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Determining the Release of Radionuclides from SRS Tank 12H Waste Residual Solids Following Tank Closure

William D. King

September 2018

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EXECUTIVE SUMMARY

Eight High Level Waste (HLW) tanks used to store radioactive waste slurries have been emptied and closed at the Savannah River Site (SRS). Performance Analyses (PA) modeling of the release of radionuclides from residual waste solids in these tanks into the environment over extended time periods indicated the most likely risk drivers for environmental contamination. Radionuclide leaching studies were desired to provide additional information regarding the residual waste solubility assumptions used in the models. This report serves to provide equilibrium solubility data for several radionuclides identified as risk drivers and adds to the database of solubility values reported in the previous analogous study with Tank 18F solids. Pore water leaching studies were conducted on actual SRS Tank 12H residual waste solids to support Liquid Waste tank closure efforts and closed tank Performance Analyses. Tank 12H was exposed to extensive mechanical cleaning, caustic aluminum dissolution, and oxalic acid chemical cleaning prior to closure. The methodology utilized for leach testing was developed during previous testing. Slurries of tank residual solids and grout-representative solids in simulated grout pore water solutions (based on SRS groundwater compositions) with pH and E_h values expected during the aging of the closed waste tank were produced. The soluble concentrations of selected radionuclides were analyzed versus time to confirm equilibrium conditions were achieved. These are the first leach studies conducted on waste tank residuals exposed to these cleaning conditions.

The target pore water leaching conditions are provided below where the initial pore water has a reducing potential and a relatively high pH (Reducing Region II = RRII). The pore water is expected to become increasingly oxidizing with time (Oxidizing Region II = ORII) and during the latter stages of aging (Oxidizing Region III = ORIII) the pH is expected to decrease. For the reducing case, tests were conducted with both unwashed and washed Tank 12H residual solids. For the oxidizing cases (Oxidizing Regions II and III), all samples were washed with simulated grout pore water solutions prior to testing, since it is expected that these conditions will occur after considerable pore water solution has passed through the system. For the reducing case, separate tests were conducted with representative ground grout solids and with calcium carbonate reagent, which is the grout phase believed to be controlling the pH. Ferrous sulfide (FeS) solids were also added to the reducing samples to lower the slurry E_h values. Calcium carbonate solids were used as the grout-representative solid phase for each of the oxidizing cases. Air purge gas with and without CO_2 removed was continually transferred through the oxidizing test samples and nitrogen purge gas was transferred through the reducing test samples during leach testing. In contrast to previous testing, the target pH values were difficult to maintain due to the fact that the samples continually consumed base equivalents which lowered the pH. Leaching studies were conducted over an E_h range of approximately 0.5 V. The lowest and highest E_h values achieved of ~-0.1 V and ~+0.4 V were significantly less positive and less negative than the target values, respectively, as was the case in previous studies. Achievement of more positive and more negative E_h values is believed to require the addition of non-representative oxidants and reductants, respectively. During testing, one ORIII sample was inadvertently exposed to a large volume of pH 12 water, but testing was continued on this highly washed sample after target conditions were re-established.

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

Soluble metal concentrations determined for slurry sub-samples collected during Tank 12H residual solids leaching studies (shown below) followed the general trends predicted for plutonium and uranium oxide phases. Data trends between porewater conditions were also generally consistent with previous leach test results, but equilibrium U and Pu concentrations were lower for Tank 12H residuals. The highest plutonium and uranium concentrations were observed for washed ORIII-A and -B conditions (excluding the highly washed ORIII-B sample) and the lowest concentrations were observed for washed and unwashed RRII-A/-B samples. The highest initial technetium concentration was observed for the unwashed reducing case with Cement, Flyash, and Slag solids (RRII-B). This was likely related to the fact that this sample had not been washed. After washing of the reducing samples, the washed oxidizing samples (ORII-A/-B and ORIII-A/-B) contained the highest technetium concentrations. The highest neptunium concentrations were observed for washed ORIII-A/-B samples (excluding the highly washed ORIII-B sample) and the lowest concentrations were observed for the reducing samples (RRII-A/-B). Below detectable levels of I-129 were observed for all but two leachate sub-samples. Comparing the solubilities of each of the metals analyzed, uranium is more soluble than all other metals analyzed in the leach studies, with a maximum average concentration of 2E-6 M, while the maximum concentrations of each of the other metals were ≤1E-7 M.

Measured pH, E_h, and Metal Concentrations for Each Condition Using Tank 12H Residual Solids.

Test Condition	Sample ID	Additives	Atmosphere/ Condition	E_h (mV)	pH	Molarity				
						Pu[a]	U[a]	Tc[a]	Np[a]	I[a]
RRII	A	$Ca(OH)_2$, $CaCO_3$, FeS	continuous N_2 purge; unwashed	+205[b]	10.8[b]	≤2E-11[b]	4E-8[b]	3E-9[b]	≤5E-11[b]	<5E-7[b]
	B	CFS[c], FeS		+145[b]	11.5[b]	≤1E-11[b]	3E-8[b]	1E-8[b]	<5E-11[b]	<2E-7[b]
	A	$Ca(OH)_2$, $CaCO_3$, FeS	continuous N_2 purge; washed	-64[d]	11.0[d]	≤3E-12[d]	9E-9[d]	≤6E-10[d]	<5E-11[d]	<3E-7[d]
	B	CFS[c], FeS		-71[d]	11.3[d]	<1E-12[d]	1E-8[d]	2E-9[d]	<5E-11[d]	<1E-7[d]
ORII	A	$Ca(OH)_2$, $CaCO_3$	continuous air purge; washed	+340[e]	10.6[e]	1E-10[e]	3E-7[e]	1E-8[e]	2E-10[e]	≤3E-8[e]
	B	$Ca(OH)_2$, $CaCO_3$		+341[e]	10.6[e]	9E-11[e]	2E-7[e]	8E-9[e]	≤1E-10[e]	<1E-7[e]
ORIII	A	$CaCO_3$	continuous air or CO_2-stripped air purge; washed	+404[e]	9.2[e]	1E-10[e]	1E-6[e]	6E-9[e]	9E-10[e]	<1E-7[e]
	B	$CaCO_3$		+406[b]	9.2[b]	1E-10[b]	2E-6[b]	6E-9[b]	1E-9[b]	≤1E-7[b]
	B	$CaCO_3$	continuous air or CO_2-stripped air purge; highly washed	+410[f]	9.2[f]	6E-11[f]	2E-8[f]	≤2E-10[f]	2E-10[f]	<1E-7[f]

[a] isotopes: Pu-238/-239/-240; U-235/-238; Tc-99; Np-237; I-129
[b] average data from first 4 weeks
[c] CFS = cement, flyash, and slag grout solids
[d] average data from final 2 weeks
[e] 8-week average
[f] average data from final 4 weeks

Comparison of the Tank 12H residual solubility data to model predictions reveals that most radionuclide concentrations were between predictions for co-precipitated iron phases and assumed pure phases under equilibrium conditions with dissolved oxygen. This indicates that a significant fraction of the radionuclides in the Tank 12H residual solids used in this testing appears to be pure metal oxide phases and not co-precipitated phases.

Analysis of the sample wash solutions revealed radionuclide concentrations in the wash comparable to the leach test samples and metal losses to the wash solutions were low (<2.5 wt. %) for all samples except for the highly washed ORIII-B sample. Evaluation of blank samples collected during leach testing revealed that the tests were successfully completed without significant contamination from Tc-99, I-129, Np-237 and Pu. Uranium sample contamination was observed in the blanks, but for most samples the level of contamination was not significant.

Based on the results, future studies are recommended for other sludge types to continue building the SRS tank residual radionuclide leaching/solubility database. The current database does not include evaluations of typical F Area Tank Farm sludge residuals or H Area sludge residuals not exposed to oxalic acid cleaning.

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LIST OF ABBREVIATIONS

AD	Analytical Development
CFS	Cement, Flyash, and Slag grout solids
DOE	Department of Energy
EM	Environmental Management
FY	Fiscal Year
HLW	High Level Waste
ICP-ES	Inductively Coupled Plasma – Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
IC	Ion Chromatography
ID	Inside Diameter
KAPL	Knolls Atomic Power Laboratory
OD	Outside Diameter
ORII	Oxidizing Region II
ORIII	Oxidizing Region III
ORP	Oxidation-Reduction Potential
PA	Performance Assessment
PVDF	Poly Vinyl Difluoride
RRII	Reducing Region II
SHE	Standard Hydrogen Electrode
SIW	Synthetic Infiltration Water
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TTQAP	Task Technical and Quality Assurance Plan
XRD	X-ray Diffraction

1.0 Introduction

Current practice for closing High Level Waste (HLW) tanks at the Savannah River Site (SRS) involves removing waste to the maximum extent practical, isolating all transfer lines and penetrations into the tanks, and filling the internal volume of the tanks with grout (concrete). Savannah River Remediation (SRR) has closed SRS Tanks 5F, 6F, 12H, 16H, 17F, 18F, 19F, and 20F. 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 technetium, iodine, uranium, neptunium, and plutonium are among the most likely risk drivers for environmental contamination.[1, 2] Waste release testing was desired 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 was described generally in the SRS Liquid Waste Facilities PA Maintenance Program FY2018 Implementation Plan.[3] In fiscal years (FY) 2014 and 2015, summary reports on method development testing using surrogates were issued.[4, 5] In FY2016, actual waste testing was conducted with Tank 18F residual solids which confirmed some of the model predictions.[6] In 2017, SRR requested that the Savannah River National Laboratory (SRNL) design and perform waste release testing for Tank 12H residual solids[7] and a Task Technical and Quality Assurance Plan (TTQAP)[8] was developed for actual waste testing following the same general protocols developed with Tank 18F residuals. Actual Tank 12H residual leaching studies were conducted in FY2018 and the results are provided in this report.

Three theoretical periods and conditions occurring at different times following tank closure have been targeted for testing based on waste release modeling conducted at SRNL.[9, 10] Reducing 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 <2,120 grout pore volumes). Oxidizing Region III (after passing >2,120 pore volumes) was the final target condition. (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 tank environment. Furthermore, a pore volume represents the total volume of the pore voids within the grout fill material inside the closed tank.) Solution pH and E_h values were predicted for each condition and testing was conducted to determine the release of radionuclides from Tank 12H residual solids exposed to conditions as near the targets as possible.

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 previous testing was also utilized for the Tank 12H leach testing. The SIW stock solution was diluted 1000:1 by volume (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)
$CaCl_2 \cdot 2H_2O$	3.68
Na_2SO_4	1.07
KCl	0.40
NaCl	2.65
$MgCl_2 \cdot 6H_2O$	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 Preparation of Grout Pore Water Simulants from SIW

The target pH and E_h values for three grout pore water solutions (based on the PA[1] and supporting modeling[9, 10]) developed from the SIW and used for radionuclide release leaching studies are provided in Table 2-3. Grout pore water simulants were prepared for each condition in Table 2-3 as described below based on methods developed previously.[5] RRII and ORII solutions were prepared from the diluted SIW by the addition of approximately 0.1-0.2 g $CaCO_3$/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 $CaCO_3$ solids (assumed composition based on modeling predictions). The RRII and ORII pore water simulants had the same chemical composition and differed only in the gaseous atmosphere ultimately used to adjust the solution E_h values. ORIII simulant was prepared from the SIW by the addition of 0.1-0.2 g $CaCO_3$/L. This resulted in a solution containing trace amounts of $CaCO_3$ solids with a pH ranging from 8-10. As needed, the ORIII solutions were purged with air resulting in the absorption of CO_2 and a reduction in the solution pH to near the target value. Alternatively, $Ca(OH)_2$ reagent was added to the ORIII solutions to raise the pH. All of the as-prepared simulants had positive solution E_h values. Previous testing and analysis revealed that these preparations result in elevated calcium concentrations ranging from 7-28 mg/L relative to the target composition of 1 mg Ca/L for the as-prepared simulant.[5]

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

The final step in the preparation of grout pore water simulants and test samples was the transfer of additional calcium carbonate or actual grout solids, and FeS solids (reducing samples only) to the solutions in the shielded cells environment prior to actual waste leach testing. Calcium carbonate reagent was utilized as a grout-representative phase in all ORII and ORIII tests and in one RRII test 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 test.

The CFS solids were initially prepared as a monolith representing the components of the grout used to fill SRS Tank 12H. The CFS solids recipe included 125 parts of Cement Type I/II, 363 parts of Fly Ash Class F, and 210 parts of Cement Grade Slag. Diutan Gum was also added as a viscosity modifier. Sand was not added as a component of the monolith since both fly ash 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. The CFS powder was stored and transferred into the shielded cells in small vials containing no head space volume to minimize air exposure of the crushed grout.

2.3 Leach Test Sample Preparation from Tank 12H Residual Waste Solids and Porewater Simulants

Actual Tank 12H residual waste solid samples archived in the SRNL shielded cells were evaluated based on available characterization data, sampling location, sample size and history in order to select samples to use for leachate testing. Multiple Tank 12H residual waste samples were collected during Tank 12H operational closure for use in tank characterization.[12] Tank 12H sample final characterization was completed in 2015 by Oji using three composites of these samples (SRNL-STI-2015-00241).[12] The composites contained material from various samples including mound samples M-L-1, M-L-2, M-L-3, M-H-1, M-H-2, and M-H-3 and floor samples F-1R, F-2R, F-3R, F-4, and F-5.

The Tank 12H sample material was re-packaged in the SRNL shielded cells in 2016 and retained for potential future use.[13] Approximately 36 grams of floor residual solids was retained from the Tank 12H samples by compositing material from samples F-1R, F-3R, F-4, and F-5 into one container. Approximately 178 grams of primary mound residual solids was retained from the Tank 12H samples by compositing material from samples M-L-1, M-L-2, M-L-3, M-H-1, M-H-2, and M-H-3 into one container. The sample compositing was performed per the residual sample material disposition plan[14] to the extent practical given the amounts of uncompromised material that were still available and the constraints affecting operations in the cells at the time of re-packaging.

Waste release test samples were prepared by mixing portions of these archived Tank 12H composite mound and composite floor residual materials in the shielded cells at an approximate 78:22 mass ratio (3.5±0.1:1) of floor:mound material. Exact reagent and sample masses used for the preparation of the individual test slurries are provided in Table 2-4. Test samples contained 7.5±0.025 g of Tank 12H residual solids floor/mound composite. Approximately 4.2 g of $CaCO_3$ or CFS solids were added to each test sample as indicated in Table 2-4. Approximately 0.8 g of FeS solids were initially added to each of the RRII test vessels. Another portion (~0.25 g) of FeS solids was added to each of the samples after the week 6 sampling event. The initial volume of each leachate slurry sample was 250 mL.

