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Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Optimized Monosodium Titanate Phase II Final Report

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Acronyms

ARP	Actinide Removal Project
ACTS	Actinide and Chemical Technology Section
BET	Brunauer Emmett Teller
BJH	Barrett Joyner Halenda
DDI	deionized and distilled
DF	decontamination factor
DWPF	Defense Waste Processing Facility
HLW	high-level waste
ITP	In-Tank Precipitation
K_d	batch distribution constant
MST	monosodium titanate
MMST	modified monosodium titanate
SNL	Sandia National Laboratories
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
TIP	titanium (IV) isopropoxide or tetraisopropoxytitanium (IV)

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1.0 Executive Summary

This document provides a final report of Phase II testing activities for the development of a modified monosodium titanate (MST) that exhibits improved strontium and actinide removal characteristics compared to the baseline MST material. The activities included determining the key synthesis conditions for preparation of the modified MST, preparation of the modified MST at a larger scale by a commercial vendor, demonstration of the strontium and actinide removal characteristics with actual tank waste supernate and measurement of filtration characteristics. Key findings and conclusions include the following.

Testing evaluated three synthetic methods and eleven process parameters for the optimum synthesis conditions for the preparation on an improved form of MST. We selected the post synthesis method (Method 3) for continued development based on overall sorbate removal performance.

We successfully prepared three batches of the modified MST using Method 3 procedure at a 25-gram scale. The laboratory prepared modified MST exhibited increased sorption kinetics with simulated and actual waste solutions and similar filtration characteristics to the baseline MST. Characterization of the modified MST indicated that the post synthesis treatment did not significantly alter the particle size distribution, but did significantly increase the surface area and porosity compared to the original MST. Testing indicated that the modified MST exhibits reduced affinity for uranium compared to the baseline MST, reducing risk of fissile loading. Shelf-life testing indicated no change in strontium and actinide performance removal after storing the modified MST for 12-months at ambient laboratory temperature. The material releases oxygen during the synthesis and continues to offgas after the synthesis at a rapidly diminishing rate until below a measurable rate after 4 months.

Optima Chemical Group LLC prepared a 15-kilogram batch of the modified MST using the post synthesis procedure (Method 3). Performance testing with simulated and actual waste solutions indicated that the material performs as well as or better than batches of modified MST prepared at the laboratory-scale. Particle size data of the vendor-prepared modified MST indicates a broader distribution centered at a larger particle size and microscopy shows more irregular particle morphology compared to the baseline MST and laboratory prepared modified MST. Stirred-cell (i.e., dead-end) filter testing revealed similar filtration rates relative to the baseline MST for both the laboratory and vendor-prepared modified MST materials. Crossflow filtration testing indicated that with MST-only slurries, the baseline MST produced between 30 – 100% higher flux than the vendor-prepared modified MST at lower solids loadings and comparable flux at higher solids loadings. With sludge-MST slurries, the modified MST produced 1.5 – 2.2 times higher flux than the baseline MST at all solids loadings.

Based on these findings we conclude that the modified MST represents a much improved sorbent for the separation of strontium and actinides from alkaline waste solutions and recommend continued development of the material as a replacement for the baseline MST for waste treatment facilities at the Savannah River Site.

2.0 Introduction

MST is an inorganic sorbent material that exhibits high selectivity for strontium and actinide elements in the presence of strongly alkaline and high sodium containing salt solutions. [1,2] The Savannah River Site (SRS) selected this material for strontium and plutonium removal from high-level waste solutions in the early 1980s as part of the In-Tank Precipitation (ITP) process.[3] In 2001, the Department of Energy (DOE) selected MST for the strontium/actinide separation step within the Salt Waste Processing Facility (SWPF).[4] Subsequently, Salt Processing Program Engineering selected MST for use in the Actinide Removal Process (ARP) to treat waste solutions low in cesium activity in a treatment facility located in Building 512-S.[5]

Original development of MST at Sandia National Laboratory (SNL) produced a dried powder. Unpublished studies conducted by L. L. Kilpatrick and D. T. Hobbs during the 1980s indicated that air drying of the MST at elevated temperature (≥100 °C) adversely impacted strontium removal performance. Principally due to the poorer sorption characteristics of MST dried at elevated temperature, procurement of MST at SRS for the ITP process specified that the vendor prepare and isolate the material without drying and deliver the MST as an aqueous solution containing 10 – 20 wt % MST solids.[6]

The proposed SWPF and existing ARP facilities have significantly different reactor configurations and process cycle times than that in the abandoned ITP operation. In particular, contact times between the MST and the alkaline waste solutions in the SWPF and ARP will be less than 12 hours versus approximately 2 weeks in the ITP process. Increased waste characterization data indicates that alpha removal characteristics (and principally plutonium removal) represent a greater challenge than that for ^{90}Sr removal. Based on recent testing at Savannah River National Laboratory (SRNL), the performance of MST to efficiently and rapidly remove alpha-emitting radionuclides serves as the limiting factor in operational throughput. Even higher alpha activities are projected for the SWPF and ARP operations as a result of initiatives to accelerate the disposal of HLW at the SRS. Due to the limited solubility of titanium in HLW borosilicate glass, there are limits on the amount of MST that can be used in SWPF and ARP facilities.[7] Consequently, the need exists for an improved Sr/alpha removal material that exhibits increased actinide capacity and removal kinetics.

In 2003 the DOE Office of Cleanup Technologies (EM-21) funded a project to develop improved sorbent materials for strontium/actinide separations at SRS.[8] This work identified a methodology for modifying the synthesis of MST that produced materials that exhibited significantly improved performance for strontium and actinide removal. Improved performance included both increased capacity and sorption kinetics. Preliminary evaluation of the use of the modified MST materials for use in the treatment of SRS high-level waste (HLW) in the ARP facility suggested that the throughput could be increased by as much as a factor of three. With these promising results, the DOE Office of Cleanup Technologies funded SRNL to continue development of the modified

MST materials under a Phase II project. Initial results from Phase II testing are documented in an earlier report.[9] This final report provides a summary of work completed as specified in the Task Technical and Quality Assurance Plan for Phase II testing.[10,11]

3.0 Experimental

3.1. Preparation of Modified MST Samples

We prepared modified MST samples by one of three methods. Method 1 added hydrogen peroxide during the synthesis of MST by the published sol-gel technique.[1,2,12] Method 2 dissolved the titanium(IV) tetraisopropoxide reagent in a sodium hydroxide solution followed by the addition of hydrogen peroxide. Method 3 added hydrogen peroxide to an aqueous suspension of MST (post synthesis).

Larger laboratory scale (25-g) and 15-kg quantities of modified MST were prepared using the Method 3 synthesis conditions. The 25-g scale preparation of modified MST used the conditions as reported for Test #14P (see section 4.1.3). Researchers filtered and washed 25 grams of MST (155 grams of Optima Batch #00-QAB-417 suspension) to remove soluble salts, suspended in deionized, distilled water (Millipore Milli-Q Element Water Purification System), adjusted to pH of 7.00 by the addition of 1 M and 0.1 M nitric acid solutions and diluted back to the original suspension weight (155 g). They placed the pH 7 suspension of MST in a 250 mL round bottom flack equipped with a magnetic stirring bar, glass addition funnel, thermocouple and condenser.

With vigorous mixing, we added 85 grams of 26 wt % hydrogen peroxide solution (Fisher Scientific) dropwise over 1 – 2 hours. The addition of the hydrogen peroxide immediately produced a yellow color and evolved a gas. The temperature of the reaction slurry increased from 22.1 °C to a maximum of 53.0 °C after adding approximately half of the hydrogen peroxide. The temperature of the reaction slurry measured about 40 °C at the conclusion of the hydrogen peroxide addition.

We mixed the reaction slurry for additional 24 hours at ambient laboratory temperature. The slurry was filtered through a disposable Nalgene filter having a 0.45-micron nylon filter membrane and solids rinsed with six 30-mL portions of deionized, distilled water. The modified MST solids were suspended in water, and personnel added quantities of 1 M and 0.1 M nitric acid solutions while stirring to bring the pH of the suspension to 4.0 ± 0.1, followed by addition of deionized, distilled water to bring the final solids concentration to 15.0 ± 0.5 wt %. The pH-adjusted modified MST slurry was then stored in plastic sample bottle.

Preparation of the vendor-prepared material by Optima Chemical Group, LLC (Douglas, GA) used the same method as described above for the preparation of the 25-scale laboratory quantity. The 15-kg quantity of modified MST received from the vendor was designated as Batch # 06-QAB-0139. Prior to shipment of the 15-kg batch of material, the vendor shipped a 1-L sub-sample for acceptance testing. SRNL designated this sub-sample as 06-QAB-0139-1L. After receipt of the 15-kg batch of modified MST at

SRNL, we obtained three additional samples during mixing the contents of the 30-gallon drum with a paddle blade attached to a hand-held drill. These three samples are designated as 06-QAB-0139-D1, 06-QAB-0139-D2 and 06-QAB-0139-D3.

3.2. Performance Testing with Simulated Waste Solution

Testing of combined strontium and actinide removal performance occurred at SRNL using simulated waste solutions having the compositions shown in Table 1. Simulant SWS-8-2004 was used during the evaluation of synthesis conditions and preparations of laboratory scale batches of modified MST. Simulant SWS-12-2005 was used for evaluating the performance of the vendor-prepared modified MST. The latter simulant was prepared for use in this program and another program evaluating cesium removal as well as strontium and actinide removal. Thus, we added ^{137}Cs to this simulant as shown in Table 1.

Table 1. Composition of Simulated Waste Solutions

Component	**Target Concentration**	**SWS-8-2004 Measured Concentration**	**SWS-12-2005 Measured Concentration**
NaNO3	2.60 M	2.44 ± 0.24 M	2.58 ± 0.26 M
NaOH	1.33 M	1.36 ± 0.14M	1.30 ± 0.13 M
Na2SO4	0.521 M	0.551± 0.055M	0.515 ± 0.052 M
NaAl(OH)4	0.429 M	0.503 ± 0.050 M	0.513 ± 0.051 M
NaNO2	0.134 M	0.116 ± 0.012 M	0.139 ± 0.014 M
Na2CO3	0.0260 M	0.016 ± 0.010 M	0.035 ± 0.0035 M
Total Na	5.6 M	5.2 ± 0.52 M	4.57 ± 0.46 M
Total Sr	0.6 mg L^{-1}	0.484 ± 0.097 mg L^{-1}	0.569 ± 0.0105 mg L^{-1}
^{85}Sr*	$\geq$10000 dpm mL^{-1}	164,000 ± 3280 dpm mL^{-1}	27,200 ± 487 dpm mL^{-1}
Total Pu	0.2 mg L^{-1}	0.218 ± 0.013 mg L^{-1}	0.200 ± 0.012 mg L^{-1}
^{237}Np	0.5 mg L^{-1}	0.461± 0.090 mg L^{-1}	0.474 ± 0.104 mg L^{-1}
Total U	10 mg L^{-1}	9.55 ± 0.33 mg L^{-1}	10.4 ± 0.57 mg L^{-1}
^{137}Cs	$\geq$10000 dpm mL^{-1}	not added	76,500 ± 4,790 dpm mL^{-1}

* Value at time solution was first prepared. ^{85}Sr has a 64.8 day half-life and, therefore, the ^{85}Sr activity in the solutions is continuously decreasing.

Reuse testing – i.e., tests involving multiple contacts of a single aliquot of MST with different solutions – featured a simulated waste solution having the same targeted chemical composition as the solutions in Table 1, but with different sorbate concentrations. Table 2 provides the sorbate composition of this simulant including the values previously reported for earlier reuse testing. Analytical results confirmed that the total strontium, plutonium, neptunium and uranium concentrations had not changed during storage of and the addition of ^{85}Sr to the simulant. Addition of the ^{85}Sr radiotracer allowed determination of strontium removal by gamma counting in addition to inductively coupled plasma mass spectrometry.

Table 2. Sorbate Composition of the Simulated Waste Solution Used in Reuse Testing

Sorbate	As Prepareda	Control Samples MST Reuse Testa	After Spiking with ^{85}Sr in Preparation for Use with Modified MST	Control Samples Modified MST Reuse Test
Total Sr (ug L^{-1})	9,270 (1,940)	9,370	9,660 (1,930)	9,920 (215)
^{238}Pu (dpm mL^{-1})	56,700 (2,880)	62,200	56,400 (2,790)	57,800 (2,010)
$^{239/240}$Pu (ug L^{-1})	128	79	105 (21.0)	96.4 (5.55)
^{237}Np ((ug L^{-1})	121 (24.2)	158	124 (24.8)	135 (5.41)
Total U (ug L^{-1})	13,800 (2,760)	13,900	13,100 (2,610)	14,300 (144)

[a] as reported in reference 15
numbers in parenthesis are single standard deviation of replicate measurements

Strontium and actinide removal testing occurred at 25 ± 2 °C with sorbent concentrations ranging from 0.1 g L^{-1} to 0.8 g L^{-1}. Test bottles were shaken at 175 rpm in the orbital shaker/waterbath. Sampling of the test bottles occurred at varying times including 2, 4, 6, 12, 24 and 168 hours of contact. Prior to sampling the test bottles, we manually agitated the contents to obtain a representative subsample of both the solids and solutions. We filtered the samples through 0.45-micron or 0.10-micron syringe filters (nylon membrane) to remove MST solids. A measured amount of the filtrate was acidified with an equal volume of 5 M nitric acid solution, mixed well and allowed to stand for a minimum of 2 hours (typically overnight) before submitting for radiochemical analyses. Gamma spectroscopy measured the ^{85}Sr and neptunium content while alpha spectroscopy measured the total alpha activity. We measured the ^{238,239,240}Pu content by radiochemical separation of the plutonium followed by alpha counting of the extracted plutonium.

3.3. Performance Testing with Actual Waste

Closure Business Unit (CBU) supplied SRNL with a three liter sample of supernate taken from Tank 39H in May, 2005 (Sample ID: HTF-049). Upon receipt, the sample was vented and allowed to stand undisturbed overnight. In preparation for characterization, we pumped the Tank 39H supernate sample from the 3-L sampler into a 4-L carboy using a Masterflex® peristaltic pump and Tygon® tubing. The total volume of Tank 39H supernate measured 3.18 L.

Visual inspection of the supernate composite showed the material to be clear and light in color with no observable solids. We determined the density of the as-received material at 1.265 ± 0.0071 g mL^{-1} using 10 mL glass Class A micro-volumetric flasks. We determined chemical composition of the material by diluting an aliquot of the as-received Tank 39H sample in either 2 M nitric acid or deionized water.

The as-received material measured 5.48 ± 0.37 M in sodium, which is consistent with measured density and within the desired range for performance testing (see Table 3). We then measured the ^{238,239,240}Pu content by radiochemical separation of the plutonium followed by alpha counting of the extracted plutonium. ^{90}Sr was determined by chemical separation and beta counting of the extracted strontium. ^{137}Cs was determined by gamma spectroscopy. Stable strontium and actinide isotopes were determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Free and total base, other base excluding carbonate, carbonate, nitrate, nitrite, sulfate, phosphate, halides, and oxalate were determined by titration and ion chromatography. Table 3 provides the measured composition of the as-received Tank 39H sample.

Table 3. Composition of the As-Received Tank 39H Supernate Sample

Analyte	Unit	Concentration	Standard Deviation
Na	M	5.48E+00	3.67E-01
OH^-	M	2.10E+00	7.00E-02
NO_3^-	M	2.47E+00	1.51E-02
NO_2^-	M	6.48E-01	6.33E-03
$Al(OH)_4^-$	M	4.23E-01	6.79E-03
CO_3^{2-}	M	5.66E-01	7.85E-03
SO_4^{2-}	M	5.18E-02	1.01E-03
PO_4^{3-}	M	2.17E-03	4.23E-05
F^-	M	bdl	-
Cl^-	M	bdl	-
^{137}Cs	pCi/mL	2.26E+08	0
^{90}Sr	pCi/mL	3.37E+05	3.64E+04
Total Pu	pCi/mL	8.25E+04	7.43E+02

bdl = below method detection level

Analytical results revealed that the tank waste sample was much lower in ^{90}Sr and alpha activity than expected given past studies involving samples from Tank 39H. Therefore, we adjusted the composition of the tank waste solution to increase plutonium and strontium content to provide a more challenging matrix for evaluating the MST performance characteristics consistent with prior studies.

Plutonium and strontium adjustment proceeded by adding three different solutions: (1) ^{238}Pu, (2) $^{239/240}Pu$ and (3) natural abundance strontium into 2.5 L of the Tank 39H waste solution. A concentrated, nitric acid solution of ^{238}Pu (3.3 mL of 1.3 E+09 dpm/mL in 15 M HNO_3) served as the source of the plutonium. After analyzing the ^{238}Pu solution for purity we added 25 mL of 0.05 M Na_2CO_3 solution slowly while stirring to obtain a slightly alkaline solution. We prepared a slightly alkaline solution of $^{239/240}Pu$ by slowly adding 10 mL of a 0.019 M Na_2CO_3 solution to a nitric acid solution of weapons-grade $^{239/240}Pu$ (1.05 mg Pu mL^{-1} in 1.3 mL of 0.5 M HNO_3). We prepared the natural abundance strontium solution by dissolving the desired quantity of strontium nitrate (0.066 g) in distilled, deionized water (10 mL). All solution volumes were minimized to reduce the degree of dilution of the Tank 39H actual waste solution.

We added the spike solutions in the following order with indicated hold times: (1) strontium solution followed by stirring for 2 hours, (2) ^{238}Pu solution followed by stirring for 1 hour, and (3) $^{239/240}Pu$ solution followed by stirring for 1 hour. We continued mixing for 13 days at ambient temperature. We collected aliquots and analyzed aliquots of the spiked solution after 6 and 13 days. Results, shown in Table 4, indicate that all analytes except possibly strontium were at or near equilibrium. Prior to use we filtered the spiked Tank 39H sample through a cartridge filter (Whatman Polycap™ 75 TF unit with 0.1 μ PTFE membrane). We analyzed additional aliquots at the start of testing and included a test bottle without added MST to serve as control samples to account for the decreasing strontium concentration and the lead time between these analytical results and the initiation of the performance tests.

Table 4. Analysis of Tank 39H Actual Waste Supernate after Spiking with Strontium and Plutonium

Analyte	Method	Units	6 day Sample	13 day Sample
^{90}Sr	Radchem	pCi/mL	3.73E+04 ± 3.8E+03	2.75E+04 ± 2.8E+03
Total Sr	ICP-MS	μg/L	2.14E+03 ± 4.3E+02	1.58E+03 ± 3.2E+02
Total Pu	PuTTA	μg/L	2.54E+02 ± 1.3E+01	2.54E+02 ± 1.4E+01
Total Pu	ICP-MS	μg/L	1.97E+02 ± 3.9E+01	2.06E+02 ± 4.1E+01
^{237}Np	ICP-MS	μg/L	1.49E+02 ± 3.0E+01	1.29E+02 ± 2.6E+01
Total U	ICP-MS	μg/L	9.99E+03 ± 2.00E+03	1.02E+04 ± 2.05E+03

Table 5 provides a listing of the first set of seven tests carried out to evaluate the performance of the laboratory prepared modified MST (Test Set #1). Testing included a single control test (no added MST), a single test with the baseline MST sample (Optima Chemical Company, Inc. Lot #00-QAB-417) at 0.2 g L^{-1}, duplicate tests with modified MST at 0.1 and 0.2 g L^{-1} MST and a final test to determine if the presence of the solvent mixture planned for use in the Caustic Side Solvent Extraction (CSSX) process influences the performance of the modified MST. For this test we mixed 0.02 grams (0.2 g L^{-1}) of modified MST with 0.050 mL (500 ppm) of the CSSX solvent.

Researchers poured 100 mL of the filtered and spiked Tank 39H waste into test bottles equipped with magnetic stirring bars. The test bottles were placed into a temperature controlled waterbath (25 ± 3 °C) and incubated overnight. We removed each bottle from the waterbath, added a pre-weighed amount of the appropriate MST, and returned the test bottle to the waterbath.

Following MST addition, we sampled each test bottle after 2, 4, 6, 12, 24 and 168-hours. At the desired sampling time, we removed a 3-mL aliquot from each test bottle. We filtered the aliquot through a syringe filter (Millex® VV 0.1-μm PVDF membrane) and collected the filtrate in a clean sample bottle. Personnel then pipetted 1-mL portions of the filtered sample into a second set of sample bottles containing 19 mL of 2 M nitric acid. The acidified samples were shaken for approximately 15 seconds and then allowed to equilibrate with periodic shaking for a minimum of 2 hours prior to submittal for analysis. The acidified samples were analyzed to determine the following, $^{238/239/240}Pu$, ^{90}Sr, stable strontium and actinides.

Table 5. Conditions for Test Set #1 Contacting Actual Waste with Laboratory-Prepared Modified MST

Test #	MST ID	[MST], g/L	Contact Time, hours
1	modified	0	0, 2, 4, 6, 12, 24 and 168
2	modified	0.1	0, 2, 4, 6, 12, 24 and 168
3	modified	0.1	0, 2, 4, 6, 12, 24 and 168
4	modified	0.2	0, 2, 4, 6, 12, 24 and 168
5	modified	0.2	0, 2, 4, 6, 12, 24 and 168
6	baseline	0.2	0, 2, 4, 6, 12, 24 and 168
7	modified	0.2*	0, 2, 4, 6, 12, 24 and 168

*with 500 ppm CSSX solvent

We conducted a supplemental set of actual waste tests evaluating the efficiency of modified MST in both multiple strike and reuse configurations using the same equipment as described for Test Set #1. The supplemental tests consisted of seven tests, which we performed in two stages. Tests S-2, S-3, and S-1C preceded Tests S-4, S-5, S-1A, and S-1B by two weeks. Tests S-1A, -1B, and -1C served as control tests (i.e., no modified MST were added). Tests S-2 and S-3 served as multiple strike tests which were facilitated by filtering the test solutions approximately 6 hours after first contacting with modified MST and then recharging the filtrate with fresh modified MST to simulate a second strike. Samples were obtained at approximately 2, 6, 8, 12, 30, and 174 h after the addition of the first strike with MST. Tests S-2 and S-3 were contacted with 0.1 g L^{-1} and 0.2 g L^{-1} MST, respectively, in each strike. Samples were prepared and analyzed as described previously.

Tests S-4 and S-5 evaluated the reuse of the modified MST sample. In these tests, we contacted the modified MST with 200-mL of the filtered, composited, residual Tank 39H actual waste solution from Test Set #1. After approximately 6 hours of contact, we separated the liquid and MST solids and then added the recovered MST solids to fresh, spiked Tank 39H actual waste solution. Samples were obtained at approximately 2, 6, 8, 12, 30, and 174 h after the first MST contact. Control tests included S-1A (fresh, spiked Tank 39H actual waste) and S-1B (filtered, composited, residual Tank 39H actual waste solution remaining from Test Set #1). Tests S-4 and S-5 featured MST concentrations of 0.1 g L^{-1} and 0.2 g L^{-1}, respectively. Samples from these tests were prepared and analyzed as described previously.

We also conducted a set of tests with the vendor-prepared modified MST using the same tank waste material described above for the laboratory-produced modified MST. Tests were similar to that in the earlier tests, except we omitted the test with the CSSX solvent and added a test with 0.4 g.L^{-1} of the baseline MST. Table 6 provides the conditions for the seven tests in this test set.

Table 6. Conditions for Actual Waste Performance Tests with Vendor-Prepared Modified MST

Test #	**MST ID**	**[MST], g/L**	**Contact Time, hours**
1	modified	0	0, 2, 4, 6, 12, 24 and 168
2	modified	0.1	0, 2, 4, 6, 12, 24 and 168
3	modified	0.1	0, 2, 4, 6, 12, 24 and 168
4	modified	0.2	0, 2, 4, 6, 12, 24 and 168
5	modified	0.2	0, 2, 4, 6, 12, 24 and 168
6	baseline	0.2	0, 2, 4, 6, 12, 24 and 168
7	baseline	0.4	0, 2, 4, 6, 12, 24 and 168

3.4 Filtration Testing

We performed filtration tests in a stirred cell filtration apparatus (see Figure 1) with a non-radioactive, simulated waste solution having the chemical composition as reported in Table 7. We added the appropriate MST sample to the solution to provide a concentration of solids of 0.55 g L^{-1}. We poured approximately 60 mL of the feed suspension into the stirred cell, agitated the cell contents, pressurized the cell to 30 psi, and measured the filtrate volume as function of time. Tests evaluated the filtration characteristics of the MST samples with the following filter media: 0.1 μ TruMem® ceramic (typical of the SpinTek rotary filter), 0.1 μ Mott sintered SS (as used in the ARP design), 0.1 μ Pall sintered SS (typical of the SWPF design), and 0.5 μ Pall sintered SS (as contained in the SRNL modified rotary microfilter). The Mott and Pall pore sizes are nominal. We performed two sets of tests with the 0.1 μ Mott and 0.1 μ Pall media using a fresh feed suspension for the second set of tests.

Table 7. Composition of Simulated Waste Solution Used in Filtration Testing

Species	Concentration (M)
Na^+ (M)	5.6
K^+ (M)	0.015
Cs^+ (M)	0.00014
OH^- (M)	1.91
NO_3^- (M)	2.14
NO_2^- (M)	0.52
AlO_2^- (M)	0.31
CO_3^{2-} (M)	0.16
SO_4^{2-} (M)	0.15
Cl^- (M)	0.025
F^- (M)	0.032
PO_4^{3-} (M)	0.01
$C_2O_4^{2-}$ (M)	0.004
SiO_3^{2-} (M)	0.004
MoO_4^{2-} (M)	0.0002

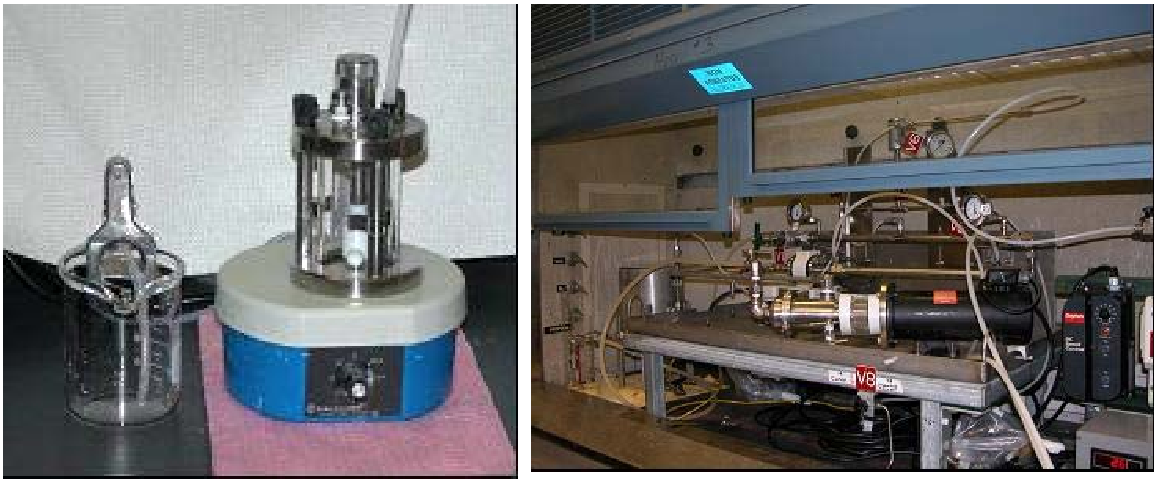

Figure 1. Stirred Cell (left) and Crossflow Filter (right) Testing Equipment

Personnel performed the crossflow filter tests in the Cold Cells Unit Filter (CUF) apparatus shown in Figure 1. They placed approximately 8 L of the simulated salt solution (Table 7) in the feed tank, added simulated SRS Sludge and the appropriate monosodium titanate material to produce the target solids composition. Table 8 shows the target solids concentrations for each of the crossflow filter tests. To ensure a good comparison in performance of the modified MST with the baseline MST, the authors made the following change in test protocol. In tests with the vendor-prepared modified MST, they collected subsamples from the vendor-prepared batch and the baseline MST, and analyzed them for total insoluble solids. They used these results to ensure comparative tests had the same solids loadings.

Table 8. Target Solids Composition for Crossflow Filter Testing

Test	Sludge (wt %)	Baseline MST (wt %)	Modified MST (wt %)
1		0.06	
2		0.29	
3		1.29	
4		5.0	
5			0.06
6			0.29
7			1.29
8			5.0
9	0.03	0.03	
10	0.15	0.15	
11	0.65	0.65	
12	2.5	2.5	
13	0.03		0.03
14	0.15		0.15
15	0.65		0.65
16	2.5		2.5

4.0 Results and Discussion

4.1 Task 1 – Identify Key Synthesis Conditions

The objective of this task was to identify the synthesis conditions that provide a modified MST material with the best strontium and actinide removal characteristics. Performance testing emphasized plutonium removal characteristics since the isotopes of this element serves as the limiting radionuclides in defining processing conditions and equipment sizing in the ARP and SWPF.

Previous Phase I testing identified several conditions under which the addition of a hydrogen peroxide provided a modified MST with improved plutonium and neptunium removal characteristics.[12] For example, addition of the hydrogen peroxide at pH conditions ranging from pH <1 to pH >11 produced materials that featured improved, but varying actinide removal characteristics. Generally, samples of the modified MST exhibited better Sr/actinide removal characteristics when produced under acidic and neutral conditions.

We prepared modified MST samples by three general routes: (1) addition of hydrogen peroxide during the sol-gel synthesis of MST, (2) addition of the hydrogen peroxide during the aqueous synthesis route and (3) addition of the hydrogen peroxide to an aqueous suspension of MST (post synthesis). Phase I testing did not explore the effects of other synthesis parameters such as the ratio of hydrogen peroxide to MST, contact time, multiple contacts of the MST with the hydrogen peroxide and post addition steps. These parameters may significantly influence the characteristics of the modified MST. Thus, this task investigated the influence of pH, mole ratio of hydrogen peroxide to titanium, and contact time on the preparation of modified MST materials.

4.1.1. Method 1 – Addition of Hydrogen Peroxide During the Sol-Gel Synthesis

Table 9 provides a summary of the 9 different syntheses carried out using this method. The reference condition in this synthetic route adds the hydrogen peroxide as a 30 wt % solution in water (i.e., no added base or acid) at a mole ratio of chemical to Ti of 3:1. Syntheses were carried out at mole ratios of 0.3, 1.0, 3.0 and 6.0. An additional preparation increased the contact/ripening time from 24 hours to 96 hours. Two tests added the hydrogen peroxide as a strongly acidic solution (0.1M HNO_3). We also prepared two samples using the reference condition with an additional step of acid adjustment with nitric acid to pH 2 and pH 4, respectively.

Figure 2 provides a plot of the 4-hour normalized decontamination factors (DF) for strontium, plutonium and neptunium, respectively, as measured upon contact with 0.4 g/L of the modified MST samples produced in Tests 1 – 9 using Method 1. Normalized DF factors are calculated by dividing the measured DF value of the modified MST sample by that of the baseline MST sample at the same sorbent concentration and sampling time. Attachment 8.1 provides a listing of the 4-hour normalized DF values and the uncertainties. Normalized strontium DF values ranged from a low of 0.85 to a high of 1.85. Normalized plutonium DF values measured over the range 0.60 – 3.05 and those for neptunium from 1.14 to 4.46.

Table 9. Method 1 – Sol-Gel Synthesis Conditions

Test #	Mole Ratio[a]	Acid/Base	Contact Time	pH Adjustment
1	3	none	24 h	no
2	3	none	96 h	no
3	0.3	none	24 h	no
4	1	none	24 h	no
5	6	none	24 h	no
6	3	0.1M HNO_3	24 h	no
7	3	0.1M HNO_3	4 h	no
8	3	none	24 h	yes (pH 2)
9	3	none	24 h	yes (pH 4)

[a] mole ratio of H_2O_2:Ti

The results indicate that this synthesis method produces samples with much improved neptunium and plutonium removal and modest improvement in strontium removal. These results are consistent with findings from Phase I testing. The sample with the best combination of strontium and actinide removal performance was that produced in Test #2, which featured a 3:1 H_2O_2:Ti ratio and contact time of 96 hours. The second best performing sample was that prepared in Test #6, which added the hydrogen peroxide in a strongly acidic nitric acid solution.

