WSRC-TR-2004-00322
Revision 0

Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Optimized Monosodium Titanate and Pharmacosiderite Phase 1 Final Report

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July 2004

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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT NO. DE-AC09-96SR18500

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Acronyms

ARP	Actinide Removal Process
CPC	Chemical Processing Cell
DF	decontamination factor
DWPF	Defense Waste Processing Facility
HA	hexylamine
HLW	high-level waste
ITP	In-Tank Precipitation
K_d	batch distribution constant
MST	monosodium titanate
Nb-SNT	niobium substituted sodium nonatitanate
SNT	sodium nonatitanate
SRS	Savannah River Site
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
TEG	tetraethylene glycol
TIP	titanium(IV) isopropoxide or tetraisopropoxytitanium(IV)
TSP	titanosilicate having pharmacosiderite structure
WPT	Waste Processing Technology

1.0 Summary

This report summarizes experiments and engineering evaluations conducted in a project funded by the Department of Energy, Office of Environmental Cleanup and Acceleration to develop improved sorbent materials for strontium/actinide separations at SRS. From the results of Phase 1 activities of the project, we offer the following conclusions and recommendations.

- Chemically modified monosodium titanate (MST) samples exhibited significantly increased actinide removal performance compared to the baseline MST. Testing results indicate that the modified MST offers the possibility of reduced MST concentrations and shorter contact times compared to the baseline MST.
- Preliminary calculations indicate that the use of the optimized MST sorbent will provide significantly increased waste throughput in the ARP facilities should shorter batch contact times and reduced MST concentrations be realized. The maximum throughput increases are realized using a 0.1-micron pore-size filter media in these facilities.
- Evaluation of the impacts of incorporating MST into DWPF operations indicates that both the baseline MST and optimized MST (4X decrease) quantities can be accommodated from Chemical Processing Cell (CPC) and glass formulation perspectives. We recommend that the MST materials be tested to determine the effects, if any, that introduction of MST has on slurry rheology, antifoam effectiveness, potential generation of hydrogen and processing time in the CPC.
- Evaluation of the impacts of MST and titanosilicate analog of pharmacosiderite (TSP) materials determined that the use of these materials showed no significant impacts on the SWPF and Saltstone facility.
- Based on the promising enhanced actinide removal performance of the chemically modified MST samples, which could have significant positive impacts on the SWPF, ARP and perhaps an in-tank deployment for Sr/actinide removal, we recommend that the Department of Energy continue funding to develop chemically modified MST materials.
- Dried MST exhibited poorer strontium and alpha removal kinetics, which may adversely impact process cycle times and waste feed throughput. Thus, we recommend that pretreatment facilities not use dried MST.
- Samples of TSP, sodium nonatitanate (SNT), templated-MST and pH-adjusted MST materials did not exhibit significantly improved strontium and actinide removal performance compared to the baseline MST. Thus, we halted further development of these materials.
- Nb-SNT exhibited evidence of chemical instability upon contact with strongly alkaline salt solutions for several days. The chemical instability could have significant impacts on downstream operations in the SWPF and DWPF.

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 process.[3] In 2001, the Department of Energy (DOE) selected MST for the strontium/actinide separation step within the 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 small treatment facility located in 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 ($\geq$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 In-Tank Precipitation (ITP) process specified that the vendor prepare and isolate the material without drying and deliver the MST to the Westinghouse Savannah River Company (WSRC) 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 24 hours versus approximately 2 weeks in the ITP process. Increased waste characterization data indicates that alpha removal characteristics (principally plutonium removal) represent a greater challenge than that for ^{90}Sr removal. Based on recent testing at SRNL, the performance of MST to efficiently and rapidly remove alpha-emitting radionuclides serves as the limiting factor in sizing the equipment and 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 Environmental Cleanup and Acceleration (EM-21) funded a project to develop improved sorbent materials for strontium/actinide separations at SRS.[8] This report assesses performance new sorbents for strontium and actinide removal characteristics as well as impacts of possible new sorbent materials on the SRS High-Level Waste (HLW) System. The assessment included impacts to Tank Farm, SWPF, ARP, DWPF, and Saltstone facilities.

