypass, early hydraulic failure due to water table rise or preferential flow through the system, and consider the impact of higher mobility forms of Pu in the natural system.
- DOE should explain differences in PORFLOW and GoldSim modeling results (e.g., Pu peak doses of around 5 mSv/yr (500 mrem/yr) in the Tanks 18/19 SA (SRR-CWDA-2010-00124) versus 7 mSv/yr (700 mrem/yr) in SRR-CWDA-2016-00086).
- DOE should evaluate the impact of the early, high concentration release of Pu or justify why the rinse sample results are not applicable to alternative conceptual models involving water table rise or preferential flow through the system.
- DOE should continue to study and develop models to account for higher mobility forms of Pu in the natural system including models that consider two fractions of Pu (relatively high mobility and low mobility forms) as well as the potential for oxidation and reduction reactions affecting the mobility of Pu in the subsurface along the flow paths away from the tank to the 1 m and 100 m compliance points.
- DOE should evaluate the impact of transport of key radionuclides from the waste zone up into the tank grout, and if found to be risk-significant, provide additional support for the transport mechanism(s).

Enclosure:
Technical Review of Real Waste Release
  Testing Results and Associated Performance
  Assessment Documentation

R. Chang   -3-

SUBJECT: TECHNICAL REVIEW OF REAL WASTE RELEASE TESTING RESULTS FOR
          TANK 18F AND ASSOCIATED PERFORMANCE ASSESSMENT
          DOCUMENTATION FOR F-AREA AND H-AREA TANK FARM FACILITIES AT
          SAVANNAH RIVER SITE, AIKEN, SOUTH CAROLINA (DOCKET NO. PROJ0734)

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Technical Review of Real Waste Release Testing Results and Associated Performance Assessment Documentation

Date: August 2018

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Primary Waste Release Documents Reviewed:

1. King W.D., and D.T. Hobbs, *Determining the Release of Radionuclides from Tank 18F Waste Residual Solids: FY2016 Report*, SRNL-STI-2016-00432, Revision 0, August 2016.
2. *Evaluation of Waste Release Testing Results against the Tank Farm Performance Assessment Waste Release Model*, SRR-CWDA-2016-00086, Revision 0, August 2016.

Summary of "Determining the Release of Radionuclides from Tank 18F Waste Residual Solids: FY2016 Report", SRNL-STI-2016-00432, Rev. 0, August 2016

Pore water leaching studies were conducted on Tank 18F wastes collected and archived prior to Tank 18F closure. A test methodology was developed to study the change in solubility of four key radionuclides during aging of closed waste tanks. Tank waste specimens were leached in shielded cells with solutions intended to simulate tank grout pore waters at three different stages of cementitious material evolution. The target leach solution test conditions are provided in Table 1. The initial leaching pore water has a reducing potential and a relatively high pH (Reducing Region II). The pore water is expected to become increasingly oxidizing with time (Oxidizing Region II) and during the latter stages of aging (Oxidizing Region III) the pH is expected to decrease. For the reducing case, tests were initially conducted with unwashed Tank 18F residual solids followed by sample washing after three weeks of leach testing. For the oxidizing cases (Oxidizing Regions II and III), all samples were washed with simulated grout pore water solutions prior to testing, because it was expected that these conditions will occur after considerable pore water solution has passed through the system. For the reducing case, separate tests were conducted with representative ground grout solids and with calcium hydroxide and calcium carbonate reagents. Ferrous sulfide (FeS) solids were also added to the reducing samples to lower the slurry E_h value. Calcium carbonate solids were used as the grout-representative solid phase for each of the oxidizing cases. Air purge-gas with and without

CO_2 removed was transferred through the oxidizing test samples and nitrogen purge-gas was transferred through the reducing test samples during leach testing. The target pH values were achieved to within 0.5 pH units for all samples. An important conclusion from the report was that the maximum and minimum E_h values (+0.5 V to −0.2 V) achieved during testing were significantly less positive and less negative then the targeted E_h values, which were targeted based on assumptions in the performance assessment (PA). The authors of the report assumed that to achieve the targeted E_h values, non-representative reductants and oxidants would be needed. One of the authors of the report (Bill King) clarified during an August 13–14, 2018 Onsite Observation (OOV) at Savannah River Site (SRS) that the E_h values assumed in the PA may not be representative of conditions following closure (i.e., the inability to achieve the targeted endpoint E_h values listed in Table 1 below was not due to experimental limitations).

Table 1. Target Pore Water Conditions

PA Target Condition	E_h (mV)	pH
Reduced Region II (RRII)	−470	11.1
Oxidized Region II (ORII)	+560	11.1
Oxidized Region III (ORIII)	+680	9.2

The results of the Plutonium (Pu) and Uranium (U) leach testing were stated as following the general predicted trends and with previous test results using simulants[1]. Pu and U concentrations were highest in Oxidized Region III (ORIII), and lowest for Reduced Region II (RRII) under grouted conditions. U was much more soluble than other metals (maximum concentration of 4×10^{-4} mol/L compared to 5×10^{-8} mol/L for other radionuclides). Technetium (Tc) concentrations were highest for oxidizing conditions and lowest for reducing conditions. Neptunium (Np) concentrations were highest in ORIII, but consistently low or non-detectable, particularly for Oxidized Region II (ORII) and RRII. With the exception of U, all of the leached test concentrations were lower than the solubilities expected when the solution is assumed to be in equilibrium with dissolved oxygen[2]. The leach testing results are presented in Table 2.

For the oxidizing cases, the highest concentrations were observed in the wash solutions (except for Tc, which had similar concentrations in both the wash solutions and ORII and ORIII leach tests). The concentrations of Pu, U, and Np in the washed solutions were higher than the expected concentrations when the solution is assumed to be in equilibrium with dissolved oxygen. These results indicate that it is possible to exceed the observed leachate concentrations during initial pore water contacts. Higher concentrations in the washes indicate

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[1] NRC staff agrees that the release concentrations generally increased from Reduced Region II to Oxidized Region II and then to Oxidized Region III, which is consistent with the predicted trend. However, as discussed in the Evaluation Section of this report, NRC staff notes that the measured concentrations were often two to three orders of magnitude higher than DOE's predicted solubilities for Pu and U (and Tc in the HTF PA, which was assumed to be coprecipitated with iron).

[2] The authors of SRNL-STI-2016-00432 state that the leach test concentrations, with the exception of U, are lower than the solubilities expected when the solution is assumed to be in equilibrium with dissolved oxygen. However, DOE has generally not assumed the solubility of Pu and Tc to be in equilibrium with dissolved oxygen in the F-Area and H-Area Tank Farm Facilities (FTF and HTF) PAs and Special Analyses. Of particular risk significance, DOE's assumed Pu solubility of 3E-11 mol/L in the HTF PA and Tank 18 and 19 Special Analysis is significantly lower than the values observed in the waste release experiments. Additionally, in the HTF PA, Tc is assumed to be coprecipitated with iron with assumed solubilities orders of magnitude below observed values (see Table 5 below). Depending on the final estimated inventories of Tc remaining in HTF tanks, the assumed solubility may be risk-significant. This is discussed in more detail in the Evaluation Section of this report.

that some portion of the metals may exist as more soluble or more kinetically accessible phases. Nonetheless, the authors noted that the leach testing results are expected to conservatively represent the levels that would be achieved during the majority of the tank aging periods of interest, although these concentrations could be exceeded upon initial contact with oxidizing solutions. The wash solution concentrations are presented in Table 3. The authors of the report noted that a substantial fraction of the U was leached during sample washing prior to the oxidizing leach experiments; therefore, the U concentrations are expected to be significantly underpredicted (i.e., the results may not be valid for U).

Observations of leachate radionuclide concentrations with time suggested that steady-state values were often not obtained. For example, plutonium concentrations were still increasing at the end of the ORII tests (Figure 3-5 of SRNL-STI-2016-00432). Tc concentrations increased throughout all oxidizing tests (Figure 3-9 of SRNL-STI-2016-00432). These patterns suggest that reported concentrations may underestimate the potential leachate concentrations.

Table 2. Measured pH, E_h, and Metal Concentrations for Each Pore Water Test Condition Using Actual Tank 18F Residual Solids

Test Condition	Sample ID	Additives	Atmosphere	E_h (mV)	pH	Pu (M)	U (M)	Tc (M)	Np (M)
RRII	E	Ca(OH)$_2$, CaCO$_3$, FeS	continuous N$_2$ purge	−208	10.9	2E−9	2E−6	<6E−10	<2E−10
RRII	F	CFS, FeS	continuous N$_2$ purge	−196	11.4	7E−11	2E−6	<6E−10	<2E−10
ORII	A	Ca(OH)$_2$, CaCO$_3$	continuous air purge	+351	11.2	4E−10	4E−6	1E−8	<2E−10
ORII	B	Ca(OH)$_2$, CaCO$_3$	continuous air purge	+328	10.8	6E−9	2E−5	1E−8	3E−10
ORIII	C	CaCO$_3$	continuous air or CO$_2$ stripped air purge	+520	9.4	1E−8	4E−4	1E−8	4E−9
ORIII	D	CaCO$_3$	continuous air or CO$_2$ stripped air purge	+493	9.3	6E−9	7E−5	6E−9	1E−9

Notes: mV=milli volts; M=mols per liter
Average data from final 4 weeks for E_h, pH, Pu, U, Tc.
Average data from final 2–3 weeks for Np.
CFS = cement, fly ash, and slag grout solids
Due to the nearly complete U dissolution during washing, the U leachate concentrations are likely well below solubility limits.

Table 3. Metal Concentrations Observed for ORII-A and ORIII-C Wash Solutions

	Pu (M)	U (M)	Np (M)	Tc (M)
ORII-A	4E−08	3.2E−04	1.3E−09	1E−08
ORIII-C	3E−07	4.6E−03	2.9E−08	9.4E−09

<u>Summary of "Evaluation of Waste Release Testing Results against the Tank Farm Performance Assessment Waste Release Model", SRR-CWDA-2016-00086, Revision 0, August 2016</u>.

The purpose of SRR-CWDA-2016-00086 was to evaluate the change in the dose projection results reported in the F-Tank Farm (FTF) and H-Tank Farm (HTF) PAs using information obtained from the waste release testing. This report discusses the real waste release experiments presented in the previous section, which were performed to support assumptions regarding solubility of key radionuclides in the FTF and HTF PAs. As described in the previous section, the solubilities of Pu, Np, U, and Tc were tested under simulated waste tank chemistry conditions using Tank 18F residual waste samples. Authors of the report noted that there may be some variance from the actual waste solubilities and the assumed solubilities in the PAs. For example, Np was—in all cases—more insoluble than assumed in the PA. The other three elements—Pu, Tc and U—appeared, in most instances, to potentially be more soluble than assumed in the PAs. The report authors concluded that, although in some cases the solubilities could be higher than assumed in the PA, the newly assigned solubilities would have a negligible impact on peak doses occurring in 1,000 or 10,000 years; therefore, the report authors thought there was no immediate need to update the current PA waste release models, and the updated results could be incorporated into the next revision to the FTF and HTF PAs.

The authors of the study also explained a partial basis for the work—to address NRC comments made during the Ronald W. Reagan National Defense Authorization Act for Fiscal Year 2005 (NDAA) Section 3116(a) (NDAA 3116) consultation process. As noted by the report authors, NRC staff's primary concern was that the timing of the FTF PA peak dose, principally associated with the residual Pu-239 inventory in Tank 18F, could occur earlier and within the compliance period if certain modeling assumptions were incorrect. The report authors reiterated NRC staff's Technical Evaluation Report (TER) recommendation for DOE to provide additional experimental support for waste release modeling assumptions to reduce uncertainty about the modeling assumptions that, if found to be significantly non-conservative, could result in the peak dose shifting into the 10,000-year performance period[3]. The NRC staff's TER designated the performance of waste release testing as a key monitoring factor (MF), and highlighted the need for continued research in this area[4]. (ML112371715).

