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We Put Science To Work

Improved Strontium and Actinide Separations

WP-2 Task # 2.1.1

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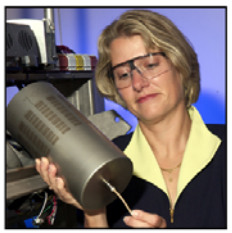
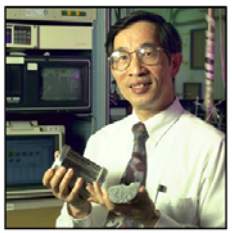
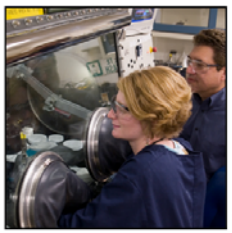
November 16, 2010

EM-Waste Processing Technical Exchange

SRNL-STI-2010-00715

Office of Environmental Management
safety ❖ performance ❖ cleanup ❖ closure

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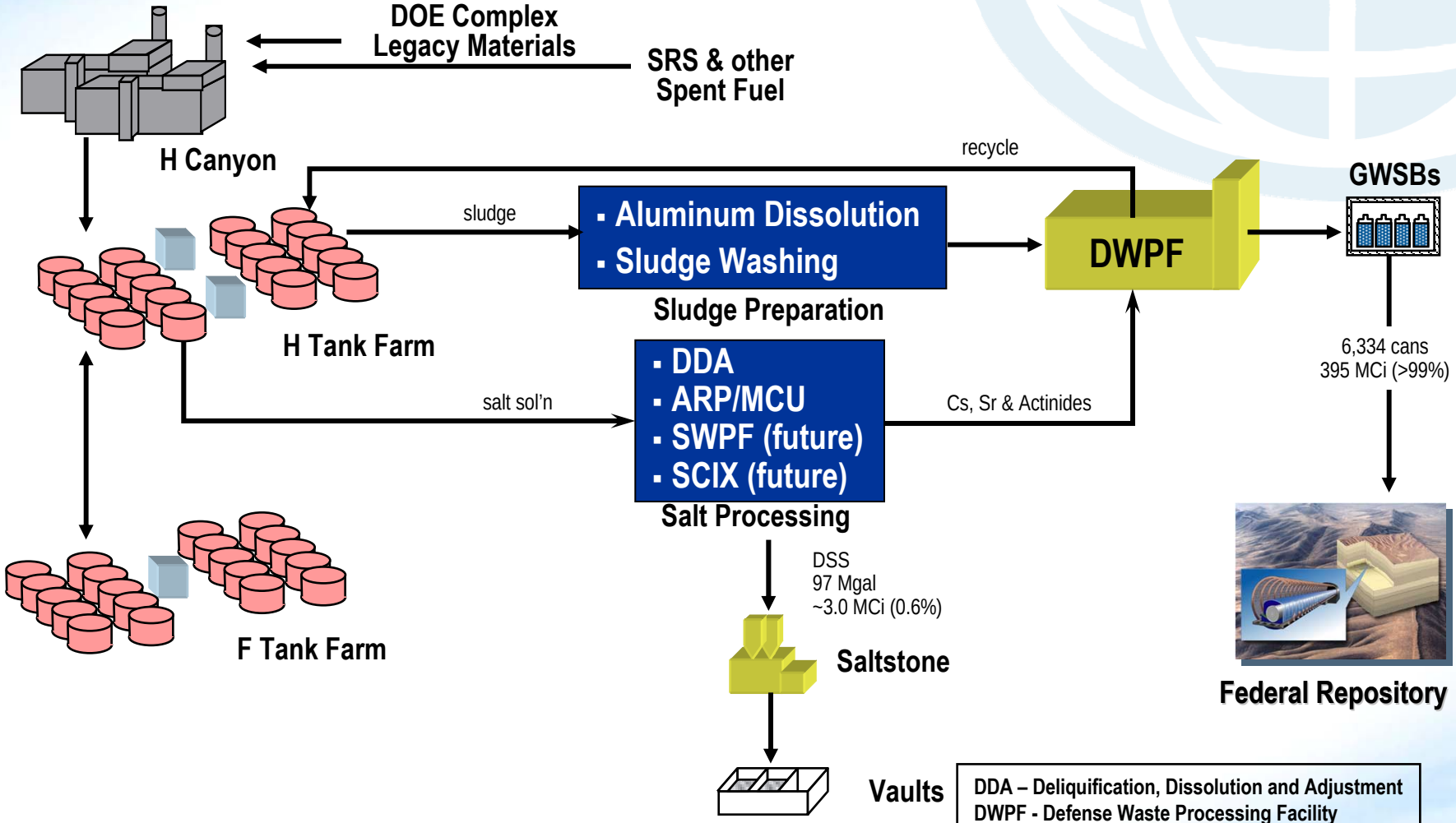
SRS High Level Waste Flowsheet



DDA – Deliquification, Dissolution and Adjustment
DWPF - Defense Waste Processing Facility
GWSB - Glass Waste Storage Building
DSS – Decontaminated Salt Solution

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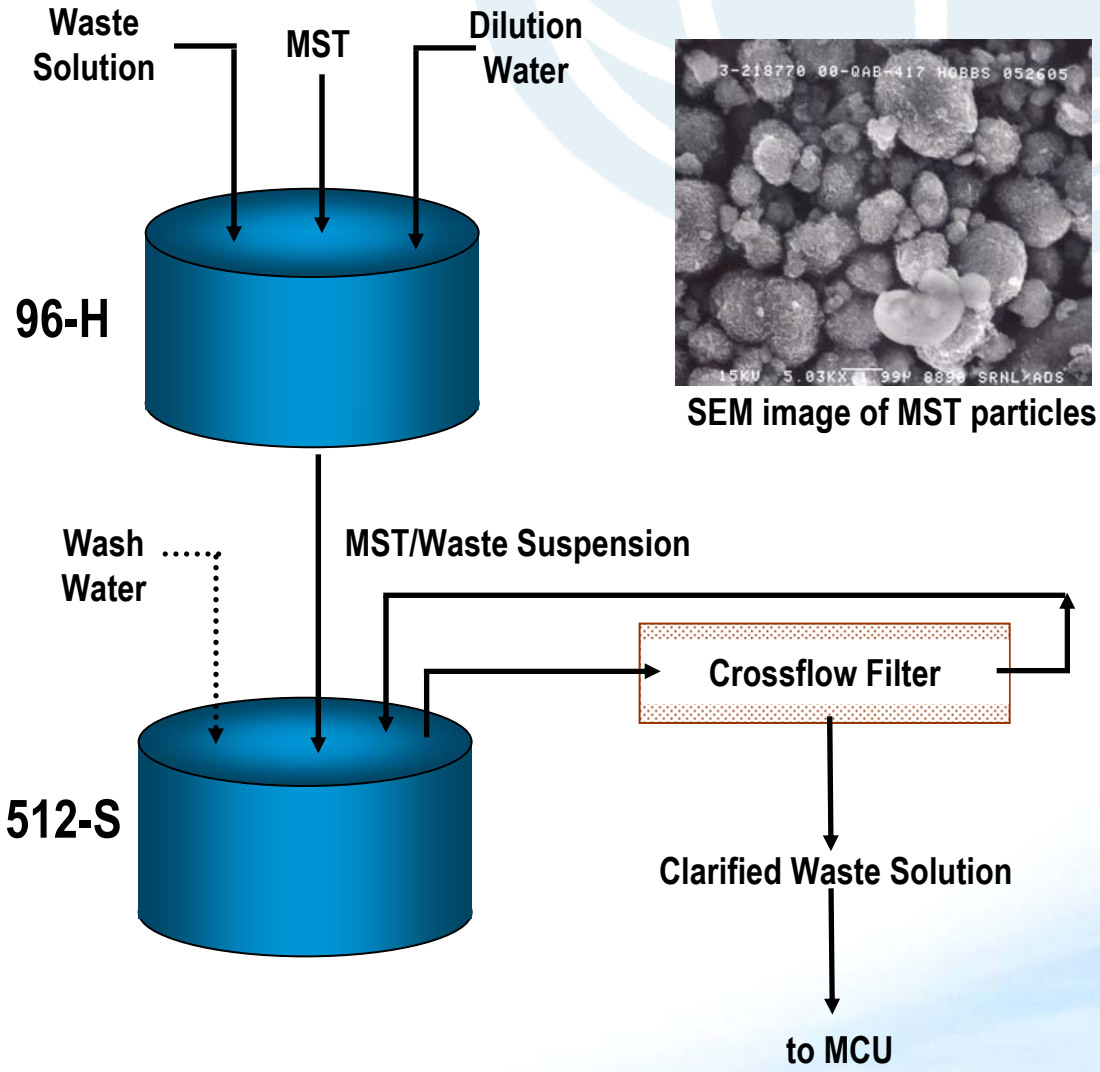
Actinide Removal Process

- ^{90}Sr and alpha-emitting radionuclides (Pu, Np, U, Am) removed by ion exchange with monosodium titanate (MST) – $NaHTi_2O_5$
- 2-stage process
  - 12-h batch contact of MST with waste solution (96-H)
  - Solids concentration and washing using crossflow filter (512-S)



SEM image of MST particles

WAC Limits - Saltstone

Sr & actinide removal from SRS HLW solutions required to meet waste disposal requirements at Saltstone Production Facility