Analysis of similar floor/mound composite samples (mass ratio 3.5:1) was conducted using two different digestion methods (aqua regia and peroxide fusion). Results are provided in Table 2-5 along with previously reported results for the composite samples with floor:mound ratios most similar to the leach test samples. Aluminum, iron, thorium, and mercury are the primary waste components, as was the case for the composite samples characterized by Oji.[12] Generally good agreement was observed between the two dissolution methods. However, the sub-sample composite used for leach testing contained considerably more Al (19 wt. %) than the samples analyzed previously (<10 wt. %). In addition, the leach test samples contained less Fe (17 wt%) than the previous composites used for characterization (20-35 wt. %). Mercury, thorium, and other actinide levels (U, Np, Pu) were comparable to previous results. Based on the leach test results, I-129 analysis of the Tank 12H residual solids is needed to determine whether iodine was lost from the sample during interim storage in the shielded cells. Insufficient floor sample was available for I-129 analysis. Therefore, a mound sample (no floor component) and a leachate test sample were analyzed for I-129 following test completion. The I-129 analysis will be reported in a revision to this report or in a separate technical memorandum.

Table 2-4. Test Sample and Reagent Masses.

Sample ID	Tank 12H Floor (g)	Tank 12H Mound (g)	Floor: Mound (g:g)	$CaCO_3$ (g)	CFS (g)	FeS (g)	Porewater Simulant Type[a]
RR2-1 (CC)	5.857	1.648	3.4:1	4.171	---	1.048[b]	RRII
RR2-2 (CFS)	5.849	1.658	3.5:1	---	4.142	1.063[b]	RRII
OR2-3	5.867	1.657	3.5:1	4.160	---	---	ORII
OR2-4	5.842	1.659	3.5:1	4.155	---	---	ORII
OR3-5	5.865	1.656	3.5:1	4.195	---	---	ORIII
OR3-6	5.839	1.644	3.6:1	4.175	---	---	ORIII

[a] 250 mL of simulant solution was initially added to each sample vessel
[b] ~0.8 g FeS added initially and another ~0.25 g added after week 6
[c] $Ca(OH)_2$ also added to all samples except RRII-CFS as needed to achieve the target pH values

Table 2-5. Tank 12H Composite Leach Test Sample Selected Elemental and Radionuclide Concentrations Versus Previous Characterization Samples.

Analyte	Aqua Regia[a]	Peroxide Fusion[a]	Average	%RSD	Composite 2[b]	Composite 3[b]
	Weight %					
Al	19.1	18.4	18.8	3	9.5	5.9
Fe	15.7	19.0	17.4	13	22.1	35.7
Hg	11.3	5.8	8.6	45	11.7	15.7
Th	6.2	5.8	6.0	5	8.2	3.3
Mn	1.0	1.1	1.0	10	1.6	1.3
Na	0.64	---	0.64	---	0.65	0.42
Ni	0.45	0.56	0.51	16	1.03	0.56
Ca	0.12	0.41	0.27	76	0.11	0.12
Si	0.11	0.16	0.13	22	0.15	0.18
Zr	0.10	---	0.10	---	0.15	0.10
U[c]	0.19	0.19	0.19	2	0.15	0.07
Np-237	1.0E-03	1.1E-03	1.1E-03	4	3.0E-03[d]	1.1E-03[d]
	uCi/g					
Tc-99	<7.1E-03	<7.2E-03	<7.2E-03	---	4.4E-03[d]	3.9E-03[d]
I-129	data to be provided separately				5.0E-03	3.9E-03
Pu-238	69.8	68.0	68.9	2	135.0	66.5
Floor:Mound (mass ratio)	3.5:1		---	---	1.9:1	4.4:1

[a] sludge residual dissolution method
[b] as reported by Oji[12]
[c] total uranium reported as the sum of U-233, U-234, U-235, U-236, and U-238 isotopes
[d] calculated from the values reported by Oji[12]

2.4 Equipment Design and Operation

Probes for the measurement of slurry pH and Oxidation-Reduction Potential (ORP) were installed in the shielded cells utilizing standard KAPL (Knolls Atomic Power Laboratory) plug penetrations through the front cell wall. Both pH and Oxidation-Reduction Potential (ORP) data were measured with a dual channel Thermo Scientific™ Orion™ Star Series meter. Slurry pH data was collected during leach testing using a sealed, double-junction Oakton pH Electrode with an Epoxy body (Model WD-35805-01). The pH meter was calibrated prior to each use with pH 4, 7, and 10 standard buffer solutions. E_h data was collected using a Thermo Scientific 9179BN Low Maintenance ORP Triode with an Epoxy body. The ORP probes were checked using Zobell's Oxidation-Reduction Potential standard solution. The standard was typically checked once during each series of ORP sample measurements and all standard measurements ranged from +210 to +217 mV (E_h range: +427 to +434 mV; reported standard E_h: +428 mV) with an average ORP of +211 mV. All reported sample E_h values are relative to the Standard Hydrogen Electrode (SHE). A standard correction of +217 mV was applied to all ORP data to convert the data to E_h format, based on the manufacturer instructions and data obtained for the ORP standard. The electrode manuals indicate that the measured ORP values may vary by as much as ±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. Under oxidizing conditions, a measurement time of several minutes was typically required for probe stabilization and data recording. Under reducing conditions, it was found that long time periods (several hours) were often needed for measurement stabilization. Once probe stabilization had been achieved under reducing conditions a second reducing sample could be analyzed relatively quickly (typically within minutes).

A test apparatus was designed and constructed to simultaneously maintain numerous actual radioactive samples under either oxidizing or reducing conditions with continuous agitation and gas purge and at constant temperature. A photograph of the test apparatus prior to transfer into the shielded cells is provided in Figure 2-1. Magnetic stir bars and multi-position stir plates were included to promote sample agitation. Glass test vessels were constructed in the SRNL glass shop for controlled-atmosphere testing that would accommodate periodic sub-sampling (see detailed discussion below).

A customized water bath was constructed from ½” thick Lexan sheets to fit over two adjacent stir plates and maintain all samples at the target temperature. The glass test vessels were immersed in the water by placing the vessels through fitted slots in the top of the bath which were directly above the sample positions on the stir plates. A rubber gasket was positioned between two Lexan plates on the top of the water bath which resulted in a close fit for the glass test vessels and helped to insulate the bath from the cell environment. The water bath was attached to a temperature-controlled water recirculator (ThermoCube Solid State Cooling System). The recirculator set temperature was maintained at 22.0 ºC throughout testing. The recirculator temperature varied little during testing ranging from 21.9 to 22.0 ºC.

A customized water bubbler manifold was constructed and attached to the back of the water baths to monitor and control gas flow through each individual vessel during testing. Low gas supply pressures (typically <5 PSI) were utilized during testing to purge the vessels. Gas flow control through the vessels was accomplished on the downstream side of each sample gas line by the adjustment of stainless steel Swagelok needle valves. Because the gas outlet lines for each sample were open to the bubbler, the gas pressures in the samples were slightly above atmospheric pressure during leach testing.

Customized glass vessels of various types were prepared for testing (see example leach test vessel in Figure 2-2). All test vessels were made of 70.2 mm ID tubing and the main (straight) portion of the vessels (excluding the tops) were ~8 cm tall. The vessels would contain ≤300 mL of solution. The vessels fit snugly into the sample slots in the top of the customized water bath. Four types of vessels were prepared for testing including: caustic scrubber, humidifier, leach sample, and probe storage vessels. Upper vessel attachments were made from #7 and #15 internal glass screw threads. Threaded Teflon fittings for the screw threads were modified to accommodate the various needed connections. Each vessel top included three to four screw thread fittings.

The purpose of the caustic scrubber vessels was to remove carbon dioxide gas from the air supply lines through gas contact with 5 M NaOH solution. Carbon dioxide removal was required to avoid impacting the test slurry pH during air gas purging. Each scrubber vessel included a single gas supply line consisting of a 12 mm OD fritted glass gas dispersion tube to promote the formation of numerous gas bubbles to enhance gas/liquid contact. A second port with a quick connect fitting was included in the scrubber vessel top for the addition of sodium hydroxide reagent. The third and final scrubber vessel attachment included a stainless steel demister suspended within a short glass column for the removal of entrained solution from

Figure 2-1. Photograph of Tank 12H Testing Equipment Prior to Installation into the SRNL Shielded Cells.

the outlet gas. When utilized, the caustic scrubbers were the first vessels that the air was passed through and the gas was then transferred to a humidifier vessel.

The humidifier vessels were filled with deionized water. The purpose of the humidifier vessels was to saturate the supply gas with water vapor at the sample temperature and minimize leach sample evaporation during testing. For oxidizing conditions, the humidifier vessels also served to isolate the leach test samples from the caustic scrubber solution. A single humidifier vessel was utilized to treat the supply gas for each sample type (RRII, ORII, and ORIII) with the water-saturated gas stream then being split between two leach test vessels. Each humidifier vessel included a single gas supply line consisting of ¼" diameter thin wall polyethylene tubing which had been heat-sealed at the end. Multiple 1/64" holes were drilled into the sides of the tubing near the bottom to produce bubbles and promote gas-liquid contact. The humidifier vessels also included a water addition port with a quick connect fitting and two gas outlet lines containing demisters. The outlet lines led to the leach test vessels.

The glass leach sample vessels (example shown in Figure 2-2) included a gas supply port, a sample/reagent addition/collection port (magnetized cap), and a single gas outlet connection identical in design to the humidifier vessels. The sample addition port was also used to insert the pH and ORP probes.

The probe storage vessels were designed similarly to the other vessels, but included open glass screw threads with no plastic fittings. Probes were immersed in water in these vessels when not in use. Reagents and samples were added to the various vessels using glass funnels or customized plastic funnels with an attached quick-connect fitting.

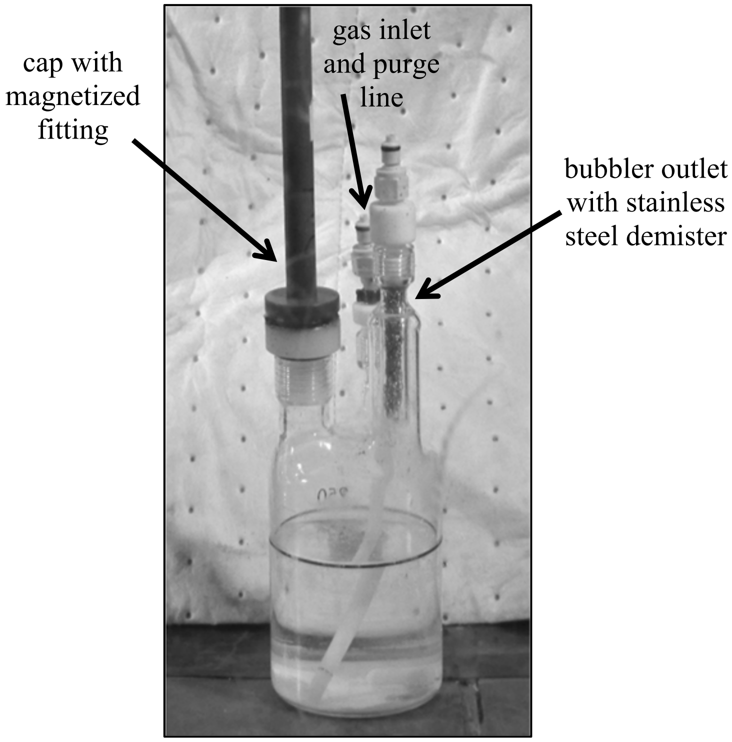


Figure 2-2. Photograph of Actual ORII Leach Test Control Sample Vessel.

A diagram of the vessel layout utilized in the test apparatus is provided in Figure 2-3. Six leach tests were conducted using two vessels for each sample type (RRII, ORII, and ORIII). As indicated in the figure, the gases were passed through a series of vessels for treatment to produce the desired conditions. The vessels in a given series were connected using 1/8” ID Tygon tubing with medical-grade check valves in the middle and quick-connect fittings (Colder Product Company PMC12 polypropylene fittings with 1/8” nominal flow) on each end to allow for vessel detachment, removal, or reconfiguration during testing. The sample vessel gas outlet lines were connected to the bubbler system using the same tubing with check valves included in each line. Blank control vessels for each sample type (RRII, ORII, and ORIII) were also incorporated into the system in the locations shown. CO_2-stripped air was used as the baseline purge gas for the oxidizing samples (ORII and ORIII). During periods when carbon dioxide was needed to lower the pH, the caustic scrubber was removed from the sequence of vessels that the air was passed through until the target pH was reached. Ultra-high purity nitrogen gas (supplied by cylinder through front wall penetrations) was used as the purge gas for the reducing samples (RRII) throughout testing.

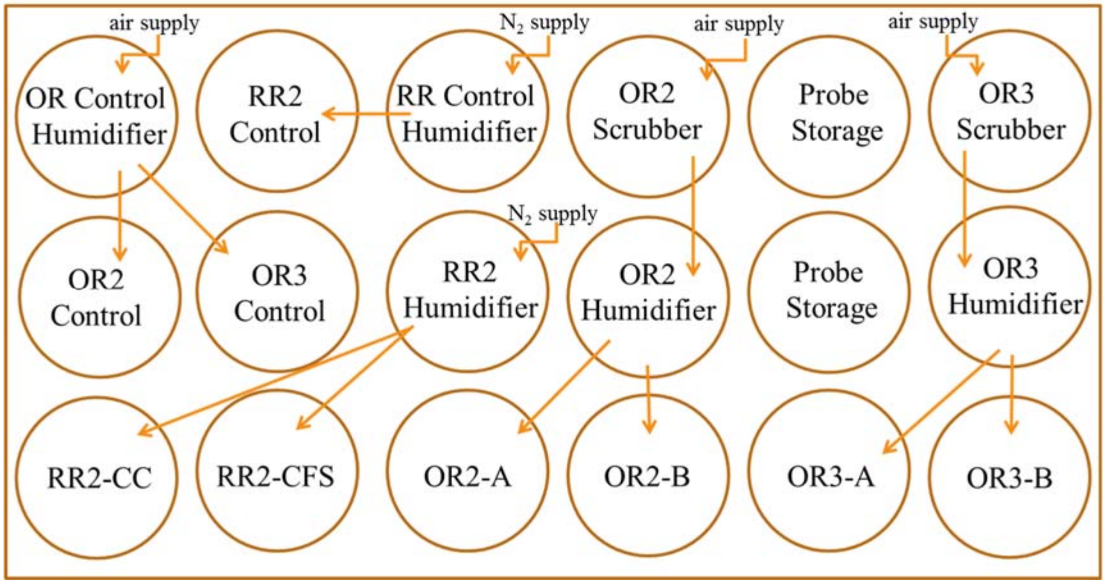


Figure 2-3. Vessel and Plumbing Layout for SRNL Shielded Cells Testing.

