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Determining the Release of Radionuclides from Tank Waste Residual Solids: FY2015 Report

William D. King

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September 2015

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EXECUTIVE SUMMARY

Methodology development for pore water leaching studies has been continued to support Savannah River Site High Level Waste tank closure efforts. For FY2015, the primary goal of this testing was the achievement of target pH and E_h values for pore water solutions representative of local groundwater in the presence of grout or grout-representative (CaCO_3 or FeS) solids as well as waste surrogate solids representative of residual solids expected to be present in a closed tank. For oxidizing conditions representative of a closed tank after aging, a focus was placed on using solid phases believed to be controlling pH and E_h at equilibrium conditions. For three pore water conditions (shown below), the target pH values were achieved to within 0.5 pH units. Tank 18 residual surrogate solids leaching studies were conducted over an E_h range of approximately 630 mV. Significantly higher E_h values were achieved for the oxidizing conditions (ORII and ORIII) than were previously observed. For the ORII condition, the target E_h value was nearly achieved (within 50 mV). However, E_h values observed for the ORIII condition were approximately 160 mV less positive than the target. E_h values observed for the RRII condition were approximately 370 mV less negative than the target. Achievement of more positive and more negative E_h values is believed to require the addition of non-representative oxidants and reductants, respectively. Plutonium and uranium concentrations measured during Tank 18 residual surrogate solids leaching studies under these conditions (shown below) followed the general trends predicted for plutonium and uranium oxide phases, assuming equilibrium with dissolved oxygen. The highest plutonium and uranium concentrations were observed for the ORIII condition and the lowest concentrations were observed for the RRII condition. Based on these results, it is recommended that these test methodologies be used to conduct leaching studies with actual Tank 18 residual solids material. Actual waste testing will include leaching evaluations of technetium and neptunium, as well as plutonium and uranium.

Target Pore Water Conditions.

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

Measured pH, E_h , and Pu and U Concentrations for Each Pore Water Test Condition Using a Tank 18 Residual Solids Surrogate.

Test Condition	Additives	Atmosphere/Vessel	Final E_h (mV)	Final pH	Final Pu (M)	Final U (M)
RRII-A	$\text{Ca}(\text{OH})_2$, CaCO_3 , FeS	N_2/Ar purge followed by zero headspace vessel	-105	9.9	6.1E-11	2.5E-05
RRII-B	CFS, FeS	N_2/Ar purge followed by zero headspace vessel	-97	11.0	<1.6E-12	1.9E-07
RRII-C	$\text{Ca}(\text{OH})_2$, CaCO_3 , FeS	continuous N_2/Ar purge	-113	10.5	4.6E-10	6.4E-05
ORII	$\text{Ca}(\text{OH})_2$, CaCO_3	excess air headspace vessel, daily venting	+515	10.8	1.2E-08	1.1E-04
ORIII	CaCO_3	excess air headspace vessel, daily venting	+523	9.4	2.2E-08	1.4E-04

CFS = cement, flyash, and slag grout solids

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LIST OF ABBREVIATIONS

AD	Analytical Development
CFS	Cement, Flyash, and Slag grout
DOE	Department of Energy
EM	Environmental Management
HLW	High Level Waste
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-ES	Inductively Coupled Plasma – Mass Spectroscopy
LDPE	Low Density Polyethylene
ORP	Oxidation Reduction Potential
PVDF	Poly Vinyl Difluoride
RPM	Rotations per Minute
SHE	Standard Hydrogen Electrode
SEM	Scanning Electron Microscopy
SIW	Synthetic Infiltration Water
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TTA	Trichloroethylene
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

Current practice for closing High Level Waste (HLW) tanks at the Savannah River Site (SRS) involves removing as much of the waste as possible, disconnecting all transfer lines and penetrations into the tanks, and filling the internal volume of the tanks with grout. Savannah River Remediation (SRR) closed SRS Tanks 17 and 20 in 1997, Tanks 18 and 19 in 2012, Tanks 5 and 6 in 2013, and is currently filling Tank 16 with grout. Performance Assessment (PA) modeling of the release of radionuclides from residual waste solids in these tanks into the environment over extended time periods indicated that uranium, plutonium, neptunium, and technetium are among the most likely risk drivers for environmental contamination.¹ The PA and supporting waste release modeling² indicated that plutonium release from SRS Tank 18 residuals (which contained relatively high Pu concentrations) was highest during the period identified as Oxidizing Region III (ORIII; predicted to occur after >2120 pore volumes of grout pore water have passed through the system) which has a pH of 9.2 and an E_h value of +680 mV (OxidationReduction Potential versus the Standard Hydrogen Electrode). At this stage, the dominant grout phase is expected to be calcite (CaCO_3). (Note: Grout pore water is defined as natural infiltrating groundwater exposed to the grout fill material and the residual waste solids layer within the closed HLW tank environment. Furthermore, a pore volume represents the total volume of the pore voids within the grout fill material inside the closed tank.)

