

May 31, 2013

MEMORANDUM TO: Janelle Jesse, Acting Chief  
Low-Level Waste Branch  
Environmental Protection  
and Performance Assessment Directorate  
Division of Waste Management  
and Environmental Protection  
Office of Federal and State Materials  
and Environmental Management Programs

THRU: Christopher McKenney, Chief **/RA/**  
Performance Assessment Branch  
Environmental Protection  
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Division of Waste Management  
and Environmental Protection  
Office of Federal and State Materials  
and Environmental Management Programs

FROM: George Alexander, Systems Performance Analyst **/RA by C. Barr for/**  
Performance Assessment Branch  
Environmental Protection  
and Performance Assessment Directorate  
Division of Waste Management  
and Environmental Protection  
Office of Federal and State Materials  
and Environmental Management Programs

SUBJECT: TECHNICAL REVIEW: WASTE RELEASE AND SOLUBILITY  
RELATED DOCUMENTS PREPARED BY UNITED STATES  
DEPARTMENT OF ENERGY TO SUPPORT FINAL BASIS FOR  
SECTION 3116 DETERMINATION FOR THE F-AREA TANK FARM  
FACILITY AT SAVANNAH RIVER SITE. PROJECT NO. PROJ0734.

The U.S. Nuclear Regulatory Commission (NRC) staff has performed a technical review of several documents prepared by the United States Department of Energy (DOE) that address NRC staff Technical Evaluation Report (TER) comments and recommendations related to waste release assumptions in the F-Area Tank Farm Facility (FTF) performance assessment (DOE, 2010). This technical review activity supports Monitoring Factors 2.1, "Solubility Limiting Phases/Limits" and 2.2, "Chemical Transition Times" in NRC staff's monitoring plan for the F-Area Tank Farm facility (FTF) (NRC, 2012).

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In 2011, NRC issued a TER for the FTF with the primary recommendation for DOE to conduct waste release experiments to support several key modeling assumptions. Following issuance of NRC staff's TER, DOE conducted a number of studies to provide additional support for several waste release assumptions. NRC staff has reviewed these additional studies and concludes, consistent with DOE plutonium solubility expert recommendations, that experimental verification of modeled solubilities of key radionuclides and solid phase analysis continues to be needed to provide support for key modeling assumptions in DOE's FTF Performance Assessment (PA).

Additionally, NRC staff has identified two follow-up actions for DOE to provide additional information related to waste release assumptions:

- DOE should provide additional information to support assumptions regarding longevity of reducing conditions in the contaminated zone. Recent studies (Cantrell and Williams, 2012) suggest that the reducing capacity of the tank grout could be depleted much earlier than assumed in the FTF PA (SRS-REG-2007-00002 Rev 1) and in more recent Pu solubility modeling performed for Tank 18 (Denham, 2012). Uncertainty in the normative mineralogy assumed in geochemical modeling should be considered under this action.
- DOE should provide additional support for the assumption that the Eh of infiltrating water will remain below a critical threshold at which Pu solubility will increase to a risk-significant value (e.g., updated geochemical modeling indicates a dramatic increase in Pu solubility occurs at Eh greater than +0.45 V). Uncertainty in the critical threshold and the Eh of infiltrating groundwater should be considered under this action.

Additional details related to NRC staff's findings and conclusions are provided in the enclosure.

Enclosure: Technical Review of Waste Release-Related Documents.

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Enclosure: Technical Review of Waste Release-Related Documents.

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## Technical Review of Waste Release Documents Supporting FTF Closure

Date: May 2013

Reviewers:

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George Alexander, NRC  
Cynthia Barr, NRC  
Bobby Pabalan, Center for Nuclear Waste Regulatory Analyses (CNWRA)  
David Pickett, CNWRA

Key Documents Reviewed:

Cantrell, K., Clark, D.L., Janecky, D.R., Psaras, J., and Runde, W. *Plutonium Solubility Peer Review Report*. LA-UR-2012-00079. Prepared for DOE Savannah River Operations Office (DOE-SR), Los Alamos National Laboratory, New Mexico, December 2011.

Denham, M. *Evolution of Chemical Conditions and Estimated Plutonium Solubility in the Residual Waste Layer During Post-Closure Aging of Tank 18*. SRNL-STI-2012-00087. Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, Aiken, SC 29808, February, 2012.

