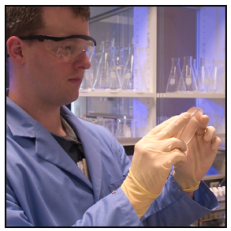
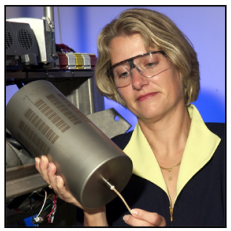
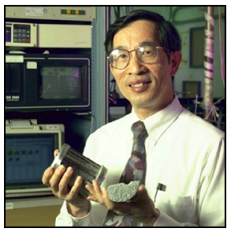
SRNL™
SAVANNAH RIVER NATIONAL LABORATORY
Operated by Savannah River Nuclear Solutions, LLC
We Put Science To Work

SRNL-MS-2010-00246

Tanks 5 and 6 Oxalic Acid Dissolution and Tank 5 and 6 Characterization

M. R. Poirier, R. Jolly, and G. D. Thaxton

November 18, 2010

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Print

Close

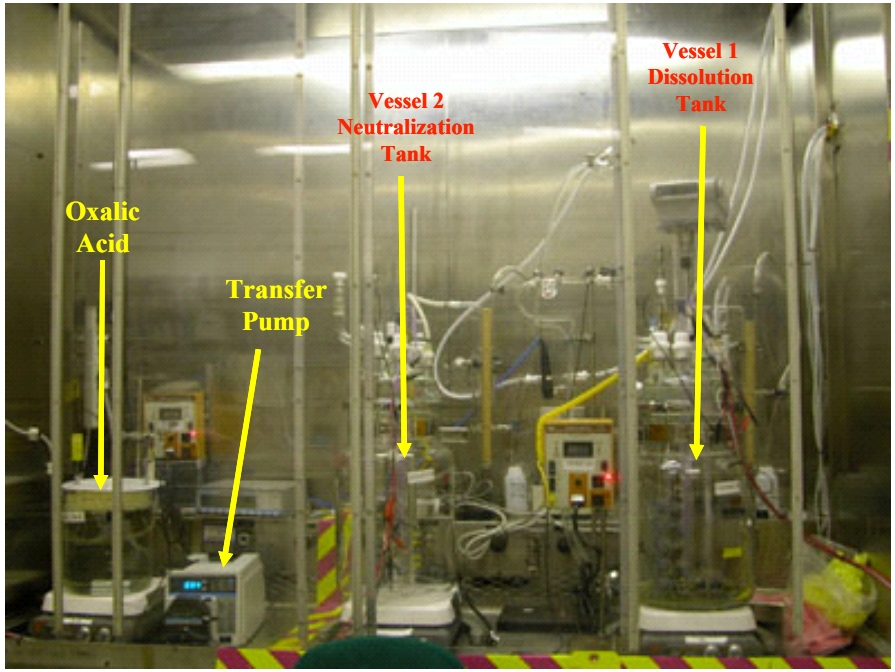
Outline of Talk

- Introduction
- Description of Testing
  - Simulant Testing
  - Actual Waste Testing
- Test Results
- Description of Oxalic Acid Cleaning in Tank Farm
- Results from Oxalic Acid Cleaning in Tank Farm
- Mechanical Cleaning
- Conclusions

Introduction

- **SRS will remove sludge as part of waste tank closure operations**
  - Bulk sludge removed by mixing it with available supernate and transporting slurry to tank for processing (i.e., “mechanical cleaning”)
    - Repeated multiple cycles with supernate being “recycled”
  - Residual heel typically remains in tank
  - Use oxalic acid solutions to disperse or dissolve sludge heel
- **Conducted demonstrations to develop and evaluate process**
  - Simulant
  - Actual waste
- **Performed chemical cleaning in two SRS waste tanks**
  - Two oxalic acid strikes
  - Spray wash
  - Water wash
  - Collected liquid and solid samples to evaluate effectiveness

Testing – Simulant Demonstration



- Simulated sludge and salt solution were placed into dissolution vessel
- Carbon steel coupons were placed in dissolution vessel for corrosion testing
- Transferred 8 wt % oxalic acid to dissolution vessel over 7 days
- Vessel not mixed until agitator blade covered
- After acid addition, dissolution continued for 50 hours
- Tests conducted at 25, 50, and 75 °C with and without mixing