Waste release testing was identified as needed to provide additional information regarding the residual waste solubility assumptions used in the SRS F- and H-Area Tank Farm PA Waste Release Models. The proposed testing is described generally in the SRS Liquid Waste Facilities PA Maintenance Program FY2015 Implementation Plan.³ This plan proposed that waste release experiments be performed with actual tank waste residuals after the completion of test method development using surrogate materials. SRR requested that the Savannah River National Laboratory (SRNL) design and perform such testing.⁴ In fiscal year (FY) 2014, a summary report on initial method development testing was issued with recommendations that additional testing be conducted with surrogates prior to actual waste testing.⁵ A Task Technical and Quality Assurance Plan (TTQAP) describing the additional tests to be conducted was subsequently issued in February of 2015.⁶ Three theoretical periods and conditions occurring at different times following tank closure were targeted for testing.² Reduced Region II (RRII) was predicted to occur initially following tank closure and to represent the conditions during the passage of the first portion (<520 pore volumes) of grout pore water through the closed tank system. Oxidizing Region II (ORII) was predicted to occur after RRII and to represent an intermediate condition (from >520 to <2120 grout pore volumes). ORIII (after >2120 pore volumes) was the final target condition. Solution pH and E_h values have been predicted for each condition. This document provides results from FY2015 method development testing targeting these conditions using a Tank 18 residual solids surrogate and makes recommendations regarding the next testing phase with the actual Tank 18 residual material.

2.0 Experimental

2.1 Preparation of Synthetic Infiltration Water

A Synthetic Infiltration Water (SIW) concentrated stock solution was prepared from ultrapure water (Milli-Q) and the reagent grade chemicals shown in Table 2-1. The SIW stock solution used for FY2014 testing was also used for FY2015 testing.⁴ The SIW stock solution was diluted 1000:1 (1 mL SIW stock diluted into 1 L deionized water) prior to use for the preparation of grout pore water formulations. The as-prepared elemental composition of the resulting SIW solution is provided in Table 2-2. The SIW was based on the average composition observed for groundwater from non-impacted wells within the SRS water table aquifer.⁴

Table 2-1. Synthetic Infiltration Water Concentrate Stock Solution Recipe.

Chemical Reagent	Concentration (g/L)
CaCl ₂ ·2H ₂ O	3.68
Na ₂ SO ₄	1.07
KCl	0.40
NaCl	2.65
MgCl ₂ ·6H ₂ O	5.51

Table 2-2. As-Prepared Elemental Composition of Synthetic Infiltration Water Simulant After Dilution.

Ion	Concentration (mg/L)
Na ⁺	1.39
K ⁺	0.21
Mg ²⁺	0.66
Ca ²⁺	1.00
Cl ⁻	5.51
SO ₄ ²⁻	0.73

2.2 Preliminary Modeling of Grout Pore Water Solutions

Prior to laboratory testing, the targeted grout pore water solutions were modeled using the OLI Thermodynamic Model in an effort to identify chemical reagents and conditions which would be expected to produce the target conditions. The intent of the modeling effort was to provide experimental direction during simulant development using the SIW as the starting simulant composition. Calcium carbonate, calcium hydroxide and ferrous sulfide (FeS) were identified as potential grout representative reagents for simulant addition. The atmosphere was controlled in OLI modeling calculations by the addition or exclusion of oxygen or carbon dioxide gases as input species. The OLI model includes a redox feature and pH and ORP are provided as output data. The modeling indicated that the target conditions could be achieved for all three cases in the presence of calcium carbonate solids at concentrations exceeding saturation. This reagent addition resulted in calcium concentrations well above the initial SIW composition. The ORII and RRII conditions required the addition calcium hydroxide to raise the pH and the ORIII condition required a carbon dioxide purge to lower the pH. In order to achieve the target E_h values for ORII and ORIII oxygen addition was required. Exclusion of oxygen and addition of FeS were required to achieve the target E_h value for RRII. The modeling indicated that a portion of the magnesium component of the SIW would precipitate for the ORII and RRII conditions.

2.3 Preparation of Grout Pore Water Simulants from SIW

The target pH and E_h values for three grout pore water solutions (based on the PA¹ and supporting modeling²) to be developed from the SIW and used for radionuclide release leaching studies are provided in Table 2-3.

Table 2-3. Target Grout Pore Water Conditions.

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

Grout pore water simulants were prepared for each condition in Table 2-3 as follows. RRII and ORII solutions were prepared from the diluted SIW by the addition of approximately 0.1 g CaCO₃/L and 0.05 g Ca(OH)₂/L to achieve a pH near 11 (reagent grade chemicals used in all cases). The resulting solution contained a trace of CaCO₃ solids (assumed based on modeling predictions). The RRII and ORII pore water simulants had the same chemical composition and differed only in the atmosphere eventually used to adjust the solution E_h values. ORIII simulant was prepared from the SIW by the addition of 0.1 g CaCO₃/L. This resulted in a solution containing trace amounts of CaCO₃ solids with a pH near 10. Subsequent, brief (~10 minutes) purging of the solution with air resulted in the absorption of CO₂ and a reduction in the solution pH to near 9. All of the as-prepared simulants had solution E_h values near +500 mV. Purging the RRII simulant with nitrogen or argon gas overnight resulted in a solution E_h value near -100 mV. Subsequent addition of reagent grade ferrous sulfide (FeS) solids while continuously purging the solution with inert gas resulted in solution E_h values near -200 mV. Analysis of the RRII/ORII pore water simulant revealed that the calcium concentration was 28 mg/L (28 times the SIW target value of 1 mg/L). Analysis of the ORIII pore water simulant revealed that the calcium concentration was 7.3 mg/L (7.3 times the SIW target value). The elevated calcium levels resulted from the addition of the calcium salts (to saturation in the case of calcium carbonate). Elevated calcium levels are expected in the grout pore water due to contact with calcium phases in the grout.