The mole ratio of H_2O_2:Ti had no discernible effect on the strontium removal. For plutonium and neptunium we observed a significant increase in removal between 0.3 and 1.0, but no significant change at higher H_2O_2 additions. The pH adjustment of the modified MST (Tests #8 and #9) exhibited slightly improved strontium and neptunium removal performance, but poorer plutonium removal performance.

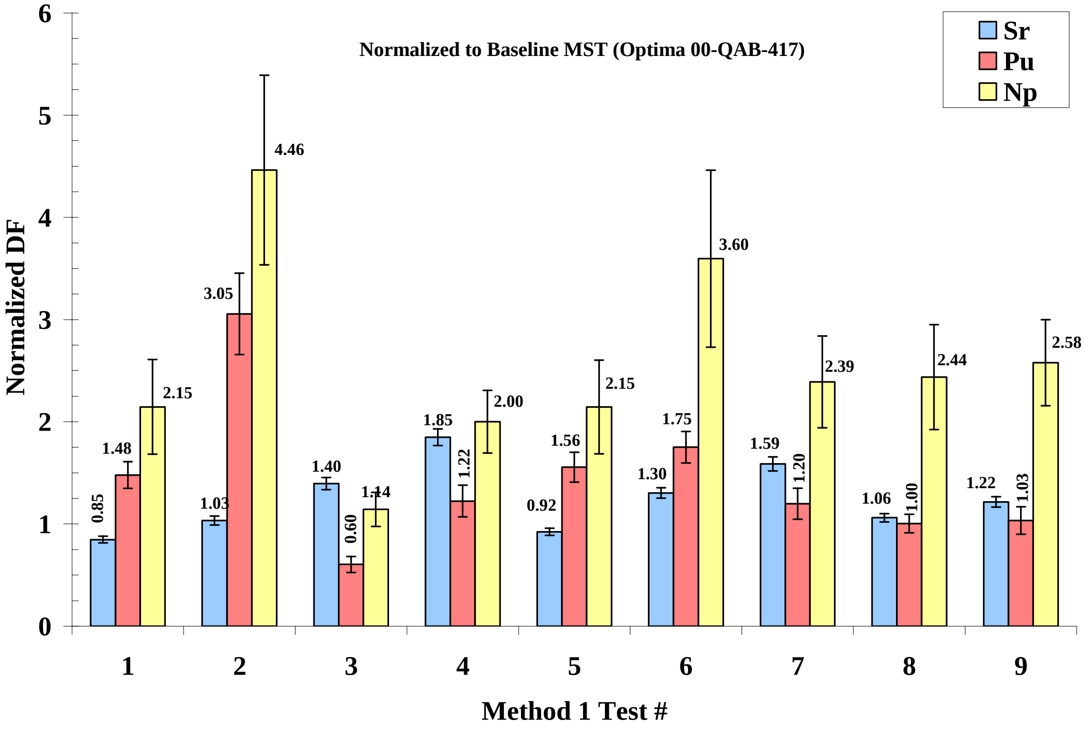

Figure 2. Normalized Decontamination Factors (DF) for Modified MST Sample Produced by Method 1 - Addition of Hydrogen Peroxide in the Sol-Gel Synthesis

4.1.2. Method 2 – Addition of Hydrogen Peroxide to a Strongly Alkaline Solution of Ti (IV)

Table 10 provides a summary of test conditions evaluated using this synthesis route. Three tests explored the influence of base concentration. We also tested the influence of post-synthesis pH adjustment, a reduced concentration of titanium in the base solution, reverse strike in which the titanium/base solution is added to a solution of the hydrogen peroxide, and the use of an inorganic titanium salt ($TiCl_4$) versus an organotitanium reagent, tetraisopropyl titanium(IV) – $Ti(OC_3H_7)_4$.

Figure 3 provides a plot of the 4-hour normalized decontamination factors (DF) for strontium, plutonium and neptunium, respectively, as measured upon contact with 0.4 g L^{-1} of the modified MST samples produced in Tests 1A – 9A using Method 2. Attachment 8.2 provides a listing of the 4-hour normalized DF values and the uncertainties. In general this synthesis route produced samples with improved sorbate removal, particularly for strontium, compared to the baseline MST sample. Compared to the samples prepared by Method 1, these samples featured better strontium removal and, in general, better plutonium, but poorer neptunium removal. Note that the sample prepared in Test 7A exhibited the highest normalized neptunium DF value (>5.19) of all of the samples prepared by Methods 1 and 2.

Table 10. Method 2 - Aqueous Modified MST Synthesis Conditions

Test #	[Base]	pH Adjustment	Other Conditions
1A	3 M NaOH	no	
2A	2 M NaOH	no	
3A	1M NaOH	no	
4A	3M NaOH	yes (pH 2)	
5A	3 M NaOH	yes (pH 4)	
6A	3M NaOH	no	0.5 x [Ti] in base
7A	3M NaOH	no	reverse strike
8A	3M NaOH	no	use $TiCl_4$ in place of $Ti(OC_3H_7)_4$
9A	3M NaOH	no	0.1 x [Ti] in base

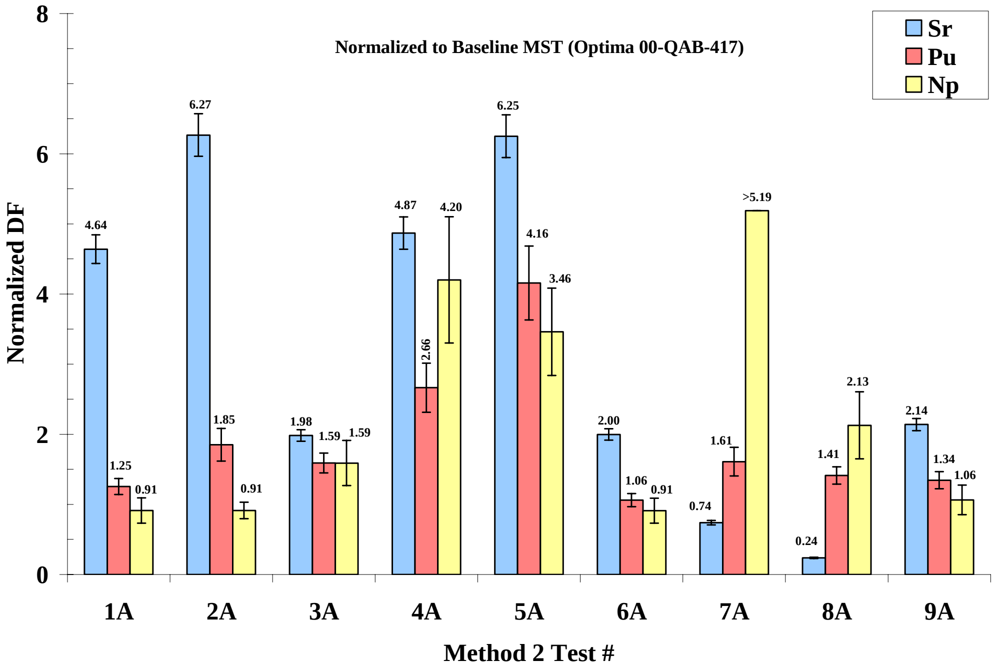

Figure 3. Normalized Decontamination Factors (DF) for Modified MST Sample Produced by Method 2 - Addition of Hydrogen Peroxide to Alkaline Solution of Titanium (IV)

Based on the normalized DF values for samples prepared in Tests 1A, 2A and 3A, a base concentration of 2 M proved best for improved strontium and plutonium removal performance and 1 M for neptunium removal. Samples in which we adjusted the pH

(Tests 4A and 5A) exhibited improved strontium, plutonium and neptunium removal performance compared to the baseline MST sample and the unadjusted modified MST sample (Test 1A). The sample prepared in Test 5A (pH 4) exhibited the best overall performance of any of the samples.

Reducing the titanium concentration (Tests 1A, 6A and 9A) resulted in decreased strontium removal, but no effect on plutonium and neptunium removal performance. The use of titanium(IV) chloride, $TiCl_4$, in place of titanium(IV) isopropoxide, $Ti(OC_3H_7)_4$, produced a material (Test 8A) that exhibited much lower strontium removal, but greater plutonium and neptunium removal than samples prepared by Method 2 with the organotitanium reagent (Test 1A) and the baseline MST sample.

4.1.3. Method 3 - Post Synthesis Addition of Hydrogen Peroxide

Table 11 provides a summary of the conditions that we tested for this synthesis method. The first seven tests explored the influence of pH during the contact of the MST with the hydrogen peroxide. The remaining tests explored the influence of the quantity of hydrogen peroxide contacted with the MST, the influence of contact time and the influence of post-treatment pH adjustment.

Table 11. Method 3 - Post Synthesis Treatment Conditions

Test #	Mole Ratio[a]	pH	Contact Time	pH Adjustment
1P	3	2	24 h	no
2P	3	3	24 h	no
3P	3	4	24 h	no
4P	3	5	24 h	no
5P	3	6	24 h	no
6P	3	7	24 h	no
7P	3	8	24 h	no
8P	0.3	4	24 h	no
9P	1	4	24 h	no
10P	6	4	24 h	no
11P	3	4	4 h	no
12P	3	4	96 h	no
13P	3	7	24 h	yes (pH 2)
14P	3	7	24 h	yes (pH 4)
15P	3.0[b]	4	24 h	no

[a] mole ratio of H_2O_2:Ti

[b] This preparation employed separate 24-h contacts of MST with the hydrogen peroxide and each contact at a mole ratio of 3:1.

Figures 4 –6 provide plots of the measured DF values for strontium, plutonium and neptunium, respectively. Attachment 8.3 provides a listing of the DF values and the uncertainties for each of the samples prepared by Method 3.

Samples prepared by this method exhibited an increase in the DF for strontium of about 2 – 5 times (see Figure 4), for plutonium of about 6 – 31 times (see Figure 5) and for neptunium of about 1.2 – 5 times (see Figure 6) compared to the baseline MST sample. These increases in strontium and actinide removal are consistent with those measured for samples prepared by this method during Phase I testing.

An increase in the initial MST slurry pH (2.0 – 8.0) appeared to produce a small decrease in the DF for strontium, but no discernible effect on the DF for plutonium and neptunium. In general, higher losses in the mass of MST occurred as the pH decreased (i.e., more acidic) as evidenced by a more intensely yellow-colored reaction solution. Thus, to minimize product losses, the pH of the MST slurry should be kept near a neutral pH condition. Within the measurement uncertainties for Tests 3P, 11P and 12P, we observed no significant differences in performance in strontium and actinide removal performance of samples prepared with reaction times of between 4 and 96 hours.

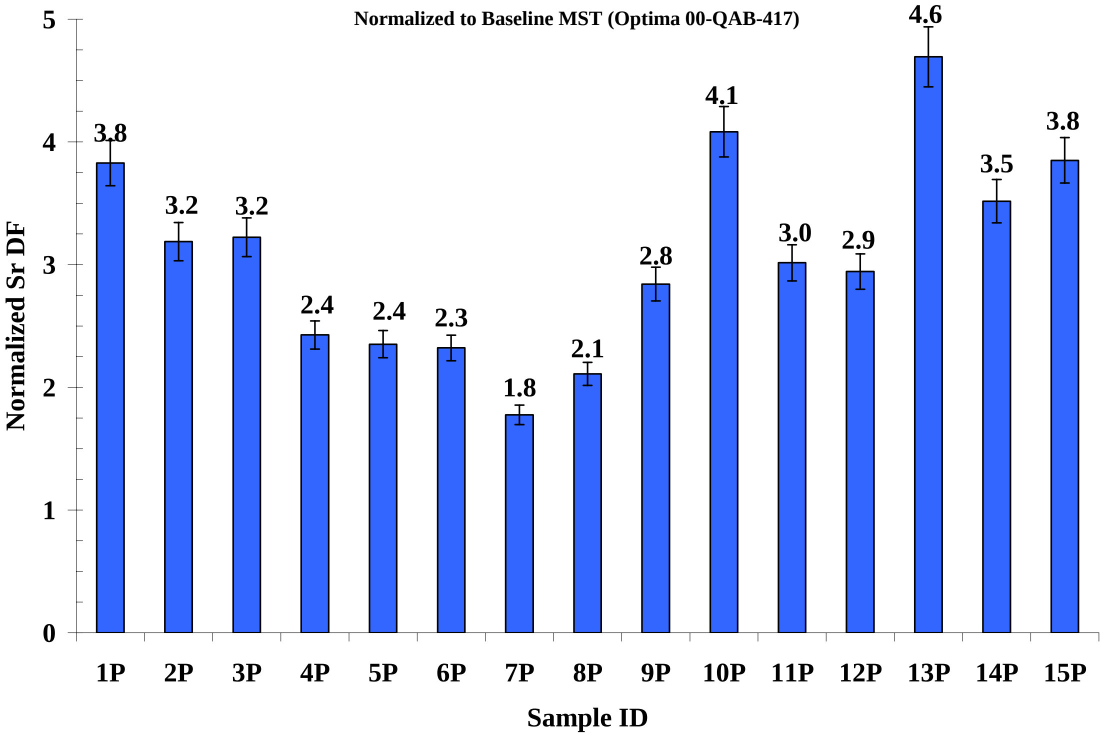

Figure 4. **Normalized Strontium Decontamination Factors (DF) for Modified MST Samples Produced by Method 3 – Post Synthesis Addition of Hydrogen Peroxide**

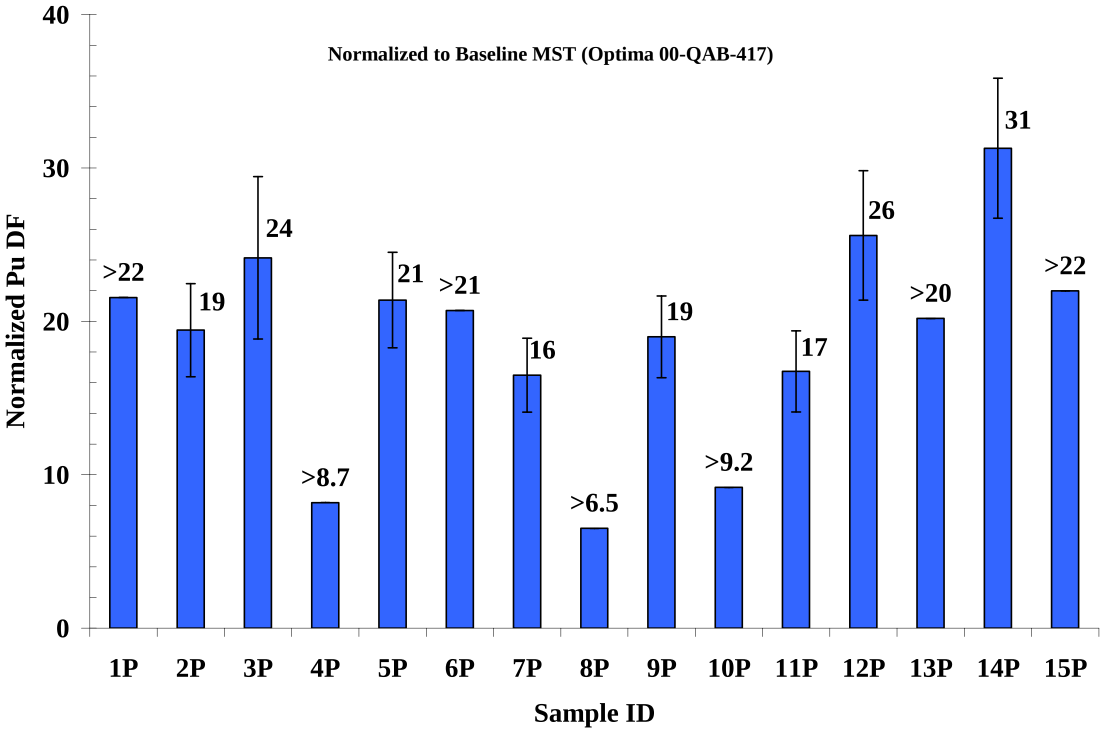

Figure 5. Normalized Plutonium Decontamination Factors (DF) for Modified MST Samples Produced by Method 3 – Post Synthesis Addition of Hydrogen Peroxide

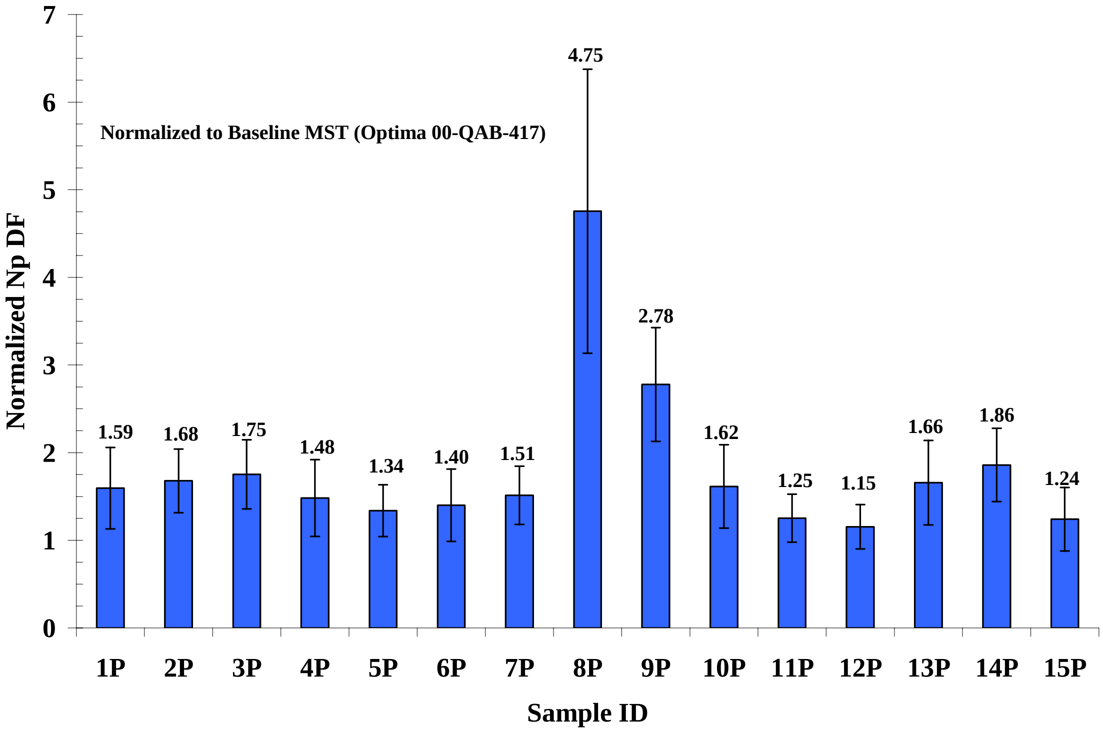

Figure 6. Normalized Neptunium Decontamination Factors (DF) for Modified MST Samples Produced by Method 3 – Post Synthesis Addition of Hydrogen Peroxide

We observed an increase in the strontium removal performance upon an increase in the amount of hydrogen peroxide used in the synthesis. Neptunium removal decreased as the amount of hydrogen peroxide increased. The influence on plutonium removal could not be quantified as the plutonium DF values for two of the five samples featured fairly high detection limits. Given the tradeoff in strontium and neptunium removal performance, we concluded that the mole ratio of H_2O_2:Ti should not exceed 3:1.

Adjustment of the pH to a lower value (pH 2 or 4) after the hydrogen peroxide addition did not affect neptunium removal, but did increase the strontium removal (Tests 6P, 13P and 14P). The effect on plutonium removal could not be quantified as two of the three plutonium measurements fell below the quantification level. However, the DF for the sample adjusted to a pH of 4 measured 31.3 ± 4.57, which is the highest value of any of the samples prepared by this method.

4.1.4. Preparation of Additional Samples using Method 2

After further review of the results from Task 1 including the findings from samples prepared by Method 3, we conducted additional preparations of modified MST samples using Method 2, but with a change in the isolation method of the precipitated solids. Previously, we isolated the precipitated solids by filtration and washed with deionized, distilled water and air dried at room temperature. Thermogravimetric analysis of the dried solids revealed that the solids contained 15 – 30 wt % water.

For the new preparations we prepared the solids in the same manner as in Test 1A (see Table 10), but did not dry the solids (Test 10A). In addition, we also performed a second strike of hydrogen peroxide after filtering and washing the initially precipitated solids (Test 12A). Finally we also prepared pH adjusted samples from these preparations (Tests 11A and 13A). Table 12 provides a summary of the preparation conditions used for the additional samples.

Table 12. Synthesis Conditions for Additional Method 2 Preparations

Test #	[Base]	pH Adjustment	Other Conditions
1A	3 M NaOH	no	
10A	3 M NaOH	no	no solids drying
11A	3 M NaOH	yes (pH = 4)	no solids drying
12A	3 M NaOH	no	2nd H_2O_2 strike, no solids drying
13A	3 M NaOH	yes (pH = 4)	2nd H_2O_2 strike, no solids drying

We tested the performance of these new samples in the same manner as before. Figure 7 provides a plot of the normalized DF for each of the samples along with that measured for the dried sample prepared in Test 1A. These slurry samples exhibited improved removal performance for three sorbates compared to both the baseline MST sample and the modified MST sample prepared earlier in Test 1A. Thus, we conclude that drying the modified MST reduces the performance of the MST as measured by the DF after 4-hours of contact. This result is consistent with previous findings with non-peroxide treated MST samples, which showed reduced sorption kinetics upon drying MST at elevated temperatures.[13]

The sample prepared in Test 13A proved to have the best combined performance for strontium, plutonium and neptunium. Plutonium removal matched that of the best performers prepared by Method 3. Strontium and neptunium removal performance of this sample exceeded that of any prepared by Method 3. Thus, this preparative route should be considered as a method for preparing modified MST materials.

The particle morphology of modified MST samples prepared by Method 2 is considerably different that that by Method 3 (post synthesis). At this time we have not determined the particle size distribution or the filtration characteristics of materials prepared by Method 2. Scanning electron micrographs (SEM) suggest that the materials prepared by Method 2 may exhibit a higher fraction of particles having small particle sizes than materials prepared by Method 3. A higher fraction of small particles may adversely impact filtration characteristics.

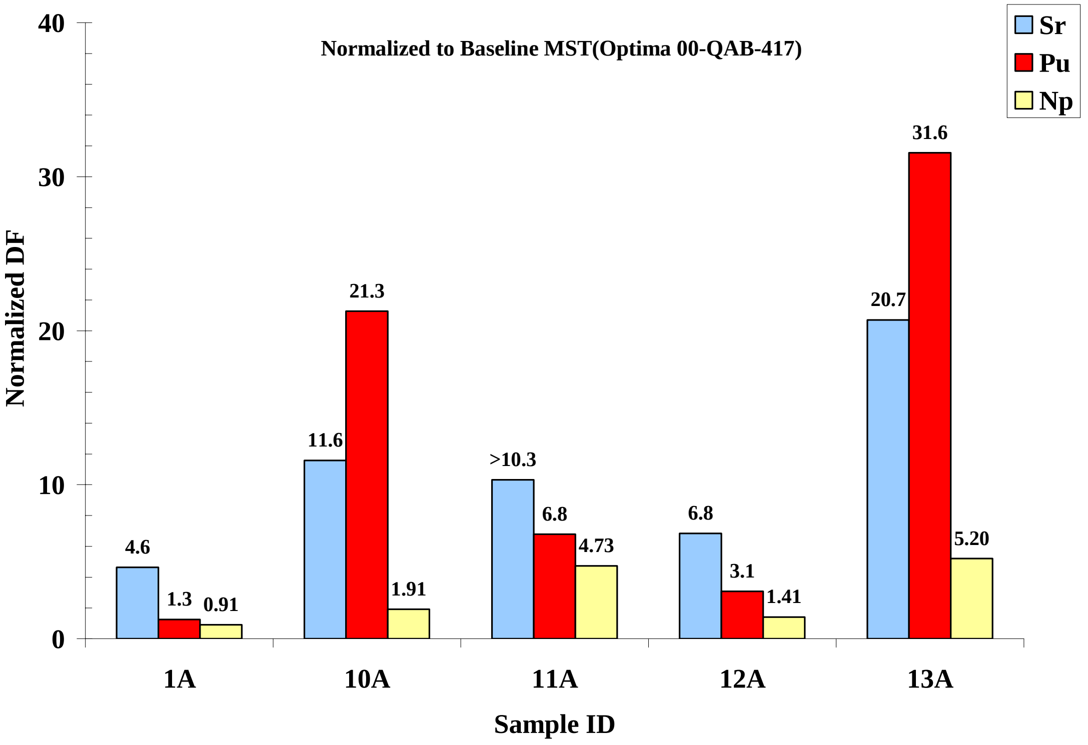

Figure 7. Normalized Decontamination Factors (DF) for Additional Modified MST Samples Prepared by Method 2 – Addition of Hydrogen Peroxide to Alkaline Solution of Titanium (IV)

4.2 Task 2 – Reproduce Performance at Larger Laboratory Scale

Based on the results from Task 1, we selected Method 3 (Post Synthesis Addition of Hydrogen Peroxide) to produce samples at a larger laboratory scale. For this task we increased the previous laboratory procedure to prepare 25 grams of modified MST per batch. This represented a 25 – 100 fold increase in batch size from previous tests.

We prepared three separate batches of the modified MST material, designated as LS-1, LS-2 and LS-3 using conditions identical to Test 14P in Task 2. Performance tests used the same simulant used in evaluating samples prepared under Task 1. The performance tests added the MST samples at two different sorbent concentrations, 0.1 and 0.2 g L^{-1}. Each performance test with the modified MST samples was performed in duplicate. A single test evaluated the performance of the baseline MST sample at each sorbent concentration. We also analyzed these materials for a variety of chemical and physical properties and filtration characteristics. Results of these analyses are presented in Section 4.4 (Task 4).

Figures 8 and 9 provide plots of the normalized 4-hour DF values for strontium and plutonium, respectively, with the three modified MST samples. The normalized DF is calculated by dividing the DF of the modified MST sample by the DF of the baseline MST sample. For strontium and plutonium, the results indicate that the modified MST samples show significantly improved performance compared to the baseline MST sample. These results are consistent with those determined with modified MST samples prepared at the smaller laboratory scale. There was very good agreement among the three different batches of modified MST indicating that the synthesis is reproducible at this scale.

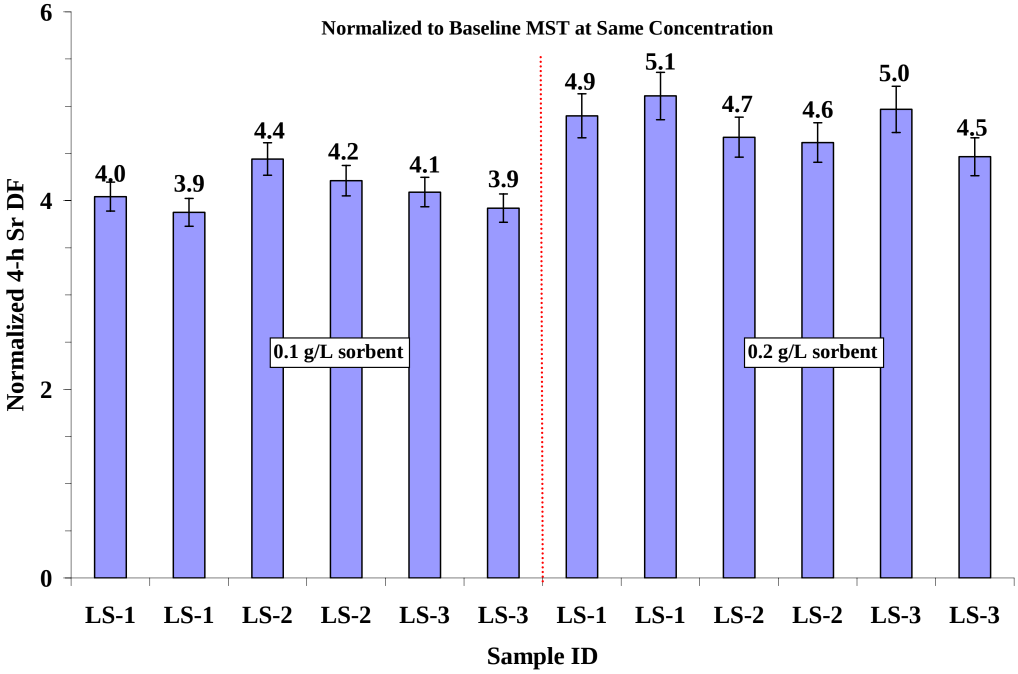

Figure 8. **Normalized 4-Hour Strontium Decontamination Factors (DF) for Modified MST Samples Produced by Method 3 at the 25-gram Scale**

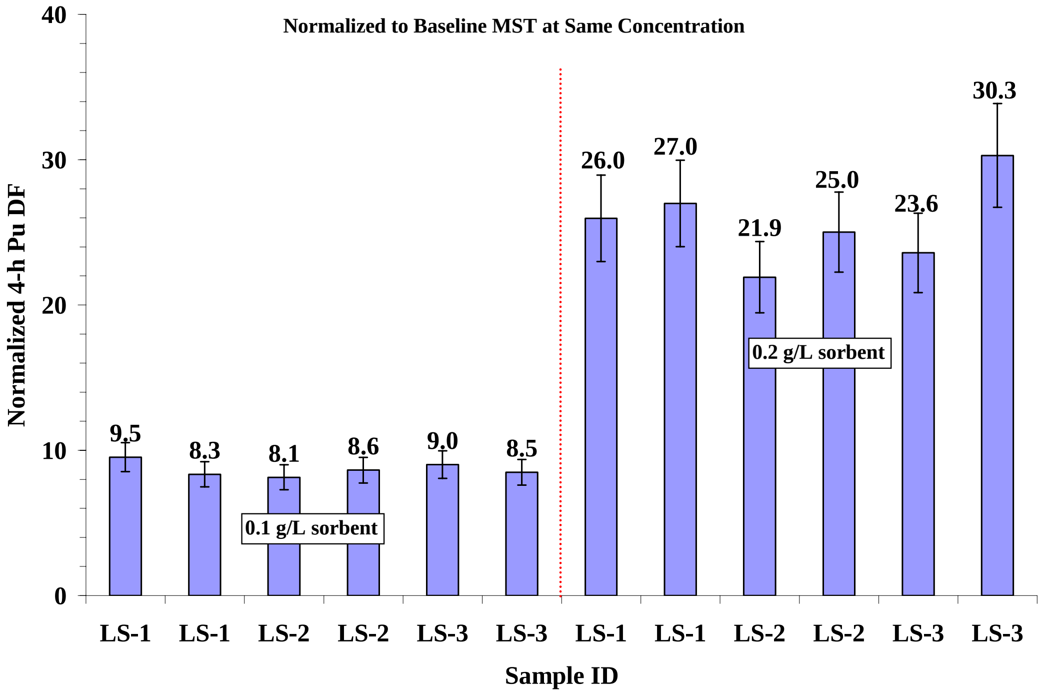

Figure 9. **Normalized 4-Hour Plutonium Decontamination Factors (DF) for Modified MST Samples Produced by Method 3 at the 25-gram Scale**

For neptunium, the normalized 4-hour DFs for the modified MST samples measured around 1.3 indicating better removal than the baseline material. However, considering the uncertainty in the normalized DF values (see Table 14), we cannot conclude that the modified MST samples exhibited improved neptunium removal after a contact time of 4 hours at the 95% confidence limit.

