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Determining the Release of Radionuclides from Tank Waste Residual Solids

D. H. Miller, K. A. Roberts, K. M. L. Taylor-Pashow, D. T. Hobbs

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EXECUTIVE SUMMARY

Current practice for closing high-level waste tanks at the Savannah River Site involves removing as much of the HLW as possible, disconnecting all transfer lines and penetrations into the tanks, and filling the internal volume of the tanks with grout. Performance assessment modeling of the release of radionuclides from tank waste solids in these tanks indicated that plutonium, neptunium, technetium, and uranium are among the most likely risk drivers. Waste release testing was identified as needed to provide additional information regarding the residual waste solubility assumptions used in the F-Area and H-Area Tank Farm Performance Assessments' waste release models. The proposed testing was described generally in the Savannah River Site Liquid Waste Facilities Performance Assessment Maintenance Program FY2014 Implementation Plan. Savannah River Remediation LLC requested that the Savannah River National Laboratory perform such testing with available tank waste residuals after method development using surrogate materials. This document reports findings from the testing completed to date and recommendations for continued work.

Key findings based on experimental work completed to date with surrogate materials include the following.

- Pore water electron transfer potentials (E_h) produced in these studies upon contact of synthetic infiltration water with surrogate tank closure solids are lower than those used in PA modeling. This suggests that in short-term experiments, kinetic controls on the E_h values of the synthetic pore waters in contact with grout solids dominate over the equilibrium controls assumed in the PA waste release modeling.

- The zero head-space method appears viable for testing the release of radionuclides from solids under reducing conditions, but not under oxidizing conditions due to oxygen depletion.

- Researchers must account for the alkalinity and redox potential of the tank waste solids to ensure target pH and E_h values will be achieved in radionuclide release testing.

- The addition of hydrogen peroxide will increase the E_h potentials of OR3, but not OR2 pore water to about +420 mV and decrease the pH by about one pH unit. These changes are transitory due to the decomposition of peroxide in alkaline solutions.

- The addition of ozone increases the potentials of OR2 and OR3 pore waters above +1000 mV as long as excess ozone is present. The addition of ozone generates acid which lowers the pH of the pore OR2 and OR3 waters.

- Under moderate reducing conditions, the quantity of Pu and U dissolved from the surrogate Tank 18 solids increased in pore water solutions that feature less reducing E_h and lower pH values.

- The presence of cement solids in the leaching tests generally reduced the dissolution of Pu and U from the surrogate Tank 18 solids.

Based on the findings and conclusions summarized in this technical report, the authors recommend that leachate testing with surrogate materials be continued and finalized prior to initiating testing with actual waste residuals. Testing with actual tank waste solids would be expected to provide additional information regarding the residual waste solubility assumptions used in the Tank Farm Performance Assessments' waste release models. The following specific actions are recommended with respect to continued waste release testing.

- Reduce the lower quantifiable limit for detection of Pu in leachates by increasing the size of the aliquot and employ longer alpha counting times.

- Determine the effect, if any; of the syringe filter pore size on Pu/U concentrations in leachates to ensure that the measured Pu/U concentrations reflect only dissolved species.

- Complete experimental studies evaluating the use of ozone to increase oxidizing E_h potentials and the use of dithionite, sulfide and ferrous ion to increase reducing E_h potentials so that surrogate pore waters have E_h potentials at the targeted values.

- Test production of surrogate pore waters using only solid phases believed to be controlling the pH and E_h at equilibrium conditions.

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LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
HLW	High-Level Waste
PA	Performance Assessment
SRR	Savannah River Remediation LLC
SRS	Savannah River Site
DOE	Department of Energy
CFS	Cement, Flyash & Slag
FY	Fiscal Year
SIW	Synthetic Infiltration Water
RR2	Reduced Region II
OR2	Oxidizing Region II
OR3	Oxidizing Region III
SCFH	Standard cubic feet per hour
LPM	Liters per minute
E_h	Electron transfer potential

1.0 Introduction

Current practice for closing high-level waste (HLW) tanks at the Savannah River Site (SRS) involves removing as much of the HLW as possible, disconnecting all transfer lines and penetrations into the tanks, and filling the internal volume of the tanks with grout. Savannah River Remediation (SRR) closed Tanks 18 and 19 in 2012 and Tanks 5 and 6 in 2013. Performance assessment (PA) modeling of the release of radionuclides from tank waste solids in these tanks indicated that plutonium, neptunium, technetium, and uranium are among the most likely risk drivers.[1] Due to the relatively high concentration of plutonium in Tank 18, the PA indicated that plutonium release was highest upon entering the oxidized region III, when the redox potential, E_h, is +680 mV and the pH is 9.2. At this stage, the dominant grout phase is calcite ($CaCO_3$).[1]

Waste release testing was identified as needed to provide additional information regarding the residual waste solubility assumptions used in the F-Area and H-Area Tank Farm Performance Assessments' waste release models. The proposed testing was described generally in the Savannah River Site Liquid Waste Facilities Performance Assessment Maintenance Program FY2014 Implementation Plan.[2] This plan proposed that waste release experiments be performed with actual tank waste residuals after method development using surrogate materials. Thus, SRR requested that the Savannah River National Laboratory (SRNL) design and perform such testing with available tank waste samples.[3] This document reports findings from this testing completed to date.