It was anticipated that very low solubilities near analysis detection limits would be observed during leach testing. As a result, a sub-sampling system and methodology were developed to allow for the isolation of filtered samples in the analysis bottles. The sampling system included a simple 10 mL syringe with a directly-attached filter (see Figure 2-4). Tubing (1/8" ID) was attached to the downstream side of the filter with a male quick-connect fitting attached to the other end of the tubing. The system also included modified, shielded analysis bottles with caps containing ¼" OD polyethylene tubing and quick-connect fittings for attachment to the syringe (see Figure 2-5). The analysis bottle required venting during sample collection via another quick-connect fitting with attached tubing and a second filter to isolate the sample from contamination on the downstream side. After sample collection, the vent line and the sub-sampling lines were removed from the analysis bottles by depressing the release tabs on the quick-connect fittings. The samples were transferred into fitted foam holders to maintain a vertical orientation during transport to analytical sample receiving. In analytical, care was taken not to contaminate the samples from personnel contact with the bottle exterior surfaces. The sample bottle caps were carefully removed with gloves following general radiological procedures. Then the analyst gloves were changed and the sample was removed from the bottle with a pipet without touching the exterior bottle surface. Using this method, the analytical bottles were never opened inside the shielded cells environment and contamination from the bottle surfaces in AD was minimized or eliminated.

During sub-sampling, the filter end of the syringe was covered with a small plastic bag to minimize the possibility of post-filtration contamination in the cell (see Figure 2-4). The bag was removed just prior to sampling and the syringe filter unit was attached directly to the analytical bottle via the quick-connect fitting. Using this system, the analysis sub-samples were removed from the leach test vessels using a plastic slurry and transferred into the top of the syringe barrel after removing the plunger. Prior to all sub-sampling events, disposable cloth wipes were laid down on the cell floor to minimize contamination. Prior to testing, and periodically during testing, the cell floors and manipulator fingers were wiped clean to remove contamination.

Figure 2-4. Photograph of Sub-Sampling System.

Figure 2-5. Photograph of Sub-Sampling System and Analysis Sample Vessels with Attached Vent Lines.

2.5 Leaching Studies

The dissolution of Tc-99, I-129, U (sum of selected isotopes), Np-237, and Pu (sum of selected isotopes) present in Tank 12H residual solids mixed with calcium carbonate or CFS solids and, for reducing cases, ferrous sulfide solids were evaluated in the grout pore water simulant solutions prepared as described in Section 2.2. CFS and calcium carbonate solids were added to each test sample at a concentration of 16.7±0.1 g/L slurry. Tank 12H solids were added to each test sample at a concentration of 30.0±0.1 g/L slurry. This phase ratio was selected based on a combination of solubility and analytical limit of detection considerations and not the actual condition in a grout-filled tank. A goal in selecting the phase ratio was ensuring that key dose contributors were not removed to any appreciable extent by the pore water flow prior to reaching the ORIII condition. FeS solid was added to RRII samples at a cumulative concentration of 4.2±0.03 g/L slurry. Initial FeS concentrations were near 3.2 g/L and additional FeS was added after 81 contact days. All test sample initial slurry volumes were 250 mL. The slurry sample volumes decreased during testing due to the removal of primarily liquid from the samples for analysis.

The ORII-A and -B leach samples were replicates for the ORII condition. The ORIII-A and -B samples were also initially replicate samples for the ORIII condition, until the -B sample was compromised during testing (see discussion below). The RRII-CC and RRII-CFS samples were both intended to represent the RRII condition, but with different grout-representative phases (calcium carbonate and Cement Flyash and Slag solids as indicated in the sample names).

As shown in Table 2-6, sample washing was conducted for the oxidizing samples (ORII and ORIII) prior to leach testing. Wash solutions were in contact with the test samples for several hours (5-12 hr) while the solids settled prior to removal from the vessels. Sample washing was not conducted for the reducing samples (RRII-CC and RRII-CFS) until after 62 days of contact. At this point the remaining free liquid simulant was removed from each leach test sample and additional simulant was added under a nitrogen gas purge to give a final slurry volume of 250 mL. This two-phased leach testing approach was intended to be representative of the earlier and latter portions of the RRII phase of aging.

Table 2-6. Test Sample Initial Wash Decant Volumes.

Date	Volume (mL)	Comments
RRII-CC	0	no wash prior to initial leach testing; after 62 contact days the remaining free liquid was removed and fresh simulant was added to the test vessels to give a final slurry volume of 250 mL
RRII-CFS	0	
ORII-A	250	ORII wash samples composited into single bottle
ORII-B	250	
ORIII-A	250	ORIII wash samples composited into single bottle; after 69 contact days the ORIII sample leach test vessel broke and the sample was exposed to approximately 8.5 liters of liquid at pH 12 for several days
ORIII-B	250	

In addition to the reagents listed in Table 2-4, calcium hydroxide was added as needed to raise the pH of the ORII and RRII-CC samples to near the target values during testing (cumulative addition of 0.35-0.55 total g per sample typically added in 0.02 g portions). Considerably less calcium hydroxide (cumulative addition of ~0.1 total g) was added to the ORIII samples to raise the pH. An air purge (without CO_2 removed) was also utilized to lower the pH of the ORIII samples, as needed. The RRII-CFS sample did not require $Ca(OH)_2$ addition during testing. Sample liquid level heights were visually monitored during testing to confirm that liquid losses to evaporation were minimal. Gas flow rates were maintained at minimum levels and liquid levels in the demister vessels were maintained at sufficient heights to minimize sample evaporation. During the entire course of the leaching studies, ≤50 volume percent of the initial sample slurries was consumed due to sub-sampling.

The dates of sample preparations and sub-sampling and comments regarding the testing are provided in Table 2-7. Prior to collection of the first analysis sample, an SRNL safety pause was initiated which

Table 2-7. Test Sample Preparation and Sub-Sampling Timeline and Comments (all activities conducted in 2018).

Date	Activity	Contact Days	Comments
4/12	sample preparation	0	leach test samples prepared; oxidizing samples washed; target pH achieved
4/17	pH adjustment	5	discovered base consumption by samples and began pH adjustments
4/18		6	continued pH adjustment with calcium hydroxide
4/19		7	
SRNL Safety Pause			
5/15	pH adjustment	33	resumed pH adjustment with calcium hydroxide
5/16		34	continued pH adjustment with calcium hydroxide
5/17		35	
5/21		39	
5/24	1st sub-sampling	42	
5/29	pH adjustment	47	continued pH adjustment with calcium hydroxide
5/30		48	
6/1	2nd sub-sampling	50	
6/5	pH adjustment	54	continued pH adjustment with calcium hydroxide
6/7	3rd sub-sampling	56	
6/11	pH adjustment	60	continued pH adjustment with calcium hydroxide
6/12		61	
6/13	4th sub-sampling	62	removed free liquid from RRII samples and added fresh simulant
6/20	pH adjustment	69	continued pH adjustment with calcium hydroxide; ORIII-B leach test vessel broke but sample recovered
6/26	pH adjustment	75	continued pH adjustment with calcium hydroxide; ORIII-B to new vessel, re-established conditions
6/27		76	
6/28	5th sub-sampling	77	
7/2	6th sub-sampling	81	
7/3	pH adjustment	82	continued pH adjustment with calcium hydroxide
7/9		88	
7/11	7th sub-sampling	90	
7/13	pH adjustment	92	continued pH adjustment with calcium hydroxide
7/16	8th sub-sampling	95	
7/19	9th sub-sampling	98	only sub-sampled reducing samples

delayed both sample pH adjustments and sub-sampling for almost a month. Therefore, the first analysis sub-samples were collected after 42 days of total contact. Sample pH adjustments were required throughout most of the testing for the RRII-CC, ORII-A, and ORII-B samples due to base consumption by the samples. After the 4th sub-sampling event, remaining free liquid was removed from the RRII samples and fresh porewater simulant was added. Also, after the 4th sub-sampling event, the ORIII-B sample vessel and the ORIII caustic scrubber vessel broke resulting in the loss of the caustic reagent and sample into the water bath solution. The solids were recovered from the solution to give a final slurry with a pH near 12. The solids were subsequently washed with fresh porewater simulant and transferred to a new test vessel and the target conditions were re-created. The ORIII-B sample recovery liquid and subsequent wash solutions were analyzed to calculate radionuclide losses resulting from contact of the ORIII-B sample solids with these liquids. Sub-sampling of the ORIII-B sample was then resumed. This sample was subsequently considered to represent a highly-washed residual sludge sample, although the pH of the contact liquid following vessel rupture was higher than any of the target conditions.

ORP measurements on the reducing samples were much higher than the target values for most of the testing. After the 6th sub-sampling event, additional FeS reagent was added to each of these samples to attempt to lower the measured ORP values. These final additions resulted in significant reductions in the measured ORP values. As a result, the later sub-samples collected from the RRII samples are closer to the target E_h values than earlier sub-samples. One additional sub-sampling event (9th sub-sampling event) was conducted for the reducing samples due to the achievement of lower E_h values toward the end of testing.

2.6 Sub-Sample Collection and Analysis

Sample aliquot volumes of 5-12 mL (depending on the volume needed for analysis) were collected from the leach test vessels for analysis after the measurement of the solution pH and E_h at approximately weekly intervals. Nine sub-sampling events (eight for oxidizing samples) were conducted over a period of nearly two months (sub-sample collection sludge:simulant contact days: 42, 50, 56, 62, 77, 81, 95, and 98). Sub-sample aliquots were filtered as described above through 0.1-µm polyvinyl difluoride (PVDF) syringe filter units without opening the bottle caps. Identically-prepared blank sub-samples were typically collected for analysis along with the leachate test samples. 5 M nitric acid volumes of 0.9-1.8 mL (adjusted for the target sample volume to give a sample:acid volume phase ratio near 6) were placed in the analysis bottles prior to cell entry to acidify the samples and avoid post-filtration precipitation of the dissolved radionuclides and metals. The isolated samples were manually shaken to promote mixing of the porewater filtrate and the diluent acid.

The acidified sub-samples were analyzed for plutonium by alpha spectroscopy following separation using thenoyltrifluoroacetone (TTA) and for uranium, technetium, and neptunium by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Reported plutonium concentrations are based on the sum of the measured Pu-238 and Pu-239/240 concentrations in dpm/mL converted to molar concentrations. For the reducing samples, plutonium concentrations were typically below detectable limits. Quantification of the total plutonium detection limits on a molar basis for the reducing samples was conducted by adjustment of the Pu-238 detection limit to total Pu based on the known isotopic ratios for this sample (Table 2-5). Total uranium concentrations were calculated as the sum of the U-235 and U-238 isotopes, since sample characterization confirmed negligibly small contributions from other uranium isotopes (U-233, -234, and -236) on a molar basis. Neptunium was calculated from the reported concentration of mass 237. Technetium was calculated from the reported concentration of mass 99. I-129 was analyzed by radio counting techniques.

Other analyses were conducted on selected samples including: Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), Ion Chromatography (IC), and Total Inorganic Carbon (TIC). Separate Tank12H residual sub-samples with the same floor:mound ratio as the leachate test samples were digested in acid (one sample by aqua regia and another by sodium peroxide fusion) to determine the elemental composition by ICP-MS, ICP-ES, beta scintillation counting (for Tc-99), and cold vapor atomic absorption for Hg. All sample chemical and physical analyses (excluding pH and ORP) were conducted by the SRNL Analytical Development (AD) section.

2.7 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 Electronic Laboratory Notebook (ELN) experiment A2341-00117-10 (SRNL Electronic Notebook Production; SRNL, Aiken, SC 29808) in accordance with the ELN Implementing Plan.[115]

3.0 Results

A test apparatus was developed and installed into the SRNL shielded cells facility to determine the leaching characteristics of actual radioactive SRS Tank 12H residual solids under conditions believed to be representative of a closed waste tank during three different aging periods after tank closure. The leach test slurries included grout-representative solids (CFS or calcium carbonate), Tank 12H residual solids, and ferrous sulfide solids (for reducing samples only). Two liquid simulants were used for testing based on the SIW composition provided in Table 2-2 with calcium carbonate reagent added to each simulant during initial preparations to just beyond saturation (dusting of solids observed in each simulant). $Ca(OH)_2$ was added to one simulant sample to produce a solution pH of 11.1 and the resulting simulant was utilized for ORII and RRII testing. A second simulant sample was prepared without $Ca(OH)_2$ addition resulting in a solution pH near 9 and this simulant was utilized for ORIII testing. Tank 12H residual sub-samples and added solids were contacted with these simulants in the leach test vessels inside the shielded cells environment. As needed, calcium hydroxide reagent and air gas sparging (without CO_2 scrubbing) were also used during testing to make any additional pH adjustments. Air gas sparging without CO_2 was only used for ORIII samples.

Sample agitation during leach studies could not be accomplished using magnetic stir bars. Stirring could not even be accomplished when the vessels were taken out of the water bath using various stir bar types and sizes. The inability to stir was apparently due to some unexpected sample characteristic, since water could be easily and vigorously stirred in these vessels using this equipment. Therefore, the samples were agitated daily by briefly lifting the vessels from the water bath and stirring manually. Continuous gas purging served to mix the samples throughout testing as well. Testing was conducted at 22 ºC over a period of approximately two months (after the Safety Pause) with sub-samples being collected periodically (approximately weekly, but varying considerably depending upon shielded cell technician availability). A photograph of the test apparatus after installation into the shielded cells and after addition of the leach test samples is provided in Figure 3-1. A photograph showing the various test vessels (scrubber, humidifier, and leach sample vessels) following leach testing is provided in Figure 3-2.