The final step in the preparation of grout pore water simulants was the transfer of additional calcium carbonate, actual grout solids, or additional FeS to the solution. Calcium carbonate reagent was utilized as a grout-representative phase in all ORII and ORIII tests and in some RRII tests to simplify the system and allow for better control of the solution pH and E_h. Cement, Fly ash, and Slag (CFS) grout solids were utilized in the remaining RRII tests. The CFS solids were initially prepared as a monolith representing the components of the grout used to fill SRS Tanks 18, 19, 5, and 6. The CFS solids recipe included 125 parts of Cement Type I/II, 210 parts of Slag Grade 100, and 363 parts of Fly Ash Class F. Sand was not added as a component of the monolith since both flyash and slag contain significant quantities of silicon. Prior to contact with the SIW, the CFS monolith was broken into pieces which were then crushed and sieved through a 100 mesh sieve.

2.4 Tank 18 Surrogate Solids

Tank 18 residual surrogate solids prepared previously during FY2014 testing were also used for the current testing. A detailed description of the preparation of these solids was provided in the FY2014 report. The composition of the solids was provided in the FY2014 report and is shown below in Table 2-4.⁴ The surrogate solids were prepared by the co-precipitation of the actinides with the other metal phases. Silicon was well below the target concentration and technetium and neptunium were below quantifiable analytical limits for these elements. As a result, FY2104 and FY2015 leaching studies focused only on the dissolution of plutonium and uranium upon contact of the solids with the three different pore water solutions.

Table 2-4. Tank 18 Surrogate Solids Composition.

Component	Target Concentration (wt. %)	Measured Concentration^a (wt. %)
Al	15.2	11.3±1.2
Ca	2.69	2.69±0.28
Fe	8.00	7.90±0.83
Mg	2.00	2.09±0.22
Mn	1.09	1.04±0.11
Na	4.48	5.96±0.62
Si	3.96	0.22±0.038
U	2.37	2.39±0.24 2.50±0.50 ^b
Pu 239/240	0.0160	0.0160±0.0009 ^c
Np-237	7.53E-4	bql
Tc-99	2.60E-4	bql

^a determined by ICP-ES

^b determined by ICP-MS

^c determined by alpha counting after removing U and Np

bql = below quantifiable limit

2.5 Equipment

E_h and pH data were collected using the following combination meters: 1) Fisher Scientific Accumet Basic AR20 pH/conductivity meter for non-radiological testing, and 2) Fisher Scientific Accumet Excel XL20 pH/conductivity meter for radiological testing. The pH measurements were obtained with one of the following: 1) an Accumet TM glass body pH probe, or 2) a Fisher Scientific Accumet TM Gel-filled pencil-thin combination electrode. The pH meter/probe combinations were calibrated daily with pH 4, 7, and 10 standard buffer solutions. E_h data was collected using either: 1) a Thermo Scientific 9179BN Low Maintenance ORP Triode with an Epoxy body, or 2) a Mettler Toledo In-lab Redox Micro ORP probe. The E_h probes were checked using Thermo Scientific TM Oxidation Reduction Potential (ORP) Standard 967901. The standard was checked once during each series of ORP sample measurements and all standard measurements ranged from +219 to +220 mV. All reported E_h values are relative to the Standard Hydrogen Electrode (SHE). A standard correction of +200 mV was applied to all ORP data to convert the data to E_h format (Oxidation Reduction Potential versus the Standard Hydrogen Electrode), based on the manufacturer instructions and data obtained for the ORP standard. The electrode manuals indicate that the measured ORP values may vary by ±60 mV.

ORP measurements were sometimes inconsistent and variable and the equipment often seemed to exhibit hysteresis effects. Careful attention was given to the electrode behavior during sample measurements to ensure that accurate data was being collected. Particularly under reducing conditions, it was found that long time periods (5-10 minutes) were often needed for measurement stabilization. Under reducing conditions it is advantageous to keep the electrode in the sample solution continuously to minimize electrode stabilization times.

Except for controlled atmosphere continuous gas purge testing, all Tank 18 surrogate leaching studies were performed in a temperature-controlled laboratory shaker oven placed in a radiological hood using a continuous horizontal orbital rotation to agitate the samples. All tests were conducted at 25 °C at a shaker rotation rate of 175 RPM. The same shaker oven was used in FY2014 testing.⁵ Larger (125 mL) sample bottles were placed in the shaker table clamps in a vertical orientation. Smaller (40 mL) glass vials used

for zero-headspace testing were placed together in plastic bags and nested on the shaker table in a horizontal orientation to facilitate better sample mixing.

As shown in Figure 2-1, a controlled atmosphere, continuous gas purge was utilized for one RRII leaching test using custom-prepared Erlenmeyer glass flasks fitted with rubber stoppers modified for insertion of a gas dispersion tube with a coarse grade porous glass frit and an E_h probe (for continuous monitoring). Nitrogen or argon gas was continually passed through the frit and into the solution at a slow rate to maintain an inert atmosphere. The outlet tubing was attached to a water-filled bubbler to isolate the system from the atmosphere in the event that flow was interrupted. Loss of sample liquid was sometimes observed with time due to evaporation resulting from continuous purging. Evaporation was nearly eliminated by saturating the purge gas with water vapor by passing the gas through a similarly designed flask containing water with a gas dispersion tube prior to introduction into the test vessel. As needed, deionized water was periodically added to the sample to maintain the original liquid level. Evaporative sample volume losses at any given time during testing were below 5% and the original liquid level was always restored prior to sampling.



