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Radionuclide Release from Savannah River Site Tank 18 Waste Residual Solids under Conditions Anticipated Following Tank Closure

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ABSTRACT

Leaching studies have been conducted with actual Savannah River Site High Level Waste Tank 18 residual radioactive sludge and grout-representative solids in pore water simulants targeting solution pH and E_h values anticipated during aging of the closed tank. Soluble metal concentrations in the leachate solutions observed after several weeks followed the general trends predicted for plutonium and uranium oxide phases, and were consistent with simulant test results. The highest uranium, neptunium, and plutonium concentrations during leaching studies were observed at average pH and E_h values of 9.4 and +506 mV, respectively. The highest technetium concentrations were observed under oxidizing conditions at E_h values ranging from +325 to +520 mV and pH values ranging from 9.3 to 11.2. The lowest concentrations for all metals were observed under reducing conditions (~-200 mV) at an average pH of 11.2. The maximum metal concentrations observed during leach testing for neptunium, plutonium, and technetium were all below the maximum predicted values, while uranium concentrations exceeded predictions. For oxidizing test conditions, the residual sludge samples were pre-washed with pore water simulants to reduce the pH prior to initiating the leaching tests. Higher metal concentrations were observed for the wash solutions than were observed for any leach test sample and the concentrations of the actinides significantly exceeded the predicted values. Mass balance calculations indicated that most of the uranium dissolved from the oxidizing test samples during washing, while <20% of each of the other elements dissolved.

INTRODUCTION

Current practice for closing High Level Waste (HLW) tanks at the Savannah River Site (SRS) involves removing waste to the maximum extent practical using mechanical sluicing methods, disconnecting all transfer lines and penetrations into the tank, and filling the internal volume of the tank with grout (concrete). As of December 2016, Savannah River Remediation has closed SRS Tanks 5, 6, 12, 16, 17, 18, 19, and 20. Performance Assessment (PA) modeling of the release of radionuclides from residual waste solids in these tanks into the environment over extended time periods indicated that uranium, neptunium, plutonium, and technetium are among the most likely risk drivers for environmental contamination.[i] The PA and supporting waste release modeling indicated that plutonium release from SRS Tank 18 residuals (which contained relatively high Pu concentrations) was highest during the tank aging period identified as Oxidizing Region III, which was predicted to occur after >2,120 pore volumes of grout pore water have passed through the system. At this stage, the dominant grout phase is expected to be calcite ($CaCO_3$). (Note: Grout pore water is defined as natural infiltrating groundwater exposed to the grout fill material and the residual waste solids layer within the closed tank environment.

Furthermore, a pore volume represents the total volume of the pore voids within the grout fill material inside the closed tank.)

In order to support SRS tank closure efforts, a test methodology was developed using simulated sludge waste solids, grout-representative solid reagents, and grout pore water solutions (based on SRS groundwater compositions) to produce slurries representing tank residuals and conditions following closure. Solution pH and E_h (Oxidation Reduction Potential versus the Standard Hydrogen Electrode) values were targeted which are expected during the various aging periods following waste tank closure. The initial pore water condition (Reducing Region II) was predicted to have an E_h of -0.45 V and a pH of 11.1. The pore water is expected to become increasingly oxidizing and less basic with increasing time and pore water throughput. The second aging period (Oxidizing Region II) was predicted to have an E_h of +0.56 V and a pH of 11.1. The final aging period following tank closure (Oxidizing Region III) was predicted to have an E_h of +0.68 V and a pH of 9.2. The target conditions for each aging period are summarized in Table 1. The target E_h values under oxidizing conditions assume equilibrium with dissolved oxygen.

The equipment designed and the test methodology developed to conduct the leach testing were successfully utilized to evaluate the metal solubilities and leaching characteristics of actual SRS Tank 18 residual sludge solids under the conditions of interest. This testing was conducted remotely within the Savannah River National Laboratory (SRNL) Shielded Cells facility. The equipment was designed for remote operation and a sampling system and methodology were utilized to rigorously exclude residual radionuclides present in the shielded cells environment from contaminating the test samples. This approach should be suitable for leach testing of other SRS waste tank residual materials within this test facility.

Table 1. Target SRS Tank 18 Pore Water Conditions.