3.0 Experimental

3.1 Drying of MST Material

All testing featured MST prepared by the Optima Chemical Company and identified as Batch #00-QAB-417. Initial tests dried the as-received MST slurry or the as-received MST after filtration and washing with three 30-mL portions of deionized water to remove soluble salts in air at ambient temperature. Subsequent MST drying experiments consisted of filtering approximately 3.3 g (targeting 0.5 g of dried solid) of the MST slurry through a Buchner filter funnel, washing the moist solids five times with 30-mL of deionized water taking care not to allow the MST solids to dry between washes and transferring the washed moist solids quickly to a preheated oven or vacuum oven and drying for 4 hours. Six samples were prepared in this manner with oven temperatures set at 55, 75, and 100 ºC and either at atmospheric pressure or at reduced pressure (0.02 atm). After drying for 4 hours at elevated temperature, we cooled the dried MST samples to ambient laboratory temperature in a desiccator and stored in tightly stoppered glass vials.

Initial characterization of the dried MST samples featured scanning electron microscopy (SEM), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and determination of the strontium decontamination factor at the Sandia National Laboratory (SNL). This testing featured either a 0.5 mg/L solution of strontium in water or a simulated waste solution having the salt concentration listed in Table 1 and spiked with ^{85}Sr radiotracer only (i.e., no actinides).

Table 1. Simulated waste solution composition for strontium and actinide removal performance testing.

Component	Target Concentration	Component	Target Concentration
$NaNO_3$	2.60 M	Uranium	10 mg L^{-1}
NaOH	1.33 M	Plutonium	0.2 mg L^{-1}
Na_2SO_4	0.521 M	Neptunium	0.5 mg L^{-1}
$NaAl(OH)_4$	0.429 M	Strontium	0.1 – 0.6 mg L^{-1}
$NaNO_2$	0.134 M		
Na_2CO_3	0.0260 M	Total Na	5.6 M

3.2 Synthesis of MST and SNT Materials

3.2.1 MST/SNT Materials Prepared at Sandia National Laboratory (SNL)

We prepared MST using the synthetic procedure provided by SRNL (Appendix 1). We prepared chemically modified MST samples by adding a proprietary chemical at varying conditions during or after the synthesis the MST.

3.2.2 MST/SNT Materials Prepared at Texas A&M University (TAMU)

We prepared MST using the synthetic procedure provided by SRNL (Attachment) with the addition of templating reagents. We tested two types of templates, hexylamine ($C_6H_{13}NH_2$, HA) and tetraethylene glycol ($C_8H_{18}O_5$, TEG). These preparations substituted washing with water in place of refluxing to remove alcohols.

Synthesis of MST-amine (DM4-46-1).

For this synthesis we modified the baseline procedure by adding 26.5 mLl (0.2 mol) of hexylamine (Aldrich) to the tetraisopropoxy titanium (IV) [$C_{12}H_{28}O_4Ti$, TIP] solution (Solution #1, see Appendix 1). After completing the refluxing step we washed the cooled slurry with 200 mL each of isopropanol (C_3H_7OH, IP) and deionized distilled (DDI) water followed by three 200-ml portions of ethanol (C_2H_5OH) and two 200-mL portions of DDI water.

Synthesis of MST-TEG-2 (Ti:TEG=1:2, DM4-48-2).
For this synthesis we modified the baseline procedure by adding 38.9 g of TEG in 47.5-mL of isopropanol in the round bottom flask prior to the addition of Solution #1) and the isopropanol and water solution (Solution #2, see Appendix 1). The final slurry was washed twice with 200 mL of isopropanol and once with 200 mL of DDI water.