Radionuclide	WAC Targets (pCi/mL)	spA (g/Ci)	Mass Conc Limit (mg/L)	Approx Solubility (mg/L)
Sr-90	**2.25E+07**	**0.0072381**	**1.63E-01**	**10**
Pu-238	**2.50E+05**	**0.058426**	**1.46E-02**	**1**
Pu-239	2.50E+05	16.122	4.03E+00	1
Pu-240	2.50E+05	4.4077	1.10E+00	1
Np-237	**2.50E+05**	**1419**	**3.55E+02**	**1000**
U-235	1.13E+04	4.63E+05	5.23E+03	50
U-238	1.13E+04	2.98E+06	3.36E+04	50
Am-241	**2.50E+05**	**2.91E-01**	**7.29E-02**	**0.5**
Am-243	2.50E+05	5.011	1.25E+00	0.5
Cm-244	**2.50E+05**	**0.012357**	**3.09E-03**	**0.5**

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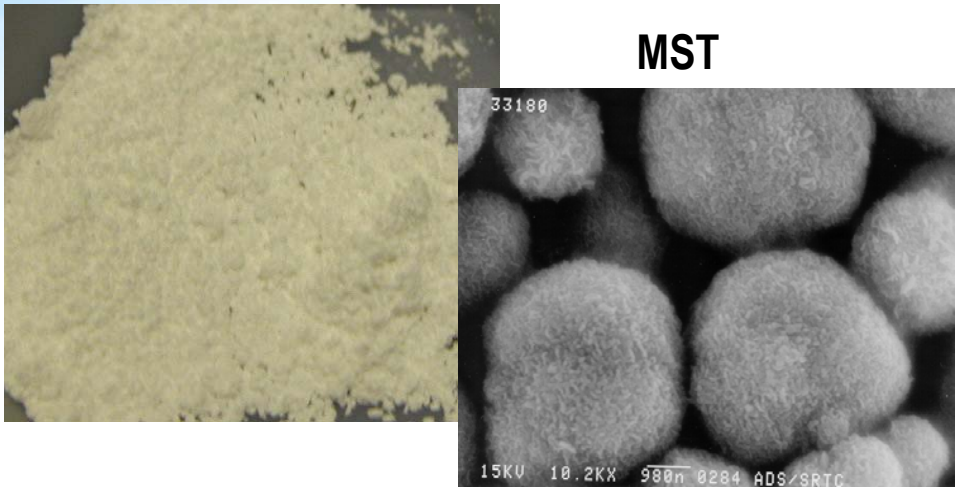
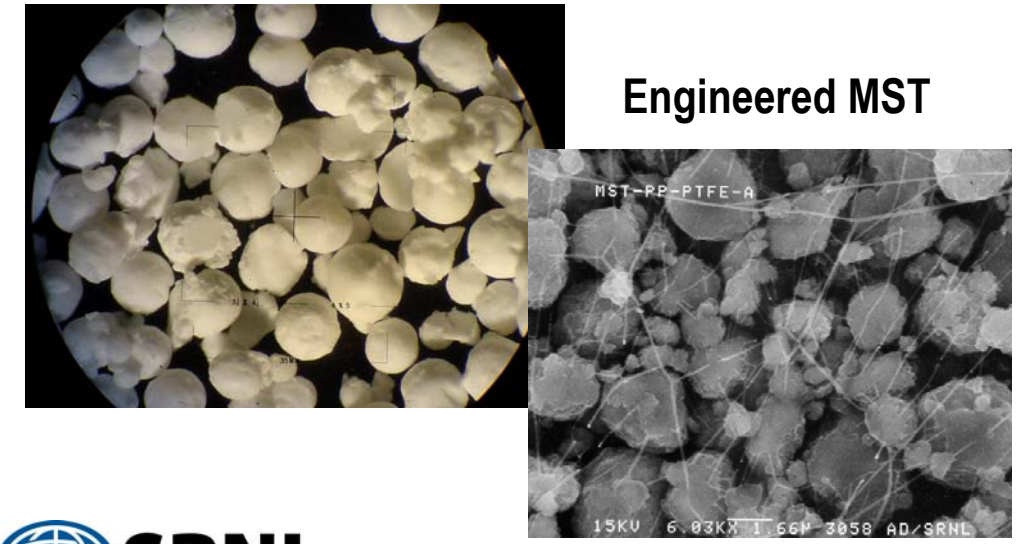
Improved Sr and Actinide Separations - Goals



MST

- Development of powder form of sorbent for direct replacement of MST



Engineered MST

- Development of engineered forms of sorbent for deployment in flow-through configuration

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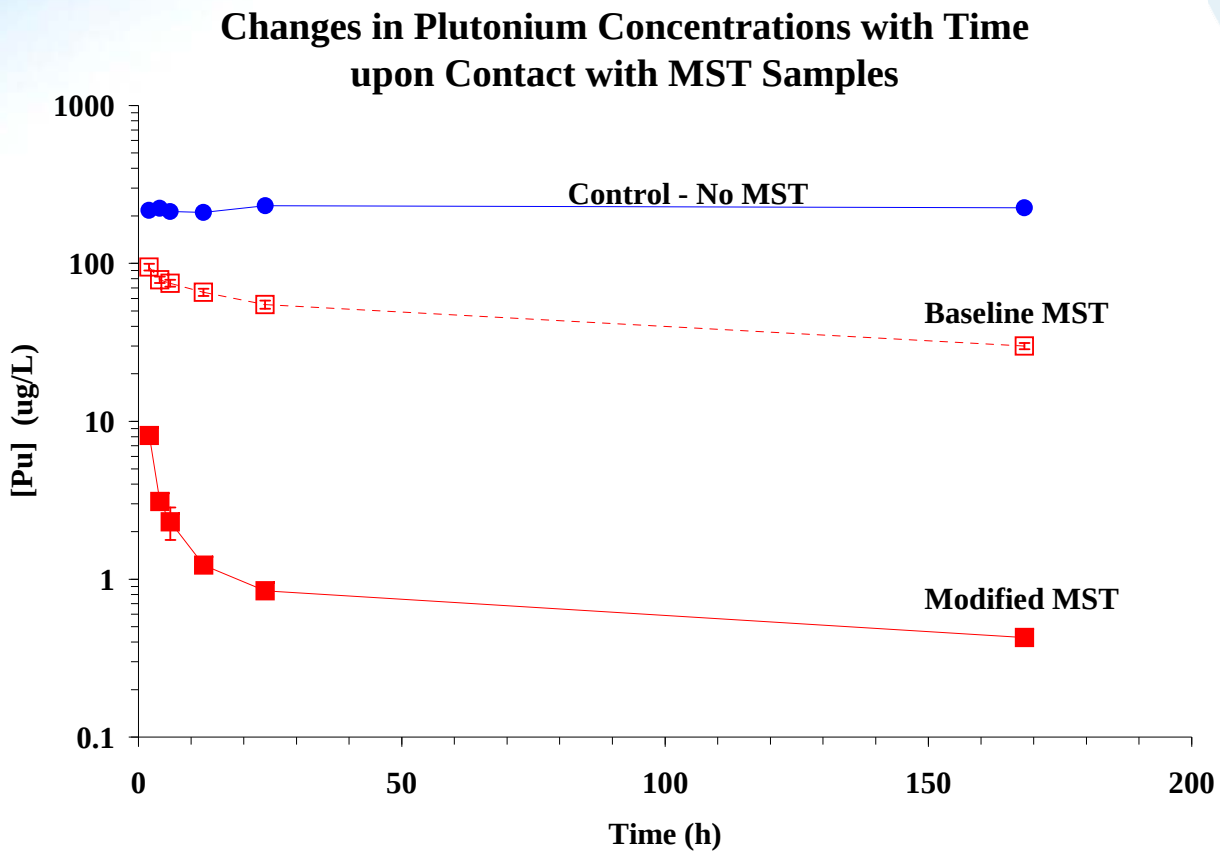
Modified MST

- Modified MST (mMST) synthesized by the treatment of MST with H_2O_2
  - Improved sorption kinetics and capacity of Sr, Np, and Pu.
  - Low affinity for U

MST

mMST

Peroxide-Modified MST (mMST)



