# Development of an Improved Sodium Titanate for the Pretreatment
## of Nuclear Waste at the Savannah River Site

D. T. Hobbs
M. R. Poirier
M. J. Barnes
T. B. Peters
F. F. Fondeur
M. E. Thompson
S. D. Fink
Savannah River National Laboratory
Westinghouse Savannah River Company
Aiken, SC 29808

M. D. Nyman
Sandia National Laboratories
Albuquerque, NM 87185

## ABSTRACT
High-level nuclear waste produced from fuel reprocessing operations at the Savannah River Site (SRS) requires pretreatment to remove Cs-137, Sr-90 and alpha-emitting radionuclides (i.e., actinides) prior to disposal onsite as low level waste. Separation processes planned at SRS include sorption of Sr-90 and alpha-emitting radionuclides onto monosodium titanate (MST) and caustic side solvent extraction, for Cs-137 removal. The MST and separated Cs-137 will be encapsulated into a borosilicate glass wasteform for eventual entombment at the federal repository. The predominant alpha-emitting radionuclides in the highly alkaline waste solutions include plutonium isotopes Pu-238, Pu-239 and Pu-240. This paper describes recent results to produce an improved sodium titanate material that exhibits increased removal kinetics and capacity for Sr-90 and alpha-emitting radionuclides compared to the baseline MST material.

## INTRODUCTION
Monosodium titanate currently serves as the baseline sorbent for the removal of Sr-90 and alpha-emitting radionuclides from high-level nuclear wastes at the Savannah River Site. This inorganic material exhibits high affinity for strontium and actinides contained in the alkaline and high ionic strength waste solutions that will be processed for disposition.[1-5] Deployment of this material occurs by a batch adsorption process in which the MST is added at a concentration of 0.4 g/L of waste solution and mixed for 24 hours. The MST solids and any entrained sludge solids are separated from the waste solution by ultra-filtration. The filtrate moves on to the cesium removal operation, which is a solvent extraction process that features a calixarene extractant. The MST solids are washed to reduce the soluble salt content in the interstitial liquid and then transferred to the Defense Waste Processing Facility (DWPF) for incorporation into a highly durable borosilicate glass wasteform.

Acceleration of waste disposal at SRS requires materials that exhibit increased loading capacities and removal kinetics for Sr-90 and alpha-emitting radionuclides compared to the baseline material, MST. Increased loading capacity and removal kinetics would result in decreased facility footprint and increased throughput for this stage of the pretreatment facility. Recent studies identified a promising new family of peroxotitanate materials with improved strontium and actinide removal characteristics.[6] Compared to the baseline MST material, the new peroxotitanate materials, referred to as modified MST or mMST, exhibit higher batch capacities and kinetics for the separation of strontium and actinides from alkaline waste solutions.[6-8] Consequently these materials offer the opportunity to reduce sorbent use and increase throughput in processing facilities. This paper describes recent results from the ongoing development of this new material for strontium and actinide separations from SRS nuclear waste solutions.

## EXPERIMENTAL
### Materials
The MST sample used in these studies is prepared using a sol-gel process developed at the Savannah River National Laboratory (SRNL) and supplied by Optima Chemical Group LLC (Douglas, GA), Lot #00-QAB-417, as a 15 wt% suspension in water containing 0.10-0.15 M NaOH and 100-150 mg $L^{-1}$ $NaNO_2$.[4] Bench-scale quantities of the mMST, identified as samples LS-1, LS-2 and LS-3, were prepared using 25 grams each of MST.[6] Chemical Group LLC (Douglas, GA) produced a pilot-scale quantity (15 kg) of mMST, Lot #06-QAB-0139, as a 15 wt% suspension in water using the same the same conditions for the bench-scale preparations.

### Evaluation of Sr and Actinide Removal Performance
We evaluated strontium and actinide removal performance by contacting simulated and actual waste solutions with a measured quantity of the peroxotitanate or MST sample. Table I provides the composition of the simulated and actual waste solutions used in these tests. We performed batch contact tests with the simulated waste solutions by shaking bottles kept at $25 \pm 3$ $^{o}$C in a waterbath. After the addition of the appropriate sample of MST, we continuously agitated the test bottles and sampled each test bottle periodically over 168 hours. All samples were filtered through 0.10-μm polytetrafluoroethylene (PTFE) membrane filters to remove MST solids. Measured aliquots of the filtrate were then diluted with an equal volume of 5 M nitric acid. Gamma spectroscopy measured the Sr-85 and Np-237 content. We measured the plutonium isotopics content by radiochemical separation of the plutonium from neptunium and uranium followed by alpha counting of the extracted plutonium.

Tests with actual waste were carried out in the Shielded Cells Facility of SRNL. The testing protocol followed that described above with simulated waste solutions. Filtration of samples used 0.1-μm PTFE-membrane syringe filters. We diluted aliquots of the filtrates by approximately a factor of 20 with 2 M nitric acid solution. The higher dilution was required to reduce radiation exposure during subsequent analyses for radiochemical content.