Target Condition	**E_h (mV)**	**pH**
Reducing Region II	-470	11.1
Oxidizing Region II	+560	11.1
Oxidizing Region III	+680	9.2

EXPERIMENTAL DETAILS

Customized glass test vessels of various types were prepared for leach testing in the SRNL shielded cells. All test vessels were made of 70.2 mm ID tubing and the main portions of the vessels were ~8 cm tall. The vessels fit snugly into sample slots in the top of a customized water bath. The water bath was positioned over two multi-position stir plates and leach sample agitation during testing was accomplished using magnetic stir bars placed in the test vessels. A water recirculator was utilized for temperature control with a set temperature of 22.1 ºC. Individual sample temperatures were measured using a K-type thermocouple near the end of testing and all samples were found to be 21 ºC. A customized water bubbler manifold was constructed and attached to the back of the water bath in order to monitor and control gas flow through each individual sample vessel during testing. Low gas supply pressures (typically <5 PSI) were utilized to purge the test vessels. Gas flow control through the vessels was accomplished on the downstream side of each sample 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 testing.

Three types of glass vessels were prepared for testing including: caustic scrubber, humidifier, and leach sample 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.

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 to avoid impacting the test slurry pH during air purging. Each scrubber vessel included a gas supply line consisting of a 12 mm OD fritted glass gas dispersion tube to promote the formation of numerous gas bubbles and high gas/liquid contact. A second port with a magnetized cap 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 the outlet gas. Scrubber vessels were not needed for reducing test conditions. 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.

Downstream vessels included the humidifier and leach test vessels. 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 humidifer vessel was utilized to treat the supply gas for each sample type with the water-saturated gas stream then being split between two leach test vessels. Each humidifier vessel included a 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 magnetized cap and two gas outlet lines containing demisters. The outlet lines led to the leach test vessels. The glass leach sample vessels included a gas supply port, a sample/reagent addition 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.

Gases were passed through a series of vessels for treatment to produce the desired sample conditions. The vessels in a given series were connected using 1/8” ID Tygon tubing with quick-connect fittings 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. Control vessels for each sample type were also incorporated into the system. CO_2-stripped air was used as the baseline purge gas for the oxidizing samples. 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 was used as the purge gas for the reducing samples throughout testing.

Based on the simulant studies and the expected solubilities of most of the metals, it was anticipated that very low metal concentrations near analysis detection limits would be observed.[ii] The need to measure very low concentrations was especially problematic for plutonium, since plutonium contamination of samples in the shielded cells is known due to high background plutonium levels within the facility. As a result, a sub-sampling system and methodology were developed to allow for the isolation of filtered samples in the analysis bottles without contamination.

The sub-sampling system involved modified, plastic shielded analysis bottles with caps containing ¼" OD polyethylene tubing and quick-connect attachments. The sampling system included a syringe with a directly-attached filter. Tubing (1/8") was attached to the downstream side of the filter with a male quick-connect fitting attached to the other end of the tubing. The filter end of the sub-sampling unit was covered with a small plastic ziploc bag to minimize the possibility of post-filtration contamination in the cell. 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. A separate vent line containing a quick-connect fitting and an in-line filter was also attached to the analysis bottle during sub-sampling to prevent sample contamination through the vent line from plutonium dust. 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. In addition, prior to testing, the cell floors were wiped clean, and prior to each sampling event, disposable cloth wipes were laid down on the cell floor to minimize contamination.

Outside of the shielded cells environment, a synthetic infiltration water simulant based on the average composition observed for groundwater collected from non-impacted wells within the SRS water table aquifer was developed and prepared from ultrapure water and reagent grade chemicals (composition provided in Table 2). Tank 18 grout pore water simulants were prepared from the infiltration water for each condition shown in Table 1 with an initial focus on achieving the target pH values of 11.1 (Reducing Region II and Oxidizing Region II) and 9.2 (Oxidizing Region III). The higher pH (11.1) pore water simulant was prepared from the infiltration water by adding $CaCO_3$ reagent to saturation and $Ca(OH)_2$ reagent until the target pH was achieved. The lower pH (9.2) pore water simulant was prepared from the infiltration water by the addition of $CaCO_3$ to saturation (no calcium hydroxide addition). This resulted in a solution containing trace amounts of $CaCO_3$ solids with a pH near 10. Subsequent, brief (~15 minutes) purging of the solution with air resulted in the absorption of CO_2 and a reduction of the solution pH to near 9.