mMST

Sorbent	Pu K_d (mL g^{-1})
MST	1.62 (0.11) E+04
mMST	1.32 (0.10) E+06

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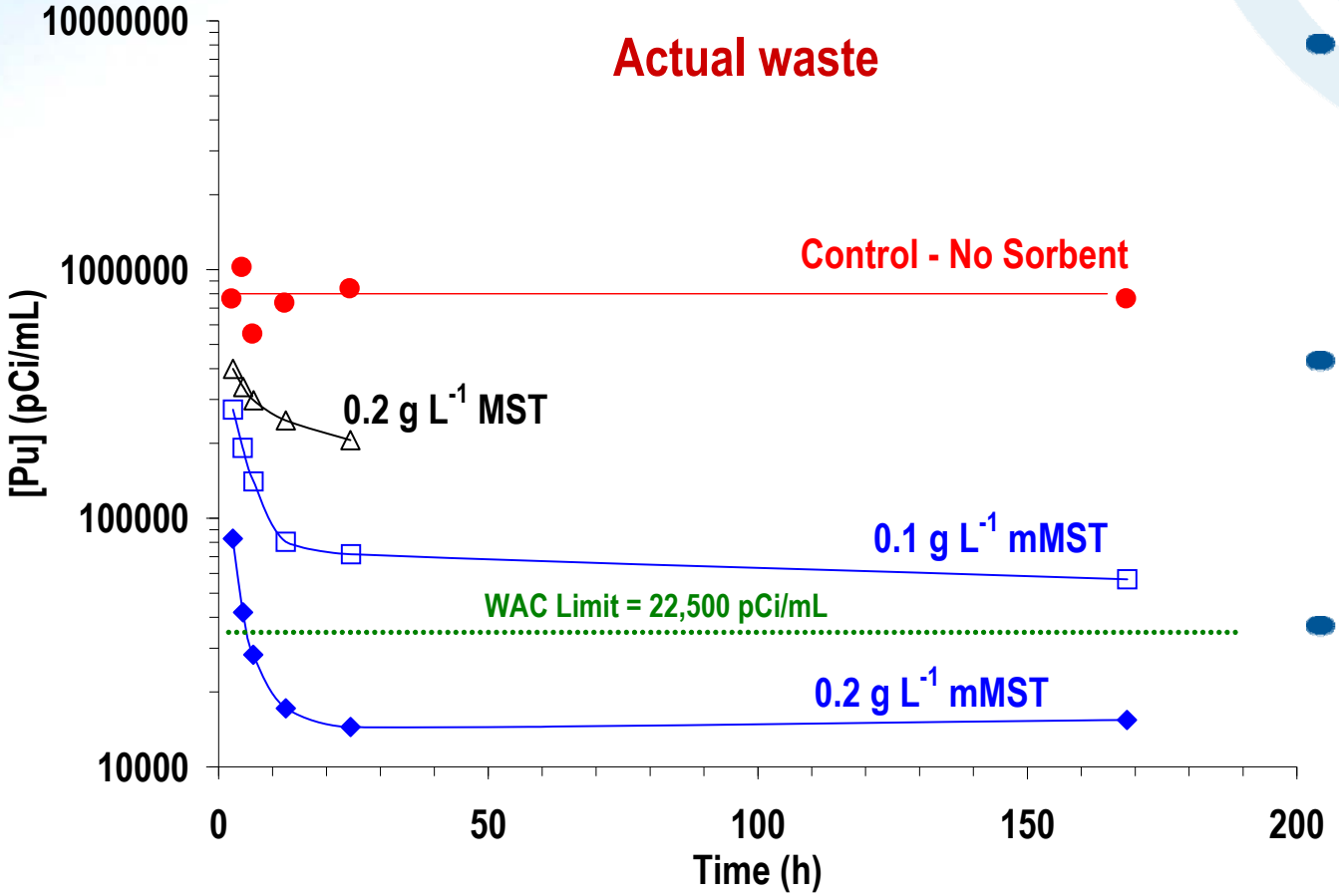
mMST Performance with Actual Waste



- mMST exhibited better Sr and Pu removal performance than the baseline MST
- mMST did not exhibit improved Np removal performance
- mMST exhibited no measurable U removal

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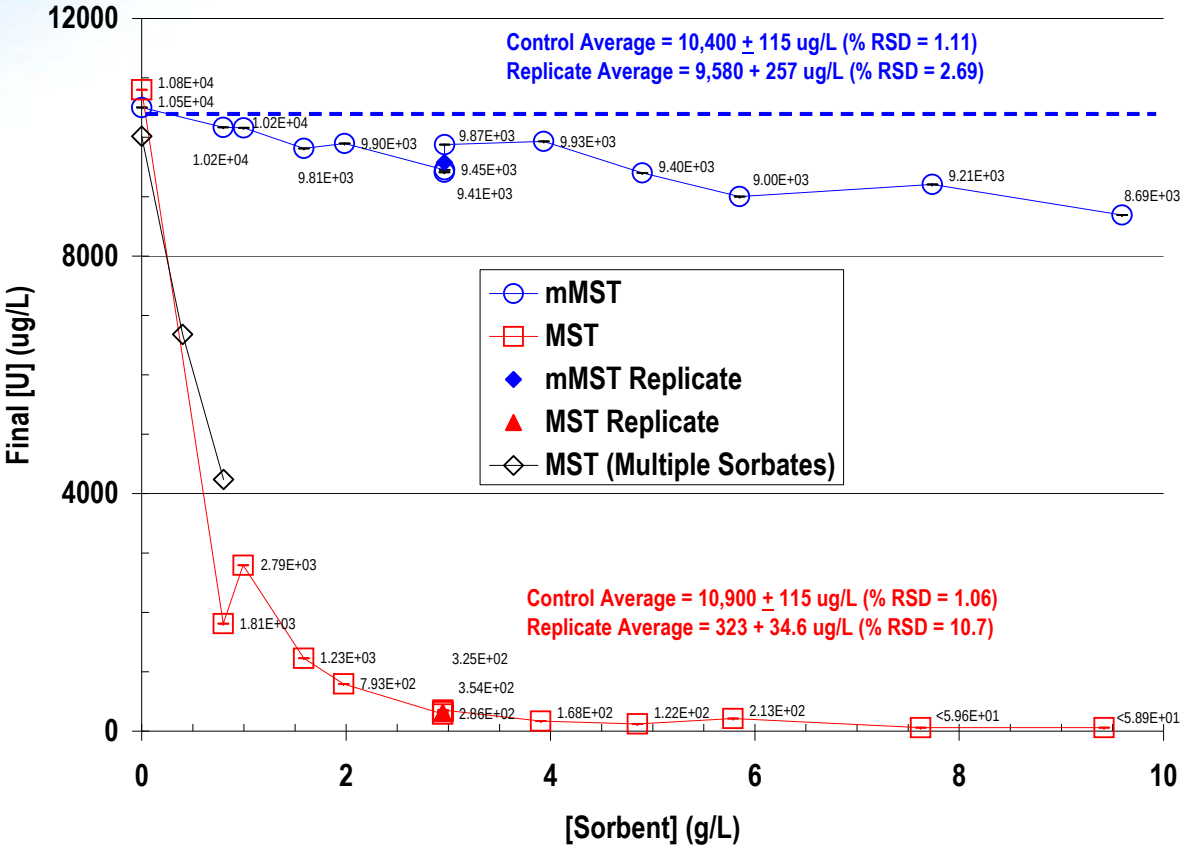
Uranium Removal



- 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

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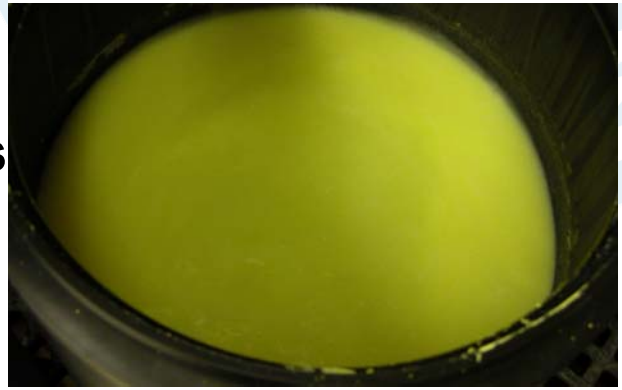
Recent Phase III Testing Activities

- XRD studies upon heating to 800 °C
- Solids settling characteristics
- Post-synthesis gas release under different conditions
- Extent of desorption under washing conditions
- Effect of gamma radiation on mMST performance
- Effect of aging on mMST performance

15 wt% mMST suspension in water



mMST dissolved in sulfuric acid

Scanning electron micrograph of mMST

Dried mMST powder

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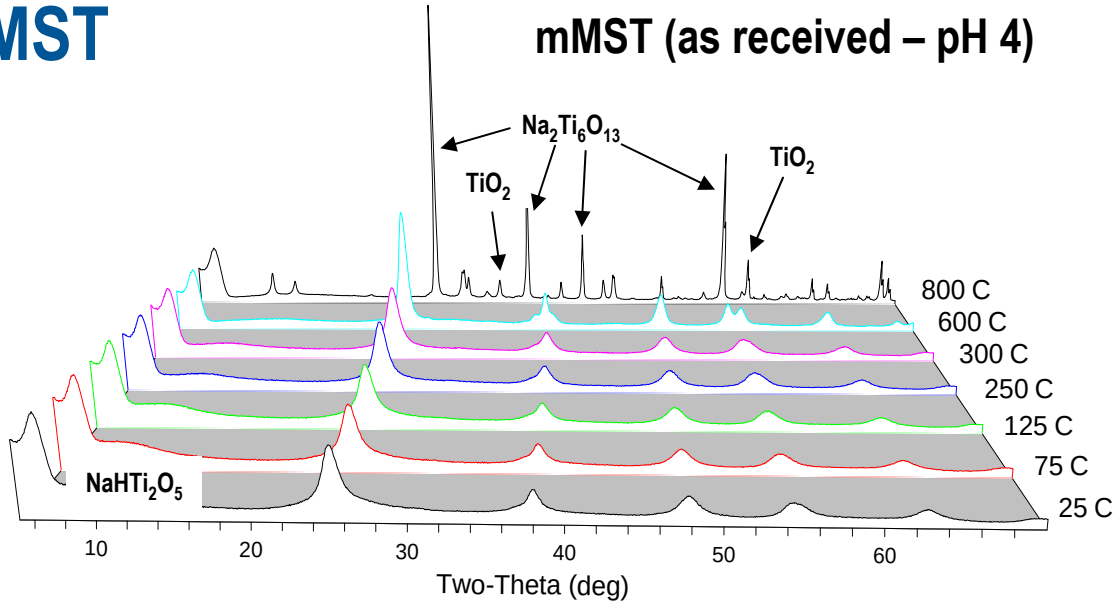
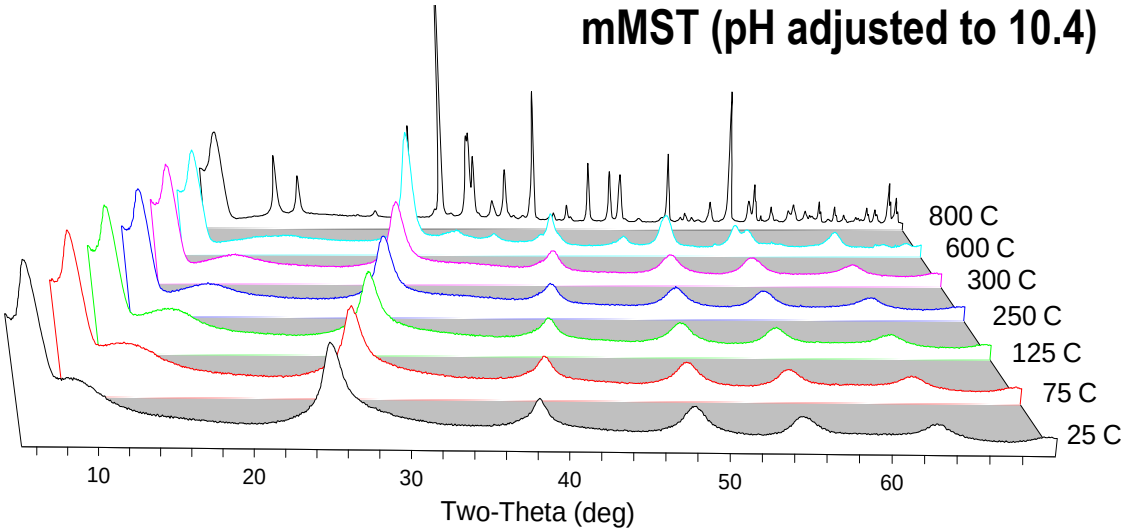
XRD Study – MST/mMST