**Table I. Composition of simulated and actual waste solutions.**

| Analyte | Unit | Simulant | Actual Waste |
|---|---|---|---|
| NaOH | M | 1.30 (0.13) | 2.10 (0.0070) |
| NaNO3 | M | 2.58 (0.264) | 2.47 (0.015) |
| NaNO2 | M | 0.139 (0.014) | 0.648 (0.0063) |
| NaAl(OH)4 | M | 0.513 (0.051) | 0.423 (0.0068) |
| Na2CO3 | M | 0.035 (0.0035) | 0.566 (0.0758) |
| Na2SO4 | M | 0.515 (0.052) | 0.0518 (0.0010) |
| Calculated Total Na | M | 5.63 (0.57) | 5.48 (0.367) |
| Sr-85 | dpm mL$^{-1}$ | 2.72E+04 (4.87E+02) | - |
| Sr-90 | dpm mL$^{-1}$ | - | 2.75E+04 (2.8E+03) |
| Total Sr | g L$^{-1}$ | 569 (11) | 1,310 (242) |
| Total Pu | g L$^{-1}$ | 200 (12) | 275 (56) |
| Np-237 | g L$^{-1}$ | 474 (104) | 131 (19) |
| Total U | g L$^{-1}$ | 10,400 (570) | 11,100 (1,740) |

[*] Numbers in parenthesis are single standard deviation of replicate measurements.

## Evaluation of Filtration Characteristics

Fig. 1 shows the apparatus used to perform the crossflow filtration tests. The equipment contains a sintered stainless steel 0.1 µ pore-size Mott crossflow filter of 0.95-cm inner diameter and 61-cm length. The filtration unit contains a feed vessel, a feed pump, a heat exchanger to control solution temperature, a magnetic flow meter to measure the filter feed rate, and three calibrated pressure gauges to measure feed, concentrate, and filtrate pressure. A graduated glass cylinder located down stream of the filter collects the filtrate. Personnel determined the filtrate flow rate, or flux, by measuring the time to collect a known volume of filtrate. The working volume of the equipment measures approximately 10 L.

Filter tests commenced by placing ~ 8L of the simulated SRS salt solution (see Table I) into the feed tank followed by the addition of MST and simulated sludge to achieve the expected solids loading of the process facility. After mixing the contents of the feed tank, the suspension was circulated through the filtration apparatus. Axial velocity and transmembrane pressure were varied to evaluate their impact on filter flux. The axial velocity ranged from 180 to 370 cm s$^{-1}$ and the transmembrane pressure ranged from 2.0 to 3.4 bar. The nominal feed temperature was 23 °C. Flow rate, pressure, and temperature data were collected and recorded every 10 minutes. Each test lasted 60 minutes. Prior to the start of each test, the filter was backpulsed with 6.2 bar air to dislodge the residual filter cake.
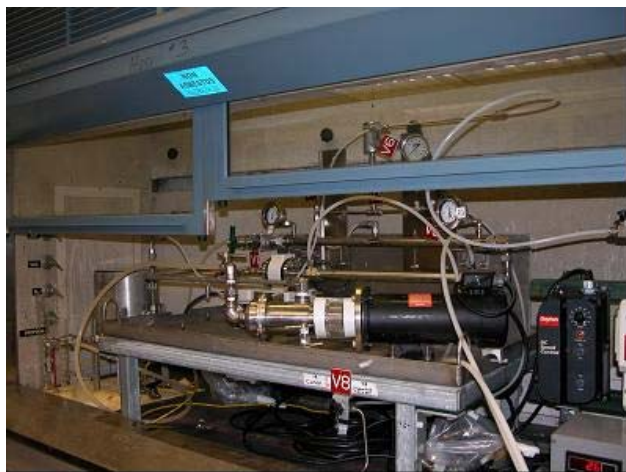
**Fig. 1.  Photograph of the crossflow filter apparatus**

RESULTS AND DISCUSSION

**Simulated Waste Tests**

Table II provides the 6-hour and 12-hour decontamination factors for the bench-scale and pilot-scale samples of mMST and the commercial lot of MST upon addition to the simulated SRS waste solution at a concentration of 0.2 g L$^{-1}$.  Both of the mMST samples exhibited much higher DF values than the baseline MST.  Also, the pilot-scale batch of mMST (06-QAB-0139) exhibited higher DFs than those of the bench-scale material (LS-1).  This finding indicates a successful scale-up of the synthesis of the mMST from the bench scale (25-grams) to pilot-scale (15-kilograms).

Fig. 2 provides a plot of the average strontium (2A) and plutonium (2B) concentrations versus time for the tests with vendor-prepared mMST added at a concentration of 0.1 and 0.2 g L$^{-1}$ and the baseline MST added at concentration of 0.4 and 0.8 g L$^{-1}$.  The control test contained no added sorbent and served as a measure of sorbate removal by a mechanism other than sorption onto the titanate such as precipitation or sorption onto bottle walls.  For all three sorbates, the mMST material performs as well as, or better than, the baseline MST when added at one-fourth the concentration.  For example, after 2 hours, the mMST materials at a concentration of 0.2 g L$^{-1}$ reduced the plutonium concentration from about 200 $\mu$g L$^{-1}$ to less than 10 $\mu$g L$^{-1}$.  At a sorbent concentration of 0.8 g L$^{-1}$, the baseline MST reduced the plutonium concentration from about 200 $\mu$g L$^{-1}$ to 100 $\mu$g L$^{-1}$.  Thus, the extent and rate of plutonium removal with the mMST greatly exceeds that of the baseline MST over the 168-hour contact time.