Figure 2-1. 80-mL Controlled Atmosphere Test Vessel during Radioactive Surrogate Testing.

2.6 Leaching Studies

The dissolution of Pu and U present in Tank 18 residual surrogate solids mixed with calcium carbonate or CFS solids and, in some cases, ferrous sulfide solids were evaluated in the grout pore water simulant solutions prepared as described in Section 2.3. CFS and calcium carbonate solids were added to each test sample at a concentration of 16.7 g/L. Tank 18 surrogate solids were added to each test sample at a concentration of 30.0 g/L. FeS solid was added to RRII samples at a concentration of 10 g/L. Leach tests were typically conducted in 40 mL, zero-headspace glass vials (RRII) or 125 mL low density polyethylene (LDPE) bottles (ORII and ORIII) with air headspace.

RRII samples were prepared for zero-headspace tests by first purging the solution with nitrogen or argon (similar E_h values observed with each) gas overnight outside of the radiological hood and then adding FeS reagent under an inert atmosphere purge. Using this procedure, it was possible to reduce the solution E_h value to as low as -217 mV. This solution was quickly transferred in air to LDPE bottles which were filled to the top and capped with no gas headspace. The capped bottles were transferred into the radiological hood to prepare glass test vials for zero-headspace testing. In the hood, these solutions were quickly transferred in air to glass vials containing Tank 18 surrogate solids, additional FeS reagent, and either calcium carbonate or CFS solids. The vials were completely filled with solution such that no air bubbles were present after capping. Typical solution transfer and air exposure times for the RRII solution were less than 2 minutes for each transfer. Duplicate zero-headspace RRII test vials were prepared and samples were agitated for five days prior to sampling. A continuous purge test was also initiated using a separate 80 mL SIW liquid sample and the test vessel shown in Figure 2-1. This test was only continued for two days prior to sampling.

For the ORII and ORIII tests, separate, duplicate samples were prepared for each sampling event. Four samples were prepared for each condition to be sampled after 1, 2, and 4 weeks, with duplicate samples for the 4 week sampling event. Solution E_h data for the ORII and ORIII samples was observed to decrease during testing over the course of 1-2 weeks. In order to maintain high E_h values, daily venting of the sample bottles (~5 minute duration) was implemented. Measured pH and E_h data collected during testing, and analytical data for the sub-samples are provided for the ORII and ORIII conditions in Appendix Tables A-1 and A-2.

ORIII test samples were prepared by first pretreating the Tank 18 solids with ORIII pore water solution to remove residual caustic. This was necessary for ORIII testing since the target pH was near 9 and residual caustic in the Tank 18 solid was observed to raise the pH to >10.5. During the washing procedure, the Tank 18 surrogate solids were placed in each test bottle and contacted with approximately 120 mL of ORIII pore water simulant. After sufficient particle settling, the solution was decanted. Four sequential pretreatment wash cycles were conducted in this manner over a 24-hour period. The time required for particle settling increased considerably for the final wash, presumably due to peptization of the solids in the low ionic strength solution. As a result, no additional washes were conducted. Analysis of the first and fourth contact solutions revealed that the sodium concentrations in these solutions were 98 and 24 mg/L, respectively. Following the fourth wash cycle, calcium carbonate solids were added along with a final volume of 30 mL of ORIII pore water simulant. No pretreatment wash was used for the ORII samples since the pH target for this condition exceeded 11.

2.7 Sample Analysis

Approximately 10-mL sample aliquots were periodically collected from the leaching test containers for analysis immediately after the measurement of the solution pH and E_h . The aliquots were filtered through 0.1- μ m poly vinyl difluoride (PVDF) syringe filter units. Nine (9.0) mL of filtrate were transferred by pipet into an analysis bottle containing 1 mL of 5 M HNO_3 . Aliquots of the acidified samples were analyzed for plutonium by alpha spectroscopy following separation using thenoyltrifluoroacetone (TTA) and for uranium by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Filtered portions of selected pore water samples (no dilution or acidification) were also collected for analysis by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES). All sample chemical analysis was conducted by the SRNL Analytical Development section (AD).

2.8 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report

Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. All pertinent instructions results and calculations were recorded in an Electronic Laboratory Notebook (ELN) experiment in accordance with the ELN Implementing Plan.⁷ Instructions and data are recorded in SRNL Electronic Notebook: A2341-00117-04, SRNL Electronic Notebook (Production); SRNL, Aiken, SC 29808 (2014).

3.0 Results and Discussion

Grout pore water simulant slurries were prepared from the dilute SIW solution shown in Table 2-2 and solid phases representative of the grout materials present within a closed HLW tank. For RRII testing, with conditions representative of the time period soon after tank closure, separate tests were conducted with both CFS and calcium carbonate solids to represent the initial grout solids and aged grout solids, respectively. Use of calcium carbonate solids instead of the CFS solids was chosen for study to limit the number of solid phases in the system and allow the system to reach the desired steady-state for easier pH control. In addition, FeS reductant, which is also present in the CFS solids (specifically as part of the slag component²), was added to all of the RRII test samples at levels exceeding solubility to promote a more reducing (i.e., negative) solution E_h value. Since ORII and ORIII conditions represent an aged tank system under oxidizing conditions, only calcium carbonate solids were added to these samples.