- Measured XRD patterns of MST and mMST from 25 – 800 °C under He purge
- Amorphous and poorly crystalline phases observed at 25 – 300 °C
- Phase changes and higher degree of crystallinity observed in 600 °C XRD patterns
- Nanocrystalline anatase (TiO_2) reported in mMST at 25 – 300 °C and $Na_2Ti_6O_{13}$ and minor amounts of TiO_2 above 300 °C





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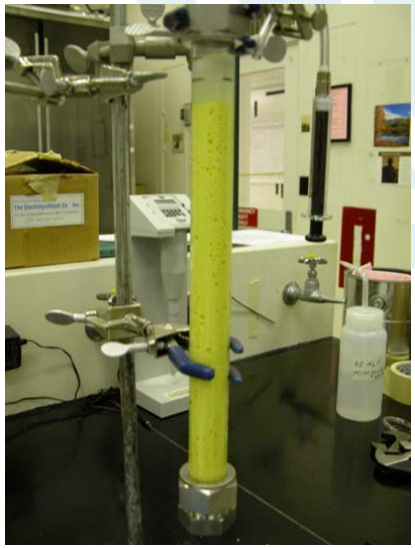
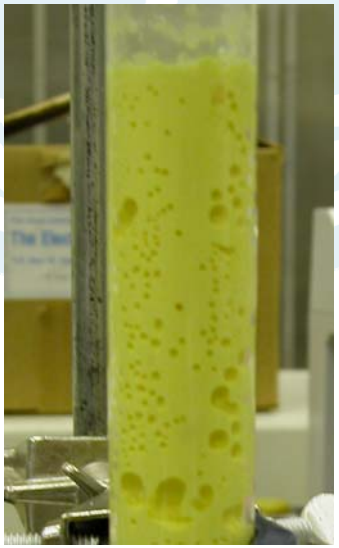
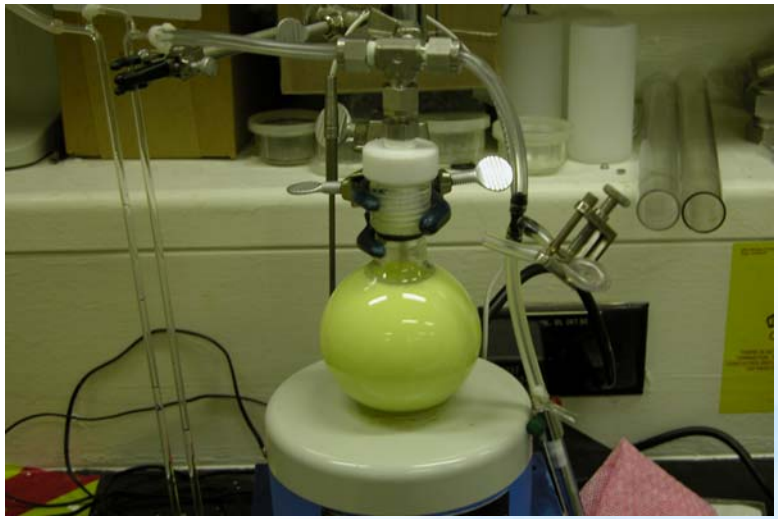
Gas Release from mMST

- Freshly prepared mMST placed in gas release apparatus
- Gas released volumes measured periodically to determine the rate (mL/min)
- Synthesis/storage conditions tested:
  - normal synthesis (neutral wash)
  - acidic wash
  - basic wash
  - elevated temperature (49 °C)







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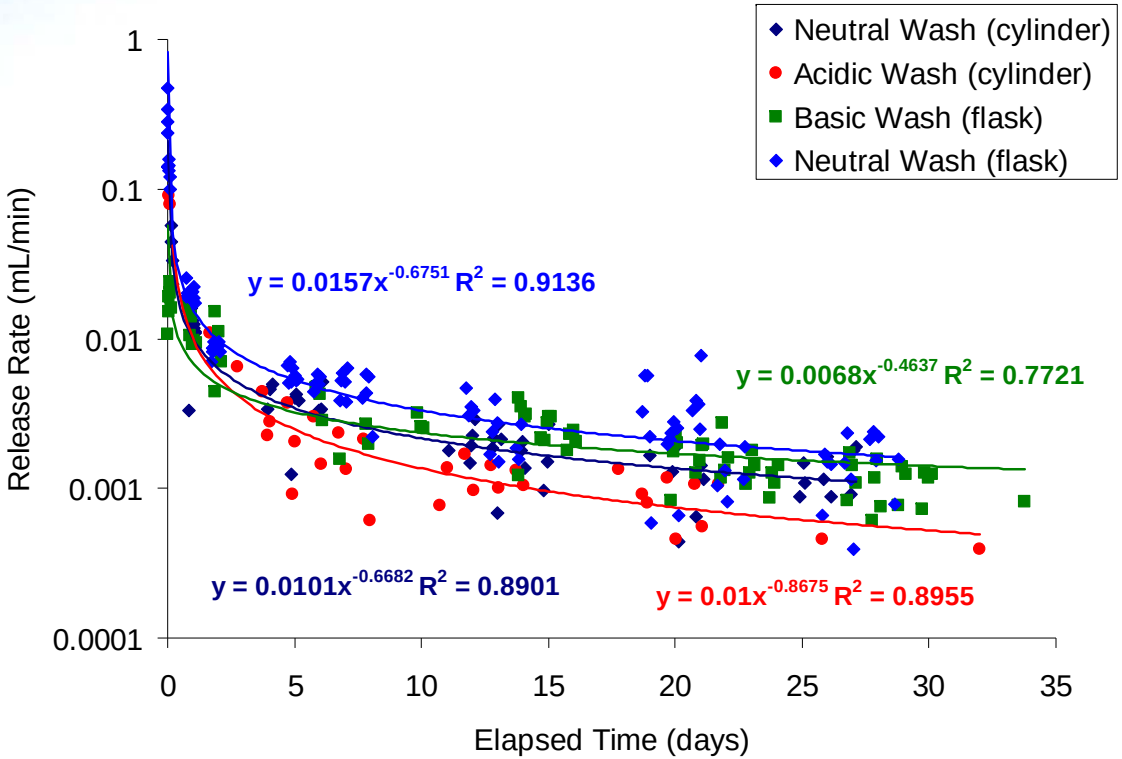
Gas Release from mMST – Room Temperature



- After production mMST suspensions release gas
  - trapped oxygen
  - decomposition of residual H_2O_2
  - decomposition of mMST (below detection limit)
- Alkaline washed mMST exhibited lower initial release rate
- After 2 days the gas release rates are not statistically different
- Recommend drum venting for transport & storage

