





UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

December 20, 2019

MEMORANDUM TO: Stephen S. Koenick, Chief
Low Level Waste Projects Branch
Division of Decommissioning, Uranium Recovery,
and Waste Programs

THRU: Christopher McKenney, Chief 
Risk and Technical Analysis Branch
Division of Decommissioning, Uranium Recovery,
and Waste Programs

FROM: Cynthia Barr, Sr. Risk Analyst 
Risk and Technical Analysis Branch
Division of Decommissioning, Uranium Recovery,
and Waste Programs

SUBJECT: TECHNICAL REVIEW OF TANK 12H WASTE RELEASE
REPORTS AND ASSOCIATED IMPACT ANALYSIS (DOCKET
NO. PROJ0734)

The U.S. Nuclear Regulatory Commission (NRC) has performed a technical review of documents prepared by the U.S. Department of Energy (DOE) that provide information about results of Tank 12H waste release experiments and associated impacts on the F-Area Tank Farm facility (FTF) H-Area Tank Farm facility (HTF) performance assessments (PAs). This technical review report is related to a previous report on Tank 18F waste release (Agencywide Documents Access and Management System (ADAMS) Accession No. ML18242A259). This technical review primarily supports Monitoring Factors 1.1, "Final Inventory and Risk Estimates," 2.1, "Solubility-Limiting Phases/Limits and Validation," 2.2, "Chemical Transition Times," and 3.2, "Groundwater Conditioning Via Reducing Grout," listed in NRC's combined FTF and HTF monitoring plan. This monitoring plan, entitled "U.S. Nuclear Regulatory Commission Plan for Monitoring Disposal Actions Taken by the U.S. Department of Energy at the Savannah River Site F-Area and H-Area Tank Farm Facilities in Accordance with the National Defense Authorization Act for Fiscal Year 2005" (ADAMS Accession No. ML15238A761), was issued in October 2015.

A previous finding in the Tank 18F waste release technical review report (ADAMS Accession No. ML18242A259) was that the NRC staff needed 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 could be met based on the results of the Tank 18F waste release experiments. This information is still needed for the FTF, where Tank 18F is located (e.g., additional information is needed to reduce uncertainty in the risk associated with

CONTACT: Cynthia Barr, NMSS/DUWP
301-415-4015

plutonium-239 in FTF Tank 18F). However, the focus of this technical review report is on the waste release testing results of an HTF tank, Tank 12H¹.

The DOE performed waste release testing from actual high-level-waste samples collected from Tank 12H to inform HTF waste release modeling results and PA assumptions. The results of the analysis improve NRC staff understanding of the waste and tank grout as chemical barriers to mitigate releases from the tank farm facilities after closure. DOE used the results of the Tank 18F and Tank 12H experiments to evaluate whether the FTF and HTF PA results were under-predicted. Notwithstanding the results of the Tank 18F waste release testing and issues associated with plutonium-239 and other key radionuclide solubility, results of both the waste release testing and PA impact analysis 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. The experiments were recommended, by several groups including by NRC staff in its technical evaluation reports (TERs) (ADAMS Accession Nos. ML112371715 and ML14094A514) and monitoring plan (ADAMS Accession No. ML15238A761), as well as an independent peer review group (LA-UR-2012-00079), to validate the waste release modeling used in the FTF and HTF PAs. The results of the two sets of 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 for the entire tank farm, as different tanks will have different waste types and a different mix of key radionuclides.

DOE should consider the following items to enhance its waste release testing, continue to address uncertainties in the current PA models and support future PA models. NRC recognizes that waste release testing and PA modeling are an iterative process. Risk insights including the impact of uncertainty should be considered in developing future tasks.

Consideration for Future Waste Release Testing:

- NRC staff supports DOE's recommendation to conduct additional leach testing on other tank waste (N-ESR-H-00040).
- DOE should consider evaluation of the impact of waste type, 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 waste release testing, if testing of multiple tank samples is impractical, DOE should develop support for the use of composite samples and discuss the limitations of use of a composite sampling approach. Ideally supporting information for use of a composite leach test sample would include solid phase characterization and aqueous phase concentrations of individual samples to better understand tank waste variability.

¹ Although the focus of the TRR is on Tank 12H waste release experimental results, DOE evaluates the impact of Tank 18F and Tank 12H waste release testing results on the FTF and HTF PAs. Therefore, NRC staff also reviewed updated information on FTF risk.

- As stated in the Tank 18F technical review report (ADAMS Accession No. ML18242A259), in future testing, DOE should consider water rinses with synthetic SRS groundwater in addition to grout conditioned groundwater to study the impact of grout bypass on waste release results.
- DOE should conduct solid phase analysis on tank waste residuals, including Tank 12H. Recommendations were provided in an independent peer review group report (LA-UR-2012-00079) with potential analysis methods.
- DOE should analyze all major ions, alkalinity, and appropriate trace components (e.g., Pu, Fe, and sulfide). If possible an anion/cation balance should be calculated to determine if an important component has been missed.
- 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. DOE should also consider how the inability to meet the target Eh endpoints assumed in modeling affect the results.
- DOE should develop additional model support that calcium carbonate maintains pH in the simulated cement-reacted solutions, both oxidizing and reducing, and how the leaching results might have been affected by this assumption.
- DOE should develop additional model support to refer to the results of the experiments (i.e., aqueous phase concentrations) as solubilities. Without a conceptual understanding of controls on radionuclide concentrations in the engineered system, it would be difficult to extrapolate the results to other conditions.
- DOE should discuss how the RR11 and OR11 conditions targeted in the leach testing differ from Conditions C and D assumed in the HTF PA for Tank 12H, and how the use of a higher pH affects the applicability of the experimental results.

Considerations for PA Modeling:

- 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 continue to study and develop alternative conceptual models to account for the various oxidation states 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 tanks to the 1 m and 100 m compliance points.

In this report, there is no significant change to the NRC staff overall conclusions from the F- and H-Tank Farm TERs regarding compliance of DOE disposal actions with the 10 CFR Part 61 Performance Objectives.

Enclosure:
Technical Review of Tank 12H Waste Release
Reports and Associated Impact Analysis

SUBJECT: TECHNICAL REVIEW OF TANK 12H WASTE RELEASE
 REPORTS AND ASSOCIATED IMPACT ANALYSIS (DOCKET
 NO. PROJ0734) **DATE December 20, 2019**

DISTRIBUTION: (w/enclosure)

LParks
 DPickett
 CDinwiddie
 MFuhrmann
 LDesotell
 THolahan
 BPham
 WIR Distribution List
 WIR Service List

ADAMS Accession No.: ML19298A092

***via email**

OFFICE	DUWP	DUWP	DUWP	DUWP
NAME	C. Barr	R. Gladney	C. McKenney	C. Barr
DATE	10/25/19	11/26/19	12/20/19	12/20/19

OFFICIAL RECORD COPY

Technical Review of Tank 12H Waste Release Reports and Associated Impact Analysis

Date: December 20, 2019

Technical Reviewers:

Cynthia Barr, Sr. Risk Analyst,
U.S. Nuclear Regulatory Commission (NRC)

David Pickett, Senior Program Manager
Center for Nuclear Waste Regulatory Analyses (CNWRA)

George Alexander, Risk Analyst,
NRC

Mark Fuhrmann, Geochemist,
NRC

Primary Documents Reviewed:

SRNL-STI-2018-00484, Rev 1, "Determining the Release of Radionuclides from SRS Tank 12H Waste Residual Solids Following Tank Closure," Savannah River Remediation LLC, Aiken, South Carolina. October 2018. [ADAMS Accession No. ML19024A505]

SRR-CWDA-2016-00086, Rev. 1, "Evaluation of Waste Release Testing Results against the Tank Farm Performance Assessment Waste Release Model," Savannah River Remediation LLC, Aiken, South Carolina. November 2018. [ADAMS Accession No. ML19024A494]

Summaries:

SRNL-STI-2018-00484, Rev. 1, Tank 12H Waste Release Experimental Report

U.S. Department of Energy (DOE)² conducted radionuclide leaching studies to provide additional information regarding the residual waste solubility assumptions used in its performance assessment (PA) models. DOE published this report to provide what it described as equilibrium solubility data for several radionuclides identified as risk drivers and adds to the database of solubility values reported in the previous analogous study with Tank 18F solids.

DOE explained that Tank 12H was exposed to extensive mechanical cleaning, caustic aluminum dissolution, and oxalic acid chemical cleaning prior to closure. The methodology utilized for leach testing was developed during previous testing of Tank 18F samples. Slurries of tank residual solids and grout-representative solids in simulated grout pore water solutions (based on Savannah River Site [SRS] groundwater compositions) with pH and E_h values expected during the aging of the closed waste tank were produced. DOE determined the concentrations of selected radionuclides versus time to assume equilibrium conditions were achieved and defined the solubility-controlled concentration of selected radionuclides. Tank 12H waste differs from that of Tank 18F waste for a variety of reasons: most notably, the type

² In most cases, work was performed by DOE contractors. The term "DOE" is used to refer to DOE as well as its contractors and is used for ease of reference.

of processing that it underwent, the types of chemical cleaning agents it was exposed to, and, perhaps most importantly, the residual elements in the heels.

The target pore water leaching conditions from the F-Area Tank Farm facility (FTF) and H-Area Tank Farm facility (HTF) PAs are provided in Table 1. The initial pore water has a reducing potential and a relatively high pH and is referred to as Reducing Region II (RRII). The pore water is expected to become increasingly oxidizing with time as the grout degrades. The first transition is to more oxidizing conditions, with the second chemical state referred to as Oxidizing Region II (ORII). The final transition is to lower pH, with the third and final chemical state referred to as Oxidizing Region III (ORIII).

