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Development of Modified Monosodium Titanate

Project #SR081301 – Improved Strontium and Actinide Separations

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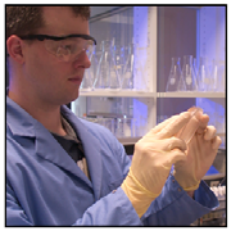
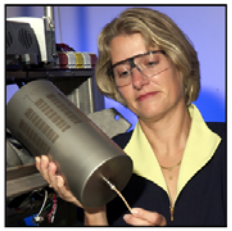
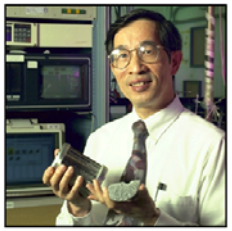
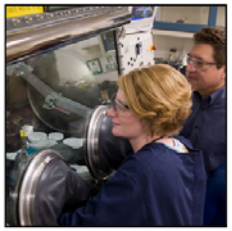
May 20, 2009

Office of Waste Processing Technical Exchange

SRNL-STI-2009-00325

Presentation Outline

- Background
- Summary of Phase II findings
- FY08 Phase III findings
- FY09 Phase III findings
- Current/Future Activities
- Acknowledgements

Background

- **MST is baseline material for Sr/actinide removal from SRS HLW solutions**
  - **Actinide Removal Process (ARP)**
  - **Salt Waste Processing Facility (SWPF)**
- **Adsorption kinetics and capacity can adversely impact pretreatment throughput and downstream operations**
- **Technical need to develop adsorbent with increased adsorption kinetics and capacities for Sr & Pu**

Background

Discovered improved sorption kinetics and capacity of peroxotitanates (FY04)

MST

mMST

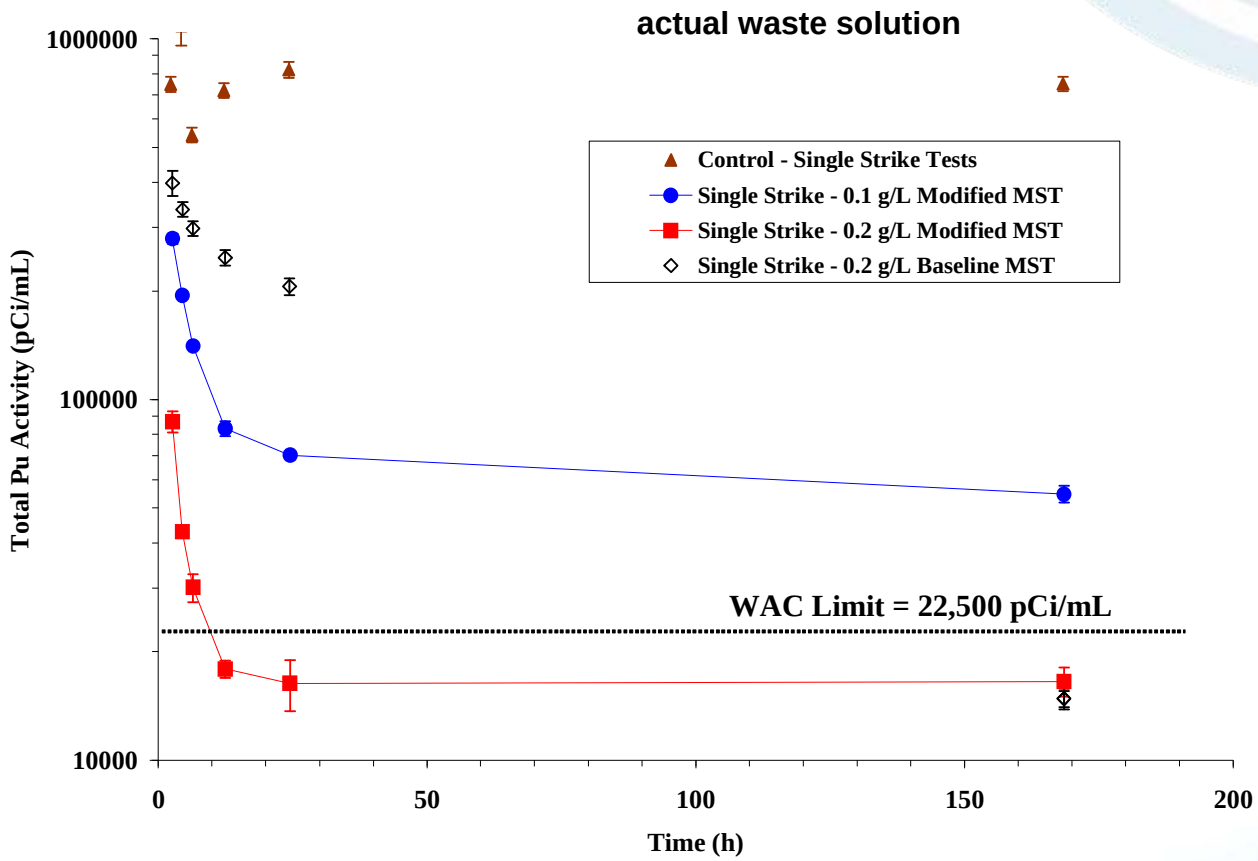
Phase I technical summary report (WSRC-TR-2004-00322)
M.D. Nyman, D.T. Hobbs, *Chem. Materials*, 2006 (18), 6425 – 6435

Phase II Findings

- mMST exhibits faster removal kinetics and higher effective capacities for Sr, Pu and Np compared to MST
  - reduce contact time (4-6 hours vs 24 hours)
  - reduce sorbent quantity (0.1-0.2 g L^{-1} vs 0.4 g L^{-1})
- mMST exhibits similar filtration characteristics as MST
  - Use of 0.1 micron media preferred
  - Slightly reduced initial flux for mMST in absence of sludge; greater flux in presence of sludge
- Successfully produced pilot-scale quantity (15 kg) of mMST by vendor (Optima Chemical Group LLC)
- mMST exhibits good lifetime upon storage under controlled temperature conditions
  - $\geq$ 30 months for lab-prepared mMST
  - $\geq$ 17 months for vendor-prepared mMST
- mMST exhibits much lower affinity for U compared to MST
  - 1.80 mmole/g (0.043 wt %) for mMST compared to 47.1 mmole/g (1.12 wt %) for MST