**Table II. Strontium, plutonium and neptunium decontamination factors for mMST and MST samples in simulated waste solution.**

| | | 6-h DF Values[a] | | |
|---|---|---|---|---|
| **Material[b]** | **Sample ID** | **Sr** | **Pu** | **Np** |
| mMST | 06-QAB-0139 | 382 (35.8) | 217 (39.7) | 3.25 (1.42) |
| mMST | LS-1 | 104 (2.90) | 78.5 (11.2) | 1.87 (0.172) |
| MST | 00-QAB-417 | 23.6 (0.593) | 3.03 (0.271) | 1.20 (0.214) |
| | | 12-h DF Values[a] | | |
| **Material[b]** | **Sample ID** | **Sr** | **Pu** | **Np** |
| mMST | 06-QAB-0139 | 507 (65.8) | 477 (113) | 3.67 (0.686) |
| mMST | LS-1 | 117 (3.20) | 148 (26.6) | 2.18 (0.330) |
| MST | 00-QAB-417 | 26.8 (0.659) | 3.65 (0.393) | 1.70 (0.449) |

[a] Numbers in parenthesis are single standard deviation of duplicate tests for the mMST sample 06-QAB-0139 and single standard deviation based on the analytical uncertainty for the mMST sample LS-1 and baseline MST sample.
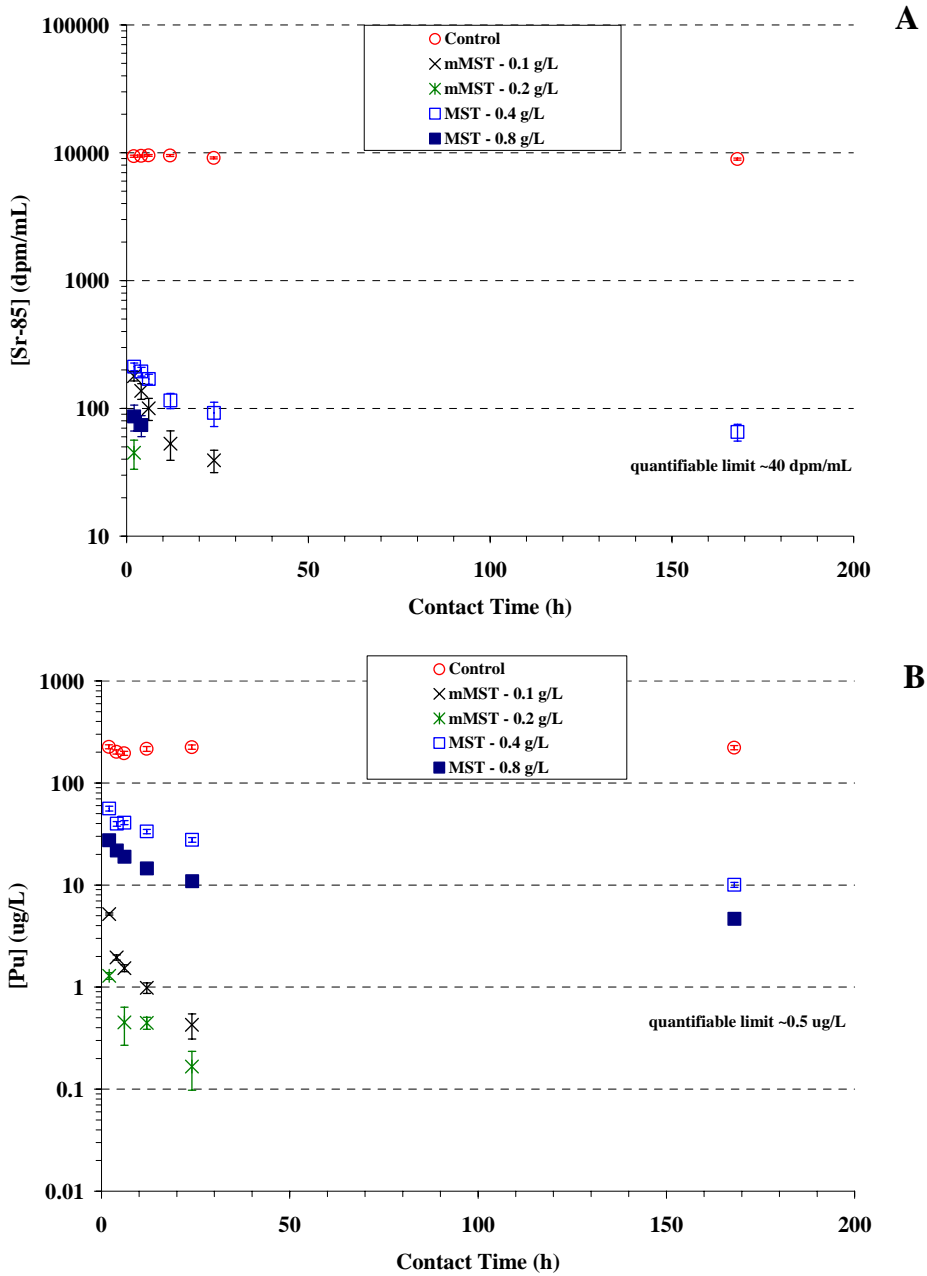[b] Sorbent added at 0.2 g $L^{-1}$. Temperature controlled at $25 \pm 3$ °C.