Hay, M.S., O'Rourke, P.E., and Ajo, H.M. *Scanning Electron Microscopy and X-Ray Diffraction Analysis of Tank 18 Samples*. SRNL-STI-2012-00123. March 2012.

Hobbs, D.T. *Form and Aging of Plutonium in Savannah River Site Waste Tank 18*. SRNL-STI-2012-00106. Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC Aiken, SC 29808, February 2012.

Millings, M., Noonkester, J., and Bagwell, L. Memo to K. Rosenberger and M. Layton. *Summary Dissolved Oxygen in Water Table Wells at SRS*. SRNL-L3200-2011-00011. Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, Aiken, SC 29808, December 2011.

### **Summaries of Technical Reports**

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

#### **Cantrell et al., 2012**

To obtain expert technical advice related to a key FTF Performance Assessment (PA) modeling assumption (plutonium solubility in Tank 18) DOE assembled a peer review group consisting of plutonium chemistry experts. A number of areas for improvement were identified in the report, including conceptual model issues, solubility assumptions, quality assurance, and communication.

Enclosure

Findings and recommendations were made in 5 major areas. The recommendations of the peer review group are summarized below.

A. Solubility Controlling Phase/Thermodynamic Database: In the PA, plutonium in residual tank waste is assumed to be co-precipitated with iron minerals in Region II, while solubility in Region III is assumed to be controlled by  $\text{PuOH}_4$ . These assumptions are not consistent with current scientific understanding or supported by experimental data. It is recommended that the contractor employ a more technically valid model using amorphous  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  (am) as the solubility controlling phase. Additionally, the thermodynamic database that was used was not appropriate. A properly vetted and internationally accepted database should be used to calculate plutonium solubility, such as the Nuclear Energy Agency (NEA) database.

B. Experimental Verification: The plutonium and grout chemistry assumptions need to be validated and verified where feasible. Residual tank waste should be characterized using advanced spectroscopic techniques. Solubility and release studies should be conducted on the waste to provide further support of plutonium and grout chemistry assumptions used for modeling.

C. Conceptual Models: Sorption of plutonium in soils should be modeled allowing for elevated pH of groundwater as a result of grout leaching. Important geochemical parameters should be evaluated, including the concentrations of oxygen and carbon dioxide. In addition, the conceptual model of degradation being controlled by the diffusion of carbon dioxide into the grout seems like a low probability scenario. Fracturing of the grout with preferential flow through the cracks would appear to be much more likely and should therefore be evaluated.

D. Quality Assurance/Quality Control (QA/QC): The plutonium solubility peer review group stated that they found no evidence of a credible quality assurance program for geochemical modeling during their on-site review. A credible QA/QC program for geochemical modeling is needed to provide confidence in the PA model results.

E. Communications: The reviewers found a lack of coordination and project integration that led to a lack of communication regarding important model assumptions and model approaches (e.g., plutonium chemists were not involved in the selection of thermodynamic data or peer reviews).

Hobbs, 2012 and Hay et al., 2012

The report by Hobbs (SRNL-STI-2012-00106) incorporates results of the solid-phase tank waste analyses from Hay, et al. (2012) in SRNL-STI-2012-00123. Hobbs reviews the history of the use of Tank 18 and discusses the forms that plutonium could take in the waste solids as a result of the major elements in the waste and the treatments (primarily neutralization with NaOH) that it received. The author states that the oxidation state of plutonium, entering the tanks, should be plutonium (IV) and that most of the plutonium is precipitated as amorphous plutonium hydroxide,  $\text{Pu}(\text{OH})_{4(\text{am})}$  or hydrous plutonium oxide,  $\text{PuO}_{2(\text{am,hyd})}$  and coprecipitated with iron and other major elements in the waste. The author also discusses that Tank 18 waste removal operations likely removed the more soluble salts and the plutonium associated with these salts. Recent Scanning Electron Microscopy (SEM) analyses disclosed small discrete plutonium particles, associated with particles of an iron oxide matrix (SRNL-STI-2012-00123). Hay et al.

(2012) discusses that these plutonium particles do not appear to account for all of the plutonium in the sample, which was determined by chemical analysis. Consequently, the authors conclude that the plutonium appears to be present as both discrete particles and distributed throughout the iron oxide matrix.