Plutonium Removal Performance

mMST exhibits excellent Pu removal with both simulated and actual waste

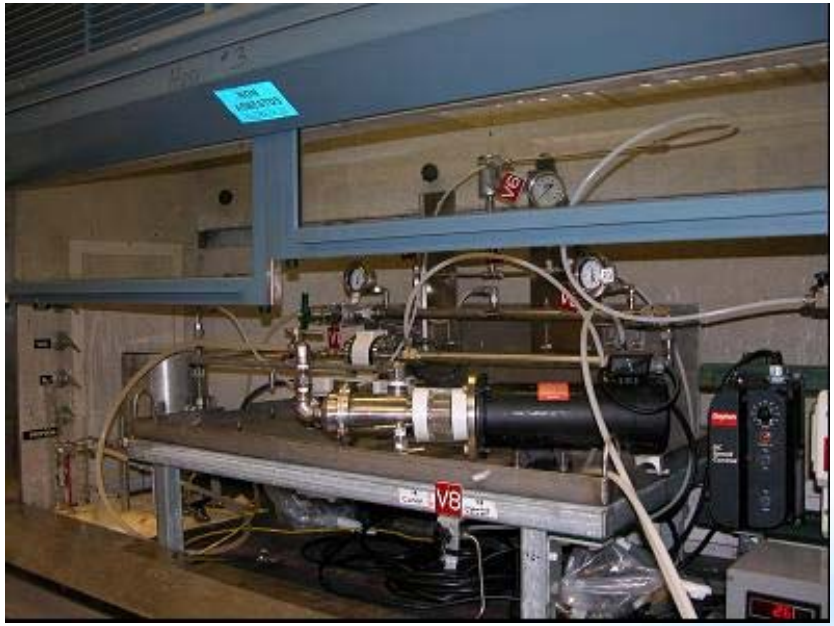


Filtration Testing

Dead-end filter apparatus

Crossflow filter

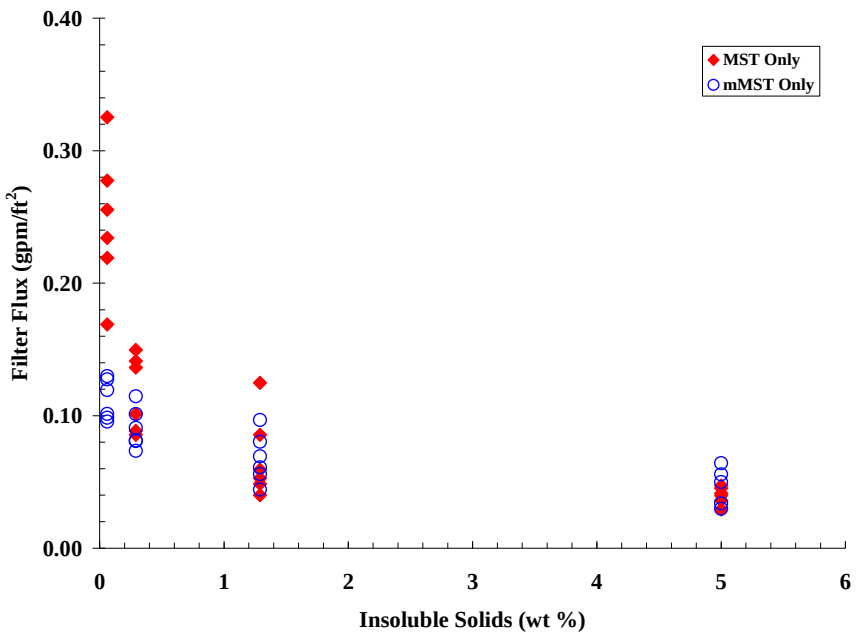
Simulated waste solution with mMST or MST (with & w/o sludge)

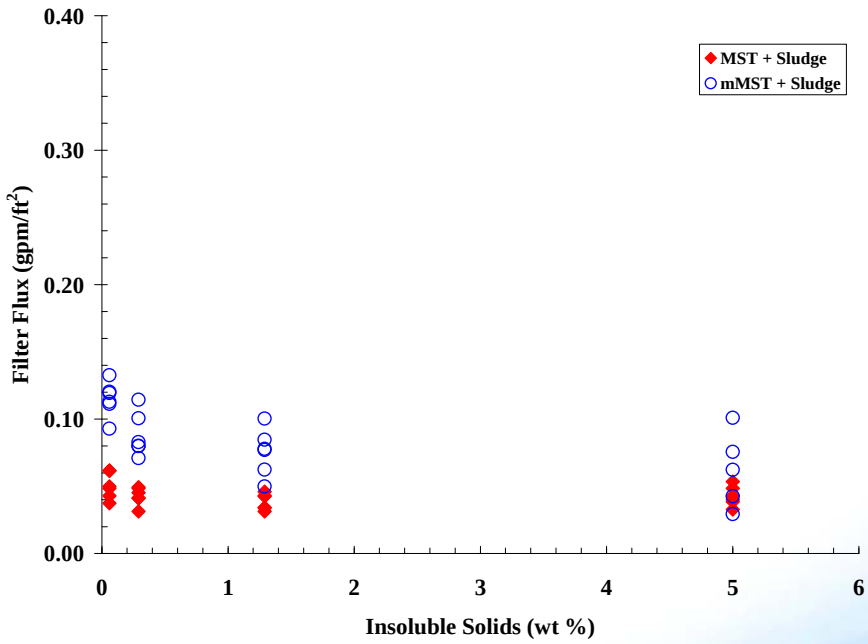


0.1-μm pore-size Mott filter membrane

Filtration Performance

Crossflow filtration tests indicated similar filtration characteristics for the vendor-prepared mMST and baseline MST samples with 0.1-m filter membranes

