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Radionuclide Release from Tank Waste Residual Solids

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Separations and Actinide Science Programs

NRC March 2014 F-Tank Farm (FTF) Onsite Observation Visit

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Project Objective, Authorization and Participants

- Objective:
  Provide additional information regarding the residual waste solubility assumptions used in the F-Area and H-Area Tank Farm Performance Assessments' waste release models by developing methods to test the solubility of Pu, Np, U, and Tc under various simulated waste tank chemistry conditions using actual Tank 18 waste residual solids.
  - Technical Task Request (TTR): HLE-TTR-2013-002, rev. 0 (2/21/2013) HLE-TTR-2013-002, rev. 1 (2/5/2014) – *Tank Waste Testing to Evaluate Residual Waste Solubility Assumptions Used in the Tank Farm PAs*
  - Task Technical and Quality Assurance Plan (TT&QAP): SRNL-RP-2013-00203, rev. 0 (approved 6/2013) – *Task Technical and Quality Assurance Plan for Determining the Radionuclide Release from Tank Waste Residual Solids*
- SRNL Participants:
  - D. Hobbs (PI, actinide and radiochemistry)
  - K. Taylor-Pashow (actinide and radiochemistry)
  - K. Roberts (leaching studies)
  - C. Langton (cementitious wasteforms)
  - M. Denham (geochemical modeling)
  - D. Kaplan (geochemistry)

FY2013 Testing Activities

- Identified two testing methodologies
  - controlled atmosphere vessel
  - zero-head space
- Prepared Tank 18 residual solids surrogate
  - U, Np, Pu & Tc
  - Al, Ca, Fe, Mg, Mn, Si
- Investigated methods to produce pore waters for three target conditions

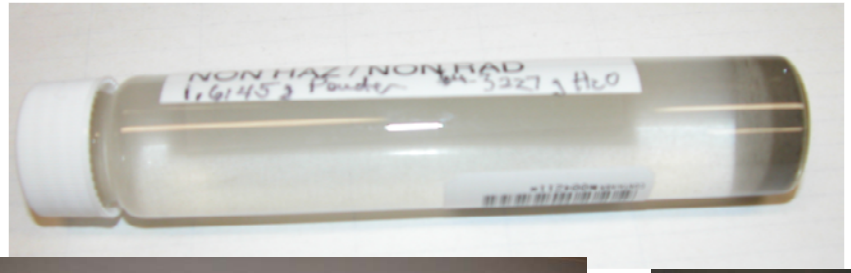
Component	Target Conc. (wt %)	Measured Conc. (wt %)
U	2.37	2.36; 2.50
Np	0.000753	bql
Pu	0.0160	0.0160
Tc	0.000260	bql
Al	15.2	11.3
Ca	2.69	2.69
Fe	8.00	7.90
Mg	2.00	2.09
Mn	1.09	1.04
Si	3.96	0.22

bql = below quantifiable limit

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

Leaching Tests – Testing Methodology & Equipment

- Prepared three pore waters targeting RR2, OR2, OR3 conditions contacted with cement/flyash/slag (CFS) solids
- Performed duplicate leaching tests with surrogate Tank 18 solids using zero head-space method
  - Leachate/waste solids ratio = 33 mL/g
  - Duplicate sets with and without CFS solids
  - Temperature and mixing controlled using incubator/shaker
    - *25.0 ± 1.0 ˚C*
    - *175 rpm*



Leaching Tests – E_h and pH Measurements

- Pore water E_h are below target values
- Pore water E_h values decrease during test to reducing values
- Identified method to prepare low pH pore water
- pH values typically increased upon addition of surrogate Tank 18 solids.