All of the as-prepared simulants had solution E_h values near +500 mV. Solutions for reducing and oxidizing test cases were subsequently purged with high purity nitrogen and air, respectively. For the Reducing Region II case, overnight nitrogen purge resulted in a solution E_h value near -100 mV. Subsequent addition of reagent grade ferrous sulfide (FeS) solids to the nitrogen-purged solution resulted

Table 2. As-Prepared Composition of Infiltration Water Simulant Based on SRS Groundwater.

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

in an E_h value near -200 mV. Analysis revealed that these preparations result in elevated calcium concentrations (measured values 7-28 mg Ca/L) relative to the initial infiltration water simulant (1 mg Ca/L).

These simulants were transferred into the SRNL Shielded Cells facility and used for leach test sample preparations. Known volumes of the simulants were transferred into the test vessels and additional calcium carbonate solids or grout solids were added to the test vessels. Calcium carbonate solids were utilized as a grout-representative phase in the oxidizing test samples (Oxidizing Regions II and III) and in one reducing test sample (Reducing Region II). These additions were made to the test samples under the appropriate gaseous atmospheres (nitrogen for reducing cases and air for oxidizing cases). Utilizing this single reagent ($CaCO_3$) to represent the grout solids simplified the system and allowed for better control of the solution pH and E_h.

Cement, Fly Ash, and Slag (CFS) grout solids were used rather than calcium carbonate reagent in one Reducing Region II test sample. The CFS solids were initially prepared as a monolith following the grout recipe utilized to fill SRS Tank 18. The recipe included 125 parts of Cement Type I/II, 210 parts of Slag Grade 100, and 363 parts of Fly Ash Class F. Sand was not added as a component of the monolith since both fly ash and slag contain significant quantities of silicon. Prior to contact with the infiltration water simulant, 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 in order to minimize air exposure of the grout.

CFS and calcium carbonate solids were added to each test sample at a concentration of 16.7±0.1 g/L slurry. FeS solid was added to reducing samples at a concentration of 3.1-3.2 g/L slurry. Total slurry volumes ranged from 200-250 mL.

An archived sample of residual radioactive sludge solids retrieved from the floor of SRS Tank 18 prior to tank closure was utilized for leach testing. The sludge sample composition is summarized in Tables 3 (elemental) and 4 (radionuclide). Tank 18 solids were added to each test sample at a concentration of 30.1±0.2 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 final tank aging condition (Oxidizing Region III).

Table 3. Major Tank 18 Residual Sludge Elemental Components as Reported by Oji.[iii]

Element	Wt. %
Al	11.0
Ca	2.9
Fe	9.8
Mg	3.8
Mn	1.0
Si	2.2
U	6.3

Table 4. Selected Tank 18 Residual Sludge Radionuclide Components as Reported by Oji.[iii]

Radionuclide	µCi/g
Tc-99	2.7E-02
Th-229	1.9E-05
Th-230	1.4E-04
U-233	1.2E-03
U-234	2.0E-02
Np-237	9.1E-03
U-238	2.0E-02
Pu-239	1.6E+01
Pu-240	3.6E+00
Pu-241	1.6E+01
Am-241	7.5E+00
Cm-244	1.2E-01

Both pH and 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. 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 E_h probes were checked using Thermo Scientific Oxidation-Reduction Potential (ORP) Standard 967901. The ORP standard was checked once during each series of sample measurements and the standard data ranged from +218 to +222 mV (E_h range: +418 to +422 mV) during testing. All reported sample E_h values are relative to the Standard Hydrogen Electrode (SHE). A standard correction of +200 mV was applied to all ORP data to convert the data to E_h format, based on the manufacturer instructions and data obtained for the ORP standard.