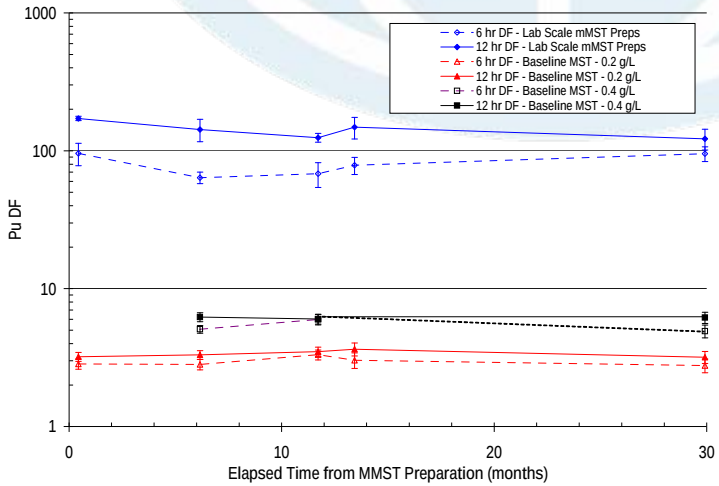


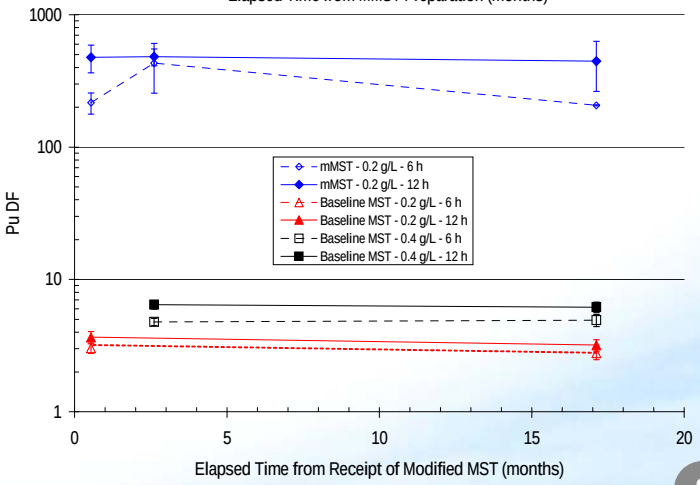


Shelf-life Testing: Sorbate Removal Performance

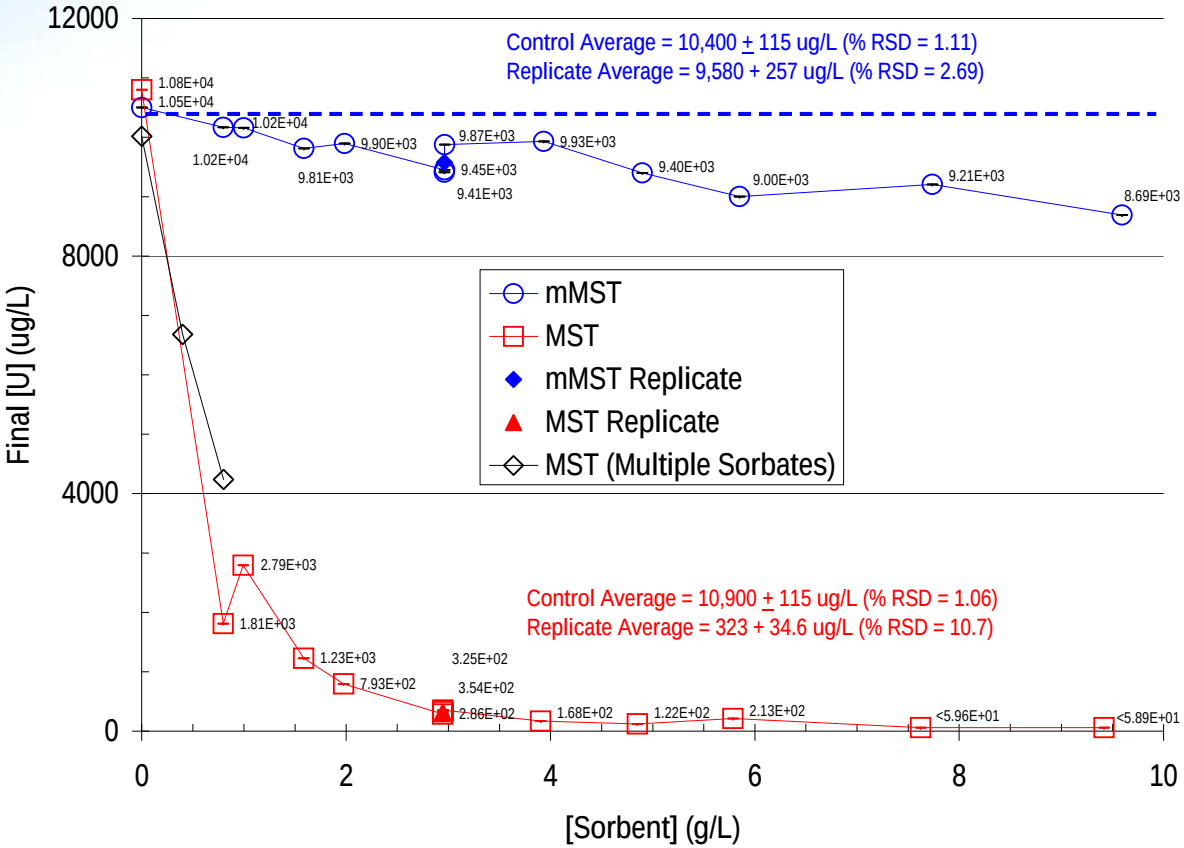
Sorbate removal performance of lab-prepared and vendor-prepared mMST remains unchanged after 30 and 17 months of storage, respectively.