In 2009, samples were collected from Tank 18 during the final heel removal. Of particular interest are the concentrations of plutonium in the liquid phase that was isolated from the samples. The concentrations of plutonium for the north and south hemisphere samples measured  $1.3 \times 10^{-8}$  and  $2.6 \times 10^{-8}$  M, respectively. The author states that these concentrations are well above the predicted solubilities for  $\text{PuO}_{2(\text{am,hyd})}$  and coprecipitated plutonium (IV). The high solubility values are attributed to possible presence of colloidal plutonium that passed through the  $0.45 \mu\text{m}$  filter or the presence of a plutonium carbonate phase. The high pH of the waste and active venting of the tank to relieve hydrogen accumulation resulted in the possibility of carbonate accumulation in the waste. Hobbs (2012) states that carbonate is an effective complexing agent for plutonium (IV) and several studies have shown that plutonium carbonate solids as well as aqueous complexes could form, thereby increasing the solubility of plutonium. Recent X-Ray Diffraction (XRD) analysis is consistent with the presence of carbon dioxide in solution as  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$  has been observed as a major crystalline component of the Tank 18 solids (SRNL-STI-2012-00123). Hobbs (2012) states that a portion of the plutonium has likely converted to a hydroxy-carbonate complex, but that upon interaction with grout (i.e., an increase in pH and decrease in carbonate concentration) the plutonium carbonate phases are expected to transform back into  $\text{PuO}_{2(\text{am, hyd})}$ .

Hobbs (2012) discusses that as precipitated solids age, they undergo Ostwald ripening and become more crystalline. The author states that this has been shown to occur for plutonium precipitates with a related lowering of solubility by about two orders of magnitude. According to Hobbs (2012), the use of grout in the tank can be expected to convert  $\text{PuO}_{2(\text{am, hyd})}$  into a more crystalline  $\text{PuO}_2$  phase. The author goes on to state that it would be an extremely slow process and the amorphous forms of plutonium would not be expected to completely convert into crystalline form due to the continual presence of water, reactions with products from the radiolysis of water, and low temperatures.

The Hobbs report concludes that there are three dominant forms of plutonium present in the Tank 18 residual waste:  $\text{PuO}_{2(\text{am, hyd})}$ , plutonium coprecipitated primarily with iron oxides, and as  $\text{PuO}(\text{CO}_3)_{(\text{am, hyd})}$ . However, Hobbs recommends X-ray Adsorption Spectroscopy (XAS) should be used to assess the form of plutonium in the waste. Hobbs recommends that if plutonium carbonate is observed, experiments should be conducted to determine if these species are converted back into  $\text{PuO}_{2(\text{am, hyd})}$  upon contact with grout.

Hobbs recommends that other tanks should be evaluated for specific conditions or operations that may alter the form of plutonium present in the residual waste. Depending on this history, characterization of the form of plutonium present in the waste solids would be appropriate. The report by Hay et al. (2012) noted that XAS could be used to determine plutonium oxidation state and local atomic coordination. The authors also discussed that leaching and solubility tests could provide information on plutonium speciation.

Millings et al. (2011)

In support of FTF PA geochemical models of infiltrating water, this study compiled available SRS data on dissolved oxygen concentrations at the water table. The dissolved oxygen in the water table wells at SRS typically ranged from 5.6 to 8.9 mg/L, which was "slightly less than the values expected for fully saturated fresh surface water (8 to 10 mg/L)." This study concluded that an assumption of equilibrium with atmospheric oxygen in DOE's grout evolution models (e.g., SRNL-STI-2012-00087) "is reasonable, if not slightly conservative." The authors also noted that because the FTF is in the vadose zone, the tanks will be exposed to a partial pressure of oxygen that is between atmospheric and the partial pressure in equilibrium with the groundwater dissolved oxygen concentrations.