2.0 Experimental Procedure

2.1 Preparation of Synthetic Infiltration Water

A synthetic infiltration water (SIW) stock solution having the composition shown in Table 2-1 was prepared using reagent grade chemicals and ultrapure water (MilliQ Element). The SIW stock solution was then diluted 1000:1 to provide the infiltration water used in pore water preparations. Table 2-2 provides the composition of the SIW, which is based on the average chemical composition of groundwater from non-impacted wells screened within the water-table aquifer on the SRS [4]

Table 2-1. Composition of Synthetic Infiltration Water Stock Solution

Chemical	Concentration (g/L)
$CaCl_2 \cdot 2H_20$	3.68
Na_2SO_4	1.07
KCl	0.40
NaCl	2.65
$MgCl_2 \cdot 6H_2O$	5.51

Table 2-2. Composition of Synthetic Infiltration Water

Component	Concentration
Na^+	1.39 mg/L
Cl^-	5.51 mg/L
Ca^{2+}	1.00 mg/L
Mg^{2+}	0.66 mg/L
K^+	0.21 mg/L
SO_4^{2-}	0.73 mg/L
pH	4.5 – 4.9

2.2 Preparation of Grout Pore Water

Table 2-3 provides the target E_h and pH values for the three pore waters to be used in the leaching tests. Note, all E_h values are relative to the standard hydrogen electrode. A monolith representing the cement, flyash and slag (CFS) components of the grout used to fill Tanks 5, 6, 18 and 19 was prepared using 125 parts of Cement Type I/II, 210 parts of Slag Grade 100 and 363 parts of Fly Ash Class F.[5] Sand was not added as a component of the monolith. Both flyash and slag contain significant quantities of silicon, which would serve as sources of silicon for dissolution into the grout pore water and the formation of silicate phases such as calcium silicate in the grout solids. Prior to contact with the infiltration water, the CFS monolith was broken into large pieces. Subsequently, the larger pieces were crushed and sieved through a 40 mesh (420 μm) or 100 mesh (149 μm) sieve.

Table 2-3. Target E_h and pH for Each Pore Water Composition

Test Condition	E_h (mV)	pH
Reduced Region II (RR2)	-470	11.1
Oxidized Region II (OR2)	+560	11.1
Oxidized Region III (OR3)	+680	9.2

The general procedure to prepare the pore waters for solids leaching consisted of placing a measured quantity of the CFS solids in a glass vial or glass vessel and adding a measured quantity of the synthetic infiltration water. For this work the concentration of CFS solids in the SIW was fixed at 16.7 g/L. Figure 2-1 provides a photograph of a vial containing the synthetic infiltration water in contact with crushed and sieved CFS solids.

The pH measurements were obtained with one of the following, (1) an Accumet™ glass body pH probe in combination with an Accumet™ Model XL20 meter or (2) Fisher Scientific™ Accumet™ Gel-filled Pencil -thin pH combination electrode connected to a Fisher Scientific™ Orion ™ 2 Star or 4 Star meter. Fisher Scientific™ pH buffers 4, 7, and 10 were used for calibration and calibration checks.

E_h measurements were obtained with one of the following, (1) a Mettler-Toledo InLab® Redox Micro probe in combination with an Accumet™ Model XL20 meter or (2) Fisher Scientific™ Orion™ Redox/ORP/Temp electrode, a Mettler Toledo™ InLab redox combination electrode (ORP) in combination with an Extech® Instruments ORP meter. Thermo Scientific™ ORP Standard (Orion 967901) was used for calibration checks of the electrodes. All reported E_h values are relative to the standard hydrogen electrode (SHE).

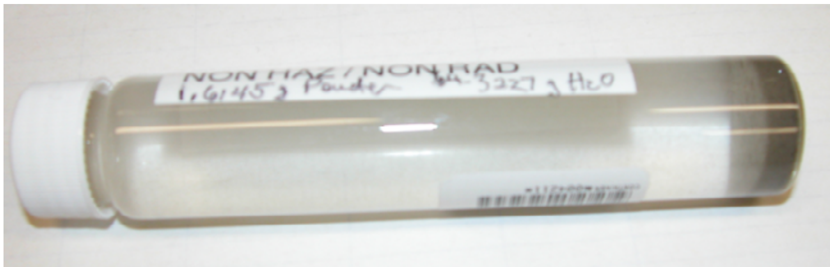

Figure 2-1. Photograph of Synthetic Infiltration Water with Crushed & Sieved CFS Solids

For the RR2 pore water, argon was bubbled through the solution to limit the partial pressure of oxygen in the system. For the OR2 pore water, air that had been treated to remove carbon dioxide was bubbled through the solution to minimize the conversion of calcium hydroxide to calcium carbonate in the cement solids. For the OR3 pore water, air that had not been treated to remove carbon dioxide was bubbled through the solution to convert calcium hydroxide in the cement to calcium carbonate. Air flowrates were controlled at 1.2 standard cubic feet per hour (scfh). Figure 2-2 shows a photograph of the equipment used to prepare approximately one liter quantities of the pore waters.