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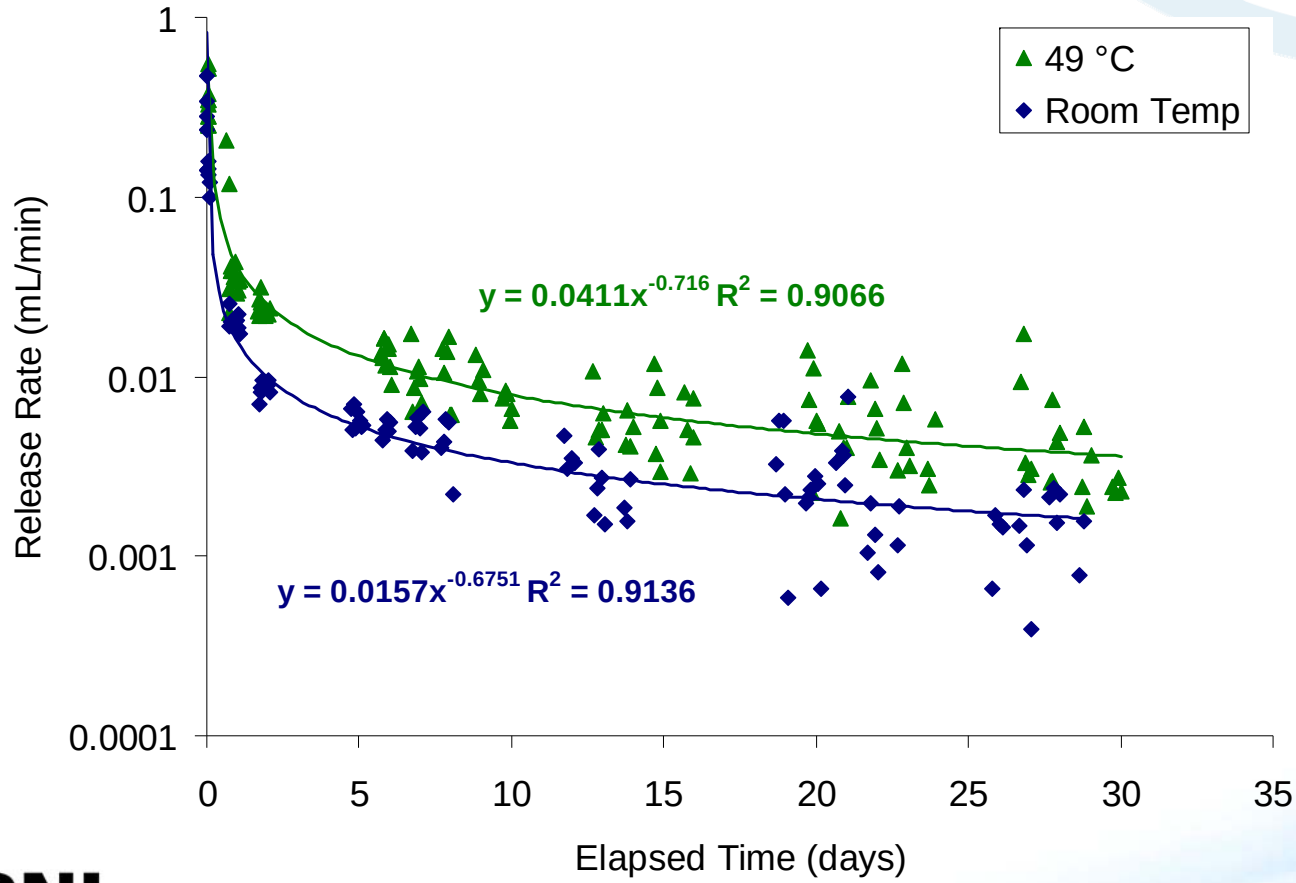
Gas Release from mMST – Elevated Temperature

Gas release rate at 49 °C consistently higher than that at room temperature over the test period (size drum vent)



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Desorption

- Objective: Determine if significant desorption occurs during the washing sequence
- Experimental Details:
  - samples of mMST loaded with Sr, Np, and Pu
  - loaded solids separated and decontaminated salt solutions diluted to give solutions representing the intermediate and final stages of washing (target [Na] of 2.8, 1.0, and 0.5 M)
  - aliquots of the diluted decontaminated salt solutions added to the loaded mMST samples and mixed for 24 hours
- Key Findings:
  - no evidence of Sr and Pu desorption
  - measured [Np] in 0.88 M Na solution suggests some desorption of Np, but solutions at lower [Na] indicate no desorption
  - uptake of U occurred (due to higher solids/solution phase ratio)

Effect of Gamma Irradiation on Performance

- Objective: Determine if gamma irradiation influences the sorption characteristics of MST and mMST
- Experimental Details
  - Samples of MST and mMST irradiated in a ^{60}Co gamma source to a total dose of 3.96E+06 R - maximum dose MST/mMST will receive in either ARP or SWPF
  - Samples irradiated in 2 different media – the as-received aqueous suspension and in simulated waste solution (SWS)
  - Irradiated and non-irradiated samples tested for Sr/actinide sorption characteristics
    - contacted with SWS containing Sr and actinides for 24 hours at 25 °C
    - MST added at 0.4 g/L; mMST added at 0.2 g/L
    - performance measured at 6, 12, and 24 hours of contact

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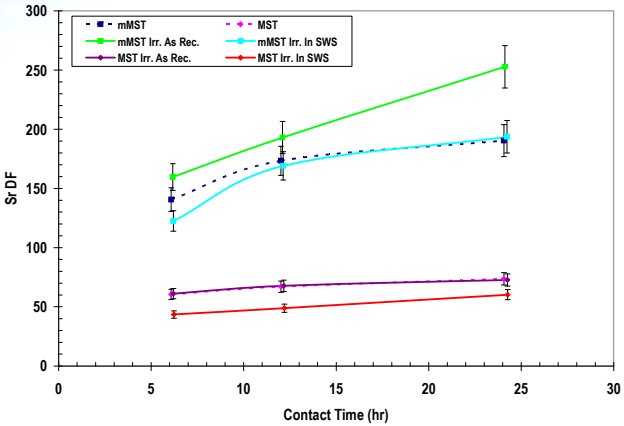
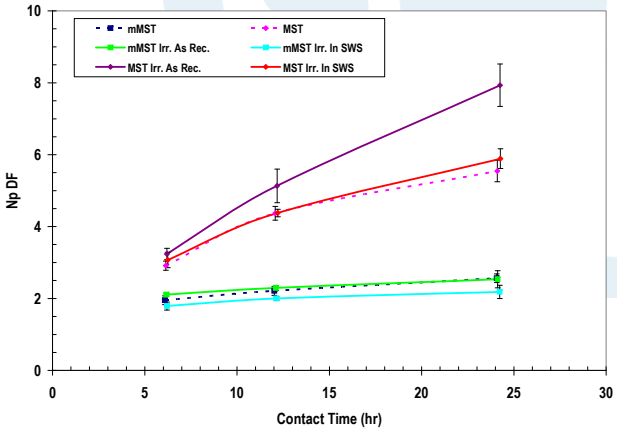
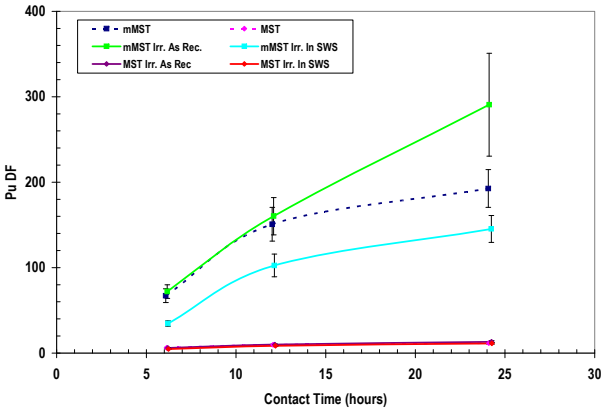
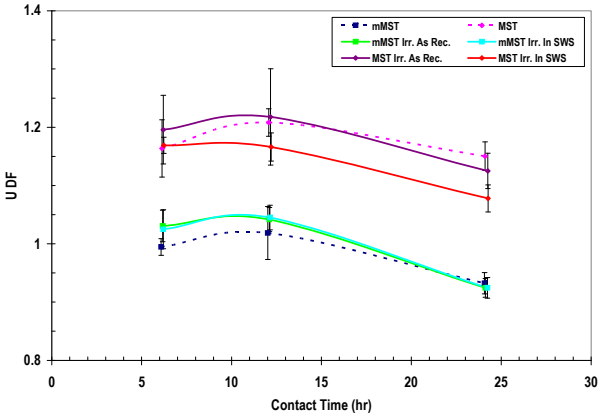
Effect of Irradiation – Sr & Np Findings