SRR-CWDA-2016-00086 explains that the conceptual model treats the waste tank reducing grout as a porous medium, and although it is recognized that cracking of the grout could lead to heterogeneous flow patterns and that fast flow might occur within preferential flow paths in the waste tank there is uncertainty about the nature and effects of grout cracking over the thousands of years of waste tank aging. This uncertainty encompasses the extent to which water passing relatively rapidly through preferential flow paths interacts with the reducing grout

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[3] NRC staff note that the timing of peak dose (and the shift of peak dose into the compliance period) is more related to assumptions regarding (i) chemical transition times in cases where the solubility of key radionuclides such as Pu-239 are assumed in DOE's PAs to increase over time and (ii) the likelihood of occurrence of alternative conceptual models, such as tank grout bypass of infiltrating ground water through preferential flow pathways (e.g., shrinkage gaps and cracks in the waste form), which could hasten the time to risk-significant release of key radionuclides into the biosphere. Transition times and likelihood of alternative conceptual models are addressed in other monitoring factors, and are not addressed by the waste release experiments that are the focus of this technical review report. Because DOE has not yet addressed other key monitoring factors related to timing of peak dose, conclusions regarding the timing of the updated peak dose of approximately 700 mrem/yr (7 mSv/yr) for the conservative case are not fully supported (i.e., peak dose occurring beyond 10,000 years).

[4] NRC staff note that the need for waste release testing was more fully developed in staff's monitoring plan under monitoring factor 2.1 "Solubility-Limiting Phases/Limits and Validation" (ML15238A761).

and how water that reaches the residual waste layer through a preferential flow path interacts with that layer. The report authors state that differing effects of grout cracks and fast flow pathways are addressed in sensitivity analyses within the PAs using information selected from the waste release model and implemented with the fate and transport modeling. Based on a review of the data, DOE contractors selected the "conservative case" solubilities in Table 5. Also presented in Table 5 are the assumed solubilities in the HTF and FTF PAs. The range of concentrations observed in the experiments discussed above is also listed in Table 5.

Select results of the updated PA modeling are presented in Figures 1 and 2 below. The results for the "Nominal" and "Conservative" solubilities that the authors of SRR-CWDA-2016-00086 selected and reported in Table 5 are included and labeled in the legend in Figures 1 and 2.
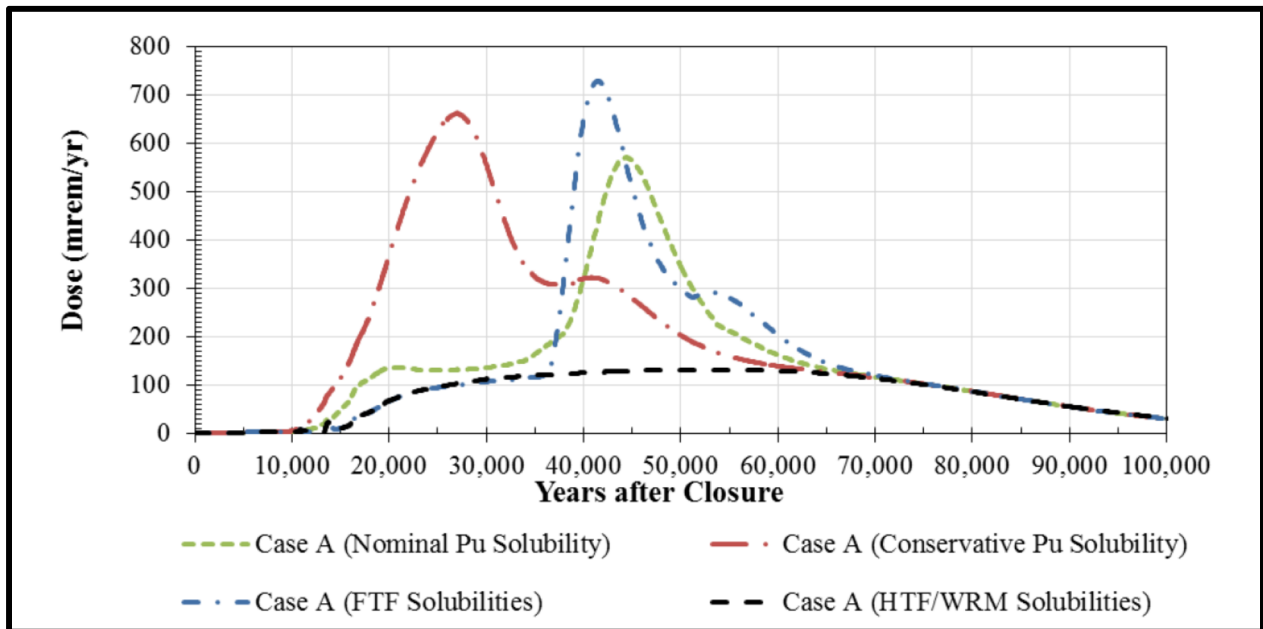

Figure 1. FTF Dose for Four Different Pu Solubilities

Table 4. Waste Release Testing Results[a]

Sample	Week	pH	E_h (mV)	Pu (M)	U (M)	Tc (M)	Np (M)
Model Value		11.1	−470	3.00E−11	5.00E−09	1.00E−14	1.00E−09
RRII-E	1	11.0	59	—	—	—	—
	2	10.9	−159	7.80E−10	6.50E−04	1.70E−09	8.50E-10
	3	10.9	−43	7.40E−10	5.90E−04	2.90E−09	1.20E−09
	4	10.9	−174	7.70E−10	1.10E−06	5.70E−09	2.40E−09
	5	10.9	−244	4.50E−09	1.70E−06	5.70E−10	2.40E−10
	6	10.9	−262	2.80E−09	2.80E−06	5.60E−10	2.40E−10
	7	10.9	−153	1.80E−09	2.70E−06	5.70E−10	2.40E−10
RRII-F (CFS)	1	11.7	−29	2.50E−12	1.30E−05	1.10E−08	2.30E−09
	2	11.7	−321	1.40E−11	1.10E−05	3.00E−09	2.40E−10
	3	11.7	−174	1.40E−10	1.10E−05	2.90E−09	1.20E−09
	4	11.3	−199	1.10E−10	2.20E−06	5.80E−09	2.40E−09
	5	11.4	−249	4.50E−11	1.90E−06	5.70E−10	2.40E−10
	6	11.4	−202	9.10E−11	1.60E−06	5.60E−10	2.30E−10
	7	11.4	−135	3.30E−11	1.50E−06	5.70E−10	2.40E−10
Model Value		11.1	560	3.00E−11	5.00E−05	1.00E−13	3.00E−07
ORII-A	1	11.4	330	6.00E−11	1.80E−06	5.40E−09	2.30E−09
	2	11.3	391	1.20E−10	2.60E−06	3.34E−09	2.40E−10
	3	11.4	356	9.30E−11	—	—	—
	4	11.4	402	1.70E−10	3.20E−06	7.70E−09	2.40E−09
	5	11.2	324	4.00E−10	4.30E−06	9.50E−09	2.40E−10
	6	11.2	320	4.70E−10	4.30E−06	1.10E−08	2.40E−10
	7	11.1	358	5.70E−10	3.60E−06	1.30E−08	2.40E−10
ORII-B	1	11.0	311	8.20E−10	2.90E−06	5.50E−09	2.30E−09
	2	11.0	291	2.60E−09	3.80E−06	6.60E−09	2.40E−10
	3	10.9	407	3.00E−09	3.50E−06	8.10E−09	1.20E−09
	4	10.9	342	4.20E−09	4.00E−06	8.80E−09	2.40E−09
	5	11.0	309	5.00E−09	6.80E−06	9.20E−09	2.40E−10
	6	10.8	317	5.00E−09	1.60E−05	1.10E−08	2.70E−10
	7	10.6	343	8.50E−09	4.20E−05	1.30E−08	3.40E−10
Model Value		9.2	680	3.00E−11	4.00E−06	2.00E−15	2.00E−06
ORIII-C	1	9.6	354	1.00E−08	2.30E−04	5.50E−09	4.50E−09
	2	9.6	304	1.60E−08	2.70E−04	4.80E−09	4.20E−09
	3	9.5	520	1.70E−08	2.60E−04	7.80E−09	4.60E−09
	4	9.2	522	1.10E−08	3.70E−04	8.00E−09	4.20E−09
	5	9.2	474	1.20E−08	4.20E−04	8.50E−09	4.80E−09
	6	9.5	536	9.80E−09	3.90E−04	1.10E−08	3.20E−09
	7	9.7	549	7.90E−09	3.30E−04	1.20E−08	3.00E−09
ORIII-D	1	9.8	348	2.00E−08	1.60E−04	5.50E−09	7.90E−09
	2	—	—	—	—	—	—
	3	9.0	520	3.20E−09	5.00E−06	2.90E−09	1.40E−09
	4	9.0	472	7.60E−09	9.50E−05	5.70E−09	2.40E−09
	5	9.1	511	8.60E−09	6.50E−05	4.40E−09	1.50E−09
	6	9.5	516	4.80E−09	6.20E−05	6.30E−09	1.20E−09
	7	9.5	472	4.50E−09	4.70E−05	6.30E−09	1.30E−09

Adapted from Table 4.1-2 in SRR-CWDA-2016-00086
[a] Minimum detection limit values are in yellow highlight (unlike actual measured values)

Table 5. Modeled and Experimentally-Derived Apparent Solubilities of Four Key Radionuclides

	Modeled			Experimental Range*			
	RRII	**ORII**	**ORIII**	**ORII and ORIII Wash**	**RRII**	**ORII**	**ORIII**
Neptunium							
FTF PA	2E−09	2E−05	1E−04	NA			
HTF PA	1E−09	3E−07	2E−06	NA			
Conservative Case	2E−10	3E−09	5E−09	1.3E−09 2.9E−08	2.3E−10 2.4E−09	2.4E−10 2.4E−09	1.2E−09 7.9E−09
Plutonium							
FTF PA	4E−12	4E−14	6E−05	NA			
HTF PA	3E−11	3E−11	3E−11	NA			
Conservative Case	5E−09	1E−08	2E−08	4E−08 3E−07	2.5E−12 4.5E−09	6.0E−11 8.5E−09	3.2E−09 2.0E−08
Nominal Case	1E−09	1E−09	1E−08				
Technetium							
FTF PA	3E−11	3E−13	No solubility control	NA			
HTF PA	1E−14	1E−13	2E−15	NA			
Conservative Case	3E−09	2E−08	2E−08	9.4E−09 1E−08	5.6E−10 1.1E−08	3.3E−09 1.3E−08	2.9E−09 1.2E−08
Nominal Case	6E−10	1E−08	1E−08				
Uranium							
FTF PA	2E−09	2E−11	3E−05	NA			
HTF PA	5E−09	5E−05	4E−06	NA			
Conservative Case	1E−03	5E−05	5E−04	3.2E−04	1.1E−06	1.8E−06	5.0E−06
Nominal Case	2E−06	4E−06	1E−04	4.6E−03	6.5E−04	4.2E−05	4.2E−04