Hydrogen peroxide and ozone were evaluated as chemical additives to increase the E_h potentials for the OR2 and OR3 pore waters. Reagent grade 30 wt% hydrogen peroxide (Fisher Scientific) served as the source of hydrogen peroxide. Ozone was provided at a flow rate of 2 liters per minute (lpm) and a concentration of approximately 6.25% by volume using an Ozone Solutions Model PS10 generator.

Figure 2-2. Photograph of Experimental Equipment to Prepare Larger Bench-Scale Quantities of Pore Waters

2.3 Preparation of Surrogate Tank 18 Solids

A Tank 18 solids surrogate was prepared using reagent grade chemicals and spiked with radionuclides at the targeted amounts based on the average composition of several Tank 18 samples analyzed by SRNL.[6,7] Table 2-4 provides the target and measured concentrations of the surrogate. Metal salts, as the respective nitrates, were dissolved in ultrapure water. Aluminum and silicon were added as sodium salts, sodium aluminate and sodium silicate, respectively. Plutonium(IV) and neptunium(V) were added as solutions in nitric acid from available stocks in SRNL. Uranium(VI) was added as uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$. ^{99}Tc as technetium(VII) was added as a solution of ammonium pertechnetate available from commercial sources.

After addition of all component chemicals and radionuclides, a solution of 19.1 M sodium hydroxide was slowly added to the nitric acid solution while mixing to precipitate the metals as metal hydroxides and hydrous metal oxides. Sodium hydroxide addition continued until the free hydroxide concentration in the supernatant was 0.1 M based on calculated base requirement. The suspension was then heated to reflux for 24 hours to convert a fraction of aluminum and the silicon to sodium aluminosilicate. The suspension was cooled to ambient temperature. At that time, mixing was discontinued and the precipitated solids were allowed to gravity settle. Gravity settling did not produce a clear supernatant liquid above the solids. Thus, the suspension was filtered through a disposable Nalgene® filter with 0.45-micron nylon membrane. The filtrate was collected and analyzed to determine the concentrations of Pu, Np, U and Tc that were not incorporated into the precipitated solids.

The concentrated solids mixture was diluted with an alkaline solution containing 0.01 M sodium hydroxide and sodium carbonate at a volume equal to that of the decanted supernatant. After mixing for several hours, the mixture was again filtered to recover the solids. The supernatant dilution and filtration was repeated three additional times. The filtered wash solutions were collected and analyzed to determine the concentrations of Pu, Np, U and Tc that were removed by the wash solutions. After the final filtration the moist solids were air dried until a dry powder was achieved. The dried solids were lightly ground, transferred to a preweighed storage container and stored until used in leaching experiments.

Analysis of the filtrates and surrogate Tank 18 residual solids indicated that solids contained Ca, Fe, Mg, Mn, U and Pu at the target concentrations. The concentration of Na was about 33% higher than the target value and likely reflects the incorporation of sodium salts from the wash solution. The concentrations of Al, Si, Np, and Tc were below the target concentrations. The low concentrations of Np and Tc, added as NpO_2^+ and TcO_4^-, respectively, were not unexpected given the solubilities of the neptunyl and pertechnetate species.

Table 2-4. Composition of Tank 18 Solids Surrogate

Component	Target Concentration (wt%)	Measured Concentration[a] (wt%)
Al	15.2	11.3 ± 1.2
Ca	2.69	2.69 ± 0.28
Fe	8.00	7.90 ± 0.83
Mg	2.00	2.09 ± 0.22
Mn	1.09	1.04 ± 0.11
Na	4.48	5.96 ± 0.62
Si	3.96	0.22 ± 0.038
U	2.37	2.39 ± 0.24 2.50 ± 0.50[b]
Pu-239/240	0.0160	0.0160 ± 0.0009[c]
Np-237	7.53E-04	bql
Tc-99	2.60E-04	bql

[a]determined by ICP-ES
[b]determined by ICP-MS
[c]determined by alpha counting after separating from U and Np
bql = below quantifiable limit

2.4 Leaching of Surrogate Tank 18 Solids

Leaching experiments were performed using the prepared Tank 18 solids surrogate and prepared pore waters representing Reduced Region II (RR2), Oxidized Region II (OR2), and Oxidized Region III (OR3). Experiments utilized zero-head space vials holding approximately 40 mL of pore water. For each experiment 1.2 g of the Tank 18 solids surrogate was added to the vial followed by the desired pore water. The vials were then capped, leaving zero head-space, and placed into a 25 °C shaker oven for agitation at 175 rpm. Figure 2-3 shows photographs of the shaker oven and the glass vials nested on the shaker table inside the oven.

A separate vial was prepared for each sampling event since air is introduced into the head space of the vial once the vial is opened and a sample is removed. Tests were conducted in duplicate for each pore water, one set using filtered pore water samples, and the second set including some of the grout solids used for preparing the pore water. Samples from the RR2 and OR3 experiments were removed after 1, 2, 3, and 4 weeks. Samples from the OR2 experiments were removed after 1 day and 1 week of contact.

The pH and E_h of the pore waters were measured just prior to starting the experiments, and then again at each of the sampling events. For sampling, approximately 10 mL of solution was filtered through a 0.1-µm PVDF syringe filter. A 9-mL aliquot of this filtrate was acidified with 1 mL of 5 M nitric acid. Aliquots of the acidified filtrate were submitted for ICP-MS and PuTTA analyses to determine the U and Pu concentrations, respectively.