Minor effects on Sr & Np removal; no effect on U sorption

Irradiation of mMST in SWS exhibited small decrease in Pu removal performance

- **statistically significant only with the 6-h data point**

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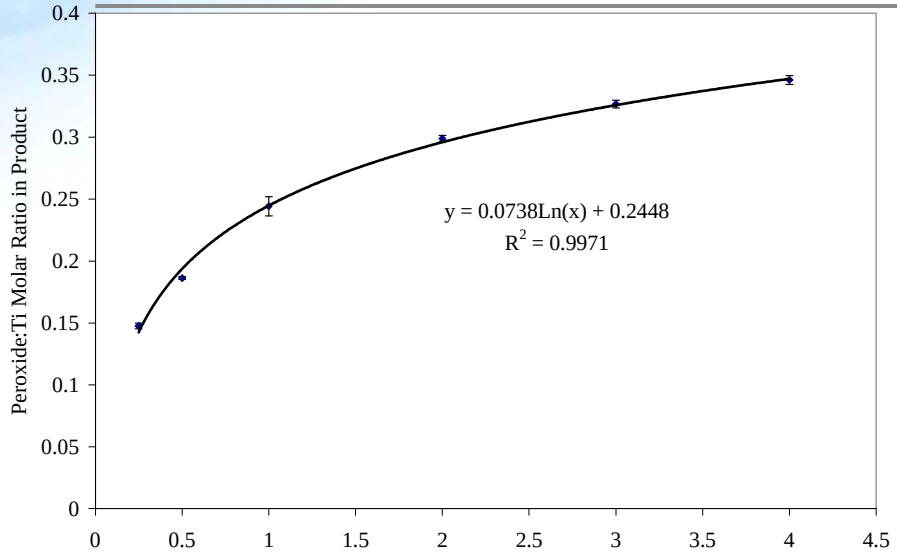
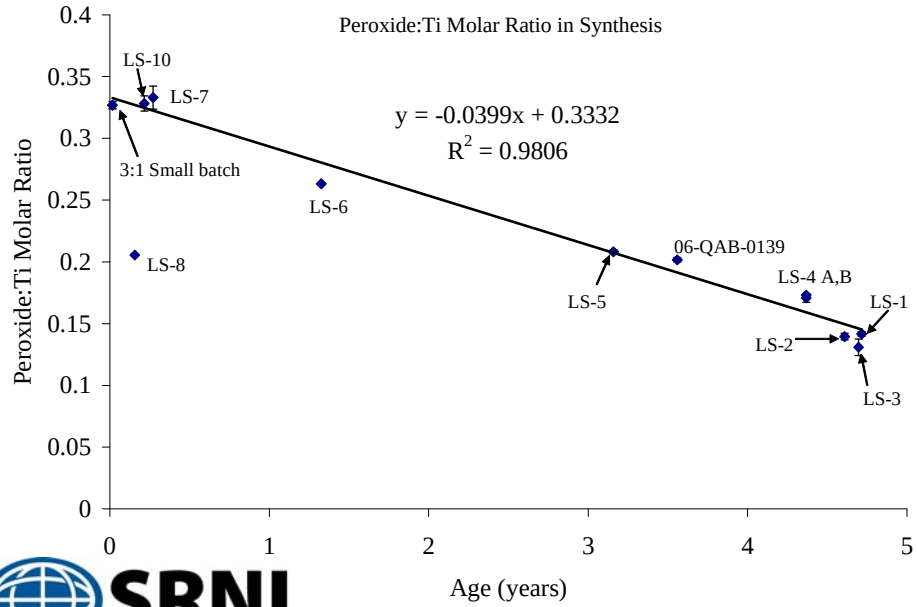
DF = decontamination factor = $[C]_0/[C]_t$

Peroxide Content in mMST





- Iodometric method
  - $H_2O_2 + 2\,I^- + 2H^+ \rightarrow I_2 + 2\,H_2O$
  - $2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI$
  - nitrite interference
- Correlation observed between peroxide:Ti ratio in product with that in synthesis
  - peroxide:Ti ratio of 0.327 at baseline synthesis condition
  - practical upper limit of peroxide:Ti ratio estimated at 0.4
- Correlation observed between peroxide:Ti ratio and age of mMST
- Peroxide content in mMST decreases upon 24-h exposure to alkaline salt solutions

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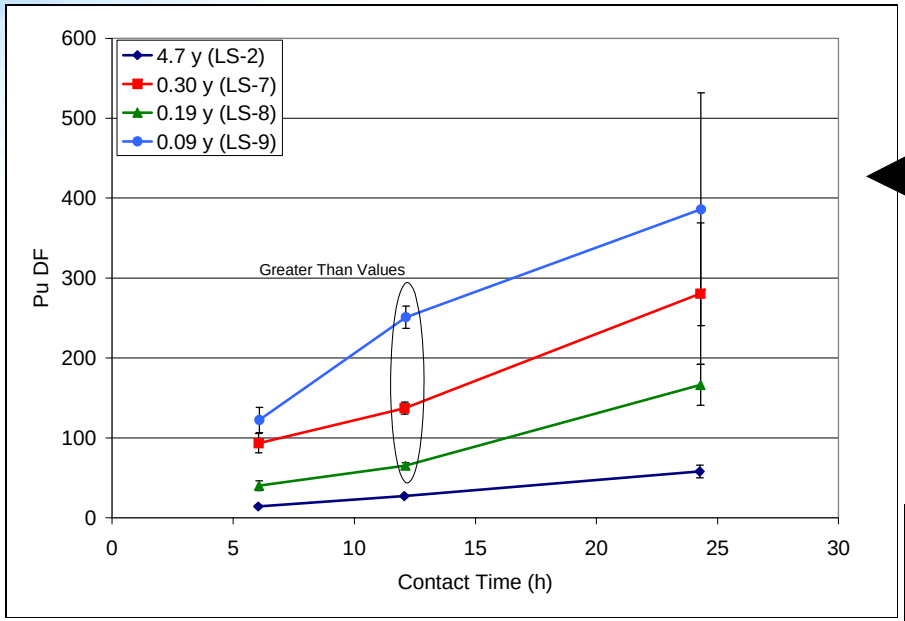
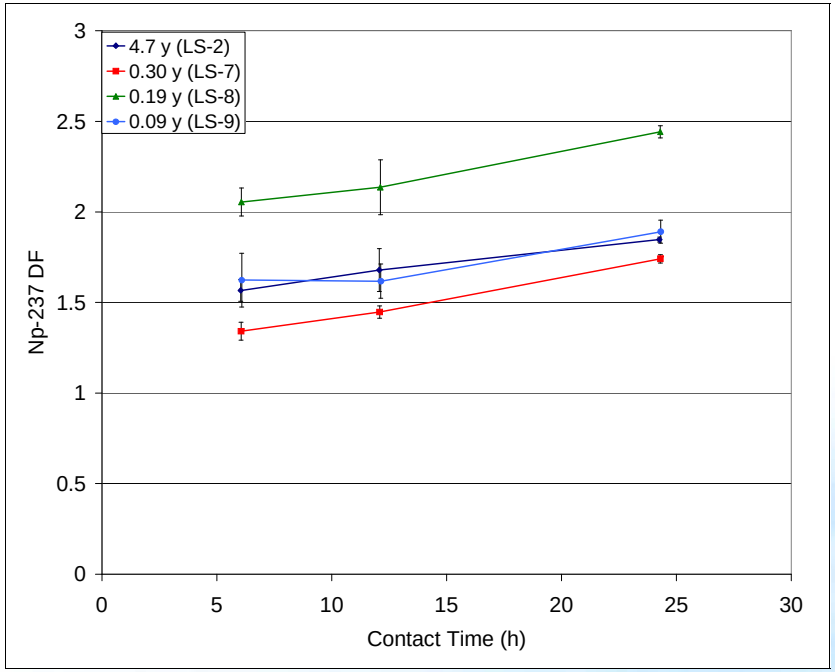
Effect of Aging on Sr, Pu and Np Removal



Aging mMST beyond 30 months resulted in decreased Sr and Pu removal performance (0.2 g/L mMST)

Np removal performance unchanged after storing mMST up to 4.7 years under laboratory conditions



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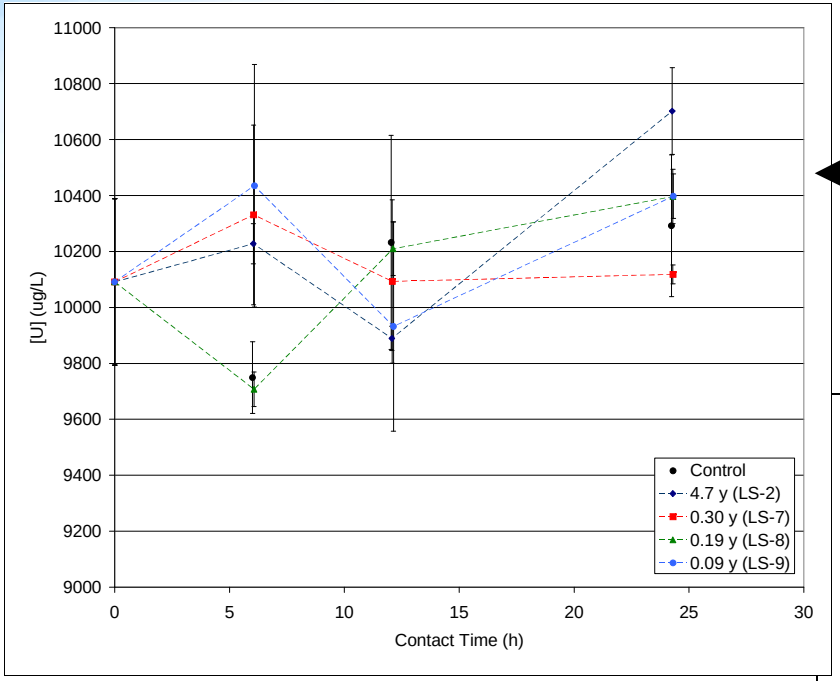
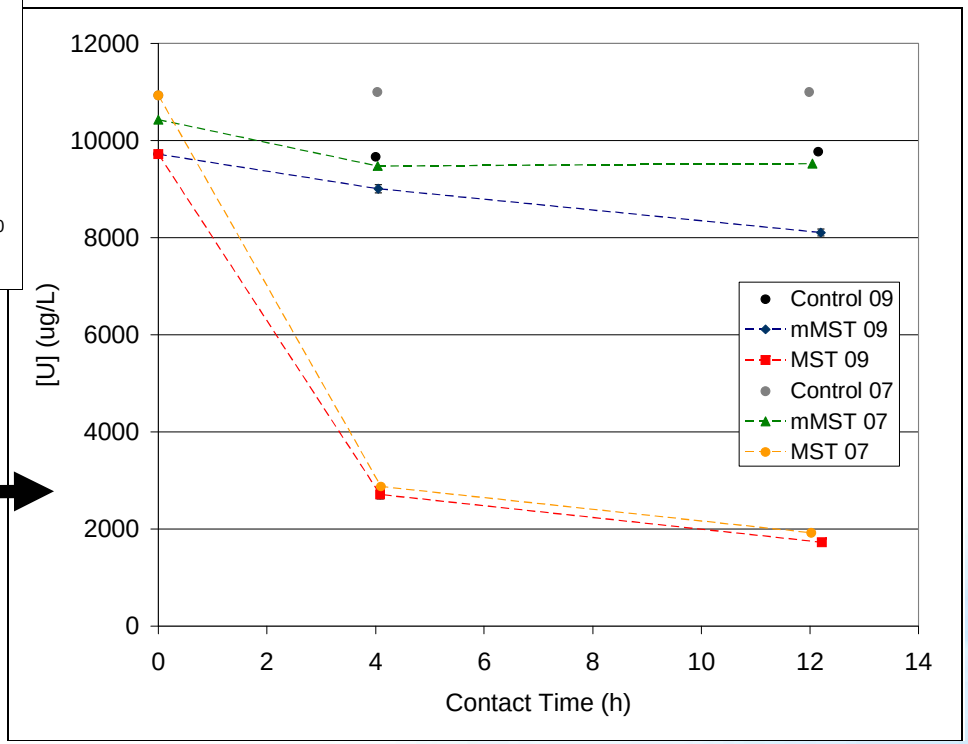
Effect of Aging on U Removal