	Contact Time = 12hours					
Storage Time (months)	mMST Pu DF	MST Pu DF	mMST Sr DF	MST Sr DF	mMST Np DF	MST Np DF
	Lab-prepared mMST					
0.44	172	3.21	128	24.8	1.83	1.25
6.2	143	3.31	137	27.8	1.24	0.74
12	124	3.49	132	28.1	1.47	0.88
13	148	3.65	117	26.8	2.18	1.70
30	122	3.19	26.1	10.7	2.20	1.14
	Vendor-prepared mMST					
0.54	477	3.65	507	26.8	3.67	1.70
2.6	483		>461		3.18	
17	447	3.19	112	10.7	3.18	1.14





Uranium Adsorption

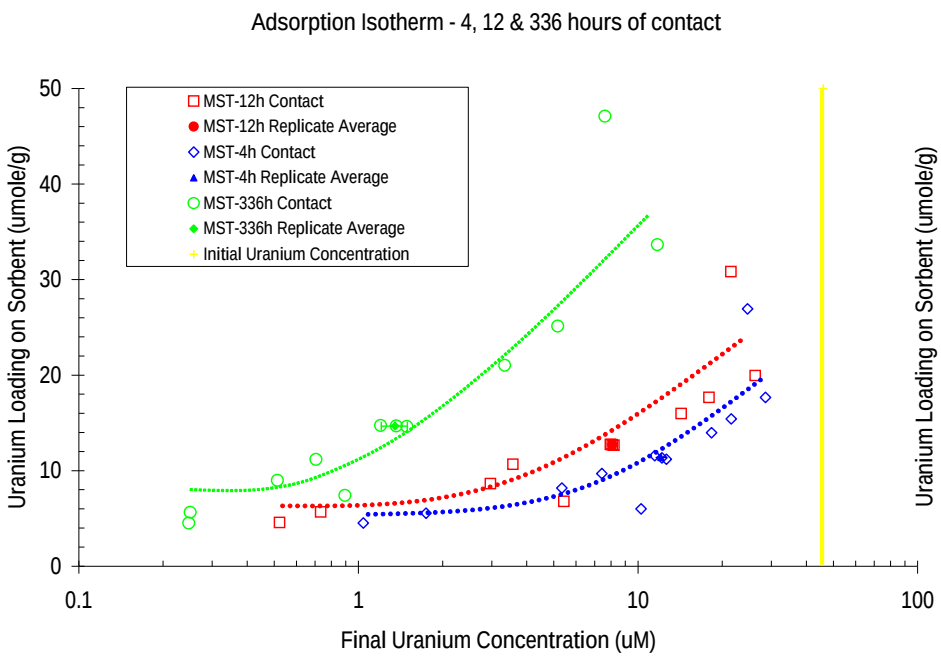


- Simulated waste solution containing only uranium (10,700 μg L^{-1})
- Varied mMST and MST concentration: 0.4 – 9.6 g L^{-1}
- Contact times: 4, 12, 336 h
- Temperature: 25 °C

Uranium Adsorption

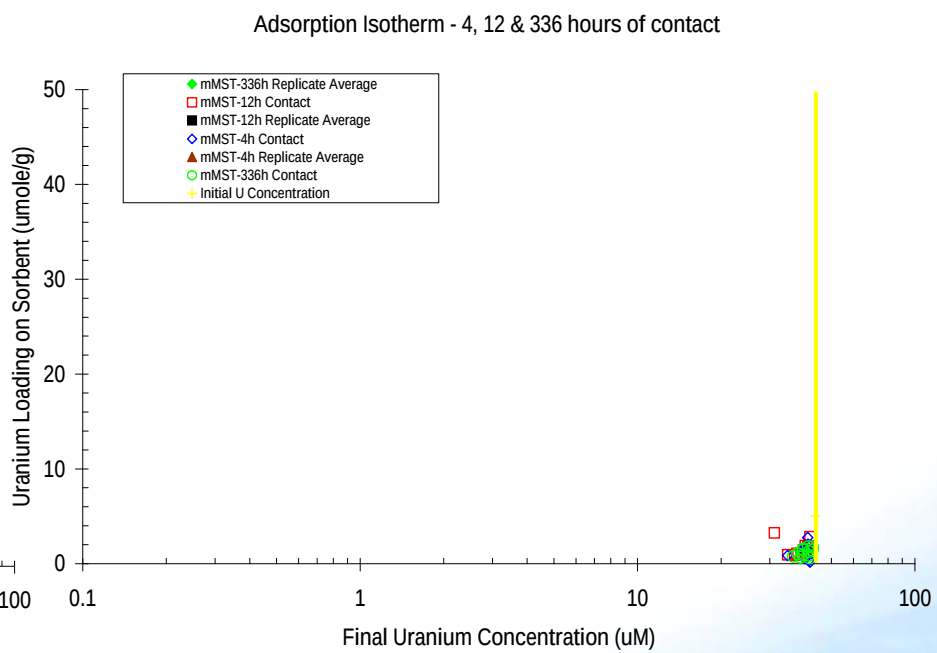
Baseline MST exhibits expected adsorption isotherm behavior

$[U]_s$ = 1.12 wt % on MST



mMST exhibits little uranium adsorption

$[U]_s$ = 0.043 wt % on mMST



Phase III Testing – FY2008

EM-21 Project #SR081301 – Improved Strontium and Actinide Separations

- Effect of temperature on Sr/actinide removal performance
- Effect of ionic strength on Sr/actinide removal performance
- Effect of acidic wash and filtration step on gas release
- Thermal stability

* Hobbs, D. T.; Fink, S. D. "Development Plan for the Use of Modified Monosodium Titanate in the Actinide Removal Project (ARP), Modular Salt Processing (MSP) and Salt Waste Processing (SWPF) Facilities", WSRC-RP-2007-00772, Rev. 0, October 2007.