Figure 2-3. Photographs of Incubator Shaker Oven and Nested Glass Vials Inside Oven Used in Zero Head Space Tests

3.0 Results ad Discussion

3.1 <u>FY13 Preparation of Pore Water</u>

FY2013 testing produced pore waters having the desired pH values, but with E_h values significantly lower than the targeted values (see Tables 3-1 and 3-2). For example, the RR2 pore water measured to have a pH of 11.40 and an E_h of -156 mV versus the target values of 11.1 and -470 mV, respectively. For the OR2 and OR3 pore waters, the pH measured 11.19 and 9.59 versus target values of 11.1 and 9.2, respectively. The measured and target E_h values for the oxidizing pore waters, OR2 and OR3, were +110 vs. +480 mV and +165 vs. +560 mV, respectively. Based on these findings, pore water E_h potentials produced in these studies are lower than those used in PA modeling. This suggests that in short-term experiments as described in this document, kinetic controls on the E_h values of the synthetic pore waters in contact with grout solids dominate over the equilibrium controls assumed in the PA waste release modeling.

3.2 <u>Zero Head Space Leaching Tests with Surrogate Tank 18 Solids</u>

Although the pore waters did not meet the target E_h values, leaching experiments were carried out to measure the release of plutonium and uranium from the surrogate Tank 18 solids. Evaluation of the release of neptunium and technetium was not possible since the concentrations of ^{237}Np and ^{99}Tc in the surrogate Tank 18 solids fell below their respective quantifiable limits. All of the leaching tests used a zero-head space methodology to limit contact of air during the testing.

Table 3-1 provides the target pH, as-prepared pH, initial pH, and pH measured after 1, 2, 3 and 4 weeks of contact with the surrogate Tank 18 solids. Table 3-2 provides the target E_h, as-prepared E_h, initial E_h, and E_h measured after 1, 2, 3 and 4 weeks of contact with the surrogate Tank 18 solids. Note, the initial pH and E_h values are those measured for the solution prior to the addition of the surrogate Tank 18 solids. From the time that the pore waters were prepared to when they were used in the leaching tests, the pH values increased and the E_h values became more reducing. In the case of the two oxidizing pore waters, OR2 and OR3, dissolved oxygen is likely being consumed resulting in more reducing potentials.

Over the leaching contact period of one to four weeks, the pH and the E_h of the RR2 pore water exhibited very little change. Over the one week contact time the pH and E_h values of the OR2 pore waters exhibited little change in pH and a small decrease in E_h indicating slightly more reducing conditions. For the leaching test with the OR3 waters, the pH and E_h values did not change appreciably. The pH and E_h values are fairly consistent across the 4-week time period for the RR2 and OR3 tests suggesting that steady-state conditions had been achieved after about one week. This confirms that the zero head space methodology can be used to maintain reducing redox potential for up to four weeks.

Table 3-1. pH Values During Zero Head Space Tests

Test Condition	Target pH	As-Prepared pH	Average Initial pH[1]	Average 1 week pH	Average 2 week pH	Average 3 week pH	Average 4 week pH
RR2	11.1	11.19	11.92	11.40	11.40	11.39	11.26
RR2 with CFS solids	11.1	11.19	11.87	11.62	11.72	11.74	11.58
OR2*	11.1	11.40	11.64	11.51*	11.40*	nm	nm
OR2 with CFS solids*	11.1	11.40	11.67	11.62*	11.64*	nm	nm
OR3	9.2	9.58	10.31	10.58	10.68	10.59	10.53
OR3 with CFS solids	9.2	9.58	10.05	10.61	10.83	10.83	10.83

[1] pH prior to addition of surrogate Tank 18 solids
*OR2 experiments are after contact with pore waters for 1 day and 1 week, respectively.
nm = not measured

Table 3-2. E_h Values During Zero Head Space Tests

Test Condition	Target E_h (mV)	As Prepared E_h (mV)	Average Initial E_h (mV)[1]	Average 1 week E_h (mV)	Average 2 week E_h (mV)	Average 3 week E_h (mV)	Average 4 week E_h (mV)
RR2	-470	-156	-215	-176	-203	-214	-189
RR2 with CFS solids	-470	-156	-207	-211	-222	-246	-215
OR2*	+560	+110	-43	-183*	-201*	nm	nm
OR2 with CFS solids*	+560	+110	-93	-197*	-224*	nm	nm
OR3	+680	+165	-36	-141	-157	-142	-138
OR3 with CFS solids	+680	+165	-13	-141	-162	-166	-142

[1] E_h prior to addition of surrogate Tank 18 solids
*OR2 experiments are after contact with pore waters for 1 day and 1 week, respectively.
nm = not measured

Tables 3-3 and 3-4 provide the measured plutonium and uranium concentrations in the leach solutions for selected test conditions and contact times. Of the 22 experimental measurements for plutonium concentration, seven of the results proved below the quantifiable limit. The values are also close to the "more realistic" solubility of amorphous plutonium oxide, 3.2E-11 molar as reported by Denham.[1] These results indicate that a larger sample aliquot should be used and perhaps longer alpha counting times to provide a lower quantification limit for the plutonium measurements.