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

Table 1. Targeted Eh and pH Pore Water Conditions for Tank 12H Waste Release Experiments (SRNL-STI-2018-00484)

For the reducing case, tests were conducted with both unwashed and washed Tank 12H residual solids. For the oxidizing cases (ORII and ORIII), all samples were washed with simulated grout pore water solutions prior to testing, since DOE expects that these conditions will occur after considerable pore water solution has passed through the system. Ferrous sulfide (FeS) solids were also added to the reducing samples to lower the slurry Eh values. Calcium carbonate solids were used as the grout-representative solid phase for each of the oxidizing cases. Air purge gas with and without carbon dioxide (CO₂) removed was continually transferred through the oxidizing test samples and nitrogen purge gas was transferred through the reducing test samples during leach testing.

In contrast to previous testing, the target pH values were difficult to maintain due to the fact that the samples continually consumed base equivalents which lowered the pH. Leaching studies were conducted over an Eh range of approximately 0.5 V. The lowest and highest Eh values achieved of ~-0.1 V and ~+0.4 V were significantly less negative and less positive than the target values, respectively, as was the case in previous studies. Achievement of more positive and more negative Eh values is believed to require the addition of non-representative oxidants and reductants, respectively. During testing, one ORIII sample was inadvertently exposed to a large volume of pH 12 water, but testing was continued on this highly washed sample after target conditions were reestablished.

Soluble metal concentrations determined for slurry sub-samples collected during Tank 12H residual solids leaching studies (shown below in Table 2) were stated to follow the general trends predicted for plutonium (Pu) and uranium (U) oxide phases. Data trends between porewater conditions were also generally consistent with previous leach test results, but steady-state U and Pu concentrations were lower for Tank 12H residuals. The highest Pu and U concentrations were observed for washed ORIII-A/B conditions (excluding the highly washed ORIII-B sample) and the lowest concentrations were observed for washed and unwashed RRII-A/B samples. The highest initial technetium (Tc) concentration was observed for the unwashed reducing case with cement, fly ash, and slag (CFS) solids (RRII-B). This was likely related to the fact that this sample had not been washed. After washing of the reducing samples, the washed oxidizing samples (ORII-A/B and ORIII-A/B) contained the highest Tc concentrations.

The highest neptunium (Np) concentrations were observed for washed ORIII-A/B samples (excluding the highly washed ORIII-B sample) and the lowest concentrations were observed for the reducing samples (RRII-A/B). Concentrations of iodine (I)-129 below detection limits for all but two leachate sub-samples. Comparing the dissolved concentrations of each of the metals analyzed, U is more soluble than all other metals analyzed in the leach studies, with a maximum average concentration of 2E-6 mol/L, while the maximum concentrations of each of the other metals were $\leq 1E-7$ mol/L.

Because steady-state conditions were not always achieved, the concentration data should be used with caution with consideration of attendant uncertainties. For example, Pu concentrations from the two ORII tests (SRNL-STI-2018-00484, Rev 1, Figure 3-7) did not attain steady state and differed by nearly an order of magnitude at times. Another factor adding uncertainty was the pH drift from solids interaction that necessitated frequent adjustments. In contrast, Tc concentrations under oxidizing conditions (Figure 3-9) and U under reducing conditions (Figure 3-8) achieved relatively stable values over time.

Test Condition	Additives	Atmosphere/ Condition	E _h (mV)	pH	Molarity				
					Pu	U	Tc	Np	I
RRII A	Ca(OH) ₂ CaCO ₃ FeS	continuous N ₂ purge; unwashed	+205 ^b	10.8 ^b	$\leq 2E-11^b$	4E-8 ^b	3E-9 ^b	$\leq 5E-11^b$	$\leq 5E-7^b$
RRII B	CFS FeS		+145 ^b	11.5 ^b	$\leq 1E-11^b$	3E-8 ^b	1E-8 ^b	$\leq 5E-11^b$	$\leq 2E-7^b$
RRII A	Ca(OH) ₂ CaCO ₃ FeS	continuous N ₂ purge; washed	-64 ^d	11.0 ^d	$\leq 3E-12^d$	9E-9 ^d	$\leq 6E-10^d$	$\leq 5E-11^d$	$\leq 3E-7^d$
RRII B	CFS FeS		-71 ^d	11.3 ^d	$\leq 1E-12^d$	1E-8 ^d	2E-9 ^d	$\leq 5E-11^d$	$\leq 1E-7^d$
ORII A	Ca(OH) ₂ CaCO ₃	continuous air purge; washed	+340 ^e	10.6 ^e	1E-10 ^e	3E-7 ^e	1E-8 ^e	2E-10 ^e	$\leq 3E-8^e$
ORII B	Ca(OH) ₂ CaCO ₃		+341 ^e	10.6 ^e	9E-11 ^e	2E-7 ^e	8E-9 ^e	$\leq 1E-10^e$	$\leq 1E-7^e$
ORIII A	CaCO ₃	continuous air or CO ₂ stripped air purge; washed	+404 ^e	9.2 ^e	1E-10 ^e	1E-6 ^e	6E-9 ^e	9E-10 ^e	$\leq 1E-7^e$
ORIII B	CaCO ₃		+406 ^b	9.2 ^b	1E-10 ^b	2E-6 ^b	6E-9 ^b	1E-9 ^b	$\leq 1E-7^b$
ORIII B	CaCO ₃	continuous air or CO ₂ stripped air purge; highly washed	+410 ^f	9.2 ^f	6E-11 ^f	2E-8 ^f	$\leq 2E-10^f$	2E-10 ^f	$\leq 1E-7^f$

a Isotopes: Pu-238/-239/-240; U-235/-238; Tc-99; Np-237; I-129

b Average data from first 4 weeks

c CFS = cement, flyash, and slag grout solids

d Average data from final 2 weeks

e 8-week average

f Average data from final 4 weeks

Table 2. Results of the Tank 12H Experiments. Note that these values are average values over different sampling periods and may underestimate release behavior because equilibrium conditions were not always demonstrably achieved. Table Credit: SRNL-STI-2018-00484 Revision 1.

DOE concluded the following:

- That a significant fraction of the radionuclides in the Tank 12H residual solids used in this testing appears to be pure metal oxide phases and not coprecipitated phases;
- Analysis of the sample wash solutions revealed radionuclide concentrations in the wash comparable to the leach test samples and metal losses to the wash solutions were low (<2.5 wt. %) for all samples except for the highly-washed ORIII-B sample;
- Evaluation of blank samples collected during leach testing revealed that the tests were successfully completed without significant contamination from Tc-99, I-129, Np-237 and Pu. U sample contamination was observed in the blanks, but for most samples, the level of contamination was not significant;
- Concentrations of radionuclides released from residual Tank 12H solids within the closed waste tank are not expected to exceed the values assumed in the PA; and
- I-129 release (a primary PA risk driver) from the closed waste tank is expected to be lower than assumed in the PA, where no solubility controls were utilized in the modeling.

SRR-CWDA-2016-00086, Rev. 1, Evaluation of the Impact of Tank 12H Waste Release Testing on the Results of the Tank Farm PAs

SRR-CWDA-2016-00086, Rev. 1, finds that I-129 in the Tank 12H residual waste sample is relatively insoluble, under both reduced and oxidized conditions, compared to the PA waste release model which conservatively assumed no solubility control for I. The other three elements tested – Pu, Tc and U - appeared in most instances to be potentially more soluble than was assumed in the waste release model. DOE concluded that newly assigned solubilities using the results of the experiments would have a negligible impact on peak doses in 1,000 or 10,000 years and that there is no immediate need to update the current model to incorporate the waste release testing data. DOE indicated that if the Tank 12H derived iodine solubility values were used in the PA model, that the HTF peak dose within 10,000 years would decrease significantly. Therefore, DOE concluded that the new waste release data could be integrated into the next revision to the FTF and HTF PAs.

N-ESR-H-00040, Rev. 2, Waste Tank Residuals Properties Report

N-ESR-H-00040, Rev. 2, discusses characteristics of residual tank waste for use in PA waste release models, as well as provides recommendations for future data collection. The report first reviews (i) the reprocessing activities that generated the liquid and sludge wastes that were originally transferred to the tanks and (ii) waste retrieval and cleaning practices, with a focus on how the histories help understand tank contents—both chemical and radiological—and their variations. The report then discusses the DOE waste release models used for evaluating closed tank compliance with performance objectives, and how chemistry-dependent solubility limits are incorporated into radionuclide release estimations.

The next section of N-ESR-H-00040, Rev. 2, summarizes and tabulates historical data on tank sludge metal and radionuclide contents, and more recent tank residuals analyses on Tanks 5F, 6F, and 12H. The report then summarizes the recent Tanks 12H and 18F waste residuals radionuclide solubility testing efforts (SRNL-STI-2016-00432 and SRNL-STI-2018-00484), and associated comparisons with PA implementation (SRR-CWDA-2016-00086), that are the subject of this technical review report (TRR).

The report ends with proposals for future testing that are, in part, responsive to published NRC staff recommendations arising from review of the Tank 18F testing report and associated PA

comparison (ADAMS Accession Nos. ML15238A761 and ML18242A259). According to the report, the key areas of interest for which more information would be useful are:

- Measured radionuclide solubility for residuals from tanks representing a variety of waste source and removal histories.
- Solubility controlling solid phases for residuals from tanks representing a variety of waste source and removal histories.
- The evolution of the chemical environment for waste residuals.
- Specifically, the report recommends the following tests:
 - Radionuclide release testing on Tank 5F residuals.
 - Radionuclide release testing on Tank 15H residuals, when available.
 - Testing on the chemical evolution (e.g., Eh and pH) of surrogates of grout and waste residuals.

NRC Staff Evaluation:

Evaluation of Waste Release Testing Results

NRC staff would start by noting the difficulty in performing this work. The experimental setup is impressive, and the implementation was well done. The results of the Tank 12H and 18F experiments contribute greatly to understanding the leaching behavior of key radionuclides found in residual waste in FTF and HTF tanks. DOE's work in this area greatly contributes to addressing Monitoring Factors (MFs), 1.1, "Final Inventory and Risk Estimates," 2.1, "Solubility-Limiting Phases/Limits and Validation," 2.2, "Chemical Transition Times," 3.2, and "Groundwater Conditioning Via Reducing Grout" listed in NRC's F-Area and H-Area Tank Farm monitoring plan (ADAMS Accession No. ML15238A761).