Denham (2012)

Denham (2012) provides updated modeling of Eh-pH transitions in aging grout and on the plutonium waste release model. The conceptual approach to contaminant release is consistent with geochemical modeling in the FTF PA. However, this modeling uses internationally accepted thermodynamic data, as recommended by the plutonium peer review group (LA-UR-12-00079), includes an updated grout formula, and considers the results of solid phase analysis of Tank 18 heels by Hay et al. (2012). Denham estimates the solubility of plutonium that is assumed to be present as discrete  $\text{PuO}_{2(\text{am, hyd})}$  particles and coprecipitated with iron in the residual waste. The estimated solubilities for  $\text{PuO}_{2(\text{am, hyd})}$  and coprecipitated plutonium under the assumed chemical conditions are reproduced from Denham (2012) in Table 1. These plutonium solubilities are characterized in the report as bounding values. The lower solubility bound is captured by the apparent solubility of plutonium coprecipitated in the iron matrix. Denham also states that the upper solubility bound is represented by  $\text{PuO}_{2(\text{am, hyd})}$  in aqueous solution equilibrated with dissolved oxygen. A series of stability diagrams indicate that for Eh values less than about +0.45 V, plutonium solubility will be relatively low. However, plutonium solubility is highly sensitive to Eh and increases significantly above an Eh of +0.45 V. The author also discusses uncertainties associated with the grout simulations and plutonium solubility estimates.

Table 1. Estimated Plutonium Solubilities (adapted from Denham, 2012)

Chemical Condition	$\text{PuO}_{2(\text{am, hyd})}$ (mol/L) Max <sup>a</sup>	$\text{PuO}_{2(\text{am, hyd})}$ (mol/L) More Realistic <sup>b</sup>	Coprecipitated (mol/L)
Reduced Region II	3.2E-11	3.2E-11	3.0E-14
Oxidized Region II	5.2E-8	3.2E-11	2.5E-13
Oxidized Region III	7.8E-8	3.2E-11	5.0E-15
a. Eh values in equilibrium with dissolved oxygen			
b. More realistic Eh values			

Denham states that the largest uncertainties include the nature of the grout and the plutonium in the future. The geochemical modeling in this report assumes that the grout is in an intact porous medium and that the bounding effects of fast flow paths are addressed within the performance assessment. As previously discussed, the nature of plutonium when the tank liner fails is considered to be discrete  $\text{PuO}_{2(\text{am, hyd})}$  particles and plutonium coprecipitated with iron. The report also discusses other forms of plutonium that may exist in the tanks. Recent

characterization of Tank 18 residual waste samples indicated that a plutonium carbonate phase may be present, based on observed concentrations of plutonium in water separated from the Tank 18 waste samples and the identification of a uranyl carbonate phase by XRD. However, Denham argues that the form of the discrete plutonium particles will be  $\text{PuO}_{2(\text{am, hyd})}$  based on its thermodynamic stability, relative to plutonium carbonate phases. Denham also discusses that the solubility of  $\text{PuO}_{2(\text{am, hyd})}$  may decrease due to dehydration and/or crystallization, although the solubility is unlikely to reach that of crystalline  $\text{PuO}_2$ .

In SRNL-STI-2012-00087, Denham discusses additional uncertainties, including pH and grout mineralogy. For Reduced Region II, the solubility of plutonium was insensitive to pH above approximately a pH of 9. Depending on the assumed Eh for Oxidized Region II, plutonium solubility can be sensitive to pH. At an Eh of +0.24V, which Denham describes as the more realistic Eh, the solubility of plutonium is constant at  $3.2\text{E-}11$  mol/L. At an Eh of +0.56V, plutonium solubility increases by approximately 3 orders of magnitude to  $5.2\text{E-}8$  mol/L. The behavior of plutonium solubility in Oxidized Region III is similar to that of Oxidized Region II. At an Eh of +0.29V and +0.68V, the solubility of plutonium is  $3.2\text{E-}11$  mol/L and  $7.8\text{E-}8$  mol/L, respectively. The assumed mineralogy is noted as influencing the pH transition.

According to this modeling, a major control on the pH transition from 11.1 to 9.2 is the amount of hydrous calcium silicates present. This in turn is influenced by the quantity of dissolved silica in the infiltrating water and the type of silica in the grout. This modeling also demonstrates that even though silica is important to pH, it has little impact on dissolved plutonium concentrations.

### **Teleconference**

On July 26, 2012, the NRC staff and representatives from DOE participated in a teleconference to discuss the staff's request for additional information pertaining to the evolution of solubility, in particular plutonium, of Tank 18 residual waste. This section provides an overview of the teleconference; the complete summary of the teleconference is available in Agencywide Documents Access and Management System (ADAMS) (ML12236A370).