For each pore water test, there is no discernible trend in the concentration of plutonium with contact time. Comparison of the RR2 and OR3 results suggests that the more oxidizing and lower pH conditions of the OR3 test may favor a higher plutonium concentration. However, the small number of sample results above the quantifiable limit for these two tests provides a high uncertainty to this statement. The measured plutonium concentrations are very similar for the RR2 and OR2 tests after 2 weeks and 1 week of contact, respectively. This finding is not unexpected since both the E_h and pH conditions are very similar for these pore water tests.

Table 3-3. Plutonium Leaching in Zero Head Space Tests

Test Condition	Average E_h (mV)	Average pH	[Pu] M after 1 week contact[1]	% Pu Leached (1 week)[1]	[Pu] M after 2 weeks contact	% Pu Leached (2 weeks)	[Pu] M after 4 weeks contact	% Pu Leached (4 weeks)
RR2	-195	11.36	1.26E-10 (3.96E-11)	0.00077 (0.00023)	4.21E-10	0.00246	<3.11E-10	<0.00192
RR2 w/ solids	-223	11.66	6.46E-11[2]	0.00040[2]	<1.40E-10	<0.00083	<4.06E-10	<0.00252
OR2*	-192	11.45	1.96E-10 (1.80E-10)	0.00119 (0.00108)	<1.04E-10	<0.00063	nm	nm
OR2 w/ solids*	-210	11.63	1.80E-10[2]	0.00110[2]	8.39E-11	0.00051	nm	nm
OR3	-144	10.59	1.25E-09 (7.97E-11)	0.00754 (0.00046)	7.38E-10	0.00441	<9.88E-10	<0.00610
OR3 w/ solids	-153	10.77	5.40E-10 (2.77E-10)	0.00323 (0.00157)	2.23E-10	0.00134	8.33E-10	0.00487

[1]Values are averages of results from replicate tests with standard deviations shown in parenthesis.
[2]Duplicate tests were performed, but only one sample was above the detection limit.
*OR2 experiments are after contact with pore waters for 1 day and 1 week, respectively.
nm = not measured

Determinations of the uranium concentrations were obtained after 1, 2 and 4 weeks of contact for the RR2 and OR3 pore water tests and one day and one week of contact for the OR2 pore water tests. The quantity of uranium dissolved from the surrogate Tank 18 solids was very similar for the RR2 and OR2 pore waters. This is the expected trend given the similar E_h and pH conditions for these two pore water tests. Note also, that the dissolution of uranium was lower for both pore waters in the presence of the CFS solids. The test mixtures for both pore tests with the CFS solids are about 20 – 25 mV lower than those in the absence of the CFS solids. This trend may reflect the influence of the redox potential on the solubility of uranium in these solutions.

For the OR3 test, the measured uranium concentrations are considerably higher than those measured in the RR2 and OR2 tests. This finding is not unexpected since the lower pH and likely higher bicarbonate/carbonate concentrations would favor dissolution of uranium from the surrogate Tank 18 solids. The much lower percentage of uranium leached for the OR3 test containing CFS solids cannot be attributed to the redox potential since the E_h values are very similar. The CFS solids may be buffering the dissolved bicarbonate/carbonate to a lower value due to the presence of excess calcium and, thereby limiting complexing of uranium by carbonate.

Table 3-4. Uranium Leaching in Zero Head Space Tests

Test Condition	Average E_h (mV)	Average pH	[U] M after 1 week contact[1]	% U Leached (1 week)[1]	[U] M after 2 weeks contact	% U Leached (2 weeks)	[U] M after 4 weeks contact	% U Leached (4 weeks)
RR2	-195	11.36	5.69E-06 (5.28E-07)	0.216 (0.016)	7.66E-06	0.279	4.67E-06	0.179
RR2 w/ solids	-223	11.66	2.93E-06 (1.68E-06)	0.113 (0.065)	2.43E-06	0.090	4.14E-06	0.160
OR2*	-192	11.45	1.06E-05* (3.90E-06)	0.402* (0.142)	5.88E-06*	0.224*	nm	nm
OR2 w/ solids*	-210	11.63	2.50E-06* (1.72E-07)	0.096* (0.007)	2.22E-06*	0.084*	nm	nm
OR3	-144	10.59	7.26E-05 (1.85E-05)	2.73 (0.703)	8.85E-05	3.30	7.64E-05	2.95
OR3 w/ solids	-153	10.77	2.10E-05 (2.13E-06)	0.789 (0.055)	2.11E-05	0.795	1.20E-05	0.440

[1]Values are averages of results from replicate tests with standard deviations shown in parenthesis.
*OR2 experiments are after contact with pore waters for 1 day and 1 week.
nm = not measured

3.3 Preparation of Pore Waters with Higher Reducing and Oxidizing Potentials

In FY2013, the E_h values for the pore waters were considerably lower than that of the target values as provided in Table 2-3. Thus, FY2014 testing focused on identifying conditions that would result in pore waters having E_h values closer to that of the target values. For oxidizing pore waters (OR2/OR3), the strategy was to determine if an increase in the partial pressure of oxygen or addition of stronger oxidants (e.g., peroxide or ozone) would produce the targeted E_h values in the presence of CFS solids. A similar strategy was planned for reducing pore water (RR2), except one would add a reducing agent (e.g., dithionite, Fe^{2+}, sulfide).