Since the oxidizing sample types represent grout aging stages where many volumes of pore water have passed through the system, these samples were washed with two portions of the appropriate simulant solutions prior to the initiation of leaching studies. Scoping studies indicated that the wash volumes used would decrease the soluble sodium concentration to near that of the as-prepared simulant composition. The reducing samples were not washed initially, since this condition represents the early portion of grout aging. After approximately three weeks of leach testing, the liquid was decanted from each of the reducing samples and fresh simulant was added. As a result, testing under reducing conditions was conducted in two phases with the second testing phase involving lower solution ionic strength. Leach test samples were monitored during testing to confirm that evaporative or entrainment sample losses associated with continuous sample gas purging were not significant. During the entire course of the leaching studies, 30-50 volume percent of the initial sample slurries was consumed due to sub-sampling. During testing, an air purge (without CO_2 removed) was periodically utilized to lower the pH of the oxidizing samples, as needed to adjust the pH to near the target values. Alternatively, additional calcium hydroxide reagent was added as needed during testing to raise the pH.

Sample aliquot volumes of 5-13 mL (depending on the volume needed for analysis) were collected from the leaching test vessels for analysis after the measurement of the solution pH and E_h at approximately weekly intervals. Seven sampling events were conducted over a period of nearly two months (sub-sample collection days: 9, 16, 23, 27, 37, 44, and 51). The aliquots were filtered as described above through 0.1-µm polyvinyl difluoride (PVDF) syringe filter units without opening the bottle caps. Blank sample analyses generally indicated that contamination from the cell environment was minimal for all metals analyzed, although uranium was consistently observed in sample blanks at relatively low levels.

Each filtered sample received an addition of 0.5-1.5 mL of 5 M nitric acid (adjusted for the target sample volume to give an acid:sample volume phase ratio near 8) to acidify the samples and avoid post-filtration precipitation. Aliquots of the acidified 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 measured combined Pu-239/Pu-240 concentrations in dpm/mL converted to molar concentrations assuming 100% Pu-239. Pu-238 concentrations were negligibly small (on a molar concentration basis) for all samples.

Additional experimental details are reported seperately.[iv]

RESULTS AND DISCUSSION

Leaching studies were conducted with actual SRS Tank 18 residual solids and grout-representative solids in pore water simulants under controlled atmosphere conditions targeting pH and E_h values representing three aging periods following tank closure. Testing was continued for approximately two months with weekly pH/E_h measurement and sample collection. The average pH, E_h, and metal concentrations (data averages from final 2-4 weeks) observed for each test sample are provided in Table 5. These concentrations were observed in the final weeks after testing following the sample washing that occurred during leach test initiation (oxidizing samples) and after the first few weeks (reducing samples).

The target pH values were achieved to within 0.5 pH units for all samples and an E_h range of approximately 0.7 V was observed for the final samples. For most test samples, steady-state pH and E_h data were observed during the final 2-3 weeks of testing. The lowest and highest E_h values observed of ~-0.2 V and ~+0.5 V were significantly less negative and less positive, respectively, than the target values (Table 1). These findings are consistent with previous tests with simulated Tank 18 sludge solids and are the result of the presence of multiple solid phases and complex solution chemistry. Based on the previous testing, achievement of more negative and more positive E_h values would require the addition of non-representative reductants and oxidants, respectively. During testing, the Oxidizing Region III-D sample was inadvertently flooded with water from the bubbler system. As a result, this sample was exposed to a larger total wash volume. This exposure resulted in lower leachate concentrations for this sample than were observed for the replicate Oxidizing Region III-C sample, as discussed below.

Table 5. Post-wash pH, E_h, and Metal Concentrations for Each Pore Water Test Condition Using Actual Tank 18F Residual Solids.

Test Sample	Additives	Atmosphere	E_h[a] (mV)	pH[a]	U[a,d] (M)	Np[b] (M)	Pu[a] (M)	Tc[a] (M)
Oxidizing Region II-A	$Ca(OH)_2$, $CaCO_3$	air	+351	11.2	4E-6	<2E-10	4E-10	1E-8
Oxidizing Region II-B			+328	10.8	2E-5	3E-10	6E-9	1E-8
Oxidizing Region III-C	$CaCO_3$	air (with/ without CO_2)	+520	9.4	4E-4	4E-9	1E-8	1E-8
Oxidizing Region III-D			+493	9.3	7E-5	1E-9	6E-9	6E-9
Reducing Region II-E	$Ca(OH)_2$, $CaCO_3$, FeS	nitrogen	-208	10.9	2E-6	<2E-10	2E-9	<6E-10
Reducing Region II-F	CFS[c], FeS		-196	11.4	2E-6	<2E-10	7E-11	<6E-10