NRC staff requested information regarding DOE plans for conducting (i) solubility and leach tests recommended by the Plutonium solubility peer review group (LA-UR-12-00079) and NRC in its Technical Evaluation Report (TER) (ADAMS accession number ML112371751), (ii) SRNL recommended solid phase analysis to determine the presence of plutonium (Pu) carbonate in the waste (SRNL-STI-2012-00106, SRNL-L3100-2012-00017), (iii) tests to determine the ability of plutonium carbonates to transform to less soluble forms upon contact with grout (SRNL-STI-2012-00106), and (iv) other test related to waste release (e.g., chemical evolution of waste zone and resultant changes in solubility). DOE indicated that PA maintenance is required by DOE Order 435.1. FTF PA maintenance items take into consideration NRC TER recommendations. Due to limited resources, feedback is needed on prioritization of activities. In reference to previous NRC staff interest in obtaining tank waste samples for analysis, DOE also expressed an interest in leveraging NRC resources to perform experimental analyses. DOE noted that it has almost 1 kg of individual and composite samples from Tank 18 that could be used for experiments.

Based on sensitivity of modeled plutonium solubility to Eh, NRC also requested clarification for the basis of the assumed Eh values. For example, according to model predictions in Denham (2012), the solubility of the assumed plutonium solid phase,  $\text{PuO}_{2(\text{am, hyd})}$ , remains relatively low if the Eh is less than +0.45 V. The solubility was shown to increase by approximately three orders

of magnitude if the Eh of the water is greater than +0.45 V. For “realistic” plutonium solubility modeling, DOE interpolates between a series of SRS groundwater data points and a hypothetical cement at pH 12.5 (Figure 9 in SRNL-STI-2012-00087). This estimation results in Eh less than +0.45 V at pH 11.1 and 9.2, and relatively low  $\text{PuO}_{2(\text{am,hyd})}$  solubilities. DOE indicated that the assumption regarding the linearity of Eh as a function of pH is consistent with Krupka and Serne (NUREG/CR-6377) and that the extrapolation of Eh between cement and natural system groundwaters does not reflect any particular Eh couple. DOE stated that the Eh of groundwater is oftentimes found to be significantly lower than one would assume based on an assumption that the groundwater is in equilibrium with oxygen. This is due to the influence of mineral phases and Eh couples present in soils and cementitious materials.

The mineral phases that are used to represent the grout (i.e., the normative grout mineralogy) in the geochemical model affect the timing and magnitude of the predicted chemical transitions. NRC staff requested information on the validation of the assumed normative grout mineralogy by comparison to actual SRS grout analyses. Denham (2012) discusses that the initial mineralogy was estimated from the proposed grout formulation and representative phases used in published cement simulations, since the actual mineralogy is unknown. In the teleconference, DOE stated that they have not attempted to validate the assumed normative mineralogy.

### **NRC Evaluation**

DOE assembled a plutonium solubility peer review group that addressed solubility and modeling assumptions in the FTF PA related to the residual plutonium in Tank 18. The peer review group provided several recommendations that are consistent with those suggested by NRC. The peer review group also raised additional concerns, such as the use of an outdated and inconsistent thermodynamic database, lack of quality assurance and control that called into question FTF PA results, and the lack of coordination and project integration across lines and contractors. In response to recommendations made by the NRC and the plutonium solubility peer review group, DOE has conducted spectroscopic analyses of residual waste samples from Tank 18 and updated the geochemical modeling for Tank 18.

The SEM and XRD analyses of Tank 18 residual waste by Hay et al. (2012) demonstrate the importance of characterizing residual waste. Information contained in Hay et al. (2012) and Hobbs (2012) indicates that the form of plutonium in the Tank 18 heels is inconsistent with the assumptions in the FTF PA. The FTF PA assumes that plutonium is initially coprecipitated with iron and constrained to very low aqueous solubility for tens of thousands of years. If this were the case, then plutonium should be dispersed within the precipitated iron oxide mass. However, the SEM analysis disclosed that a fraction of the plutonium was present as small discrete particles, suggesting that plutonium is present both as a unique plutonium phase and distributed within the iron matrix. Although the concentration of the crystalline plutonium phase(s) was below the XRD detection limit, a uranyl carbonate phase,  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ , was detected. The presence of  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$  suggests that plutonium in Tank 18 residual waste may have also been converted into a more soluble carbonate phase.