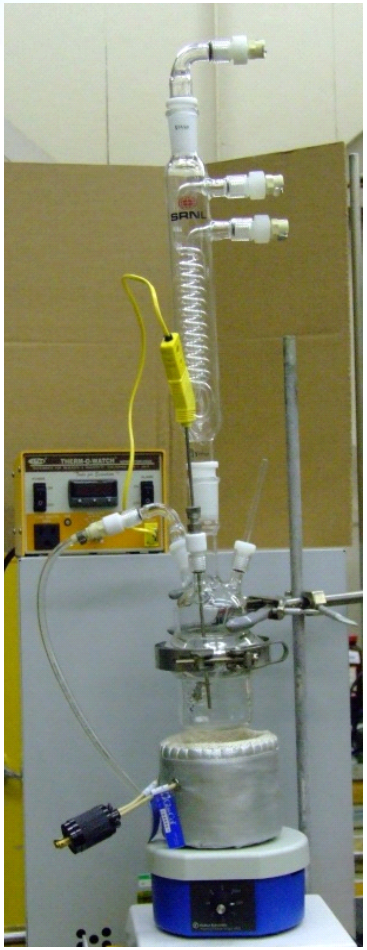
SRNL™

Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Print

Close

Testing – Actual Waste Test



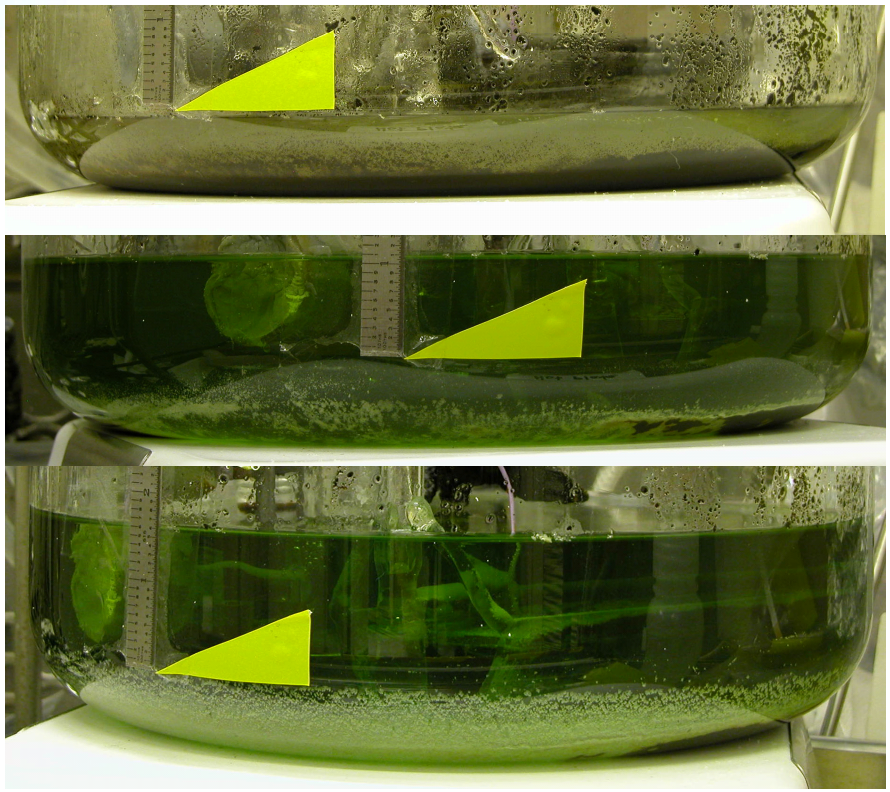
- Occurred via remote handling in the SRNL's Shielded Cells
- Carbon steel coupon was placed in contact with the solution for the duration of each test
- Reactor heated using a heating mantle for heating to 50 and 75 °C
- Solution temperature monitored during test
- Reactors mixed with stir bar rather than impeller; mixing less vigorous than simulant tests
- Oxalic acid added as batch

Test Conditions

Test	Sludge/Surface Area (gal/ft^2)	Oxalic Acid/Surface Area (gal/ft^2)	Oxalic Acid/Sludge + Supernate Volume
Actual Waste	0.1	4.2	20.7
Simulant	0.25	8.8	10.1
Tank 5 (nominal)	0.56	11.8	8.8
Tank 5 (actual)	0.3	9.6	32
Tank 6 (actual)	0.2	9.6	32

Attempted to match sludge to surface area, oxalic acid to surface area, and oxalic acid to sludge + supernate volume ratios