Average slurry pH and E_h data and metal concentrations for filtered sub-samples obtained throughout the testing period are provided in Tables 3-1 and 3-2. Slurry pH values varied considerably during testing due to base consumption by the samples. Base consumption was likely the result of the dissolution of insoluble metals (such as aluminum) from the residual sludge to form soluble hydroxy complexes. Initial and final pH values measured for the samples during testing are provided in Tables 3-3 and 3-4 along with the average pH data for each testing period. The average, initial, and adjusted sample pH data values are plotted in Figures 3-3, 3-4, and 3-5, respectively. Inspection of these figures and tables reveals the high degree of variability in the slurry pH values during testing. Trends in the slurry E_h data are provided in Figure 3-6. The highest E_h values were observed for the ORIII samples and the lowest values were observed for the

Figure 3-1. Photograph of Tank 12H Testing Equipment After Installation in the SRNL Shielded Cells.

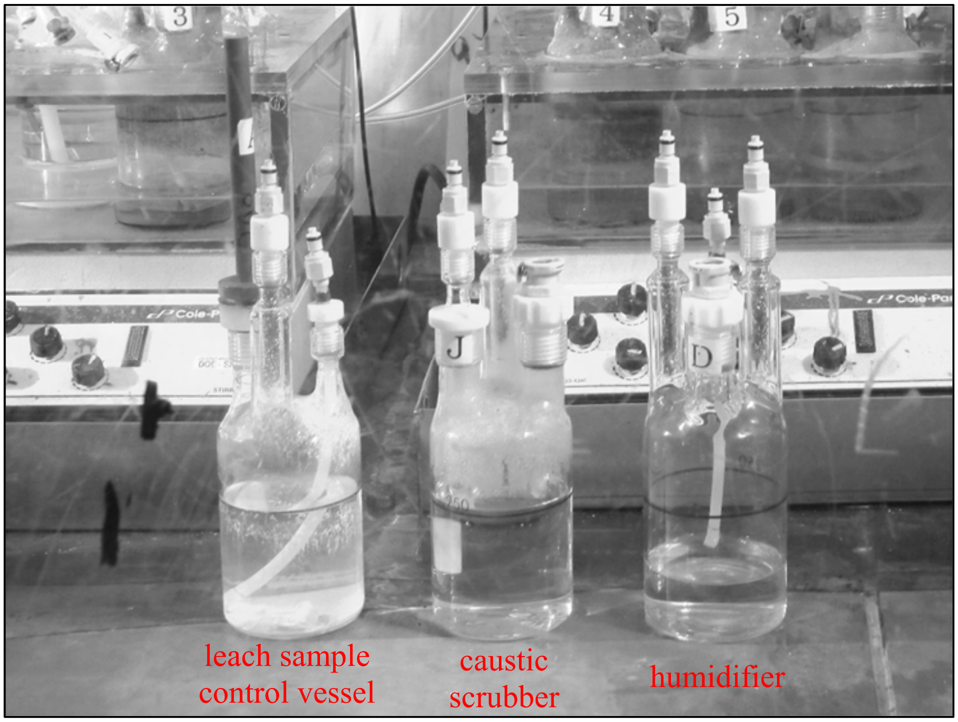


Figure 3-2. Photograph of Test Vessels in the SRNL Shielded Cells at Test Conclusion.

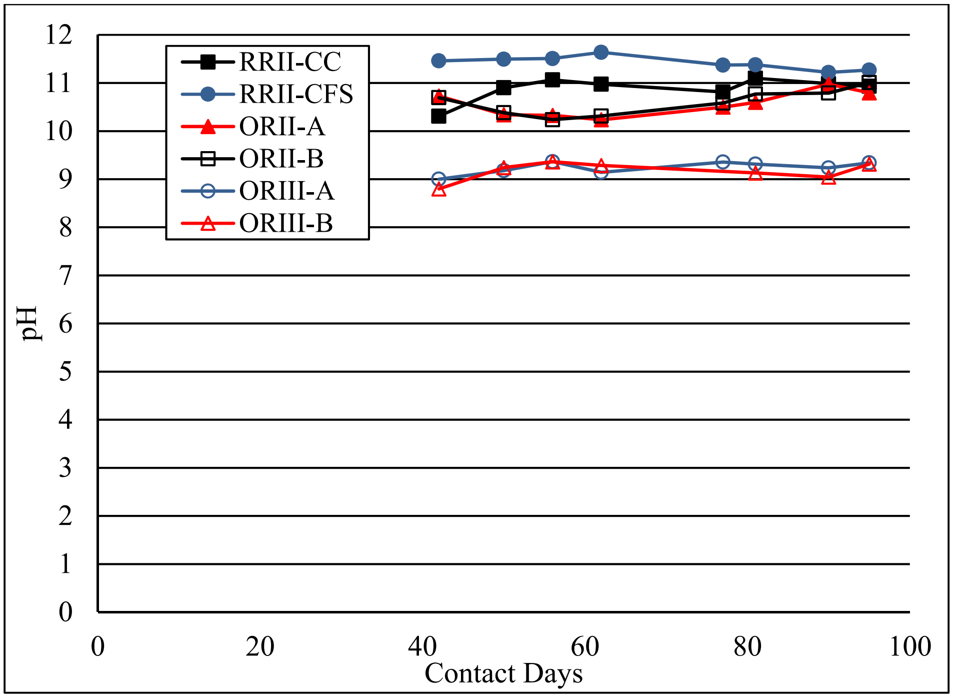


Figure 3-3. Average Slurry pH Data Collected During Tank 12H Residual Solids Leaching Studies.

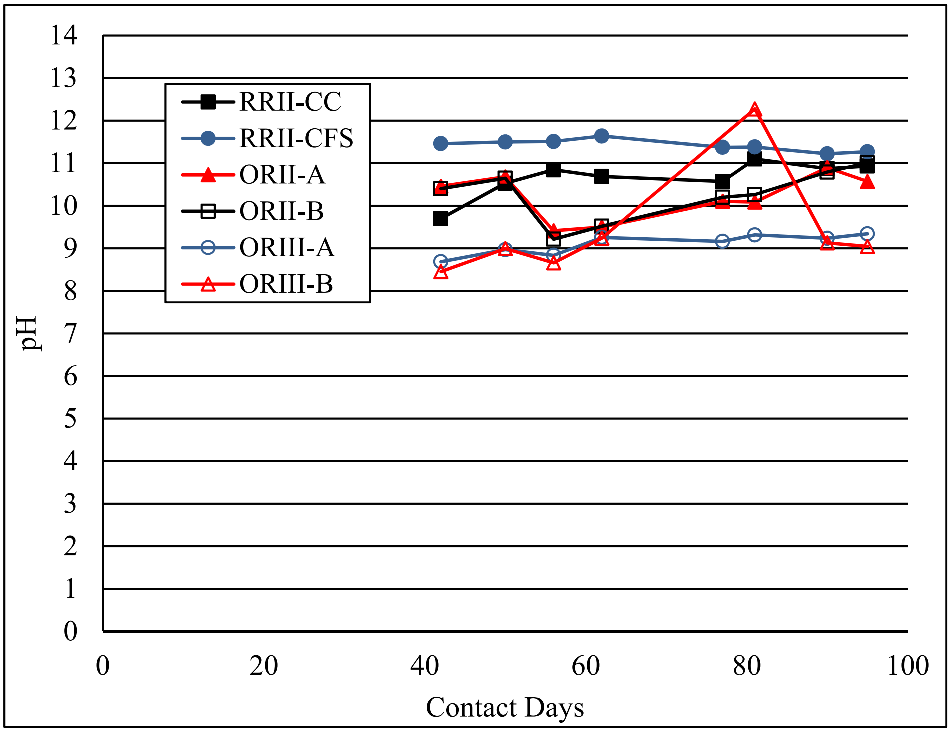


Figure 3-4. Initial Slurry pH Data Collected During Tank 12H Residual Solids Leaching Studies <u>Prior to</u> Periodic pH Adjustments.

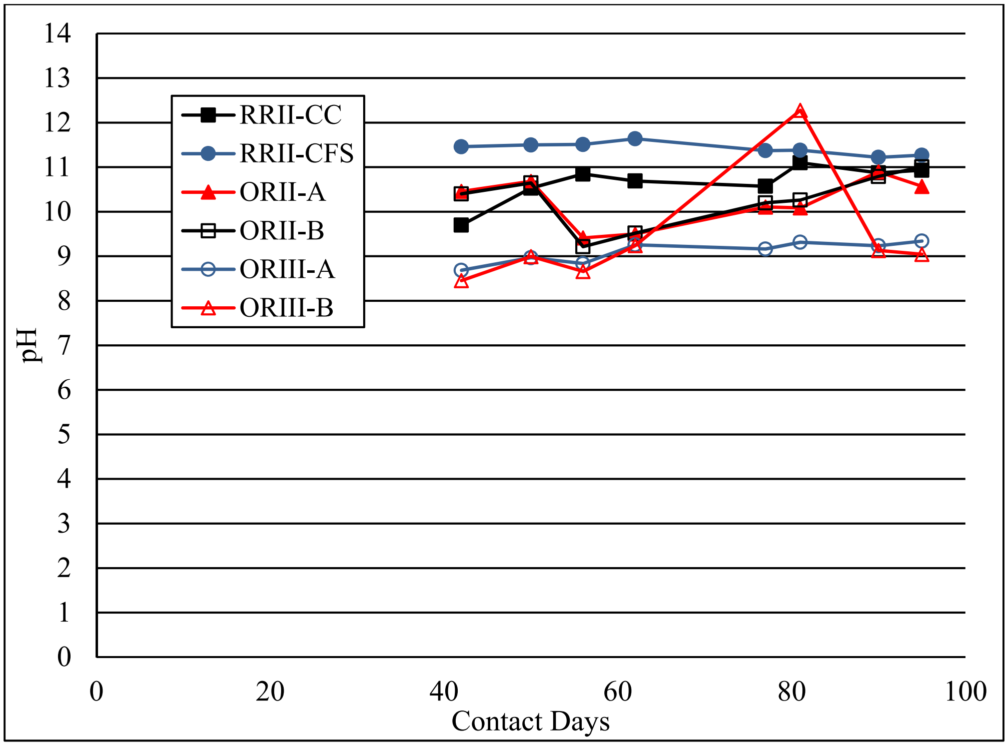


Figure 3-5. Adjusted Slurry pH Data Collected During Tank 12H Residual Solids Leaching Studies Following Periodic pH Adjustments.

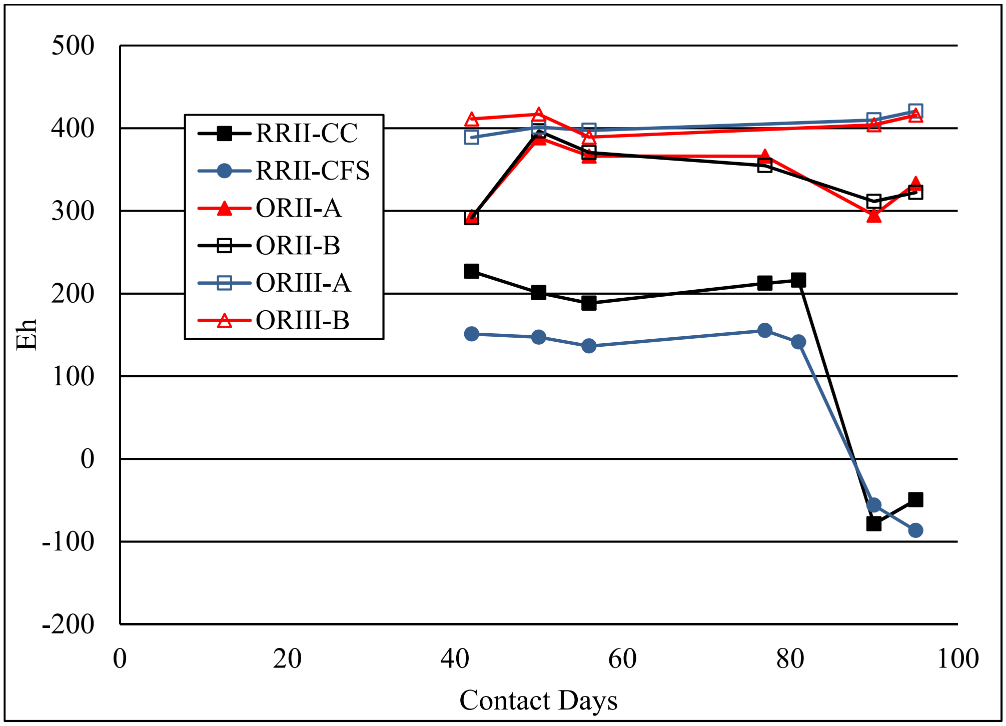


Figure 3-6. Slurry E_h Data Collected During Tank 12H Residual Solids Leaching Studies.

RRII samples, with the ORII samples having intermediate E_h values. The dramatic decrease in the E_h values for the reducing samples after contact day 81 is evident following sample washing and the addition of a second portion of FeS reagent to each bottle.

Blank control samples were maintained under the same conditions as the leachate samples throughout the testing with sub-samples being collected periodically for analysis. Analysis results for the control samples are provided in Table 3-5. The concentrations of Tc-99, I-129, Np-237, and Pu were generally below detectable limits for all control samples. For technetium, the detection limit was 1-2 orders of magnitude below the concentrations observed for most samples. The exception being the highly washed OR3-B samples toward the end of testing for which the measured technetium concentrations were near the detection limit. Almost all leachate samples contained I-129 concentrations below detectable limits, as was the case for the control samples. For neptunium, control sample detection limits were generally 1-2 orders of magnitude lower than the Np-237 concentrations observed for the oxidizing samples (reducing samples typically contained less than detectable concentrations of Np-237). Detection limits for plutonium were generally 2-3 orders of magnitude lower than the Pu concentrations observed for the oxidizing samples (reducing samples typically contained less than detectable concentrations of Pu). Detectable U-238 contaminations were observed for all control samples. The detection limits were corrected to total uranium based on the known isotopic ratios of the uranium isotopes in the Tank 12H solids. The corrected total uranium detection limits were typically an order of magnitude lower than the concentrations observed for reducing test sub-samples and 2-4 orders of magnitude lower than the uranium concentrations observed for oxidizing test sub-samples. Based on these observations, sub-sample contamination is not believed to have compromised the test results for most samples, although background uranium contamination could have influenced some of the results for the reducing samples.