Test Condition	Target E_h (mV)	As Prepared E_h (mV)	Average Initial E_h (mV)	Average 1 week E_h (mV)	Average 3 week E_h (mV)
RR2	-470	-156	-215	-176	-214
RR2 w/ solids		-156	-205	-211	-246
OR2 *	+560	+110	-43	-183	-201
OR2 w/ solids *		+110	-93	-197	-224
OR3	+680	+165	-35	-141	-142
OR3 w/ solids		+165	-13	-141	-166

Test Condition	Target pH	As-Prepared pH	Initial pH	1 week pH	3 week pH
RR2	11.1	11.19	11.92	11.40	11.39
RR2 w/ solids			11.87	11.62	11.74
OR2 *	11.1	11.40	11.64	11.51	11.37
OR2 w/ solids *			11.67	11.62	11.64
OR3	9.2	9.58	10.36	10.58	10.59
OR3 w/ solids			10.05	10.61	10.83

* OR2 experiments are after contact with pore waters for 1 day and 1 week

Leaching Tests – Plutonium Measurements

Target Condition	Average E_h (mV)	Average pH	[Pu] M after 2 weeks contact	% Pu Leached
RR2	-214	11.39	4.26×10^{-10}	0.00246
RR2 w/ solids	-246	11.74	$<1.40 \times 10^{-10}$	<0.00083
OR2 *	-201	11.37	$<1.00 \times 10^{-10}$	<0.00063
OR2 w/ solids *	-224	11.64	8.40×10^{-11}	0.00051
OR3	-142	10.59	7.41×10^{-10}	0.00441
OR3 w/ solids	-166	10.83	2.22×10^{-10}	0.00134

* After 1 week of contact with pore waters

- Measured Pu concentrations are at or just above quantifiable limits of analytical method
- Quantity of Pu leached similar for RR2 and OR2 conditions (similar E_h and pH)
- Quantity of Pu leached may be increased for OR3 condition (less reducing E_h and lower pH)
- Presence of CFS solids generally reduces leaching of Pu

Leaching Tests – Uranium Measurements

Target Condition	Average E_h (mV)	Average pH	[U] M after 2 weeks contact	% U Leached
RR2	-214	11.39	5.69×10^{-6}	0.217
RR2 w/ solids	-246	11.74	2.93×10^{-6}	0.112
OR2 *	-201	11.37	1.06×10^{-5}	0.402
OR2 w/ solids *	-224	11.64	2.50×10^{-6}	0.096
OR3	-142	10.59	7.27×10^{-5}	2.74
OR3 w/ solids	-166	10.83	2.10×10^{-5}	0.789

* After one day of contact with pore waters

- Quantity of U leached similar for RR2 and OR2 conditions (similar E_h and pH)
- Quantity of U leached increased for OR3 condition (lower E_h and pH)
- Presence of CFS solids generally reduces leaching of U

Summary of Preliminary Testing Observations

- Pore water E_h potentials are lower than target potentials
- Reducing E_h maintained over 3-week period in zero head-space tests
- Zero head space tests for OR2 and OR3 regions showed E_h moved to reducing values and pH moved to higher values upon standing and upon contact with Tank 18 surrogate solids
  - depletion of dissolved oxygen
  - surrogate solids are alkaline
- Quantity of Pu leached similar for RR2 and OR2 conditions and may be higher for OR3 (less reducing E_h and lower pH)
- Quantity of U leached similar for RR2 and OR2 conditions and higher for OR3 (less reducing E_h and lower pH)
- Presence of cement solids generally reduces leaching of Pu and U

Planned FY14 Testing Activities

- Reduce lower quantifiable limit for detection of Pu in leachates
- Determine effect, if any, of filter pore size on Pu/U concentrations in leachates
- Determine influence of pore water chemistry on E_h potentials
  - produce more reducing RR2 potential
  - produce more oxidizing OR2 and OR3 potentials
- Extend conditioning times for preparation of pore waters
  - ensure pore water is in equilibrium with CFS solids
- Perform OR2 and OR3 leaching tests utilizing surrogate solids in open containers
  - maintain dissolved oxygen throughout leaching test