[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 may not represent saturation

Leachate uranium concentrations for each sample were higher by several orders of magnitude than all other metals. The maximum uranium concentration of 4E-4 M was observed for the Oxidizing Region III-C sample. Presumably due to excessive washing (and removal of uranium), the uranium concentration for the Oxidizing Region III-D sample was significantly lower than the replicate -C sample. Intermediate uranium concentrations were observed for the Oxidizing Region II samples (-A and -B) while the lowest uranium concentrations (2E-6M) were observed for the Reducing Region II samples. The uranium concentrations observed versus time for the Oxidizing Region II-B sample were not stabilized at test conclusion while concentrations of other samples were generally stable.

The initial leachate solutions for the Reducing Region II samples were decanted from the test vessels after approximately three weeks of contact in order to provide two sets of results representing the early portion of this aging period where higher ionic strength is expected and the later portion with lower ionic strength. Much higher uranium concentrations were observed for the reducing samples during the first contact phase than those reported in Table 5 from the second phase. The uranium concentrations for the first contact phase ranged from 1E-5 M for the Reducing Region II-F sample to 7E-4 M for the Reducing Region II-E sample. The lower concentration observed for the Reducing Region II-F sample is presumably associated with the CFS solids and indicates that the presence of grout solids results in lower leachate uranium concentrations during this early phase of tank aging. Significantly lower uranium concentrations (2E-6 M) were observed following decantation of the first leachate solution (as shown in Table 5). It is unknown whether this difference is associated with ionic strength differences between the first and second leachates or is associated with variability in the uranium speciation and accessiblity within the sample.

Surprisingly, the control sample analysis indicated that uranium contamination occurred for the later control samples. However, the highest uranium concentration in the control samples of 1E-7 M is significantly lower than all leach test sample concentrations observed.

For oxidizing test conditions, the Tank 18 samples were washed with pore water simulants prior to initiating the leaching tests. As shown in Table 6, higher metal concentrations were observed for the wash solutions than were observed for any leach test sample and the concentrations of uranium, neptunium, and plutonium significantly exceeded the maximum values in the PA. Mass balance calculations based on these concentrations indicated that nearly all of the uranium from the Oxidizing Region III test samples dissolved during the washing step. However, <20% of each of the other metals dissolved. These results indicate that it is possible to exceed the observed leachate concentrations during initial pore water contacts.

Significant uranium solubility is typically observed in tank sludge wash solutions and commonly observed uranium crystalline sludge phases include Clarkeite, $Na((UO_2)O)(OH)\cdot H_2O$, and sodium diuranate, $Na_2U_2O_7\cdot 6H_2O$. The Tank 18F residual sample used for testing included both the Clarkeite uranium phase and a uranium carbonate phase, Cejkaite, $Na_4UO_2(CO_3)_3$, not previously observed in other tank waste samples. Carbonate phases such as this would be expected to be more soluble than typical oxide phases. A review of the Tank 18 processing history prior to closure indicated that the conditions favored the formation of carbonate complexes of the actinide metals.

Leachate neptunium concentrations were 4-5 orders of magnitude lower than the uranium concentrations observed under the same conditions. The maximum neptunium concentration of 4E-9 M was observed for the Oxidizing Region III-C sample. Lower than detectable amounts of neptunium (<2E-10 M) were observed for the Reducing Region II samples and the Oxidizing Region II-A sample. Neptunium activity levels in the original sample (Table 4) on a curie basis were lower than any of the four radionuclides analyzed, but mass balance calculations indicate that only a small percentage of the total neptunium dissolved during testing.