Influence of Temperature

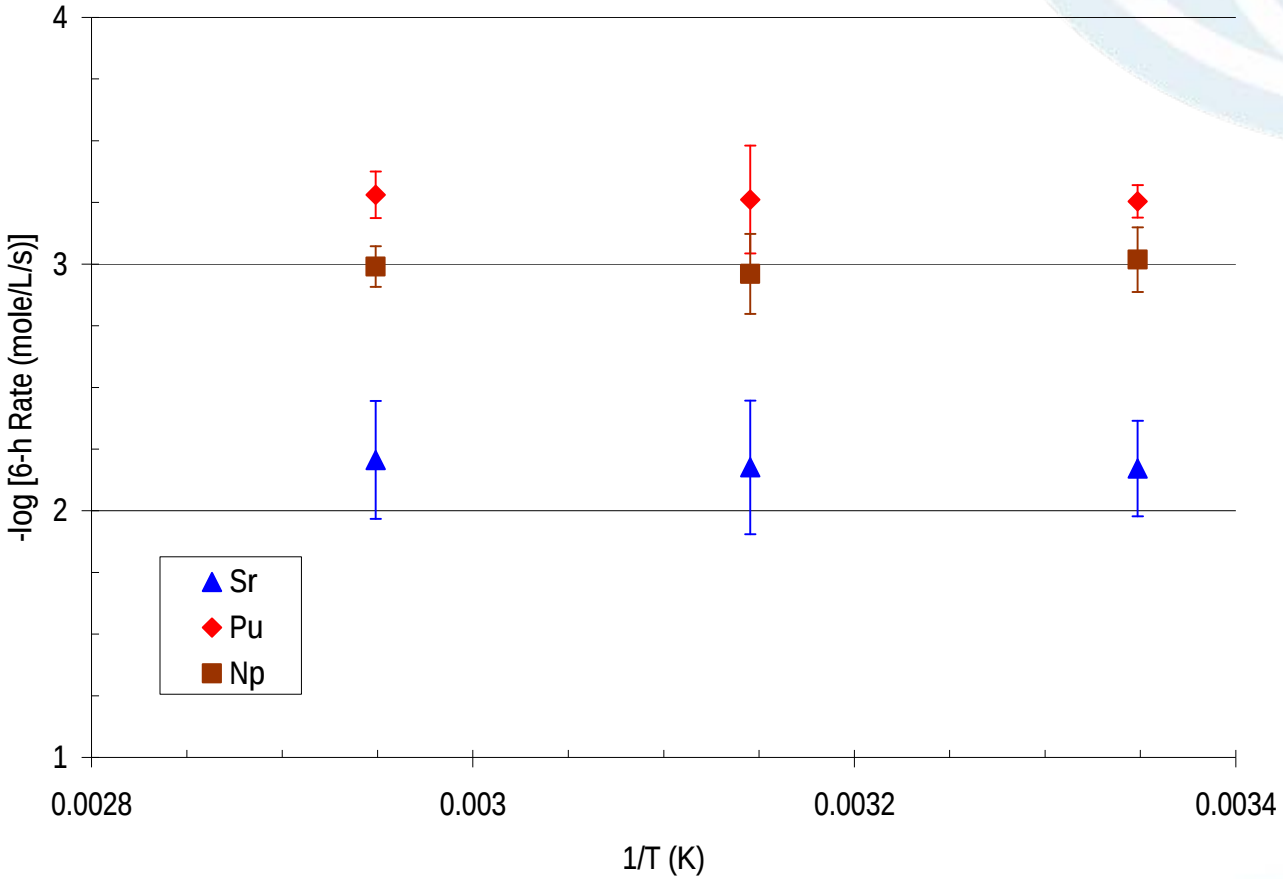
From tests conducted with mMST over the temperature range of 26 – 66 °C in contact with 5.6M Na simulated waste solution

- Increasing temperature has a small, but positive influence on the removal of Sr
- Increasing temperature provided no statistically significant influence on the removal of Pu
- Np removal was unaffected by an increase in temperature from 26 to 45 °C and exhibited only a small decrease at a temperature of 66 °C
- No measurable removal of U occurred over the temperature range and mMST concentration of 0.2 g L^{-1}
- Temperature did not affect the rate of adsorption of Sr, Pu & Np

D. T. Hobbs, "Improved Strontium and Actinide Separations Modified Monosodium Titanate Final Report of FY2008 Testing Activities", SRNL-STI-2008-00390, Rev. 0, December 2008.

Influence of Temperature – Adsorption Kinetics

Adsorption kinetics unaffected by temperatures ranging from 26 – 66 °C



Effect of Ionic Strength

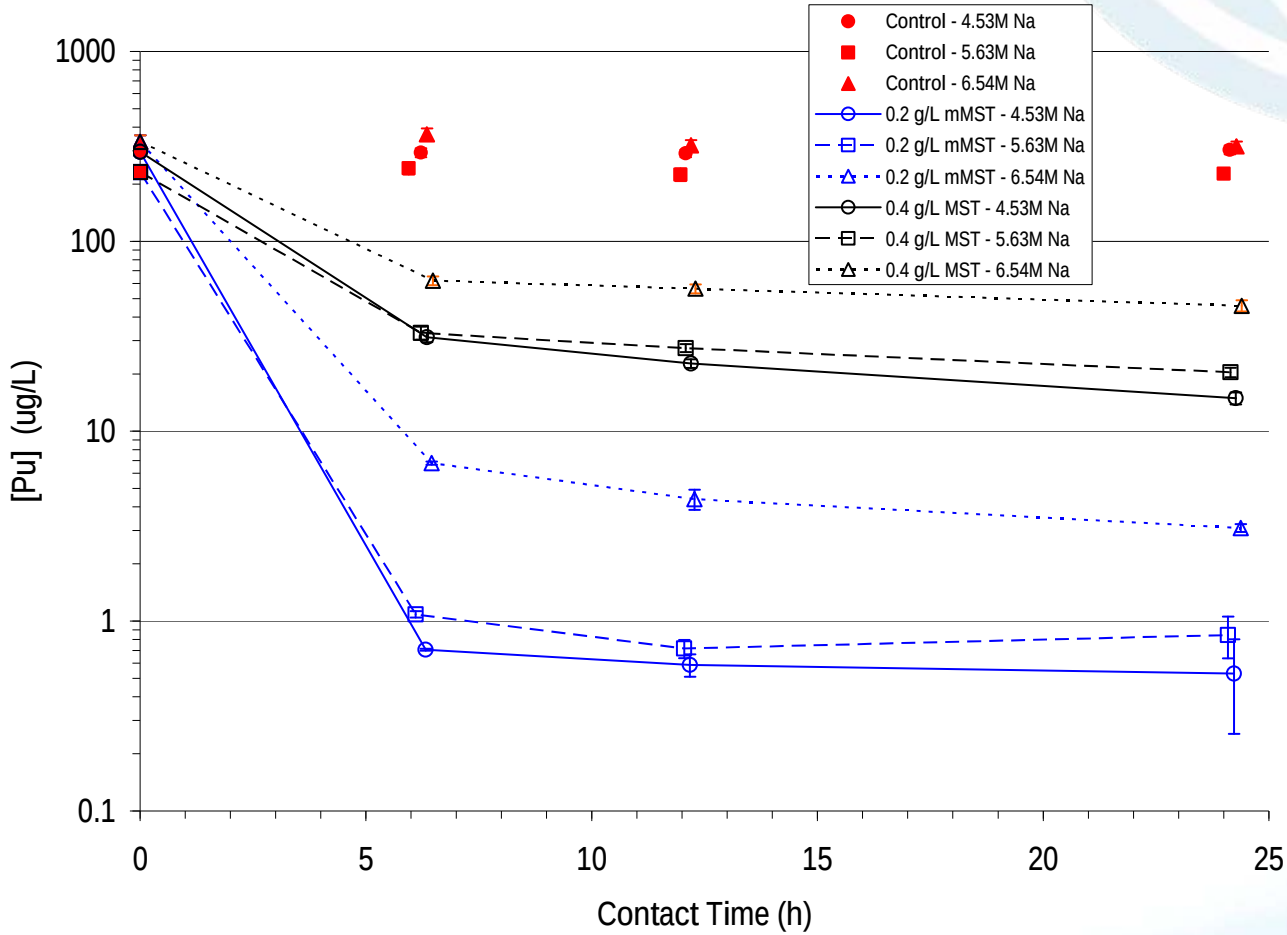
Testing featured simulated waste solutions having ionic strengths (Na concentrations, densities) ranging from 4.93 M (4.49 M in Na, d = 1.20 g mL^{-1}) to 7.14 M (6.54 M in Na, d = 1.29 g mL^{-1}):