The uranium removal characteristics for the modified MST samples proved indeterminate in this test set. Given the analytical uncertainty in the uranium measurement by ICP-MS and the variance among duplicate tests, we observed no statistical difference among the uranium concentrations measured in samples from tests with and without MST. Note that we did not analyze for uranium in the samples from tests with 0.2 g/L MST at contact times other than 4 hours. At longer contact times (e.g., 168-hours), there may have been sufficient uranium sorption by the MST samples to provide a measurable difference in the uranium concentrations remaining in solution.

In addition to the 4-hour sample, we also pulled and analyzed samples after 2, 6, 12, 24 and 168 hours of contact with the MST samples to evaluate removal kinetics. Table 13 provides a summary of the average strontium, plutonium and neptunium DF values for the modified and baseline MST samples at each sampling time and each sorbent concentration. Table 14 provides the average normalized DF value for the modified MST at each sampling time and sorbent concentration.

Comparison of the baseline MST and modified MST samples at each time and concentration revealed that the modified MST consistently exhibited very high DF values for strontium and plutonium. For strontium, the DF value for the modified MST consistently measured between factors of 4 to 5 higher than that of the baseline MST (see Table 12). The modified MST exhibited exceptionally good plutonium removal with DF values of 24.0 and 49.3 upon contact with 0.1 g L^{-1} of at 6 and 12-hours, respectively, at a sorbent concentration of 0.1 g L^{-1} and values of 95.7 and 172, respectively, at a sorbent concentration of 0.2 g L^{-1} (see Table 11). Thus, the modified MST samples exhibited plutonium DF values between 10 and 50 times higher than those of the baseline MST sample (see Table 12).

The average neptunium DF values for the modified MST samples measured higher than the baseline MST sample at both sorbent concentrations at each sampling time. In some cases, however, the difference between the modified and baseline DF values was not statistically significant. Thus, the modified MST samples exhibited a small increase of no more that about a factor of 2 in neptunium removal compared to that of the baseline MST sample. This trend is consistent with that previously measured for samples prepared by Method 3.[13]

Table 13. Average Strontium and Plutonium Decontamination Factors for Modified MST Samples Produced by Method 3 at the 25-gram Scale

Strontium

	Baseline MST @ 0.1 g/L		Modified MST @ 0.1 g/L		Baseline MST @ 0.2 g/L		Modified MST @ 0.2 g/L	
Time (h)	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**
2	5.42	0.13	20.6	1.18	17.8	0.45	84.6	2.57
4	6.19	0.16	25.4	1.28	21.7	0.60	104	5.26
6	8.50	0.21	27.4	1.57	21.4	0.56	113	14.0
12	6.88	0.18	30.6	1.36	24.8	0.71	128	5.80
24	8.45	0.22	37.4	1.88	29.9	0.87	147	12.0
168	11.1	0.30	47.6	2.09	37.7	1.2	200	14.8

Plutonium

	Baseline MST @ 0.1 g/L		Modified MST @ 0.1 g/L		Baseline MST @ 0.2 g/L		Modified MST @ 0.2 g/L	
Time (h)	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**
2	1.52	0.13	5.44	0.38	2.29	0.16	26.9	2.86
4	1.73	0.13	15.1	0.87	2.83	0.20	72.6	8.22
6	1.85	0.13	24.0	2.60	2.85	0.20	95.7	17.6
12	2.11	0.16	49.3	2.69	3.21	0.24	172	6.16
24	2.54	0.20	89.6	7.32	4.23	0.35	276	20.8
168	7.15	0.49	119	11.3	7.49	0.49	528	39.0

Neptunium

	Baseline MST @ 0.1 g/L		Modified MST @ 0.1 g/L		Baseline MST @ 0.2 g/L		Modified MST @ 0.2 g/L	
Time (h)	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**	**Average**	**Std Dev**
2	1.13	0.067	1.43	0.056	1.22	0.070	1.60	0.114
4	1.19	0.096	1.55	0.146	1.29	0.098	1.65	0.271
6	1.30	0.270	1.64	0.170	1.05	0.063	1.77	0.252
12	0.89	0.143	1.62	0.234	1.25	0.100	1.83	0.155
24	1.30	0.265	2.06	0.102	1.47	0.118	2.46	0.338
168	1.72	0.419	3.00	0.319	2.07	0.229	5.34	1.27

Modified MST results are average and standard deviation of six trials
Baseline MST results are single determinations with reported analytical uncertainty

Table 14. Average Normalized DF Values for Modified MST Samples

	Normalized DF - Strontium			
	[MST] = 0.1 g/L		[MST] = 0.2 g/L	
Time (h)	**Average**	**Std Dev**	**Average**	**Std Dev**
2	3.80	0.22	4.75	0.14
4	4.10	0.21	4.79	0.24
6	3.23	0.18	5.31	0.66
12	4.45	0.20	5.16	0.23
24	4.43	0.22	4.93	0.40
168	4.30	0.19	5.30	0.39

	Normalized DF - Plutonium			
Time (h)	**[MST] = 0.1 g/L**		**[MST] = 0.2 g/L**	
2	3.59	0.25	11.8	1.25
4	8.69	0.50	25.6	2.90
6	13.0	1.41	33.6	6.18
12	23.3	1.28	53.5	1.92
24	35.3	2.88	65.3	4.92
168	16.7	3.16	70.5	5.20

	Normalized DF - Neptunium			
Time (h)	**[MST] = 0.1 g/L**		**[MST] = 0.2 g/L**	
2	1.26	0.049	1.31	0.094
4	1.30	0.123	1.28	0.211
6	1.26	0.131	1.70	0.241
12	1.81	0.262	1.46	0.124
24	1.58	0.079	1.67	0.230
168	1.75	0.186	2.58	0.611

Normalized DF values calculated by dividing the measured DF value for the modified MST to that measured for the baseline MST sample (Optima 00-QAB-417) at the same test condition.

Figures 10 – 12 provide plots of solution concentrations of strontium, plutonium and neptunium, respectively, versus time upon contact of the simulated waste solution with 0.1 and 0.2 g L^{-1} of MST sorbent. For the modified MST samples, we observed excellent agreement among the duplicate for the different preparation batches at each sample time. The concentrations plotted in Figures 10 – 12 are average concentrations of the six tests at each sorbent concentration. Error bars in these figures –shown, but not easily discernible - are the single standard deviation of the six values for the modified MST samples, the pooled single standard deviation of the six control samples taken over the entire test and the analytical uncertainty reported for each sample measurement in the baseline MST test.

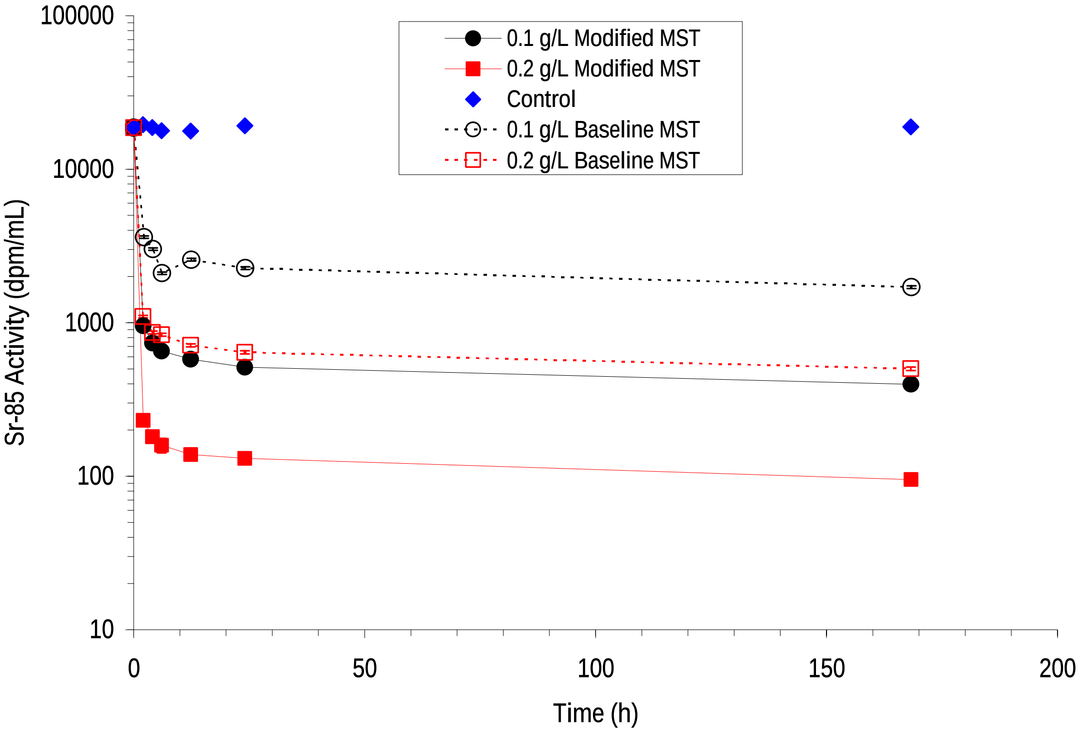

Figure 10. Strontium Removal Kinetics for Modified and Baseline MST Samples

The modified MST samples exhibited faster strontium removal kinetics than the baseline MST sample. For example, after two hours of contact the modified MST samples had removed more than 95% and 99% of the strontium at concentrations of 0.1 and 0.2 g L^{-1}, respectively, compared to 82% and 94% for the baseline MST sample. After two hours both the modified and baseline MST samples show a decrease in the rate of removal, which is typical behavior for adsorption of solution species onto solids.

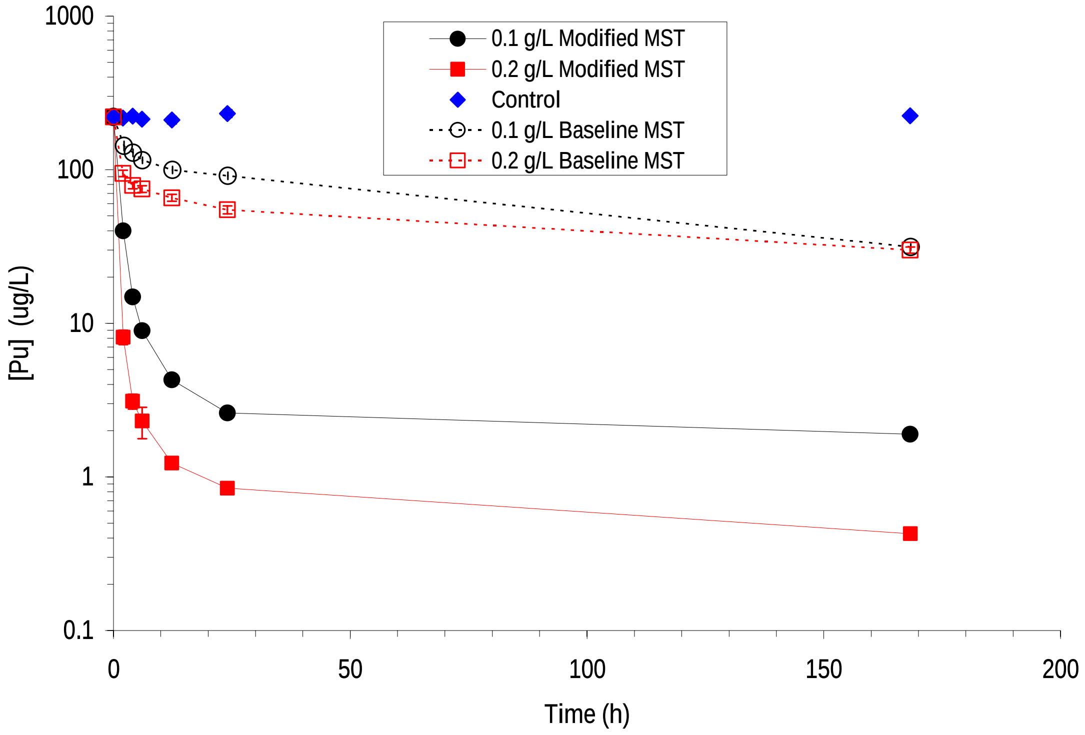

Figure 11. Plutonium Removal Kinetics for Modified and Baseline MST Samples

As with strontium, the modified MST samples exhibited much faster plutonium removal compared to the baseline MST. For example, at a MST concentration of 0.1 g L^{-1}, we observed that the modified MST samples removed on average 56% of the plutonium after 2 hours compared to 34% for the baseline MST. At a MST concentration of 0.2 g L^{-1}, the removal of plutonium increased to 96% for the modified MST samples compared to 82% for the baseline MST sample after 2 hours of contact. Note that after 12 hours of contact, the modified MST samples removed on average 98% and 99% of the plutonium, respectively, compared to 53% and 69%, respectively, at MST concentrations of 0.1 g L^{-1} and 0.2 g L^{-1}.

Figure 12 provides a plot of the neptunium concentration versus time for the tests conducted at a sorbent concentration of 0.1 g L^{-1}. The modified MST samples consistently removed neptunium faster than the baseline MST sample. Furthermore, the neptunium concentrations measured for the tests with the modified MST samples measured consistently below those of the baseline MST sample. Two of the data points for the baseline MST tests (6-h at 0.2 g L^{-1} and 12-h at 0.1 g L^{-1}) measured higher than expected based on the other time samples. The corresponding data for ^{85}Sr and plutonium data at these times did not exhibit a similar increase. Thus, we have no basis for excluding these results.

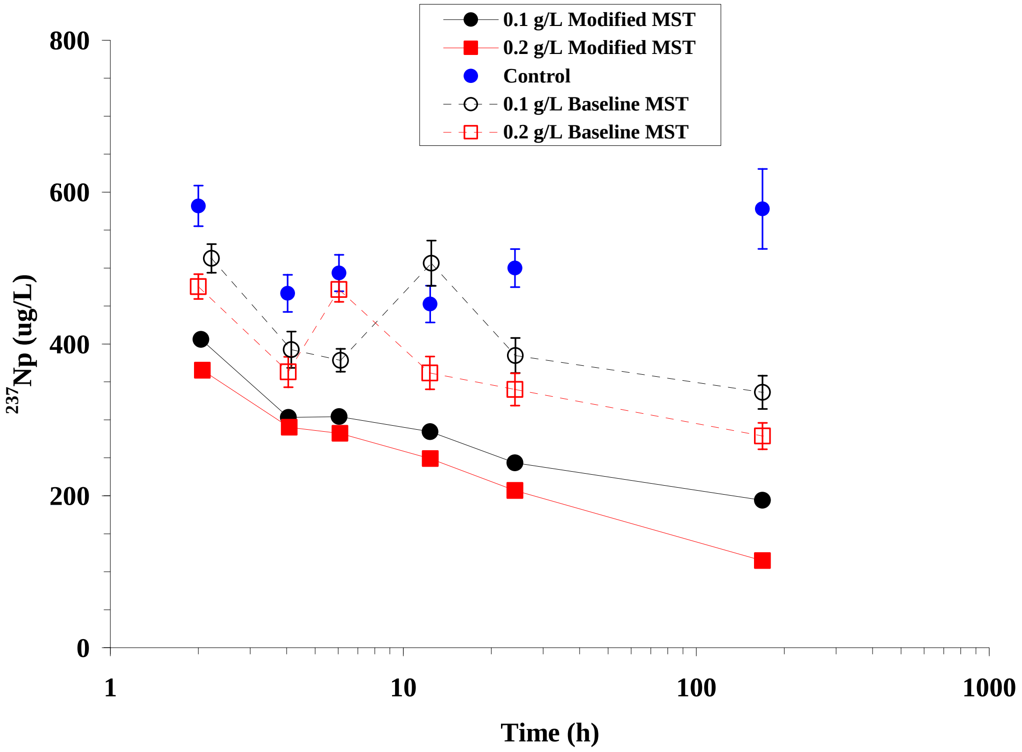

Figure 12. Neptunium Removal Kinetics for Modified and Baseline MST Samples

4.3 Task 3 – Verify Performance of Modified MST with Actual Waste

We carried out two sets of tests with actual waste to evaluate the performance of the laboratory prepared modified MST material. Test Set #1 evaluated the performance at MST loadings of 0.1 and 0.2 g L^{-1} and in the presence of the CSSX solvent. Test Set #2 (Supplemental Tests) evaluated the performance of the modified MST in multiple strike and reuse configurations. These tests used a 3-L sample of supernate taken from Tank 39H (HTF-049) in May 2005.

We selected this tank waste for testing since previous samples from this tank proved high in ^{90}Sr and plutonium.[14] Analysis of the supernate sample revealed that the supernate was much more dilute in salt content, ^{90}Sr and plutonium than the supernate sample analyzed in 2003. A review of tank transfer records revealed that most of the supernate present in Tank 39H when sampled in 2003 had been transferred to either Tank 26F or Tank 27F. Over the time period of 2003 – 2005 Tank 39H received fresh canyon waste, which was much more dilute in salt content and contained much less ^{90}Sr and plutonium.

The sodium concentration of the Tank 39H supernate measured 5.48 $\pm$ 0.37 M, which is the desired concentration for testing. Therefore, the waste did not require any dilution. To increase strontium and plutonium content we added a solution of strontium nitrate and two separate solutions of plutonium(IV) nitrate to the waste sample with stirring and allowed the material to equilibrate (see Section 3.3 for details).

4.3.1 Actual Waste Test Set #1

In this set of tests we contacted the actual waste supernate with the LS-1 modified MST sample and the Optima #00-QAB-417 baseline MST sample at the conditions detailed in Table 5. The modified MST tests were conducted in duplicate at 0.1 and 0.2 g L^{-1}. The baseline MST test featured a sorbent concentration of 0.2 g L^{-1}. We also included a test in which a small amount of the solvent planned for use in Caustic Side Solvent Extraction process was added in addition to the modified MST.

Table 15 provides a summary of the measured DF values for strontium, plutonium and neptunium in the actual waste tests. Table 16 provides the normalized DF values at each sampling time. Greater than values are reported when the measured concentrations for a sorbate fell below the analytical method detection value. The values for the tests with the modified MST samples at the 0.1 and 0.2 g L^{-1} concentrations are the average of duplicate tests. The uncertainties for tests with a single replicate are the reported analytical uncertainties.

Figure 13 provides a plot of the total strontium concentration (μg L^{-1}) versus time for the actual waste tests. For the tests with the modified MST sample, we plot the average of the duplicate trials. For these plots, the total strontium concentration derives from the ICP-MS analytical results. We also analyzed the filtrate samples for ^{90}Sr. However, the ^{90}Sr data proved very scattered as the values were very close to the analytical method detection limit. Consequently the ^{90}Sr data provides no insight into the performance of the MST samples for strontium removal.

The graph indicates that similar strontium removal occurred when the waste was contacted with 0.1 g L^{-1} of the modified MST or 0.2 g L^{-1} of the baseline MST. At a modified MST concentration of 0.2 g L^{-1}, the test results indicated strontium concentrations about 2 – 3 times lower than those of the baseline MST at 0.2 g L^{-1} or modified MST at 0.1 g L^{-1}. Unfortunately, the strontium concentration fell below the analytical method detection limit at sampling times after 4 hours. Thus, we cannot provide a quantitative value as to the performance of the modified MST at 0.2 g L^{-1} for these times.

At the sorbent concentration of 0.2 g L^{-1}, the strontium DF values for the modified MST sample measured about 2.7 times higher than those of the baseline MST sample. Tests with the modified MST at a sorbent concentration of 0.1 g L^{-1} resulted in strontium DF values comparable to those of the baseline MST sample. We also observed that the strontium DF values in the test with the modified MST and CSSX solvent proved very similar to those without the CSSX solvent. Thus, we conclude that the presence of the CSSX solvent did not adversely influence strontium removal by the modified MST sample.

In earlier tests with simulated waste solution, the modified MST exhibited a factor of about 5 higher strontium removal than the baseline MST sample (see Table 12). We attribute the lower increase in strontium removal performance in the actual waste tests to the higher initial total sorbate concentration, which results in greater overall loading of the sorbent. The actual waste solution contained a total cation equivalent concentration for the four sorbates of 128 ± 21 μM, which is 32% higher than that of 97 ± 15 μM for the simulated waste solution.

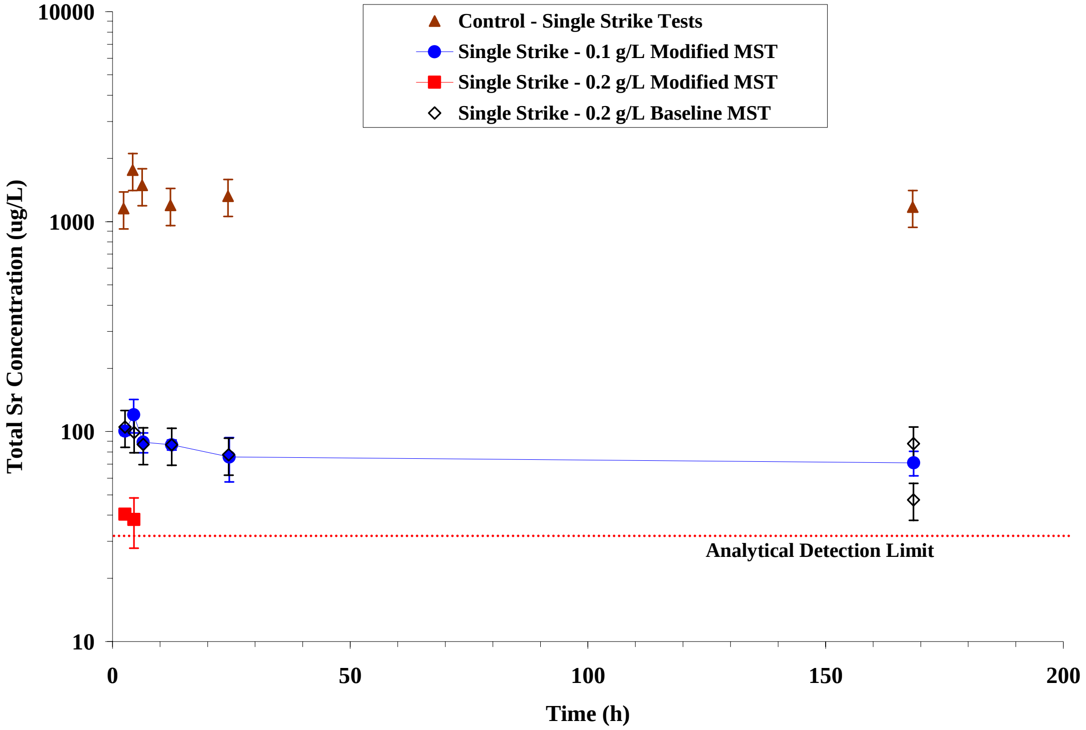

Figure 13. Total Strontium Concentration versus Time in Actual Waste Test Set #1

Figure 14 provides a plot of the total plutonium activity (pCi mL^{-1}) versus time for the actual waste tests. For the tests with the modified MST samples, the plot provides the average of the duplicate trials. As with strontium, the modified MST sample exhibited increased plutonium removal compared to the baseline MST. Within 12-hours, the plutonium activity decreased to below the current Waste Acceptance Criteria (WAC) limit of 22,500 pCi mL^{-1} when the waste solution was contacted with 0.2 g L^{-1}. At this time the plutonium activity in the test with the baseline MST sample remained more than an order of magnitude higher than the WAC limit. Contact of this actual waste with 0.1 g L^{-1} MST produced plutonium concentrations above the WAC limit at all contact times, but still about a factor of 2 – 3 lower at the 6 and 12-hour sampling times than that of the baseline MST sample, which was added at 0.2 g L^{-1}.

The 168-hour result for the baseline MST tests showed a significant decrease in plutonium activity compared to the earlier sampling times. Additional analyses confirmed the low plutonium result. We have not observed this type of behavior with the baseline MST in other tests with simulants or tank wastes. Thus, we believe this result is in error.

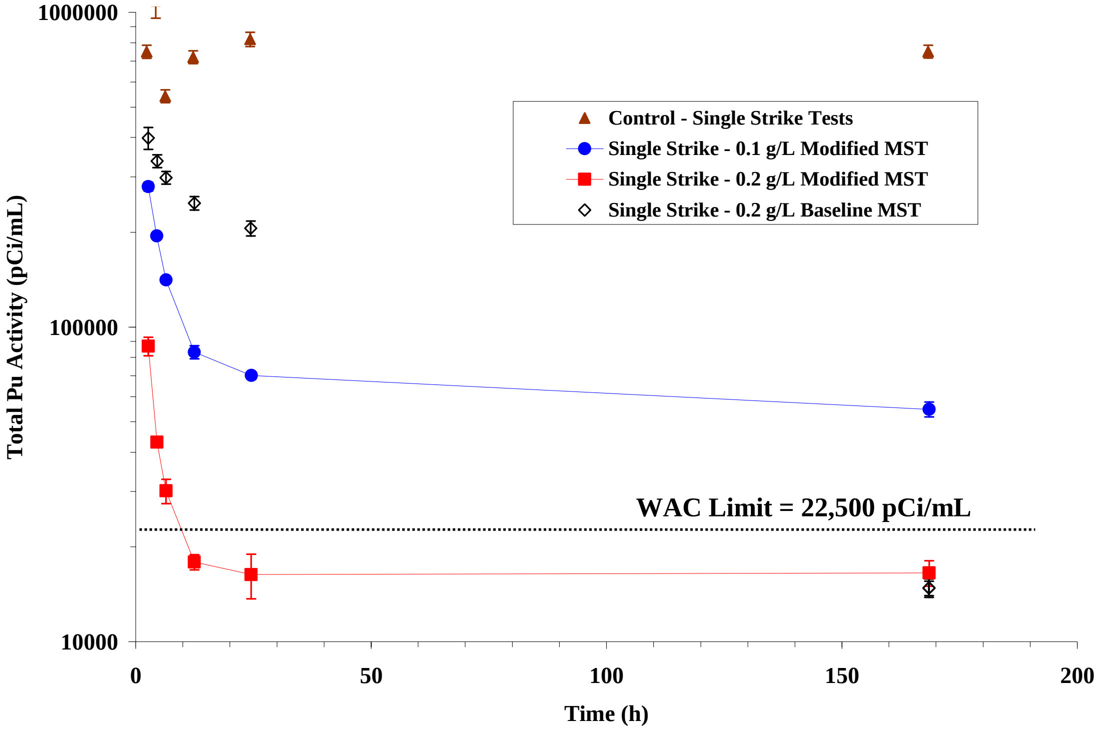

Figure 14. Total Plutonium Activity versus Time in Actual Waste Test Set #1

At a sorbent concentration of 0.2 g L^{-1} the plutonium DF values for the modified MST sample measured between 5 and 11 times higher than those of the baseline MST sample (see Tables 15 and 16). Tests with the modified MST at a sorbent concentration of 0.1 g L^{-1} resulted in plutonium DF values between 1.5 and 3.5 times higher than those of the baseline MST sample at 0.2 g L^{-1}. Given these results, we conclude that the modified MST sample clearly demonstrated improved plutonium removal performance compared to the baseline MST sample.

We also observed that the plutonium DF values in the test with the modified MST and CSSX solvent proved very similar to those without the CSSX solvent. Thus, we conclude that the presence of the CSSX solvent did not adversely influence plutonium removal by the modified MST sample.

In earlier tests with simulated waste solution, the modified MST exhibited a factor of 11 to 70 times higher in the plutonium DF value than the baseline MST sample (see Table 14). For the actual waste tests the modified MST sample exhibited increases in the DF values of between 5 and 11 times that of the baseline MST sample. As with strontium, we attribute the lower increase in plutonium removal performance in the actual waste tests to the higher initial total sorbate concentration in the actual waste. As noted earlier, the plutonium DF values for the modified MST sample at 0.1 g L^{-1} measured 1.5 – 3.5 times that of the baseline MST at the higher sorbent concentration of 0.2 g L^{-1}. In the case of strontium, the DF values were very similar for the two MST samples at the respective concentrations. The actual waste solution measured about 25% higher in plutonium concentration than that in the simulant (275 ± 56 versus 218 ± 13 µg L^{-1}). These findings confirm that the modified MST sample clearly exhibits increased capacity for plutonium compared to the baseline MST sample.

We observed similar neptunium DF values for the modified MST sample in each of the tests. The baseline MST sample exhibited higher DF values for neptunium than the modified MST at each of the sampling times (see Table 15). In previous simulant tests we observed that the modified MST sample exhibited higher DF values than the baseline MST sample (see Table 13). The initial neptunium concentration in the actual waste solution measured more than one-third lower than that in the simulant tests (131 ± 19 versus 461 ± 90 µg L^{-1}). Given the lower neptunium concentration and the previous findings with the simulated waste solution, the results with the modified MST sample are surprising. Perhaps the higher loading of strontium and plutonium reduced the sorption of neptunium onto the modified MST.

We observed no measurable removal of uranium in any of the tests. Previous testing with simulated waste solutions at low sorbent concentrations also showed no measurable uranium removal. Given the similar initial uranium concentrations in both the actual waste (9,550 ± 333 µg L^{-1}) and simulated waste (10,200 ± 2,040 µg L^{-1}) solutions, the lack of measurable uranium removal is not unexpected. Higher sorbent concentrations are needed to determine uranium removal performance of the modified MST sample with actual waste solutions.

Table 15. Strontium, Plutonium and Neptunium Decontamination Factors in Actual Waste Tests Set #1

Strontium Decontamination Factors

	Baseline MST @ 0.2 g/L		Modified MST @ 0.2 g/L		Modified MST @ 0.2 g/L with CSSX Solvent		Modified MST @ 0.1 g/L	
Time (h)	Value	Uncertainty	Average	Std Dev	Value	Uncertainty	Average	Std Dev
2.6	1.10E+01	3.10E+00	2.86E+01	1.60E+00	2.68E+01	7.57E+00	1.15E+01	5.57E-01
4.5	1.78E+01	5.03E+00	4.80E+01	1.29E+01	3.94E+01	1.11E+01	1.49E+01	2.70E+00
6.4	1.71E+01	4.85E+00	>4.54E+01		>4.52E+01		1.69E+01	1.84E+00
12.4	1.39E+01	3.92E+00	>2.30E+01		>2.33E+01		1.39E+01	7.70E-01
24.5	1.71E+01	4.83E+00	>4.02E+01		>4.07E+01		1.80E+01	4.29E+00
168.5	2.48E+01	7.02E+00	>3.56E+01		>3.57E+01		1.67E+01	2.22E+00

Plutonium Decontamination Factors

	Baseline MST @ 0.2 g/L		Modified MST @ 0.2 g/L		Modified MST @ 0.2 g/L with CSSX Solvent		Modified MST @ 0.1 g/L	
Time (h)	Value	Uncertainty	Average	Std Dev	Value	Uncertainty	Average	Std Dev
2.6	1.84E+00	2.05E-01	9.58E+00	5.78E-01	8.69E+00	1.48E+00	2.82E+00	1.45E-01
4.5	2.99E+00	2.12E-01	1.66E+01	1.19E+00	1.47E+01	1.43E+00	4.96E+00	3.69E-02
6.4	1.86E+00	1.36E-01	1.22E+01	2.09E+00	1.08E+01	1.14E+00	3.53E+00	1.95E-01
12.4	2.35E+00	1.79E-01	2.67E+01	9.54E-01	3.32E+01	4.79E+00	8.20E+00	4.62E-01
24.5	4.46E+00	4.43E-01	3.96E+01	1.28E+01	4.01E+01	6.26E+00	7.87E+00	5.55E+00
168.5	3.37E+01	5.13E+00	2.70E+01	8.99E+00	3.22E+01	4.56E+00	7.62E+00	5.36E+00

Neptunium Decontamination Factors

	Baseline MST @ 0.2 g/L		Modified MST @ 0.2 g/L		Modified MST @ 0.2 g/L with CSSX Solvent		Modified MST @ 0.1 g/L	
Time (h)	Value	Uncertainty	Average	Std Dev	Value	Uncertainty	Average	Std Dev
2.6	2.21E+00	6.26E-01	1.59E+00	1.57E-01	1.55E+00	4.38E-01	1.35E+00	3.97E-02
4.5	2.87E+00	8.13E-01	2.21E+00	1.03E-01	2.42E+00	6.83E-01	1.64E+00	4.25E-01
6.4	2.55E+00	7.21E-01	1.60E+00	6.56E-02	1.49E+00	4.21E-01	1.35E+00	2.05E-02
12.4	3.24E+00	9.17E-01	1.88E+00	3.76E-02	1.80E+00	5.09E-01	1.59E+00	2.80E-02
24.5	3.10E+00	8.76E-01	1.82E+00	1.66E-01	2.00E+00	5.65E-01	1.38E+00	4.35E-01
168.5	4.84E+00	9.67E-01	2.30E+00	1.74E-01	2.04E+00	4.07E-01	1.62E+00	5.13E-02

Modified MST results are average and standard deviation of six trials; Baseline MST results are single determinations with reported analytical uncertainty

Table 16. Average Normalized Strontium and Plutonium DF Values

	Normalized DF Value			
	Strontium		Plutonium	
Time (h)	Average	Std Dev	Average	Std Dev
2.6	2.61E+00	1.45E-01	5.21E+00	3.14E-01
4.5	2.70E+00	7.29E-01	5.54E+00	3.99E-01
6.4	>2.65E+00		6.53E+00	1.12E+00
12.4	>1.66E+00		1.13E+01	4.06E-01
24.4	>2.35E+00		8.88E+00	2.87E+00
168.4	>1.44E+00		8.02E-01	2.67E-01

4.3.2 Supplemental Actual Waste Tests - Test Set #2

Supplemental actual waste tests (Test Set #2) evaluated the performance of modified MST in both double-strike and reuse configurations. Seven tests in all were conducted in two stages. Tests S-2, S-3, and S-1C occurred approximately two weeks prior to Tests S-4, S-5, S-1A, and S-1B. Tests S-1A, -1B, and -1C are control tests (i.e., no modified MST was added).