3.3.1 OR3 Pore Water

For OR3, the target E_h is +680 mV and pH is 9.2. A total of 1.4 liters of the SIW (pH 6.62 and E_h +508 mV) and 23.3 grams of large pieces removed from a CFS monolith were placed in the glass vessel as shown on the right side of Figure 3-1. Upon addition of the CFS solids, the pH measured 10.5 and the E_h measured +205 mV. Initially the apparatus was opened to the room air allowing oxygen to freely contact the mixture of the SIW and CFS solids. Periodic measurements of the pH and E_h were made and recorded. Mixing was stopped during the off-shift time periods, but the vessel remained open to the laboratory atmosphere. During the initial 8 days of contact, the pH decreased to 9.88 and the E_h decreased to about +150 mV.

After 8 days, the CFS solids were removed from the vessel, ground to a fine powder, seived through a 100 mesh sieve, and returned to the vessel. Over the next 13 days, the pH and E_h did not change appreciably. Thus, it was decided to bubble air through the mixture to ensure the solution was saturated in oxygen. Air was bubbled through the stirred mixture at a rate of 1.2 standard cubic feet per hour (SCFH). Agitation and air sparging were stopped during off-shift time periods.

Upon bubbling air into the mixture, the E_h immediately increased to about +225 mV and remained at this potential over the next 13 days. During the 13-day time period, the pH of the mixture decreased from 9.8 to about 8.1. Since the E_h had appeared to reach steady-state condition, it was decided to see if the E_h could be increased by the addition of hydrogen peroxide. Small additions of 30 wt% hydrogen peroxide to provide 0.1 – 10 millimolar concentration of peroxide did not exhibit any effect on the E_h. However, upon the addition of 2.0 grams of hydrogen peroxide (100 mM), the E_h immediately increased to +300 mV. The higher E_h persisted for a few minutes and then decreased reaching +220 mV after 3.5 hours and +202 mV the following morning. The E_h remained at about +200 mV for the next four days. During this time the pH of the mixture ranged between 8.28 to 8.49.

The addition of another 2.0 grams of hydrogen peroxide (100 mM) increased the E_h to +430 mV and maintained an E_h at or above +400 mV for 4 – 5 hours. After 24 hours, the E_h measured +310 mV and after about 33 hours the E_h had decreased to +226 mV. The pH remained unchanged in the range of 8.19 to 8.47.

Two final tests with hydrogen peroxide determined if daily additions of hydrogen would maintain an E_h of +400 mV and to determine if the E_h could be maintained at about +420 mV and if even higher E_h potentials could be achieved by increased quantities of hydrogen peroxide. Successive additions of 2.0 grams of hydrogen peroxide over the 3-day period confirmed that the E_h was maintained between +402 and +422 mV with no observed change in the pH. Addition of 4.0 grams of hydrogen peroxide produced similar E_h value (+414 mV) as 2.0 grams of hydrogen peroxide. Since the E_h did not respond to the higher concentration of hydrogen peroxide no further experiments with hydrogen peroxide were carried out.

A brief test was carried out to determine if ozone would serve to increase the E_h and what affect, if any, it had on the pH of the pore water. Bubbling ozone (~ 6.25 vol%) at a flowrate of 2 lpm resulted in an immediate increase in the E_h to +760 mV which rose to a final reading of +1045 mV. This is well above the target value of +680 mV. Simultaneously with an increase in the E_h, the pH of the mixture decreased to a value of 7.44 after 75 minutes of ozone bubbling. Upon stopping the ozone bubbling, the E_h rapidly decreased to +461 mV after 65 minutes and +481 mV after 205 minutes. The pH of the OR3 mixture measured 7.42 after 65 minutes and 7.57 after 205 minutes indicating a slow response, if any, to stopping the ozone bubbling.

Figures 3-1 and 3-2 provide plots of the measured pH and E_h versus the date for the OR3 pore water during the various evolutions described above.