**Fig. 2. Sr-85 (A) and plutonium (B) concentrations versus time upon contact of simulated waste solution with mMST and MST samples. Eerror bars represent single standard deviation of replicate measurements or analytical uncertainty for single measurements.**

**Actual Waste Tests**

Given the excellent performance of the peroxotitanate samples with simulated waste solutions we tested performance with actual SRS waste supernate. In this set of tests we contacted the actual waste supernate (see Table III) with the samples of the mMST at 0.1 and 0.2 g L$^{-1}$ and the baseline MST at 0.2 and 0.4 g L$^{-1}$. Table 3 provides a summary of the DF values for the tests with actual waste. The actual waste tests were conducted in two separate test sets. The first test set (Dataset #1) used the bench-scale mMST (LS-1), whereas the second test set (Dataset #2) featured the vendor-prepared mMST (O6-QAB-0139).

Inspection of Table III indicates that the strontium removal with 0.2 g L$^{-1}$ of the baseline MST in Dataset #2 is about a factor of 2 – 3 lower than that measured in Dataset #1. In the test with 0.4 g L$^{-1}$ of baseline MST, the measured strontium DF values were much higher than those measured at 0.2 g L$^{-1}$ and about a factor of 3 higher than those measured in Dataset #1 at 0.2 g L$^{-1}$. Similar trends are also observed with plutonium and neptunium removal. These findings suggest that the 0.2 g L$^{-1}$ baseline MST in the second test set may have received less sorbent than the target concentration.

Comparison of the strontium DF values measured for the bench-scale mMST (Dataset #1) and the pilot-scale mMST (Dataset #2) are limited by the small population of quantifiable results in Dataset #2. The average strontium DF values measured at 2 and 12-hours for the pilot-scale mMST exceeded those measured for the bench-scale mMST. This finding suggests that the pilot-scale mMST performs as good as or better than that of the bench-scale MST with respect to strontium removal.

Fig. 3 shows the total plutonium concentration versus time for the actual waste tests with the pilot-scale mMST (Dataset #2). The results indicate more rapid removal of plutonium by the mMST compared to the baseline MST. Also, at earlier contact times, the mMST exhibits a much higher DF value than the baseline MST even at the lower sorbent concentration. After 6 and 12 hours of contact with 0.1 and 0.2 g L$^{-1}$ of the modified MST, respectively, the Pu-239,240 content fell below the quantifiable limit. Thus, at the longer contact times we could not quantify the total plutonium concentration in solution. Consequently, we used the Pu-238 concentration to evaluate plutonium DF values for vendor-prepared modified MST tests as reported in Table III.

Comparison of the plutonium DF values for the bench and pilot-scale mMST samples reveals that the pilot-scale sample of mMST exhibited higher values over the entire contact time at both sorbent concentrations (0.1 and 0.2 g L$^{-1}$). Further inspection of Table 3 reveals that the vendor-prepared modified MST exhibited higher plutonium DF values when added at 0.1 g L$^{-1}$ versus a 0.4 g L$^{-1}$ concentration for the baseline MST. Thus, we conclude that the vendor-prepared modified MST exhibits excellent plutonium removal performance with actual waste solution.

In general, we observed that an increase in the concentration of the mMST from 0.1 g L$^{-1}$ to 0.2 g L$^{-1}$ produced an 11% increase in the quantity of neptunium removed from the actual waste solution.  Neptunium removal by the bench-scale and pilot-scale mMST samples proved similar to the baseline MST at the same sorbent concentration (0.2 g L$^{-1}$).  This trend is not consistent with that observed in tests with simulated waste solution.  Given the similar DF values, we conclude that the neptunium removal characteristics of the bench-scale and pilot-scale MST samples are comparable to one another and to that of the baseline MST with actual waste solutions.
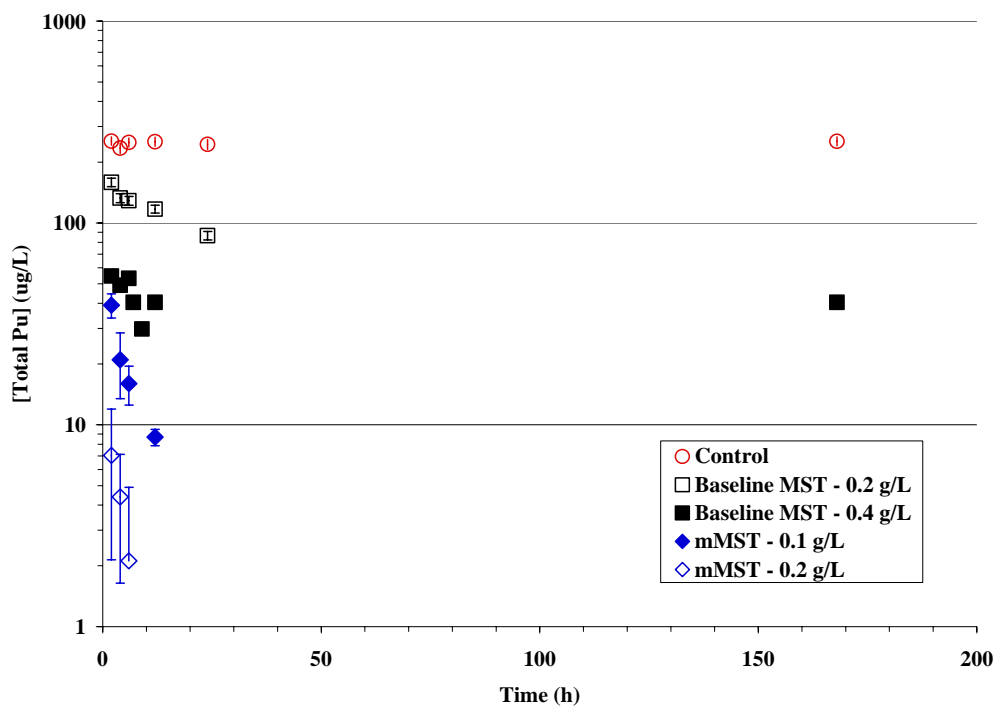