Tests S-2 and S-3 are double-strike tests conducted by filtering the test solutions approximately 6 hours after first contacting with modified MST and then adding fresh modified MST to the filtrate. Tests S-2 and S-3 added 0.1 g L^{-1} and 0.2 g L^{-1} modified MST, respectively, in each strike (see Attachment 8.4 for the measured radiochemical concentrations).

Tests S-4 and S-5 used filtered, composited, residual Tank 39H actual waste solution remaining from the Actual Waste Test Set #1 (see Attachment 8.4). These reuse tests filtered the decontaminated test solutions approximately 6 hours after first contacting with modified MST and then added the collected MST solids to fresh, spiked Tank 39H actual waste solution. Tests S-4 and S-5 used 0.1 g L^{-1} and 0.2 g L^{-1} modified MST, respectively. This test design mimics the proposed operations in the Alpha Finishing Process of the SWPF.

Personnel obtained samples from all tests except Control Test 1C at approximately 2, 6, 8, 12, 30, and 174 h after the first MST contact. Control Tests S-1A (using fresh, spiked Tank 39H actual waste) and S-1B (using filtered, composited, residual Tank 39H actual waste from earlier testing) were also sampled at the start of testing (time = 0 h). Control Test 1C (fresh, spiked Tank 39H actual waste) was sampled at 2, 8, and 174 h. All tests were conducted at 25 ± 3 °C.

As with the previous test set, the ^{90}Sr data is scattered and provides no discernible trends in performance. The total strontium data, while limited by the method detection limit, appears well behaved. The total plutonium data from both PuTTA and ICP-MS methods show reasonable agreement, although the PuTTA method provides a lower detection limit compared to the ICP-MS method.

Figures 15 and 16 provide plots of strontium concentration and plutonium activity, respectively, versus time for the single and double strike tests. We observed good agreement between the 2 and 4-h sample results in the single-strike tests (Test Set #1) and that for the first strike of the double-strike tests (Test Set #2). Unfortunately, the first sample after the second modified MST addition resulted in the total strontium falling below the analytical method detection limit. Thus, we cannot quantitatively assess the magnitude of the strontium removal upon the second strike of modified MST.

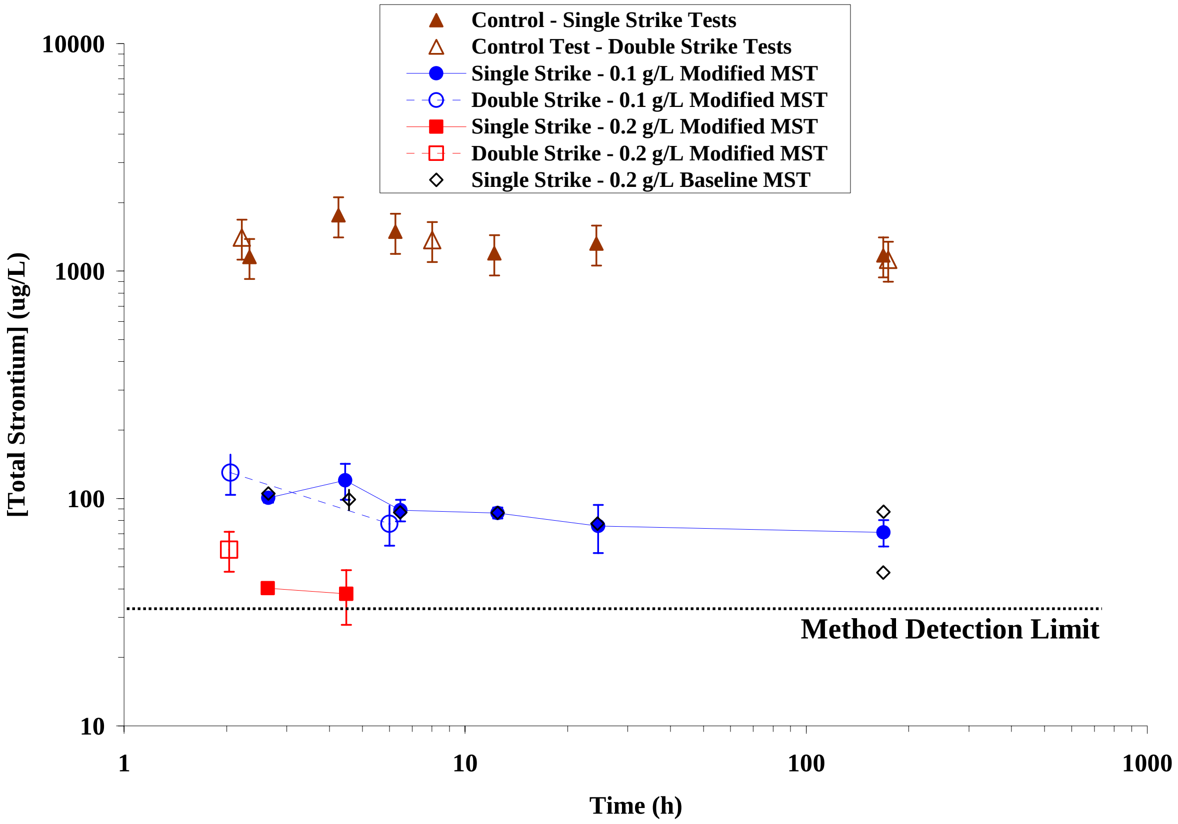

Figure 15. Total Strontium Concentration versus Time for the Single and Double Strike Tests with Actual Waste

We observe good agreement between the 2 and 4-h sample results for the single strike tests (Test Set #1) and that for the first strike of the double strike tests (Test Set #2) with respect to plutonium activity. Upon the addition of the second strike of modified MST, the plutonium activity decreased to a value well below the total alpha activity WAC limit at both MST concentrations (see Figure 16). The 30-h result for the double-strike test indicates a higher plutonium concentration than the previous two samples and the 170-h sample which is below the method detection limit. We believe this value is in error, most likely the result of cross contamination during sample handling within the Shielded Cells.

Table 17 provides a summary of the measured DF values for strontium, plutonium and neptunium in the double strike tests. Greater than values are given when the measured concentrations for a sorbate are below the analytical method detection limit. Uncertainties for the single replicate tests are determined from the analytical uncertainties. Strontium, plutonium, and neptunium DFs for the two double-strike tests (S-2 and S-3) exhibit the expected increase with time. The large increase in DF between the 6 and 8-hour sampling time resulted from the removal of the modified MST solids from the first strike and addition of fresh MST.

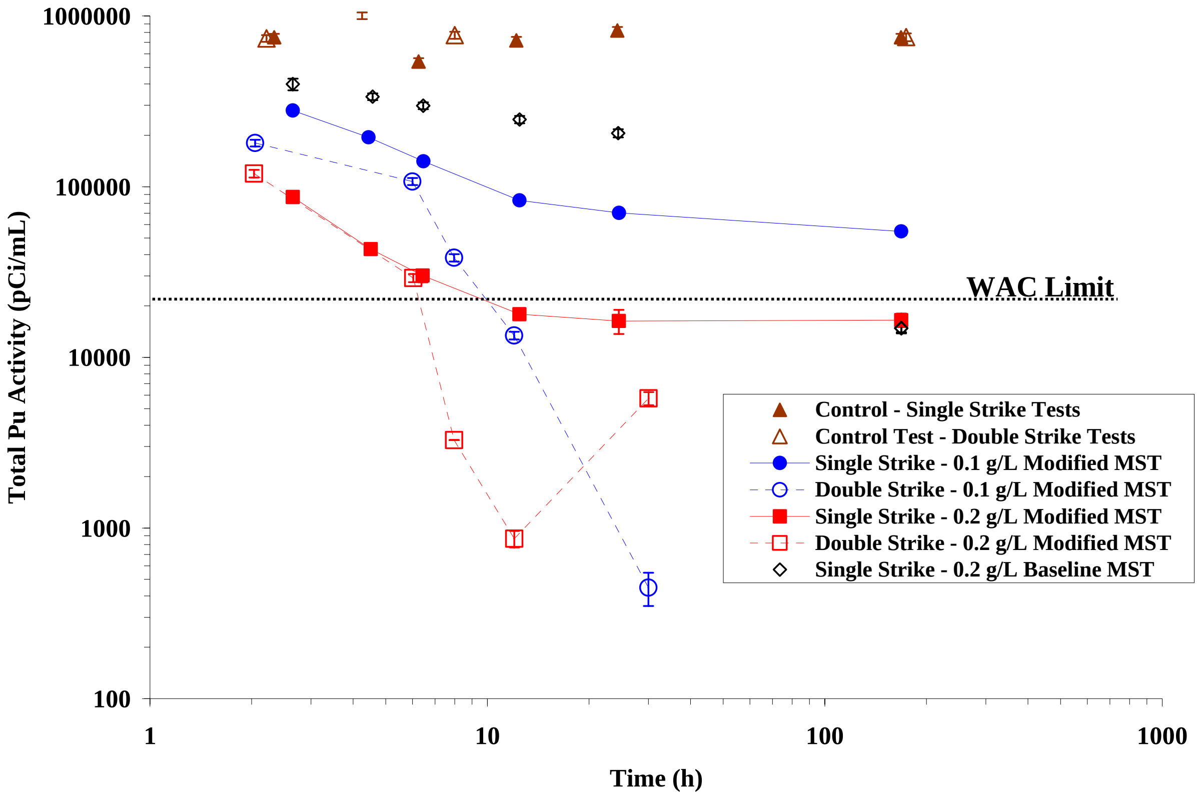

Figure 16. Total Plutonium Activity versus Time for the Single and Double Strike Tests with Actual Waste

Table 17. Strontium, Plutonium and Neptunium Decontamination Factors in Double Strike Actual Waste Tests

		Decontamination Factors (DFs)					
		Total Sr		Total Pu*		^{237}Np	
Test Description	Time (h)	Value	Uncertainty	Value	Uncertainty	Value	Uncertainty
Supplemental Test S-2 Double-strike test with 0.1 g/L Modified MST	2.1	1.00E+01	2.83E+00	4.18E+00	2.78E-01	1.40E+00	3.95E-01
	6.0	1.68E+01	4.74E+00	7.02E+00	4.77E-01	1.55E+00	4.37E-01
	8.0	>2.49E+01		1.97E+01	1.36E+00	1.86E+00	5.27E-01
	12.0	>2.62E+01		5.63E+01	3.99E+00	1.96E+00	5.53E-01
	30.0	>2.66E+01		1.69E+03	3.83E+02	2.21E+00	6.24E-01
	174	>8.12E+01		>1.04E+02		2.41E+00	6.82E-01
Supplemental Test S-3 Double-strike test with 0.2 g/L Modified MST	2.0	2.18E+01	6.17E+00	6.31E+00	4.48E-01	1.34E+00	3.79E-01
	6.0	>2.43E+01		2.59E+01	1.87E+00	1.50E+00	4.23E-01
	8.0	>2.64E+01		>2.31E+02		2.60E+00	7.35E-01
	12.0	2.20E+01	6.24E+00	8.71E+02	1.06E+02	2.79E+00	7.89E-01
	30.0	>2.64E+01		1.31E+02	1.34E+01	3.29E+00	9.29E-01
	174	>8.06E+01		>7.61E+02		4.62E+00	1.31E+00

DF calculated using average concentrations of Control Test 1C
*Calculated from PuTTA data for ^{238}Pu and $^{239/240}$Pu

Single tests (S-4 at 0.1 g L^{-1} and S-5 at 0.2 g L^{-1}) evaluated the performance of the modified MST upon reuse. In these tests we first contacted the modified MST with a filtered composite of the residuals from Test Set #1, which had a reduced radioactivity compared to the initial waste. After approximately six hours, we recovered the MST solids from the waste solution, and added the solids to a fresh batch of the Tank 39H waste solution at the original spiked concentrations (i.e., same material as used in the Test Set #1 and Supplemental Tests S-2 and S-3). Figure 17 provides a plot of the total plutonium activity as a function of total test time for the reuse tests. Included in Figure 17 are the curves measured for plutonium removal in the single-strike tests (Test Set #1) allowing for a 6-hour offset from the beginning of the experiment.

The observed changes in plutonium activity with time during the test met expectations. Initially, the plutonium activity decreases for the first two samples. After separating the solids and contacting the recovered MST solids with fresh Tank 39H supernate, the plutonium activity increased reflecting the higher plutonium activity in the fresh waste versus that of the initial strike which had a much lower initial plutonium activity (8.18 ± 0.44 E+05 versus 3.02 ± 0.16 E+04 pCi mL^{-1}). Subsequent samples showed decreasing plutonium activity with time.

Comparison of the plutonium activity changes with time in the reuse and single strike tests indicates that less removal of plutonium occurs in the reuse test. Generally, the plutonium activity is about a factor of 10 higher in the tests with the reused MST compared to a single strike of fresh MST. The results indicate that a higher MST concentration is required to achieve the WAC limit if the material is previously used in the Alpha Finishing Process.

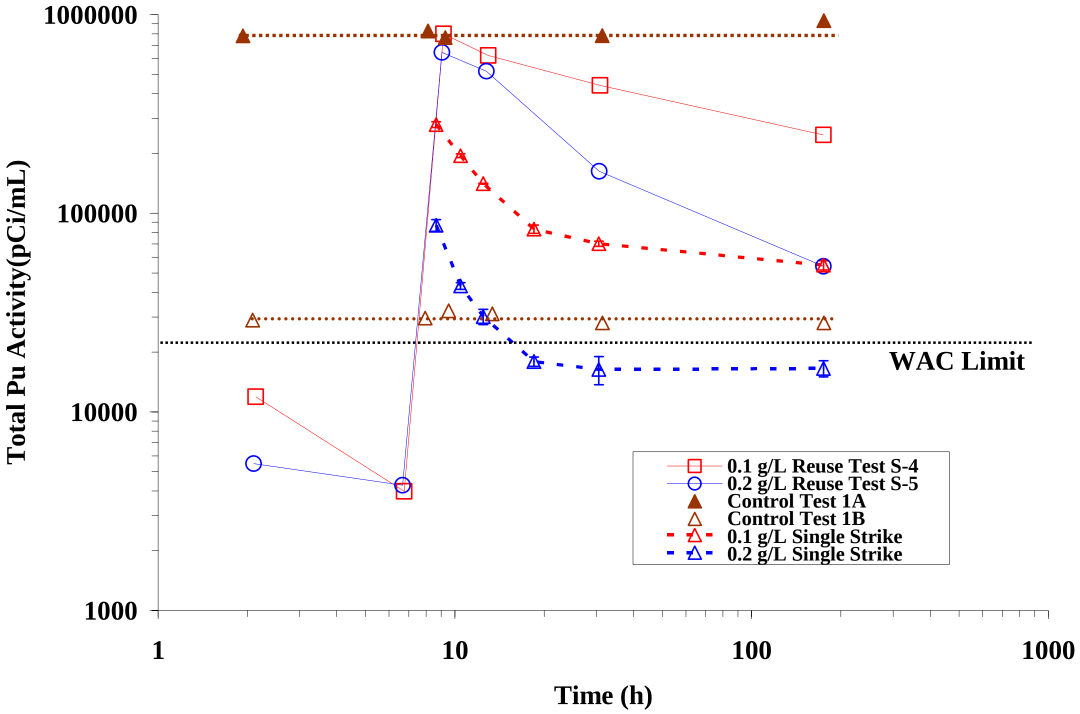

Figure 17. Total Plutonium Activity versus Time in the Modified MST Reuse Tests

Figure 18 provides a plot of the total strontium concentration versus total test time for the reuse tests. Included in Figure 18 are the data measured for strontium removal in the single-strike tests (Test Set #1) allowing for a 6-hour offset from the beginning of the experiment. Data points designated with filled symbols are the method detection values reported by the Analytical Development Section for that sample and corrected for dilution. Unfortunately, a large number of the samples fell below the detection limit. This prevents obtaining a quantitative measure of the influence of the reuse on strontium removal.

From the available data we see that the removal of strontium by the reused MST is less than that measured in the single-strike tests. This result is consistent with the trend observed with plutonium. From Figure 18 we estimate that after 2 hours of contact the reused MST lagged that of fresh MST by a factor of 10. After 6 and 24 hours of contact the reused MST lagged the fresh MST by a factor of about 2 – 3.

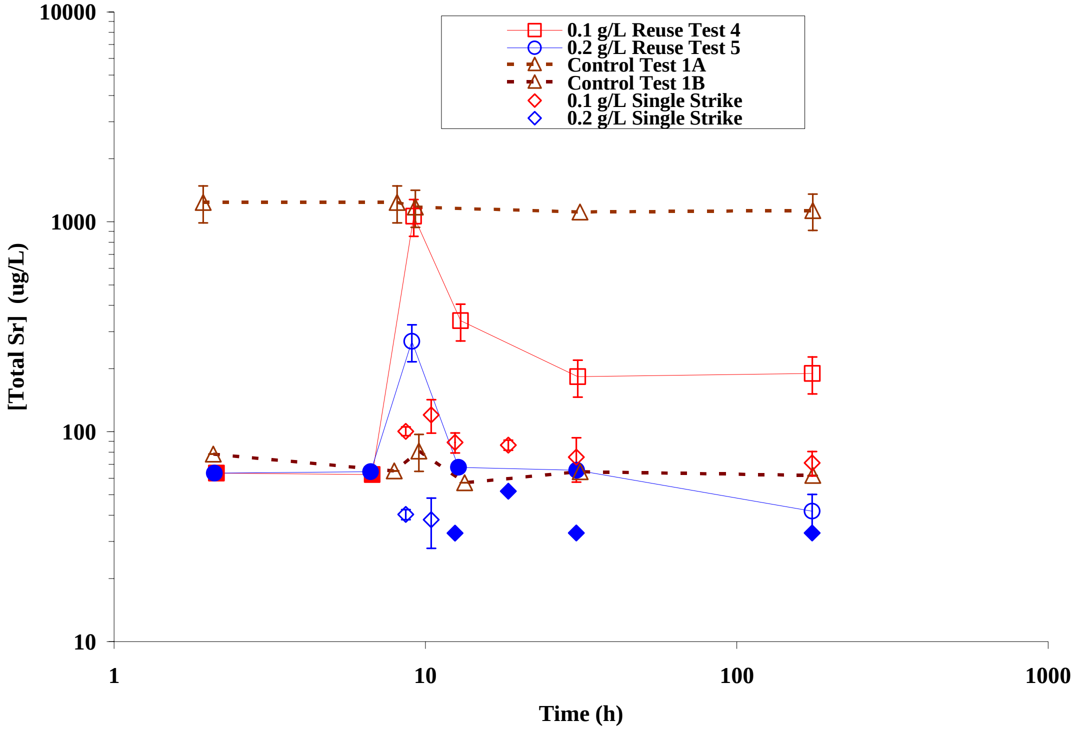

Figure 18. Total Strontium Concentration versus Time in the Modified MST Reuse Tests

4.4 Acceptance Testing of Vendor-prepared Modified MST

Acceptance testing of the batch of vendor-prepared modified MST consisted of measuring the insoluble solids content, pH, particle size distribution and strontium/actinide removal performance upon contact for 6 and 12 hours. Table 18 provides a summary of the solids content and pH of the vendor-prepared modified MST samples.

Table 18. Solids Content and pH of the Vendor-prepared Modified MST Samples

Sample ID	Wt % Insoluble Solids	pH
06-QAB-0139-1L	16.9 (0.021)	4.18 (5/2/06)
		4.86 (8/15/06)
06-QAB-0139-D1	15.8 (0.277)	4.81 (8/15/06)
06-QAB-0139-D2	15.64 (0.144)	4.78 (8/15/06)
06-QAB-0139-D3	15.43 (0.337)	4.52 (8/15/06)

The initial sub-sample of modified MST (Optima #06-QAB-0139-1L) measured 16.9 ± 0.021 wt % in insoluble solids and pH 4.18, which met the purchase specifications of 15 ± 3 wt % insoluble solids and pH of 4.0 – 4.3. Given these results we measured the particle size distribution. Particle size measurements with the Microtrac S3000 instrument in water revealed that the material slightly exceeded the lower limit (<7% with a particle size of 1.0 μ) and the upper size limit (<1% greater than 35 μ) established for the procurement specification. However, we judged the variances to be acceptable and continued forward in the acceptance testing for strontium and actinide removal.

Strontium and actinide removal performance consisted of contacting a simulated waste solution (SWS-12-2005) with 0.2 g L^{-1} of the vendor-prepared modified MST. Similar tests were conducted with the baseline MST (Optima 00-QAB-417) and the laboratory scale modified MST identified as Batch #LS-1. We measured strontium and actinide removal performance at contact times of 6 and 12 hours.

Table 19 provides a summary of the measured DF values for the materials in the acceptance testing. The vendor produced modified MST exhibited significantly improved strontium and plutonium removal performance compared to the baseline MST sample. Furthermore, the vendor-prepared materials generally exhibited higher removal of strontium and plutonium removal after 6 and 12 hours of contact compared to the laboratory-produced modified MST sample (LS-1). Decontamination factors were also higher for the vendor-prepared modified MST compared to the laboratory prepared modified and baseline MST samples. Considering the experimental uncertainties, the neptunium DF values are not statistically different and, thus, we cannot conclude that the vendor-prepared sample of modified MST exhibits improved neptunium removal.

Table 19. Decontamination Factors for Modified and Baseline MST Samples Measured in the Acceptance Testing

		6-h DF Values[a]		
Material[b]	**Sample ID**	**Sr**	**Pu**	**Np**
Modified MST	06-QAB-0139-1L	382 (35.8)	217 (39.7)	3.25 (1.42)
Modified MST	LS-1	104 (2.90)	78.5 (11.2)	1.87 (0.172)
Baseline 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**
Modified MST	06-QAB-0139-1L	507 (65.8)	477 (113)	3.67 (0.686)
Modified MST	LS-1	117 (3.20)	148 (26.6)	2.18 (0.330)
Baseline 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 modified MST sample 06-QAB-0139 and single standard deviation based on the analytical uncertainty for the modified MST sample LS-1 and baseline MST sample.
[b] Sorbent added at 0.2 g L^{-1}. Temperature controlled at 25 ± 3 °C.

Since the acceptance testing sample of the vendor-prepared modified MST met the purchase specifications and exhibited excellent strontium and plutonium removal characteristics, WSRC authorized the vendor to ship the batch of modified MST to SRNL. The drum of modified MST was received at SRNL and passed visual inspection. Three additional sub-samples of the drum contents were taken from the drum identified as 06-QAB-0139-D1, 06-QAB-0139-D2 and 06-QAB-0139-D3.

We determined the weight percent insoluble solids content, pH and particle size distribution of these three samples and compared these to the one-liter sample, 06-QAB-0139-1L (see Table 18). We observed that the pH of the modified MST sample, 06-QAB-0139 from 4.18 to 4.86 during storage for just over 3 months. The pH values measured for the three drum samples were similar to that of the 06-QAB-0139-1L sample measured on the same day. The increase in pH over the 3-month period may reflect further exchange reactions between the MST solids and the solution, which consume acid in solution and raise the pH slightly.

Each of the three drum samples exhibited lower insoluble solids content than the acceptance testing sample. We first thought that the lower solids content reflected the addition of water by the vendor to transfer all of the solids from the processing tank to the shipping drum. However, a discussion with the vendor revealed that no water was added during the filling of the drum. Thus, the higher solids content of the acceptance testing sample likely represents incomplete suspension of the material during the sampling event at the vendor.

Table 20 presents the particle size characteristics of the modified MST samples as well as that of the baseline MST in comparison to that specified for the procurement of the modified MST. The average of the four modified MST samples indicates that the modified MST meets the lower particle size specification of < 7% below 1 micron and slightly exceeds the upper size specification of < 1% greater than 37 microns. Note that the baseline MST sample exceeded the lower size limit, but met the upper size limit.

Table 20. Particle Size Characteristics of MST Samples[a]

Material	Sample ID	% <1 μ	% >37 μ
	Specification	< 7	< 1
Modified MST	06-QAB-0139-1L	7.09	1.9
Modified MST	06-QAB-0139-D1	6.89	4.12
Modified MST	06-QAB-0139-D2	4.83	0.27
Modified MST	06-QAB-0139-D3	5.4	0.79
	Average	6.05 + 1.11	1.77 + 1.71
Baseline MST	00-QAB-417	8.8	0.02

[a] Measured in deionized, distilled water using a Microtrac S3000 instrument.

4.5 Performance Testing of Vendor-prepared Modified MST with Simulated Waste Solution

We conducted an additional set of tests with the vendor-prepared modified MST with simulated waste solution (SWS-12-2005) to provide a more complete description of the adsorption kinetics and verify if uranium adsorption occurs. In this test set, we measured the performance of the modified MST sample at sorbent concentrations of 0.1, 0.2, 0.4 and 0.8 g L^{-1} versus that of the baseline MST sample at 0.4 and 0.8 g L^{-1}. Figures 19 – 22 provide graphs of solution concentrations versus contact time for ^{85}Sr, plutonium, neptunium and uranium, respectively. Table 21 provides the calculated decontamination factors for the baseline MST at concentrations of 0.4 g L^{-1} and 0.8 g L^{-1} and the modified MST at concentrations of 0.1 and 0.2 g L^{-1}.

Strontium removal with the vendor-prepared modified MST proved more rapid than the baseline MST when added at one-fourth the concentration of the baseline MST material (0.1-0.2 g L^{-1} for MMST vs. 0.4-0.8 g L^{-1} for MST). Generally the decontamination factors for the modified MST measured about twice that of the baseline MST. The analogous experiment with laboratory prepared modified MST (see Table 13) used a different simulated waste solution and tested the baseline MST material at 0.1 and 0.2 g L^{-1} concentrations. Thus, we cannot make a direct comparison between the vendor and laboratory prepared materials between these two datasets. Given the strontium removal performance in the acceptance testing results (see Table 19) and the excellent strontium removal characteristics in this test, we conclude that the vendor-prepared batch of modified MST material represents successful scale up from the 25-gram scale (laboratory) to the 15-kilogram scale (vendor).

As with strontium, plutonium removal with the vendor-prepared modified MST proved more rapid than the baseline MST when added at one-fourth the concentration of the baseline MST material (0.1-0.2 g L^{-1} for modified MST vs. 0.4-0.8 g L^{-1} for MST). Generally the decontamination factors for the modified MST measured more than an order of magnitude higher than those of the baseline MST. The analogous experiment with laboratory prepared modified MST (see Table 13) used a different simulated waste solution and tested the baseline MST material at 0.1 and 0.2 g L^{-1} concentrations. Thus, we cannot make a direct comparison between the vendor and laboratory prepared materials between these two datasets. Given the plutonium removal performance in the acceptance testing results (see Table 19) and the excellent plutonium removal characteristics in this test, we conclude that the vendor-prepared batch of modified MST material represents successful scale up from the 25-gram scale (laboratory) to the 15-kilogram scale (vendor).

As shown in Figure 21, neptunium removal with the vendor-prepared modified MST proved more rapid than the baseline MST when added at the same concentration as the baseline MST material (0.4 and 0.8 g L^{-1}). Generally the decontamination factors for the modified MST measured about 2 – 3 times that of the baseline MST except at the 168-h result at 0.8 g L^{-1}. The analogous experiment with laboratory prepared modified MST (see Table 13) used a different simulated waste solution and tested the baseline MST material at 0.1 and 0.2 g L^{-1} concentrations. Thus, we cannot make a direct comparison between the vendor and laboratory prepared materials between these two datasets. Given the neptunium removal performance in the acceptance testing results (see Table 19) and the excellent neptunium removal characteristics in this test, we conclude that the vendor-prepared batch of modified MST material represents successful scale up from the 25-gram scale (laboratory) to the 15-kilogram scale (vendor).