The maximum plutonium concentration of 1E-8 M was observed for the Oxidizing Region III-C sample. A gradual increase in Pu concentration was observed during testing for both Oxidizing Region II test samples versus time (not shown), and it is unclear based on the data whether saturation and equilibrium were achieved during the testing period. In addition, the Pu concentrations observed for the Oxidizing Region II-A sub-samples were consistently an order of magnitude lower than the -B samples. This difference is not understood, since nearly identical sample preparation methods and amounts were used for each sample. The lowest plutonium concentrations were observed for the Reducing Region II samples with the sample containing CFS solids (-F) exhibiting much lower soluble plutonium levels (7E-11 M) than the sample containing calcium carbonate solids (-E sample; 2E-9 M Pu). As was observed for the uranium samples, this result indicates that the presence of grout solids may serve to inhibit plutonium leaching into the pore water, at least during the first tank aging stage under reducing conditions.

Only one control sample contained plutonium above detectable limits. This control sample contained plutonium at levels just above detection and well below most leach test sample results. This observation indicates that the test methodology and sub-sample design successfully eliminated plutonium contamination and the plutonium concentrations observed for the samples can be attributed to the metal leaching from the Tank 18F residual solids.

The highest leachate technetium concentration of 1E-8 M was observed for both Oxidizing Region II and III samples (-A through -C). Analysis and mass balance calculations for the wash solutions indicate that 17% of the technetium may have been lost from this sample during washing. The data trends in the technetium concentrations for the oxidizing samples indicate that the technetium concentration did not

Table 6. Metal Concentrations Observed for ORII-A and ORIII-C Wash Solutions.

Test Sample	Pu (M)	U (M)	Np (M)	Tc (M)
Oxidizing Region II-A	4.0E-08	3.2E-04	1.3E-09	1.0E-08
Oxidizing Region III-C	3.0E-07	4.6E-03	2.9E-08	9.4E-09

stabilize during testing but continued to gradually increase. Lower than detectable amounts of technetium (<6E-10 M) were observed for the Reducing Region II samples.

To support Performance Assessment modeling of the closed waste tank, metal solubilities were calculated by Denham[v] for pure metal oxide phases under oxidizing conditions assuming equilibrium with dissolved oxygen, as well under non-equilibrium conditions which is believed to be more realistic. Solubility predictions were calculated for the pure metal oxide phases under these conditions and apparent solubilities were calculated for the metals co-precipitated with Fe phases. The apparent solubilities are based on the primary iron phase solubility and the ratio of the metals of interest to the iron phase. The predicted apparent solubilities for the co-precipitated phases were much lower than the solubilities for the pure phases.

In general, the predicted metal concentrations for co-precipitated phases are all lower than were experimentally observed. Thus we conclude that a significant fraction of the in the Tank 18 residual solids sample used in this testing appears to be pure metal oxide phases and not co-precipitated phases. Uranium concentrations observed under oxidizing conditions exceeded the maximum predicted values, indicating that the uranium speciation in the Tank 18 residuals may be dominated by a more soluble species (such as a carbonate phase) than assumed in the PA modeling. Maximum neptunium and plutonium concentrations did not exceed the predicted values for the cases where dissolved oxygen is assumed. Data trends for technetium indicated that equilibrium and saturation had not been achieved. No solubility limit was reported by Denham for technetium under oxidizing conditions, due to the high solubilities of oxidized forms of technetium.

CONCLUSIONS

Leaching studies were completed for actual SRS Tank 18F 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. 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 plutonium, technetium, and neptunium in washed samples were below the maximum predicted concentrations utilized for PA modeling, although trends in the technetium data indicate that equilibrium and saturation were not achieved during the 2-month testing period. Observed uranium concentrations were high and significantly exceeded predictions, presumably due to the differences between the actual and assumed chemical speciation. After test conclusion it was discovered that significant losses of uranium to the wash solutions occurred for oxidizing samples and that the concentrations of uranium, plutonium and neptunium were higher in the wash solutions than in any leachate samples analyzed. The metal concentrations in the wash samples also exceeded the maximum predicted concentrations assumed and utilized for PA modeling. This was an unexpected result and is presumably associated with the fact that more soluble chemical forms of these metals are present. Due to the uranium losses to the wash and the apparent near depletion of uranium from the samples, the uranium concentrations reported for the oxidizing samples are not believed to represent solubility limits. Despite the discovery of high metal concentrations in the wash solutions the measured leachate concentrations for the remaining metals (neptunium, plutonium, and techentium) are believed to be representative of the maximum concentrations that might be observed during the major portion of the tank aging time periods of interest.

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