Analytical results from residual waste liquid samples showed plutonium concentrations of  $1.3 \times 10^{-8}$  and  $2.6 \times 10^{-8}$  M (Hobbs, 2012). These measured Pu concentrations in washed Tank 18

residuals are greater than initial solubilities assumed in DOE's revision 1 PA<sup>1</sup> and comparable to what is described as "conservative" solubilities in DOE's Tanks 18 and 19 Special Analysis or SA (SRR-CWDA-2010-00124). Simulations using "conservative solubilities" in DOE's Tanks 18 and 19 SA lead to risk-significant peak doses of around 2 and 5 mSv/yr (200 and 500 mrem/yr)<sup>2</sup>. Additionally, the measured Pu concentrations could have been higher if dissolved Pu was not at equilibrium at the time of analysis.

Hobbs (2012) discusses that any plutonium carbonate phases, which formed during active venting, are expected to transform back into  $\text{PuO}_{2(\text{am, hyd})}$  under grouted conditions. Denham (2012) provides thermodynamic evidence that at the time of tank closure,  $\text{PuO}_{2(\text{am, hyd})}$  will be the stable phase under the assumed conditions. The subsequent solubility calculations for plutonium are based on the assumption that  $\text{PuO}_{2(\text{am, hyd})}$ , not plutonium carbonate species, are present. However, based on the potential risk significance of plutonium solubility, the thermodynamic potential may not be a sufficient basis. Although  $\text{PuO}_{2(\text{am, hyd})}$  may be thermodynamically favored, several factors may inhibit or preclude transformation of plutonium carbonate species to less soluble forms. The assumption that plutonium carbonate species will convert to  $\text{PuO}_{2(\text{am, hyd})}$  could be undermined in several scenarios, including (i) thermodynamic or kinetic limitations to  $\text{PuO}_{2(\text{am, hyd})}$  formation, or (ii) greater-than-assumed carbonate ion concentrations due to infiltrating water bypassing the grout or water table rise. Accordingly, NRC staff disagree that the values reported in Table 1 (Denham, 2012) for  $\text{PuO}_{2(\text{am, hyd})}$  and coprecipitated plutonium under Reduced Region II represent bounding solubilities for plutonium based on observation of higher aqueous phase Pu concentrations in washed Tank 18. Therefore, depending on the amount of plutonium that has reacted with carbonate, the assumption of plutonium transformation under grouted conditions may be risk significant. Monitoring factor 2.1 in NRC staff's FTF monitoring plan (2013) addresses the transformation of plutonium carbonate species to  $\text{PuO}_{2(\text{am, hyd})}$ .

Hobbs (2012) suggests that other methods (e.g., XAS) for solids analysis would provide valuable information on plutonium chemistry in the waste. Hobbs also recommends that if the presence of plutonium carbonate phase is confirmed, that experiments be conducted to determine if plutonium carbonates are transformed back into  $\text{PuO}_{2(\text{am, hyd})}$  upon contact with grout. NRC staff thinks that additional solid phase analysis and waste release experiments are necessary to define the speciation and forms of major radionuclides in the waste, which in turn are needed to better constrain estimates of radionuclide solubility and potential releases rates. These types of analyses should also be applied to the residual waste in other tanks that contain risk significant concentrations of radionuclides consistent with NRC staff recommendations in the FTF TER and monitoring plan (NRC, 2011; NRC, 2012).

Denham (2012) addresses several recommendations made by the DOE plutonium solubility peer review group (Cantrell et al., 2011), groundwater data developed by Strom and Kaback (1992) and Millings et al. (2011) and analyses by Hay et al. (2012) and Hobbs (2012). In SRNL-STI-2012-00087, Denham states that the geochemical analyses assume that flow is through an intact grout matrix and that the impact of preferential flow paths is addressed in sensitivity analyses within the PA. The influence of fast flow paths is addressed in the PA as a low

<sup>1</sup> The actual, dissolved plutonium concentrations measured in Tank 18 significantly exceed the modeled solubility of plutonium for Reduced and Oxidized Region II. The Pu solubility is assumed to be  $4.1 \times 10^{-12}$  M for Reduced Region II and  $4.0 \times 10^{-14}$  M for Oxidized Region II. Region II conditions are assumed to last from the time of closure until approximately 30,000 years in the future for Tank 18.