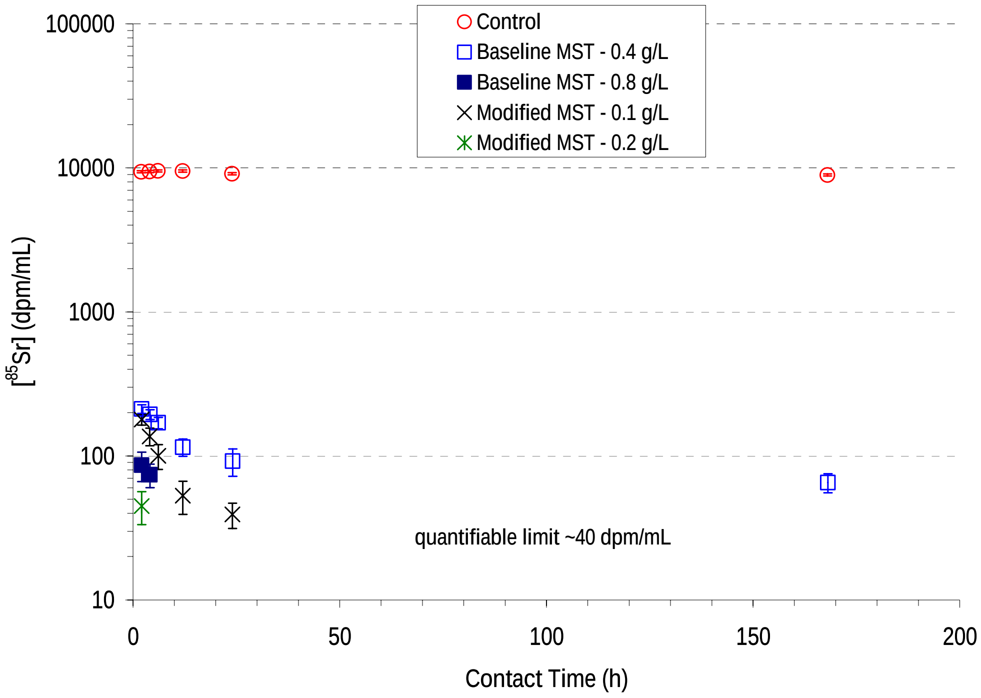

Figure 19. ^{85}**Sr Activity Versus Time for Baseline and Vendor-prepared Modified MST**

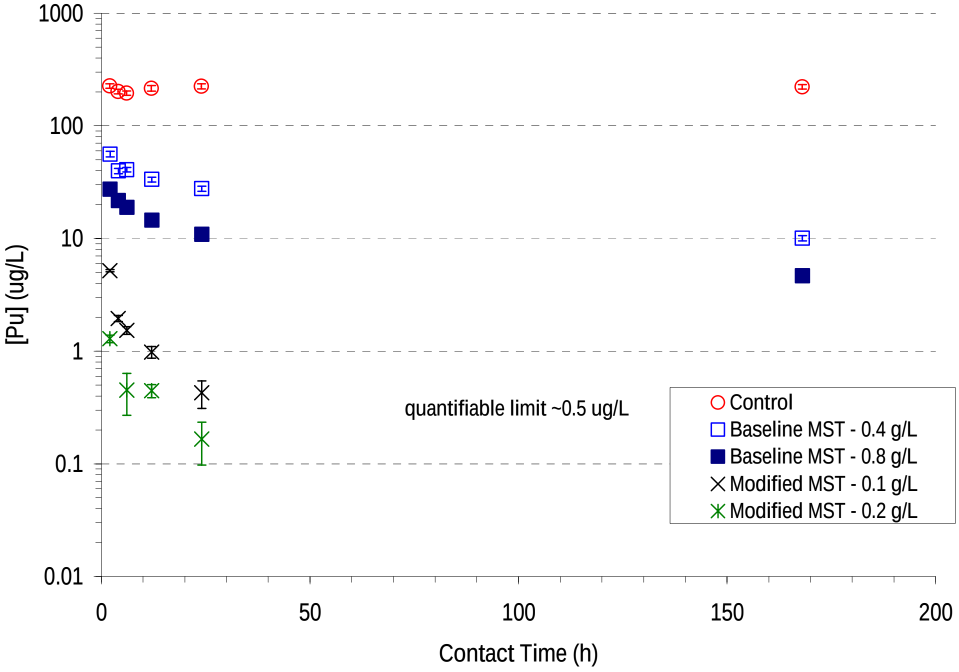

Figure 20. Plutonium Concentration Versus Time for Baseline and Vendor-prepared Modified MST

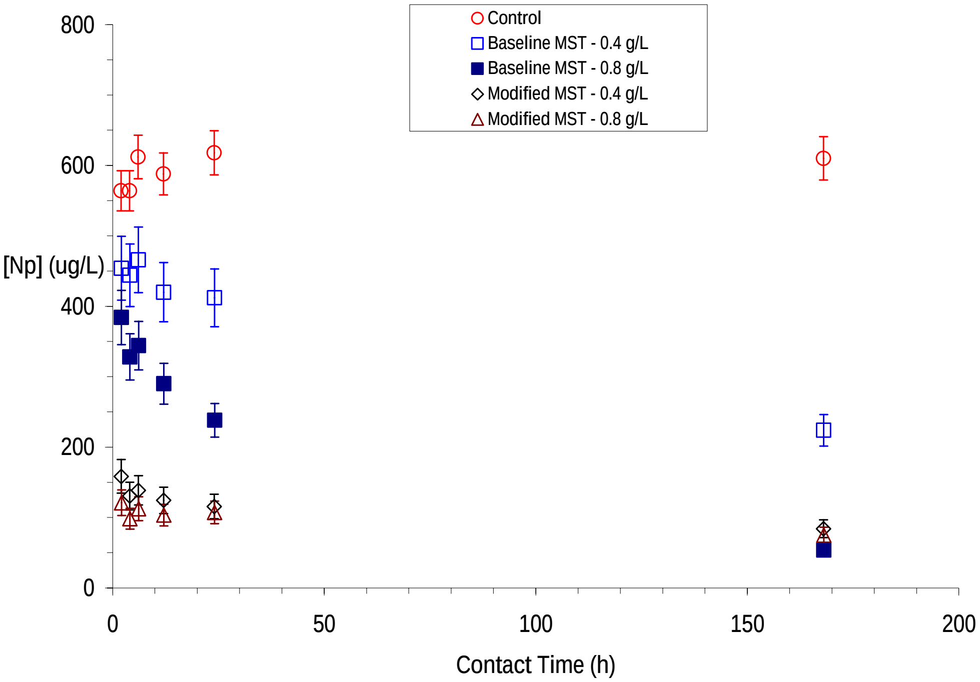

Figure 21. Neptunium Concentration Versus Time for Baseline and Vendor-prepared Modified MST

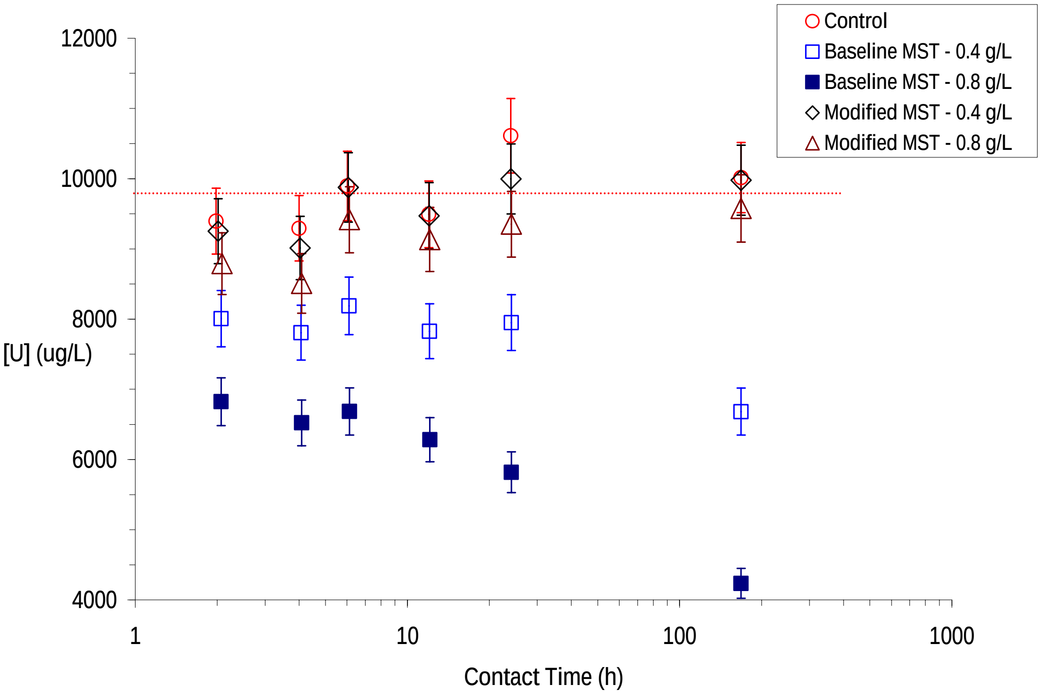

Figure 22. Uranium Concentration Versus Time for Baseline and Vendor-prepared Modified MST

Table 21. Decontamination Factors for Baseline MST and Vendor-prepared Modified MST

	Sr DF			
	MST		MMST	
Time (h)	**0.4 g/L**	**0.8 g/L**	**0.1 g/L**	**0.2 g/L**
2	4.44E+01	1.09E+02	5.25E+01	2.09E+02
4	4.87E+01	1.28E+02	6.91E+01	>2.72E+02
6	5.62E+01	>2.45E+02	9.51E+01	>2.46E+02
12	8.27E+01	>2.34E+02	1.80E+02	>4.61E+02
24	9.91E+01	>3.50E+02	2.32E+02	>2.60E+02
168	1.37E+02	>1.98E+02	>2.15E+02	>2.46E+02

	Pu DF			
	MST		MMST	
Time (h)	**0.4 g/L**	**0.8 g/L**	**0.1 g/L**	**0.2 g/L**
2	4.02E+00	8.23E+00	4.35E+01	1.75E+02
4	5.06E+00	9.29E+00	1.03E+02	>2.63E+02
6	4.78E+00	1.03E+01	1.27E+02	4.32E+02
12	6.45E+00	1.48E+01	2.19E+02	4.83E+02
24	8.11E+00	2.06E+01	5.25E+02	1.35E+03
168	2.21E+01	4.77E+01	>2.49E+02	>5.21E+02

	Neptunium DF			
	MST		MMST	
Time (h)	**0.4 g/L**	**0.8 g/L**	**0.4 g/L**	**0.8 g/L**
2	1.24E+00	1.47E+00	3.56E+00	4.66E+00
4	1.27E+00	1.72E+00	4.32E+00	5.74E+00
6	1.31E+00	1.78E+00	4.42E+00	5.44E+00
12	1.40E+00	2.03E+00	4.73E+00	5.69E+00
24	1.50E+00	2.60E+00	5.35E+00	5.76E+00
168	2.72E+00	1.13E+01	7.26E+00	8.16E+00

We conducted a reuse test with the vendor-prepared modified MST using the same simulant and test methodology previously reported with the baseline MST (see Table 2).[15] Due to the limited quantity of simulant we scaled the solution volumes from 1.0 L in the previous study to 0.4 L in this study and performed duplicate tests only with the modified MST in duplicate. Previous testing established that the CSSX solvent did not affect modified MST performance and, therefore, we omitted the addition of the CSSX solvent in this test sequence. The reuse test consisted of contacting the modified MST with the simulated waste solution at a sorbent concentration of 0.2 g L^{-1} for six hours at ambient laboratory temperature, separating the solids from the solution by filtration and adding fresh modified MST solids (0.2 g L^{-1}) to the filtrate from the first contact. After mixing for six hours we again filtered the test suspensions and isolated the solids and filtrate. The partially-loaded solids from the second contact were then added to fresh simulated waste solution, contacted for six hours and then filtered to separate the solids and simulated waste solution. We isolated the solids from the first contact and third contacts and determined the amount of strontium and actinide adsorbed onto the solids. Samples of each of the filtrates were also analyzed to determine sorbate concentrations.

Table 21 provides a summary of the measured DF values for this test and those previously reported for the baseline MST. The measured DF values follow the expected trends. As previously observed, the modified MST exhibits greater strontium and plutonium removal than the baseline MST. For example, the strontium DF value for the modified MST measured about 4 times that of the baseline MST in Contact #1 even at one-half the sorbent concentration (0.2 g L^{-1} vs. 0.4 g L^{-1}). The plutonium DF value for the modified MST represents 99.5% removal of the plutonium versus 90.1% removal for the baseline MST.

Given the greater strontium removal during Contact #1, we cannot compare strontium removal between the two materials during Contact #2. The lower plutonium DF value for the modified MST (4.24) compared to the baseline MST (11.5) reflects the low initial plutonium concentration for the solution used in Contact #2 (filtrate from Contact #1). Strontium and plutonium DF values for the modified MST in Contact #3 are much lower than those in Contact #1. Note that the neptunium DF values for the modified MST appear similar to that of the baseline MST. Solution analyses for uranium indicated some removal of uranium in the first contact, but not in the later contacts with the modified MST.

Table 22. Average Decontamination Factors for Modified and Baseline MST[a] Determined in the Reuse Tests

		Average Decontamination Factor							
		Sr		**Pu**		**Np**		**U**	
Contact	**Analytical Method**	**Modified MST (0.2 g/L)**	**Baseline MST (0.4 g/L)**	**Modified MST (0.2 g/L)**	**Baseline MST (0.4 g/L)**	**Modified MST (0.2 g/L)**	**Baseline MST (0.4 g/L)**	**Modified MST (0.2 g/L)**	**Baseline MST (0.4 g/L)**
1	**Counting**	48.9	11.5	244	10.1	>2.08	-	-	-
	ICP-MS	44.9	10.4	>12	>1.6	3.67	>1.75	1.05	1.14
2	**Counting**	>29.2	109	4.24	11.5	ND	-	-	-
	ICP-MS	>22.8	109	ND	ND	1.76	ND	0.968	1.14
3	**Counting**	2.17	5.13	3.97	4.80	>1.46	-	-	-
	ICP-MS	2.08	5.23	3.28	>2.1	2.02	1.75	1.00	1.05

[a] decontamination factors for the Baseline MST are those reported in reference 15

ND = not determinant Blank entry (-) indicates not measured

Table 23 provides the measured and calculated sorbent loadings for each of the sorbates for single use (Contact #1) and after reuse (solids after Contacts #2 and #3). We observed very good agreement between the measured and calculated loadings except for uranium after the reuse test. The low calculated value from the reuse test (85.5 ± 3.83 μg g^{-1}) reflects no measurable removal based on the solution analyses. The measured uranium loadings (ca. 2,270 and 2,790 μg g^{-1}) after a single contact and two contacts represents the first data confirming that the modified MST does adsorb uranium. Note that these values are about a factor of 2.8 lower than the baseline MST, which was added at twice the concentration as the modified MST.

The reduced affinity of the modified MST for uranium is also evident when one compares the molar ratios of strontium to the actinides in the simulant and the sorbent solids. Table 23 also provides the molar ratios of Sr:Pu, Sr:Np and Sr:U for the simulants and modified MST. For plutonium and neptunium the affinity index (i.e., molar ratio in the solids divided by that in the simulant) are near unity for both single and two contacts suggesting that the modified MST has the same relative affinity for strontium, plutonium and neptunium. Uranium exhibits an index of about 30 indicating much more strontium adsorbed onto the solids than uranium. Thus, we conclude that the modified MST exhibits lower affinity for uranium compared to the other sorbates.

Table 23. Sorbent Loadings and Affinity Index for Modified and Baseline MST

	Sorbent Loading (ug/g)				
	Modified MST - Single Contact		**Modified MST - After Reuse**		**Baseline MST - After Reuse**
Sorbate	**Measured**	**Calculated**	**Measured**	**Calculated**	**Measured**
Sr	44,700 + 7,240	49,800 + 2,550	29,200 + 4,570	27,300 + 3,790	39,500 + 566
Pu	411 + 53.1	394 + 34.3	338 + 67.6	296 + 47.1	171 + 2.83
Np	496 + 134	503 + 57.5	599 + 134	426 + 79.2	>84
U	2,270 + 198	3550 + 59.6	2,790 + 334	85.5 + 3.83	7,240 + 2,440

	Contact 1			**Contact 3**		
	Simulant	**Solids**	**Affinity Index**			**Affinity Index**
	(umol/umol)	**(umol/umol)**		**(umol/umol)**	**(umol/umol)**	
Sr:Pu	280	300	1.1	290	240	0.83
Sr:Np	200	240	1.2	160	140	0.88
Sr:U	1.9	54	28	0.96	29	30

4.6 Performance Testing of Vendor-Prepared Modified MST with Actual Waste

Performance testing of the vendor-prepared modified MST consisted of the seven tests in which we contacted the Tank 39H waste solution with modified MST and baseline MST at the concentrations specified in Table 6. Test 1 served as the control test with no added sorbent. Tests 2 and 3 added the modified MST at 0.1 g L^{-1}, Tests 4 and 5 added the modified MST at 0.2 g L^{-1} and Tests 6 and 7 added the baseline MST at 0.2 and 0.4 g L^{-1}, respectively.

Table 24 provides the measured sorbate concentrations for each of the samples taken from the control test. The ^{238}Pu and ^{238}U concentrations varied by less than 5% and the ^{237}Np exhibited a RSD of 9.45%. ^{90}Sr measurements exhibited the most variation with a RSD on 25%. The much higher RSD for the ^{90}Sr analyses is attributed to the high ^{137}Cs content, which necessitated additional sample preparation steps. The high variance in ^{90}Sr analyses in tank waste samples was previously observed in the tank waste testing with the laboratory prepared MST and characterization of tank waste supernate samples. Comparison of the analyte concentrations in this dataset agree closely with those measured in the previous dataset (Dataset #1). This confirms that the sorbate concentrations did not change during storage of the actual waste solution between the test sets.

Table 24. Analyte Concentrations in the Actual Waste Control Test Samples Measured in Dataset #2

Sampling Time (hours)	Total Pu (µg/L)	Total U (µg/L)	^{237}Np (µg/L)	^{90}Sr (dpm/mL)	Total Sr (µg/L)
0	2.56E+02 (5.18%)	9.37E+03	1.68E+02	5.29E+04 (15.2%)	1.30E+03
2	2.54E+02 (4.76%)	9.38E+03	1.68E+02	8.97E+04 (20.8%)	1.35E+03
4	2.35E+02 (6.00%)	8.90E+03	1.49E+02	9.21E+04 (3.42%)	1.37E+03
6	2.51E+02 (5.41%)	9.73E+03	1.72E+02	6.30E+04 (12.1%)	1.29E+03
12	2.53E+02 (5.30%)	9.31E+03	1.88E+02	5.91E+04 (14.2%)	1.36E+03
24	2.45E+02 (6.01%)	9.48E+03	1.92E+02	6.53E+04 (14.0%)	1.37E+03
168	2.54E+02 (5.26%)	9.21E+03	1.53E+02	5.03E+04 (3.68%)	1.30E+03
Average	2.50E+02	9.34E+03	1.70E+02	6.75E+04	1.33E+03
Std Dev	6.86E+00	2.51E+02	1.61E+01	1.68E+04	3.62E+01
% RSD	2.75	2.69	9.45	25.0	2.72
Average of Control Samples from Dataset 1	2.754E+02	1.10E+04	1.31E+02	4.97E+04	1.31E+03
Std Dev	5.59E+01	1.73E+03	1.88E+01	9.96E+03	2.42E+02

Analysis of the filtrate samples from tests with baseline and modified MST for ^{90}Sr proved very scattered as the values were very close to the analytical method detection limit. Consequently the ^{90}Sr data provided no insight into the performance of the MST samples for strontium removal. Figure 23 provides a plot of the total strontium concentration versus contact time for the seven tests, where the total strontium derived from the ^{88}Sr data measured by ICP-MS. Table 25 provides the calculated DF values for the baseline and modified MST materials in this dataset (Dataset #2) as well as that for the earlier dataset (Dataset #1). A large number of the strontium data points, including all of the samples from the 0.2 g L^{-1} modified MST tests fell below the method quantifiable limits. These results were omitted from the plot in Figure 23. Given that the tests with 0.2 g L^{-1} vendor-prepared modified MST fell below the quantifiable limit within the first 2-hour sampling event, we conclude that vendor-prepared modified MST exhibits faster strontium removal than the baseline MST. This finding is consistent with the previous tests with the laboratory prepared modified MST. The available data indicate that 0.1 g L^{-1} of the vendor-prepared modified MST achieved the same degree of strontium removal as 0.4 g L^{-1} of the baseline MST.

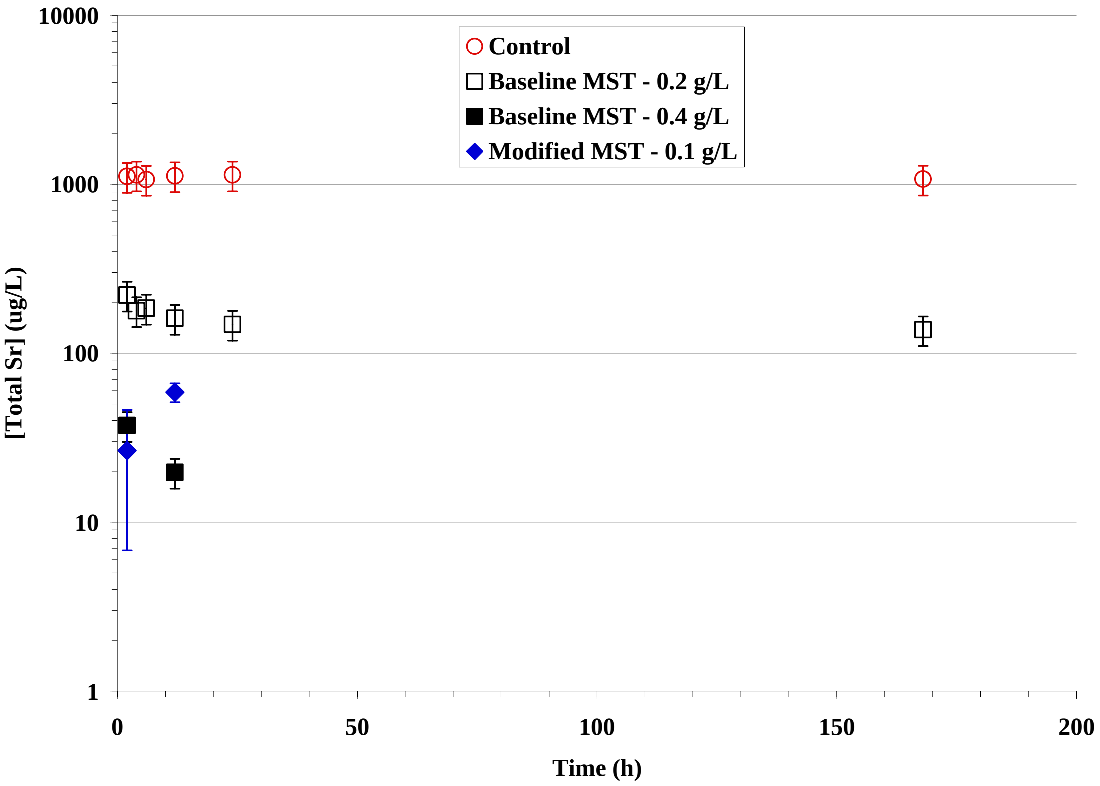

Figure 23. Strontium Concentration Versus Contact Time in Actual Waste Tests with Vendor-prepared Modified MST and Baseline MST

Inspection of Table 25 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 this test set may have received less sorbent than the target concentration.

Table 25. Decontamination Factors for Baseline MST, Laboratory Prepared Modified MST and Vendor-prepared Modified MST with Actual Waste

	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		Laboratory Prepared Modified MST @ 0.2 g/L		Vendor Prepared Modified MST @ 0.2 g/L		Laboratory Prepared Modified MST @ 0.1 g/L		Vendor Prepared Modified MST @ 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		Laboratory Prepared Modified MST @ 0.2 g/L		Vendor Prepared Modified MST @ 0.2 g/L		Laboratory Prepared Modified MST @ 0.1 g/L		Vendor Prepared Modified MST @ 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		Laboratory Prepared Modified MST @ 0.2 g/L		Vendor Prepared Modified MST @ 0.2 g/L		Laboratory Prepared Modified MST @ 0.1 g/L		Vendor Prepared Modified MST @ 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

Modified MST results are average and standard deviation of six trials
Baseline MST results are single determinations with reported analytical uncertainty
Values in red are calculated from ^{238}Pu results as the determination of $^{239/240}$Pu fell below quantifiable limit

Comparison of the strontium DF values measured for the laboratory prepared modified MST (Dataset #1) and the vendor-prepared modified MST (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 vendor-prepared modified MST exceeded those measured for the laboratory prepared modified MST. This finding suggests that the vendor-prepared modified MST performs as good as or better than that of the laboratory prepared modified MST with respect to strontium removal.

Figure 24 shows the total plutonium concentration versus time for the seven tests. The results indicate more rapid removal of plutonium by the modified MST compared to the baseline MST. Also, at earlier contact times, the modified MST 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 $^{239/240}$Pu 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 ^{238}Pu concentration to evaluate plutonium DF values for vendor-prepared modified MST tests as reported in Table 25.

Comparison of the plutonium DF values for the laboratory and vendor-prepared modified MST samples revealed that the vendor-prepared sample exhibited higher values over the entire contact time at both sorbent concentrations (0.1 and 0.2 g L^{-1}). Further inspection of Table 25 revealed 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.

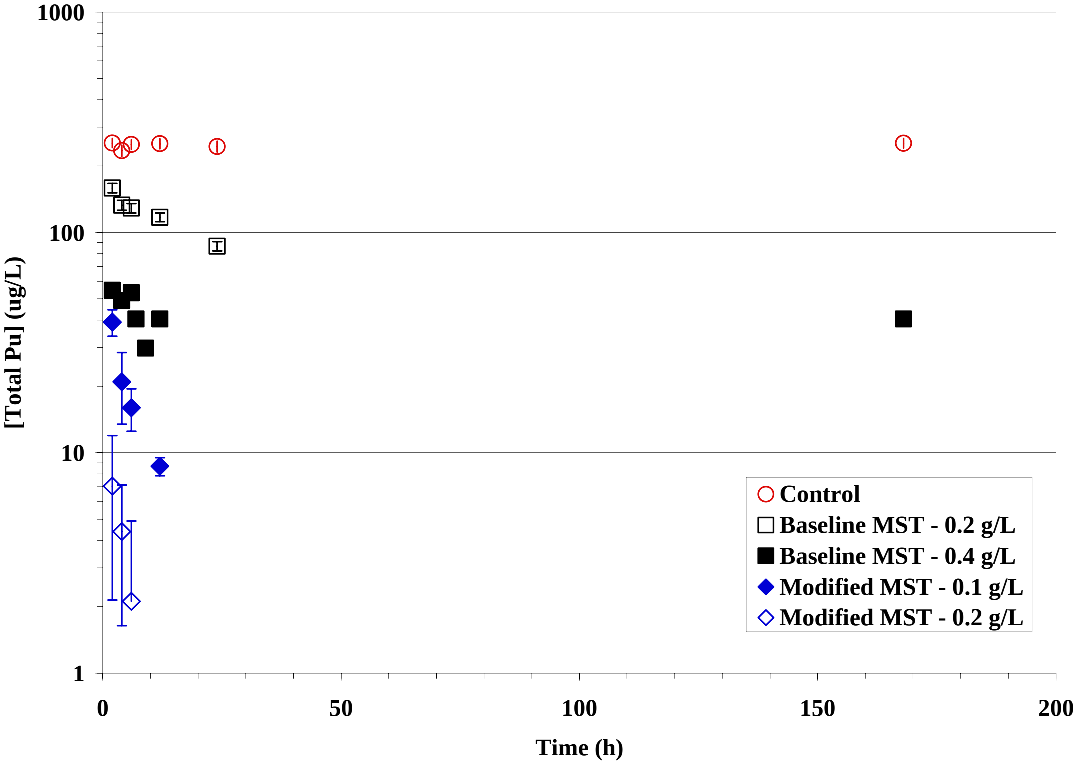

Figure 24. Total Plutonium Concentration Versus Time for the Vendor-prepared Modified MST and Baseline MST Samples with Actual Waste Solution

Figure 25 shows a plot of the ^{237}Np concentration versus contact time for the tests. The modified MST concentrations are the average of duplicate tests. Error bars for the modified MST data are the single standard deviation of the duplicates. The control samples include the reported analytical uncertainty of ± 20% for the ICP-MS analytical method. We omitted the analytical uncertainty bars for the baseline MST for clarity.

In general we observed that an increase in the concentration of the modified MST 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 (see Fig 25). Neptunium removal by the vendor-prepared modified MST 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 (see Fig. 21), but is consistent with the earlier actual waste tests (see Section 4.3.1). Thus, the measured DF values in this test set for the vendor-prepared modified MST are very similar to those measured for the laboratory prepared modified MST in Dataset #1 (see Table 25). Based on these findings, we conclude that the neptunium removal characteristics of the vendor-prepared modified MST are comparable to that of the laboratory prepared modified MST and the baseline MST with actual waste solutions.

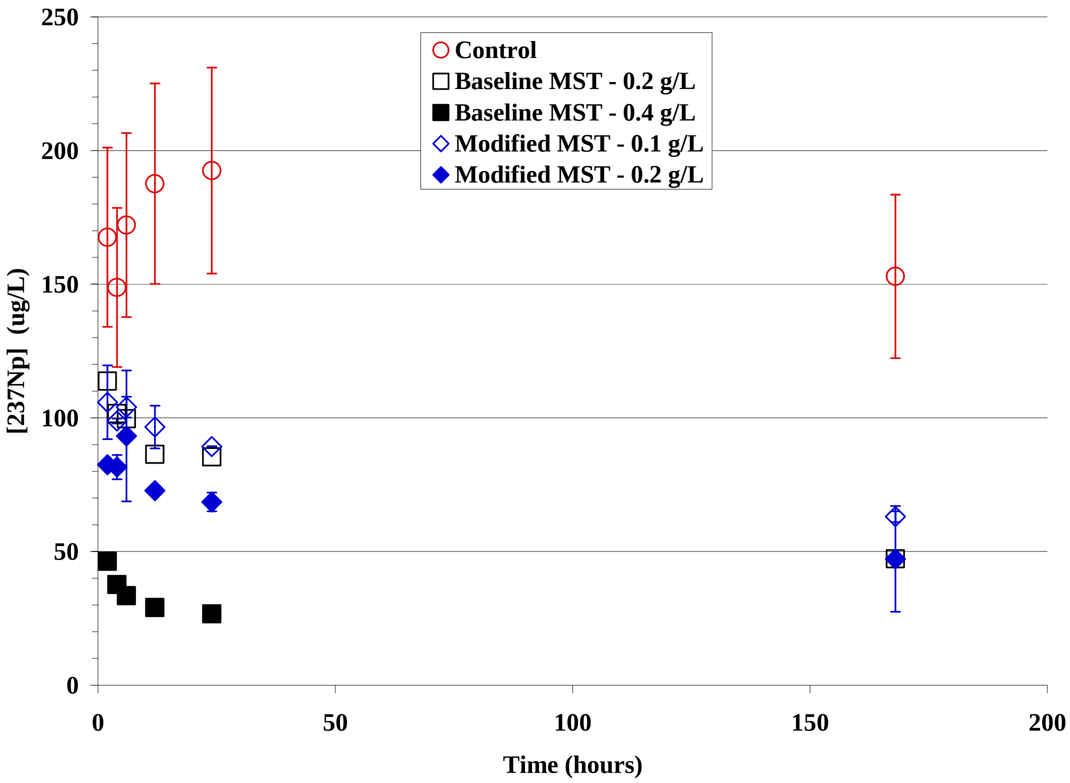

Figure 25. ^{237}**Np Concentration Versus Time for the Vendor-prepared Modified MST and Baseline MST Samples with Actual Waste Solution**

Figure 26 shows a plot of the ^{238}U concentration versus contact time for the seven tests. As with earlier tests with actual and simulated waste solutions, we observed no discernible uranium removal when the modified MST was added at 0.1 or 0.2 g L^{-1}. Tests with the baseline MST material did exhibit measurable amounts of removed uranium. Given these results we conclude that the modified MST material exhibits lower affinity for uranium than the baseline MST, which is consistent with those found with laboratory prepared modified MST.

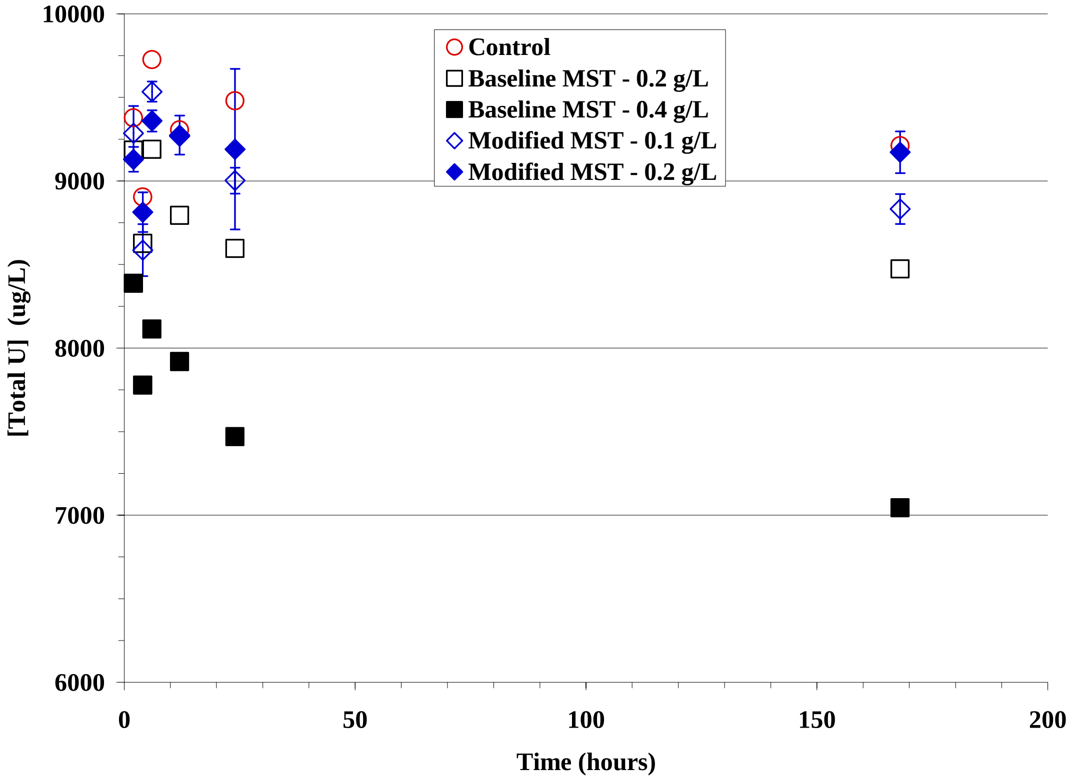

Figure 26. ^{238}U Concentration Versus Time for the Vendor-prepared Modified MST and Baseline MST Samples with Actual Waste Solution

4.7 Task 4 – Characterization of Modified MST Samples

4.7.1 Particle Size Distribution, Particle Morphology and Surface Area

We measured the particle size distribution of the three modified MST samples prepared at the 25-gram scale using a Microtrac S3000 instrument. Figure 27 provides a graph of the volume distribution data for these three samples as well as a sample of the baseline MST material (Optima Chemicals, Inc. Batch #00-QAB-417). For all materials, we diluted the sample into deionized and distilled (DDI) water for the particle size measurement. Note that the three modified MST samples were synthesized by treating 25-gram quantities of the Optima Batch #00-QAB-417 MST with hydrogen peroxide (Method 3).