Waste release test samples were prepared by mixing portions of the archived Tank 12H composite mound and composite floor residual materials in the shielded cells at an approximate 78:22 mass ratio (3.5±0.1:1) of floor:mound material. While a certain mass is required to conduct the leaching experiments, as discussed in the Tank 12H inventory and special analysis TRR (ADAMS Accession No. ML17277B235), NRC identified potential issues with the representativeness of the composite samples used to determine the Tank 12H inventory (e.g., lack of collection of a sample from the actual Tank 12H mound [samples were obtained from boulders on the way to the mound] and lack of consideration of density uncertainty as well as potentially inappropriate consideration of volume uncertainty in the volume proportional compositing methodology). These concerns extend to the use of a composite sample for waste release testing and may be amplified given the fact that over-representation of a highly washed floor sample in the composite may obscure more risk-significant concentrations that may have been released had the relatively less washed mound sample been leach tested. Samples with different solid phase assemblages and radionuclide contents may behave differently in ways that are not reflected in sample mixtures. Therefore, the full range of potential radionuclide release characteristics may not be represented by the tests. DOE did not discuss the limitations of the compositing methodology used to analyze the high-level waste samples in Tank 12H. At a minimum, if DOE is unable to perform leach tests on individual waste segments (e.g., well washed residual waste remaining on tank bottoms, relatively unwashed residual waste remaining in mounds, and waste associated with tank walls, and cooling coils) expected to have significantly different release behavior, DOE should provide information supporting use of the measured concentrations from the composite samples, which may underestimate risk. Ideally,

this information would include solid phase analysis³ of the different waste segments in the tank and aqueous phase concentrations from previous characterization efforts. This information would be useful in assessing the representativeness of the composite sample and potential variability between samples.

SRNL-STI-2018-00484, Rev. 1, states (pages 7 and 11) that for oxidizing cases (both ORII and ORIII) that all samples were washed with simulated grout pore water solutions prior to leach testing to reflect considerable volumes of pore water solution passing through the system⁴. It is unclear why samples were washed prior to testing when the samples come from a tank that has been subjected to extensive cleaning. Furthermore, it is unclear that pre-leach washing performed under oxidizing conditions is representative of tank conditions. Because NRC staff is interested in the early release fraction and alternative scenarios including by-pass flow, washing the samples prior to the experiments with oxidizing fluids may lead to release of risk-significant concentrations and a loss of activity as was the case for U in the Tank 18F waste release experiments. This concern is partially mitigated by the fact that for Tank 12H (i) radionuclide wash concentrations are generally⁵ similar to leach test results (cf. Table 2 and Table 3) and (ii) with the exception of the inadvertent long-duration ORIII-B wash, wash solutions removed only a few percent of radionuclide sample inventories (see Table 4). Nevertheless, DOE should consider conducting leach tests without prior washing.

³ Recommendations were also provided in an independent peer review group report (LA-UR-2012-00079) with respect to use of X-ray spectroscopic analyses [e.g., Extended X-Ray Absorption Fine Structure or (EXAFS)] of Pu and other metals, such as iron in waste residues. X-ray Absorption Near Edge Structure (XANES) may also be especially useful in determining oxidation states of elements in samples used in the leaching experiments.

⁴ The wash solution was ORII (target pH 11.1) or ORIII (target pH 9.2) water, prepared from synthetic infiltration water by addition of $\text{CaCO}_3 + \text{Ca}(\text{OH})_2$ and CaCO_3 , respectively (page 2 of report SRNL-STI-2018-00484, Revision 1). Washing was achieved by leaving solution in contact with the solids for 5 to 12 hours as solids settled prior to removal from the vessels.

⁵ This is with the exception of Np-237 which was more than an order of magnitude higher for ORIII wash solutions ($3\text{E}-08$ wash solution concentration versus $1\text{E}-09$ to $2\text{E}-10$ mol/L for leach test concentration). NRC staff would also note that for Tank 18F, the highest Pu solubility observed was in the wash solutions at a value of $3\text{E}-07$ mol/L, which was orders of magnitude above leach test results and several orders of magnitude higher than that assumed in the PA.

Wash Sample	Molarity				
	Tc-99	I-129	U (total)	Np-237	Pu (total)
Initial ORII Composite Wash	1E-09	<1E-07	3E-08	1E-09	1E-10
Initial ORIII Composite Wash	1E-09	1E-08	2E-06	3E-08	1E-10
ORIII-B Sample Water Bath Recovery Solution	9E-10	<4E-08	2E-06	4E-10	1E-10
ORIII-B Sample Second Wash After Recovery	5E-10	7E-09	2E-07	1E-10	5E-11

Notes:
For each pair of OR leach tests, the wash solutions were combined before analysis (see Table 2-7, SRNL-STI-2018-00484). Therefore, it must be assumed that the percent leached was the same for both cases of ORII and of ORIII.
After 69 contact days, the ORIII sample leach test vessel broke and the sample was exposed to approximately 8.5 liters of liquid at pH 12 for several days. The solids were subsequently washed with 1 L of simulant to restore the sample to the target conditions.

Table 3 Radionuclide Concentrations in Tank 12H Residual Wash Solutions. Table Credit: Table 3-6 SRNL-STI-2018-00484, Rev. 1.

Wash Sample	Mass Percent				
	Tc-99	I-129	U (total)	Np-237	Pu (total)
Initial ORII Composite Wash	1.6	1.9	0.01	0.08	0.0012
Initial ORIII Composite Wash	1.2	0.21	0.82	2.1	0.0015
ORIII-B Sample Water Bath Recovery Solution	44.3	<25.5	34.1	0.99	0.068
ORIII-B Sample Second Wash After Recovery	3.1	0.5	0.41	0.03	0.0035
ORIII-B Wash Composite	48.6	<26.2	35.3	3.1	0.073

Notes:
For each pair of OR leach tests, the wash solutions were combined before analysis (see Table 2-7, SRNL-STI-2018-00484). Therefore, it must be assumed that the percent leached was the same for both cases of ORII and of ORIII.
After 69 contact days, the ORIII sample leach test vessel broke and the sample was exposed to approximately 8.5 liters of liquid at pH 12 for several days.

Table 4 Estimated Metal Losses to Tank 12H Residual Wash Solution. Table Credit: Table 3-7 SRNL-STI-2018-00484, Rev. 1.

SRNL-STI-2018-00484, Rev. 1 (pages 3 and 7) indicates that for the reducing case, separate tests were conducted with representative ground grout solids and with calcium carbonate reagent, which is the grout phase believed to be controlling the pH. Ferrous sulfide (FeS) solids were also added to the reducing samples to lower the slurry Eh values. Calcium carbonate solids were used as the grout-representative solid phase for each of the oxidizing cases (ORII and ORIII) and in one RRII test to simplify the system and allow for better control of the solution pH and Eh. CFS grout solids were utilized in the remaining RRII test. For Regions II and III, calcium carbonate would not be expected to be controlling system pH. Denham and Millings (SRNL-STI-2012-00404) state that pH in Regions II (11.2 to 11.6) and III (9.2) is controlled by cement phases. SRNL-STI-2018-00484, Rev. 1, Figures 3-3, 3-4, and 3-5 show that the RRII-CC solutions consistently had lower pH than the RRII-CFS solutions. DOE should discuss its choice of calcium carbonate to maintain pH in the simulated cement-reacted solutions, both oxidizing and reducing, and how the leaching results might have been affected.

On page ix and page 30 (SRNL-STI-2018-00484, Rev. 1), DOE indicate that a significant fraction of the radionuclides in the Tank 12H residual solids used in this testing appears to be pure metal oxide phases and not coprecipitated phases. Under oxidizing conditions (ORII and ORIII), Pu solubilities observed for Tank 18F residuals ($4\text{E}-10$ to $1\text{E}-08$ M) were higher than the solubilities observed with Tank 12H solids ($2\text{E}-11$ to $4\text{E}-10$ M). The difference in Pu (and other key radionuclide) concentrations between the tanks is surprising but could be attributed to a number of factors (i.e., differences in degree of washing, waste processing/type, chemical cleaning). The Pu and other results suggest that there is something inherent to the sample that drives leachate radionuclide concentrations. It is not necessarily a "solubility," but a release concentration perhaps controlled by multiple processes (e.g., dissolution of certain phases, sample-specific coprecipitation, or sorption). Nonetheless, a better understanding of the factors leading to the rather stark differences in leached radionuclide concentrations between tank wastes is needed. NRC staff would note that DOE largely refers to the results of the experiments (i.e., aqueous phase concentrations) as solubilities. It would be more appropriate to refer to these as "steady-state" concentrations, provided they are reasonably consistent, since no mechanistic information is provided to establish solubility control as limiting aqueous concentrations in the pore water. Furthermore, without a conceptual understanding of controls on radionuclide concentrations in the engineered system, it would be difficult to extrapolate the results to other conditions.

NRC staff noted in the August 2018 Onsite Observation Visit (OOV) (ADAMS Accession No. ML18311A184), that the targeted experimental conditions were different than those assumed in the PA for submerged tanks at HTF (ADAMS Accession No. ML13044A313). For submerged tanks in the HTF PA, DOE assumed that the chemical conditions in the waste zone transitioned from what was called Condition C, to Condition D, to ORIII. Due to the submergence of the waste zone, Condition C assumes that groundwater flows laterally, directly into the contaminated zone (CZ) with no effect from the concrete vault and mixes with a small amount of RRII grout pore fluid. Condition D assumes that groundwater flows directly into the residual waste layer with no effect from the concrete vault and mixes with a small amount of ORII grout pore fluid. DOE used Geochemist's Workbench[®] to simulate the mixing of groundwater with grout pore fluid, and selected the composition at 90 percent groundwater and 10 percent pore fluid for Conditions C, and D. The mixture compositions are used as input to Geochemist's Workbench modeling of grout degradation—similar to that conducted for the non-submerged waste tanks—to determine the change in pore water composition (and associated radionuclide solubilities) over time, as the water reacts with the reducing grout. The targeted and actual pH achieved for RRII in these experiments, however, is significantly higher than modeled in the PA. Table 5 shows the difference in the experimental versus assumed values in the PA. DOE should discuss how lower pH values and other differences may have affected the experimental results.