Results – Simulant Test Visual Results



- Formation of white colored solids under acid addition point
- More acid led to formation of bright yellow solids
- Solids spread throughout vessel
- White layer across residual sludge solids
- Brown/rust solids
- Emerald green solution color (iron oxalate)

Results – Actual Waste Test Visual Results

- **At end of oxalic acid addition to the sludge, layer of whites solids with slight blue color remained at bottom**
  - Raman spectra indicate the presence of sodium oxalate, iron oxalate and iron hydroxide
  - XRD indicates the presence of calcium oxalate
- **Sodium oxalate due to large concentration of sodium that exceeds solubility in oxalic acid**

Sludge Dissolution during Demonstrations

Test	Uranium	Iron	Manganese	Nickel
Simulant 25 °C w/mixing	100 %	99 %	32 %	0.2 %
Simulant 50 °C w/mixing	100 %	99 %	43 %	0.6 %
Simulant 75 °C w/mixing	99 %	94 %	24 %	0.06 %
Simulant 25 °C w/o mixing	99 %	100 %	57 %	2.0%
Simulant 50 °C w/o /mixing	99 %	96 %	33 %	0.5 %
Simulant 75 °C w/o mixing	99 %	98 %	37 %	0.2 %
Actual Waste 50 °C w/mixing	73 %	62 %	40 %	0.1 %
Actual Waste 75 °C w/mixing	87 %	76 %	59 %	0.1 %

- Good removal of uranium and iron – removal better in simulant tests
- Poor removal of nickel – good agreement between simulant and actual waste
- Good agreement between simulant and actual waste for manganese removal

SRNL™

Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Chemical Cleaning in SRS Waste Tanks

Acid Strike 1 – Addition of 8% OA to waste tank with soaking and mixing

Acid Strike 2 – Addition of 8% OA to waste tank with soaking

Spray Wash – Addition of 8% OA through 2 spray masts, followed by water addition and soaking.

Water Wash – Addition of well water to waste tank with mixing.

Liquid Samples from Tank 5

- **Sample pH measured 4 following Strike 1 rather than 1 – 2**
  - Residual sludge heels, interstitial liquid, films on tank walls and residual base will titrate oxalic acid to reduce effective H_3O^+ concentration.
- **pH measured 2 following Strike 2**
- **Liquid samples showed good dissolution of U, Fe, Al, Na, Mn, ^{137}Cs, and ^{90}Sr**
  - Except for Fe, solution concentrations decreased significantly following subsequent strikes
- **Measured oxalate about half of expected**
  - Likely formed metal precipitates

Liquid Samples from Tank 6

- **pH of sample measured 2 following Strikes 1 and 2 as expected**
- **Liquid samples showed good dissolution of U, Fe, Al, Na, Mn, ^{137}Cs, and ^{90}Sr**
  - Concentrations decreased significantly following subsequent strikes
- **Measured oxalate about half of expected**
  - Likely formed metal precipitates

Solid Samples from Waste Tanks

- **70 wt % solids**
- **Major cation constituents were Fe, Ni, and Mn**
- **Concentrations of ^{90}Sr, ^{241}Am, ^{244}Cm, and ^{137}Cs higher than other radionuclides**
- **XRD analysis of Tank 6 residual solids showed primary species, in order, are**
  1. Hematite
  2. Maghemite
  3. Nickel Oxalate Hydrate
  4. Goethite
- **Performed mass balance to calculate the fraction removed during chemical cleaning**

$$X = \frac{\sum \left(C_{liq-removed}\right)\left(V_{liq-removed}\right)}{\left[\sum \left(C_{liq-removed}\right)\left(V_{liq-removed}\right)\right] + \left(C_{solid}\right)\left(V_{solid}\right) + \left(C_{liq-remaining}\right)\left(V_{liq-remaining}\right)}$$

Fraction Removed and Sludge Remaining in Tank 5

Species	Removed	Remaining
Al	90%	33 kg
Fe	32%	4,830 kg
Mn	48%	875 kg
Na	98%	43 kg
Ni	1%	2,138 kg
U	99%	46 kg
Hg	n.m.	37 kg

n.m. not measured

Species	Removed
^{90}Sr	83%
^{99}Tc	37%
^{137}Cs	97%
$^{239/240}Pu$	6%
^{238}Pu	5%
^{241}Am	1%
^{242m}Am	1%
^{242}Cm	1%
^{244}Cm	3%

- Good removal of U, Na, and Al
- Poor removal of Ni
- Most of remaining sludge mass is Fe and Ni