The particle size data indicate very little change in the particle size distribution of the modified MST samples compared to the baseline MST sample. The modified MST samples exhibit a similar bimodal distribution of particle volumes as compared to the baseline MST. Two of the three modified MST samples (LS-1 and LS-3) exhibited a slightly smaller fraction of particles smaller than 1 micron and larger than 10 microns. This may indicate some removal of fines and larger particles during the synthesis of the modified MST samples. However, the amount of change is very small. These findings suggest that the post treatment synthesis method introduces little change in the primary particle size of the MST.

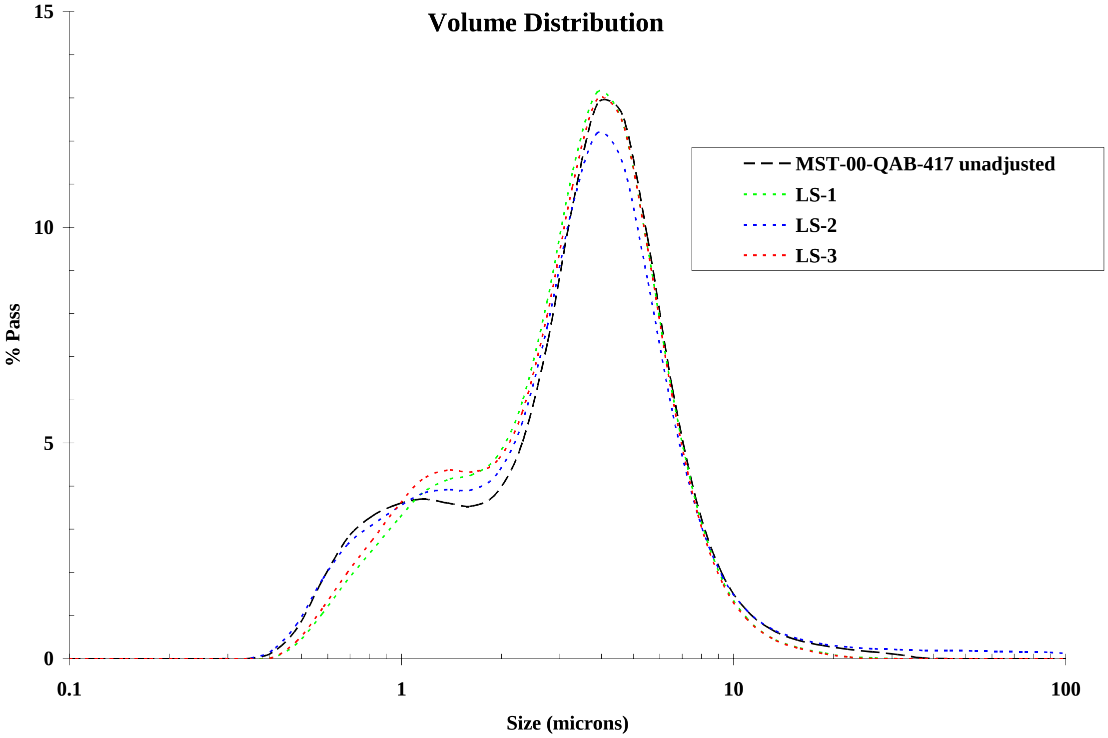

Figure 27. Particle Size Distribution of Laboratory Prepared Modified MST (LS-1, LS-2 and LS-3) and Baseline MST (Optima 00-QAB-417) Samples in Water

Plots of the particle size distribution for each of the samples from the vendor-prepared modified MST suspended in water are shown in Figure 28. The graphs indicate that the particle size distributions are very similar for each of the four modified MST samples and reveal a trimodal distribution. The largest fraction of the modified MST samples is centered at a particle size of about 12 microns. The baseline MST exhibits a bimodal distribution with the larger fraction centered at about 4 microns.

We attribute the difference in particle size characteristics between the baseline and modified MST samples to the difference in the particle size of the vendor-prepared MST from which the modified MST derives and to post synthesis particle classification. As described above, we observed little change in distribution of laboratory-prepared modified MST samples and the baseline MST from which they derived. The vendor did not retain a sample of the initial MST material prior to treating with hydrogen peroxide and, therefore, we cannot compare the particle size distribution of the original MST materials.

Analysis of sub-samples of the modified MST prior to the delivery of the 1-L acceptance test sample revealed that the material exhibited a much higher fraction of larger particles than allowed by the purchase specification. The vendor contracted with another company to perform wet classification of the material to reduce the fraction of large particles. Two evolutions of the classification reduced the fraction of large particle size. The post-synthesis classification likely produced some additional fines that result in the appearance of an additional peak (total of 2 peaks) at the low end of the distribution compared to one for the baseline MST.

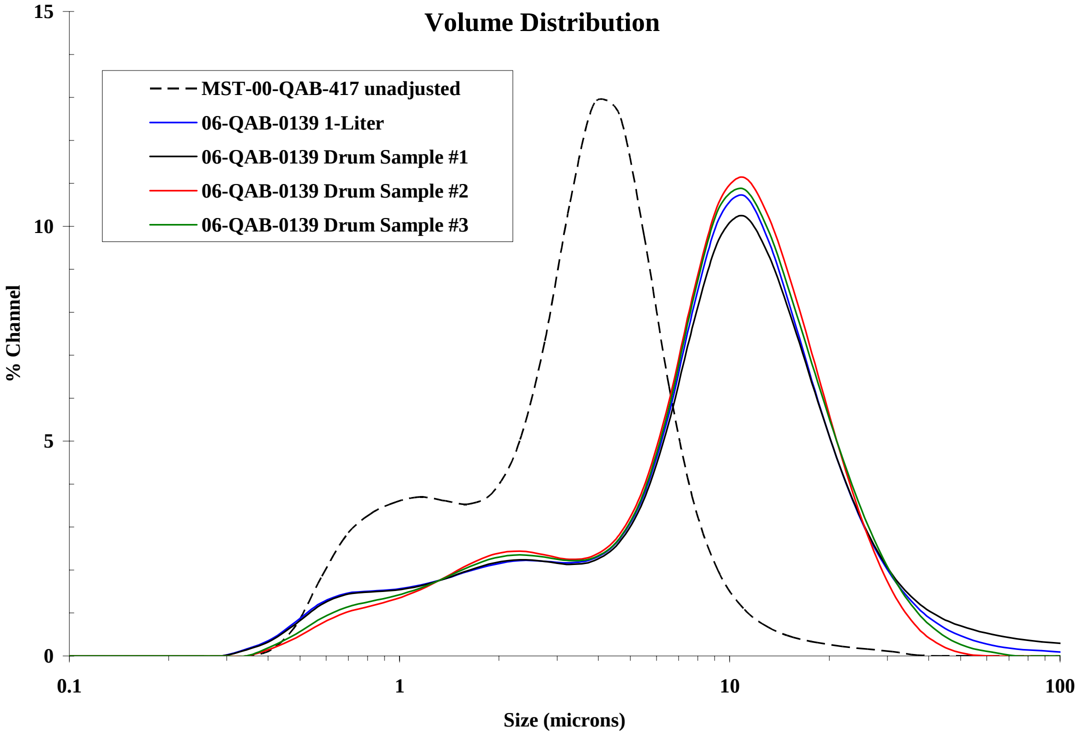

Figure 28. Particle Size Distribution of Vendor-prepared Modified MST (Optima #06-QAB-0139-1L, 06-QAB-0139-D1, 06-QAB-0139-D2 and 06-QAB-0139-D3) and Baseline MST (Optima 00-QAB-417) Samples in Water

To provide a comparison of particle sizes of the baseline and modified MST materials under processing conditions, we measured the particle size of the samples suspended in a 5.6 M sodium salt solution having the same chemical composition as that shown in Table 1, but without any radioactive components. Suspension of the MST solids in this highly alkaline salt solution would convert proton forms of the modified MST samples to the sodium forms. The particle size distribution measured in this solution will provide an indication of the distribution present during adsorption and filtration stages during pretreatment of alkaline waste solutions.

Figure 29 provides a plot of the particle size distributions of the MST (Optima #00-QAB-417) and the three laboratory-scale modified MST materials (LS-1, LS-2 and LS-3) derived from the MST in both salt solution and water. The particle size distribution for each of the materials in salt solution exhibits a narrower and less pronounced bimodal distribution compared to that in water. Interestingly, the fraction of both small (<1 μ) and large (>10 μ) particles is reduced in salt solution compared to water.

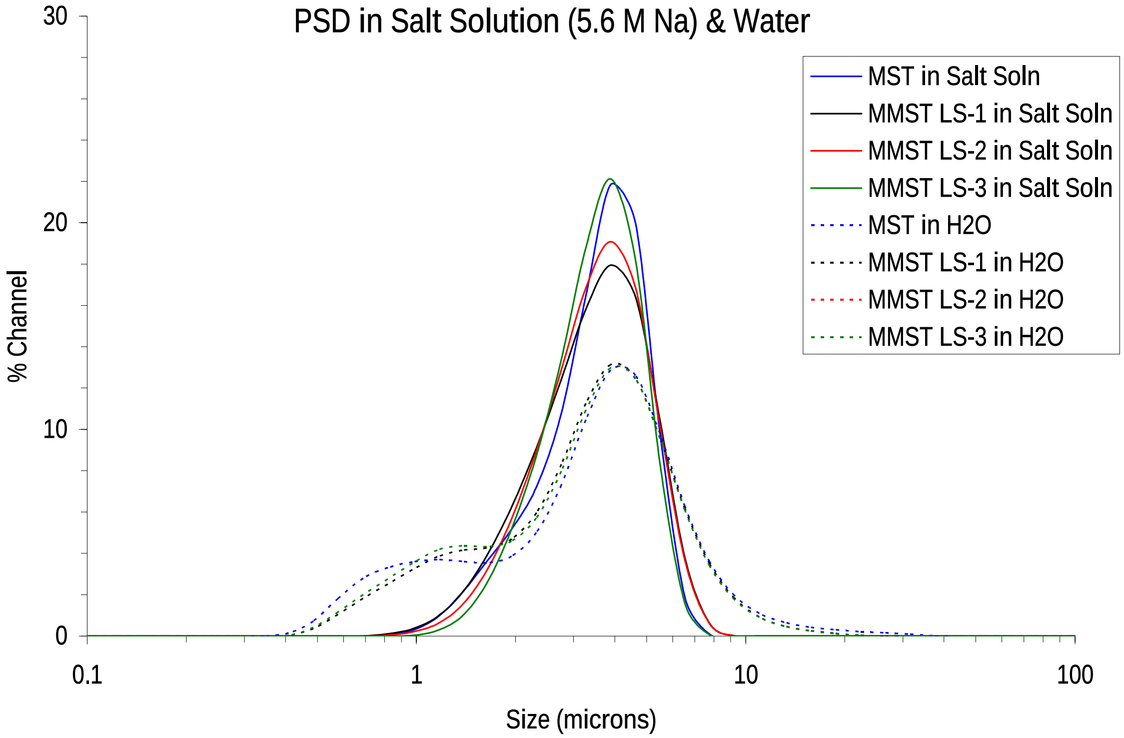

Figure 29. Particle Size Distribution of MST (Optima #00-QAB-417) and Laboratory Scale Modified MST Samples (LS-1, LS-2 and LS-3) in Salt Solution and Water

Figure 30 provides a plot of the particle size distributions of the four vendor-prepared modified MST materials (Optima #06-QAB-0139-1L, 06-QAB-0139-D1, 06-QAB-0139-D2 and 06-QAB-0139-D3) in both salt solution and water. The particle size distribution for each of the materials in salt solution exhibits a narrower and bimodal distribution compared to broader and trimodal distribution in water. As observed with the baseline MST and laboratory produced modified MST samples, the fraction of both small (<1 μ) and large (>10 μ) particles is reduced in salt solution compared to water.

Inspection of both Figures 29 and 30 indicates that the vendor-prepared modified MST exhibits a broader distribution of particle sizes (1 – 20 μ) in salt solution compared to that of the baseline MST and laboratory prepared modified MST samples (1 – 8 μ). Figure 31 provides a plot of the particle size distribution of the laboratory and vendor-prepared modified MST samples in the 5.6 M sodium salt solution. Clearly, the vendor-prepared modified MST exhibits both a broader distribution and larger particle size than the laboratory prepared modified MST samples and the baseline MST from which the laboratory prepared modified MST were produced. The broader distribution of particle sizes of the vendor-prepared modified MST suggest that this material may produce a denser cake (i.e., particles may packed together tighter) than the baseline MST or the laboratory prepared modified MST materials. The formation of a denser filter cake could result in reduced filter flux (see Section 4.7.4).

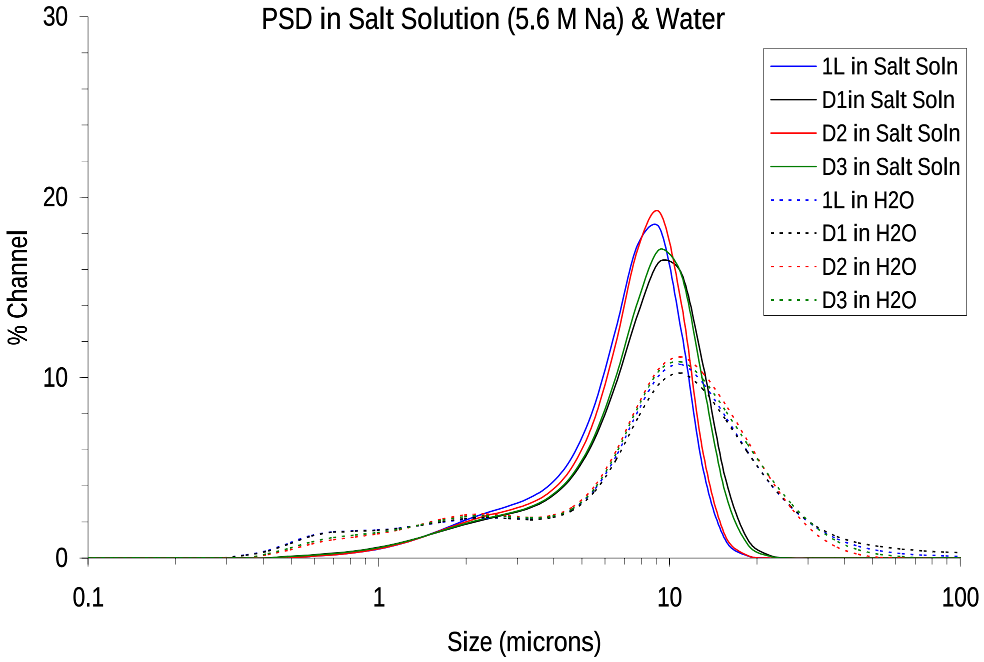

Figure 30. Particle Size Distribution of Vendor-Prepared Modified MST Samples (Optima #06-QAB-0139-1L, 06-QAB-0139-D1, 06-QAB-0139-D2 and 06-QAB-0139-D3) in Salt Solution and Water

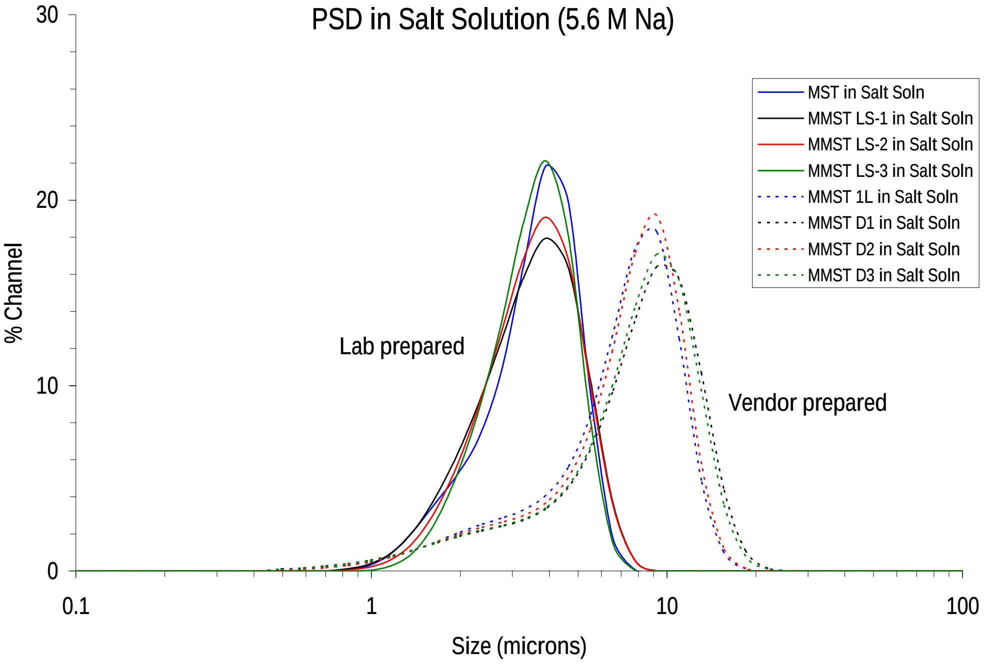

Figure 31. Particle Size Distribution of Baseline MST (Optima #00-QAB-417), Laboratory Prepared Modified MST (LS-1, LS-2 and LS-3) and Vendor-Prepared Modified MST Samples (Optima #06-QAB-0139-1L, 06-QAB-0139-D1, 06-QAB-0139-D2 and 06-QAB-0139-D3) in Salt Solution

We evaluated the particle morphology of the modified and baseline MST materials using scanning electron microscopy (SEM). Figures 32 – 34 provide selected SEM images obtained with the MST samples. The baseline MST (Fig. 32) exhibits a spherical shape consisting of a tightly woven network of smaller irregularly-shaped particles. The laboratory prepared modified MST sample, LS-1 (Fig. 33) exhibits a more irregular shaped morphology and less spherical shape than the baseline MST sample. Also, the smaller particles in the network appear with higher definition and more intra-particle porosity. This change in appearance is consistent with surface area measurements, which indicate a much higher surface area and micro-porosity than the baseline MST (see below). The vendor-prepared modified MST (Fig. 34) exhibits an irregular-shaped morphology with a ‘cauliflower’-like appearance for the primary particles. This morphology would be expected to exhibit a relatively high surface area and porosity similar to that observed for the laboratory prepared modified MST.

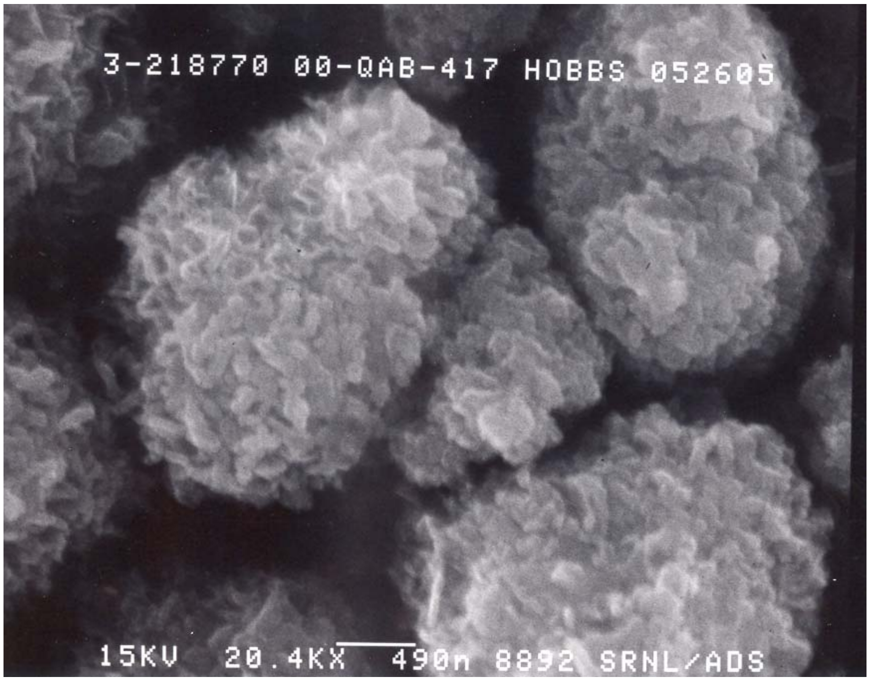

Figure 32. SEM Image of Baseline MST – Optima #00-QAB-417 (Magnification 20,400X)

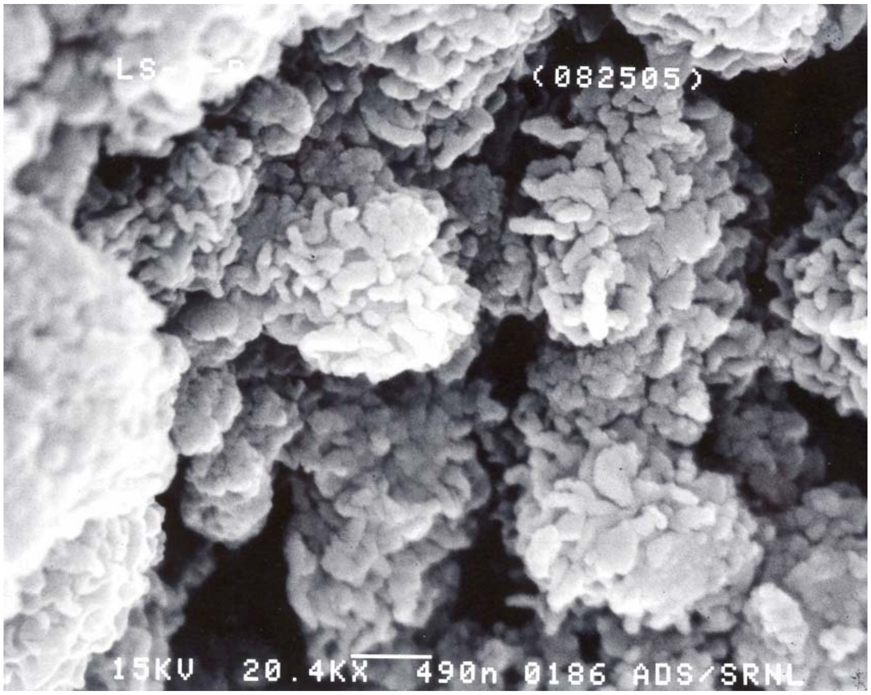

Figure 33. SEM Image of Modified MST – Laboratory Prepared Sample LS-1 (Magnification 20,400X)

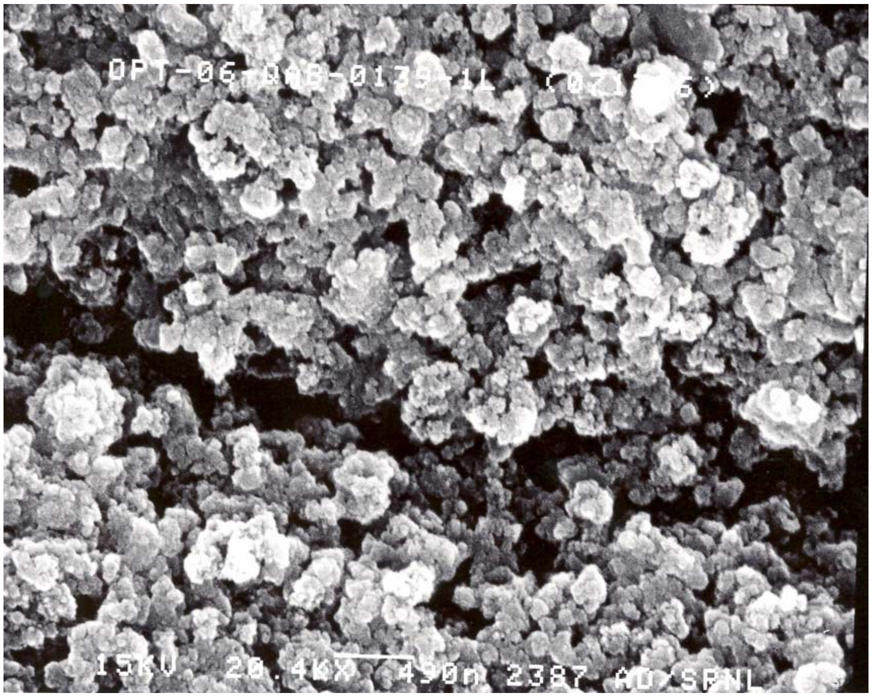

Figure 34. SEM Image of Modified MST – Vendor-prepared Sample #06-QAB-0139-1L (Magnification 20,400X)

Surface area (SA) measurements were obtained by the Brunauer-Emmett-Turner (BET) method for analysis of adsorption isotherms on a Micromeretocs ASA2010 Porosimeter Analyzer at the University of South Carolina. Nitrogen was used as the adsorbate, and samples were outgassed under vacuum at room temperature over night prior to analysis. Micropore surface areas were determined by T-plot analysis and average pore size were obtained via the Barrett-Joyner-Halenda (BJH) method of analysis of desorption isotherms. Table 26 provides a summary of the results for the baseline MST and the laboratory prepared modified MST.

Surface area measurements revealed that the peroxide treatment of the baseline MST produced modified MST samples having much higher surface areas. Furthermore, the pore size of the modified MST measured 27.2 – 36.9 Å compared to 206 Å for the baseline MST starting material. The much smaller pore size for the modified MST samples is consistent with the introduction of intra-particle porosity in contrast to the relatively large pore size for the baseline MST indicative of inter-particle porosity. These results are consistent with the findings from the SEM images and suggest that the improved strontium/actinide removal performance of the modified MST materials derives largely from increased surface area and porosity.

Table 26. Surface Area and Porosity of Baseline and Modified MST Samples

Sample ID	BET SA ($m^2\ g^{-1}$)	BJH Pore Size (Å)
MST #00-QAB-417	16.7	206
MMST #LS-1	106	27.2
MMST #LS-2	176	28.8
MMST #LS-3	178	36.9

If the improved sorption kinetics and apparent capacity of the modified MST largely results from the increased surface area and porosity of the modified MST compared to the baseline MST, we would expect that both materials would show the same or very similar sorbate removal at equilibrium. For the lower surface area and less porous material, the time to reach equilibrium may be well in excess of 168 hours, which is the typical maximum contact time that we analyze for sorbate removal. To test this hypothesis, we carried out a long contact test in which we contacted simulated waste solution (SWS-8-2004) with 0.2 g L^{-1} of the modified MST (LS-1) and baseline MST (00-QAB-417) at ambient laboratory temperature for 7,224 hours or 301 days. Over the course of this test, we obtained 11 solution samples from each test bottle beginning at 24 hours. Each of the samples was prepared as previously described and analyzed for plutonium content.

Figure 35 provides a plot of the plutonium concentration versus time for the extended contact test. Plutonium concentrations shown at contact times less than 24 hours come from previously reported tests with the same sorbents, sorbent concentrations and simulated waste solution. The 24-h and 168-h sample results show greater removal of plutonium for the test with modified MST compared to that with the baseline MST, which is consistent with results in earlier tests (see Fig. 11). The test with the modified MST appears to be at equilibrium after about 24 hours.

The baseline MST test continues decreasing in concentration and after 504 hours (36 days) the difference in plutonium concentrations between the modified and baseline MST tests has narrowed significantly. After 672-hours (28 days), the baseline MST has removed plutonium from solution to the same degree as the modified MST and remains at this condition over the remainder of the test. Note that the samples taken at 2738-hours (114-days) and 3533-hours (147-days) for both tests exhibited much higher plutonium concentrations suggesting some desorption and release of plutonium into solution. Reanalysis of these samples confirmed the reported results. We do not have an explanation for the cause of the increased concentrations at the 114 and 147-day sampling events.

After about 5000 hours the plutonium concentrations in the two tests have decreased again and measure well below 5 ug L^{-1} and remain at the low concentrations for the next 91-days at which time the test was terminated. For plutonium, these findings provide support to our hypothesis that the chemical modification of the baseline MST produces materials with significantly faster plutonium adsorption kinetics (i.e., makes adsorption sites more accessible), but does not change the total number of adsorption sites for plutonium.

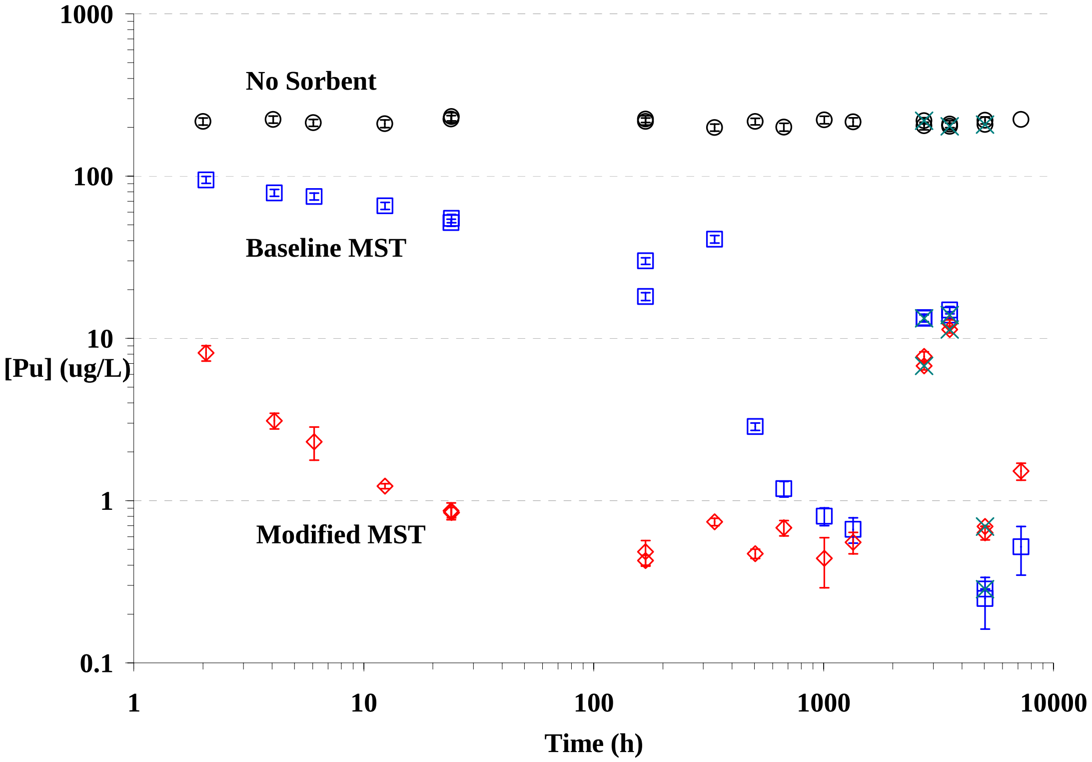

Figure 35. Plot of Plutonium Concentration Versus Time in the Extended Contact Test

4.7.2. Gas Release During and After Preparation of Modified MST

During the synthesis of the modified MST we observed the formation and release of gas bubbles. We conducted a test to identify the composition of the gas formed during synthesis. For this test, we prepared a 25-g batch of the modified MST using the same procedure and equipment as described in the experimental section and collected two gas samples for analysis during the addition of the hydrogen peroxide. Gas samples were collected by locating a glass sampling bulb between the reactor and bubbler such that any gases formed pass through the sample bulb before venting to the atmosphere through the bubbler.