No uptake of U observed with any of the aged samples (0.2 g/L mMST)

Increase in U removal (17% vs. 9.1%) observed upon contact of 3.0 g/L mMST with U-only simulant after additional 27 months of storage under laboratory conditions



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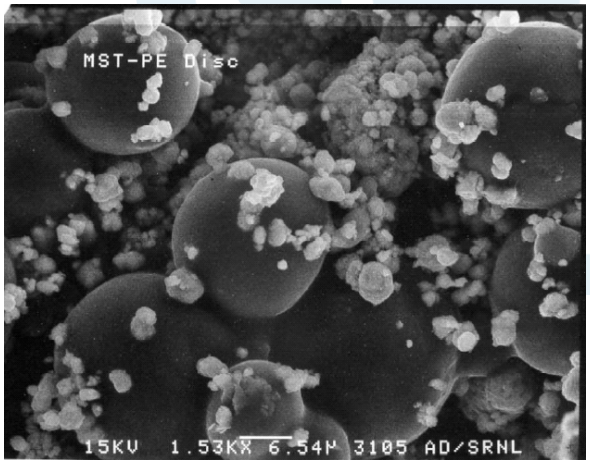
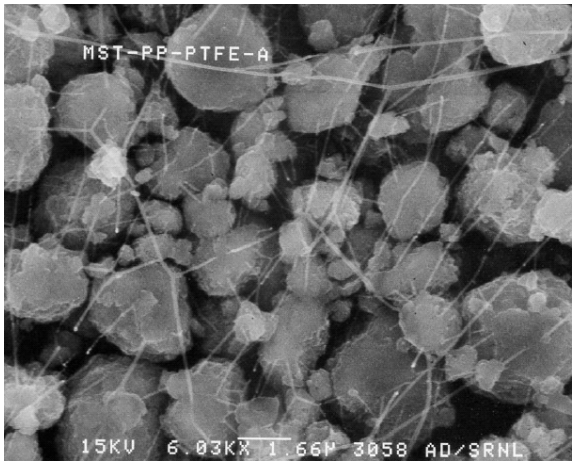
Engineered Titanates

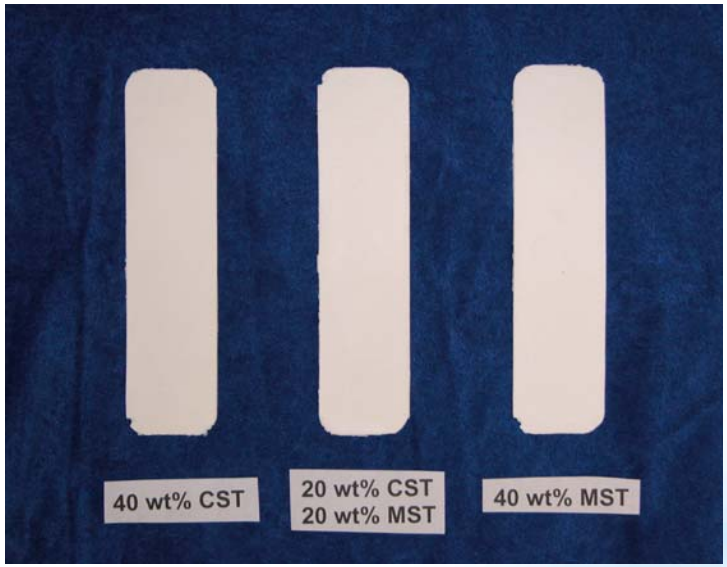
Titanates Incorporated into Porous Substrates

- Cellulose
- Polyethylene (PE)
- Polytetrafluoroethylene (PTFE)





MST in PP/PTFE membrane



MST/CST in PE membrane

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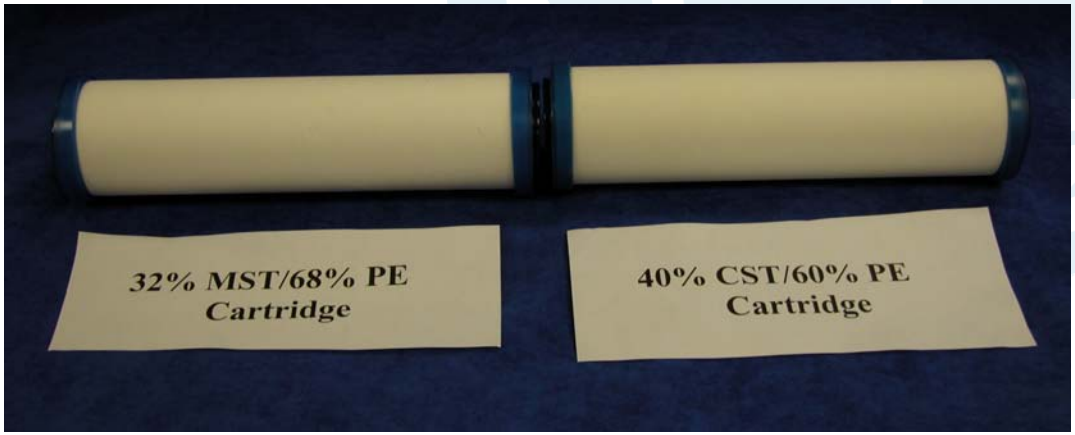
Filter Membrane Performance

- Measure ^{137}Cs & ^{85}Sr removal from radioactive simulants
- Influence of ionic strength, flowrate, single/multiple pass and sorbent sequence on performance



MST & CST PTFE Cartridges

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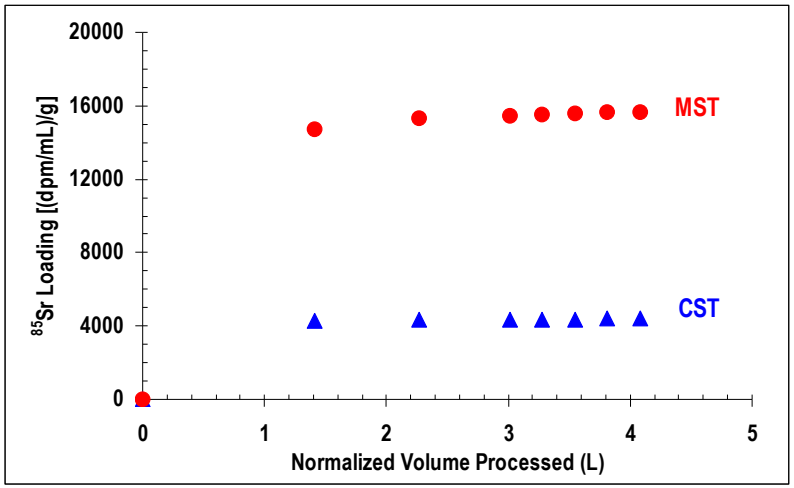
Cs/Sr Removal Performance by Porous Membranes

Batch Contact Testing		% Removed	
IX Material & Polymer Matrix	Solution	Sr	Cs
20 wt% each MST & CST in PE	water	99.99	99.98
20 wt% each MST & CST in PTFE	water	97.0	88.0

Filter Cartridge Testing		% Removed	
IX Material & Polymer Matrix	Salt Solution	Sr	Cs
32 wt% MST in PE	0.29M Na	97.5	-
40 wt% CST in PE	0.29M Na	99.7	98.0
32 wt% MST in PFTE	0.29M Na	96.2	-
85 wt% CST in PTFE	0.29M Na	97.6	49.0



- Good removal of Sr and Cs in water and dilute salt solution by MST and CST incorporated into porous membranes
- Filter cartridges using PE membranes performed better than the PTFE membranes for the removal of Sr & Cs
- PE membrane cartridges required higher operating pressure than PTFE membrane cartridges

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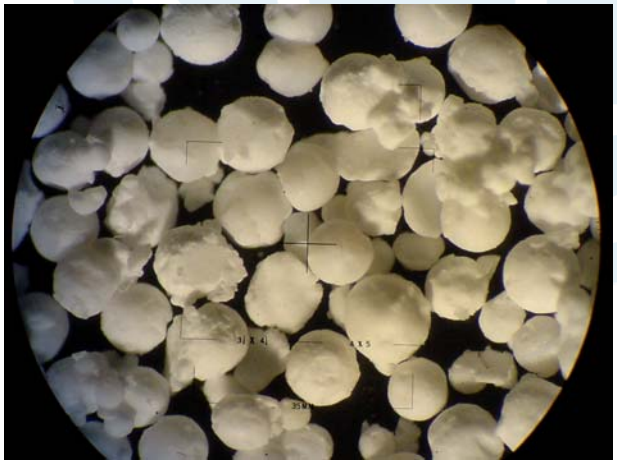
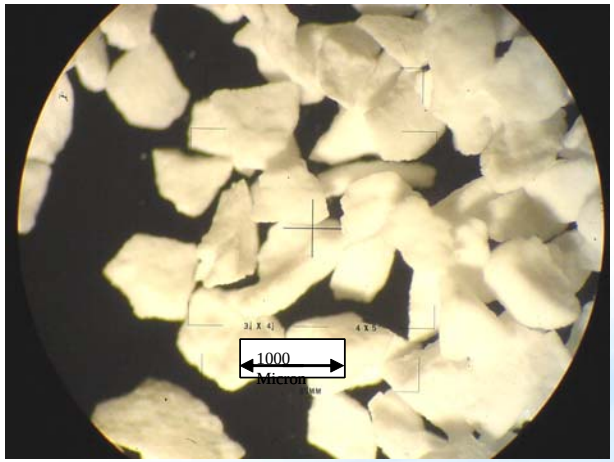
Engineered MST/mMST for Column Deployment

- Goal is to produce engineered form of MST/mMST that can be deployed in column
- Particle size: 250 – 600 microns
- MST/mMST content: ≥45 wt%
- C & N content: <2 wt%
- Candidates
  - internal gelation (ORNL) – hydrous Ti oxide binder
  - internal hydrolysis – Porocel Al_2O_3
  - SrTreat®
  - others?