*Note the minimum and maximum observed values in the experimental range may not reflect equilibrium conditions (e.g., the minimum values may have occurred early during the experiment with concentrations increasing over time as the system approached equilibrium conditions, and if the experiments were continued, maximum concentrations could be higher). Therefore, the observed concentrations may or may not be representative of the expected concentrations leaching from the HLW tanks in the real system. For additional information about the change in observed concentration over time due to reaction kinetics and other phenomena, please see Table 4 in this technical review report and data, tables, and figures in SRNL-STI-2016-00432 and SRR-CWDA-2016-00086.
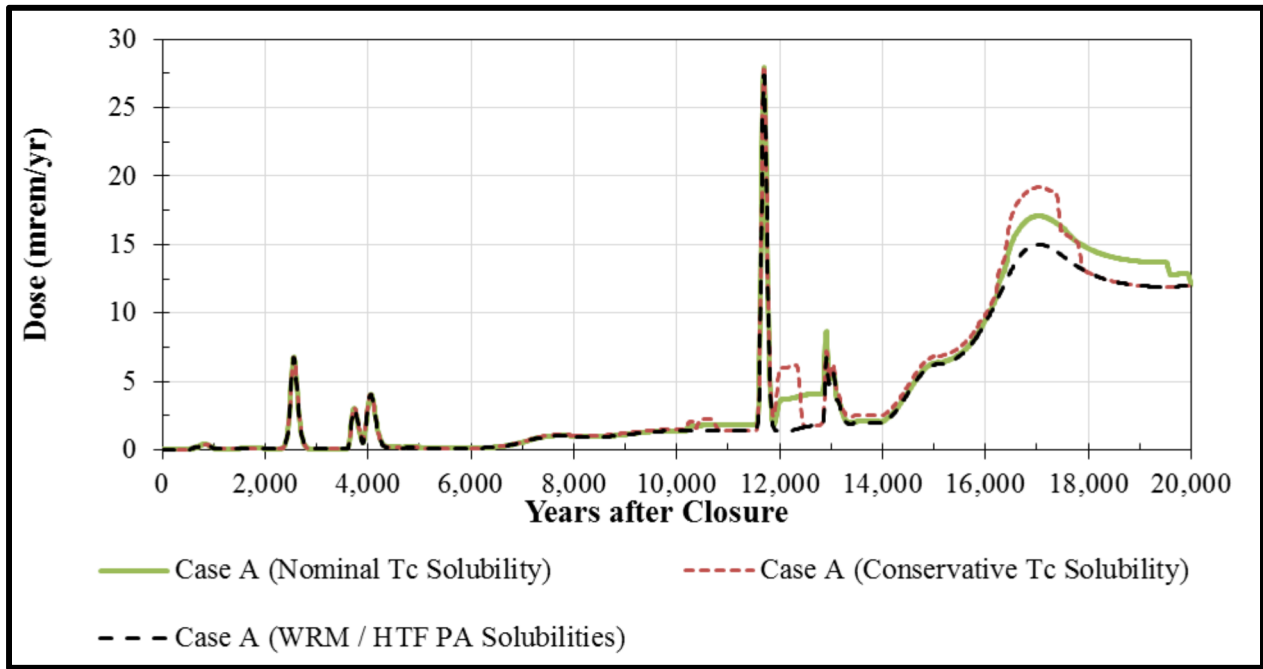
Figure 2. HTF Dose for Four Different Tc Solubilities

<u>NRC Staff Evaluation</u>:

Background on Previous Reviews and Barrier Analysis

SRNL-STI-2016-00432 reports results of leaching experiments conducted on actual SRS Tank 18F residual waste (i.e., "real waste"). The experiments simulated water infiltration through tank grout and the residue at the base of the waste tank during three grout degradation periods: RRII, ORII, and ORIII. To provide context for NRC staff's review of SRNL-STI-2016-00432, some background information on the assumed solubility values in previous PA documentation is provided next.

Table 6 below provides information on the assumed Pu solubility in the FTF PA (see column "Base Case"), as well as revised Pu solubilities developed by DOE in response to NRC staff's TER comments (see all other columns). The "realistic E_h" Pu solubilities were later used as the base case Pu solubility in the HTF PA as well. The updated solubility modeling was reviewed in NRC staff's waste release Technical Review Report (TRR) (ML12272A082). The associated Tanks 18F and 19F Special Analysis (SA) used the updated solubility values to estimate dose for comparison to FTF PA results. NRC staff reviewed the Tanks 18F and 19F SA in a separate TRR (ML13100A230). In its waste release TRR, NRC staff reiterated the need for additional support for the assumed chemical transition times (see discussion in the next paragraph), and experimental validation for the assumed solubilities given uncertainty in the geochemical modeling. The need for additional support for key barrier performance assumptions was also reiterated in the Tanks 18F and 19F SA TRR (e.g., basemat, and natural system K_ds). In fact, the results of the waste release experiments showed that in most cases, the assumed solubilities used in the PAs and in the Tanks 18F and 19F SA were overly optimistic as discussed in more detail below; and DOE has not yet addressed technical issues associated with support for key barriers affecting the timing and magnitude of peak dose (i.e., the basemat and natural system K_ds).

Figures 3 and 4 (see green and red dashed, vertical lines in Figure 4) illustrate the two transition times between the three grout degradation periods at which time E_h and pH markedly change, and the resulting three chemical regimes assumed in the FTF PA for Type IV tanks, such as Tank 18F. Figure 3 presents additional details regarding the assumed phases controlling Pu solubility, as well as the assumed chemistry of the groundwater in contact with grout solids. Table 7 presents information on the assumed chemical transition times in the HTF PA in comparison to the FTF PA. With the exception of the iron (Fe) coprecipitation column listed in Table 6, the Pu solubilities are assumed to either stay the same or increase with time. As can be seen in these figures and tables, DOE oftentimes relies on the chemical performance of the tank grout for tens of thousands of years. Therefore, the timing of chemical transitions to higher solubility are oftentimes risk-significant in DOE's PAs. Uncertainty in chemical transition times are addressed in NRC staff's Monitoring Plan under MFs 2.2, "Chemical Transition times," and 3.2, "Groundwater Conditioning via Reducing Grout" (ML15238B403).

Additionally, Figure 4 illustrates the importance of the steel liner, basemat, and natural system in delaying the timing of peak dose from Pu. Uncertainty in steel liner performance is addressed in NRC staff's monitoring plan, MF 3.1, "Hydraulic Performance of Concrete Vault and Annulus (As it Relates to Steel Liner Corrosion and Waste Release)." Uncertainty in basemat performance is addressed by MF 3.5, "Vault and Annulus Sorption." And uncertainty in natural system performance is addressed by MF 4.1, "Natural Attenuation of Key Radionuclides". While awaiting the results of the waste release experiments which addressed NRC staff's highest priority MF 2.1, "Solubility Limiting Phases/Limits and Validation", DOE has not yet addressed these other high priority MFs[5].

A peak dose ranging from approximately 1 to 7 mSv/yr (100 to 700 mrem/yr) results depending on the assumed solubility of Pu (see Figure 1). Additionally, the timing of the peak dose varies tens of thousands of years (e.g., "conservative" case versus "nominal" or "HTF" case) depending in large part on whether risk-significant solubilities are assumed initially or later in time, demonstrating again the importance of chemical barrier performance on the results[6].

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[5] NRC staff notes that the need for work on the other high priority MFs was dependent on the results of the waste release experiments; therefore, NRC staff did not expect DOE to address these other high priority MFs until the results of the waste release experiments were evaluated. For example, if the observed solubilities of key radionuclides was below levels of concern, no additional work would be needed. However, because of the risk-significance of the Pu concentrations observed in the waste release experiments, NRC staff finds that additional work is needed to address other high priority MFs.

[6] It is important to note that the results presented in Figure 1 were based on GoldSim modeling reported in SRR-CWDA-2016-00086, while the results reported in the FTF PA (SRS-REG-2007-00002, Rev. 1) and Tanks 18F and 19F SA (SRR-CWDA-2010-00124) are based on PORFLOW modeling, leading to differences in the reported peak doses with GoldSim typically resulting in higher peak doses compared to PORFLOW. Additionally, following preparation of the FTF PA, a higher, final estimated Pu inventory was developed for use in the Tanks 18F and 19F SA. The higher estimated Pu inventory was based on actual residual waste sampling following waste retrieval.

Table 6. Assumed Solubility of Pu for Different Chemical Regimes and Different Assumed Phases from the Tank 18F SA (SRR-CWDA-2010-00124).*

E_h/pH Regime	Base Case (mol/L)	Fe Coprecipitation (mol/L)	$PuO_{2(am,hyd)}$ (conservative E_h) (mol/L)	$PuO_{2(am,hyd)}$ (realistic E_h) (mol/L)
Reduced Region II	4.1E−12	3.0E−14	3.2E−11	3.2E−11
Oxidized Region II	4.0E−14	2.5E−13	5.2E−08	3.2E−11
Oxidized Region III	5.7E−05	5.0E−15	7.8E−08	3.2E−11

* The chemical transitions proceed as follows: Reduced Region II, Oxidized Region II, Oxidized Region III. Table 7 provides information on the timing of the chemical transitions.

Table 7. Assumed Chemical Transition Times. Taken from Table 3-2 in the Tank Farms Monitoring Plan (ML15238A761).

Submergence of Tank	Transition	Number of Pore Volumes Required [CZ Transition Time (Year)]	
		HTF PA	**FTF PA**
Partially and Nonsubmerged	Reduced Region II to Oxidized Region II	523 (7,900 Type IV; 9,200 Type II NL; 15,000 Type II; 16,000 Type III)	371[†] (10,500 Type IV; 15,500 Type I; 15,500 Type III/IIIA)
	Oxidized Region II to Oxidized Region III	2,119 (19,000 Type II NL; 22,000 Type IV; 25,000 Type II; 28,000 Type III)	2,063[‡] (20,000 Type IV; 20,000 Type I; 20,000 Type III/IIIA)[§]
Submerged	Reduced Region II to Oxidized Region II (Condition C to D)	1,787 (7,700 Type I NL; 12,000 Type I)	NA
	Oxidized Region II to Oxidized Region III (Condition D to Oxidized Region III)	2,442 (8,100 Type I NL; 12,000 Type I)	NA

Notes:
[†]Transition to Oxidized Region II occurs at 371 DPV in original FTF PA (SRR–CWDA–2010–00128) but changed to 523 DPV in the Tanks 18 and 19 Special Analysis (SRR–CWDA–2010–00124), consistent with what was later used in the HTF PA.
[‡]Transition to Oxidized Region III occurs at 2,063 DPV in original FTF PA (SRR–CWDA–2010–00128) but changed to 2,119 DPV in Tanks 18 and 19 Special Analysis (SRR–CWDA–2010–00124), consistent with what was later used in the HTF PA.
[§]Although the calculated chemical transition time based on the displaced pore volume count would occur after 20,000 years, the final chemical transition was assumed to occur at 20,000 years, because most of the simulations ended prior to the transition from Oxidized Region II to Oxidized Region III. DOE did provide results to 100,000 years in one simulation.