**Fig. 3.  Total plutonium activity versus time upon contact of actual waste with mMST and MST. Eerror bars represent single standard deviation of replicate measurements or analytical uncertainty for single measurements.**

**Table III. Decontamination factors for baseline MST and mMST samples prepared at the bench and pilot scales.**

| | Strontium Decontamination Factors | | | | | | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Set #1 Baseline MST @ 0.2 g/L | | Set #2 Baseline MST @ 0.2 g/L | | Set #2 Baseline MST @ 0.4 g/L | | Bench Scale mMST @ 0.2 g/L | | Pilot Scale mMST @ 0.2 g/L | | Bench Scale mMST @ 0.1 g/L | | Pilot Scale mMST @ 0.1 g/L | |
| Nominal Time (h) | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty | Average | Std Dev | Value | Std Dev | Average | Std Dev | Average | Std Dev |
| 2 | 1.10E+01 | 3.10E+00 | 5.05E+00 | 1.43E+00 | 2.98E+01 | 7.45E+00 | 2.86E+01 | 1.60E+00 | >4.30E+01 | | 1.15E+01 | 5.57E-01 | 2.65E+01 | 1.97E+01 |
| 4 | 1.78E+01 | 5.03E+00 | 6.35E+00 | 1.80E+00 | >3.04E+01 | | 4.80E+01 | 1.29E+01 | >2.78E+01 | | 1.49E+01 | 2.70E+00 | >3.10E+01 | |
| 6 | 1.71E+01 | 4.85E+00 | 5.78E+00 | 1.63E+00 | >1.12E+01 | | >4.54E+01 | | >1.07E+01 | | 1.69E+01 | 1.84E+00 | >1.12E+01 | |
| 12 | 1.39E+01 | 3.92E+00 | 6.98E+00 | 1.97E+00 | 5.68E+01 | 3.95E+00 | >2.30E+01 | | >9.12E+01 | | 1.39E+01 | 7.70E-01 | 5.87E+01 | 7.53E+00 |
| 24 | 1.71E+01 | 4.83E+00 | 7.67E+00 | 2.17E+00 | >1.72E+01 | | >4.02E+01 | | >1.68E+01 | | 1.80E+01 | 4.29E+00 | >1.70E+01 | |
| 168 | 2.48E+01 | 7.02E+00 | 7.79E+00 | 2.20E+00 | >1.57E+01 | | >3.56E+01 | | >1.57E+01 | | 1.67E+01 | 2.22E+00 | >1.60E+01 | |
| | Plutonium Decontamination Factors | | | | | | | | | | | | | |
| | Set #1 Baseline MST @ 0.2 g/L | | Set #2 Baseline MST @ 0.2 g/L | | Set #2 Baseline MST @ 0.4 g/L | | Bench Scale mMST @ 0.2 g/L | | Pilot Scale mMST @ 0.2 g/L | | Bench Scale mMST @ 0.1 g/L | | Pilot Scale mMST @ 0.1 g/L | |
| Nominal Time (h) | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty | Average | Std Dev | Value | Std Dev | Average | Std Dev | Average | Std Dev |
| 2 | 1.84E+00 | 2.05E-01 | 1.60E+00 | 1.08E-01 | 4.67E+00 | 3.08E-01 | 9.58E+00 | 5.78E-01 | 2.31E+01 | 9.58E+00 | 2.82E+00 | 1.45E-01 | 6.24E+00 | 7.57E-01 |
| 4 | 2.99E+00 | 2.12E-01 | 1.77E+00 | 1.39E-01 | 4.79E+00 | 3.90E-01 | 1.66E+01 | 1.19E+00 | 4.92E+01 | 1.08E+01 | 4.96E+00 | 3.69E-02 | 1.23E+01 | 2.85E+00 |
| 6 | 1.86E+00 | 1.36E-01 | 1.94E+00 | 1.38E-01 | 4.71E+00 | 3.28E-01 | 1.22E+01 | 2.09E+00 | 1.14E+02 | 7.57E+01 | 3.53E+00 | 1.95E-01 | 1.68E+01 | 2.63E+00 |
| 12 | 2.35E+00 | 1.79E-01 | 2.16E+00 | 1.49E-01 | 6.25E+00 | 4.43E-01 | 2.67E+01 | 9.54E-01 | 9.18E+01 | 3.81E+01 | 8.20E+00 | 4.62E-01 | 2.88E+01 | 6.30E+00 |
| 24 | 4.46E+00 | 4.43E-01 | 2.84E+00 | 2.12E-01 | 8.22E+00 | 8.35E-01 | 3.96E+01 | 1.28E+01 | 1.16E+02 | 4.49E+01 | 7.87E+00 | 5.55E+00 | 3.67E+01 | 8.90E+00 |
| 168 | 3.37E+01 | 5.13E+00 | 1.63E+01 | 1.30E+00 | 4.14E+01 | 2.93E+00 | 2.70E+01 | 8.99E+00 | 9.71E+01 | 4.62E+01 | 7.62E+00 | 5.36E+00 | 3.83E+01 | 3.58E+00 |
| | Neptunium Decontamination Factors | | | | | | | | | | | | | |
| | Set #1 Baseline MST @ 0.2 g/L | | Set #2 Baseline MST @ 0.2 g/L | | Set #2 Baseline MST @ 0.4 g/L | | Bench Scale mMST @ 0.2 g/L | | Pilot Scale mMST @ 0.2 g/L | | Bench Scale mMST @ 0.1 g/L | | Pilot Scale mMST @ 0.1 g/L | |
| Nominal Time (h) | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty | Average | Std Dev | Value | Std Dev | Average | Std Dev | Average | Std Dev |
| 2 | 2.21E+00 | 6.26E-01 | 1.47E+00 | 4.17E-01 | 3.61E+00 | 1.02E+00 | 1.59E+00 | 1.57E-01 | 2.03E+00 | 4.04E-03 | 1.35E+00 | 3.97E-02 | 1.60E+00 | 2.08E-01 |
| 4 | 2.87E+00 | 8.13E-01 | 1.46E+00 | 4.14E-01 | 3.95E+00 | 1.12E+00 | 2.21E+00 | 1.03E-01 | 1.83E+00 | 1.02E-01 | 1.64E+00 | 4.25E-01 | 1.51E+00 | 1.33E-02 |
| 6 | 2.55E+00 | 7.21E-01 | 1.73E+00 | 4.88E-01 | 5.15E+00 | 1.46E+00 | 1.60E+00 | 6.56E-02 | 1.91E+00 | 5.03E-01 | 1.35E+00 | 2.05E-02 | 1.66E+00 | 6.15E-02 |
| 12 | 3.24E+00 | 9.17E-01 | 2.17E+00 | 6.15E-01 | 6.45E+00 | 1.83E+00 | 1.88E+00 | 3.76E-02 | 2.58E+00 | 4.13E-02 | 1.59E+00 | 2.80E-02 | 1.95E+00 | 1.62E-01 |
| 24 | 3.10E+00 | 8.76E-01 | 2.25E+00 | 6.38E-01 | 7.22E+00 | 2.04E+00 | 1.82E+00 | 1.66E-01 | 2.81E+00 | 1.43E-01 | 1.38E+00 | 4.35E-01 | 2.16E+00 | 4.38E-03 |
| 168 | 4.84E+00 | 9.67E-01 | 3.23E+00 | 9.15E-01 | >6.15E+00 | | 2.30E+00 | 1.74E-01 | 3.55E+00 | 1.49E+00 | 1.62E+00 | 5.13E-02 | 2.43E+00 | 7.81E-02 |