With respect to E_h , DOE notes that significantly higher E_h values were achieved for the oxidizing conditions (ORII and ORIII) than were previously observed. For the ORII chemical condition, the target E_h value was nearly achieved (within 50 mV). However, E_h values observed for the ORIII chemical condition were approximately 160 mV less positive than the target. E_h values observed for the RRII chemical condition were approximately 370 mV less negative than the target. See Table 2 (and Table 5) for additional information. As discussed in the Tank 18F waste release TRR (ADAMS Accession No. ML18242A259), the results of Tank 18F and 12H waste release experiments suggest that the results of the geochemical modeling, which supported the PA, are unrealistic. Therefore, the performance assessment assumptions regarding the E_h endpoints need to be revised in future updates.

Additionally, for submerged tanks such as Tank 12H, the grout pore water *Eh* transitions from -0.47 volts to +0.54 volts after 1,787 pore volumes of fluid reacted (i.e., Condition C to Condition D) and the pH transitions from 11.3 to 9.3 at 2,442 pore volumes (i.e., Condition D to Oxidized Region III). While for non-submerged tanks such as Tank 18F, the *Eh* transition was projected to occur at 523 pore volumes and the pH transition to occur at 2119 pore volumes. In contrast, for the Tank 18F waste release experiments, a larger volume of wash solution was actually used (approximately 9.3 g of sample were washed with 600 mL of decant solution) compared to the Tank 12H waste release experiments (approximately 7.5 g of sample were washed with a total volume of 250 mL). DOE should explain the rationale for the relative change in wash volumes for Tank 18F and Tank 12H.

	Measured Quantity	HTF PA (for Submerged Tanks such as Tank 12H)	Target Experimental Conditions	Actual Experimental Conditions
Condition C (HTF PA) or RRII (Target)	pH	8.8	11.1	10.8 - 11.5
	<i>Eh</i> (mV)	-310	-470	-71 to +205
Condition D (HTF PA) or ORII (Target)	pH	8.8	11.1	10.6
	<i>Eh</i> (mV)	+360	+560	+340
ORIII	pH	9.2	9.2	9.2
	<i>Eh</i> (mV)	+290	+680	+410

Table 5. PA Modeled/Assumed Conditions versus Targeted and Actual Experimental Conditions.

The measured radionuclide concentrations from the Tank 12H waste release experiments generally varied by greater than an order of magnitude from the projected solubility values in the HTF performance assessment. The measured concentrations were both lower and greater than the projected solubilities, depending on the radionuclide and test condition (i.e., RRII, ORII, ORIII). The maximum observed concentrations that are higher than the projected solubilities for Pu, U, Tc, Np, and I are listed in red in Table 6. For RRII conditions, measured U and Tc concentrations exceeded as-modeled projections and Pu, Np, and I were less than the detection limits and the as-modeled projections. For ORII and ORIII, measured Pu and Tc concentrations exceeded as-modeled projections and U, Np, and I were less than the as-modeled projections. The magnitude of the differences between measured concentrations and projected solubilities continues to demonstrate the importance of actual waste release testing. There is significant uncertainty in applying geochemical models and databases to systems that differ from the experiments that were relied upon to develop the underlying databases.

Although there are limitations in applying these waste release results to the actual system, the waste release experiments reported in SRNL-STI-2018-00484, Rev. 1 significantly reduce the uncertainty in the HTF PA projections. Uncertainties in the geochemical modeling remain significant, including a lack of information of solid phases present in the tanks and potentially limited thermodynamic data for key phases. There are also limitations to applying leach test data to PA models that include: (1) experimental conditions that varied from as-modeled geochemical tank conditions, (2) uncertainty in the as-modeled geochemical conditions, (3) uncertainty in future tank conditions, and (4) uncertainty in conditioning of groundwater. The observed *Eh* and pH for RRII, ORII, and ORIII all varied from the as-modeled or targeted geochemical conditions without the addition of non-representative reducing and oxidizing agents. It is unclear what affect the differences in *Eh* and pH and addition of non-

representative agents may have on waste release. Further, the as-modeled geochemical conditions are also based on model projections that relied on thermodynamic databases that may differ from actual conditions, currently or in the future as the system evolves over time. DOE assumed in the HTF PA that the water contacting the residual waste would be conditioned to some extent by the reducing grout. However, NRC staff are concerned that the presence of fast pathways (e.g., due to grout shrinkage and construction joints), could result in relatively unconditioned groundwater interacting with the residual waste. This could result in release concentrations similar to the wash solutions and oxidizing solutions.

Test Condition	PA Assumed Molarity*					Molarity (average values, see table 3-1 and 3-2 of SRNL-STI-2018-00484 Rev.1)				
	Pu	U	Tc	Np	I	Pu	U	Tc	Np	I
RRII A	3.0E-11	4E-09	3E-12	1E-09	NA	≤2E-11	4E-8	3E-9	≤5E-11	<5E-7
RRII B						≤1E-11	3E-8	1E-8	<5E-11	<2E-7
RRII A						≤3E-12	9E-9	≤6E-10	<5E-11	<3E-7
RRII B						<1E-12	1E-8	2E-9	<5E-11	<1E-7
ORII A	3.0E-11	2.0E-06	1.0E-15	2.0E-05	NA	1E-10	3E-7	1E-8	2E-10	≤3E-8
ORII B						9E-11	2E-7	8E-9	≤1E-10	<1E-7
ORIII A	3.0E-11	4.0E-06	2.0E-15	2.0E-06	NA	1E-10	1E-6	6E-9	9E-10	<1E-7
ORIII B						1E-10	2E-6	6E-9	1E-9	≤1E-7
ORIII B						6E-11	2E-8	≤2E-10	2E-10	<1E-7
Wash Max						1E-10	2E-06	1E-09	3E-08	<1E-07 1E-08

*Test conditions for the Tank12H waste was based on RRII, ORII, and ORIII. However, Tank 12H is modeled as a submerged tank in the HTF PA and was projected to transition from Condition C, to Condition D, to ORIII. The assumed solubilities listed here are for submerged tanks. These solubilities are similar between RRII and Condition C, ORII and Condition D, but differ slightly as shown in Table 4-4 of the HTF Technical Evaluation Report (ADAMS Accession No. ML14094A514).

Table 6. PA Modeled/Assumed Solubility Limited Waste Release Concentrations versus Tank 12H Experimentally Observed Concentrations.

Evaluation of Waste Tank Characterization

NRC staff generally agrees with DOE recommendations made in a waste tank characterization report, N-ESR-H-00040, Rev. 2. The waste tank characterization report (N-ESR-H-00040) lists the following recommendations:

1. Measured radionuclide solubility for residuals from tanks representing a variety of waste source and removal histories.
2. Solubility controlling solid phases for residuals from tanks representing a variety of waste source and removal histories.
3. The evolution of the chemical environment for waste residuals.
4. Specifically, the report recommends the following tests:
 - a. Radionuclide release testing on Tank 5 residuals.
 - b. Radionuclide release testing on Tank 15 residuals, when available.
 - c. Testing on the chemical evolution (e.g., E_h and pH) of surrogates of grout and waste residuals.

As stated in the conclusions of this TRR and the related Tank 18F waste release TRR (ADAMS Accession No. ML18242A259), NRC staff endorses recommendations 1 and 2. Recommendation 3 is directly related to MFs 2.2, "Chemical Transition Times", and 3.2,

“Groundwater Conditioning via Reducing Grout” listed in NRC’s Tank Farms Monitoring Plan (ADAMS Accession No. ML15238B403). NRC staff should discuss prioritization of future waste release testing with DOE (Recommendation 4a and 4b). With regard to Recommendation 4c, NRC has sponsored related research with the CNWRA (Walter and Dinwiddie, 2019). NRC should discuss the results of CNWRA testing and DOE experimental designs in this area at a future teleconference(s).

Evaluation of DOE’s PA Impact Analysis

The results of the waste release testing reveal significant differences between modeled and experimentally derived release concentrations, as well as significant differences between Tank 18F and Tank 12H release concentrations. This suggests that many factors, which have not been considered explicitly in previous modeling efforts, have an influence on the observed release concentrations. Furthermore, the waste release testing results indicate that release concentrations are tank- or waste segment- specific suggesting that use of a single release concentration for each key radionuclide may be inappropriate.⁶

In general, Tank 12H concentrations were significantly lower than the Tank 18F concentrations observed in the waste release tests. Nonetheless, in some cases the Tank 12H results revealed higher concentrations than assumed in the HTF PA. DOE developed nominal and conservative values to evaluate the impact of higher solubilities for Tank 12H key radionuclides such as Pu (for ORII and ORIII) and Tc (for RRII, ORII, and ORIII). U concentrations were higher for RRII; however, overall the impact of the assumed U solubility had no significant impact on the PA results. Concentrations for Np and I were lower than assumed in the PA; therefore, the following evaluation focuses on DOE’s impact analysis of Pu and Tc solubility.