The leach sample wash solutions were analyzed to calculate radionuclide losses to the wash. Wash solution analysis results are provided in Table 3-6. The initial ORII and ORIII wash solutions correspond to 410 and 450 mL of composite wash solution, respectively, from the combined washes of the duplicate ORII and duplicate ORIII samples prior to leach testing initiation. Except for the neptunium concentration for the ORIII wash, the radionuclide concentrations in these wash solutions were comparable to those observed for the leachate samples. The neptunium concentration in the ORIII wash solution of 3E-08 M was nearly an order of magnitude higher than the most concentrated leachate sample (1E-9 M). Additional wash solutions were isolated from the ORIII-B sample after the test vessel broke following contact day 62 when the solution was exposed to a large volume (8.75 L) of caustic-contaminated (pH 12) water bath solution. The solids were subsequently washed with 1.05 L of simulant to restore the sample to the target condition. The radionuclide concentrations in the ORIII-B water bath recovery solution (>8 L) and the ORIII-B sample second wash after recovery (>1 L) are also provided in Table 3-6. The radionuclide concentrations for these solutions were in the ranges observed for the leachate samples. Estimated radionuclide losses to the four wash solutions are provided in Table 3-7. Losses of the radionuclides of interest (Tc-99, I-129, U, Np-237, and Pu) to the initial ORII and ORIII wash solutions were all minimal (<2.5%) and were greatest for Np-237. Losses to the wash for the RRII leachate samples following contact day 62 can be calculated from the leachate concentrations for the first four sub-sampling events and are also minimal. Significant metal losses were observed for the ORIII-B sample after exposure to the water bath solution. These losses were primarily due to the large volumes of the wash solutions. Total metal losses for the ORIII-B sample following exposure to the water bath solution were greatest for Tc-99 (49%) and lowest for Np-237 (3%).

Table 3-1. Measured pH and E_h Data and Metal Concentrations for RRII-CC, RRII-CFS, and ORII-A Conditions with Actual Tank 12H Residual Solids.

Sample	Contact Days	pH	E_h	Molarity				
				Tc-99	I-129	U (total)	Pu (total)	Np-237
RRII-CC	42	10.3	227	4E-09	<2E-07	6E-08	3E-11	6E-11
	50	10.9	201	4E-09	<3E-07	4E-08	<5E-11	<5E-11
	56	11.1	188	2E-09	<7E-07	3E-08	<3E-12	<5E-11
	62	11.0	---	2E-09	<7E-07	3E-08	<6E-13	<5E-11
	Average	10.8	205	3E-09	<5E-07	4E-08	≤2E-11	≤5E-11
	% RSD	3.3	9.6	38	---	28	---	---
	77	10.8	212	1E-09	<3E-07	9E-09	<2E-12	<5E-11
	81	11.1	216	1E-09	<3E-07	9E-09	<6E-13	<5E-11
	90	11.0	-79	<1E-10	<4E-07	9E-09	<2E-12	<5E-11
	95	10.9	-50	<1E-10	<2E-07	8E-09	<4E-12	<5E-11
	98	---	---	3E-10	<3E-07	7E-09	7E-12	<5E-11
	Average	11.0	75	≤6E-10	<3E-07	9E-09	≤3E-12	<5E-11
	% RSD	1	215	99	---	9	---	---
RRII-CFS	42	11.5	151	1E-08	<2E-07	4E-08	4E-13	<4E-11
	50	11.5	147	1E-08	<6E-08	3E-08	<4E-11	<5E-11
	56	11.5	136	1E-08	<1E-07	3E-08	<1E-12	<5E-11
	62	11.6	---	9E-09	<5E-07	3E-08	<8E-13	<5E-11
	Average	11.5	145	1E-08	<2E-07	3E-08	≤1E-11	<5E-11
	% RSD	1	5	8	---	6	---	---
	77	11.4	155	2E-09	<2E-07	1E-08	<2E-12	<5E-11
	81	11.4	141	2E-09	<2E-07	1E-08	<8E-13	<5E-11
	90	11.2	-56	1E-09	<4E-08	1E-08	<3E-13	<5E-11
	95	11.3	-87	4E-10	<2E-08	2E-08	<2E-12	<5E-11
	98	---	---	1E-09	<1E-07	2E-08	<9E-13	<5E-11
	Average	11.3	38	2E-09	<1E-07	1E-08	<1E-12	<5E-11
	% RSD	1	332	51	---	17	---	---
ORII-A	42	10.7	293	8E-09	<8E-08	3E-08	2E-11	<4E-11
	50	10.3	388	8E-09	<4E-08	6E-07	1E-10	3E-10
	56	10.3	366	8E-09	<3E-08	5E-07	1E-10	3E-10
	62	10.2	---	9E-09	<3E-08	5E-08	8E-11	7E-11
	77	10.5	366	1E-08	<1E-08	6E-07	4E-10	3E-10
	81	10.6	---	1E-08	1E-08	2E-07	7E-11	1E-10
	90	11.0	295	9E-09	<5E-08	2E-07	1E-10	2E-10
	95	10.8	333	1E-08	<1E-08	3E-07	1E-10	2E-10
	Average	10.6	340	1E-08	≤3E-08	3E-07	1E-10	2E-10[a]
	% RSD	2	12	19	---	76	78	49[a]

[a] average and %RSD excluding 42-day sample

Table 3-2. Measured pH and E_h Data and Metal Concentrations for ORII-B, ORIII-A, and ORIII-B Conditions with Actual Tank 12H Residual Solids.

Sample	Contact Days	pH	E_h	Molarity				
				Tc-99	I-129	U (total)	Pu (total)	Np-237
ORII-B	42	10.7	292	8E-09	<1E-07	3E-08	5E-11	<4E-11
	50	10.4	397	8E-09	<2E-07	6E-07	1E-10	3E-10
	56	10.2	371	9E-09	<7E-08	5E-07	1E-10	2E-10
	62	10.3	---	9E-09	<1E-07	6E-08	2E-10	1E-10
	77	10.6	355	9E-09	<6E-08	9E-08	5E-11	8E-11
	81	10.8	---	9E-09	<6E-08	4E-08	3E-11	5E-11
	90	10.8	311	7E-09	<5E-07	2E-08	2E-11	<5E-11
	95	11.0	322	7E-09	<2E-08	4E-08	6E-11	6E-11
	Average	10.6	341	8E-09	<1E-07	2E-07	9E-11	≤1E-10
	% RSD	3	12	9	---	135	85	---
ORIII-A	42	9.0	389	5E-09	<1E-07	1E-06	<6E-11	1E-09
	50	9.2	401	6E-09	<1E-07	2E-06	1E-10	1E-09
	56	9.4	397	6E-09	<2E-07	2E-06	1E-10	9E-10
	62	9.1	---	7E-09	<2E-07	2E-06	2E-10	9E-10
	77	9.4	---	8E-09	<1E-07	2E-06	1E-10	8E-10
	81	9.3	---	7E-09	<1E-07	1E-06	9E-11	7E-10
	90	9.2	410	6E-09	<5E-08	1E-06	1E-10	7E-10
	95	9.3	421	6E-09	<4E-08	1E-06	1E-10	7E-10
	Average	9.2	404	6E-09	<1E-07	1E-06	1E-10[a]	9E-10
	% RSD	1	3	12	---	13	26[a]	23
ORIII-B	42	8.8	411	5E-09	2E-08	2E-06	<4E-11	1E-09
	50	9.2	417	5E-09	<2E-08	2E-06	7E-11	1E-09
	56	9.4	389	7E-09	<2E-07	2E-06	8E-11	9E-10
	62	9.3	---	7E-09	<3E-07	2E-06	2E-10	9E-10
	Average	9.2	406	6E-09	≤1E-07	2E-06	1E-10[a]	1E-09
	% RSD	3	4	20	---	3	49[a]	26
	77	---	---	2E-10	<5E-08	6E-09	6E-11	7E-11
	81	9.1	---	4E-10	<7E-08	2E-08	4E-11	3E-10
	90	9.0	404	<1E-10	<2E-07	3E-08	3E-11	3E-10
	95	9.3	416	<1E-10	<2E-07	4E-08	1E-10	3E-10
	Average	9.2	410	≤2E-10	<1E-07	2E-08	6E-11	2E-10
	% RSD	2	2	---	---	61	51	47

[a] average and %RSD excluding 42-day sample

Table 3-3. Leachate Slurry pH Data Collected During Testing for First Six Sub-Sampling Events.

Sub-Sampling Event	Contact Days	Sample	Average pH		
			Initial	Overall	Adjusted
1	42	RRII-1	9.7	10.3	11.0
		RRII-2	11.5	11.5	---
		ORII-3	10.5	10.7	11.1
		ORII-4	10.4	10.7	11.0
		ORIII-5	8.7	9.0	9.4
		ORIII-6	8.5	8.8	9.2
2	50	RRII-1	10.5	10.9	11.2
		RRII-2	11.5	11.5	---
		ORII-3	10.7	10.3	11.2
		ORII-4	10.6	10.4	11.5
		ORIII-5	9.0	9.2	9.6
		ORIII-6	9.0	9.2	9.9
3	56	RRII-1	10.7	11.1	11.3
		RRII-2	11.5	11.5	---
		ORII-3	9.4	10.3	11.2
		ORII-4	9.2	10.2	11.2
		ORIII-5	8.8	9.4	9.9
		ORIII-6	8.7	9.4	10.1
4	62	RRII-1	10.7	11.0	11.3
		RRII-2	11.6	11.6	---
		ORII-3	9.5	10.2	11.0
		ORII-4	9.5	10.3	11.1
		ORIII-5	9.3	9.1	9.0
		ORIII-6	9.2	9.3	9.3
5	77	RRII-1	10.6	11.0	11.5
		RRII-2	11.4	11.4	---
		ORII-3	10.1	10.5	11.1
		ORII-4	10.2	10.6	11.2
		ORIII-5	9.2	9.4	9.7
		ORIII-6	12.3	---	---
6	81	RRII-1	11.1	11.1	---
		RRII-2	11.4	11.4	---
		ORII-3	10.1	10.6	11.1
		ORII-4	10.3	10.8	11.3
		ORIII-5	9.3	9.3	---
		ORIII-6	9.1	9.1	---

Table 3-4. Leachate Slurry pH Data Collected During Testing for Seventh and Eighth Sub-Sampling Events.

Sub-Sampling Event	Contact Days	Sample	Average pH		
			Initial	Overall	Adjusted
7	90	RRII-1	10.9	11.0	11.2
		RRII-2	11.2	11.2	---
		ORII-3	10.9	11.0	11.1
		ORII-4	10.8	10.8	---
		ORIII-5	9.2	9.2	---
		ORIII-6	9.0	9.0	---
8	95	RRII-1	10.9	10.9	---
		RRII-2	11.3	11.3	---
		ORII-3	10.6	10.8	11.0
		ORII-4	11.0	11.0	---
		ORIII-5	9.3	9.3	---
		ORIII-6	9.3	9.3	---

Table 3-5. Leaching Study Blank Control Sample Analysis Results.

Control Sample	Contact Days	Molarity				
		Tc-99	I-129	U[a]	Pu[b]	Np-237
RRII	50	1E-10	---	4E-10	<4E-13	<5E-11
ORII	50	<1E-10	---	6E-10	<9E-13	<5E-11
ORII	56	<1E-10	---	7E-10	<5E-13	<5E-11
ORIII	56	<1E-10	---	2E-09	<2E-12	<5E-11
ORII	62	<1E-10	---	2E-09	5E-13	<5E-11
ORIII	62	<1E-10	---	6E-10	<8E-13	<5E-11
RRII	77	---	<5E-09	---	---	---
ORII	77	---	<9E-09	---	---	---
RRII	81	1E-10	---	5E-10	7E-13	<5E-11
RRII	90	<1E-10	---	3E-10	<7E-13	<5E-11
ORIII	90	<1E-10	---	4E-10	<5E-13	<5E-11
RRII	95	<1E-10	---	7E-10	<9E-13	<5E-11
ORIII	95	---	<6E-09	---	---	---
RRII	98	1E-9		1E-09	<2E-12	<5E-11

[a] total uranium calculated from the measured U-238 concentrations adjusted to account for the U-235 contributions based on known isotopic ratios

[b] total plutonium calculated from the measured Pu-238 concentrations adjusted to account for the Pu-239/-240 contributions based on known isotopic ratios

Table 3-6. Radionuclide Concentrations in Tank 12H Residual Wash Solutions.

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

Table 3-7. Estimated Metal Losses to Tank 12H Residual Wash Solutions.

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

Plutonium concentrations observed for the oxidizing ORII and ORIII leach test sub-samples as a function of contact days are provided in Figure 3-7. Results for reducing samples are not plotted in the figure since most samples did not contain plutonium above detectable concentration limits. Plutonium concentrations ranged from 2E-11 to 4E-10 M for all oxidizing samples. Average concentrations over all eight sub-sampling events for the ORII-A ORII-B, and ORIII-A samples ranged from 9E-11 to 1E-10 M. The lower plutonium concentrations observed for the ORII-B sub-samples from contact days 77-95 are not understood. The average plutonium concentration for the ORIII-B sample during the first 62 days of testing (1E-10 M) was similar to the other oxidizing samples. The average concentration for the ORIII-B sample from contact days 77-95 was lower (4E-11 M), presumably due to the extensive sample washing that occurred with this sample following test vessel rupture after contact day 69. The plutonium concentration for the final ORIII-B sub-sample increased to 1E-10 M, indicating that extensive washing did not greatly change the equilibrium plutonium concentration for this sample. Plutonium concentrations for almost all of the reducing test samples (RRII-CC and RRII-CFS) were below detectable limits. Observed detection limits for the initial 62 days of testing using unwashed Tank 12H sludge were near 1E-11 M. Detection limits for contact days 77-95 using washed Tank 12H sludge with reducing test samples at lower E_h values were near 3E-12 M. Assuming that the measured leach test solubility data is representative of the leachate concentrations that would be observed from the closed waste tank, the results indicate that very little plutonium should leach from Tank 12H during the early tank aging stages under reducing conditions. During later tank aging stages under oxidizing conditions (ORII and ORIII), plutonium concentrations in the leachate will probably be near 1E-10 M.