Hydrous TiO_2 containing 50 wt% MST



Porous Al_2O_3 containing 9.9 wt% MST

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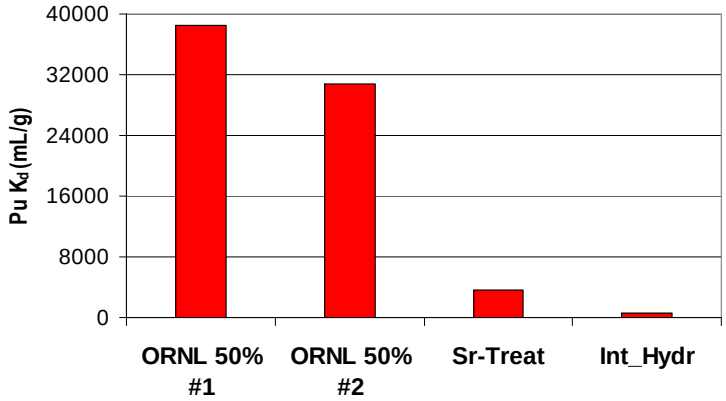
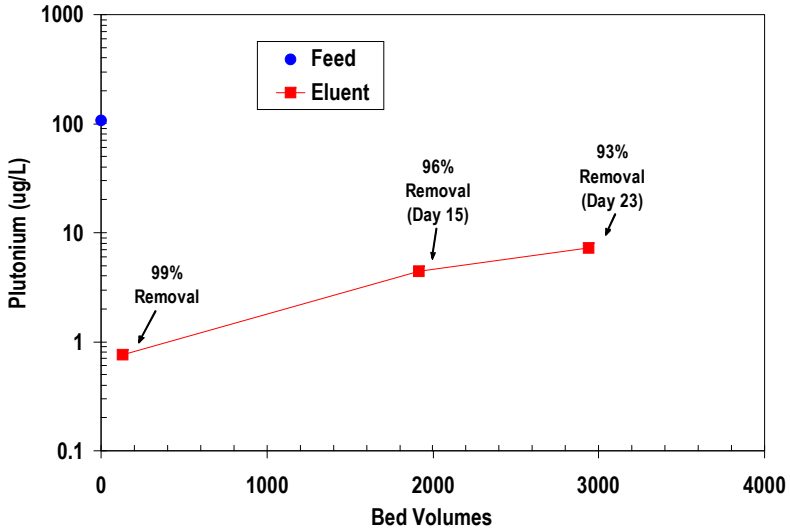
Engineered Titanates Performance -Tank Waste (FY04)





- ℰMST produced by internal gelation process (ORNL) exhibited excellent Sr & Pu removal performance in batch and column testing
  - no Sr and minimal Pu break through after 2900 bed volumes
- SrTreat® and ℰMST produced by internal hydrolysis with porous aluminia exhibited good Sr removal, but inconsistent Pu removal

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Planned FY11 Activities

- Measure effects of ionic strength and Sr loading capacity on existing inventory of ℰMST
- Produce new quantities of ℰMST & ℰmMST at ORNL
- Test performance of ℰMST & ℰmMST
- Identify alternate sorbents or technologies for producing ℰMST & ℰmMST
- Develop predictive model for performance of sorbents in column configuration

Bench-scale internal gelation equipment at ORNL

gelation column with silicon carbide beads

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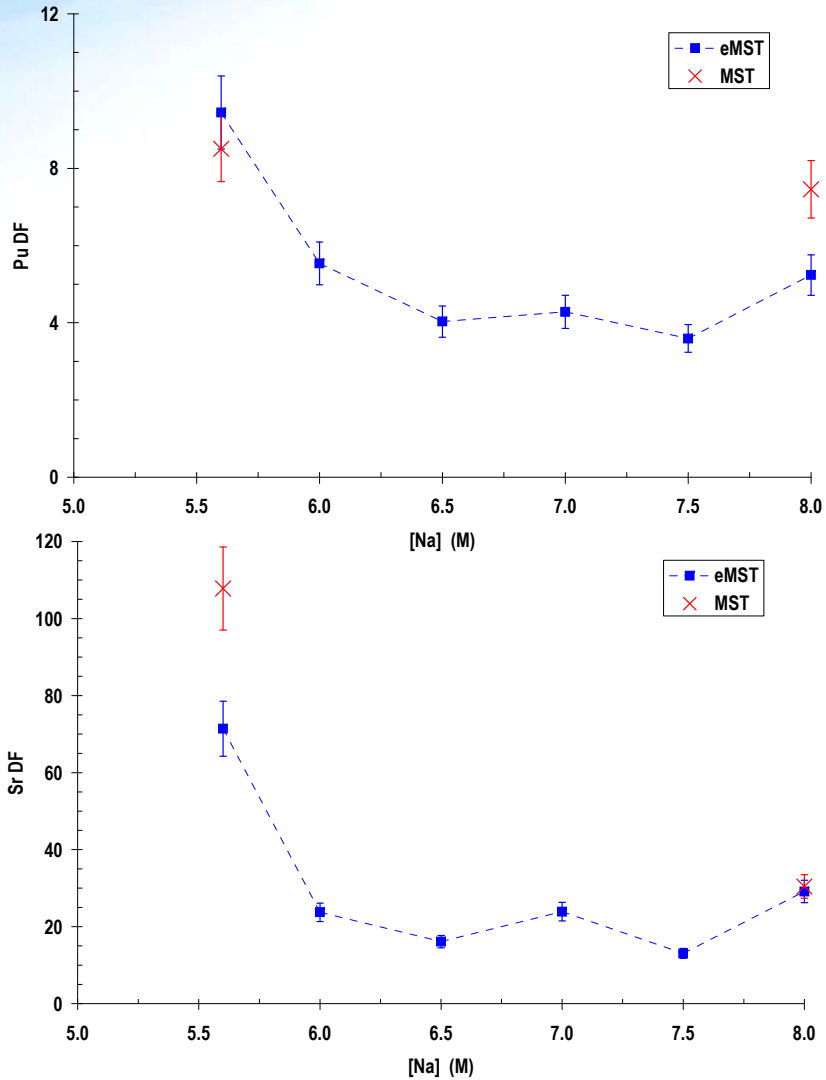
Effect of Ionic Strength – Preliminary Findings



- Pu removal decreases with increased ionic strength for ℰMST, but not for MST
- Sr removal decreases with increased ionic strength for both ℰMST and MST
- Sorption of Pu and Sr somewhat slower in ℰMST than MST

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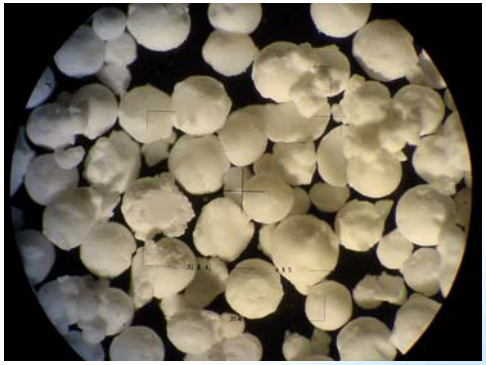
Conclusions and Recommendations

- mMST exhibits improved performance for the removal of Sr and Pu compared to MST from alkaline salt solutions
- Recommend use of mMST in ARP and SWPF
- Perform pilot-scale mixing, settling and rheology testing of mMST and determine impacts, if any, that mMST has on hydrogen production in DWPF
- Demonstrated feasibility of producing engineered forms of MST by incorporating into porous polymer matrices and hydrous titanium oxide (internal gelation)
- Recommend continued development of ^{E}MST produced by internal gelation process for deployment in a column configuration



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Acknowledgements

- Funding provided by Department of Energy
  - Office of Environmental Management, Office of Waste Processing (EM-31)
  - SRNL LDRD Program – filter membranes
- David DiPrete, Ceci DiPrete, Curtis Johnson, Mark Jones – chemical and radioanalytical measurements
- Mona Blume, Debbie Marsh – experimental testing
- Kofi Adu-Wusu & Mark Crowder (SRNL)
  Rodney Hunt & Jack Collins (ORNL) – engineered titanates

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