mMST results are average and standard deviation of 2-6 replicate trials

Baseline MST results are single determinations with reported analytical uncertainty

Values in red are calculated from Pu-238 results as the determination of Pu-239,240 fell below quantifiable limit

**Shelf-Life**
The baseline MST appears to have a very long shelf-life when stored as an aqueous suspension.  For example, the sample of MST used in these studies for comparison to the peroxotitanate samples was produced about 10 years ago and has shown no loss in strontium and actinide separations performance during this time period.  Given the good shelf-life of MST, we evaluated the shelf-life of the bench-scale mMST samples by measuring strontium and actinide removal performance after storing at ambient laboratory conditions as an aqueous slurry for six and twelve months.

We used the same simulant (see Table I) that we used when we first tested the performance of the freshly prepared mMST samples. Prior to each test set we added a small amount of Sr-85 radiotracer.  This addition was necessary to bring the Sr-85 activity to a level similar to that when we tested the performance of the samples in the earlier test set.  The addition of the Sr-85 radiotracer provides an insignificant increase in the total stable strontium concentration of the simulant.  For these tests we limited the mMST testing to a single MST concentration ($0.2 \text{ g L}^{-1}$) in duplicate for each sample (LS-1, LS-2 and LS-3) with sampling events at 6 and 12-hours.