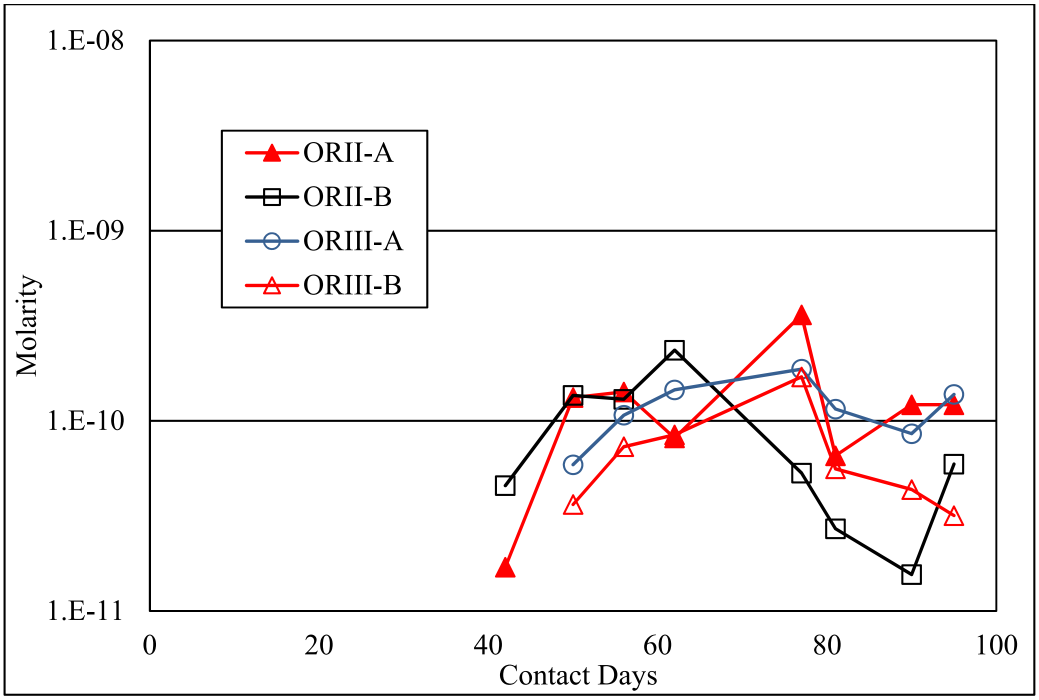


Figure 3-7. Plutonium Concentrations Versus Contact Time During Tank 12H Residual Solids Leaching Studies for Oxidizing Conditions (ORII and ORIII).

Measured uranium concentrations for all samples (reducing and oxidizing) are plotted versus contact time in Figure 3-8. The uranium concentrations for all test samples were generally higher than the concentrations observed for the other radionuclides. The highest uranium concentrations were observed for the ORIII condition. The average uranium concentration observed for the ORIII-A sub-samples over the entire 95-day test period was 1E-06 M. The average uranium concentration observed for the ORIII-B sub-samples over the first 62 days of 2E-06 M was similar to the average observed for ORIII-A sub-samples. Following extensive washing and exposure to pH 12 solution on contact day 69 the ORIII-B sub-sample concentrations decreased significantly to approximately 2E-08 M. The average uranium concentrations observed for both the ORII-A and ORII-B sub-samples over the entire 95-day test period was 2E-07 to 3E-07 M, although the concentrations observed for the two samples were notably different from each other during contact days 77-98. The average uranium concentrations observed for the reducing samples (RRII-CC and RRII-CFS) ranged from 3E-08 to 6E-08 M during the first 62 days of contact. Following washing and after decreasing the E_h values for the samples during contact days 77 through 98, the average uranium concentrations for the reducing samples decreased slightly and ranged from 9E-09 to 1E-08 M. Overall, the results indicate that uranium concentrations in porewater leachates from Tank 12H residuals during the early tank aging stages under reducing conditions should be near 4E-08 M. During intermediate tank aging stages under oxidizing conditions (ORII conditions), uranium concentrations in the leachate will probably be near 3E-07 M. During the latest tank aging stage under ORIII conditions, uranium concentrations in the leachate will probably be near 2E-06 M, until significant amounts of the uranium have been removed and the leachate concentration begins to decrease (represented by the highly washed ORIII-B sub-samples).

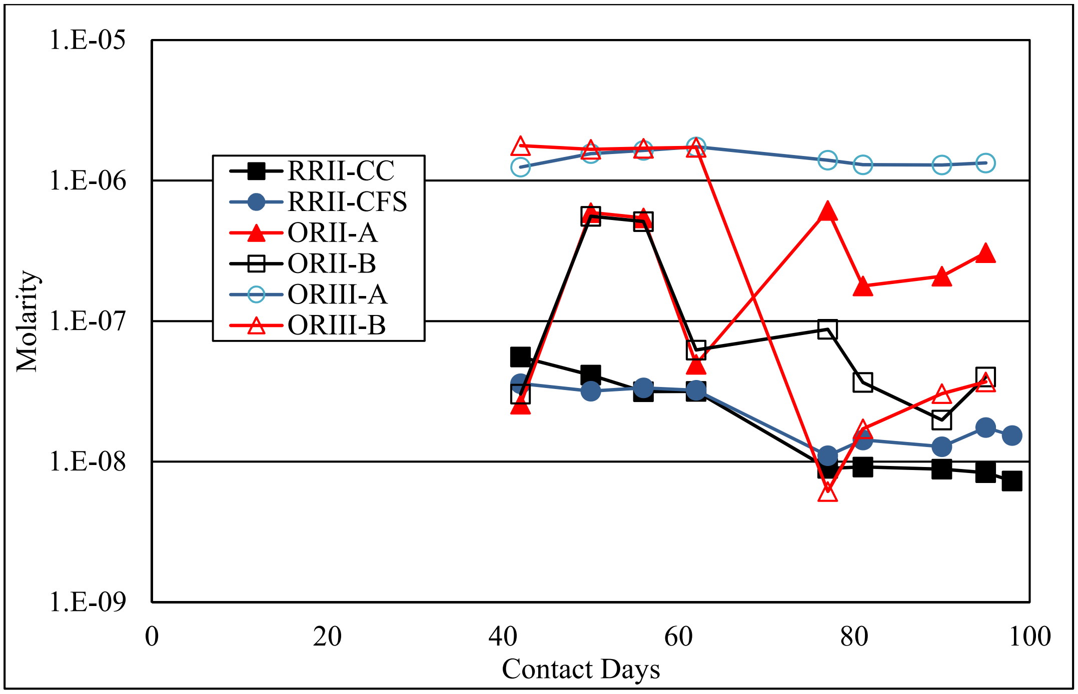


Figure 3-8. Uranium Concentrations Versus Time During Tank 12H Residual Solids Leaching Studies.

Measured technetium (Tc-99) concentrations for all samples (reducing and oxidizing) are plotted versus contact time in Figure 3-9. Technetium concentrations observed for the ORII-A, ORII-B, and ORIII-A test sub-samples ranged from 5E-09 to 1E-08 M across the entire 95-day testing period. During the first 62 contact days, the average uranium concentration in the ORIII-B sub-samples of approximately 6E-09 M was similar to the other oxidizing samples. After exposure to significant wash volumes following the 62-day sub-sampling event, the average technetium concentration in the ORIII-B sub-samples decreased to ≤2E-10 M (contact days 77-95) presumably due to removal of significant amounts of soluble technetium during extensive washing. The average technetium concentration for the unwashed reducing samples containing calcium carbonate solids (RRII-CC) during the first 62 contact days was 3E-09 M. The average technetium concentration for the unwashed reducing samples containing CFS solids (RRII-CFS) during the first 62 contact days of 1E-08 M was significantly higher than the RRII-CC sub-sample average and was similar to the oxidizing sub-sample concentrations. Following sample washing, the technetium concentrations of both reducing samples decreased with the CC sub-samples containing lower technetium concentrations than the CFS sub-samples during each sub-sampling event. The technetium concentrations appeared to decrease as the E_h values for the reducing samples decreased toward the end of testing. The average technetium concentrations observed for contact days 77 through 98 ranged from ≤6E-10 to 2E-09 M for the reducing samples. Overall, the results indicate that technetium concentrations in porewater leachates from Tank 12H residuals during the early tank aging stages under reducing conditions may be near 2E-09 M after significant porewater volumes have passed through the system. Under oxidizing conditions (ORII and ORIII) the technetium concentrations will likely increase again to near 1E-08 M until significant amounts of the technetium are washed away.

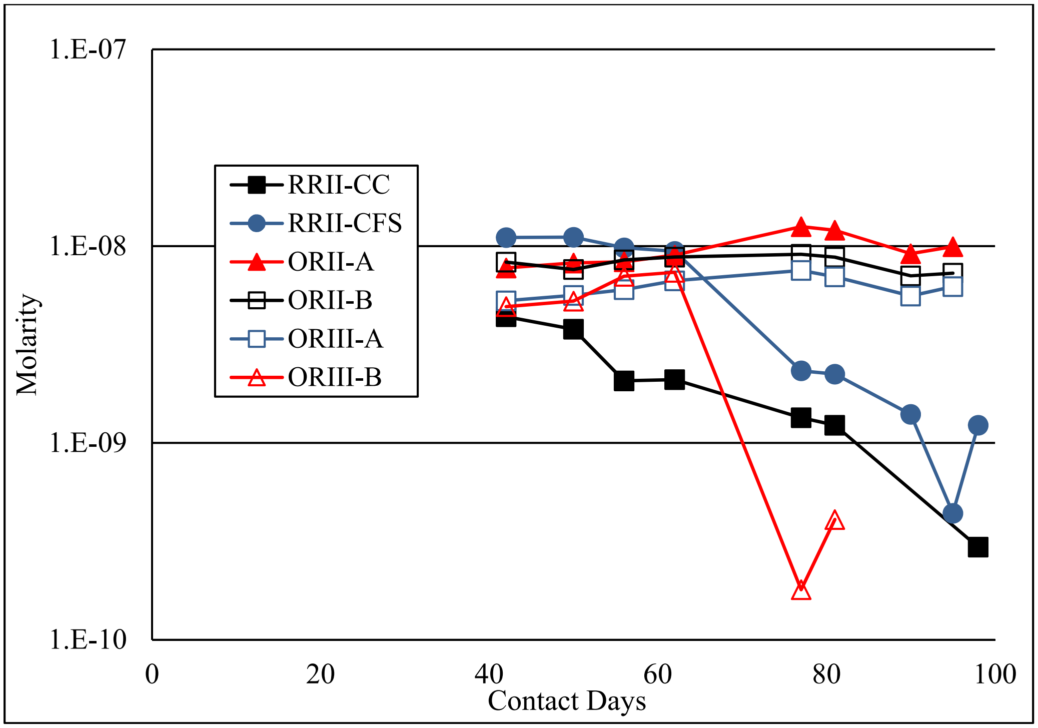


Figure 3-9. Technetium Concentrations Versus Time During Tank 12H Residual Solids Leaching Studies.

Neptunium (Np-237) concentrations observed for the leach test sub-samples from the oxidizing samples (ORII and ORIII) versus contact time are provided in Figure 3-10. Results for reducing samples are not plotted in the figure since most samples did not contain neptunium above detectable concentration limits. The highest neptunium concentrations were observed for the ORIII sub-samples. The average neptunium concentration for the ORIII-A sub-sample during the entire 95-day test duration was 9E-10 M. The average neptunium concentration for the ORIII-B sample over the first 62 days of testing was 1E-09 M. Following extensive washing, the average ORIII-B leachate sub-sample neptunium concentration was 2E-10 M, indicating that significant soluble neptunium was lost to the wash. The average neptunium concentrations observed for the ORII-A and ORII-B sub-samples ranged from ≤1E-10 to 2E-10 M. Nearly all reducing sub-samples (RRII-CC and RRII-CFS) contained below detectable concentrations of neptunium (typically <5E-11 M). Overall, the results indicate that neptunium concentrations in porewater leachates from Tank 12H during the early tank aging stages under reducing conditions may be very low (<5E-11 M). Under intermediate oxidizing conditions (ORII) the neptunium concentrations will likely increase to near 2E-10 M. In the latter tank aging stages (ORIII), the neptunium concentrations will likely increase to near 1E-09 M.

Iodine (I-129) concentrations in nearly every leachate sub-sample were below detectable limits (ranging from <1E-8 to <7E-7 M). Two leachate samples were observed to contain above detectable levels of I-129. The 81-day ORII-A sub-sample contained an I-129 concentration of 1E-08 M. The 42-day ORIII-B sub-sample contained an I-129 concentration of 2E-08 M. Based on these results, it appears that the leachate samples may contain iodine at concentrations near, but generally below the detectable concentration limit.

Selected leachate samples were also analyzed to determine the soluble metal concentrations and the concentrations of various anions. The concentrations of various dissolved metals in the ORII-A and -B samples and the ORIII-A sample after 90 contact days are provided in Table 3-8. As expected, the concentrations of all metals were low (<200 mg/L). The sodium concentrations ranged from 90-190 mg/L (≤8.3E-03 M) with the lowest Na concentration being observed for the ORIII-A sample. The sodium source was the Tank 12H residual solids since the original porewater sodium concentration was only 1.4 mg/L. The concentrations of all other metals were ≤6 mg/L, including Al, B, and Si which are components of the glass vessels. These results also indicate that significant Al dissolution did not occur from the Tank 12 residual solids. Calcium concentrations were only slightly elevated relative to the original simulant composition (1 mg/L) due to addition of calcium salts to the samples. At test conclusion, two leachate samples were analyzed to determine the soluble anion concentrations. Results are provided in Table 3-9. The concentrations of all anions measured including oxalate were below detectable limits (50-100 mg/L) for the ORII-A sample. The concentrations of all anions except sulfate (86 mg/L) were below detectable limits for the ORIII-A sample.