- Increase in the ionic strength produced a decrease in the removal of Sr & Pu
- Np removal was unaffected by changes in the ionic strength of the solution
- No measurable U removal at any ionic strength

D. T. Hobbs, "Improved Strontium and Actinide Separations Modified Monosodium Titanate Final Report of FY2008 Testing Activities", SRNL-STI-2008-00390, Rev. 0, December 2008.

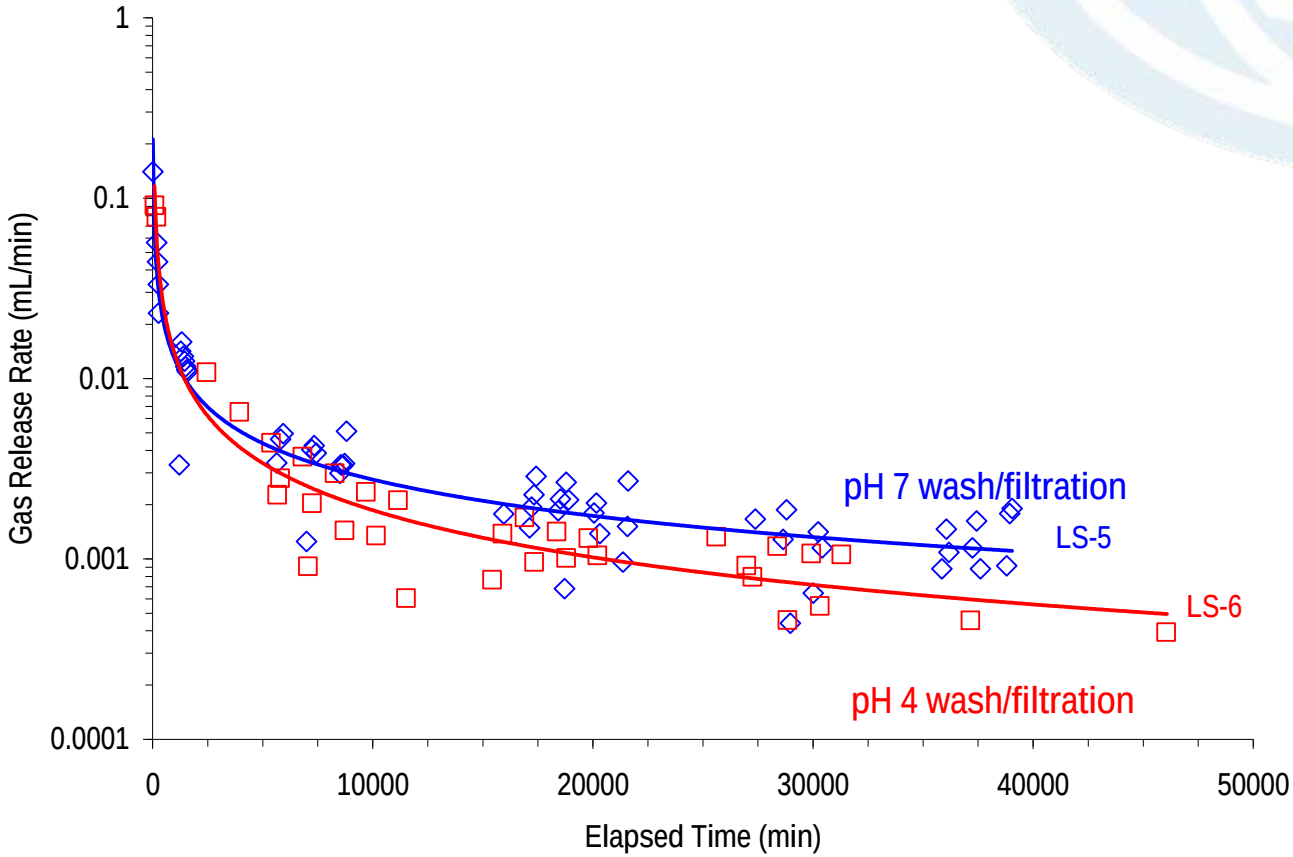
Ionic Strength Influence – Plutonium Removal