NL=no liner, HTF = H-Area Tank Farm, FTF = F-Area Tank Farm, CZ = Contaminated Zone, PA = Performance Assessment
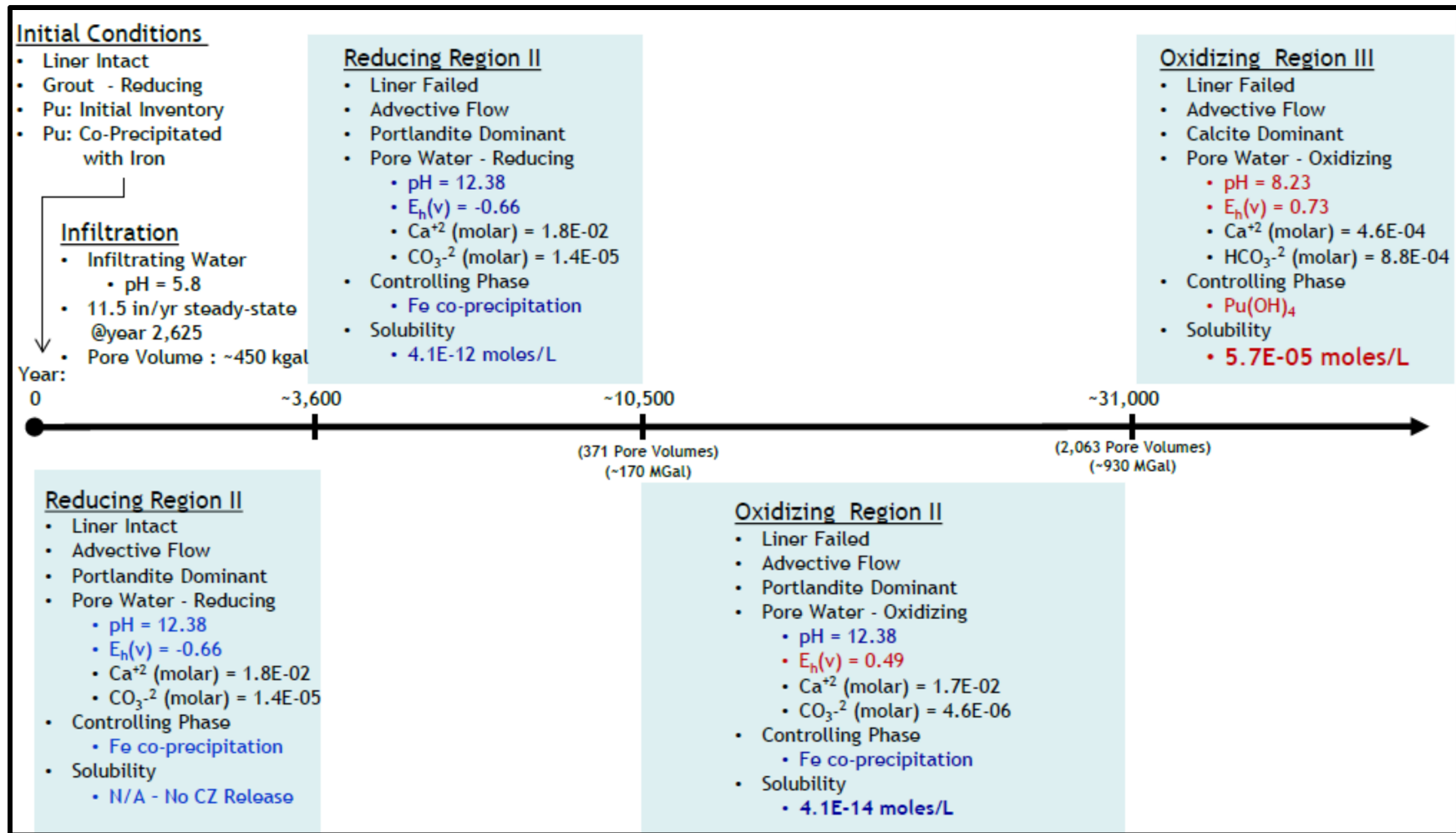
Initial Conditions
- Liner Intact
- Grout - Reducing
- Pu: Initial Inventory
- Pu: Co-Precipitated
  with Iron

Infiltration
- Infiltrating Water
  - pH = 5.8
- 11.5 in/yr steady-state
  @year 2,625
- Pore Volume : ~450 kgal

Reducing Region II
- Liner Failed
- Advective Flow
- Portlandite Dominant
- Pore Water - Reducing
  - pH = 12.38
  - $E_h(v) = -0.66$
  - Ca^{+2} (molar) = 1.8E-02
  - CO_3^{-2} (molar) = 1.4E-05
- Controlling Phase
  - Fe co-precipitation
- Solubility
  - 4.1E-12 moles/L

Oxidizing Region III
- Liner Failed
- Advective Flow
- Calcite Dominant
- Pore Water - Oxidizing
  - pH = 8.23
  - $E_h(v) = 0.73$
  - Ca^{+2} (molar) = 4.6E-04
  - HCO_3^{-2} (molar) = 8.8E-04
- Controlling Phase
  - $Pu(OH)_4$
- Solubility
  - 5.7E-05 moles/L

Year:
0   ~3,600   ~10,500   ~31,000

(371 Pore Volumes)   (2,063 Pore Volumes)
(~170 MGal)   (~930 MGal)

Reducing Region II
- Liner Intact
- Advective Flow
- Portlandite Dominant
- Pore Water - Reducing
  - pH = 12.38
  - $E_h(v) = -0.66$
  - Ca^{+2} (molar) = 1.8E-02
  - CO_3^{-2} (molar) = 1.4E-05
- Controlling Phase
  - Fe co-precipitation
- Solubility
  - N/A – No CZ Release

Oxidizing Region II
- Liner Failed
- Advective Flow
- Portlandite Dominant
- Pore Water - Oxidizing
  - pH = 12.38
  - $E_h(v) = 0.49$
  - Ca^{+2} (molar) = 1.7E-02
  - CO_3^{-2} (molar) = 4.6E-06
- Controlling Phase
  - Fe co-precipitation
- Solubility
  - 4.1E-14 moles/L

Figure 3. Type IV Tank Pu Solubility Modeling Parameters in the FTF PA. Taken from Figure 6.3-16 in the FTF PA SRS-REG-2007-00002, Revision 1.
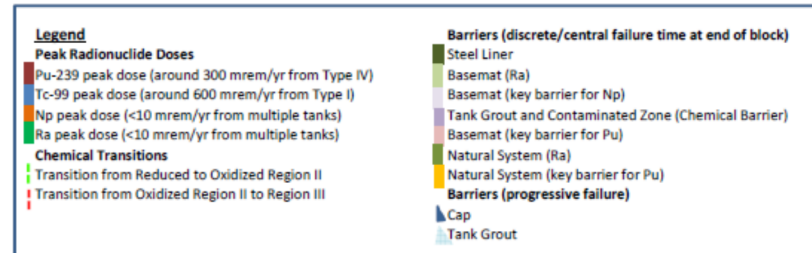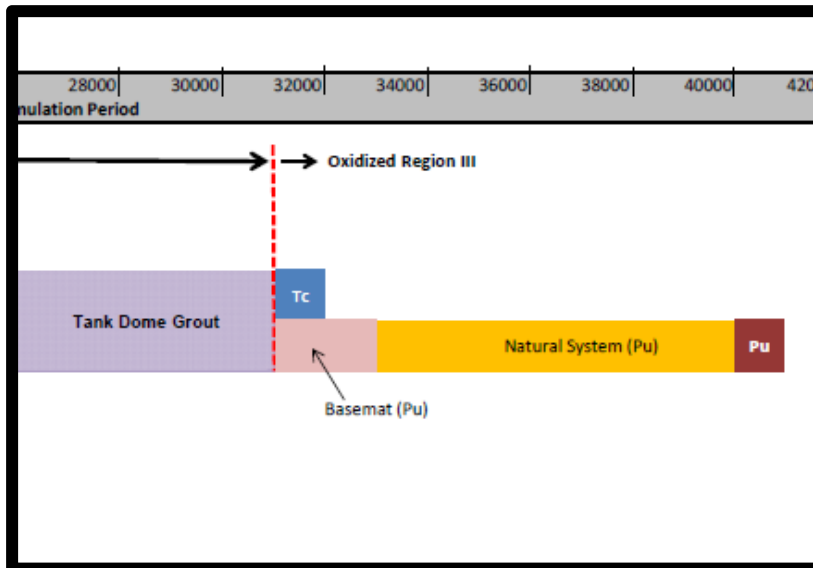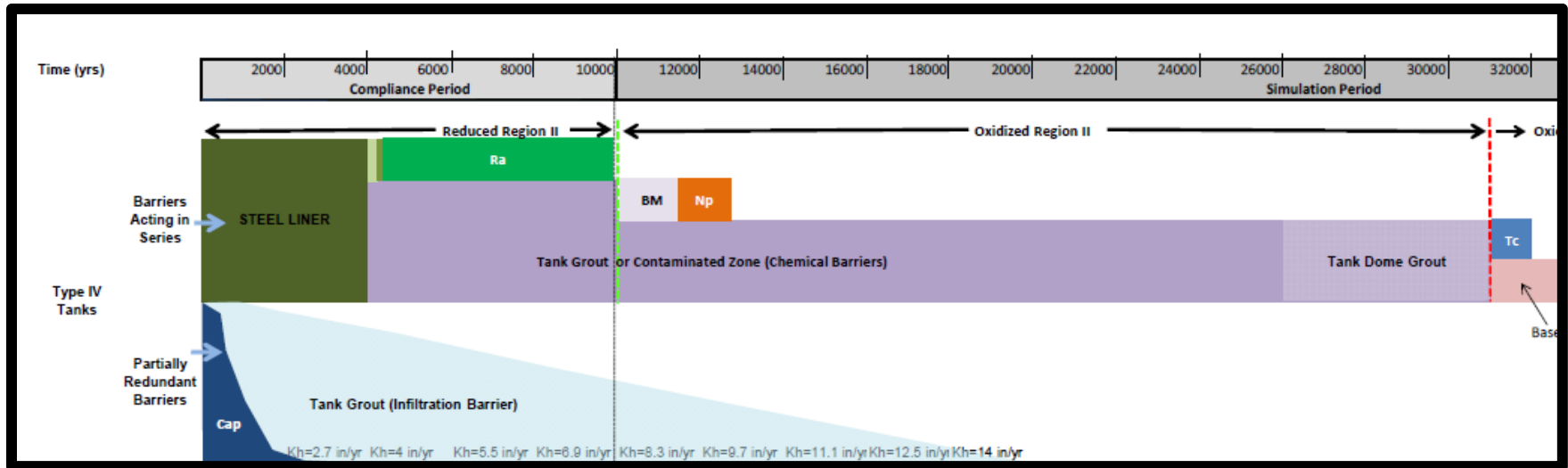
Figure 4. NRC Staff's Interpretation of Performance of Barriers to Timing of Peak Dose in DOE's FTF PA. Adapted from Figure 3-5 in the Tank Farms Monitoring Plan (ML15238A761).

NRC Evaluation of Real Waste Release Testing

The results presented in SRNL-STI-2016-00432 are intended to be useful for selecting radionuclide release models and parameters for PAs of waste tanks containing residual waste incidental to reprocessing. The simulated grout pore waters that were mixed with the waste residue samples were based on modeling conducted to support the PAs. NRC staff agree that using geochemical modeling as a starting point for chemical conditions is reasonable; however, NRC staff also understands that there is uncertainty in modeling geochemical conditions. In fact, deviations between modeled and experimental chemical conditions were indicated by initial testing and later in final waste release experiments, which showed that the targeted E_h endpoints could not be achieved without the introduction of what was deemed to be non-representative reducing and oxidizing agents (SRNL-STI-2015-00446). During the August 13–14, 2018, OOV, DOE contractors provided a presentation on follow-on Tank 12 real waste release testing that has since been conducted (ML18247A080). Early results from this testing also demonstrate the difficulty DOE contractors had in achieving the targeted E_h endpoints and corroborate earlier statements by the investigators regarding the unrealistic assumptions regarding lower and higher endpoint E_h values in the real system.

The Tank 18F real waste release experiments were conducted after an extended period of design development. The investigators faced a variety of challenges, including working with highly radioactive material, establishing and maintaining solution E_h and pH values, accurately measuring these parameters in leach solutions, controlling CO_2 in the gas phase above the solutions, and avoiding plutonium contamination from the shielded cells. The investigators recognized potential sources of uncertainty and experimental artifacts and developed apparatus and methods for addressing the uncertainties. The report appropriately concludes that the developed methods and equipment are well designed for their intended purpose. The investigators also reported a variety of other analytical data that provided useful characterization information. Some of these data (e.g., XRD and SEM) also aided in interpreting the leach test results.