<sup>2</sup> Differences in peak dose are based on differences in assumed natural system  $K_d$ .

probability scenario; however, NRC staff agrees with the plutonium solubility peer review group comment that fracturing of the grout with preferential flow through the cracks is much more likely than flow through an intact grout matrix over very long time periods. The implementation of the NEA thermodynamic database in the geochemical modeling provides additional confidence in the model results. However, several key assumptions in Denham's report need additional support. Monitoring factors 3.2 and 3.3 in NRC staff's FTF monitoring plan (2013) address the likelihood and performance impact of preferential pathways.

The updated geochemical modeling results (Denham, 2012) indicate that plutonium solubility is primarily influenced by Eh and pH to a lesser extent. The solubility of plutonium was predicted to increase by approximately three orders of magnitude for infiltrating water with an Eh greater than +0.45 V. Evaluation of whether the Eh of infiltrating water is above or below the critical threshold is important because Denham's "realistic" Pu solubilities lead to significantly lower peak doses of limited concern. If "max" or "conservative"<sup>3</sup> Pu solubilities are used, then the peak dose is significantly higher (2 and 5 mSv/yr in SA sensitivity cases). There is significant uncertainty with respect to the Eh of infiltrating water and therefore, the likelihood that Eh will be above or below the critical threshold at which Pu solubility increases to risk-significant values. Given these uncertainties there may not be a good basis for labeling one Eh (or Pu solubility) "max"/"conservative" while another "realistic". DOE uses data from Strom and Kaback (1992) to evaluate the likelihood and conservatism of Eh (and Pu solubilities) evaluated in the SA. Difficulty in selecting a "reasonable" range of assumed Eh and Pu solubility results from the following uncertainties:

- Uncertainty in thermodynamic modeling calculations and the threshold Eh value of +0.45 V where Pu solubility increases to risk-significant values
- Uncertainty introduced by the small (eight) sample size of water table well data compiled by Strom and Kaback (1992) with one of eight measurements above the (uncertain) critical Eh threshold and other measurements potentially within the range of error
- Uncertainty associated with the reported Eh measurements provided in Strom and Kaback (1992)
- Uncertainty in the representativeness of the Eh data from Strom and Kaback (1992) for infiltrating groundwater

As stated above, the measured water table well data are not necessarily representative of waters infiltrating the waste tanks. The Eh of the infiltrating water is a function of the DO and the mineral species interacting with the water. The Eh of the infiltrating water may be greater than that of the water table because of the different mineral phases present in the grout and vadose zone soils. In addition to the mineral phase differences, the DO is expected to be greater in the vadose zone, than in the water table. Millings et al. (2011) discussed that the tanks will be exposed to a partial pressure of oxygen between atmospheric oxygen and the partial pressure in equilibrium with the groundwater. For these reasons, NRC staff thinks additional information is needed to support the selection of Pu solubility based on the expected Eh and updated geochemical modeling. DOE should provide additional support for the assumption that the Eh of infiltrating water will remain below a critical threshold at which the solubility will increase to a risk-significant value considering the uncertainties listed above.

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<sup>3</sup> Instead of the description "max" used in Denham (2012), the Tanks 18 and 19 SA (SRR-CWDA-2010-00124) uses the term "conservative Eh".

The slow hydration kinetics of the grout and the use of equilibrium thermodynamic models contribute to model uncertainty. Denham (2012) discussed the uncertainty in the assumed silica phase, which could affect the timing of the pH transition. Although the release of plutonium in the current modeling by Denham does not show a significant sensitivity to pH changes, the transition of Region II to Region III could potentially be important, depending on future model assumptions. In addition to the uncertainty in the pH transition, recent research by Cantrell and Williams (2012) indicates that the use of pyrite or pyrrhotite to represent the reduced sulfur-bearing phase may lead to an overestimate of the Eh transition time.

The transition from reduced to oxidized conditions is largely dependent on the reducing capacity of components within the blast furnace slag. In recent saltstone-related experiments, Cantrell and Williams (2012) observed reduced sulfur species in leachates. Although the experiments conducted by Cantrell and Williams were for a saltstone simulant, rather than a tank grout formulation, both materials use a similar blast furnace slag. These results suggest that a portion of the reducing capacity in the blast furnace slag used by DOE may be more soluble than assumed by the use of pyrite or pyrrhotite in geochemical modeling. Accordingly, the transition to oxidizing conditions could occur more quickly than assumed in the geochemical modeling by Denham if this sulfur phase(s) is leached from the system prior to reacting with oxygen. DOE should provide additional information regarding the potential early release of reduced sulfur species from the grout, which could be determined during the waste release experiments recommended by NRC staff and the plutonium solubility peer review group.