Increase in the ionic strength produced a decrease in plutonium removal



Effect of Low pH Wash & Filtration on Gas Release

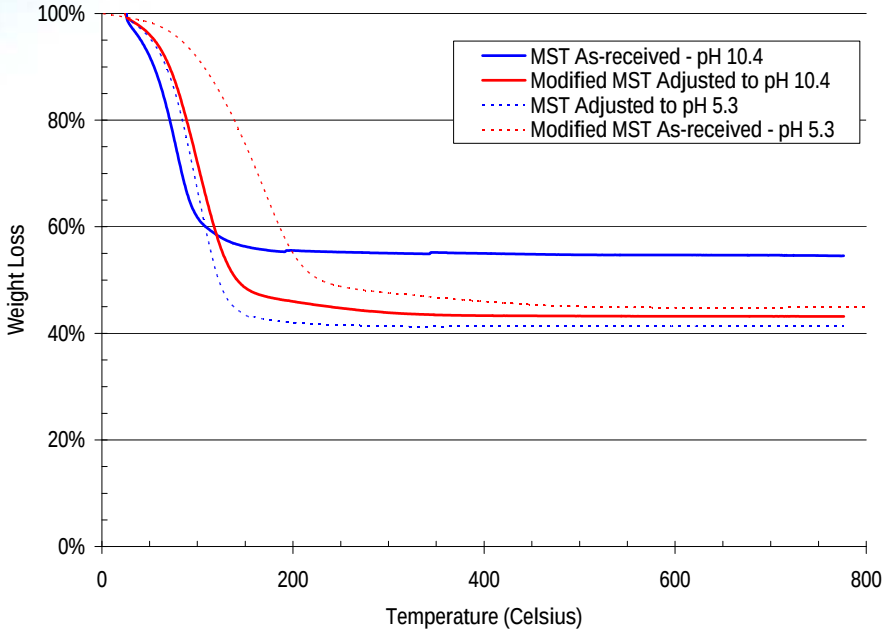
Low pH wash (pH 4) and filtration step did not significantly reduce post-synthesis oxygen gas release

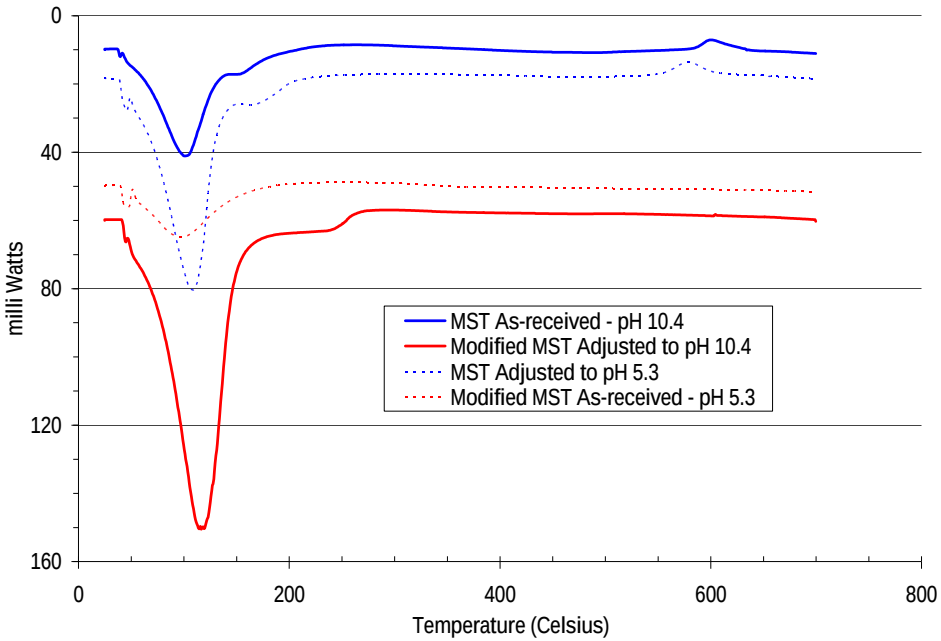


D. T. Hobbs, "Improved Strontium and Actinide Separations Modified Monosodium Titanate Final Report of FY2008 Testing Activities", SRNL-STI-2008-00390, Rev. 0, December 2008.

Thermal Stability of mMST

mMST exhibits excellent thermal stability





XRD study in progress

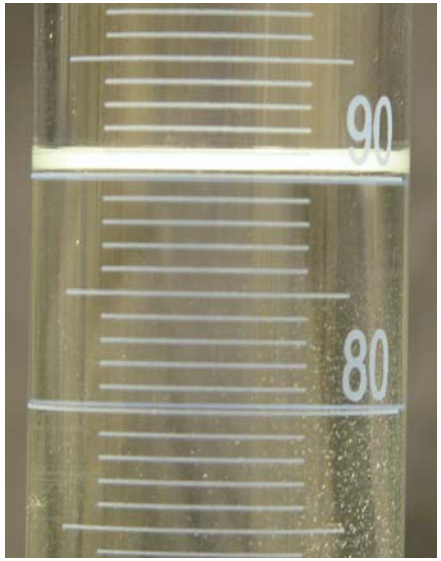
FY09 Planned Testing

- Measure solids settling characteristics
- Measure desorption characteristics
- Determine if high pH wash and filtration step decreases gas release
- Measure sorption kinetics under reduced mixing conditions
- Measure gas release characteristics at higher storage temperature
- Determine effect of radiation on mMST performance
- *Perform radioactive tests with engineered form of MST/CST for Cs, Sr, actinide separations*

Solids Settling – Gravity

- mMST fines settle slower than MST fines
  - simulants with [Na] = 4.6, 5.6 and 6.6 M
  - mMST particles more adherent to glass walls
- Additional tests in progress

Early stage of settling test



Late stage of settling showing clear supernate, settled solids and solids adhering to glass walls

Solids Settling - Centrifugal

	Settled Solids Conc (g/mL) Average (1 s) Centrifuge Speed = 6.3 x g	
Suspended Solids Concentration (g/mL)	**Settling Fluid [Na] = 5.6 M**	**Settling Fluid [Na] = 0.5 M**
0.03	0.188 (0.007)	0.212 (0.015)
0.09	0.201 (0.002)	0.214 (0.005)
0.15	0.197 (0)	0.197 (0)