Regarding the main thrust of the report—radionuclide leaching from real Tank 18F waste—the investigators found that typical leachate concentrations of U and Pu exceeded solubilities modeled as coprecipitating with an iron phase. For RRII conditions, U and Pu exceeded the modeled pure-phase solubility limits for UO_2 and PuO_2 shown in Table 3-4 of SRNL-STI-2016-00432 and the values used in the more recent HTF PA by factors of approximately 400[7] and 70, respectively. Based on these results, the assumed solubility limits for U and Pu that were used in the FTF and HTF PAs lack support. For oxidizing conditions, the Pu leachate concentrations were bounded by modeled pure-phase solubilities, but not the base case solubilities assumed in the HTF PA (and "realistic E_h" solubilties assumed in the Tanks 18F and 19F SA). Additionally, high U concentrations in ORIII leachates are consistent with the presence of a phase more soluble than hydrous uranyl oxide, which was used for PA solubility models.

For RRII conditions, Tc and Np were below detection limits in leachates. Because the detection limits were higher than iron coprecipitation solubilities, but below pure-phase solubilities shown in Table 3-6 of SRNL-STI-2016-00432, the results suggest that using these pure-phase solubility limits in the PA is conservative. The results for Tc and Np for ORII and ORIII were not conclusive, but nevertheless showed that iron phase coprecipitation models under-predict released concentrations.

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[7] The U concentration was a factor of 1000 higher than the assumed solubility in the FTF PA.

The report discussed the effect of wash solutions (i.e., solutions resulting from nearly complete removal of supernate) on leaching results. For all four oxidized region residue samples, washing took place prior to leaching. The real waste release report acknowledged that washing affected the quantity of U available for leaching and therefore limited interpretation of U data. Direct observations of the elimination of U solids after washing support the marked effect of washing on U concentrations. The measured wash solution concentrations also generally exceeded leachate concentrations for the other three radioelements. The fact that significant losses of radionuclides occurred during washing suggests that waste retrieval methods were not effective in the portion of the tank where sample FTF-1, the sample used in the waste release experiments, was collected. This is not unexpected as FTF-1 was collected at the periphery of the tank to the southeast with waste accumulating on the periphery of the tank (see Figure 5). DOE selected FTF-1, because this sample contained the highest concentrations of key radionuclides.

The two reduced region residue samples were washed midway through the leach tests. The main apparent effects of these washings were that Tc and Np were not detectable in subsequent leachates, and U leachate concentrations dropped markedly. Again, washing had a marked effect on U, and the pre-wash U concentrations in RRII solutions were well above modeled solubility limits. The NRC staff agrees that the post-wash U leach results are unlikely to represent solubility limits that would be appropriate for PA modeling. Although the investigators deemphasized the potential performance effects of high radioelement concentrations in initially contacting solutions, this observed effect warrants further consideration in future PAs. In the following section, NRC staff evaluates the impact of potentially higher, earlier solubility in the waste zone.

Oxidation of the samples could have affected the results, and it was unclear to NRC staff the extent to which the samples may have been exposed to ambient air inside the shielded cell throughout the course of the experiment. During the August 13–14, 2018 OOV, the investigators indicated that oxidation of the samples was not a concern during the very short time period these samples were subjected to ambient air due, in part, to continuous nitrogen purging of the experiments (ML18235A538). Investigators also agreed to document their evaluation of an issue raised by NRC staff regarding the non-representative solids-to-water ratios[8] used in the experiments in the upcoming Tank 12 waste release report. NRC staff also expressed a technical concern regarding the potential loss of Pu during filtering performed to prevent cross-contamination of the sample with Pu present in the laboratory. In response to this concern, DOE indicated that controls were used that provide support that only Pu associated with contamination in the laboratory was filtered, and not Pu associated with the sample.

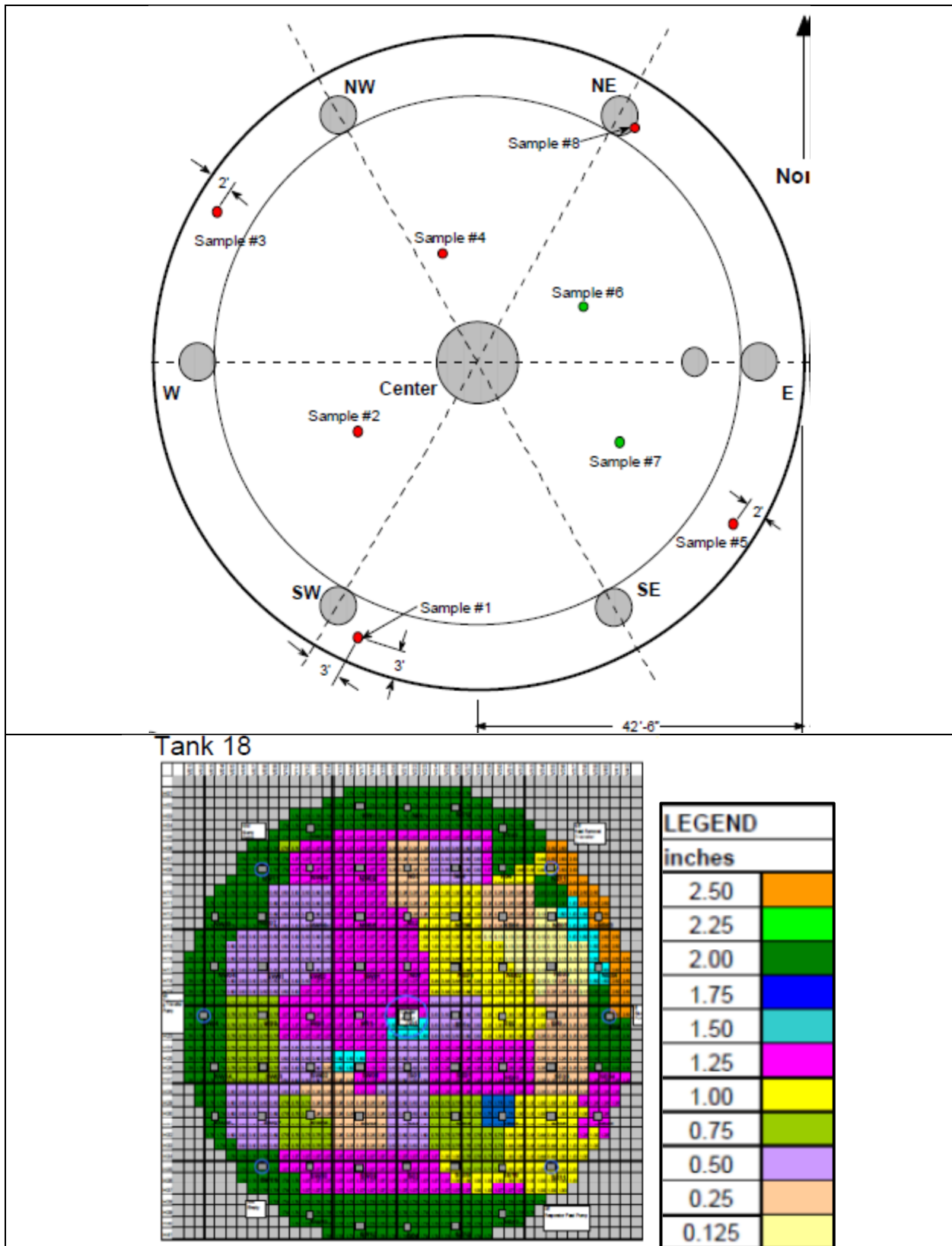[8] NRC staff also notes that the solids to liquid ratio changed over time due to sampling.

Figure 5 Location of Sample FTF-1 and Distribution of Residual Waste in Tank 18F

As shown in Figure 3-5 of SRNL-STI-2016-00432, Pu concentrations were still increasing at the end of the ORII experiments (see Figure 6). A gradual increase in Pu concentration with time was observed for both ORII test samples, and based on the data, it is uncertain whether saturation and equilibrium were achieved during the test period. In addition, the Pu concentrations observed for the ORII-A sample were consistently an order of magnitude lower than for the ORII-B samples. This difference is not understood, because nearly identical sample preparation methods and amounts were used for each. Plutonium concentrations observed for the ORIII test samples (C and D) were more stable and were typically the highest values observed (near 1×10^{-8} M) of any samples tested. Due to the gradual increases observed for the ORII-B samples, the final sample analyzed was also near 1×10^{-8} M. The Pu concentration results still exhibit a significant level of uncertainty, and indicate a complexity not easily captured in a model using a single solubility value to represent the contaminated zone at each time step. It is possible that the Pu results reflect the fact that the residual sample includes two or more types of Pu with differing solubilities. The differing solubilities could be associated with oxidation state, chemical speciation, or matrix differences. For example, a significant fraction of the Pu in the sample could be coprecipitated with other metals present in the residual solids or imbedded deep within the solid matrix (SRNL-STI-2016-00432). Inability to achieve steady state concentrations can also be seen on ORII-B U results and in all Tc results. The investigators should explore approaches to resolving the lack of steady-state observations and provide justification for use of the results in PA modeling.
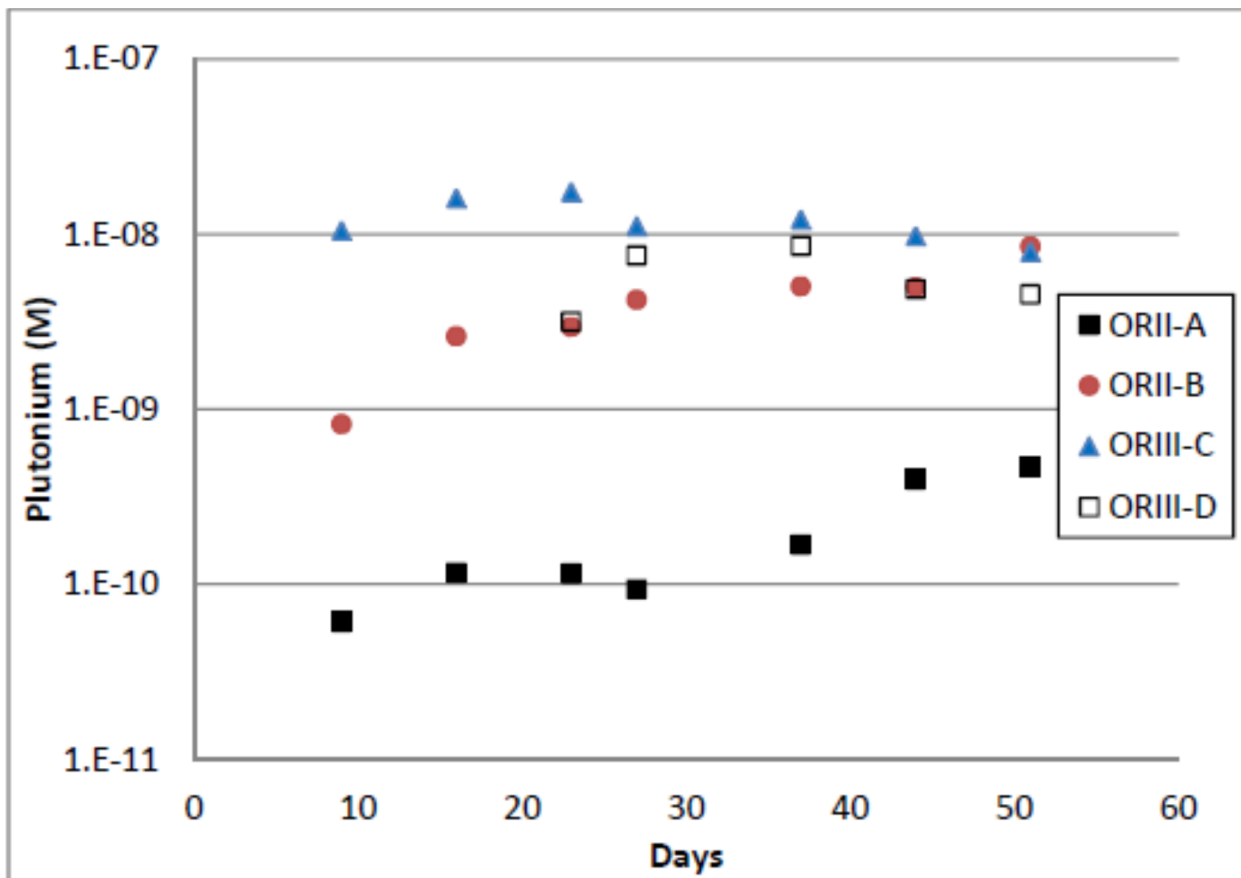