Figure 36 provides a photograph of the experimental equipment. Hydrogen peroxide solution was added dropwise from the addition funnel to the well-agitated MST suspension contained in the reaction vessel. Evolved gases pass out of the reactor vessel through the gas sampling bulb and exit through the water bubbler. After collection of the gas sample, both stopcock valves on the gas sample bulb are closed, the bulb removed from the system and delivered to the Analytical Development Department for analysis.

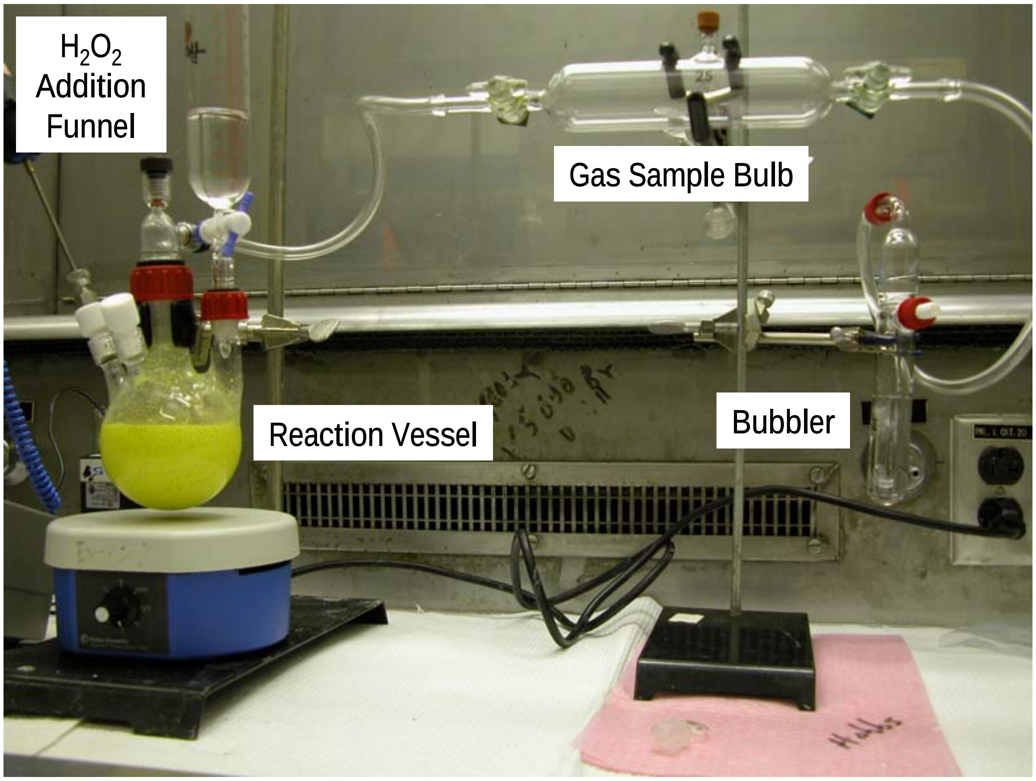

Figure 36. Photograph of Equipment for Collecting Gas Samples During the Synthesis of the Modified MST

Gas Sample #1 was collected up until one-half of the hydrogen peroxide had been added to the reaction flask. Gas Sample #2 was collected from during the second half of the hydrogen peroxide addition. Both gas samples were analyzed in duplicate by the Analytical Development Department of SRNL. Analysis indicated that both samples were principally oxygen (95 – 98%) with small amounts of nitrogen (5 – 8 %). The small amount of nitrogen results from residual air that had not been displaced by the evolved oxygen. No hydrogen (<0.1%) was detected in either sample. The high concentration of oxygen and absence of hydrogen is consistent with the decomposition of hydrogen peroxide to produce oxygen and water.

In addition to gas evolution during the synthesis of the modified MST by Method 3, we observed continued gas release during the storage of the modified MST samples for several weeks. Gas bubbles were seen on the walls of containers containing the modified MST slurry. Upon gentle shaking of the bottles, the gas bubbles easily released to the vapor space. Gas formation appeared to decrease with time. Possible sources of the gas release include trapped oxygen from the synthesis of the modified MST and decomposition of a titanium-peroxide species to release oxygen.

To evaluate the quantity and time dependent behavior for the formation of oxygen, we constructed a test chamber that allowed for the measurement of gas released to the vapor space. Figure 37 provides a photograph of the system. A cylindrical plastic tube was filled with a freshly prepared 25-g batch of modified MST. The system was closed to the atmosphere so that any gas produced and released to the vapor space displaced water in the attached U-tube. The volume of displaced liquid was measured periodically by pulling the released gas into a gas-tight 1.0-mL syringe, which returns the liquid levels to their original position in the U-tube. After recording the volume, the system was vented to the atmosphere and then closed again. Time intervals were recorded between each set of measurements.

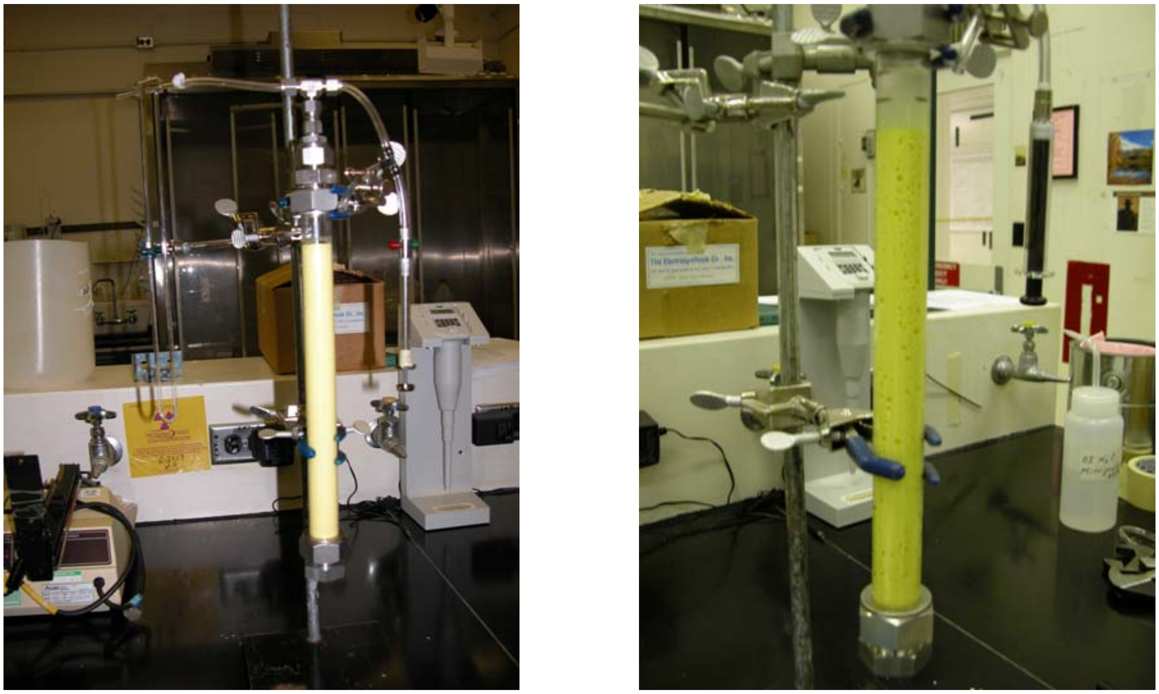

Figure 37. Photographs of Gas Release Equipment. Left photograph is a view of the entire system including the water filled U-tube, the plastic cylinder containing the modified MST suspension and the gas-tight syringe. Right photograph is a close-up view showing gas bubbles in the modified MST suspension after standing overnight.

Over the course of the experiment, gas accumulated in the slurry resulting in an overall increase in the height of the suspension. Periodically, we tapped the walls of the cylindrical tube to release this trapped gas. In addition to releasing trapped gas, tapping also suspends some fraction of the settled solids. After 12 days, we opened the system and mixed the contents of the cylindrical tube with a stainless steel rod to re-suspend the solids. After mixing, the system was again closed and gas release measurements continued for another 15 days for a total of 27 days.

Figure 38 provides a plot of the measured gas release rate (mL min^{-1}) versus elapsed time (days) for the freshly prepared batch of modified MST. Initially the release rate measured approximately 0.15 mL min^{-1} (per 125 g of 15 wt % slurry) and rapidly decreased by an order of magnitude within 2 days and two orders of magnitude after about 20 days. Four weeks after the preparation of the modified MST, the gas release rate is 0.0011 mL min^{-1}. Thus, after four weeks the gas release rate per gram of modified MST slurry containing 15 wt% solids measured 8.6E-06 mL min^{-1} g^{-1}. Using a value of 1.10 g mL^{-1} for the density of 15 wt % slurry of modified MST, the release rate on a slurry volume basis is 50 mL day^{-1} L^{-1}.

We kept the modified MST slurry in the gas measuring equipment and allowed the suspension to stand unattended at ambient laboratory temperature. Periodically we inspected the equipment and observed gas bubbles within the slurry indicating continued gas formation from the solids. With time, the quantity of gas bubbles in the slurry continued to diminish. After approximately 4 months, we observed no additional gas bubbles in the slurry. To confirm that gas formation and release had ceased, we closed the system to the atmosphere and monitored the system for release of gas. Over the course of one week, we observed no gas release. Thus, we conclude that gas formation of the laboratory produced modified MST slurry decreases below a measurable quantity within four months of the synthesis.

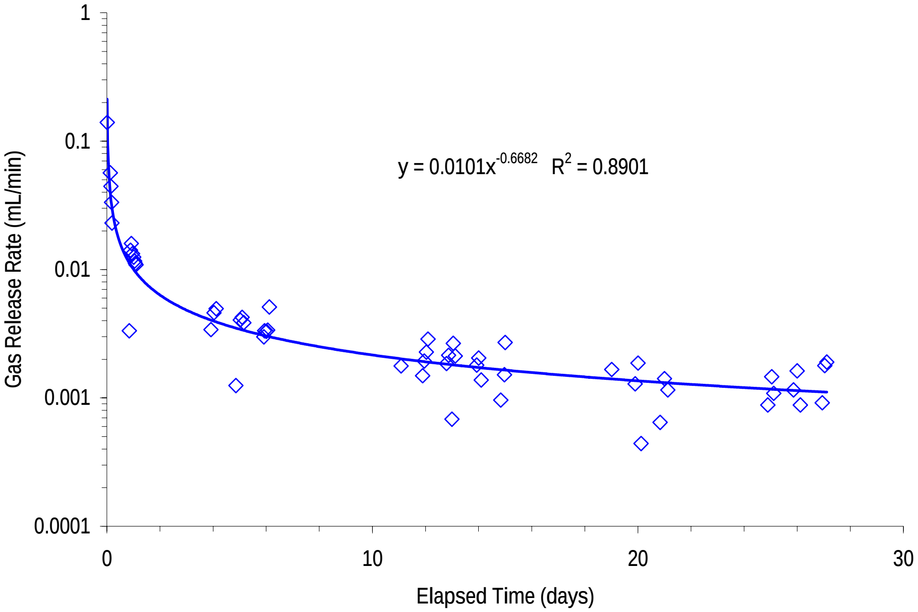

Figure 38. **Gas release rate (mL min^{-1}) versus elapsed time (days) for freshly prepared modified MST.**

4.7.3 Solids Settling Characteristics

We measured the settling characteristics of the baseline and modified MST in aqueous solution over a range of pH values. The baseline and modified MST suspensions used in this test were Optima Batch #00-QAB-417 and Optima Batch #06-QAB-0139, respectively. The pH of the as-received baseline and modified MST suspensions measured 10.47 and 4.84, respectively. We prepared suspensions of each MST sample at pH values as 6, 7, 8, 9 and 10 by adding 2M nitric acid solution to the baseline MST suspension and 2 M NaOH solution to the modified MST suspension. After mixing for 30 minutes, we pipetted approximately 11-mL aliquots from each of the as-received and pH-adjusted suspensions into separate 15-mL glass centrifuge tubes. The suspensions stood at ambient laboratory temperature undisturbed for 50 days. We periodically inspected each tube and measured the height of the settled solids.

Figure 39 provides plots of the height of the settled solids (mm) versus settling time (hours) for the extreme pH conditions tested with each sorbent material. Initially, the height of each of the suspensions measured 17.5 mm. After 2 hours of settling, the height of the settled MST solids measured about 50% of the initial suspension height. The MST suspensions slowly settled after this time to about 40% of the initial height. We observed little difference in settling characteristics among the MST solids adjusted to a pH of between 6 and 10.47. The modified MST solids settled to a lesser degree than the baseline MST solids. After about 2 hours of settling, the height of the modified MST solids measured about 58% of the initial height. The suspensions containing the modified MST solids settled at a slower rate than the suspensions containing the baseline MST reaching between 48 – 56% of the initial height at the conclusion of the test. Unlike the baseline MST suspensions, the extent of solids settling correlated linearly with pH with increased settling occurring with an increase in the pH of the modified MST suspension. The overall reduced extent of settling for the modified MST solids suggests that the modified MST particles have a lower apparent density than the baseline MST material, which results in reduced gravity settling in aqueous suspensions.

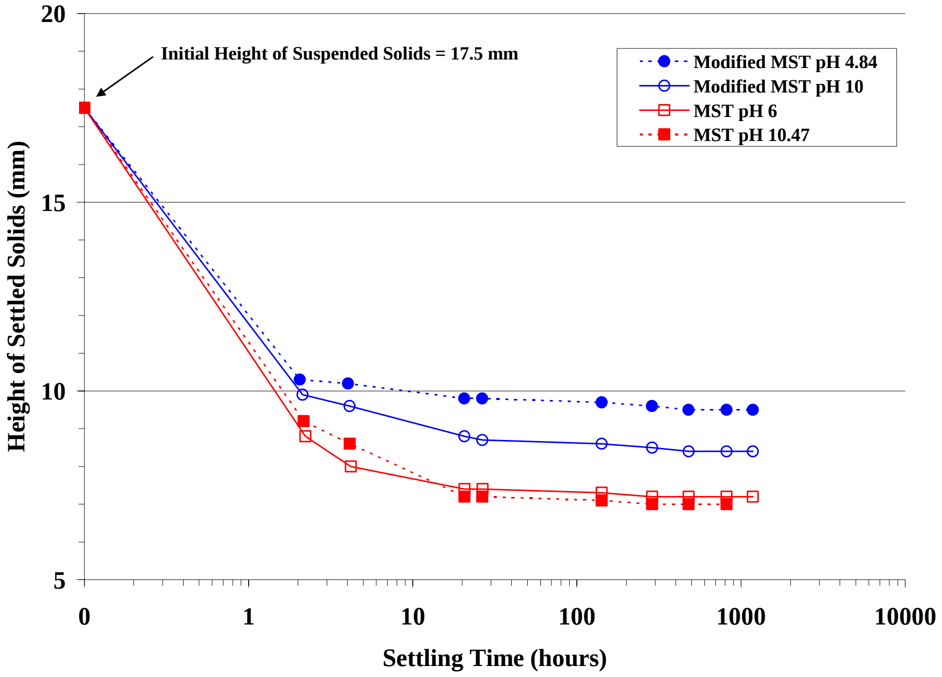

Figure 39. Height of Settled Solids Versus Settling Time for Modified and Baseline MST.

4.7.4 Filtration Characteristics

4.7.4.1 Tests with Laboratory Prepared Modified MST

Previous SRNL work shows that dead-end filters, such as the stirred cell, can provide a reliable qualitative comparison of the filterability of different feed slurries.[16,17] Using the stirred cell (see Figure 1) as a screening tool allows performing many tests in a short time and at much lower cost than performing all of the tests with a prototypical crossflow filter. These tests used a simulated waste solution having the chemical composition shown in Table 7 and laboratory prepared (25-g scale) samples of modified MST designated as LS-1, LS-2 and LS-3.

Figure 40 shows the results from the tests conducted in triplicate with the TruMem® media. We observed no difference in filtrate rate between the baseline MST and the modified MST with the TruMem® media.

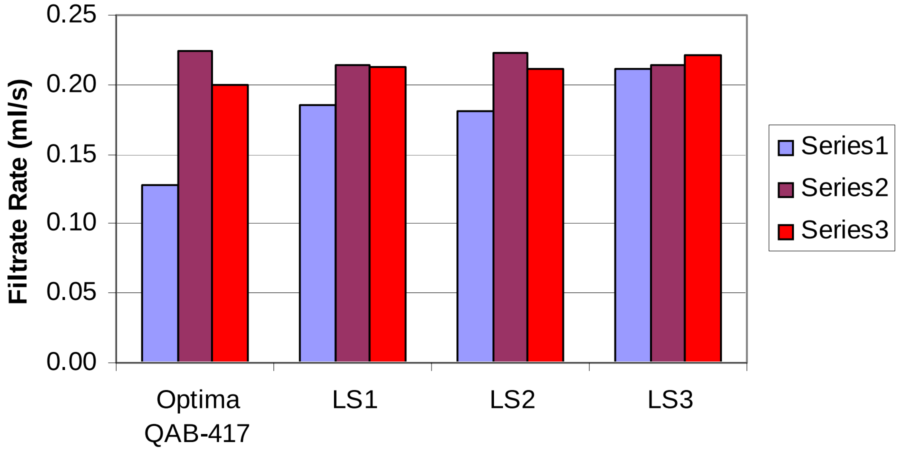

Figure 40. Filtration Rate with 0.1-μm TruMem® Media (each MST sample tested in triplicate).

Figure 41 shows the results from the tests conducted with the Mott media. We performed two sets of tests each in triplicate with this filter media. In general we observe a decrease in filtration rate in the second test set compared to the first set. This offset is likely due to differences in the feed slurry for the two tests. Preparation of the feed slurry includes preparing simulated supernate, collecting samples of MST from a slurry (~ 15 wt %), adding the MST to the supernate, and mixing the MST-supernate slurry. Differences between the two supernates are likely to have minimal effect on filtration rate. Given that the MST slurry is ~ 15 wt % and that the solids settle and compact tightly, there could be differences in the particle size of the MST added to the supernate, which would impact the filtration rate. However, within each test set, we observe no difference in filtrate rate between the baseline MST and the modified MST.

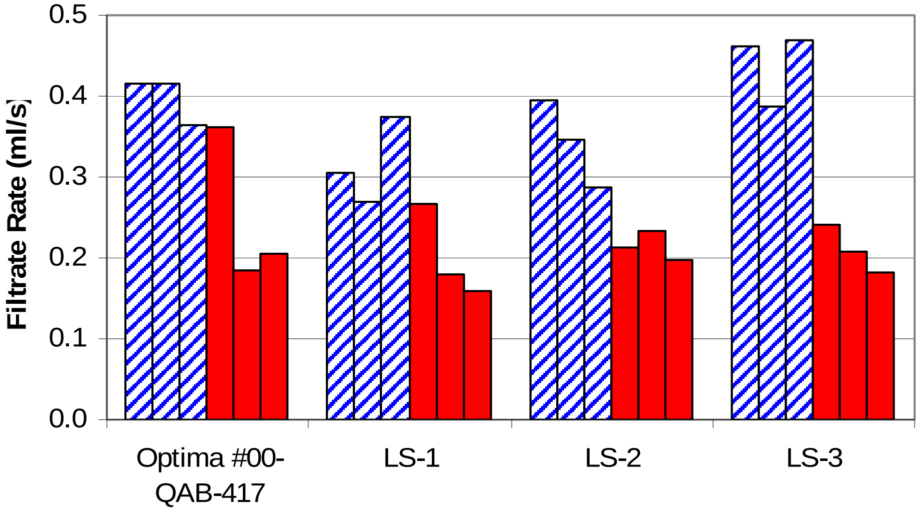

Figure 41. Filtration Rate with 0.1 micron Mott Media (each MST sample tested in triplicate in two different test sets).

Figure 42 shows the results with the 0.1 micron Pall media. The modified MST shows a lower filtration rate than the baseline MST for both sets of tests.

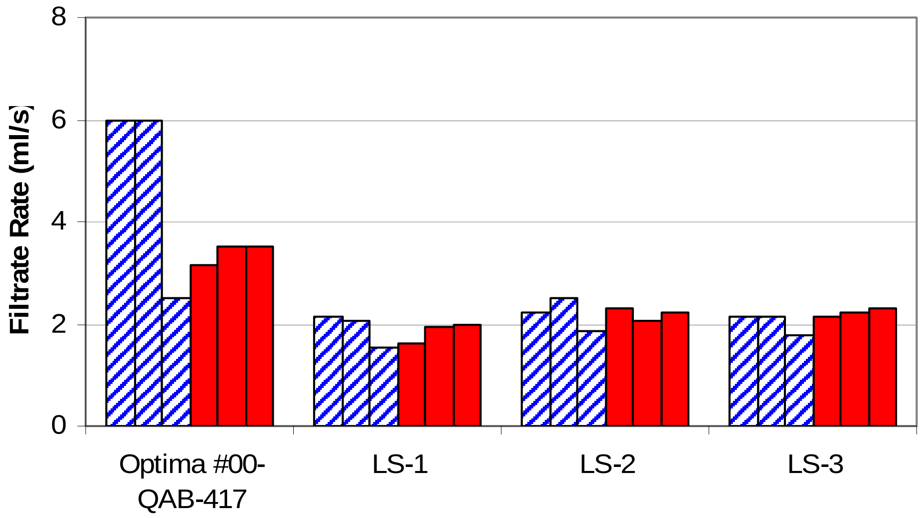

Figure 42. Filtration Rate with 0.1 micron Pall (each MST sample tested in triplicate in two different test sets).

Figure 43 shows the results for the 0.5 micron Pall media. The modified MST shows a lower filtration rate than the Baseline MST.

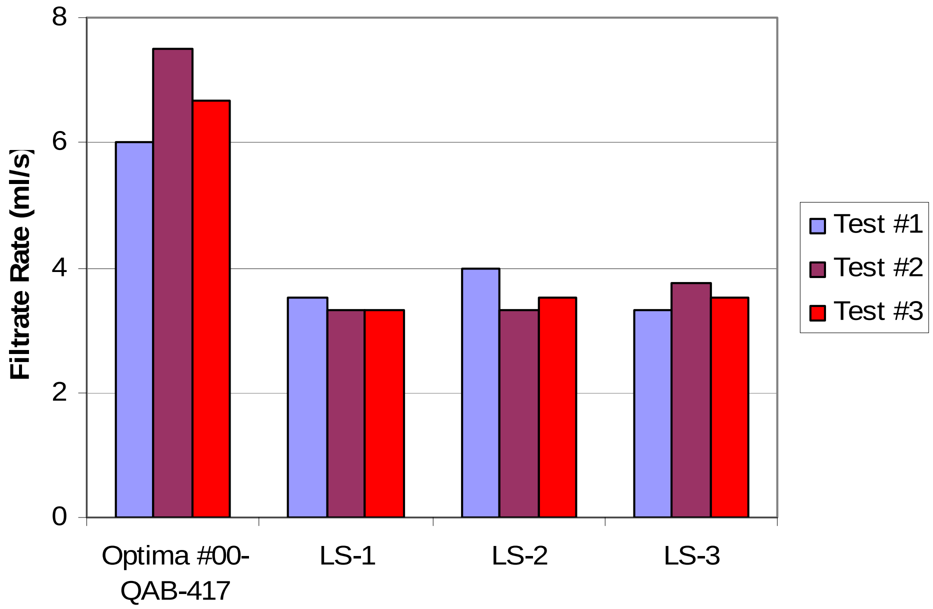

Figure 43. Filtration Rate with 0.5 micron Pall (each MST sample tested in triplicate).

The filter media with smaller absolute pore size (TruMem® and Mott) show no difference in the filtration rates between the baseline MST and the modified MST. The larger pore size media (Pall) show a decrease in filtrate rate with the modified MST. To determine whether there is a correlation between filter absolute pore size and filterability of the modified MST, the authors plotted the normalized filtrate rate (i.e., normalized rate = modified MST filtrate rate/baseline MST filtrate rate) as a function of absolute pore size in Figure 43.

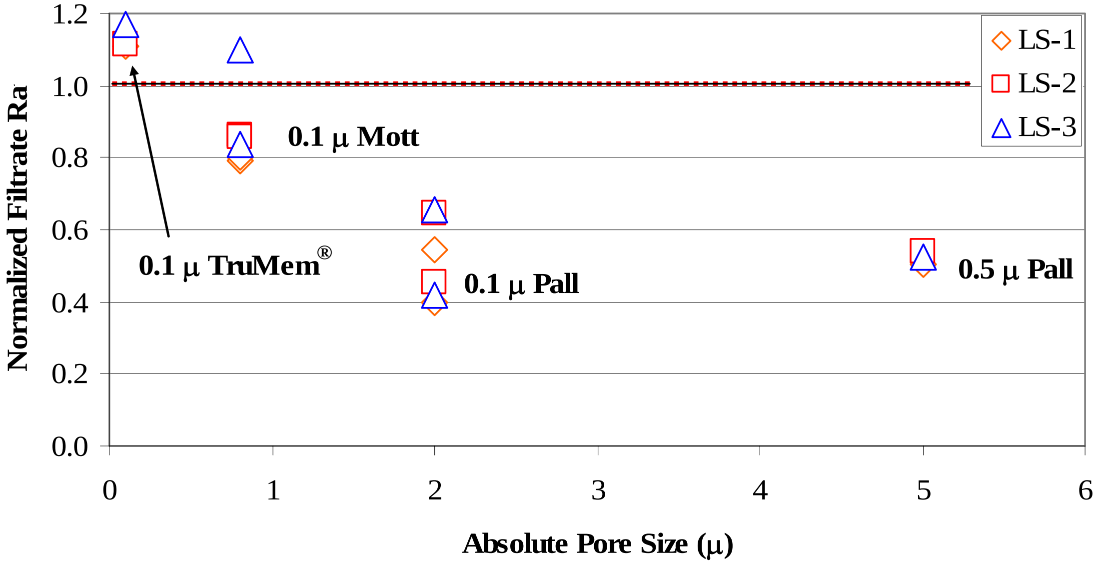

Figure 44. Normalized Filtration Rate of Modified MST as a Function of Absolute Pore Size.

Figure 44 shows a correlation between absolute pore size and normalized filtration rate of the optimized MST. When the absolute pore size is less than 1 μ, there is no significant difference in filtration rate for modified and baseline MST. When the absolute pore size is greater than 1 μ, the modified MST filters more slowly than the baseline MST. This result suggests that the modified MST may have more fine particles than the baseline MST when dispersed in the simulated salt solution. Note that when dispersed in salt solution the particle size data show a minor, but perhaps statistically insignificant, increase in fines between the baseline and laboratory prepared modified MST samples (see Figure 29). The variance appears in the 1 to 2 micron range, which one might expect to be most important for these filters.

4.7.4.2 Tests with Vendor-prepared Modified MST

Figure 44 shows the results from the stirred cell tests with a 0.1-micron Mott filter membrane for the baseline and vendor-prepared modified MST (sample 06-QAB-0139-1L). The average filtrate rate with the baseline MST measured 8.7 ± 3.3 mL min^{-1} compared to 8.8 ± 2.4 mL min^{-1} for the modified MST. The filtrate collected was clear and did not show any solids. Thus, we conclude that the vendor-prepared modified MST exhibited the same filtration characteristics as the baseline MST in the stirred cell testing apparatus. Note, that the filtration rates in this dataset are much higher than those in the previous dataset (see Fig. 39). Thus, we cannot make a direct comparison of the filtration rates between the laboratory and vendor-prepared modified MST samples using the stirred cell filtration equipment. Given the good filtration performance of the vendor-prepared modified MST in the stirred cell test, we proceeded to test the performance of this material in a single tube crossflow filter apparatus (see Section 3.4 and Fig. 1).

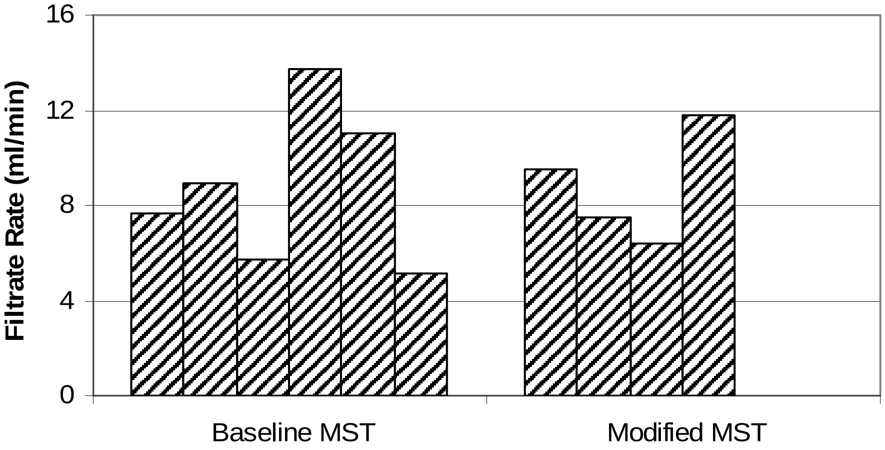

Figure 45. Filtrate Rates for the Baseline MST and Vendor-prepared Modified MST in the Stirred Cell Apparatus.

Figure 46 shows the crossflow filter flux (corrected, using viscosity, to 25 °C) during tests with the baseline and modified MST materials without any sludge solids. The filtrate samples collected were clear and did not show any solids. The baseline MST shows higher flux (1.3 – 2X) than the modified MST at low solids loadings (0.06 and 0.29 wt %). At higher solids loadings (1.29 and 5.0 wt %), we observed the same flux for both materials.

Using the filter flux data measured for sludge and MST slurries, the authors calculated the filtrate time required to concentrate salt solution containing 0.6 g/L sludge and 0.4 g/L MST for the ARP facility. They used the following inputs for the calculation.

- 20 filtration cycles
- 3800 gallons of feed per cycle (76,000 gallons total)
- Initial solids loading of 0.079 wt %
- All solids remain in the filter feed tank
- Final solids loading 5 wt %
- Filtration occurs at 25 °C.
- Filter surface area of 230 ft^2

They calculated the filer flux at solids loadings between 0.079 and 5.0 wt% by interpolating the measured flux data. They numerically integrated the filtration rate as a function of time to calculate the time needed to concentrate the slurry from 0.079 wt % to 5.0 wt %. The cycle time with the baseline MST was 121 hours, and the cycle time with the modified MST was 55 hours.

The authors performed a statistical analysis of the filter flux data with the JMP software. The analysis showed the insoluble solids concentration had the strongest effect. It was statistically significant with higher solids loadings producing lower filter flux. The analysis also showed the MST had a statistically significant effect with the baseline MST producing a higher flux than the modified MST. The TMP and axial velocity did not have statistically significant effects.

The modified MST has a larger particle size than the baseline MST (see Fig. 30). All other factors being the same, a filter cake with larger particles will have higher permeability. However, the vendor-prepared modified MST has a broader particle size distribution and more irregular shape. This broader distribution and more irregular shape can lead to a denser filter cake and lower permeability. At this time we cannot quantify the relative contribution of these two effects.