DOE indicated that the Pu concentration results 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 (SRR-CWDA-2016-00086). DOE goes on to state that the Pu results likely reflect the possibility that residual samples from different tanks may contain different Pu forms with differing solubilities, or that a residual sample from a single tank includes two or more types of Pu with differing solubilities. The different solubilities could be associated with oxidation state, chemical speciation, or matrix differences. For example, DOE hypothesizes that a significant fraction of the Pu in a single tank sample could be co-precipitated with other metals present in the residual solids or imbedded deep within the solid matrix. [SRNL-STI-2016-00432]. As explained in the Tank 18F waste release TRR, NRC staff believes the Tank 18F waste sample used in the waste release testing was likely representative of areas of the tank where washing was relatively ineffective. Due to the variability in waste release testing results between Tank 18F and Tank 12H, NRC staff concludes that additional waste release testing and updated geochemical modeling is needed to have confidence in the PA results. Updated probabilistic analysis that considers the results of Tank 18F and 12H waste release testing and other factors (e.g., tank/waste type, cleaning method, and characterization results) can be used to determine tanks where additional waste release testing may be most beneficial. Further, DOE should critically evaluate the appropriateness of compositing tank waste samples in future waste release testing if tank waste segments are suspected of having significantly different solubility or release behavior.

SRR-CWDA-2016-00086 indicates that the solubility testing results for RRII, ORII, and ORIII also indicate that the waste tank Pu residuals might not be as insoluble as assumed in the PA

⁶ Assuming a single, demonstrably conservative release concentration for all key radionuclides and tanks, would be appropriate although this approach may not lead to compliant results.

waste release model, especially with respect to Tank 18F. DOE goes on to state that the waste release testing does seem to demonstrate that the worst case (i.e., Tank 18F) solubility of Pu in ORII and ORIII chemical conditions will not exceed the values calculated for the Pu phase in equilibrium with dissolved oxygen. The solubility of the Pu phase in equilibrium with dissolved oxygen (PuO₂(amorphous, hydrous)) is 5E-8 moles/liter for ORII and 8E-8 moles/liter for ORIII, per Table 12 of SRNL-STI-2012-00404. DOE indicates that prior to residual waste testing there was a concern that Pu might exist in a much more soluble phase, as may be the case if the Pu existed in the residual waste as a carbonate phase. The solubility of the Pu carbonate phase (Pu(OH)₂CO₃) in ORII chemical conditions was calculated to be 4.8E-5 moles/liter in "Form and Aging of Plutonium in Savannah River Site Waste Tank 18F" (SRNL-STI-2012-00106).

Although the solubilities seen during the waste release testing are higher than the PuO₂(am,hyd) solubility calculated for and documented in the PA waste release model, DOE states that the solubility testing results for Tanks 18F and 12H are all at least 4-5 orders of magnitude lower than the Pu(OH)₂CO₃ solubility of 4.8E-5 moles/liter. NRC staff would note that the presence of carbonate phases in the waste has not yet been ruled out. In fact, DOE is unable to definitively state what chemical phases are present or what mechanisms are responsible for controlling aqueous phase concentrations of key radionuclides in the tank waste. NRC staff would also note that the maximum observed average concentration for Pu in waste release testing of 3E-07 mol/L (ADAMS Accession No. ML18242A259) is higher than the DOE reported Pu solubilities in equilibrium with dissolved oxygen, and orders of magnitude higher than the assumed solubility limiting phases for Pu in the latest PA documentation. Furthermore, because the ultimate degradation product of these grouts is calcium carbonate and a few recalcitrant minerals from the fly ash such as quartz and mullite are present, it is likely that current phases in the waste will, over time react to form other compounds with greater or lesser stability. DOE should identify and demonstrate the stability of existing compounds controlling Pu solubility, or should evaluate forms of Pu that are associated with a higher solubility compound, such as Pu carbonate, that will likely form over time.

Finally, NRC would note that DOE sensitivity analyses conducted for Tank 18F show that Pu solubilities in the range of no solubility control to 1E-06 mol/L lead to lower doses compared to lower solubilities. This counter-intuitive result occurs due to upwards diffusion of relatively high solubility Pu into the tank grout in DOE's Type IV tank, near-field model prior to tank failure. In fact, the Pu concentration leading to the highest dose was found by DOE to be approximately 1E-07 mol/L (see Figure 1 below). Therefore, concentrations higher than 1E-07 mol/L would lead to lower doses using DOE's Type IV tank near-field model. Because Pu concentrations up to 3E-07 mol/L in wash solutions were observed during the Tank 18F waste release experiments (see discussion in ADAMS Accession No. ML18242A259), NRC staff is concerned that there is a potential for the most risk-significant release of Pu from Tank 18F based on DOE's PA modeling. NRC staff will continue to evaluate the reasonableness of DOE PA model assumptions which indicate that no solubility control could lead to lower doses for Pu in Type IV tanks such as Tank 18F.

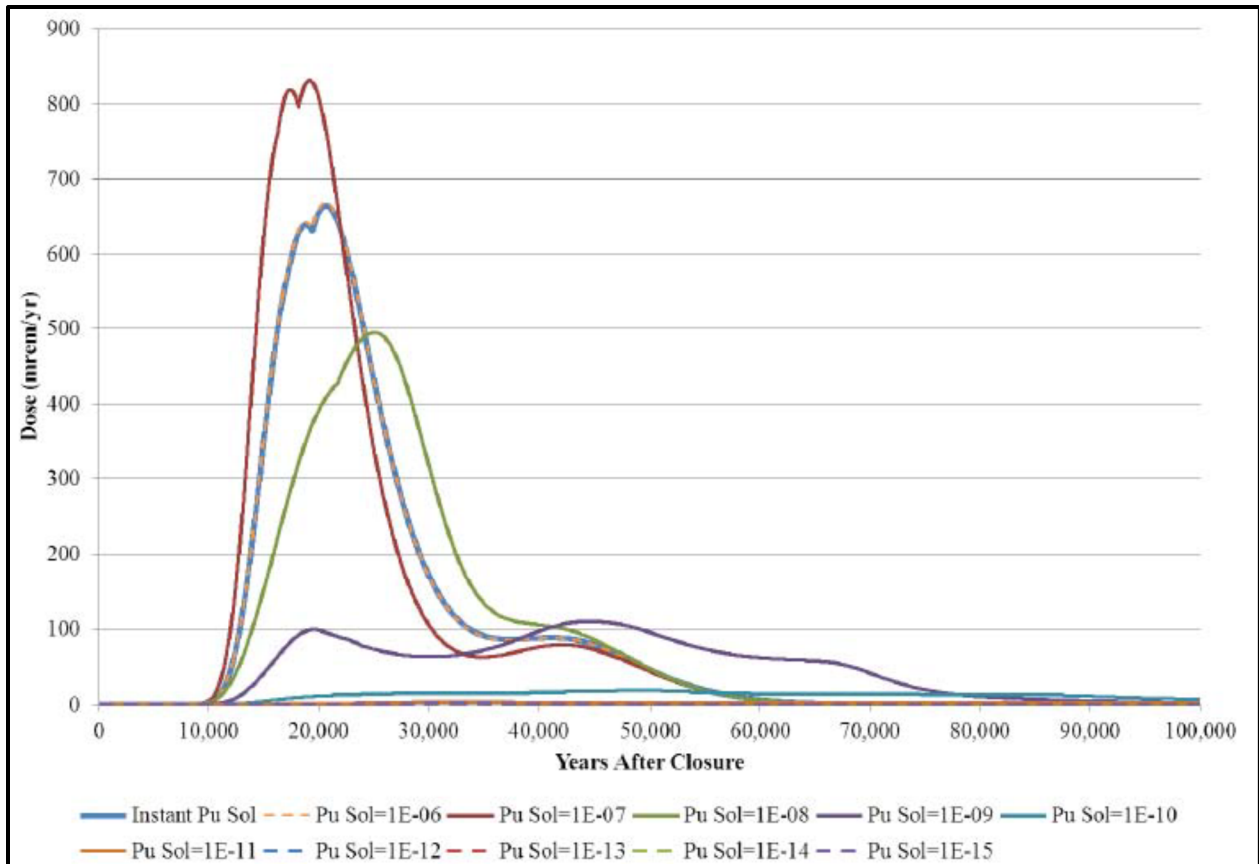


Figure 1. DOE Sensitivity Analysis on Pu Solubility (SRR-CWDA-2010-00124, Figure 6.3-23).

DOE goes on to state that that while Pu might not be quite as insoluble as assumed in the tank farm PA, it is still relatively insoluble and would therefore not be expected to contribute to the peak doses within 10,000 years (SRR-CWDA-2016-00086). Because solubility primarily affects magnitude and not timing of peak dose, this statement is unclear. Additionally, the most risk-significant release concentration of $3E-07$ mol/L observed in the Tank 18F waste release testing was for a washed sample prior to leach testing which suggests the highest release concentration might be associated with an early release fraction of relatively oxidized groundwater in contact with the waste (an alternative conceptual model in DOE's PA).

DOE evaluated the impact of potentially higher solubility values using the HTF and FTF GoldSim™ models in a deterministic mode (SRR-CWDA- 2018-00075). See Figure 2 below. The results for FTF are similar to results presented in the Tank 18F waste release PA impact report with doses over 0.25 mSv/yr just after 10,000 years and approaching 7 mSv/yr (700 mrem/yr) over longer time periods (20,000 to 30,000 yrs)⁷. The Tank Farm solubility values used in these new base case model runs are presented in SRR-CWDA-2016-00086, Rev. 1, Table 4.3.2-1, along with the solubility values used in HTF (SRR-CWDA-2010- 00128) and FTF (SRS-REG-2007-00002) PA modeling. See Table 7 below for ease of reference. The "Tank

⁷ Uncertainty in the timing of risk-significant concentrations and dose is also an NRC staff concern. For example, consideration of higher mobility forms of Pu could lead to doses above the 0.25 mSv/yr performance objective within 1000s of years. Additionally, the updated GSA PORFLOW (2018) model shows that peak concentrations and dose could be a factor of two higher than shown in Figure 2.