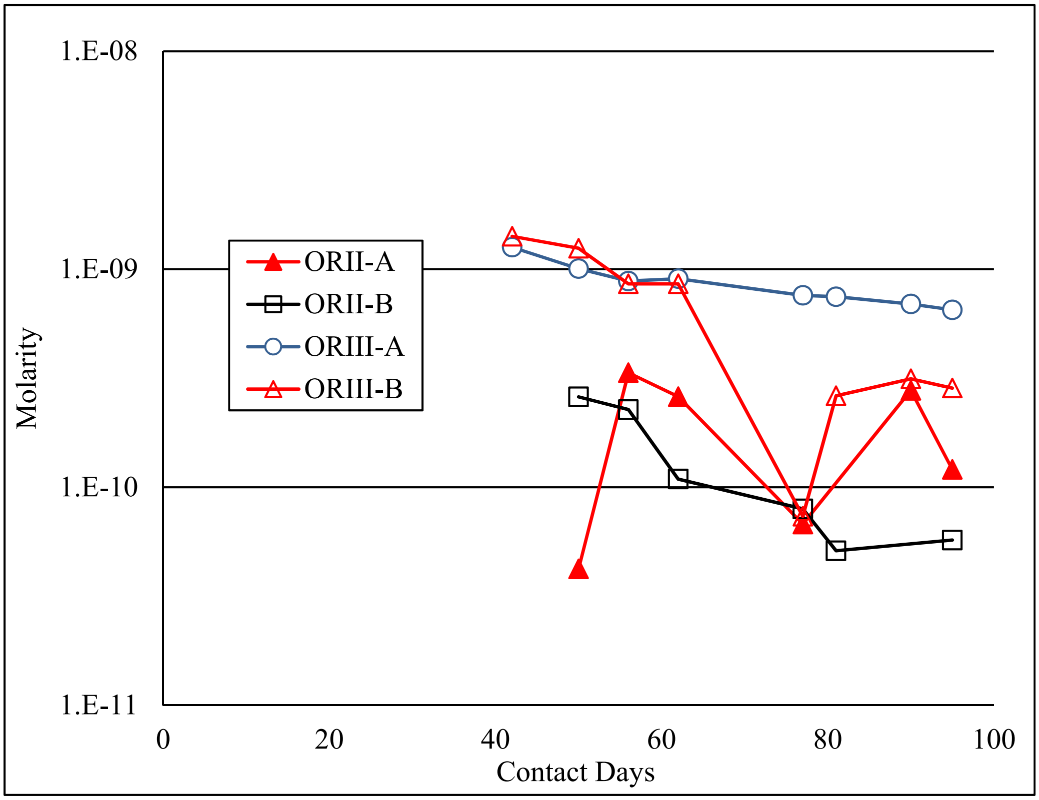


Figure 3-10. Neptunium Concentrations versus Time during Tank 12H Residual Solids Leaching Studies for Oxidizing Conditions (ORII and ORIII).

Table 3-8. Soluble Metal Concentrations in Selected Leachate Samples After 90 Contact Days.

Sample ID	mg/L		
	ORII-A	ORII-B	ORIII-A
Al	5.2	3.7	<0.44
B	4.1	1.3	0.54
Ca	1.2	2.4	2.6
Fe	0.31	0.34	0.11
Mg	0.05	0.07	0.18
Na	190	125	90
Si	1.4	0.59	0.72

Table 3-9. Soluble Anion Concentrations in Selected Leachate Samples at Test Conclusion.

Sample ID	mg/L	
	ORII-A	ORIII-A
F^-	<50	<50
Cl^-	<50	<50
Br-	<50	<50
NO_2^-	<50	<50
NO_3^-	<50	<50
PO_4^{3-}	<50	<50
SO_4^{2-}	<50	86
$C_2O_4^{2-}$	<50	<50
CHO_2^-	<50	<50
CO_3^{2-}	<100	<100

.

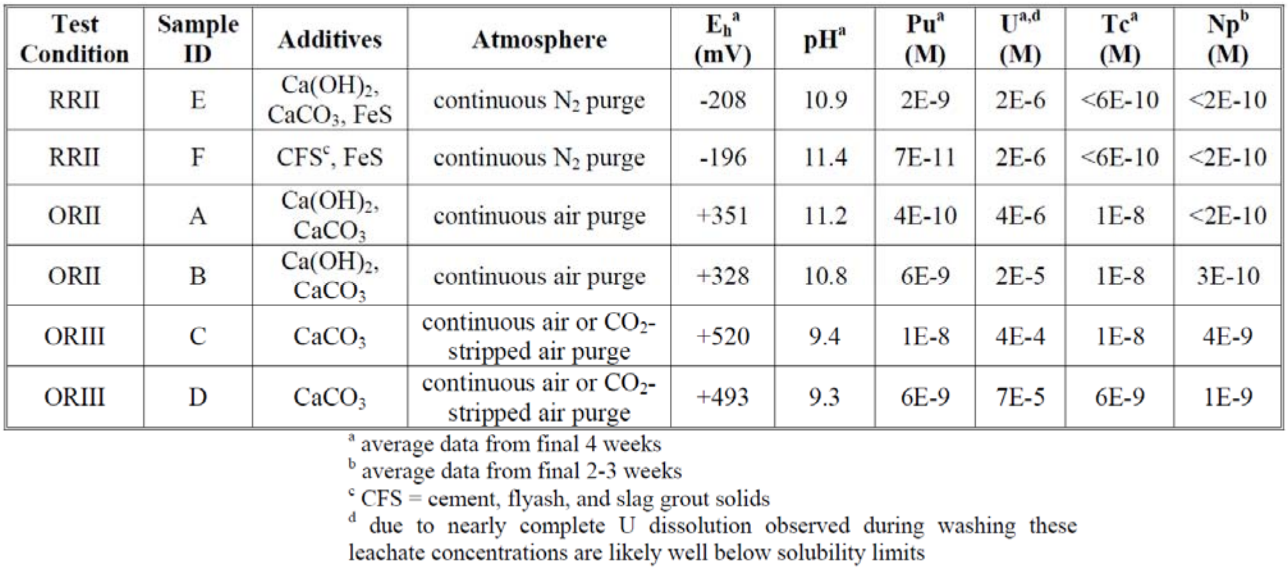
4.0 Discussion

Measured radionuclide solubilities for SRS Tank 18F residual solids were reported previously and are summarized in Table 4-1.

Tc-99 solubilities reported for Tank 18F residual solids under reducing conditions were below detectable concentration limits (<6E-10 M). Average technetium solubilities under reducing conditions (RRII) ranged from 3E-09 to 1E-08 M for unwashed Tank 12H residual samples and from ≤6E-10 to 2E-09 M for washed samples. Higher technetium concentrations may have been associated with the fact that much higher E_h values were observed for the reducing Tank 12H samples during most of the leach testing. Under oxidizing conditions (ORII and ORIII), Tc-99 solubilities observed for Tank 18F residuals (6E-09 to 1E-08 M) were comparable to the average solubilities observed with Tank 12H solids (2E-10 to 1E-08 M excluding highly washed sub-samples).[6]

I-129 solubilities with Tank 12H residual solids in grout porewater simulants were generally below detectable concentration limits (average of all data <2E-07 M). No iodine leachate analysis was conducted for the Tank 18F residual solids.[6] Short-term leaching tests were conducted using distilled water during Tank 12H characterization studies conducted by Oji.[12] Approximately 0.5 g of composite Tank 12H solids were contacted with 30 g of de-ionized water (1.7 g sludge per L of water slurry versus 30 g sludge/L of simulant slurry for Tank 12H testing) with periodic agitation. The residual sludge composite samples characterized by Oji contained Tank 12H floor:mound mass ratios ranging from 1.9 to 5.6 versus the Tank 12H leachate samples which had a floor:mound ratio of 3.5. The water slurries were filtered and analyzed by Oji and the reported I-129 concentrations ranged from 2.2E-03 to 2.9E-03 wt. %. In addition, a composite liquid fraction was isolated from Tank 12H floor residuals which contained 20 dpm/mL of I-129. The Tank 12H leachate sub-samples isolated during porewater leaching studies typically contained below detectable concentrations of I-129 (<9 dpm/mL average value). Four Tank 12H leachate and wash samples contained values above detectable amounts ranging from 0.3 to 1.0 dpm/mL. An I-129 concentration of 1 dpm/ml in the leachate corresponds to an iodine concentration of 4E-06 to 9E-06 wt. % in the original solid (depending on slurry volume) assuming that all I-129 leached from the sample. The measured I-129 concentrations from the current leaching studies were 3 orders of magnitude lower than those reported by Oji for water washes even though the sludge concentration in the leach test slurries was much higher (30 g/L versus 2 g/L for Oji characterization studies).

Table 4-1. Measured pH, E_h, and Metal Concentrations for Each Pore Water Test Condition Using Actual Tank 18F Residual Solids (data reported by King, 2016[6]).



Test Condition	Sample ID	Additives	Atmosphere	E_h[a] (mV)	pH[a]	Pu[a] (M)	U[a,d] (M)	Tc[a] (M)	Np[b] (M)
RRII	E	$Ca(OH)_2$, $CaCO_3$, FeS	continuous N_2 purge	-208	10.9	2E-9	2E-6	<6E-10	<2E-10
RRII	F	CFS[c], FeS	continuous N_2 purge	-196	11.4	7E-11	2E-6	<6E-10	<2E-10
ORII	A	$Ca(OH)_2$, $CaCO_3$	continuous air purge	+351	11.2	4E-10	4E-6	1E-8	<2E-10
ORII	B	$Ca(OH)_2$, $CaCO_3$	continuous air purge	+328	10.8	6E-9	2E-5	1E-8	3E-10
ORIII	C	$CaCO_3$	continuous air or CO_2-stripped air purge	+520	9.4	1E-8	4E-4	1E-8	4E-9
ORIII	D	$CaCO_3$	continuous air or CO_2-stripped air purge	+493	9.3	6E-9	7E-5	6E-9	1E-9

[a] average data from final 4 weeks
[b] average data from final 2-3 weeks
[c] CFS = cement, flyash, and slag grout solids
[d] due to nearly complete U dissolution observed during washing these leachate concentrations are likely well below solubility limits

This discrepancy in the I-129 leachate concentrations is not currently understood. It is expected that pH differences in the leachate solutions used (pH 5-6 in the water leachates used by Oji and pH 9-11 in the porewater leachates used in this study) would impact the I-129 solubility, but a solubility difference exceeding 3 orders of magnitude was unexpected. Other differences in the Tank 12H leaching studies and those conducted by Oji include the addition of grout or grout-representative phases and the manipulation of the ORP with the Tank 12H samples. It has been postulated that the drying of the Tank 12H residual samples during handling and subsequent storage may have resulted in the loss of iodine vapor from the samples. Characterization efforts are in progress to determine if the residual sample used for Tank 12H leaching studies contains a significantly reduced I-129 concentration relative to the initial characterization sample.

Uranium solubilities reported for Tank 18F residual solids were compromised by the fact that most of the uranium in the samples was lost to the wash solution prior to testing.[6] Despite this fact, uranium solubilities observed for Tank 18F residuals under reducing conditions (2E-06 M) exceeded those observed with Tank 12H solids (7E-09 to 6E-08 M) by at least 2 orders of magnitude, even though more reducing conditions were observed with the Tank 18F solids than the Tank 12H solids (~-200 mV vs ~-100 mV with Tank 12H solids). Under oxidizing conditions (ORII and ORIII), uranium solubilities observed for Tank 18F residuals

(4E-06 to 4E-04 M) were also higher than the solubilities observed with Tank 12H solids (6E-09 to 2E-06 M), even though significant uranium was removed from the Tank 18F leach test samples during preliminary washing.[6]

Np-237 solubilities observed under reducing conditions (RRII) for Tank 18F residual solids were below detectable concentration limits (<2E-10 M).[6] Neptunium solubilities for Tank 12H solids were also typically below detectable concentration limits under reducing conditions (<5E-11 M). Under oxidizing conditions (ORII and ORIII), Np-237 solubilities observed for Tank 18F residuals (<2E-10 to 4E-09 M) were comparable to the solubilities observed with Tank 12H solids (<4E-11 to 1E-09 M).

Under reducing conditions (RRII), plutonium solubilities observed for Tank 18F residuals (7E-11 to 2E-09 M) exceeded those observed with Tank 12H solids (<3E-13 to <5E-11 M, excluding 42-day data points) even though more reducing conditions were observed with the Tank 18F solids.[6] Under oxidizing conditions (ORII and ORIII), plutonium solubilities observed for Tank 18F residuals (4E-10 to 1E-08 M) were higher than the solubilities observed with Tank 12H solids (2E-11 to 4E-10 M).

A summary of predicted solubilities for assumed plutonium and uranium species reported by Denham[9, 10] at various E_h values is provided in Table 4-2. The E_h values 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 oxidizing samples for the more realistic cases where equilibrium with dissolved oxygen does not exist and the E_h values are lower. The more realistic E_h values were +240 mV for the ORII condition and +290 mV for the ORIII condition. The average experimentally observed E_h values for the ORII condition with Tank 12H residuals ranged from +340 to +341 mV and the average values observed for the ORIII condition ranged from +404 to +410 mV. These data are intermediate between the values used by Denham for these conditions.

Solubility predictions were calculated for pure Pu and U phases and apparent solubilities were also calculated for the actinides co-precipitated with Fe phases. [9, 10] The apparent solubilities are based on the primary iron phase solubility and the ratio of the actinides to the iron phase. In all cases, the predicted uranium solubility is greater than the 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, $PuO_2(OH)_2 \cdot H_2O$. 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, $UO_3 \cdot 2H_2O$, 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.

Average experimentally observed pH, E_h, and leachate metal concentrations for each Tank 12H residual test sample are provided in Table 4-3. The pH values were within 0.5 pH units of the target values for all samples, although considerable pH variability was observed during much of the testing period (see previous discussion). The experimentally observed average E_h value for the two RRII samples during the final 2 weeks of testing was -68 mV (earlier values were considerably higher). The experimentally observed average E_h value for the two ORII samples was +341 mV. The experimentally observed average E_h value for the two ORIII samples was +405 mV. Based on these results, the speciation would be expected to be

Table 4-2. 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 $UO_3{\cdot}2H_2O$	+240	3E-11	5E-05
ORII[b]	PuO_2[d] or $UO_3{\cdot}2H_2O$	+560	5E-08	6E-05
ORII[c]	Maghemite co-precipitate	+240	7E-12	2E-11
ORIII[a]	PuO_2[d] or $UO_3.2H_2O$	+290	3E-11	4E-06
ORIII[b]	PuO_2[d] or $UO_3.2H_2O$	+680	8E-08	4E-06
ORIII[c]	Maghemite co-precipitate	+290	1E-13	5E-13

[a] from Table 11 of SRNL-STI-2012-00404[2]; E$_h$ values represent more realistic, non-equilibrium conditions with dissolved oxygen

[b] from Table 12 of SRNL-STI-2012-00404[2]; E$_h$ values represent equilibrium conditions with dissolved oxygen

[c] from Table 14 of SRNL-STI-2012-00404[2]; represents apparent solubility based on primary iron phase solubility and Fe:Pu:U ratio

[d] solubility based on hydrous, amorphous plutonium oxide phase

Table 4-3. Measured pH, E$_h$, and Metal Concentrations for Each Pore Water Test Condition Using Actual Tank 12H Residual Solids.