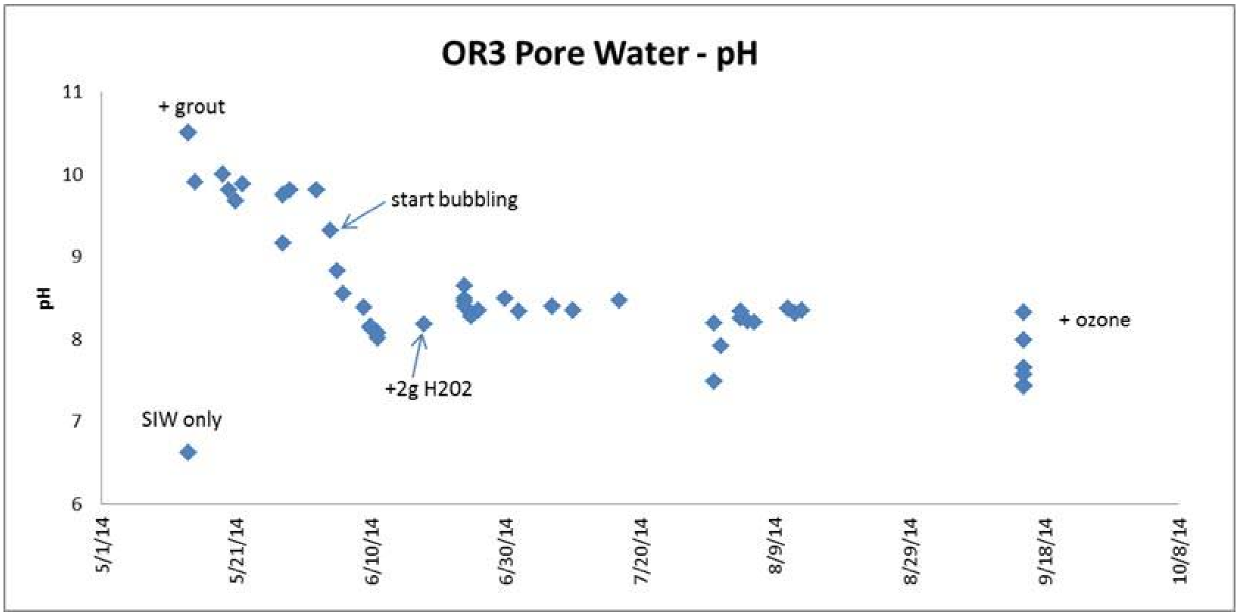

Figure 3-1. Plot of pH versus Date in the Preparation of the OR3 Pore Water

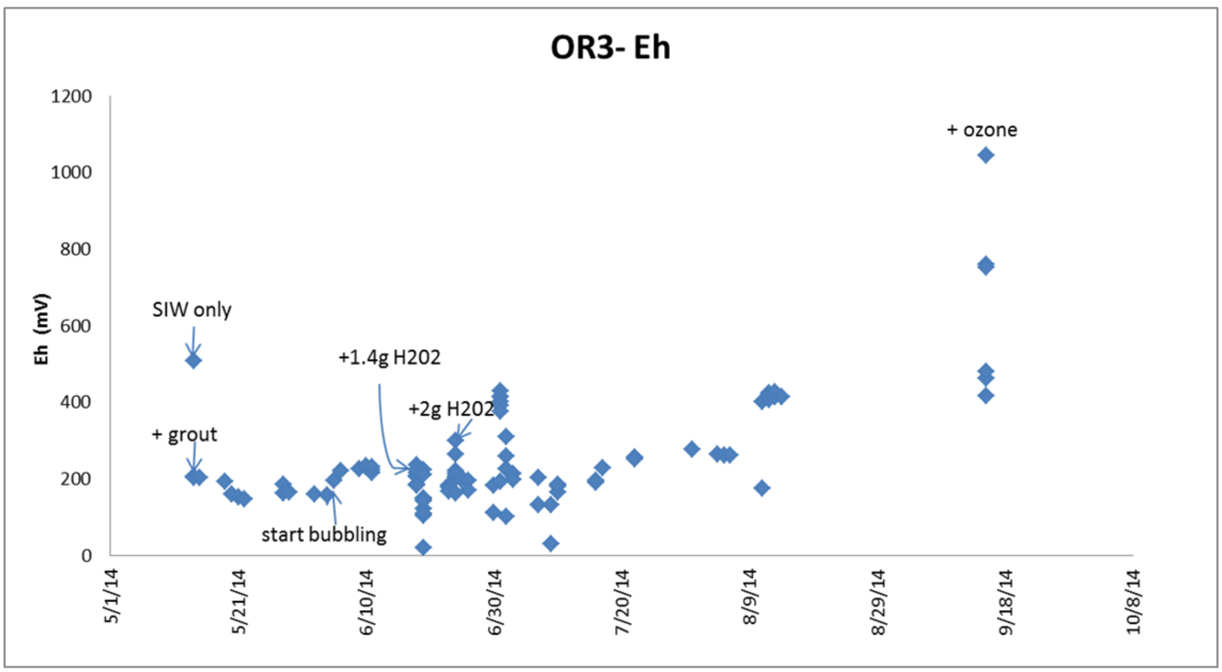

Figure 3-2. Plot of E_h versus Date in the Preparation of the OR3 Pore Water

3.3.2 OR2 Pore Water

For OR2, the target E_h is +560 mV and pH is 11.1. A total of 1.2 liters of the SIW and 20.0 grams of the CFS solids were placed in the glass vessel as shown on the left side of Figure 2-2. One hour after the addition of the CFS solids, the pH measured 11.48 and the E_h measured +135 mV. Carbon dioxide-free air was bubbled through the mixture of the SIW and CFS solids at a flowrate of 1.5 scfh. Carbon dioxide was removed to maintain a higher pH and limit the conversion of $Ca(OH)_2$ to $CaCO_3$. Periodic measurements of the pH and E_h were made and recorded. Mixing was stopped during the off-shift time periods, but the vessel remained open to the laboratory atmosphere.

Over the next 16 days, the E_h ranged from about +90 to +135 mV and the pH 11.76 to 11.10. On successive days, hydrogen peroxide additions of 2.0 and 4.0 grams, respectively, resulted in measureable increase in the E_h. The pH of the mixture measured 10.92 after the second hydrogen peroxide addition. At this time the sodium hydroxide bubbler was replaced to ensure effective removal of the carbon dioxide from the air. During this time the E_h potential increased to +155 mV.