Numerous scoping studies were conducted to evaluate the behavior of the ORP probes and determine the conditions required to achieve the target E_h values. Based on these studies, the following pore water and Tank 18 surrogate solids pretreatment steps were developed. Extensive purging of the RRII simulant with an inert gas atmosphere (N_2 or Ar) and the addition of FeS under an inert gas purge were required to produce reducing E_h values. In order to achieve the target pH for ORIII samples, extensive washing of the Tank 18 surrogate solids to remove residual caustic and air purging of the grout pore water solution to promote CO_2 absorption were required. Air exposure of the ORII and ORIII pore water simulants was found to produce E_h values approaching the target for ORII, but lower than the target for ORIII.

The final pH and E_h values achieved for RRII test conditions during leaching studies with Tank 18 surrogate residual solids are summarized in Table 3-1. RRII-A was a zero headspace test in which calcium carbonate and ferrous sulfide solids were added to a solution that had been exposed to a continuous nitrogen or argon purge (both gases used at various times with similar results). RRII-B was a zero headspace test using inerted solution and CFS solids. The RRII-A and -B data provided are based on analysis of samples following five days of contact with Tank 18 surrogate solids. RRII-C was a continuous argon purge test with calcium carbonate added as the grout-representative phase. The RRII-C data provided is based on analysis of samples following only two days of contact with Tank 18 surrogate solids. The pH values for the RRII tests ranged from 9.9-11.0 versus the target value of 11.1. The lowest pH was observed for test RRII-A. The low pH result for this sample was unexpected. E_h values for the three RRII tests (A through C) ranged from -97 to -113 mV. All of these results are considered to be the same based on the reported measurement uncertainty (± 60 mV). These E_h values are significantly less negative than the target value for RRII of -470 mV. During the pretreatment of the RRII simulants, prior to contact with the Tank 18 surrogate solids, lower E_h values near -220 mV were achieved. It is not understood why less negative E_h values were observed in the presence of the surrogate solids. Based on this result, it appears that achieving the highly reducing target value for RRII would require the addition of non-representative reductants. Pu and U concentrations measured for the RRII sub-samples were all very low ($<5E-10$ M Pu and $<6E-5$ M U) indicating that leaching of the actinides under moderately reducing conditions will be low, as predicted by modeling² and observed in previous testing⁵. Significantly lower Pu and U concentrations were observed for RRII-B, which contained the CFS solids. Given the similar results observed for the RRII-A and RRII-C tests conducted, both zero-headspace and continuous purge test methods could be considered for real waste testing of this condition. Longer contact times are recommended for the actual waste leaching studies to ensure that equilibrium has been achieved. Shorter times were considered sufficient for the surrogate leaching studies.

The data provided in Table 3-1 for the ORII condition was based on analysis of samples following approximately four weeks of contact with Tank 18 surrogate solids. A final solution pH value of 10.8 was achieved for the ORII condition during Tank 18 surrogate solids leaching studies versus the target value of 11.1. The final E_h value observed was +515 mV, versus the target value of +560 mV. Thus, the test conditions achieved for ORII were near the target values for both pH and E_h . These conditions were achieved by the addition of calcium carbonate reagent at levels above saturation and the addition of calcium hydroxide to adjust the pH. The samples were maintained under an air atmosphere in bottles with significant headspace. In addition, it was discovered during the first couple of weeks of leach testing that daily bottle venting to the atmosphere was needed to maintain the E_h value (E_h gradually decreased with time in closed system).

Pu and U analysis results versus time are provided for the ORII condition in Figure 3-1. The concentrations of both Pu and U were observed to increase after the implementation of bottle venting. Although periodic bottle venting did appear to allow higher E_h values to be achieved for the ORII condition and show that significantly higher E_h values were possible than were previously observed⁵, this method also likely resulted in variable oxygen concentrations and E_h values in the test solutions. As a result, the recommended test method for actual waste testing is a continuous purge of CO₂ free air.

The data provided in Table 3-1 for the ORIII condition was based on analysis of samples following nearly five weeks of contact with Tank 18 surrogate solids. A final solution pH value of 9.4 was achieved for the ORIII condition during Tank 18 surrogate solids leaching studies versus the target value of 9.2. This pH was achieved through the addition of calcium carbonate solids and exposure of the solution to a brief air purge to promote carbon dioxide absorption prior to contact with the Tank 18 surrogate solids. Following contact with the washed Tank 18 surrogate, the pH was observed to increase to near 10, so the sample was exposed to a second brief air purge during the leach testing to lower the pH to near the target value. As was the case for ORII, after approximately two weeks of contact with the Tank 18 residual surrogate solids, it was discovered that daily bottle venting was needed to maintain a high E_h value.