Farm conservative case” and “Tank Farm nominal case” values were presented in SRR-CWDA-2016-00086, Rev. 1, Table 4.3.2-1 based upon what was described as a considered evaluation (by the author) of the data presented in SRR-CWDA-2016-00086, Rev. 1, Figure 4.3.2-7. As stated in the Tank 18F waste release TRR (ADAMS Accession No. ML18242A259), DOE neglected to consider the highest concentrations of Pu observed in the ORIII wash solutions of $3E-07$ mol/L and did not consider two discrete fractions of Pu in the natural system (relatively high and relatively low mobility forms of Pu), which have been corroborated by lysimeter experiments. Consideration of higher mobility forms of Pu could lead to higher concentrations with the 10,000-year compliance period. NRC staff has issued a separate TRR, which among other topics, evaluates the results of the lysimeter experiments (ADAMS Accession No. ML19280A059).

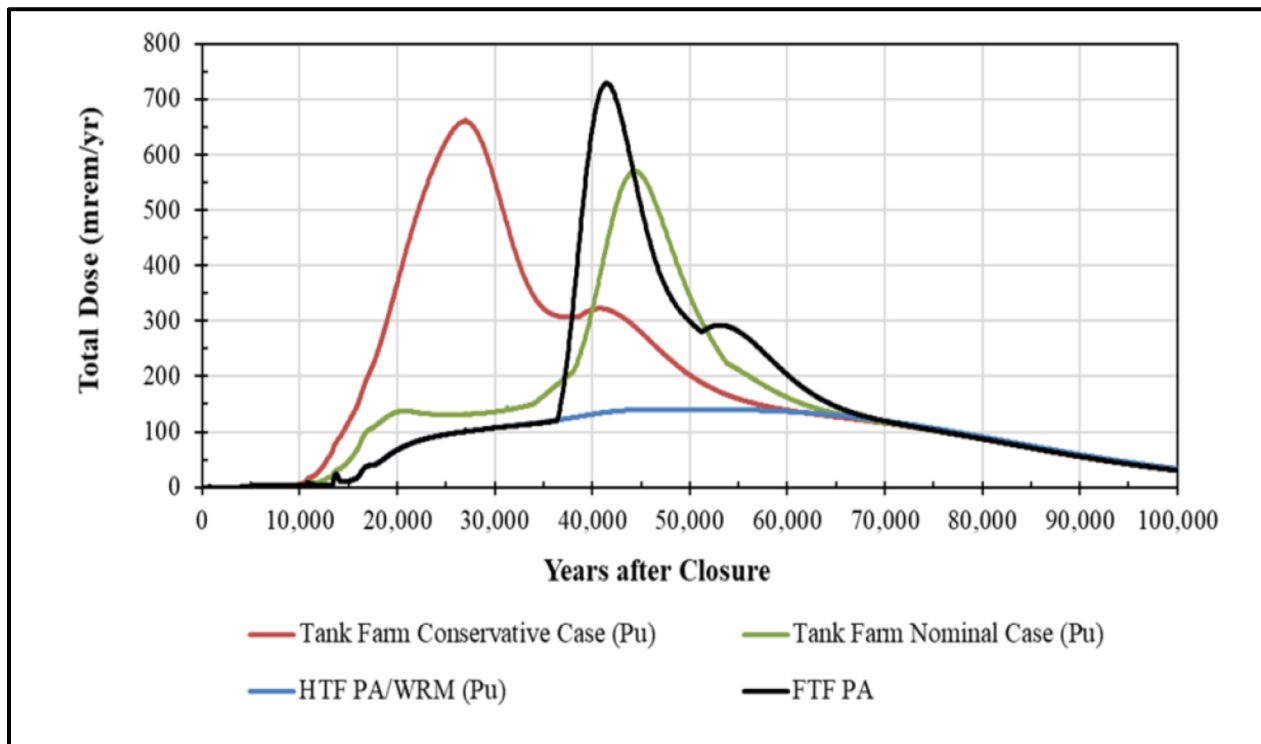


Figure 2. FTF Peak MOP Doses for Various Pu Solubility Values. See Figure 4.3.2-8 in SRR-CWDA-2016-00086, Rev. 1.

	RRII (mol/L)	ORII (mol/L)	ORIII (mol/L)
FTF PA	4E-12	4E-14	6E-05
HTF PA/WRM	3E-11	3E-11	3E-11
Tank 18F Conservative Case	5E-09	1E-08	2E-08
Tank 18F Nominal Case	5E-09	1E-09	1E-08
Tank 12H Conservative Case	5E-11	4E-10	2E-10
Tank 12H Nominal Case	5E-12	1E-10	1E-10
Tank Farm Conservative Case	5E-09	1E-08	2E-08
Tank Farm Nominal Case	1E-09	1E-09	1E-08

Table 7. Pu Solubilities Evaluated in SRR-CWDA-2016-00086, Rev. 1. See Table 4.3.2-1 in SRR-CWDA-2016-00086, Rev. 1.

While DOE performed a sensitivity analysis to evaluate the impact of sandy soil K_d on the results, as stated previously, multiple fractions of varying mobility were not considered independently as discussed in NRC staff's FTF Technical Evaluation Report (TER) (ADAMS Accession No. ML112371715), Appendix E of FTF and HTF Monitoring Plan (ADAMS Accession No. ML15238B403), and the NRC's Tank 18 special analysis and waste release TRRs (ADAMS Accession Nos. ML13100A230 and ML18242A259). Additional model support is needed for DOE's selection of K_d values as well as their treatment of different oxidation states of Pu with significantly different mobility in the natural system. Based on NRC staff analysis, use of an average K_d is generally inappropriate when the magnitude of the K_d varies orders of magnitude.

DOE also evaluated the impact of potentially higher Tc concentrations on the results. Table 8 below provides information on the assumed solubilities used in the GoldSim™ simulations. Given the limited inventory of Tc, the impact of higher assumed Tc solubilities had no significant impact on the FTF PA results (see Figure 3) and minimal impact on the HTF PA results (see Figure 4) within 20,000 years.

	RRII (mol/L)	ORII (mol/L)	ORIII (mol/L)
FTF PA	3E-11	3E-13	NA (no solubility control)
HTF PA/WRM	1E-14	1E-13	2E-15
Tank 18F Conservative Case	3E-09	2E-08	2E-08
Tank 18F Nominal Case	6E-10	1E-08	1E-08
Tank 12H Conservative Case	2E-09	1E-08	8E-09
Tank 12H Nominal Case	1E-09	1E-08	8E-09
Tank Farm Conservative Case	3E-09	2E-08	2E-08
Tank Farm Nominal Case	1E-09	1E-08	1E-08

Table 8. Tc Solubilities Evaluated in the Impact Analysis. See Table 4.3.3-1 in SRR-CWDA-2016-00086, Rev. 1.

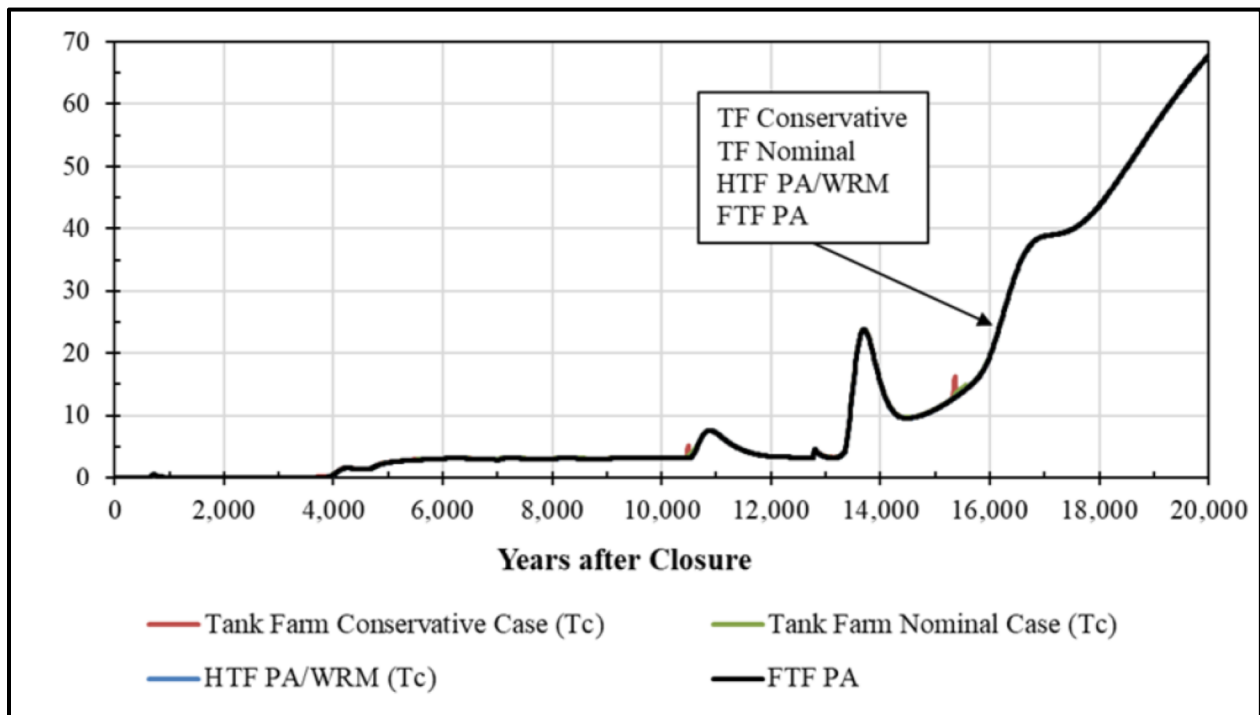


Figure 3. FTF Peak Member of the Public Doses for Various Tc Solubility Values—20K Years. Image credit: Figure 4.3.3-8 of SRR-CWDA-2016-00086, Rev. 1.

