

Summary

The U.S. Nuclear Regulatory Commission (NRC) staff appreciated the opportunity to provide comments on the U.S. Department of Energy (DOE) experimental plan in SRNL-RP-2013-00203, Rev. 0, "Task Technical and Quality Assurance Plan for Determining the Radionuclide Release from Tank Waste Residual Solids." The NRC staff believes that, in general, the experimental plan was reasonable and carefully developed. As with any experimental plan, NRC staff understands the need for flexibility to adapt to unforeseen challenges and unanticipated results. The researchers' plan to use surrogate samples to refine experimental methods is a sound approach. It will provide an important opportunity for the researchers to refine/modify the experiments for the actual waste residual solids. NRC staff would appreciate the opportunity to discuss the results of using the surrogate samples as a mock-up (e.g., key observations, lessons learned, unexpected results, revisions to laboratory protocol) with the researchers prior to start of the F-Tank Farm (FTF) Tank 18 solids experiments. See below for the NRC staff general and specific comments that were binned according to their respective Task Activities in the experimental plan.

General Comments:

NRC staff believes that an "objectives" section in the experimental plan for the research would help the reader understand why the research will be conducted (e.g., to validate solubility modeling) and how the study will support key modeling assumptions in the FTF performance assessment (PA) as well as in the H-Tank Farm PA.

NRC staff suggests that DOE describe in more detail in the experimental plan the conceptual model for the chemical evolution of the tank grout and contaminated zone used in the FTF PA. NRC staff identified inconsistencies between the assumed PA modeling assumptions and experimental plan. For example, the relatively low plutonium solubilities reported in the second Table 3 on page 9 of 14 of the experimental plan were reflective of Eh values less than the critical threshold of +0.45 V reported in SRNL-STI-2012-00087 and SRNL-STI-2012-00404 for all three chemical states; while, the experimental conditions reported in the first Table 3 on page 7 were assumed to be greater than +0.45 V for Oxidized Region II and III. Further, the Table 4 pore water activities for plutonium in the experimental plan appear to be consistent with the values reported in SRNL-STI-2012-00087 and SRNL-STI-2012-00404; but, they are not consistent with the constant solubilities reported in the second Table 3 on page 9 of 14 of the experimental plan. NRC staff believes that the experimental plan would also benefit from mapping of the parameter space (e.g., Eh, pH) that defines key radionuclide solubility against the proposed experimental conditions. That would lead to a better understanding of the sensitivity of the results to the proposed experimental conditions.

NRC staff suggests that DOE consider uncertainty in the geochemical modeling in the design of the experiments. The proposed experiments are designed to provide support for FTF PA assumptions related to key radionuclide solubility. However, given uncertainty in the geochemical modeling used to predict key radionuclide solubility, it is not clear to the NRC staff that experiments designed to mimic the modeled geochemical conditions will be reflective of actual conditions in the field. Due to the uncertainties in the geochemical modeling and the

difficulty in reproducing field conditions, NRC staff suggests that DOE consider the uncertainty in the geochemical modeling in order to increase the usefulness of the experimental results. NRC staff believes that consideration of geochemical modeling uncertainty could be accomplished through evaluation of a broader range of potential conditions than those represented in the reference case that may occur in the field. For example, identification of a critical Eh threshold where solubility is expected to increase to risk-significant levels for redox sensitive radionuclides would greatly inform the FTF PA results. NRC staff believes that DOE should be judicious in its selection of experimental conditions to ensure the greatest utility of the results. NRC staff believes that FTF PA results could be used to inform the number and range of values selected.

NRC suggests that DOE discuss the experimental plan with DOE's plutonium solubility peer review group. NRC staff believes that review of the experimental plan by experts who have performed similar types of experiments may be beneficial in identifying potential improvements and increasing the usefulness of the results.

Based on the: (1) level of effort required to conduct the planned experiments, (2) potential variability between the residual waste in FTF Tank 18 versus FTF Tanks 5/6, and (3) risk-significance of the residual waste in FTF Tanks 5/6, NRC suggests that DOE consider conducting a similar study with residual waste samples from FTF Tanks 5/6.

Comments on Section 4.1: Fabrication of Tank Waste Leaching Test Vessel:

NRC staff believes that the proposed glass apparatus described in Section 4.5 of the experimental plan may affect the leach results. That is because the dissolution of silica caused by the high pH of solution could result in the formation of new phases. NRC staff suggests that a vessel constructed of Teflon, nylon, or high-density polyethylene may be preferable.

Comments on Section 4.2: Preparation of Tank 18 Residue Surrogate:

In addition to the characterization of the FTF Tank 18 residue solids, NRC staff suggests that X-ray Diffraction (XRD) and elemental analysis of the surrogate samples could help inform the experiments and results from the FTF Tank 18 residue samples.