Table IV provides the average and standard deviation of the strontium, plutonium and neptunium DF values for the mMST and baseline MST samples at the three testing dates.  Note, we did not test the performance of the baseline MST sample at $0.4 \text{ g L}^{-1}$ at the initial time date.  Inspection of Table IV indicates excellent agreement for the average strontium DF values at the 6-h and 12-h sampling times across the three datasets.  This finding indicates no loss in strontium removal performance during storage of the bench-scale mMST at ambient laboratory temperature.  For strontium, we observed that the mMST exhibited an average DF value 5 times greater than that of the baseline MST sample after 6 and 12-hours of contact at a $0.2 \text{ g L}^{-1}$ sorbent concentration at the initial, 6-month and 12-month testing dates.  Comparison of the mMST results at $0.2 \text{ g L}^{-1}$ with that of the baseline MST at the higher concentration of $0.4 \text{ g L}^{-1}$ revealed that the mMST exhibited a strontium DF value of 1.5 times that of the baseline MST.

The average plutonium DF values at the 6-hour and 12-hour sampling times after storing the mMST samples for six and twelve months are lower than those determined in the initial test set (see Table IV).  However, at the 95% confidence level the range of plutonium DF values overlap indicating the DF values are not statistically different.  Note, that for the 6-h and 12-h sampling events, the measured plutonium concentration varied between about 1 and 4 $\mu\text{g L}^{-1}$, which corresponds to DF values of about 50 - 200.  Thus, at the low plutonium concentrations that are achieved by the mMST, small changes in the measured plutonium concentration can result in large change in the DF value.  Given the overlap and the experimental uncertainty in the plutonium measurements at the $1 - 4 \mu\text{g L}^{-1}$ range, we conclude that the plutonium removal performance did not decrease over the 12-month storage time.  For these datasets, the mMST added at $0.2 \text{ g L}^{-1}$ exhibited at least 20-fold and 10-fold increases in DF values compared to the baseline MST material added at 0.2 and $0.4 \text{ g L}^{-1}$, respectively.

We observed no significant differences among the measured 6-h and 12-h neptunium DF values for the bench-scale mMST samples over the three datasets.  Thus we conclude that the neptunium removal characteristics did not change over the 12-month storage period. Comparison of the average DF values for the mMST and baseline MST samples suggest a slight improvement in neptunium removal by the mMST.  However, the 12-h samples for the baseline MST tests in both the 6-month and 12-month datasets indicate no measurable removal of neptunium. Thus, it is difficult to quantify the degree of improved performance given the available neptunium data.

**Filtration Characteristics**
Filtrate rates from the stirred cell (i.e., dead end filter) tests with a 0.1-micron Mott filter membrane measured $8.7 \pm 3.3$ mL min$^{-1}$ for the MST material and $8.8 \pm 2.4$ mL min$^{-1}$ for the pilot-scale sample of mMST.  The filtrate collected was clear and did not show any solids.  Given the good filtration performance of the mMST in the stirred cell test, we proceeded to test the performance of this material in a single tube crossflow filter apparatus.

Fig. 4 shows the crossflow filter flux (gpm ft$^{-2}$) as a function of the insoluble solids concentration (wt %) for tests with MST and mMST materials in the absence (A) and presence (B) of sludge solids.  Both sets of tests were carried out over the same range of pressures and axial velocities.  In the absence of sludge solids, the MST exhibited a higher flux (1.3 – 2X) than the mMST at low solids loadings (0.06 and 0.29 wt %) and the same flux at higher solids loadings (1.29 and 5.0 wt %).  In the presence of the sludge solids, the mMST-sludge suspension exhibited a higher filter flux than the MST-sludge suspensions at all solids concentrations.

The higher fluxes for the mMST-sludge suspensions compared to the MST-sludge suspensions are somewhat surprising given that the results in the absence of sludge solids.  Previous testing indicated that mixtures of the MST and sludge filter more slowly than MST alone.[9]  This dataset confirms this trend for MST (see Fig. 3).  In contrast, the filter fluxes for the mMST-sludge suspensions are very similar to those measured in mMST-only suspension.  This suggests that the sludge-sorbent interactions (e.g., particle packing) are reduced with the mMST material compared to that with the MST and, consequently, crossflow filtration of the modified MST-sludge mixture is equal to or better than that of the MST-sludge mixture.

**Table IV. Strontium, plutonium and neptunium DF values for the baseline MST and mMST samples at the initial synthesis, 6-month storage and 12-month storage times.**