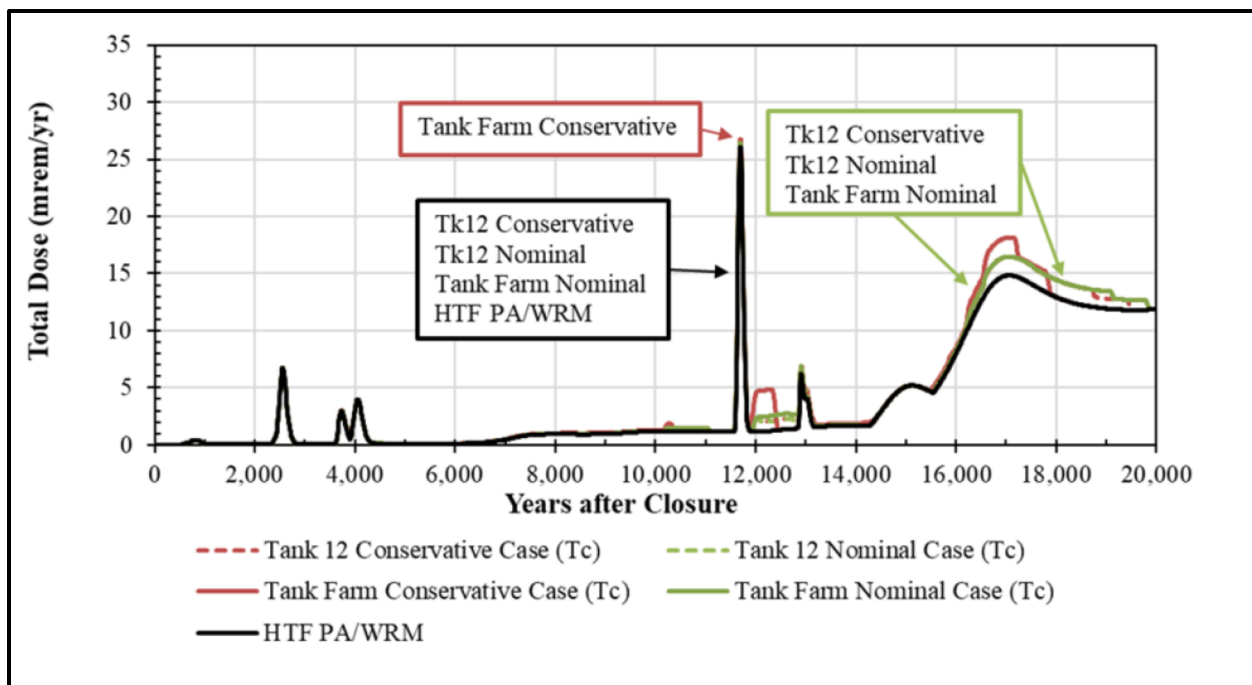


Figure 4. HTF Peak Member of the Public Doses for Various Tc Solubility Values—20K Years. Image Credit: Figure 4.3.3-9 of SRR-CWDA-2016-00086, Rev. 1.

DOE notes that the I-129 solubilities with Tank 12H residual solids in grout porewater simulants were generally below detectable concentration limits ($<6E-07$ M). No measurable iodine was observed for any of the reducing samples (RRII-CC and RRII-CFS), and iodine was detected only twice in the oxidizing samples (one for sample ORII-3 and one for sample ORIII-6). SRR-CWDA-2016-00086 indicates that iodine can form solubility-limiting solid phases with several metals that are present in residual tank waste. While the I-129 results for nearly all samples were below detectable concentration limits, two oxidizing samples were observed to contain I-129 above the limits (concentrations ranging from $1E-08$ M to $2E-08$ M). DOE indicates that these concentrations were below the predicted solubility for Hg_2I_2 .

Overall, the solubility testing results for RRII, ORII, and ORIII indicate iodine is much less soluble than assumed in the TF PAs. A table of values simulated using GoldSim™ to assess the impact of various iodine solubilities on the PA results is provided in Table 9 below. The AgI and Hg_2I_2 iodine solubility cases were based on the findings of SRNL-STI-2015-00339 but did non-mechanistically assume that iodine solubility controls were present in RRII and/or submerged Region C (SRR-CWDA-2016-00078). As seen in Figure 5 below, assuming the Tank 12H derived I solubility values (i.e., using the I solubility values from Table 9) decreases the peak dose (accounting for all sources and all radionuclides) within 10,000 years for HTF.

	RRII	ORII	ORIII
FTF PA/HTF PA/WRM	NSC	NSC	NSC
AgI Above Water	2.7E-07	2.7E-07	3.8E-08
AgI Submerged	9.8E-09	9.8E-09	3.8E-08
Hg₂I₂ Above Water	2.0E-05	2.0E-05	1.2E-04
Hg₂I₂ Submerged	1.8E-07	1.8E-07	1.8E-07
Tank 12H Conservative Case	7.0E-07	5.0E-07	2.0E-07
Tank 12H Nominal Case	5.0E-07	5.0E-08	5.0E-08

NSC=No solubility control

Table 9. Iodine Solubilities Evaluated in the Impact Analysis. See Table 4.3.5-1 in SRR-CWDA-2016-00086.

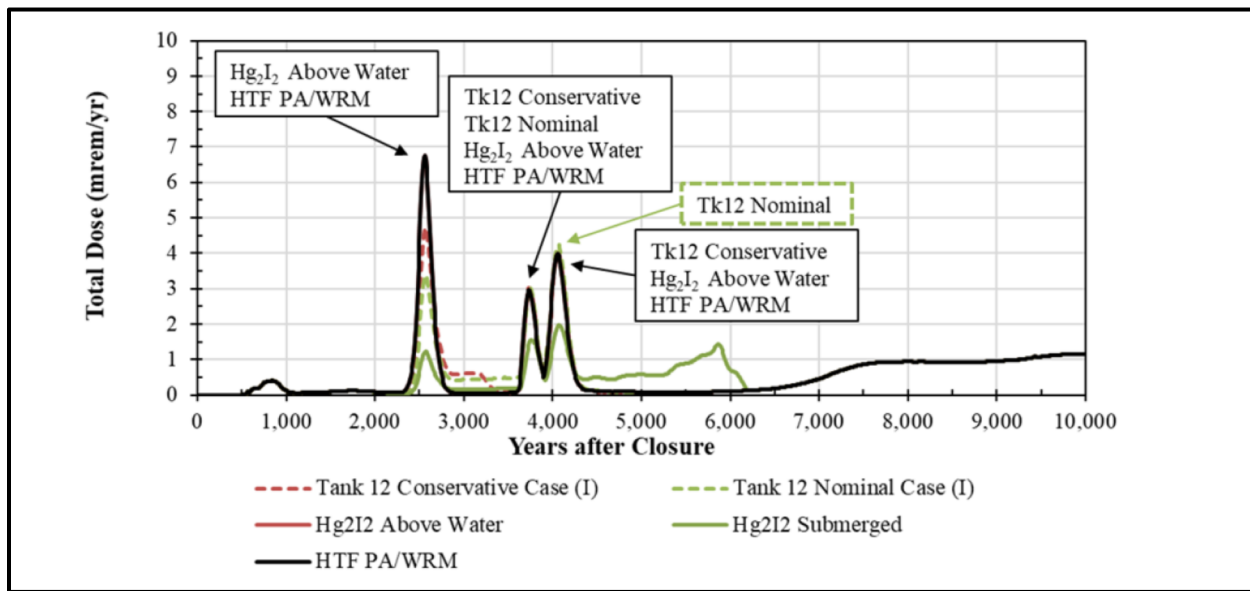


Figure 5. HTF Peak Member of the Public Doses for Various I Solubility Values—10K Years. Image credit: Figure 4.3.5-5 in SRR-CWDA-2016-00086.

Evaluation of Iodine Solubility and Sorption

In typical performance assessments for radioactive waste disposal, iodine is considered to be a mobile radioelement because of its generally high solubility and low sorption. DOE indicated that analyses of the residual waste sampled from the Tank 12H floor and cooling coils revealed higher than anticipated I-129 inventories (SRR-CWDA-2015-00166), suggesting that iodine release from waste tanks may be solubility-controlled. The SRNL report *Potential Solubility Controls for I-129 in Residual Tank Waste* (SRNL-STI-2015-00339) documented a scoping analysis of possible controls on the release of I-129 from Tank 12H residual waste. Estimates of solubility controls on I-129 suggest the possibility that silver or mercury in the residual waste can limit the release of I-129 under certain conditions. Under various oxidizing conditions the calculated solubility of silver iodide (AgI) ranges from 9.8E-9 to 2.7E-7 moles/liter and the calculated solubility of mercury iodide (Hg₂I₂) ranges from 1.2E-7 to 1.2E-4 moles/liter.

In SRR-CWDA-2016-00086, Rev. 1, DOE concluded that the fact that the iodine in floor residual waste samples from Tank 12H was removed (during characterization) with a deionized (DI) water leach (SRNL-STI-2015-00241) is not inconsistent with active solubility controls on I-129

solubility. DOE calculated an average iodine concentration of $3.6\text{E-}6$ moles/L in 30 ml of water when washed with DI water. DOE stated that this is within the range of solubility controlled by mercury iodide compounds.

Although not directly related to the tank farm PAs, DOE performed laboratory work to study the mobility of iodine in the natural system for the Saltstone Disposal Facility (SDF). SREL Doc. R-17-0004 Version 1 documents laboratory studies at the Savannah River Ecology Laboratory aimed at refining the technical basis for partition coefficient (K_d) values for redox-sensitive I-129. Batch sorption experiments were performed on a representative SDF soil using four test solutions that mimic aqueous chemical conditions during progressive cementitious material degradation. The tests are therefore designed to be relevant for modeling transport below the SDF of I-129 released from saltstone. In addition, sorption tests were conducted on ground concrete representative of Saltwaste Disposal Unit construction. The tests used two different starting host solutions to represent pore waters associated with early stages of concrete and saltstone degradation. The solutions were prepared by equilibrating water with portlandite and saltstone. Two other solutions mimic late-stage cementitious material degradation (calcite equilibration) and groundwater unaffected by cementitious material (simulated site groundwater). Solutions were prepared under both oxic and anoxic conditions. The latter conditions were maintained by conducting the tests in a glove box with an oxygen-free N_2 atmosphere with 2 percent H_2 .