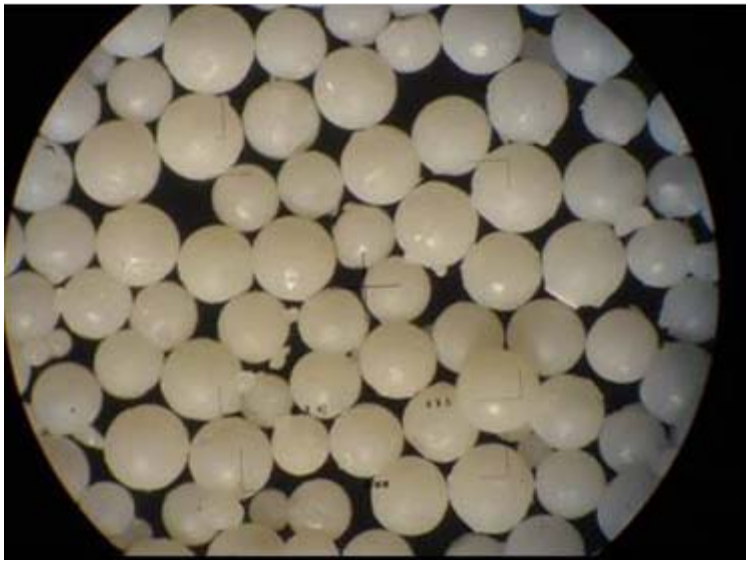
	Settled Solids Conc (g/mL) Average (1 s) Centrifuge Speed = 1400 x g	
Suspended Solids Concentration (g/mL)	**Settling Fluid [Na] = 5.6 M**	**Settling Fluid [Na] = 0.5 M**
0.03	0.300 (0.020)	0.318 (0.004)
0.09	0.338 (0.004)	0.342 (0.002)
0.15	0.365 (0.012)	0.348 (0.005)

Desorption Experiment

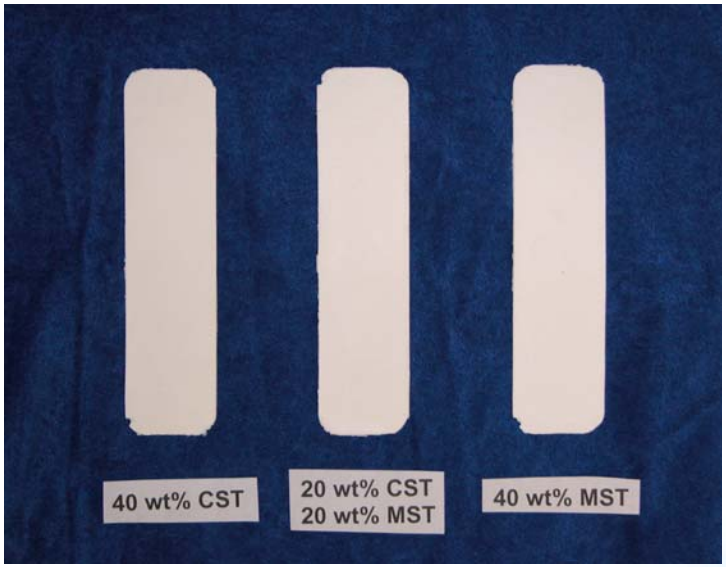
- Load mMST solids with Sr, Pu, Np & U by contacting mMST with 5.6 M salt solution
- Isolate sorbate-loaded mMST solids from sorbate-depleted salt solution
- Contact loaded mMST solids with diluted, sorbate-depleted salt solution representing 3 stages of washing sequence
  - 2.8 M in Na salt solution (2.0x dilution)
  - 1.0 M in Na salt solution (5.6x dilution)
  - 0.5 M in Na salt solution (11x dilution)
- Data Pending

Engineered Forms of MST

- Identified methods to produce engineered forms of MST
  - Internal gelation (ORNL) and porous substrate [C. Nash]
  - Incorporate MST/CST into filter membranes [L. Oji – LDRD]



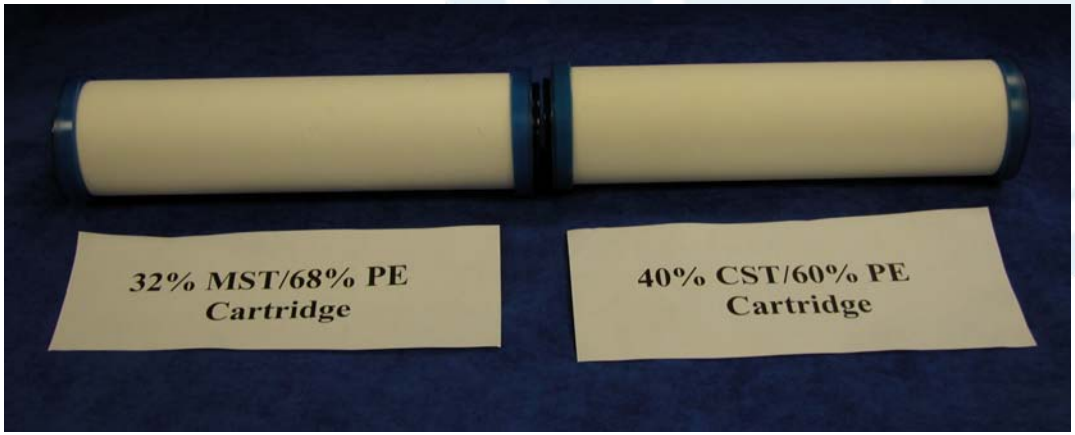
MST in hydrous titania spheres



MST/CST in PE membrane

Filter Membrane Performance

- Measure ^{137}Cs & ^{85}Sr removal from radioactive simulants



- Influence of ionic strength, flowrate, single/multiple pass and sorbent sequence on performance

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Deployment Opportunities

- Radiochemical Separations
  - High Level Nuclear Waste
    - *Actinide Removal Process (ARP) – 2010*
    - *Salt Waste Processing Facility (SWPF) – 2013*
    - *Enhanced Processes for Radionuclide Removal (EPRR)*
      SCIX (engineered form) or In-tank (powder)
  - Low level Nuclear Waste
    - *Small volume - filter membrane*
    - *Large volume - engineered form*
- Metal Separations
  - Industrial wastewater
  - Contaminated groundwater

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- Funding provided by DOE EM-21 Office of Waste Processing
- David DiPrete, Ceci DiPrete, Curtis Johnson – radioanalytical measurements
- Mona Blume and Kim Wyszynski – experimental testing
- Larry Oji and Keisha Martin - filter membrane development (LDRD)
- Charles Nash & Kofi Adu-Wusu (SRNL), Jack Collins & Rodney Hunt (ORNL), Edgar Buck (PNNL) – engineered MST

Questions?

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