Test Condition	Sample ID	Additives	Atmosphere/ Condition	E$_h$ (mV)	pH	Molarity				
						Pu[a]	U[a]	Tc[a]	Np[a]	I[a]
RRII	A	$Ca(OH)_2$, $CaCO_3$, FeS	continuous N_2 purge; unwashed	+205[b]	10.8[b]	≤2E-11[b]	4E-8[b]	3E-9[b]	≤5E-11[b]	<5E-7[b]
	B	CFS[c], FeS		+145[b]	11.5[b]	≤1E-11[b]	3E-8[b]	1E-8[b]	<5E-11[b]	<2E-7[b]
	A	$Ca(OH)_2$, $CaCO_3$, FeS	continuous N_2 purge; washed	-64[d]	11.0[d]	≤3E-12[d]	9E-9[d]	≤6E-10[d]	<5E-11[d]	<3E-7[d]
	B	CFS[c], FeS		-71[d]	11.3[d]	<1E-12[d]	1E-8[d]	2E-9[d]	<5E-11[d]	<1E-7[d]
ORII	A	$Ca(OH)_2$, $CaCO_3$	continuous air purge; washed	+340[e]	10.6[e]	1E-10[e]	3E-7[e]	1E-8[e]	2E-10[e]	≤3E-8[e]
	B	$Ca(OH)_2$, $CaCO_3$		+341[e]	10.6[e]	9E-11[e]	2E-7[e]	8E-9[e]	≤1E-10[e]	<1E-7[e]
ORIII	A	$CaCO_3$	continuous air or CO_2-stripped air purge; washed	+404[e]	9.2[e]	1E-10[e]	1E-6[e]	6E-9[e]	9E-10[e]	<1E-7[e]
	B	$CaCO_3$		+406[b]	9.2[b]	1E-10[b]	2E-6[b]	6E-9[b]	1E-9[b]	≤1E-7[b]
	B	$CaCO_3$	continuous air or CO_2-stripped air purge; highly washed	+410[f]	9.2[f]	6E-11[f]	2E-8[f]	≤2E-10[f]	2E-10[f]	<1E-7[f]

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

[b] average data from first 4 weeks

[c] CFS = cement, flyash, and slag grout solids

[d] average data from final 2 weeks

[e] 8-week average

[f] average data from final 4 weeks

dominated by the hydrous, amorphous PuO_2 phase and the very soluble U(VI) phase, $UO_3 \cdot 2H_2O$ across the range of test conditions. Comparison of the average results observed experimentally for Pu and U to the predicted solubilities reported by Denham[9, 10] reveals the following.

Pu concentrations for the reducing RRII samples were typically below detectable concentration limits. During the final four testing weeks the average Pu concentrations ranged from <3E-13 to 7E-12 M (Table 3-2). The predicted Pu solubility at an E_h of -470 mV for both pure PuO_2 and the co-precipitate phase ranged from 8E-13 to 3E-11 M. The plutonium solubility appears to be near or below the predicted range, even though the measured E_h values were significantly higher than the values used for the calculations. Observed average U concentrations for the reducing RRII samples after washing ranged from 7E-09 to 2E-08 M. These results are higher than the predicted values at -470 mV for this condition for both pure UO_2 and the co-precipitate phase which ranged from 2E-12 to 5E-09 M.

For the ORII condition, observed Pu concentrations for the filtered leachate samples ranged from 2E-11 to 4E-10 M (Table 3-2), which is in the range of the predicted values for the pure PuO_2 and the co-precipitate phase (7E-12 to 5E-08 M). Observed U concentrations for the ORII leachate samples ranged from 2E-08 to 6E-07 M, which is intermediate in value relative to the predicted values for both pure $UO_3 \cdot 2H_2O$ and the co-precipitate phase which ranged from 2E-11 to 6E-05 M.

For the ORIII condition, observed Pu concentrations for the filtered leachate samples ranged from 3E-11 to 2E-10 M (Table 3-2), which is in the range of the predicted values for the pure PuO_2 and the co-precipitate phase which ranged from 1E-13 to 8E-08 M. Observed U concentrations for the ORIII leachate samples ranged from 6E-09 (highly washed sample) to 2E-06 M. Most measured uranium concentrations were near the highest predicted uranium concentration of 4E-06 M for $UO_3 \cdot 2H_2O$ (oxygen equilibrium or non-equilibrium conditions).

In general, the predicted Pu and U concentrations for co-precipitated phases are all lower than were experimentally observed. Thus, the author concludes that a significant fraction of the Pu and U in the Tank 12H residual solids sample used in this testing appears to be pure Pu and U oxide phases and not co-precipitated phases. Plutonium concentrations for both oxidizing cases (where higher solubilities were expected) did not exceed the predicted values for the cases where dissolved oxygen is assumed. Uranium concentrations observed for the RRII condition exceeded the predicted values, although the higher E_h values for these samples may explain this result. Uranium concentrations for the oxidizing cases did not exceed the predicted values for the cases where dissolved oxygen is assumed.

Technetium, iodine, and neptunium predicted solubilities as reported by Denham[9, 10] are provided in Table 4-4. Dramatic shifts in technetium solubility were predicted as the system shifts from reducing to oxidizing conditions due to speciation changes from hydrated TcO_2 to highly soluble oxidized species such as TcO_4^-. Likewise, neptunium solubility was predicted to increase significantly due to speciation changes from the hydrated NpO_2 phase to the Np(V) species, $NpO_2(OH)$. No solubility-controlling phases were identified for iodine under any of the expected conditions (RRII, ORII, or ORIII) in initial waste release modeling.[9] However, analyses of the residual waste sampled from the Tank 12H floor revealed higher than anticipated I-129 inventories,[16] suggesting that iodine release from waste tanks may be solubility-controlled.

Iodine can form solubility-limiting solid phases with several metals that are present in residual tank waste. A scoping analysis[10] of possible controls on the release of I-129 from Tank 12H residual waste provided estimates of solubility controls on I-129 based on the presence of silver and mercury. Under various oxidizing conditions, the calculated solubility of silver iodide (AgI) ranges from 9.8E-09 to 2.7E-07 M and the calculated solubility of mercury (I) iodide (Hg_2I_2) ranges from 1.3E-07 to 1.2E-04 M. The lower solubilities in the ranges are associated with conditions for tanks in which the waste layer is below the water table. Under reducing conditions, the elemental forms of silver and mercury are stable, and no solubility limitations from AgI or Hg_2I_2 are applicable.

Under reducing conditions (RRII), observed technetium concentrations were initially similar (contact days 42-62) to oxidizing conditions with average solubilities ranging from 3E-09 to 1E-08 M. From contact days 77-98 (following sample washing and more FeS addition), the average concentration range decreased to ≤6E-10 to 2E-09 M. These results are in the range of predicted solubilities for pure phase $TcO_2 \cdot 1.6\ H_2O$ and the co-precipitate phase which ranged from 1E-14 to 1E-08 M. Under reducing conditions (RRII), observed neptunium concentrations were below detectable concentration limits (<5E-11 M) and the detection limit was intermediate between the predicted solubilities for pure-phase NpO_2 and the co-precipitate phase which ranged from 5E-15 to 1E-09 M.

Table 4-4. Predicted Solubilities of Assumed Tc and Np Phases.

Condition	Initial Phase	E_h (mV)	Tc (M)	I (M)[e]	Np (M)
RRII[a]	$TcO_2 \cdot 1.6\ H_2O$, $NpO_{2\ (am,\ hyd)}$[d], AgI or Hg_2I_2	-470	1E-08	no limit	1E-09
RRII[c]	Maghemite co-precipitate	-470	1E-14	---	5E-15
ORII[a]	no Tc solubility controlling phase; $NpO_{2\ (am,\ hyd)}$[d]	+240	no limit	2.7E-07 (AgI) 2.0E-05 (Hg_2I_2)	3E-07
ORII[b]	$NpO_2(OH)_{(am,\ aged)}$[d]	+560	---	---	7E-07
ORII[c]	Maghemite co-precipitate	+240	1E-13	---	4E-14
ORIII[a]	no Tc solubility controlling phase; $NpO_{2\ (am,\ hyd)}$[d]	+290	no limit	3.8E-08 (AgI) 1.2E-04 (Hg_2I_2)	2E-06
ORIII[b]	$NpO_2(OH)_{(am,\ aged)}$[d]	+680	---	---	5E-05
ORIII[c]	Maghemite co-precipitate	+290	2E-15	---	9E-16

[a] from Table 11 of SRNL-STI-2012-00404[9]; E_h values represent more realistic, non-equilibrium conditions with dissolved oxygen

[b] from Table 12 of SRNL-STI-2012-00404[9]; E_h values represent equilibrium conditions with dissolved oxygen

[c] from Table 14 of SRNL-STI-2012-00404[9]; represents apparent solubility based on primary iron phase solubility and Fe:Tc:Np ratio

[d] solubility based on hydrous (hyd), aged, and amorphous (am) neptunium oxide and oxy-hydroxide phases

[e] from Table 2 of SRNL-STI-2015-00339[10]

No solubility limit was reported by Denham[9, 10] for technetium under oxidizing conditions, due to the high solubilities of oxidized forms of technetium such as TcO_4^-. However, only a portion of the Tc-99 was removed from the Tank 12H residual samples during washing and leach testing (Table 3-7), indicating that Tc dissolution is solubility-controlled under the test conditions. For the ORII condition, average neptunium concentrations ranged from ≤1E-10 to 2E-10 M, and these values are intermediate between the predicted solubilities for pure phase NpO_2 and the co-precipitate phase which ranged from 4E-14 to 7E-07 M. For the ORIII condition (excluding the highly washed sub-samples), average neptunium concentrations ranged from 9E-10 to 1E-09 M, which is intermediate between the predicted solubilities for pure phase NpO_2 and the co-precipitate phase which ranged from 9E-16 to 5E-05 M.

In general, the predicted Tc and Np concentrations for co-precipitated phases are all lower than were experimentally observed. Thus the author concludes that a significant fraction of the Tc and Np in the Tank

12H residual solids used in this testing appears to be pure Tc and Np oxide phases and not co-precipitated phases. Tc and Np concentrations for both of the oxidizing cases (where higher solubilities were expected) did not exceed the predicted values for the cases where equilibrium with dissolved oxygen is assumed.

I-129 results for nearly all samples were below detectable concentration limits. Two oxidizing samples were observed to contain I-129 above the limits (concentrations ranging from 1E-08 M to 2E-08 M). These concentrations are well below the predicted solubility for H_2I_2, but in the range of solubility for AgI.

5.0 Conclusions

Leaching studies were completed for actual SRS Tank 12H residual solids using customized test equipment and a sub-sampling system and sample handling methodology designed to minimize or eliminate sample contamination from the SRNL shielded cells test facility. Tank 12H was exposed to extensive mechanical cleaning operations, low temperature aluminum dissolution (caustic additions), and bulk oxalic acid cleaning operations prior to tank closure and grouting. Very low leachate metal concentrations (near analytical detection limits in some cases) were analyzed along with blank samples to confirm the suitability of the testing approach. Results indicate that the concentrations of all radionuclides analyzed (I-129, Tc-99, U, Np-237, and Pu) were below the maximum predicted concentrations utilized for PA modeling. In contrast to Tank 18F leaching studies, analysis of preliminary wash solutions indicated minimal losses of the radionuclides to the wash.

Uranium was the most soluble radionuclide analyzed with average concentrations as high 2E-06 M being observed. The maximum uranium leachate concentration was significantly lower than was observed for Tank 18F residual solids, presumably due to speciation differences between the samples (XRD analysis confirmed that Tank 18F residuals contained a more soluble uranium carbonate phase). I-129 concentrations were generally below detectable concentration limits (≤6E-7 M). Observed Tank 12H leachate plutonium concentrations (near 1E-11 M for oxidizing samples) were lower than the other radionuclides analyzed. Plutonium solubilities observed for Tank 12H residuals were considerably lower than were observed for Tank 18F residuals. Np-237 and Tc-99 leachate concentrations in the oxidizing Tank 12H samples were intermediate in concentration relative to U and Pu and were similar to those observed with Tank 18F residuals, with the exception of the reducing technetium samples which had higher solubilities than the Tank 18F residuals (likely due to higher E_h values for Tank 12H samples). The lack of significant I-129 in the Tank 12H leachate solutions is inconsistent with previous leaching studies in water. Additional characterization of the Tank 12H residuals used for testing is in progress to understand this discrepancy.

Comparison of the Tank 12H residual solubility data to model predictions reveals that most radionuclide concentrations were between predictions for co-precipitated iron phases and assumed pure phases under equilibrium conditions with dissolved oxygen. Under reducing conditions, technetium concentrations were in the predicted range even though solution E_h values were higher than the targets. Under oxidizing conditions, technetium was predicted to be highly soluble, but results indicated that only a portion of the Tc-99 dissolved. Under reducing conditions, uranium concentrations exceeded predictions by less than an order of magnitude, but this is likely associated with the fact that E_h values were higher than the targets. The trends in the solubilities indicate that a significant fraction of the radionuclides in the Tank 12H residual solids used in this testing appears to be pure metal oxide phases and not co-precipitated phases.

6.0 Recommendations, Path Forward, and Future Work

Based on the results, it is believed that the current testing methods and equipment were successfully utilized to evaluate the leaching properties of Tank 12H residual solids. Alternative methods may need to be considered for sample agitation in future testing. Additional waste testing could provide general information regarding how various tank closure factors impact elements of concern in waste tank residuals and their associated solubilities. Solubility testing on a range of tank samples, reflecting varying tank cleaning techniques and different tank residual constituents, would help to develop a broader database of the leaching properties of SRS tank residual solids into the groundwater aquifer. For instance, the current database does not include evaluations of typical F Area Tank Farm sludge residuals (Tank 18F was a unique tank composition). Likewise, H Area sludge residuals not exposed to oxalic acid cleaning have not been evaluated.

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