Given the risk significance and uncertainty of the solubility of plutonium and consistent with previous NRC recommendations, as well as recommendations made by DOE's plutonium solubility peer review team (Cantrell et al., 2011) and other DOE experts, NRC continues to believe that experimental verification of modeled plutonium solubility under a range of chemical conditions potentially relevant to the contaminated zone should be undertaken as described in NRC staff's monitoring plan (NRC, 2013) under monitoring factor 2.1. Tank wastes should be characterized using advanced spectroscopic techniques such as Scanning Electron Microscopy (SEM)/Energy Dispersive X-Ray Analysis (EDAX), X-Ray Diffraction (XRD), X-Ray Absorption Near Edge Structure (XANES) or Extended X-Ray Absorption Fine Structure (EXAFS). Leach tests and solubility tests should be conducted on the waste residuals and solid phase analysis should be repeated after the leach tests are completed.

In addition to the experiments listed above, NRC finds that additional information is needed regarding (i) the assumed longevity of reducing conditions in the contaminated zone, and (ii) the assumption that the Eh of infiltrating groundwater remains below a critical threshold above which Pu solubility increases to risk-significant levels. These additional studies that are not specifically discussed in the FTF monitoring plan (NRC, 2013), but that are pertinent to closure of monitoring factors 2.1 and 2.2, are listed in the follow-up actions section.

### **Follow-up Actions**

Related to closure of monitoring factors 2.1 and 2.2 listed in NRC staff's monitoring plan (NRC, 2013), DOE should also perform the following actions:

- DOE should provide additional information to support assumptions regarding longevity of reducing conditions in the contaminated zone. Recent studies (Cantrell and Williams, 2012) suggest that the reducing capacity of the tank grout could be depleted much

earlier than assumed in the FTF PA (SRS-REG-2007-00002 Rev 1) and in more recent Pu solubility modeling performed for Tank 18 (Denham, 2012). Uncertainty in the normative mineralogy assumed in geochemical modeling should be considered under this action.

- DOE should provide additional support for the assumption that the Eh of infiltrating water will remain below a critical threshold at which Pu solubility will increase to a risk-significant value (e.g., updated geochemical modeling indicates a dramatic increase in Pu solubility occurs at Eh greater than +0.45 V). Uncertainty in the critical threshold and the Eh of infiltrating groundwater should be considered under this action.

### **Open Issues**

There are currently no open issues.

### **Conclusions**

In 2011, NRC issued the FTF TER with the primary recommendation for DOE to conduct waste release experiments to increase support for several key modeling assumptions related to: (i) the evolution of pH and Eh in the grouted tank system over time; (ii) identification of HRR association with solid phases comprising the residual wastes; and (iii) solubility of HRRs under a range of expected conditions. NRC's FTF monitoring plan (2013) provides additional details regarding these TER recommendations under monitoring factors 2.1 and 2.2. DOE has provided additional support for several waste release assumptions including convening a plutonium solubility peer review that provided expert technical advice related to residual plutonium in Tank 18, spectroscopic analyses of residual waste samples from Tank 18, and revising the geochemical modeling. However, these additional support activities have not obviated the need for experimental verification of modeled waste release. In fact, these activities have further illustrated the need for experimental support. Analyses of residual waste indicate that plutonium exists in the residual waste with a solubility that is potentially risk-significant and inconsistent with assumptions in the PA. In addition, geochemical modeling indicates that the predicted Eh threshold for increased plutonium solubility is within the range of observed Eh values. Given the risk significance of the solubility of plutonium and consistent with previous NRC recommendations, as well as recommendations made by DOE's plutonium solubility peer review group (Cantrell et al., 2011) and other DOE experts, NRC continues to believe that experimental verification of modeled plutonium solubility under a range of chemical conditions potentially relevant to the contaminated zone should be undertaken.

NRC staff have identified two follow-up actions for DOE to provide additional information regarding the longevity of reducing conditions afforded by the tank grout considering uncertainty in the normative mineralogy and additional support for the assumption that the Eh of infiltrating water will remain below a critical threshold (e.g., +0.45 V identified in Denham (2012)) considering uncertainties in geochemical modeling and infiltrating groundwater Eh.

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