Pu and U analysis results versus time are provided for the ORIII condition in Figure 3-1. The concentrations of both Pu and U were observed to increase after the implementation of bottle venting, as was the case for the ORII condition. In addition, (results not shown), analysis of the first two pretreatment wash solutions revealed that the average Pu and U concentrations in the wash solutions were 5E-9 and 8E-6 M, respectively, indicating that Tank 18 residual surrogate solids washing prior to the leach tests did not remove significant amounts of the actinides (<0.5% Pu and <2.5% U in first two washes). The final E_h value observed in the ORIII leaching test was +523 mV, versus the target value of +680 mV. Although periodic bottle venting did appear to allow higher E_h values to be achieved and show that significantly higher E_h values were possible than were previously observed⁵, this method also likely resulted in variable oxygen concentrations and E_h values in the test solutions. As a result, the venting method is not recommended for future testing. A continuous purge of CO₂ free air is recommended for actual waste testing, except during periods (as discussed above) when an air purge without CO₂ removed is needed for pH adjustment. Continuous sample purging with air containing CO₂ has been observed to decrease the pH to near 8.5.

Separate Tank 18 surrogate solids leaching tests conducted with ORIII simulant and added permanganate revealed that the addition of permanganate results in a short-lived increase in the E_h value to +610 mV, but after 1 week, the E_h had decreased to near +500 mV. This solution was not analyzed to determine the Pu and U concentrations. Additional scoping studies conducted as part of this work revealed that exposure of the ORIII simulant to a pure oxygen gas purge does not generate more positive E_h values than air exposure. No additional studies were conducted using pure oxygen or permanganate. Based on these results and the previously reported tests with hydrogen peroxide and ozone⁵, it appears that the generation of an E_h value near the target value of +680 mV requires the addition of non-representative oxidants that

produce transient E_h results. Furthermore, the addition of these oxidants can alter the pH to values well away from that of the target value of 9.2.

Table 3-1. Measured pH and E_h Data and Pu and U Concentrations for Each Pore Water Condition with Tank 18 Residual Solids Surrogate.

Test Condition	Additives	Atmosphere/Vessel	Final E_h (mV)	Final pH	Final Pu (M)	Final U (M)
RRII-A ^a	Ca(OH) ₂ , CaCO ₃ , FeS	N ₂ /Ar purge followed by zero headspace vessel	-105	9.9	6.1E-11	2.5E-05
RRII-B ^a	CFS ^b , FeS	N ₂ /Ar purge followed by zero headspace vessel	-97	11.0	<1.6E-12	1.9E-07
RRII-C ^c	Ca(OH) ₂ , CaCO ₃ , FeS	continuous N ₂ /Ar purge	-113	10.5	4.6E-10	6.4E-05
ORII ^d	Ca(OH) ₂ , CaCO ₃	excess air headspace vessel, daily venting	+515	10.8	1.2E-08	1.1E-04
ORIII ^d	CaCO ₃	excess air headspace vessel, daily venting	+523	9.4	2.2E-08	1.4E-04

^a average of duplicate results, Tank 18 surrogate contact time: 5 days

^b CFS = cement, flyash, and slag grout solids

^c average of duplicate results, Tank 18 surrogate contact time: 2 days

^d average of duplicate results, Tank 18 surrogate contact time: 4 weeks

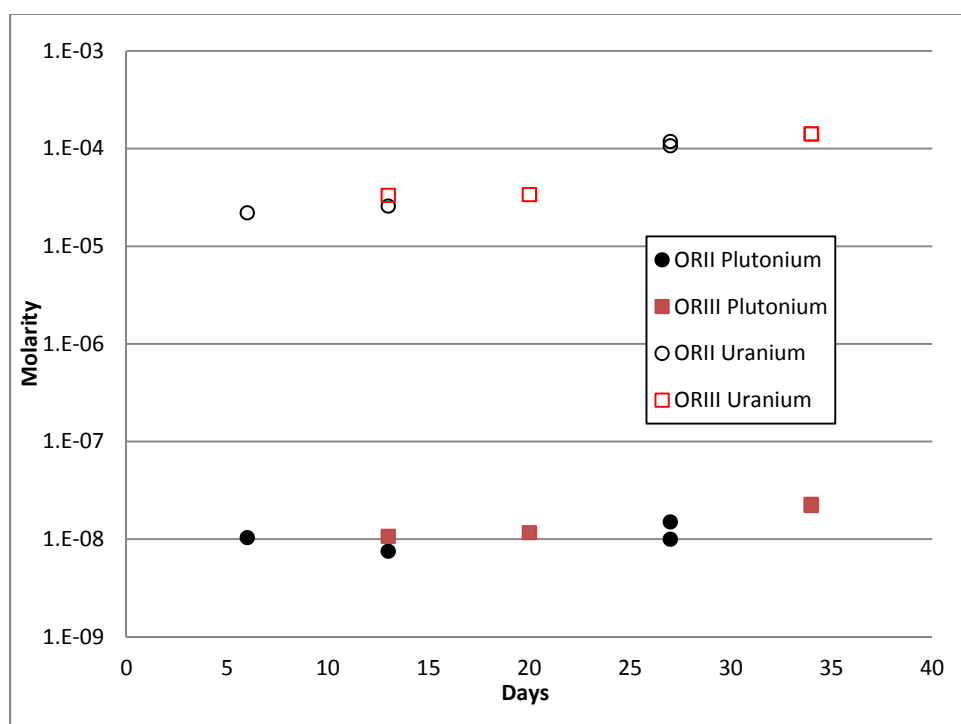


Figure 3-1. Pu and U Concentrations versus Time during Tank 18 Residual Solids Surrogate Leaching Tests for Oxidizing Conditions (ORII and ORIII).