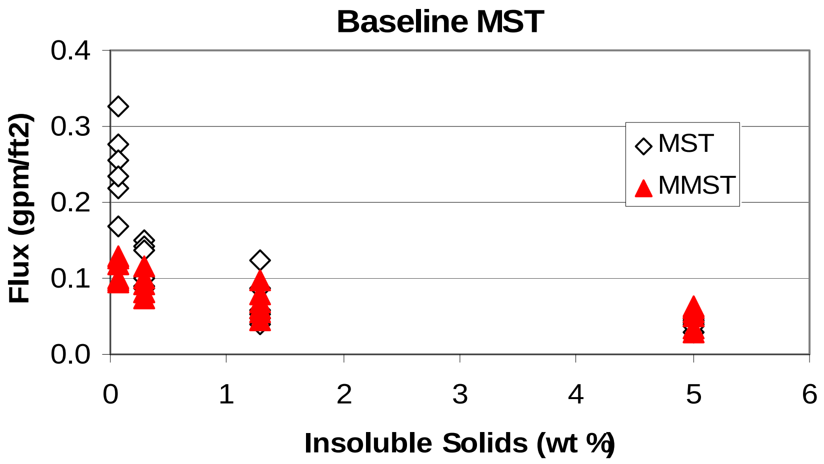

Figure 45. Crossflow Filter Flux for Slurries Containing Only MST Solids.

Figure 47 shows the crossflow filter flux (corrected, by viscosity, to 25 °C) measured with tests containing both sludge and MST solids. The vendor-prepared modified MST-sludge slurries show higher flux than the baseline MST-sludge slurries at all solids loadings. The authors performed a statistical analysis of the filter flux data with the JMP software. The analysis showed the MST had a statistically significant effect with the modified MST producing a higher flux than the baseline MST. The insoluble solids concentration was also statistically significant with higher solids loadings producing lower filter flux. The TMP and axial velocity did not have statistically significant effects.

The higher fluxes for the modified MST-sludge mixture result are somewhat surprising given that the previous results with MST-only suspensions. Previous testing indicated that mixtures of the baseline MST and sludge filter more slowly than MST alone. This dataset confirms this trend for the baseline MST (compare Figs. 45 and 46 for baseline MST). In contrast, the filter fluxes for the modified MST-sludge mixture are very similar to those measured in MST-only suspension. This suggests that the sludge-MST interactions are reduced with the modified MST material compared to that with the baseline MST and, consequently, crossflow filtration of the modified MST-sludge mixture is equal to or better than that of the baseline MST-sludge mixture.

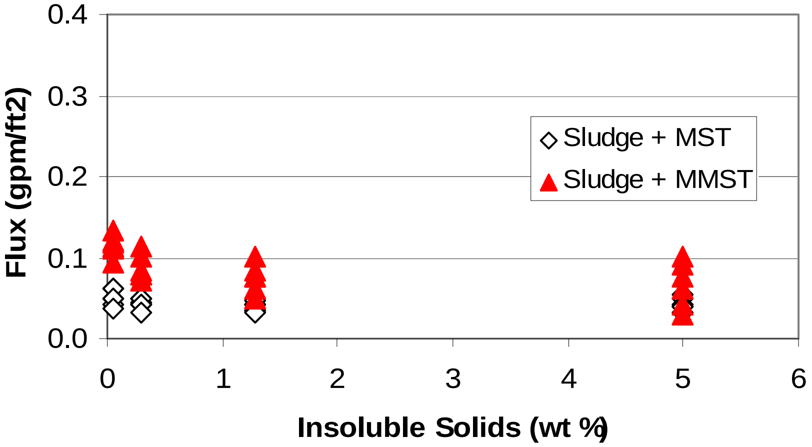

Figure 47. Crossflow Filter Flux for Slurries Containing Both Sludge and MST Solids.

4.7.5 Shelf-Life of Laboratory Prepared Modified MST

This task measured the strontium and actinide removal performance of the laboratory modified MST samples, LS-1, LS-2 and LS-3, prepared by Method 3 at the 25-gram scale after storage for six and twelve months at ambient laboratory temperature (see Section 4.2 Task 2). We used the same simulant used when first testing the performance of the modified MST samples. Prior to each test set we added a small amount of ^{85}Sr radiotracer. This addition was necessary to bring the ^{85}Sr activity to a level similar to that when we tested the performance of the samples at the earlier test set. The addition of the ^{85}Sr radiotracer provides an insignificant increase in the strontium concentration of the simulant.

For these tests we limited the modified MST testing to a single sorbent concentration (0.2 g L^{-1}) in duplicate for each sample with sampling events at 6 and 12-hours. For the baseline MST sample we tested at both 0.2 and 0.4 g L^{-1}. Table 27 provides the average and standard deviation of the strontium, plutonium and neptunium DF values for the modified MST and baseline MST samples on both testing dates. Note, we did not test the performance of the baseline MST sample at 0.4 g L^{-1} at the initial time date. Figure 47 provides a plot of the average plutonium concentration for the modified MST (average of 6 trials) and baseline MST (single trial) samples at the initial, 6-month and 12-month time intervals. Figure 48 provides a plot of the plutonium concentrations for the six individual trials at the 6 and 12-hour sampling times for each test set.

Inspection of Table 27 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 laboratory prepared modified MST at ambient laboratory temperature. For strontium, we observed that the modified MST 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 g L^{-1} sorbent concentration at the initial, 6-month and 12-month testing dates. Comparison of the modified MST results at 0.2 g L^{-1} with that of the baseline MST at the higher concentration of 0.4 g L^{-1} revealed that the modified MST 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 modified MST samples for six and twelve months are considerably lower than those determined in the initial test set (see Table 27). However, at the 95% confidence level the range of plutonium DF values overlap indicating the DF values are not statistically different. This overlap is evident in Figure 48, which shows each of the individual data points for the laboratory prepared modified MST samples. Note, that for the 6-h and 12-h sampling events, the measured plutonium concentration varied between about 1 and 4 μg L^{-1}, which corresponds to DF values of about 50 - 200. Thus, at the low plutonium concentrations that are achieved by the modified MST, small changes in the measured plutonium concentration can result in large change in the calculated decontamination factor. Given the overlap and the experimental uncertainty in the plutonium measurements at the 1 – 4 μg L^{-1} range, we conclude that the plutonium removal performance did not decrease over the 12-month storage time. For these datasets, the modified MST added at 0.2 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 g L^{-1}, respectively.

We observed no significant differences among the measured 6-h and 12-h neptunium DF values for the laboratory prepared modified MST 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 modified and baseline MST samples suggest a slight improvement in neptunium removal by the modified MST. 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.

Table 27. Strontium, Plutonium and Neptunium DF Values for the Modified and Baseline MST Samples at the Initial Synthesis, 6-month Storage and 12-month Storage Times.

	Strontium DF											
	Modified MST @ 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											
	Modified MST @ 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	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											
	Modified MST @ 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

Modified MST results are average and standard deviation of six trials

Baseline MST results are single determinations with reported analytical uncertainty

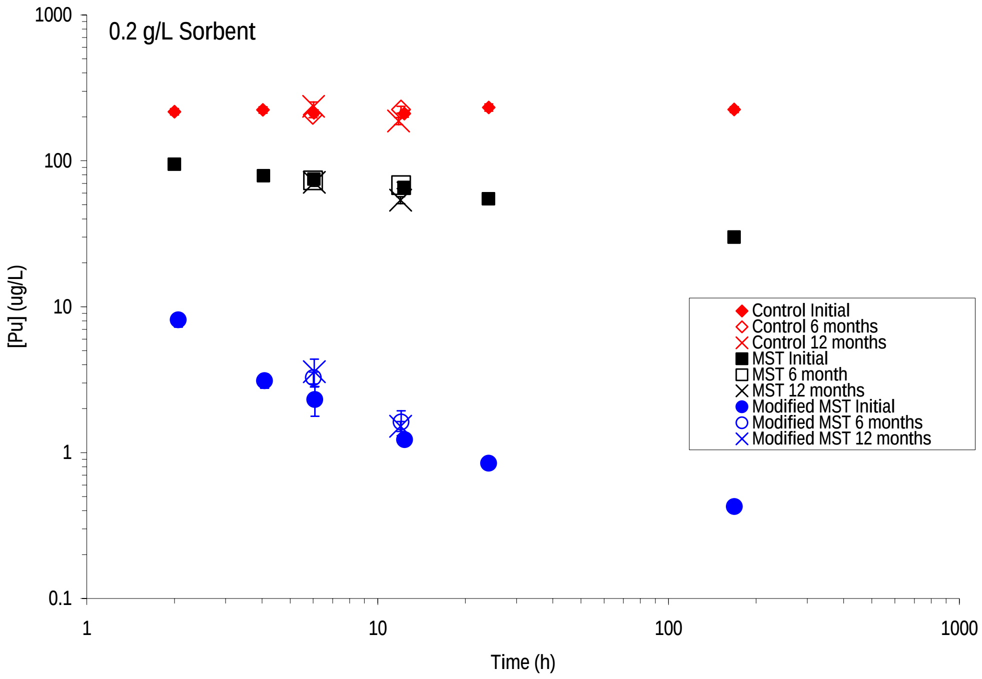

Figure 48. Plot of Average Plutonium Concentration versus Time for Tests with Modified and Baseline MST Samples at the Initial Synthesis, 6-month Storage and 12-month Storage Times.

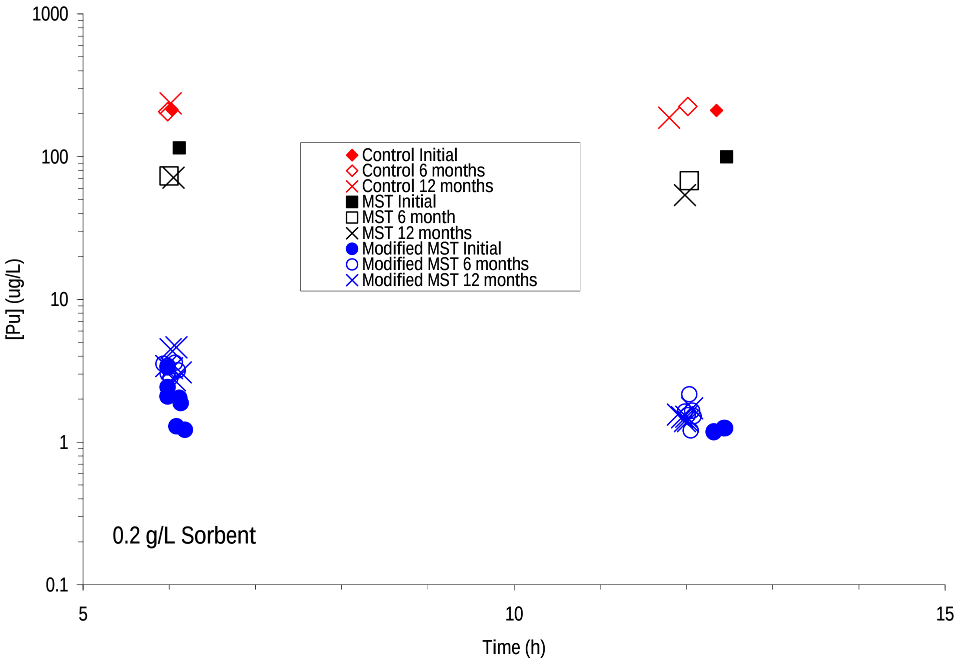

Figure 49. Plot of Individual Plutonium Concentrations at the 6 and 12 Hours Sampling Times for Tests with Modified and Baseline MST Samples at the Initial Synthesis, 6-month Storage and 12-month Storage Times.

5.0 Summary of Finding and Recommendations

This document provides a final report of Phase II testing activities for the development of a modified monosodium titanate (MST) that exhibits improved strontium and actinide removal characteristics compared to the baseline MST material. The activities included determining the key synthesis conditions for preparation of the modified MST, preparation of the modified MST at a larger scale by a commercial vendor, demonstration of the strontium and actinide removal characteristics with actual tank waste supernate and measurement of filtration characteristics. Key findings and conclusions include the following.

Testing evaluated three synthetic methods and eleven process parameters for the optimum synthesis conditions for the preparation on an improved form of MST. We selected the post synthesis method (Method 3) for continued development based on overall sorbate removal performance.

We successfully prepared three batches of the modified MST using post-synthesis addition of hydrogen peroxide at a 25-gram scale. The laboratory prepared modified MST exhibited increased sorption kinetics with simulated and actual waste solutions and similar filtration characteristics to the baseline MST. Characterization of the modified MST indicated that the post synthesis treatment did not significantly alter the particle size distribution, but did significantly increase the surface area and porosity compared to the original MST. Testing indicated that the modified MST exhibits reduced affinity for uranium compared to the baseline MST. Shelf-life testing indicated no change in strontium and actinide performance removal after storing the modified MST for 12-months at ambient laboratory temperature. Oxygen is released during the synthesis of the modified MST and continues after the synthesis at a rapidly diminishing rate until below a measurable rate after 4 months.

Optima Chemical Group LLC prepared a 15-kilogram batch of the modified MST using the post synthesis procedure. Performance testing with simulated and actual waste solutions indicated that the material performs as well as or better than batches of modified MST prepared at the laboratory-scale. Particle size and morphology data of the vendor-prepared modified MST indicates a broader distribution centered at a larger particle size and more irregular particle morphology compared to the baseline MST and laboratory prepared modified MST. Stirred-cell (dead-end) filter testing revealed similar filtration rates relative to the baseline MST for both the laboratory and vendor-prepared modified MST materials. Crossflow filtration testing indicated that with MST-only slurries, the baseline MST produced between 30 – 100% higher flux than the vendor-prepared modified MST at lower solids loadings and comparable flux at higher solids loadings. With sludge-MST slurries, the modified MST produced 1.5 – 2.2 times higher flux than the baseline MST at all solids loadings.

Based on these findings we conclude that the modified MST represents a much improved sorbent for the separation of strontium and actinides from alkaline waste solutions and recommend continued development of the material as a replacement for the baseline MST for waste treatment facilities at the Savannah River Site.

6.0 Acknowledgements

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7.0 Reviews and Approvals

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W. L. Isom, Jr., Manager, Salt Disposition Engineering Date

8.0 Attachments

8.1 Decontamination Factors and Uncertainties for Modified MST Samples Prepared by Method A – Addition of Hydrogen Peroxide in the Sol-Gel Synthesis

Test ID	Strontium DF	Uncertainty Strontium DF	Plutonium DF	Uncertainty Plutonium DF	Neptunium DF	Uncertainty Neptunium DF
1	0.85	0.032	1.48	0.13	2.15	0.46
2	1.03	0.044	3.05	0.40	4.46	0.93
3	1.40	0.060	0.60	0.078	1.14	0.17
4	1.85	0.081	1.22	0.16	2.00	0.31
5	0.92	0.036	1.56	0.15	2.15	0.46
6	1.30	0.051	1.75	0.15	3.60	0.87
7	1.59	0.069	1.20	0.15	2.39	0.45
8	1.06	0.041	1.00	0.091	2.44	0.51
9	1.22	0.052	1.03	0.13	2.58	0.42

8.2 Decontamination Factors and Uncertainties for Modified MST Samples Prepared by Method B – Addition of Hydrogen Peroxide to a Strongly Alkaline Solution of Titanium (IV)

Test ID	Strontium DF	Uncertainty Strontium DF	Plutonium DF	Uncertainty Plutonium DF	Neptunium DF	Uncertainty Neptunium DF
1A	4.64	0.204	1.25	0.11	0.91	0.18
2A	6.27	0.305	1.85	0.23	0.91	0.12
3A	1.98	0.082	1.59	0.143	1.59	0.32
4A	4.87	0.230	2.66	0.35	4.20	0.90
5A	6.25	0.305	4.16	0.53	3.46	0.62
6A	2.00	0.081	1.06	0.09	0.91	0.18
7A	0.74	0.031	1.61	0.20	>5.19	
8A	0.24	0.009	1.41	0.123	2.13	0.48
9A	2.14	0.086	1.34	0.12	1.06	0.21

8.3 Decontamination Factors and Uncertainties for Modified MST Samples Prepared by Method C – Post Synthesis Treatment of MST with Hydrogen Peroxide

Test ID	Strontium DF	Uncertainty Strontium DF	Plutonium DF	Uncertainty Plutonium DF	Neptunium DF	Uncertainty Neptunium DF
1P	3.83	0.18	>21.5		1.59	0.46
2P	3.19	0.16	19.4	3.03	1.68	0.36
3P	3.22	0.16	24.1	5.29	1.75	0.39
4P	2.43	0.11	>8.2		1.48	0.44
5P	2.35	0.11	21.4	3.12	1.34	0.30
6P	2.32	0.10	>20.7		1.40	0.41
7P	1.78	0.080	16.5	2.42	1.51	0.33
8P	2.11	0.094	>6.5		4.75	1.62
9P	2.84	0.14	19.0	2.67	2.78	0.65
10P	4.08	0.21	>9.2		1.62	0.48
11P	3.01	0.15	16.7	2.64	1.25	0.27
12P	2.94	0.14	25.6	4.22	1.15	0.25
13P	4.69	0.24	>20.2		1.66	0.48
14P	3.52	0.18	31.3	4.57	1.86	0.42
15P	3.85	0.19	>22.0		1.24	0.36

Attachment 8.4

^{90}Sr, Pu and ^{237}Np Concentrations Measured for Supplemental Actual Waste Tests

Test	Time (h)	Concentration (pCi/mL)							
		^{90}Sr	±	Total Pu*	±	Total Pu**	±	^{237}Np	±
Test S-2 (Restrike Test w/ 0.1 g/L MST)	2.1	3.20E+03	3.20E+02	1.80E+05	8.18E+03	3.21E+03	6.41E+02	6.50E+01	1.30E+01
	6.0	1.24E+03	1.73E+02	1.07E+05	5.10E+03	1.66E+03	3.32E+02	5.87E+01	1.17E+01
	8.0	7.84E+02	1.62E+02	3.83E+04	1.89E+03	< 1.76E+03	idl	4.87E+01	9.74E+00
	12.0	1.94E+03	2.85E+02	1.34E+04	6.93E+02	< 1.67E+03	idl	4.64E+01	9.28E+00
	30.0	3.29E+03	3.91E+02	4.47E+02	9.92E+01	< 1.65E+03	idl	4.11E+01	8.22E+00
	174	< 2.37E+02	mda	< 7.26E+03	mda	< 8.11E+02	idl	3.76E+01	7.52E+00
Test S-3 (Restrike Test w/ 0.2 g/L MST)	2.0	1.70E+03	2.04E+02	1.19E+05	6.19E+03	2.13E+03	4.27E+02	6.77E+01	1.35E+01
	6.0	5.57E+02	1.11E+02	2.92E+04	1.57E+03	< 1.81E+03	idl	6.06E+01	1.21E+01
	8.0	1.67E+03	2.80E+02	< 3.26E+03	mda	< 1.66E+03	idl	3.49E+01	6.98E+00
	12.0	1.15E+03	2.14E+02	8.65E+02	9.64E+01	< 1.72E+03	idl	3.25E+01	6.50E+00
	30.0	1.09E+03	1.90E+02	5.75E+03	5.15E+02	< 1.66E+03	idl	2.76E+01	5.52E+00
	174	2.06E+03	2.39E+02	< 9.91E+02	mda	< 8.17E+02	idl	1.96E+01	3.92E+00
Test S-1C (Control for Tests S-2 & S-3)	2.2	1.89E+04	1.89E+03	7.39E+05	3.41E+04	1.24E+04	2.48E+03	8.54E+01	1.71E+01
	8.0	2.06E+04	2.06E+03	7.72E+05	3.64E+04	1.27E+04	2.55E+03	9.41E+01	1.88E+01
	174	1.72E+04	1.74E+03	7.51E+05	3.92E+04	1.19E+04	2.38E+03	9.26E+01	1.85E+01
	Average	1.89E+04	1.89E+03	7.54E+05	3.66E+04	1.24E+04	2.47E+03	9.07E+01	1.81E+01
Test S-1A (Control for Tests S-4 & S-5)	1.9	2.24E+04	2.28E+03	7.82E+05	3.68E+04	1.23E+04	2.45E+03	9.17E+01	1.83E+01
	8.1	2.68E+04	3.48E+03	8.28E+05	4.65E+04	1.25E+04	2.49E+03	8.57E+01	1.71E+01
	9.3	2.54E+04	2.90E+03	7.65E+05	3.60E+04	1.31E+04	2.62E+03	8.92E+01	1.78E+01
	13.3	bad sample data		bad sample data		bad sample data		bad sample data	
	31.4	2.34E+04	2.67E+03	7.83E+05	3.77E+04	1.20E+04	2.40E+03	8.84E+01	1.77E+01
	175	2.15E+04	2.15E+03	9.32E+05	6.09E+04	1.11E+04	2.21E+03	8.30E+01	1.66E+01
	Average	2.39E+04	2.70E+03	8.18E+05	4.36E+04	1.22E+04	2.43E+03	8.76E+01	1.75E+01
Test S-1B (Control for Tests S-4 & S-5)	0.0	1.72E+03	2.72E+02	3.35E+04	1.96E+03	< 1.68E+03	idl	3.44E+01	6.88E+00
	2.1	9.08E+03	1.09E+03	2.90E+04	1.64E+03	< 1.98E+03	idl	4.14E+01	8.28E+00
	7.9	1.93E+03	2.50E+02	2.97E+04	1.50E+03	< 1.65E+03	idl	3.93E+01	7.86E+00
	9.5	3.98E+03	4.78E+02	3.22E+04	1.70E+03	< 1.69E+03	idl	4.01E+01	8.02E+00
	13.4	3.36E+04	3.57E+03	3.11E+04	1.66E+03	< 1.65E+03	idl	3.63E+01	7.27E+00
	31.4	1.59E+03	2.10E+02	2.80E+04	1.41E+03	< 1.63E+03	idl	4.32E+01	8.64E+00
	175	1.42E+03	1.98E+02	2.80E+04	1.39E+03	< 1.69E+03	idl	3.50E+01	7.01E+00
	Average	7.62E+03	8.66E+02	3.02E+04	1.61E+03	< 1.63E+03	idl	3.85E+01	7.71E+00
Test S-4 (Reuse Test w/ 0.1 g/L MST)	2.1	4.66E+02	9.31E+01	1.19E+04	6.90E+02	< 1.61E+03	idl	4.02E+01	8.04E+00
	6.8	1.56E+03	2.19E+02	3.98E+03	2.71E+02	< 1.59E+03	idl	2.73E+01	5.47E+00
	9.2	2.37E+04	2.49E+03	8.00E+05	4.17E+04	1.16E+04	2.32E+03	9.13E+01	1.83E+01
	13.0	6.64E+03	7.43E+02	6.24E+05	2.88E+04	9.22E+03	1.84E+03	7.41E+01	1.48E+01
	30.8	5.06E+03	5.82E+02	4.40E+05	2.17E+04	7.41E+03	1.48E+03	7.05E+01	1.41E+01
	175	1.09E+04	1.09E+03	2.48E+05	1.29E+04	3.18E+03	6.36E+02	5.98E+01	1.20E+01
Test S-5 (Reuse Test w/ 0.2 g/L MST)	2.1	8.83E+02	1.55E+02	< 5.48E+03	mda	< 1.61E+03	idl	2.81E+01	5.62E+00
	6.7	3.34E+03	4.54E+02	4.27E+03	2.72E+02	< 1.64E+03	idl	3.04E+01	6.08E+00
	9.0	5.82E+03	6.17E+02	6.46E+05	3.04E+04	1.05E+04	2.11E+03	8.33E+01	1.67E+01
	12.8	3.67E+03	4.15E+02	5.18E+05	2.50E+04	8.43E+03	1.69E+03	7.93E+01	1.59E+01
	30.6	2.20E+03	2.49E+02	1.63E+05	9.23E+03	2.86E+03	5.72E+02	6.09E+01	1.22E+01
	175	7.99E+02	1.28E+02	5.40E+04	2.81E+03	< 1.69E+03	idl	4.84E+01	9.68E+00

*Sum of PuTTA data for ^{238}Pu and $^{239/40}$Pu

**ICP-MS data for ^{239}Pu only. The mass of ^{240}Pu was below the detection limit for all samples.

mda signifies the minimum detectable analysis of a isotope

idl indicates the mass was below the instrument detection limit.

Attachment 8.5

Gas Release Data for Freshly Prepared Modified MST

Date & Time	Temp. (C)	Cumulative Elapsed Time (days)	Gas Release Rate (mL/min)		Date & Time	Temp. (C)	Cumulative Elapsed Time (days)	Gas Release Rate (mL/min)
10/19/2006 13:23	21.90				10/31/2006 14:13	22.23	12.03	2.27E-03
10/19/2006 13:38	21.96	0.01	1.40E-01		10/31/2006 15:40	22.21	12.10	2.87E-03
10/19/2006 16:25	21.99	0.13	5.67E-02		11/1/2006 8:25	22.20	12.79	1.85E-03
10/19/2006 17:05	22.16	0.15	4.44E-02		11/1/2006 10:12	22.28	12.87	2.15E-03
10/19/2006 17:42	21.99	0.18	3.33E-02		11/1/2006 13:15	22.05	12.99	6.83E-04
10/19/2006 17:55	21.98	0.19	2.31E-02		11/1/2006 14:30	22.04	13.05	2.67E-03
10/20/2006 9:42	21.80	0.85	3.33E-03		11/1/2006 16:16	22.05	13.12	2.12E-03
10/20/2006 10:45	21.89	0.89	1.42E-02		11/2/2006 11:35	22.42	13.93	1.80E-03
10/20/2006 11:27	21.98	0.92	1.60E-02		11/2/2006 13:25	22.27	14.00	2.05E-03
10/20/2006 12:34	21.83	0.97	1.33E-02		11/2/2006 15:50	22.07	14.10	1.38E-03
10/20/2006 13:37	21.69	1.01	1.25E-02		11/3/2006 9:30	21.35	14.84	9.63E-04
10/20/2006 14:26	21.57	1.04	1.17E-02		11/3/2006 12:48	21.36	14.98	1.52E-03
10/20/2006 15:06	21.54	1.07	1.12E-02		11/3/2006 13:25	21.52	15.00	2.70E-03
10/20/2006 15:47	21.54	1.10	1.09E-02		11/7/2006 13:45	21.74	19.02	1.67E-03
10/23/2006 11:27	19.72	3.92	3.41E-03		11/8/2006 10:50	21.77	19.89	1.29E-03
10/23/2006 14:12	20.56	4.03	4.61E-03		11/8/2006 13:25	21.77	20.00	1.87E-03
10/23/2006 16:11	20.89	4.12	4.96E-03		11/8/2006 16:15	22.24	20.12	4.41E-04
10/24/2006 10:00	21.29	4.86	1.25E-03		11/9/2006 9:30	20.22	20.84	6.45E-04
10/24/2006 13:55	21.71	5.02	4.04E-03		11/9/2006 13:20	20.93	21.00	1.41E-03
10/24/2006 15:35	21.67	5.09	4.25E-03		11/9/2006 16:22	21.12	21.12	1.15E-03
10/24/2006 17:11	21.68	5.16	3.85E-03		11/13/2006 10:55	18.50	24.90	8.82E-04
10/25/2006 11:14	21.37	5.91	2.99E-03		11/13/2006 14:20	19.31	25.04	1.46E-03
10/25/2006 11:53	21.58	5.94	3.33E-03		11/13/2006 16:15	19.77	25.12	1.09E-03
10/25/2006 13:30	21.37	6.00	3.30E-03		11/14/2006 10:00	18.38	25.86	1.15E-03
10/25/2006 14:44	21.59	6.06	3.38E-03		11/14/2006 13:20	19.60	26.00	1.62E-03
10/25/2006 16:14	21.43	6.12	5.11E-03		11/14/2006 16:10	19.59	26.12	8.82E-04
10/30/2006 15:18	21.60	11.08	1.78E-03		11/15/2006 12:00	19.43	26.94	9.17E-04
10/31/2006 10:45	22.41	11.89	1.49E-03		11/15/2006 14:20	19.87	27.04	1.79E-03
10/31/2006 12:23	22.31	11.96	1.94E-03		11/15/2006 16:05	20.26	27.11	1.90E-03

9.0 References

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[1] Lynch, R. W.; Dosch, R. G.; Kenna, B. T.; Johnstone, J. K.; Nowak, E. J. Sandia Solidification Process: A Broad Range Aqueous Waste Solidification Method. In *Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vol.*, IAEA Symposium on the Management of Radioactive Waste, Vienna, Austria, March 22, 1976, IAEA, Vienna, 1976, p 360-372.

[2] Lynch, R. W. *Sandia Solidification Process – Cumulative Report July 1974 – January 1976*; Technical Report Sandia National Laboratory, SAND-76-0105, Albuquerque, NM, January 1976.

[3] Walker, D. D.; Schmitz, M. A. “Technical Data Summary In-Tank Precipitation Processing of Soluble High-Level Waste,” DPSTD-84-103, May 19884.

[4] Record of Decision: Savannah River Site Salt Processing Alternatives (Salt Processing SEIS, DOE/EIS-0082-S2), Federal Register, Vol. 66, No. 201, October 17, 2001.

[5] “Actinide Removal Process Alternative Study and Selection (U),” G-ADS-G-00007, Rev. 0, January 2002.

[6] Harris, J. B. “Specification for Procurement of Monosodium Titanate,” Specification No. Z-SPP-H-00001, Rev. 2, May 1992.

[7] Lorier, T.H.; Jantzen, C. M. “Evaluation of the TiO_2 Limit for DWPF Glass”, WSRC-TR-2003-00396, Revision 0, October 30, 2003.

[8] Hobbs, D. T.; Nyman, M.; Clearfield, A. “Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Optimized Monosodium Titanate and Pharmacosiderite,” Volume 1 – Technical Proposal, WSRC-SRTC-PR-02-21-02, February 7, 2003.

[9] Hobbs, D.T.; Nyman, M.D.; Poirier, Barnes, M.J.; Thompson, M.E.; “Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Optimized Monosodium Titanate Phase II Interim Report for External Release,” WSRC-STI-2006-00072, Rev. 0, August 2006.

[10] Hobbs, D. T.; Poirier, M. J. “Task Technical and Quality Assurance Plan for Phase II Testing – Modified Monosodium Titanate (MST),” WSRC-RP-2004-00627, Rev. 1, June 2005.

[11] Hobbs, D. T. “Task Technical and Quality Assurance Plan for Phase II Supplemental Actual Waste Testing – Modified Monosodium Titanate (MST),” WSRC-RP-2005-01614, Rev. 0, May 2005.

[12] Hobbs, D. T.; Barnes, M. J.; Pulmano, R. L.; Marshall, K. M.; Edwards, T. B.; Bronikowski, M.G.; Fink, S. D.; “Strontium and actinide separations from high level nuclear waste solutions using monosodium titanate 1. simulant testing,” *Separation Science and Technology*, **2005** (40), 3093-3111.

[13] Hobbs, D. T.; Nyman, M. D.; Clearfield, A. “Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Optimized Monosodium Titanate and Pharmacosiderite Phase 1 Final Report,” WSRC-TR-2004-00322, Revision 0, July 2004.

[14] Stallings, M. E.; Barnes, M. J.; Peters, T. B.; DiPrete, D. P.; Fondeur, F. F.; Hobbs, D. T.; Fink, S. D. “Characterization of Supernate Samples from High Level Waste Tanks 13H, 30H, 37H, 39H, 45F, 46F and 49H”, WSCR-TR-2004-00386, Rev. 2, June 15, 2005.

[15] Peters, T. B.; Hobbs, D. T.; Fink, S. D. “Results of Supplemental Studies,” WSRC-STI-2006-00012, Rev. 0, July 24, 2006.

[16] Poirier, M.R and Hobbs, D. T. “Filterability of Monosodium Titanate Supplied by Blue Grass Chemical Specialties”, WSRC-TR-2004-00214, April 13, 2004.

[17] Poirier, M.R. “Improving the Filtration of Sludge/Monosodium Titanate Slurries by the Addition of Flocculants”, WSRC-TR-2001-00175, March 27, 2001.