Figure 6. Pu Concentrations versus Time for ORII and ORIII Experiments (Reproduced from Figure 3-5 of SRNL-STI-2016-00432, Rev. 0)

The investigators conducted XRD, SEM, and particle size analyses of the real waste before leaching for one oxidizing and one reducing sample. With the XRD analyses, uranium phases such as Clarkeite and Cejkaite were observed prior to leaching. The investigators noted that Cejkaite, which is a uranium carbonate phase, has been observed in other waste samples collected from the Tank 18F floor. However, Cejkaite has not been observed in waste samples collected from other tanks. The investigators also discussed that carbonate phases such as Cejkaite would be expected to be more soluble than the commonly observed uranium oxide phase, Clarkeite, and the uranium phases assumed in the geochemical modeling by DOE (see Table 3-4 of SRNL-STI-2016-00432). Although not observed in the XRD analysis, the investigators stated that the formation of plutonium and neptunium carbonate phases[9] is also likely in Tank 18F. After both RRII and ORIII leaching, the XRD scan showed that no uranium minerals remained. These analyses, especially coupled with waste release experiments such as the ones reported in SRNL-STI-2016-00432, provide insight into waste release concentrations and mechanisms for Tank 18F as well as other tanks. Results from XRD analyses of other tank wastes could be used to update the predicted mineral phases used in geochemical models. Results from the waste release experiments could be used to evaluate the appropriateness of the thermodynamic data in the geochemical model. Model updates would significantly reduce uncertainty in tank waste release modeling.

XRD analyses showed the presence of calcite before and after leaching for the RRII-E and ORIII-C samples. However, it is not clear to NRC staff how the results from the waste release experiments may have been influenced by the potential incorporation of trace radioelements during the formation of calcite compared to sorption of these trace radioelements onto the surface of pre-existing calcium carbonate phases. Additional information related to any potential experimental artifacts due to the addition of calcium carbonate would be helpful.

DOE conducted a particle size analysis of Sample FTF-1 (p. 27 of SRNL-STI-2016-00432). Before leaching, the mean particle size was 112 µm with a range of <10 µm to approximately 700 µm. The authors of the report noted that the mean particle size for Sample FTF-1 was much larger than typical tank waste samples, which have average particle diameters of <10 µm. The post-leaching results from the particle size analysis for both the RRII-E and ORIII-C samples showed that all of the remaining particles were less than 100 µm and that the mean particle diameters were much smaller than the original sample. However, the post-leaching particle diameters were stated as still being large relative to typical sludge. It is not clear what caused the reduction in particle size during leaching, but DOE should consider potential implications of leach test sample particle sizes. Because of the potential for non-conservative waste release results from the use of samples with larger-than-typical particle sizes, NRC staff note that the use of a composite sample could help mitigate this concern (i.e., use of composite samples could provide results that are more representative of the entire tank contents including wastes of varying particle size and chemical composition). Efforts should be made to avoid grinding the samples which could influence the results.

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[9] XRD analysis is typically not sensitive enough to detect phases in low concentrations as would be expected for any Pu and Np phases.

With regard to how the experimental results impact PA assumptions, NRC staff notes the following:

- The waste release testing results demonstrate the importance of the waste release experiments, which were recommended by NRC staff in its TER (ML112371715) and monitoring plan (ML15238A761), as well as an independent peer review group under contract with the DOE (LA–UR–2012–00079). The experiments were recommended to validate the waste release modeling used in the FTF and HTF PAs. In many cases, the results of the waste release experiments demonstrate the difficulty in projecting solubility of key radionuclides for these unique tank wastes, notwithstanding use of the best thermodynamic data available in the literature for the geochemical modeling.

- In particular, the results of the Tank 18F experiments show that the Fe coprecipitation model for radioelement release concentrations is likely inappropriate and is expected to underpredict release rates.

- Assuming the pure-phase solubility values shown in Table 3-6 of SRNL-STI-2016-00432 in future PAs is likely reasonable or conservative for Tc, and Np.

- Observed U concentrations in wash solutions and leachates suggest U solubilities assumed in the PAs are potentially nonconservative and identification of the solubility-limiting solid in tank wastes is needed.

- Inability to achieve equilibrium concentrations at the end of ORII tests for Pu and the discrepant final concentrations for Pu in the two different ORII test results demonstrate the level of complexity involved when modeling Pu release. Additional work to address uncertainty in Pu solubility would be beneficial.

- An important finding in SRR-CWDA-2016-00086 is that Np, Pu, and U solubility appear to be more correlated to pH compared to E_h. This finding is contrary to the results of geochemical modeling which shows a dependence of Np and U solubility on E_h. These results should be investigated further and the geochemical modeling updated as warranted to have confidence in the results.

- In general, radioelement release appears to be tank-specific. For example, Tank 18F residue contains calcite and cejkaite, which according to the investigators are not typical in SRS tank residues. Cejkaite is expected to be relatively soluble compared to more typical uranium oxide phases and the presence of carbonates could also increase Pu and Np mobility. The presence of soluble phases such as cejkaite in tank wastes should be evaluated.

- DOE should consider the following: (1) comparison of the experimental conditions against those for which the NEA's thermodynamic database is based to better understand differences in the modeled and experimental results, and (2) update the assumed phases and geochemical modeling as warranted. Understanding factors that influence radionuclide solubility is important to extrapolating the Tank 18F real waste release experimental results to other wastes in other tanks.

- Waste samples from other tanks should be characterized and modeled.

- Evaluation of concentrations in rinse solutions reveals that, in some cases, the highest concentrations are observed for freshly washed waste, suggesting the potential importance of initial concentrations. DOE should study the impact of higher initial concentrations of waste. NRC staff evaluates the impact of higher initial concentrations in the next section.

<u>NRC Evaluation of Updated PA Modeling Using Results from the Waste Release Testing</u>

Insights With Regard to the Uncertainty in Geochemical Modeling

The primary purpose of the Tank 18F waste release experiments was to provide information about the expected solubility of key radionuclides given a set of modeled chemical conditions. As discussed above, in many cases and for many assumed chemical states, the solubility of key radionuclides was higher than expected based on geochemical modeling, while in other cases and for certain chemical states, the solubility of the key radionuclides was lower than expected. The results of the waste release experiments are useful in better understanding the uncertainty in the geochemical modeling that may be reflective of lack of knowledge about the unique chemical composition of the tank wastes, as well as the lack of information available in the thermodynamic databases used to simulate these systems. For example, in the Tanks 18F and 19F SA, DOE evaluated a conservative case with Pu solubility of 5×10^{-8} mol/L and 8×10^{-8} mol/L for ORII and ORIII, respectively, and characterized a solubility for all three chemical conditions of 3.2×10^{-11} mol/L as being more realistic (see Table 6). The waste release experimental results reported in SRNL-STI-2016-00432 do not support the "realistic" solubility value reported in the Tanks 18F and 19F SA based on updated geochemical modeling using the best available thermodynamic data available in the literature (all of the experimental results approached values that were orders of magnitude higher than the "realistic" solubility values used in the Tanks 18F and 19F SA). The results of the waste-release testing, therefore, demonstrate the importance of experimental validation of the geochemical modeling results for risk-significant tanks and radionuclides.

While the results of the waste-release testing are informative and provide valuable inputs to the updated PA modeling, NRC staff note that the highest Pu solubility value observed in the experiments occurred for a washed sample, suggesting that initial concentrations of Pu that may be released from the tanks may be the most risk-significant. Concentrations observed for washed samples may be appropriate as input for alternative cases where the ground water conditioning properties of the tank grout are bypassed, such as may occur due to water table rise or due to fast flow of infiltrating ground water through preferential flow pathways (shrinkage gaps, or cracks or other pathways through the tank grout). Because the rinsed samples had Pu concentrations higher than those DOE assumed for the "conservative" case in the updated PA modeling results reported in SRR-CWDA-2016-00086, and DOE did not evaluate the impact of these Pu concentrations, NRC staff performed its own independent analysis (see discussion below).

Uncertainty in Geochemical Modeling Assumptions (Grout Degradation and Near-field Flow Conceptual Models; and Ability of Grout to Condition Ground water)

As discussed above, MF 2.2, "Chemical Transition Times" (ML15238A761) evaluates DOE's PA assumption based on geochemical modeling that the tank grout will condition infiltrating ground water to relatively low E_h and high pH to ensure the low solubility of key radionuclides for long periods of time. As part of this monitoring factor, NRC staff indicated that it would evaluate the assumption regarding the capability of the grout components to react with and condition infiltrating ground water.

In addition to providing information about key radionuclide solubility, the Tank 18F waste release experiments provided useful information about the capability of the reducing tank grout components to condition the ground water to pH and E_h values assumed in DOE's geochemical

modeling. The extent to which reductants in the waste form are capable of influencing E_h and the solubility of key radionuclides is not yet apparent. The real waste release experiments demonstrate uncertainty in the capability of the system to achieve the PA-assumed high and low E_h endpoints. During the August 13–14, 2018, OOV, the investigators clarified that they think the modeled endpoint E_hs listed in Table 1 cannot be achieved in the field after tank closure, because nonrepresentative oxidants and reductants would be needed to achieve those E_h endpoints. An inability to achieve the targeted E_h endpoints in the laboratory may partially explain the differences in observed versus modeled results. Additional testing focusing on the capability of the reducing tank grout to condition infiltrating ground water would be beneficial to reducing the uncertainty associated with the chemical performance of reducing tank grout.

Another factor that influences the capability of the reducing tank grout to condition infiltrating ground water is related to the conceptual model for flow through a grouted tank. MF 3.2, "Groundwater Conditioning via Reducing Grout" (ML15238A761) addresses the conceptual model for flow through the tank grout and the capability of reducing tank grout to condition infiltrating ground water. As addressed in the Tanks 18F and 19F SA TRR, a key uncertainty affecting flow through a grouted tank is related to the conceptual model for tank grout degradation. DOE assumes that the grout monolith degrades homogenously with time, leading to an increase in the grout matrix hydraulic conductivity that facilitates infiltration of water throughout the monolith. If, instead, the grout is initially heterogeneous due to the manner in which the tank was grouted, or if initially homogeneous grout degrades heterogeneously via cracking, and flow throughout the monolith is primarily through preferential fast flow pathways, the reductive capacity of the grout along crack faces may be depleted significantly earlier than predicted by PA models. The end result would be significantly expedited chemical transitions (see Table 7 for basecase chemical transition times).