| | Strontium DF | | | | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | mMST @ 0.2 g/L | | | | Baseline MST @ 0.2 g/L | | | | Baseline MST @ 0.4 g/L | | | |
| | 6-hours | | 12-hours | | 6-hours | | 12-hours | | 6-hours | | 12-hours | |
| | Average | Std Dev | Average | Std Dev | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty |
| Initial | 1.13E+02 | 1.40E+01 | 1.28E+02 | 5.80E+00 | 2.14E+01 | 5.63E-01 | 2.48E+01 | 7.12E-01 | nd | - | nd | - |
| 6-month | 1.10E+02 | 3.50E+00 | 1.37E+02 | 5.74E+00 | 2.36E+01 | 5.97E-01 | 2.78E+01 | 7.47E-01 | 7.35E+01 | 2.02E+00 | 9.00E+01 | 3.44E+00 |
| 12-month | 1.11E+02 | 7.16E+00 | 1.32E+02 | 1.04E+01 | 2.52E+01 | 6.59E-01 | 2.81E+01 | 7.45E-01 | 7.72E+01 | 2.31E+00 | 8.87E+01 | 2.87E+00 |
| | Plutonium DF | | | | | | | | | | | |
| | mMST @ 0.2 g/L | | | | Baseline MST @ 0.2 g/L | | | | Baseline MST @ 0.4 g/L | | | |
| | 6-hours | | 12-hours | | 6-hours | | 12-hours | | 6-hours | | 12-hours | |
| | Average | Std Dev | Average | Std Dev | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty |
| Initial | 9.57E+01 | 1.76E+01 | 1.72E+02 | 6.16E+00 | 2.85E+00 | 1.97E-01 | 3.21E+00 | 2.41E-01 | nd | - | nd | - |
| 6-month | 6.38E+01 | 6.14E+00 | 1.43E+02 | 2.66E+01 | 2.82E+00 | 1.82E-01 | 3.31E+00 | 2.43E-01 | 5.08E+00 | 3.23E-01 | 6.22E+00 | 4.66E-01 |
| 12-month | 6.82E+01 | 1.39E+01 | 1.24E+02 | 9.25E+00 | 3.32E+00 | 3.11E-01 | 3.49E+00 | 2.72E-01 | 5.99E+00 | 5.28E-01 | 6.02E+00 | 4.90E-01 |
| | Neptunium DF | | | | | | | | | | | |
| | mMST @ 0.2 g/L | | | | Baseline MST @ 0.2 g/L | | | | Baseline MST @ 0.4 g/L | | | |
| | | | | | | | | | | | | |
| | Average | Std Dev | Average | Std Dev | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty | Value | Uncertainty |
| Initial | 1.77E+00 | 2.52E-01 | 1.83E+00 | 1.55E-01 | 1.05E+00 | 6.27E-02 | 1.25E+00 | 9.99E-02 | nd | - | nd | - |
| 6-month | 1.83E+00 | 3.93E-01 | 1.24E+00 | 2.07E-01 | 1.10E+00 | 2.52E-01 | 7.44E-01 | 2.19E-01 | 1.24E+00 | 1.90E-01 | 8.79E-01 | 1.80E-01 |
| 12-month | 1.98E+00 | 4.07E-01 | 1.47E+00 | 1.37E-01 | 1.30E+00 | 3.33E-01 | 8.82E-01 | 1.95E-01 | 1.46E+00 | 2.06E-01 | 1.02E+00 | 1.21E-01 |

nd = not determined

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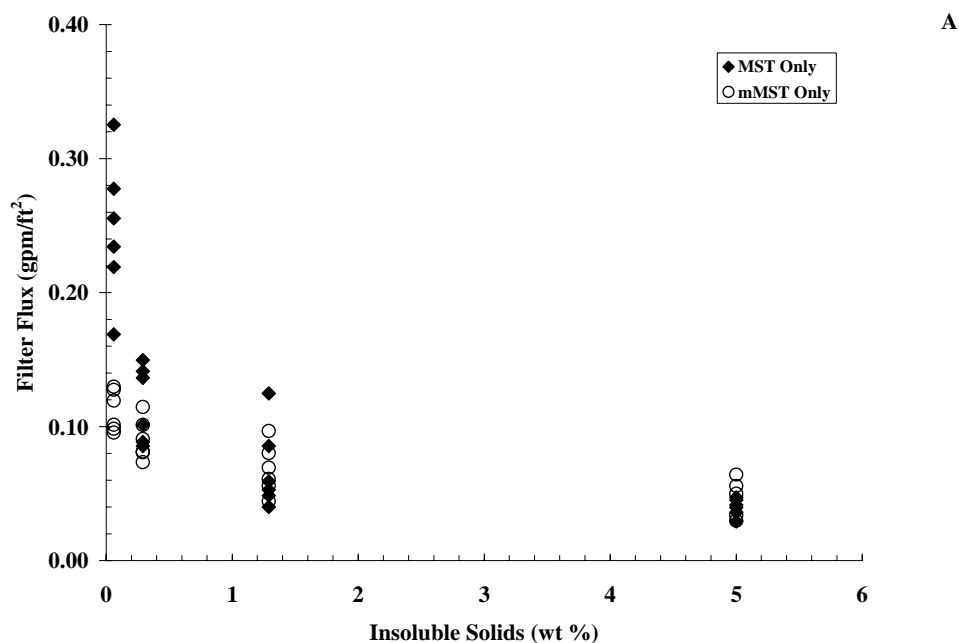
**Fig. 4. Crossflow filter flux as a function of insoluble solids content with sludge solids absent (A) and present (B).**

## CONCLUSIONS

Testing demonstrated that the preparation of an improved inorganic sorbent, referred to as modified MST, can be reproduced at the pilot-scale. In addition to excellent removal characteristics with simulated waste solutions, the new peroxotitanate materials demonstrated improved performance with actual tank waste. Filtration characteristics of the peroxotitanate samples proved similar to that of the baseline MST. Also, after 12 months of storage in the laboratory, the peroxotitanates continue to show excellent strontium and actinide removal performance. Based on these results we conclude that the peroxotitanate material appears an excellent candidate for replacing the baseline MST material for waste processing at the SRS.

## ACKNOWLEDGEMENTS

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