- Good removal of Cs and Sr
- Poor removal of Tc, Pu, Am, and Cm
- Most of remaining activity ^{90}Sr

SRNL™

Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Print

Close

Fraction Removed and Sludge Remaining in Tank 6

Species	Removed	Remaining
Al	90%	48 kg
Fe	73%	1900 kg
Mn	49%	267 kg
Na	98%	31 kg
Ni	2%	1219 kg
U	98%	42 kg
Hg	n.m.	93 kg

n.m. not measured

- Good removal of U, Na, and Al
- Poor removal of Ni
- Better Fe removal than Tank 5
- Most of remaining sludge mass is Fe and Ni

Species	Removed
^{90}Sr	86%
^{99}Tc	2.0%
^{137}Cs	86%
$^{239/240}Pu$	14%
^{238}Pu	14%
^{241}Am	6%
^{243}Am	7%
^{242m}Am	7%
^{244}Cm	7%
^{241}Pu	6%

- Good removal of Cs and Sr
- Poor removal of Tc, Pu, Am, and Cm
- Better Pu, Am, and Cm removal than Tank 5
- Most of remaining activity ^{90}Sr

SRNL™

Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Comparing Oxalic Acid Dissolution in Tank Farm with Demonstrations

Species	Tank 5	Tank 6	Actual Waste Demonstration	Simulant Demonstration
Fe	21%	69%	62%	99%
U	89%	80%	73%	100%
Mn	40%	46%	40%	43%
Ni	0.6%	1.6%	0.1%	0.6%
Na	88%	76%	96%	96%
Al	81%	85%	84%	n.m.
^{238}Pu	3.5%	13%	2.9%	n.m.
$^{239/240}Pu$	4.4%	13%	3.2%	n.m.

n.m. not measured

- Tank Farm removal efficiencies are for first strike
- Except for Fe, good agreement between Tank 5 chemical cleaning and actual waste demonstration

SRNL™

EM Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

Comparing Oxalic Acid Dissolution in Tank Farm with Laboratory Demonstrations

- **Waste tank samples showed less iron removal than in simulant demonstration**
  - Iron in simulant demonstration added as ferric hydroxide (easily dissolved by oxalic acid)
  - Iron in SRS waste tanks primarily magnetite and hematite
  - Hematite more difficult to dissolve by oxalic acid
- **Testing and waste tank samples show poor nickel removal**
  - Nickel forms precipitate with oxalic acid (nickel oxalate)
- **Testing and waste tank samples show poor plutonium removal**
  - Plutonium forms precipitate with oxalate

Phase 2 Mechanical Cleaning

- SRR performed additional heel removal (Phase II Mechanical Cleaning) by a “Feed and Bleed” process in Tank 5
- Process included addition of well water, tank mixing and liquid removal.
- Sludge heel started at estimated 3300 gallons waste. After Feed and Bleed Process, Tank 5 contained 4065 gallons of liquid.
- Heel sample collected and sent to SRNL for characterization.
- Final mapping of tank planned in future.

Composition of Solids Remaining after Feed and Bleed

Species	Conc. (mg/kg)	Species	Conc. (Ci/g)
Al	4941	^{90}Sr	1.4×10^{-2}
Fe	469,000	^{99}Tc	1.7×10^{-9}
Hg	2060	^{137}Cs	3.0×10^{-4}
Mn	38,000	^{238}Pu	2.2×10^{-6}
Ni	64,000	$^{239/240}Pu$	9.5×10^{-6}
U	10,700	^{241}Am	7.3×10^{-5}
		^{242m}Am	1.7×10^{-7}
		^{242}Cm	1.6×10^{-7}
		^{244}Cm	4.2×10^{-5}

Conclusions

- **With exception of iron, dissolution of sludge components from Tank 5 agreed with results from actual waste demonstration**
  - Fraction of iron removed from Tank 5 by chemical cleaning was significantly less than fraction removed in demonstrations
  - Likely cause of difference is higher pH in the initial oxalic acid strike and different iron species in the waste
  - Subsequent strikes removed additional iron
- **Most of sludge mass remaining in tanks is Fe and Ni**
- **Remaining sludge contains significant amounts of Ba, Cr, & Hg**
- **Most of radioactivity remaining in tanks is derived from ^{90}Sr.**
- **Chemical cleaning efficient at removing U, Al, Ca, Na, Sr, & Cs**
- **Chemical cleaning not efficient at removing Ni, Hg, Pu, Am, & Cm**
- **Mechanical cleaning is now complete for Tank 5.**