For 10 years, NRC's contactors at the Center for Nuclear Waste Regulatory Analyses (CNWRA) have developed physical analog models of tank grout at the bench-, meso- and intermediate-scale, and have measured and monitored the post-placement evolution of these grout monoliths to develop practical insights into the flow behavior and risk-significant physicochemical properties of reducing tank grouts that are similar to or the same as those in use by DOE to stabilize tank waste at SRS and Idaho National Laboratory. Experimental results from these investigations provide NRC staff with additional technical bases for evaluating and monitoring DOE's PAs and tank closure activities. One key concern driving these studies is the potential for preferential fast flow pathways (e.g., cracks, shrinkage gaps, and annuli) to develop within a grout monolith, which may then allow rapid movement of air and water into and through the grout mass. Grout monolith specimens have been inspected for cracks, annuli, and void spaces, and gas injection has been performed to characterize grout hydraulic conductivity and shrinkage gap annuli that form around tank internals, such as pipes, tank walls, and cooling coils (Walter et al. 2009; 2010). Voids and gaps are observed to occur at lift boundaries in CNWRA's physical analog models (Walter et al., 2009). Annuli are observed to develop between internal fixtures and grout in all specimens, including pipe-grout specimens. The greater the volume of grout in a monolith, the more potential the grout has to undergo drying shrinkage, and the larger the annular apertures within the grout become (Walter et al., 2009).

Preferential fast flow pathways may develop as tank grout ages as a result of heterogeneities near obstacles, vesicles and vugs within the grout mass, and void space at lift separations and flow lobe interfaces. Grout placed into tanks at CNWRA typically exhibit grout flow lobes[10] (Walter et al., 2009; 2010); grout lobes split to flow around obstacles inside tanks and do not merge together at lobe seams on the downstream side of obstacles because of the non-Newtonian rheology of grout. Each flow lobe within a tank is a discrete unit of grout, separate from its adjacent neighboring lobes. A 20-m-diameter, intermediate-scale grout monolith poured into a tank at the CNWRA exhibited flow lobes and mounding beneath the tremie, which was accentuated by limited capability of the reducing grout to self-level and incomplete lateral delivery of grout as it flowed outward toward the tank wall. Cracks that formed in the grout at the top of this monolith were a response to its non-self-leveling topography (Dinwiddie et al., 2011). An extensive network of cracks developed in the intermediate-scale grout monolith, enabling applied water to permeate the grout and emerge as seepage along its perimeter when dye-tracer tests were conducted (Dinwiddie et al., 2012). Within this nominally 30-inch-high grout monolith, staff observed that grout quality was depth dependent along the tank axis because grout compaction and minimization of gap and void sizes occurs with sufficient overburden, even absent grout vibration, which suggests that less compacted grout at the top of waste tanks will have different hydraulic properties than more compacted grout deeper within monoliths. CNWRA staff examined bonding between this grout monolith and the tank wall, and found it to be variable along the perimeter and with depth, indicating variability in the presence of air gaps between the grout and the tank wall (Dinwiddie et al., 2011). Based upon experimental and operational observations documented to date, tank-waste-stabilizing grout monoliths are composed of non-self-leveling grout that is laterally and vertically heterogeneous, consisting of hundreds to thousands of separate grout flow lobes that are prone to localized shrinkage and fast flow at their seams (Dinwiddie et al., 2012).

NRC is concerned with tank grout heterogeneities, including those associated with mounds of grout that form beneath tremie pipes and grout flow lobes because Dinwiddie et al. (2011; 2012) indicate that the lobe interfaces, as well as interfaces between grout lifts poured on different days, are subject to shrinkage during the thermal contraction and drying processes, potentially forming high hydraulic conductivity, preferential flow paths through the grout. High hydraulic conductivity zones, such as shrinkage gaps at flow lobe interfaces and annuli around pipes, cooling coils, and other internal fixtures are expected to focus inflow of ground water relative to lower conductivity zones. Grout mounded high in a waste tank will hydrate in a relatively dry microclimate, whereas grout submerged understanding bleedwater at a tank perimeter will hydrate in a wetter microclimate; because of this, tank grout properties are unlikely to be uniform along a tank radius. NRC staff is concerned with the potential for bleedwater segregation to deliver a different quality of tank grout to the periphery of waste tanks, with a different water-to-cement ratio that may enhance shrinkage along tank walls and focus flow around, rather than through, reducing tank grout, potentially resulting in less grout water-conditioning of infiltrating ground water than if the water slowly flowed through a uniform, intact grout matrix, as assumed in DOE's PAs (ML13269A365).

Just as an open network of shrinkage gaps may develop around the numerous, individual grout flow lobes and lifts that are stacked within grouted tanks, cracks and crack networks that develop within tank and annulus grout are also potential preferential fast flow pathways that may route infiltrating water rapidly to the contaminated zone at the base of a waste tank. If ground

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[10] A grout flow lobe is a channel-to-fan-shaped mass of grout that forms on a slope by the changing position of the grout source; grout flow lobes were also observed to have formed within DOE's grouted waste tanks (ML13269A365, ML14342A784, and ML16231A444).

water flow occurs primarily through cracks, annuli, and shrinkage gaps in the tank grout, a small fraction of the total volume of reducing grout may come into contact with infiltrating ground water, potentially expending the local, along-crack-face reductive and buffering capacity of the tank grout much earlier than intended due to flow focusing and frequent exposure of a few grout surfaces to relatively rapidly flowing water. Because DOE assumes that the solubilities of certain key radionuclides are dependent on the chemistry of the infiltrating ground water, with lower solubilities expected for adequately conditioned ground water, the extent of interaction between infiltrating ground water and reducing tank grout is risk-significant.

The impact of fast, bypassing flow through tank grout as it impacts the capability of the reducing tank grout to condition ground water is also being investigated by CNWRA staff, who have performed bench-scale water-conditioning experiments using a synthetic SRS ground water interacting with (i) an early generation reducing grout and (ii) tank grout prepared with Grade 100 slag cement, and (iii) tank grout prepared with Grade 120 slag cement (i.e., according to C-SPP-F-00055). Dynamic flow tests on early generation reducing grout specimens indicated that the pH of synthetic SRS ground water increases to a value above 10 pH units almost immediately after contacting the grout (Walter and Necsoiu, 2015). Static tests of nominally 0.06 in^3 (1 cm^3) cubes or chunks of tank grout with a grout-to-water-mass ratio of 0.7 resulted in a steady E_h of −77 mV after 5 days with dissolved oxygen concentrations <8 ug/L. Two subsequent static tests using the same grout specimens resulted in steady E_h values of −10 to −20 mV after 3 to 4 days. A 130-day-long test conducted during FY2018 on tank grout that had been prepared with 120 grade slag resulted in a steady E_h of approximately −250 mV. Testing during FY2018 also indicated that E_h is controlled by the dissolved oxygen concentration until very low dissolved oxygen concentrations are achieved, after which yet-to-be-identified redox reactions reduce E_h even further. The recent tests also demonstrated that oxidation reactions involving the tank grout can reduce dissolved oxygen concentrations to less than the detection limit of the DO probe {nominally 0.004 mg/L [0.004 ppm]}. Although static tests were designed to maximize the interaction between tank grout and synthetic SRS ground water through use of small cubes or chunks of grout, the low, initial E_h values of −470 mV assumed in DOE's PA documents were not achieved during these laboratory tests.

Evaluation of Updated PA Modeling

DOE indicates that while Pu may not be as insoluble as assumed in the tank farm waste release model, it is still relatively insoluble and would therefore not be expected to contribute to the TF peak doses within 10,000 years. To substantiate this hypothesis, new HTF and FTF base case model runs were performed by DOE with higher solubility values using the HTF and FTF GoldSim models in a deterministic mode (SRR-CWDA-2016-00084). The solubility values used in these new model runs are presented in Table 5, along with the solubility values used in HTF (SRR-CWDA-2010-00128) and FTF (SRS-REG-2007-00002) PA modeling. The conservative case and nominal case values presented in Table 5 were stated to be based upon a considered evaluation of the data obtained from the Tank 18F real waste release experiments (SRR-CWDA-2016-00086, Revision 0). The NRC staff does not agree with the statement regarding the relative insolubility of Pu affecting the timing of peak dose within 10,000 years. Solubility primarily affects magnitude and not timing of peak dose. Additionally, the solubility of Pu is risk-significant compared to the dose standard (leading to peak doses of a few to several mSv/yr in DOE's simulations versus a dose standard of 0.25 mSv/yr), so the characterization of Pu as relatively insoluble does not clearly communicate the risk-significance of Pu activity remaining in Tank 18F.

DOE concludes that the PA does not need to be updated in the near future, because the results demonstrate that the dose within 20,000 years is not significantly different from previous PA predictions. Because the peak dose is an order of magnitude or more greater than the performance objective and DOE is relying on the dose being above the performance objective occurring outside of the compliance period, other factors influencing the timing of the peak dose which might lead to unacceptable doses within the compliance period need to be evaluated to support DOE's conclusions. The NRC staff's Tank 18F SA TRR lists the other technical issues related to timing of peak dose, which must be addressed for the NRC staff to have reasonable assurance that the performance objectives can be met.

As discussed above, the results of the Tank 18F waste release testing indicate that the solubility of Pu is risk-significant at the time of tank closure. Previous simulations conducted by DOE showed that when the assumed solubility occurs at time t = 0 years and is held constant, the highest doses occur when the solubility is approximately 1E−07 mol/L (see Figure 8). However, the peak dose is lower with an assumed solubility of 1E−06 mol/L, which is an order of magnitude lower than the highest assumed solubility of 1E−07 mol/L. This counter-intuitive result occurs due to the transport of Pu into the tank grout overlying the waste zone early during the simulation period. After the steel liner fails thousands of years later (and water flow through the system increases), Pu is transported vertically downward out of the engineered system, but at lower concentrations than would occur if the Pu did not migrate into the overlying tank grout early on in the simulation. Scoping calculations performed by NRC staff show that if the steel liner and tank grout does not perform as well as assumed in the base case (see Figure 4, which indicates DOE gets credit for tank grout performance for thousands of years), then the Pu release rates could be significantly higher (e.g., the release rates could be 5× higher if the full flow rates are realized after 500 years). These scoping calculations demonstrate the importance of assumptions regarding the conceptual model for fluid flow through the system and the assumptions regarding engineered barrier performance in DOE's base case PA (e.g., MFs 3.1, and 3.2 [ML15238A761]).

Although the DOE simulations are instructive on the impact of initial Pu solubility on peak dose, the simulations do not show the importance of other barrier assumptions on the results. For example, the impact of basemat bypass and impact of natural system K_d on timing of peak dose was not evaluated in SRR-CWDA-2016-00086. If ground water bypasses the attenuating capacity of the basemat, and a fraction of the waste has a low K_d of 3 L/kg (Demirkanli et al., 2007) the Pu peak dose could occur much earlier in time, and be above the performance objective within 10,000 years. MFs related to vault and natural system performance (MF 3.5 "Vault and Annulus Sorption" and MF 4.1 "Natural Attenuation of Key Radionuclides") are important because if the basemat and natural system do not perform as well as assumed in the PA, the peak release will occur earlier in time and the dose could be above the performance objectives within the compliance period. Scoping calculations show that if 100 percent of the mobile fraction is assumed, and basemat bypass occurs (and full flow occurs early during the simulation at 500 years), the peak dose could be orders of magnitude higher than the performance objective significantly earlier in time (well within 10,000 years and potentially within 1000 years). While this case is not realistic, it points to the fact that only a small fraction of high mobility Pu can be present and still meet the performance objectives. Additionally, alternative conceptual models that would hasten the time to peak dose (e.g., groundwater table rise and basement bypass) are also risk-significant. Thus, the extent which high mobility forms of Pu exist in SRS groundwater, as well as the stability of these high mobility forms[11], should be