Comments on Section 4.3: Characterization of Compositing Tank 18 Residue Solids:

NRC staff agrees with the researchers that XRD characterization of the residue solids before and after experimentation will likely provide important insights.

Comments on Section 4.4: Pore Water Compositions:

NRC staff is concerned that the pore water composition may not be representative of field conditions. The researchers described contacting the synthetic infiltrate with the grout components. It is not clear to NRC staff whether the researchers plan to mix the grout components and crush them prior to contacting the infiltrate or to contact the infiltrate with the individual grout components. NRC staff believes that the latter approach could result in significant differences from field conditions. Additionally, NRC staff is concerned that the synthetic infiltrate may not be in contact with a grout formulation containing admixtures.

Contacting the synthetic infiltrate with a grout formulation, which is as similar to as-emplaced materials as is practicable, is expected to reduce experimental artifacts and uncertainties. However, it may be necessary to develop a synthetic leachate from chemical reagents versus contacting the solution with the grout, in order to produce a leachate with the appropriate composition.

It is not clear to NRC staff how the researchers intend to adjust Eh and pH.

NRC staff suggests that, for the Reduced Region II water, simply equilibrating the water with cement, fly ash, and slag may impose Region I conditions (i.e., pore water high in sodium and potassium and $\text{pH} > 12.5$). It is not clear to NRC staff whether the excess alkalis in the solution will be flushed, whether the pH adjustment to 11.1 will be done in a way to preserve the integrity of the pore water equilibration, and whether the solids used for equilibrating the water will be characterized.

It is not clear to NRC staff why, for the Oxidized Region II water, fly ash is excluded from the solid assemblage for equilibration. SRNL-STI-2012-00087 indicates that it is the fly ash and slag that are responsible for the absence of portlandite [$\text{Ca}(\text{OH})_2$] in the Region II assemblage. Both WSRC-STI-2007-00544 and SRNL-STI-2012-00087 indicate that calcium-silicate-hydrate phases, and not $\text{Ca}(\text{OH})_2$, will control pH in Region II. Those reports on the grout evolution model appear to the NRC staff to be inconsistent with the description that indicates that equilibrium with $\text{Ca}(\text{OH})_2$ is desired for Oxidized Region II. It is not clear to NRC staff that equilibration with an assemblage of cement alone affords a good simulation of Oxidized Region II.

For the Oxidized Region III water, the pH is 9.2 because the model pH has changed from 8.23 to 9.2 (see WSRC-STI-2007-00544 and SRNL-STI-2012-00087 documents). That is because pH is now considered to be controlled by OH-hydroxalite rather than calcite. NRC staff believes that is inconsistent with: (1) the statement in Section 2.1 that calcite is “the dominant grout phase” in Oxidized Region III; and (2) the use of calcite as the contacting solid for producing the Oxidized Region III water. If contacting with calcite does not give a pH of 9.2 and if calcite is not considered in models to be the pH controlling solid for Oxidized Region III, then it is not clear to the NRC staff why calcite is used. Note that it may be true that calcite is the controlling solid, but that is not the current model and was not the basis for the target pH of 9.2.

Comments on Section 4.5: Leach Testing:

Section 4.1 of the experimental plan includes the statement, “... to provide a low oxygen content inert gas to assist in maintaining a reducing environment.” It is not clear to the NRC staff what specific atmosphere the researchers intend to use. For example, it is not clear whether the researchers intend to include hydrogen gas and a catalyst to maintain reducing conditions and if so, whether the researchers intend to conduct any control samples to verify that the reducing atmosphere is not providing any artificial reducing capacity to the experiments.

The experimental plan includes the statement, "... these tests will also provide experience with the time required for the experimental system to achieve a steady-state condition." NRC staff expects that the surrogate and FTF Tank 18 solid samples will likely contain different phases and will therefore likely require differing amounts of time to reach steady-state conditions. It is not clear to NRC staff what the anticipated basis for determination of steady state conditions will be.

References:

Denham, M., "Conceptual Model of Waste Release from the Contaminated Zone of Closed Radioactive Waste Tanks," WSRC-STI-2007-00544, Rev. 2, 2010, Savannah River Site, Aiken, South Carolina.

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, 2012, Savannah River National Laboratory, Aiken, South Carolina.

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, Rev. 0, 2012, Savannah River National Laboratory, Aiken, South Carolina.

Hobbs, D., Taylor-Pashow, K., Roberts, K., and C. Langton, "Task Technical and Quality Assurance Plan for Determining the Radionuclide Release from Tank Waste Residual Solids," SRNL-RP-2013-00203, Rev. 0, 2013, Savannah River National Laboratory, Aiken, South Carolina.