After an additional five days, without any further hydrogen peroxide additions, the E_h potential measured about +194 mV. The increase in the E_h was attributed to a composition change in the E_h standard resulting in a lower E_h. Over the next 13 days, the measured E_h ranged from +184 to +210 mV. Thus, we concluded that the addition of hydrogen peroxide is not effectively increasing the E_h of the OR2 pore water. This lack of change in the E_h may reflect a shorter lifetime of the peroxide in this mixture due to the higher alkalinity (higher pH).[8]

A brief test was carried out to determine if ozone would serve to increase the E_h potential and what affect, if any, it had on the pH of the pore water. Bubbling ozone (~ 6.25 vol%) at a flowrate of 2 lpm resulted in an increase in the E_h potential to +1039 mV. This is well above the target value of +560 mV. Simultaneously with an increase in the E_h, the pH of the mixture decreased from 10.66 to a value of 9.61 after 180 minutes of ozone bubbling. Upon stopping the ozone bubbling, the E_h potential rapidly deccreased to +412 mV after 140 minutes. The pH of the OR2 mixture measured 9.82 after 140 minutes.

Unlike hydrogen peroxide, ozone is increasing the oxidizing potential of the OR2 pore water. The degree of increase is well above the target for the OR2 pore water. However, the introduction of ozone is producing acid that is reacting with base and reducing the pH well below the target value of 11.1. Further testing with ozone needs to be carried out in the presence of the surrogate and actual Tank 18 solids to determine if these solids will serve to moderate the decrease in pH and allow the pH to be controlled close to the target value.

3.3.3 *RR2 Pore Water*

For RR2, the target E_h is -470 mV and pH is 11.1. A total of 0.8 liters of the SIW and 13.03 grams of the ground and sieved (40 mesh) CFS solids were placed in a glass vessel similar to the vessels shown in Figure 2-2. Argon was bubbled through the mixture at a flowrate of 4.0 lpm for 68 days. After 68 days, the E_h measured 126 mV. One gram of the reducing agent, sodium dithionite, $Na_2S_2O_4$, was added to the mixture to provide a sodium dithionite concentration of 0.0071 molar. After stirring the mixture for 2.25 hours while maintaining the argon purge, the E_h was measured at -95 mV. The mixing was stopped overnight and resumed the following morning. After stirring for the mixture for 20 minutes, the E_h and pH measured +150 mV and 10.43, respectively. This indicates that the dithionite addition provided a transitory reduction in the E_h of the mixture.

At this time researchers decided to make a second addition of sodium dithionite using an increased quantity of the reagent. Thus, 2.25 grams of sodium dithionite was added to the mixture to provide a sodium dithionite concentration of 0.016 molar. After stirring the mixture for three hours, the E_h and pH of the mixture measured +110 mV and 9.20, respectively. The second and larger addition produced a much smaller decrease in the E_h and reduced the pH of the mixture from 10.43 to 9.20. This result suggests the addition of sodium dithionite will not likely achieve the target E_h value of -470 mV.

4.0 Conclusions

Based on the findings reported in this document the authors conclude the following.

- Pore water E_h potentials produced in these studies upon contact of synthetic infiltration water with surrogate tank closure solids are lower than those used in PA modeling. This suggests that in short-term experiments, kinetic controls on the E_h values of the synthetic pore waters in contact with grout solids dominate over the equilibrium controls assumed in the PA waste release modeling.
- The zero head-space method appears viable for testing the release of radionuclides from solids under reducing conditions, but not under oxidizing conditions due to oxygen depletion.
- Researchers must account for the alkalinity and redox potential of the tank waste solids to ensure target pH and E_h values will be achieved in radionuclide release testing.
- The addition of hydrogen peroxide will increase the E_h potentials of OR3, but not OR2 pore water to about +420 mV and decrease the pH by about one pH unit. These changes are transitory due to the decomposition of peroxide in alkaline solutions.
- The addition of ozone increases the potentials of OR2 and OR3 pore waters above +1000 mV as long as excess ozone is present. The addition of ozone generates acid which lowers the pH of the pore OR2 and OR3 waters.
- Under moderate reducing conditions, the quantity of Pu and U dissolved from the surrogate Tank 18 solids increased in pore water solutions that feature less reducing E_h and lower pH values.
- The presence of cement solids in the leaching tests generally reduced the dissolution of Pu and U from the surrogate Tank 18 solids.

5.0 Recommendations

Based on the findings and conclusions summarized in this technical report, the authors recommend that leachate testing with surrogate materials be continued and finalized prior to initiating testing with actual waste residuals. Testing with actual tank waste solids would be expected to provide additional information regarding the residual waste solubility assumptions used in the Tank Farm Performance Assessments' waste release models. The following specific actions are recommended with respect to continued waste release testing.

- Reduce the lower quantifiable limit for detection of Pu in leachates by increasing the size of the aliquot and employ longer alpha counting times.
- Determine the effect, if any; of the syringe filter pore size on Pu/U concentrations in leachates to ensure that the measured Pu/U concentrations reflect only dissolved species.
- Complete experimental studies evaluating the use of ozone to increase oxidizing E_h potentials and the use of dithionite, sulfide and ferrous ion to increase reducing E_h potentials so that surrogate pore waters have E_h potentials at the targeted values.
- Test production of pore waters using only solid phases believed to be controlling the pH and E_h at equilibrium conditions.

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