I-129 sorption was weak but measurable, ranging from 0.2 to 1.1 mL/g, under only 3 of the tested conditions: in oxic and anoxic groundwater (pH 4.66 and 5.22) and in oxic calcite water (pH 5.74). In all other cases, including in the concrete tests, sorption was too weak to be statistically indistinguishable from a zero K_d .

The new iodine sorption tests were appropriately designed to provide information useful for SDF PAs. The data can also be considered for transport models below SRS tank farms, to the extent that (i) the selected soil is within the range of soil types below tank farms and (ii) the Saltwaste Disposal Unit concrete is similar to tank farm concretes. These factors should be explicitly considered on a case-by-case basis. The saltstone leachate tests in this report are not applicable to tank farm models, but the other three experimental solutions are more generic in nature and potentially relevant.

In the tests, I-129 sorption was measurable only at pH less than 6, suggesting that a K_d of zero is appropriate for modeling all other conditions. The NRC staff has recommendations that would be needed to support a non-zero K_d , and also has suggestions for clarifying the report.

- Knowledge of solution chemistry before and after the tests, beyond only pH, would aid interpretation of the results in that they would reveal the extent of solid-solution reaction. In particular, oxidation-reduction potential measurements would help understanding of how iodine behavior reflects actual solution redox, such as may be imposed by the soils or cementitious materials. Establishing and maintaining reducing conditions—which is a target of the study, given the intended focus on reduced iodine—is experimentally challenging. (For example, in the anoxic tests the transfer of solutions outside the glove box, even in closed tubes, introduces the possibility of oxygen contamination.) Solution Eh measurements would provide useful information that would aid in interpreting the results and would help support the use of a non-zero K_d in more acidic anoxic conditions.
- Because the study was intended to focus on the iodide species, knowledge of the actual aqueous iodine speciation during the experiments would be useful.

- The report should state clearly whether the saltstone used to prepare the saltstone leachate solution is actual or simulated saltstone and provide a reference for its preparation. Presumably actual saltstone was not used because its intrinsic I-129 content would affect the tests.
- For all tests, it is unclear why most supernatant is removed after initial equilibration between the soil and the starting solution, and then fresh starting solution is added along with the I-129. Presumably this procedure is aimed at minimizing any strong effect of initial reaction between the soil and the experimental solution, but it is unclear whether the test solutions are therefore representative of soil equilibration.

Teleconference or Meeting:

No teleconference or meeting was held on this TRR.

Follow-up Actions:

There are no follow-up action items.

Open Issues:

There are no open issues resulting from this TRR.

Conclusions:

In conclusion, the DOE performed waste release testing from actual high-level-waste samples collected from Tank 12H to inform HTF waste release modeling results and PA assumptions. The results of the analysis improve NRC staff understanding of the waste and tank grout as chemical barriers to mitigate releases from the tank farm facilities after closure. DOE used the results of the Tank 18F and Tank 12H experiments to evaluate whether the FTF and HTF PA results were under-predicted. Notwithstanding the results of the Tank 18F waste release testing and issues associated with Pu-239 and other key radionuclide solubility, results of both the waste release testing and PA impact analysis 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 TERs (ADAMS Accession Nos. ML112371715 and ML14094A514) and monitoring plan (ADAMS Accession No. 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. The results of the two sets of waste release experiments demonstrate the difficulty in using models to predict the 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 for the entire tank farm, as different tanks will have different waste types and a different mix of key radionuclides.

DOE should consider the following items to enhance its waste release testing, continue to address uncertainties in the current PA models and support future PA models. NRC recognizes that waste release testing and the PA modeling are an iterative process. Risk insights including the impact of uncertainty should be considered in developing future tasks.

Considerations for Future Waste Release Testing

- NRC staff supports DOE's recommendation to conduct additional leach testing on other tank waste (N-ESR-H-00040).
- DOE should consider evaluation of the impact of waste type, 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 waste release testing, if testing of multiple tank samples is impractical, DOE should develop support for the use of composite samples and discuss the limitations of use of a composite sampling approach. Ideally supporting information for use of a composite leach test sample would include solid phase characterization and aqueous phase concentrations of individual samples to better understand tank waste variability.
- As stated in the Tank 18F TRR (ADAMS Accession No. ML18242A259), in future testing, DOE should consider water rinses with synthetic SRS groundwater in addition to grout conditioned groundwater to study the impact of grout bypass on waste release results.
- DOE should conduct solid phase analysis on tank waste residuals, including Tank 12H. Recommendations were provided in an independent peer review group report (LA-UR-2012-00079) with potential analysis methods.
- DOE should consider analyzing all major ions, alkalinity, and appropriate trace components (e.g., Pu, Fe, and sulfide). If possible an anion/cation balance should be calculated to determine if an important component has been missed.
- 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. DOE should also consider how the inability to meet the target Eh endpoints assumed in modeling affect the results.
- DOE should develop additional model support that calcium carbonate maintains pH in the simulated cement-reacted solutions, both oxidizing and reducing, and how the leaching results might have been affected by this assumption.
- DOE should develop additional model support to refer to the results of the experiments (i.e., aqueous phase concentrations) as solubilities. Without a conceptual understanding of controls on radionuclide concentrations in the engineered system, it would be difficult to extrapolate the results to other conditions.

- DOE should discuss how the RRII and ORII conditions targeted in the leach testing differ from Conditions C and D assumed in the HTF PA for Tank 12H, and how the use of a higher pH affects the applicability of the experimental results.

Considerations for PA Modeling

- 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 continue to study and develop alternate conceptual models to account for various oxidation states 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.

In this report, there is no significant change to the NRC staff overall conclusions from the F- and H-Tank Farm TERs regarding compliance of DOE disposal actions with the 10 CFR Part 61 Performance Objectives.

References

Denham, M. and Millings M., "Evolution of Chemical Conditions and Estimated Solubility Controls on Radionuclides in the Residual Waste Layer During Post-Closure Aging of High-Level Waste Tank," SRNL-STI-2012-00404, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina, 2012.

ML112371715, *Technical Evaluation Report for F-Area Tank Farm Facility, Savannah River Site, South Carolina*, U.S. Nuclear Regulatory Commission, Washington, DC, October 2011.

ML14094A514, *Technical Evaluation Report for the U.S. DOE Savannah River Site Draft Section 3116 Waste Determination for the H-Area Tank Farm Facility*, U.S. Nuclear Regulatory Commission, Washington, DC, June 2014.

ML15238A761, *U.S. Nuclear Regulatory Commission Plan for Monitoring Disposal Actions Taken by the U.S. Department of Energy at the Savannah River Site F-Area and H-Area Tank Farm Facilities in Accordance with the National Defense Authorization Act for Fiscal Year 2005*, U.S. Nuclear Regulatory Commission, Washington, DC, October 2015.

ML17277B235, *Technical Review: Final Inventory and Special Analysis Documentation for Tank 12*, U.S. Nuclear Regulatory Commission, Washington, DC, January 2018.

ML18235A538, *U.S. Nuclear Regulatory Commission August 13-14, 2018, Onsite Observation Visit Report for the Savannah River Site Combined F and H Tank Closure*, US NRC, Washington, DC, 2018.

N-ESR-H-00040, *Waste Tank Residuals Properties*, Savannah River Site, Aiken, SC, Rev. 2, November 2018.

Oji, L.N., et al., *Tank 12H Residuals Sample Analysis Report*, SRNL-STI-2015-00241, Savannah River National Laboratory, Aiken, SC, June 2015.

SREL Doc.: R-17-0004, *Impact of Cementitious Material Leachate on Iodine Partitioning*, Savannah River Ecology Laboratory, University of Georgia, Aiken, SC, September 2017.

SRNL-MS-2018-00142, *SRS Tank 12H Residual Radionuclide Release Testing Status*, Savannah River Nuclear Solutions, Aiken, SC, August 13, 2018.

SRNL-STI-2015-00241, Rev. 0., *Tank 12H Residuals Sample Analysis Report*, Savannah River National Laboratory, Aiken, SC, June 2015.

SRNL-STI-2015-00339, *Potential Solubility Controls for I-129 in Residual Tank Waste*, Savannah River National Laboratory, Aiken, SC, July 2015.

SRNL-STI-2012-00106, *Form and Aging of Plutonium in Savannah River Site Waste Tank 18F*, Savannah River National Laboratory, Aiken, SC, February 2012.

SRR-CWDA-2010-00124, Rev. 0. *Tank 18/Tank 19 Special Analysis for the Performance Assessment for the F-Tank Farm at the Savannah River Site*. Savannah River Remediation: Aiken, SC, 2012.

SRR-CWDA-2015-00166, *Updated Radionuclide and Chemical Inventories in Tanks 9, 10, 11, 13, 14, 15, Rev. 0*, Savannah River Remediation, Savannah River Site, Aiken, SC, January 2016.

SRR-CWDA-2016-00078, *Type I and II Tanks Special Analysis for the Performance Assessment for the H-Tank Farm at the Savannah River Site, Rev. 0*, Savannah River Remediation, Savannah River Site, Aiken, SC, Rev. 0, August 2016.

SRR-CWDA-2010-00128, *Performance Assessment for the H-Area Tank Farm at the Savannah River Site, Rev. 1*, Savannah River Remediation, Savannah River Site, Aiken, SC, November 2012.

Walter, G.R. and C.L. Dinwiddie, *Tank Grout Water-Conditioning Tests—Status Report*, Center for Nuclear Waste Regulatory Analyses, San Antonio, Texas, January 2019. [\[ML18285A834\]](#)