A summary of predicted solubilities for assumed plutonium and uranium species reported by Denham² at various E_h values is provided in Table 3-2. The E_h values selected include the target values for each condition provided in Table 2-3. For the oxidizing cases (ORII and ORIII), the target conditions provided in Table 2-3 assume equilibrium with dissolved oxygen. In addition, actinide solubilities were calculated for the more realistic cases where equilibrium with dissolved oxygen does not exist and the E_h values are lower. Solubility predictions were calculated for pure Pu and U phases and apparent solubilities were calculated for the actinides co-precipitated with Fe phases. The apparent solubilities are based on the primary iron phase solubility and the ratio of the actinides to the iron phase. In all cases, uranium solubility is greater than plutonium solubility. Predicted apparent solubilities for the co-precipitated phases are much lower than the solubilities for the pure phases. The highest Pu solubility (8E-08 M) is predicted for the ORIII condition in equilibrium with dissolved oxygen. The highest U solubility (6E-05 M) is predicted for the ORII condition in equilibrium with dissolved oxygen. The initial assumed Pu phase was hydrous, amorphous PuO_2 , however, it is reported that E_h values above +450 mV for ORII and +530 mV for ORIII result in conversion of increasingly greater amounts of the Pu to higher oxidation states, such that the solubility-controlling phase near +600 mV is the Pu(VI) phase, $\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$. The sensitivity of U solubility to E_h is almost a step change with similar predicted changes in uranium speciation. Below an E_h of approximately -400 mV, the controlling phase is U(IV) oxide (UO_2) and solubility is predicted not to vary with more reducing E_h values. Above an E_h of approximately -200 mV, the much more soluble U(VI) phase, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, dominates and the U solubility is predicted not to vary with increasing (i.e., more oxidizing) E_h values such as those represented by ORII and ORIII.

Comparison of the experimentally observed E_h data provided in Table 3-1 to the E_h values used for the prediction of Pu and U solubility by Denham (Table 3-2) reveals the following. The E_h value achieved experimentally for RRII of approximately -100 mV is significantly less negative than the targeted value of -470 mV and is in the range where the less soluble Pu(IV) and the more soluble U(VI) species are expected to dominate. Consistent with these expectations, the plutonium solubility is very low for all RRII tests and the uranium solubility (at least for RRII-A and RRII-C) is significantly higher.

The E_h value achieved for ORII of approximately +515 mV is approaching the target value of +560 mV for the case where equilibrium with dissolved oxygen exists. The measured Pu and U concentrations for the ORII condition are in the same order of magnitude as the predicted values, with the Pu value being lower than (25% of predicted value for equilibrium conditions) the predicted value and U being higher than (90% higher than predicted for equilibrium conditions) the predicted value.

The E_h value achieved for ORIII of approximately +523 mV was considerably lower than the target value of +680 mV and intermediate between this value and the E_h value used to represent the more realistic, non-equilibrium case of +290 mV. The measured Pu concentration for ORIII was on the same order of magnitude as the predicted value (28% of predicted value for equilibrium conditions). The predicted U concentration for ORIII is nearly two orders of magnitude lower than the measured value. In general, the predicted Pu and U concentrations for co-precipitated phases are all lower than were experimentally observed. Thus we conclude that a significant fraction of the Pu and U in the Tank 18 residual surrogate solids used in this testing appears to be pure Pu and U oxide phases and not co-precipitated phases. This is not unexpected, since the surrogate solids generally received limited washing during preparation. In contrast, the residual tank solids in SRS Tank 18 received multiple contacts with solutions over the course of tank cleaning operations. Thus, testing with actual tank materials is needed to assess the available Pu and U for dissolution during contact with pore waters.

Table 3-2. Predicted Solubilities of Assumed Pu and U Phases.

Condition	Initial Phase	E _h (mV)	Pu (M)	U (M)
RRII ^a	PuO ₂ ^d or UO ₂	-470	3E-11	5E-09
RRII ^c	Magnetite co-precipitate	-470	8E-13	2E-12
ORII ^a	PuO ₂ ^d or UO ₃ ·2H ₂ O	+240	3E-11	5E-05
ORII ^b	PuO ₂ ^d or UO ₃ ·2H ₂ O	+560	5E-08	6E-05
ORII ^c	Maghemite co-precipitate	+240	7E-12	2E-11
ORIII ^a	PuO ₂ ^d or UO ₃ ·2H ₂ O	+290	3E-11	4E-06
ORIII ^b	PuO ₂ ^d or UO ₃ ·2H ₂ O	+680	8E-08	4E-06
ORIII ^c	Maghemite co-precipitate	+290	1E-13	5E-13

^a from Table 11 of SRNL-STI-2012-00404²; E_h values represent more realistic, non-equilibrium conditions with dissolved oxygen

^b from Table 12 of SRNL-STI-2012-00404²; E_h values represent equilibrium conditions with dissolved oxygen

^c from Table 14 of SRNL-STI-2012-00404²; represents apparent solubility based on primary iron phase solubility and Fe:Pu:U ratio