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[11] In SRS sediment, it is thought that Pu cycles repeatedly through lower and higher mobility forms of Pu,

studied in detail to construct a technically defensible far-field transport model for NRC to have reasonable assurance that the performance objectives in Title 10 of the *Code of Federal Regulations* (10 CFR) Part 61, Subpart C can be met. NRC also recommends that DOE perform multi-variate sensitivity analysis to better understand uncertainty in the dose projections and factors important to facility performance.
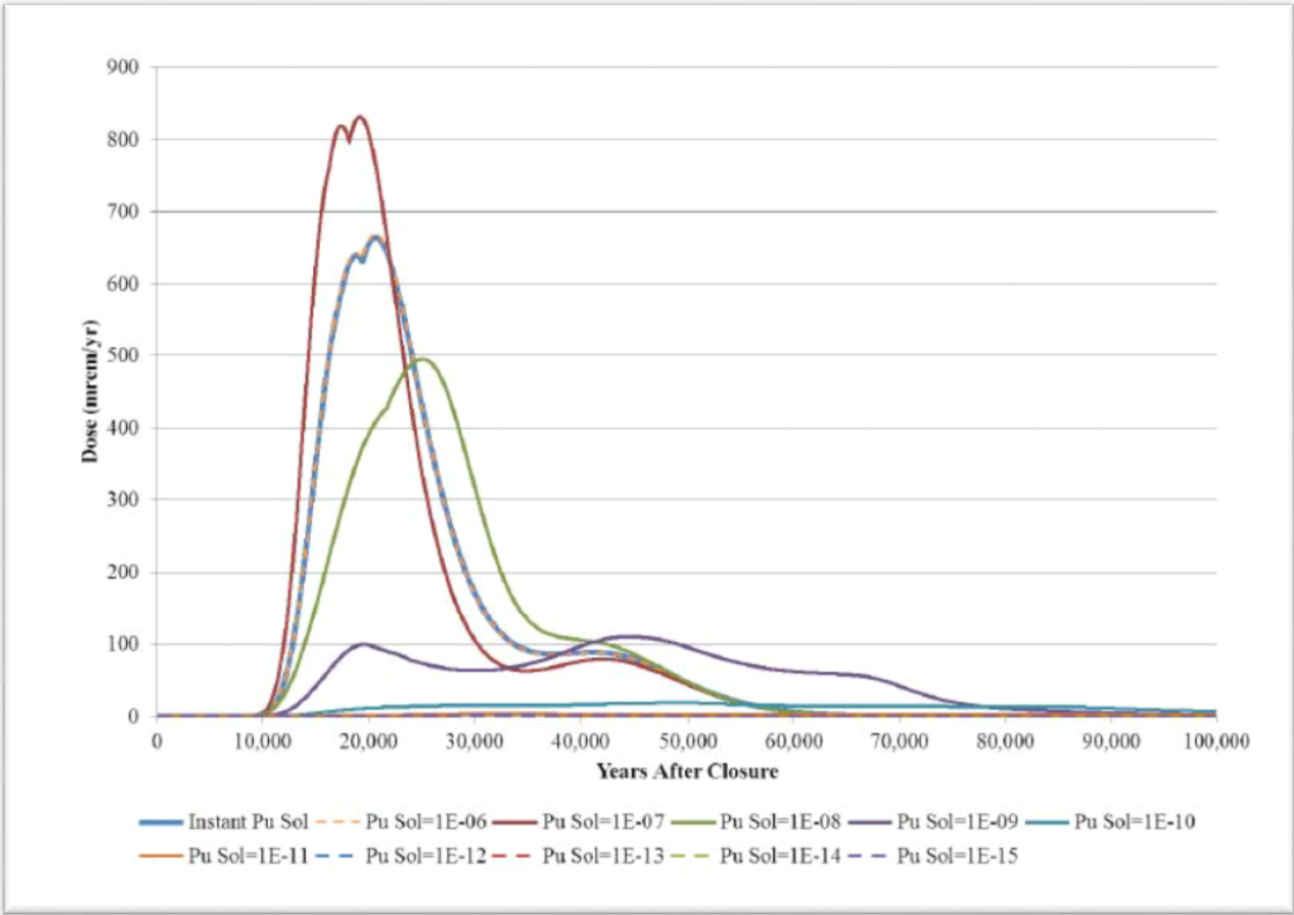

Figure 8 Peak Dose versus Time for Various Assumed Pu Solubilities. Taken from SRR-CWDA-2010-00124, Figure 6.3-23.

Conclusions and Recommendations Related to Performance Assessment Modeling

- DOE should consider a larger range of uncertainty in key radionuclide solubility due to experimental limitations (e.g., substantial metal losses of uranium during leach testing which compromised the utility of the uranium data collected from the experiments and apparent lack of ability to achieve equilibrium conditions particularly for Pu and Tc).
- DOE should perform probabilistic or multi-variate sensitivity analysis considering uncertainty in performance of multiple barriers including scenarios that evaluate basemat bypass, early hydraulic failure due to water table rise or preferential flow through the system, and consider the impact of higher mobility forms of Pu in the natural system.

the Pu (IV) and Pu (V) oxidation states, respectively, in response to wet/dry cycles (WSRC-MS-2003-00889).

- DOE should explain differences in PORFLOW and GoldSim modeling results (e.g., Pu peak doses of around 5 mSv/yr (500 mrem/yr) in the Tanks 18/19 SA (SRR-CWDA-2010-00124) versus 7 mSv/yr (700 mrem/yr) in SRR-CWDA-2016-00086.
- DOE should evaluate the impact of the early, high concentration release of Pu or justify why the rinse sample results are not applicable to alternative conceptual models involving water table rise or preferential flow through the system.
- DOE should continue to study and develop models to account for higher mobility forms of Pu in the natural system including models that consider two fractions of Pu (relatively high mobility and low mobility forms) as well as the potential for oxidation and reduction actions affecting the mobility of Pu in the subsurface along the flow path to the 1 m and 100 m compliance points.
- DOE should evaluate the impact of transport of key radionuclides up into the tank grout, and if found to be risk-significant provide additional support for this transport mechanism.

Teleconference or Meeting:

The NRC staff discussed technical issues associated with these reports at the August 13–14, 2018 OOV. The OOV report is documented in ML18235A538.

Follow-up Actions:

NRC staff plans to follow-up with DOE regarding progress on the Tank 12H waste release experiments, as well as follow-up questions found in Appendix A of this report related to the Tank 18F waste release experiments.

Open Issues:

There are no open issues resulting from this TRR.

Conclusions:

In conclusion, DOE performed waste release testing from actual high-level-waste samples collected from Tank 18F to inform waste release modeling results and PA assumptions. The results of the analysis greatly improve understanding of the waste and tank grout as a chemical barrier to mitigate releases from the tank farm facilities after closure. The results of the experiments were used to evaluate whether the FTF and HTF PA results were under-predicted. Results of the analyses are informative to the NRC staff in assessing the ability of the disposal facilities to meet performance objectives in 10 CFR Part 61, Subpart C.

The waste release testing results demonstrate the importance of the waste release experiments, which were recommended by NRC staff in its TER (ML112371715) and monitoring plan (ML15238A761), as well as an independent peer review group under contract with the DOE (LA–UR–2012–00079). The experiments were recommended to validate the waste release modeling used in the FTF and HTF PAs. In many cases, the results of the waste release experiments demonstrate the difficulty in projecting solubility of key radionuclides for these unique tank wastes, notwithstanding use of the best thermodynamic data available in the literature for the geochemical modeling. Therefore, additional waste release testing and updated geochemical modeling are needed for NRC staff to have confidence in the PA results. The NRC staff offer the following additional conclusions and comments related to waste release testing and PA modeling.

Conclusions and Comments for Future Waste Release Testing and Modeling

- Although DOE only used a single sample (FTF-1) for the Tank 18F waste release testing, their rationale (e.g., good characterization, and high concentrations of key radionuclides) is reasonable. In future waste release testing, if testing of multiple samples is impractical, DOE should consider compositing samples to get representative results for the entire tank contents rather than just a small portion of the waste.
- DOE should consider the impact of waste treatment methods, grout additives, and other chemical constituents that may increase radionuclide solubility (e.g., oxalates and carbonates) in designing and evaluating the results of future experiments.
- In future testing, DOE should consider water rinses with synthetic SRS ground water in addition to grout conditioned ground water to study the impact of grout bypass on waste

release results. DOE should also consider evaluating the change in concentration over time for the rinse solutions.

- DOE should continue to conduct solid phase analysis of residual waste to inform waste release assumptions for other tanks.
- As recommended by an independent peer review group (LA-UR-2012-00079), DOE should consider conducting spectroscopic analyses [e.g., Extended X-Ray Absorption Fine Structure or (EXAFS)] of plutonium (Pu) and other metals such as iron (Fe) in waste residues.
- DOE should analyze all major ions, alkalinity, and appropriate trace components (e.g., Pu, Fe, and sulfide).
- DOE should consider the following: (1) comparison of the experimental conditions against those for which the Nuclear Energy Agency's (NEA's) thermodynamic database is based to better understand differences in the modeled and experimental results, and (2) updating the assumed phases and thermodynamic data in the geochemical modeling as warranted.
- DOE should consider performing updated geochemical modeling using information gained from characterization of the tanks, and knowledge gained from comparisons of the experimental to previously modeled results.

Conclusions and Comments Related to Performance Assessment Modeling

- DOE should consider a larger range of uncertainty in key radionuclide solubility due to experimental limitations (e.g., substantial metal losses of uranium during leach testing which compromised the utility of the uranium data collected from the experiments and apparent lack of ability to achieve equilibrium conditions particularly for Pu and Tc).
- DOE should perform probabilistic or multi-variate sensitivity analysis considering uncertainty in performance of multiple barriers including scenarios that evaluate basemat bypass, early hydraulic failure due to water table rise or preferential flow through the system, and consider the impact of higher mobility forms of Pu in the natural system.
- DOE should explain differences in PORFLOW and GoldSim modeling results (e.g., Pu peak doses of around 5 mSv/yr (500 mrem/yr) in the Tanks 18/19 SA (SRR-CWDA-2010-00124) versus 7 mSv/yr (700 mrem/yr) in SRR-CWDA-2016-00086).
- DOE should evaluate the impact of the early, high concentration release of Pu or justify why the rinse sample results are not applicable to alternative conceptual models involving water table rise or preferential flow through the system.
- DOE should continue to study and develop models to account for higher mobility forms of Pu in the natural system including models that consider two fractions of Pu (relatively high mobility and low mobility forms) as well as the potential for oxidation and reduction reactions affecting the mobility of Pu in the subsurface along the flow paths away from the tank to the 1 m and 100 m compliance points.
- DOE should evaluate the impact of transport of key radionuclides from the waste zone up into the tank grout, and if found to be risk-significant, provide additional support for the transport mechanism(s).

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Appendix A: Additional Questions Related to the Review of SRNL-STI-2016-00432

The relationships among wash solution volumes in Tables 2-7 and 2-8 are not clear.
For example, Table 2-7 implies that samples A, B, and C would have 300–315 mL of wash solutions, not the 600–650 mL shown in Table 2-8.

Please provide discussion on the applicability of the waste release results to tank bottom conditions, given the solid-to-solution ratios used in the tests.

It is noted at the bottom of page 10 that 30 to 50 percent of the sample slurries were consumed during testing. Was the solution selectively sampled relative to the solids, so that the ratio changed during the test? Could this have affected the results?

Please explain how the metal loss percentages in Tables 3-3 and 3-10 were calculated. Were they based on bulk concentrations in the original residue (Table 3-11)? How is it possible that a value above 100 percent was obtained for U in Table 3-10?

Has DOE subsequently gained any new insights into the unexplained differences in Pu concentrations, and U concentration patterns, between ORII-A and ORII-B leachates?

U concentrations were initially similar in ORII-A and ORII-B solutions (Figure 3-7), but late in the tests the ORII-B U concentrations increased more rapidly while ORII-A U leveled off. Has DOE subsequently gained any new insights into this contrasting behavior in similar solutions?

For U and Pu, RRII-F leachate values are lower than for RRII-E. Was sorption on CFS a factor? More generally, was the impact of sorption on the results and their application in PAs considered?

What was responsible for the low Tc concentrations in ORII and ORIII leachates? Could it be redox kinetics alone?