^d solubility based on hydrous, amorphous plutonium oxide phase

4.0 Conclusions

Methodology development for pore water leaching studies has been continued to support Savannah River Site High Level Waste tank closure efforts. For FY2015, the primary goal of this testing was the achievement of target pH and E_h values for pore water solutions representative of local groundwater in the presence of grout or grout-representative (CaCO₃ or FeS) solids as well as waste surrogate solids representative of residual solids expected to be present in a closed tank. For oxidizing conditions representative of a closed tank after aging, a focus was placed on using solid phases believed to be controlling pH and E_h at equilibrium conditions. For all three pore water conditions (RRII, ORII, and ORIII), the target pH values were achieved to within 0.5 pH units. Tank 18 residual surrogate solids leaching studies were conducted over an E_h range of approximately 630 mV. Significantly higher E_h values were achieved for the oxidizing conditions (ORII and ORIII) than were previously observed. For the ORII condition, the target E_h value was nearly achieved (within 50 mV). However, E_h values observed for the ORIII condition were approximately 160 mV less positive than the target. E_h values observed for the RRII condition were approximately 370 mV less negative than the target. Achievement of more positive and more negative E_h values is believed to require the addition of non-representative oxidants and reductants, respectively. Plutonium and uranium concentrations measured during Tank 18 residual surrogate solids leaching studies under these conditions followed the general trends predicted for plutonium and uranium oxide phases, assuming equilibrium with dissolved oxygen. The highest plutonium and uranium concentrations were observed for the ORIII condition and the lowest concentrations were observed for the RRII condition. Based on these results, it is recommended that these test methodologies be used to conduct leaching studies with actual Tank 18 residual solids material. Actual waste testing will include leaching evaluations of technetium and neptunium, as well as plutonium and uranium.

5.0 Recommendations, Path Forward, and Future Work

Based on the results, it is recommended that testing with actual Tank 18 residual solids be conducted using the methodologies developed herein. Continuous purge, controlled atmosphere testing is recommended for ORII and ORIII testing using CO₂-stripped air and air purges to achieve conditions similar to those observed with the Tank 18 residual surrogate solids. RRII testing may be conducted using both continuous inert gas purge and zero headspace methods. This testing will require final

development and installation of test equipment in the SRNL shielded cells. In addition, pretreatment washing methods will need to be developed for the actual Tank 18 residual solids to establish the desired pH conditions.

6.0 References

1. "Performance Assessment for the H-Area Tank Farm at the Savannah River Site", SRR-CWDA-2010-00128, Rev. 1, November 2012.
2. M. E. Denham and M. R. Millings, "Evolution of Chemical Conditions and Estimated Solubility Controls on Radionuclides in the Residual Waste Layer during Post-Closure Aging of High-Level Waste Tanks", SRNL-STI-2012-00404, August 2012.
3. K. H. Rosenberger, "Savannah River Site Liquid Waste Facilities Performance Assessment Maintenance Program FY2015 Implementation Plan", SRR-CWDA-2014-00133, January 2015.
4. Technical Task Request, "Tank Waste Testing to Evaluate Residual Waste Solubility Assumptions used in the Tank Farm PAs", HLE-TTR-2013-002, Rev. 2, December 2014.
5. D. H. Miller, K. A. Roberts, K. M. L. Taylor-Pashow, and D. T. Hobbs, "Determining the Release of Radionuclides from Tank Waste Residual Solids", SRNL-STI-2014-00456, September 2014.
6. D. T. Hobbs, K. A. Roberts, K. M. L. Taylor-Pashow, "Task Technical and Quality Assurance Plan for Determining the Radionuclide Release from Tank Waste Residual Solids", SRNL-RP-2013-00203, Rev. 2, February 2015.
7. ELN Implementing Plan, SRNL-RP-2011-01699, Revision 1.

Appendix A. Supplementary Data

Table A-1. Pu and U Concentrations versus Time for the ORII Condition.

Sample	1	2	3A	3B	3A/B Average
Days	6	13	27	27	27
pH	11.0	11.0	10.6	11.0	10.8
E _h (mV)	+290	+527	+518	+512	+515
Pu (M)	1.0E-08	7.5E-09	1.0E-08	1.5E-08	1.2E-08
U (M)	2.2E-05	2.6E-05	1.1E-04	1.2E-04	1.1E-04

Table A-2. Pu and U Concentrations versus Time for the ORIII Condition.

Sample	1	2	3A	3B	3A/B Average
Days	13	20	34	34	34
pH	10.2	10.2	9.3	9.5	9.4
E _h (mV)	+531	+511	+520	+525	+523
Pu (M)	1.1E-08	1.2E-08	2.3E-08	2.2E-08	2.2E-08
U (M)	3.3E-05	3.4E-05	1.4E-04	1.4E-04	1.4E-04

Distribution:

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M. K. Layton, 705-1C
T. W. Coffield, 705-1C
J. C. Griffin, 773-A
A. P. Fellingner, 773-42A
T. B. Brown, 773-A
D. H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
M. E. Stone, 999-W
P. R. Jackson, DOE-SR, 703-46A
J. A. Crenshaw, 703-46A
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A. W. Wiggins, 1C241-168H
B. T. Butcher, 773-43A
D. A. Crowley, 773-42A
G. P. Flach, 773-42A
L. L. Hamm, 735-A
R. A. Hiergesell, 773-42A
G. K. Humphries, 730-4B
D. I. Kaplan, 773-42A
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