Synthesis of MST-TEG-1 (Ti:TEG=1:1, DM5-261-1).
For this synthesis we modified the baseline procedure by adding a total of 9.09 g of TEG in 23.7 mL of IP in a round bottom flask prior to addition of Solutions #1 and #2. We mixed the reaction product with DDI H_2O for 2 days and adjusted the pH of the final slurry to a pH of 10 using 10 M NaOH solution.

Synthesis of MST-TEG-0.3 (Ti:TEG=1:0.3, DM5-271-1).
For this synthesis we modified the baseline procedure by adding a total of 3.1 g of TEG to Solution #2 in place of the water. After adding half of Solutions #1 and #2 into the round bottom flask, we added 2.2 mL of water to trigger precipitation. We washed the reaction product with isopropanol followed by DDI water as previously described.

Synthesis of MST-TEG-0.29 (Ti:TEG=1:0.29, DM5-28-1).
We prepared this sample using the same procedure as described about for DM5-271-1 with a slightly smaller amount of TEG (2.9 g). We washed the reaction product with isopropanol followed by DDI water as previously described.

Synthesis of MST-TEG-0.58 (Ti:TEG=1:0.58, DM5-281-1).
We prepared this sample using the same procedure as described about for DM5-271-1 using a greater amount of TEG (5.84 g). We washed the reaction product with isopropanol followed by DDI water. We adjusted the pH of the final slurry to a pH of 10 using 10 M NaOH solution.

3.2.3 Synthesis of SNT

We prepared SNT samples by a hydrothermal technique from the gel with composition of 1.0 TiO_2 : 4.63 Na_2O : 120.0 H_2O at temperatures 165 – 180 ^oC. The time of hydrothermal treatment varied from 21 – 72 hours. In a typical procedure a source of titanium, usually TIP, was added to DDI H_2O under vigorous stirring. To this mixture we added the desired quantity of 50 wt % NaOH solution. We placed the mixture in a pressure reactor, sealed the vessel and heated to temperature for the desired reaction time.

After heating, we followed the following steps for all of the samples. We cooled the pressure vessels/reaction flasks to near ambient temperature, separated the solids by filtration and washed the solids with 150 – 200 mL of DDI water. We converted the samples into the H-form ($Na_2H_2Ti_9O_{20}$) by treatment with 200 mL of 0.0035 M nitric acid solution, with the exception of Na-SNT, which was washed only with DDI H_2O. Sodium analysis of the acid treated SNT sample confirmed conversion to the H-form as the sample measured 5.53 wt% in sodium, which is good agreement with the theoretical value of 5.76 wt%. The theoretical sodium content for the sodium form of SNT ($Na_4Ti_9O_{20}$) is 10.86 wt%.

3.2.4 Synthesis of SNT-TS Mixture

In a typical SNT-TS synthesis the gel with composition of $1.0TiO_2:1.98SiO_2:6.77Na_2O:218H_2O$ was prepared by mixing of 3.5 ml of titanium isopropoxide in 20mL of DDI H_2O, 8.5 mL of 10 M NaOH with 27 mL of 0.86 M silica solution in 2.6 M NaOH. The resulting mixture was treated hydrothermally at 200 ^oC for 10 hours.

3.2.5 Synthesis of TSP Materials

We prepared three different pharmacosiderite phases in the potassium form for strontium removal using the methods detailed below.

Synthesis of K-TS-P
A total of 0.66 mL (6 mmol) of $TiCl_4$ (Alfa Aesar) was mixed with 40 mmol of HCl in deionized, distilled (DDI) water in a plastic beaker. To this solution, 5 ml of 30 wt % H_2O_2 was added under constant stirring followed by 10 mL of 10 M KOH solution and 20 mL of 1.06 M solution of silicic acid (Fisher Scientific Cat #A288-500) in 3 M KOH. The mixture was vigorously stirred for 15 minutes followed by the addition of 5 ml of 10 M KOH solution. It was placed in a Teflon lined stainless steel pressure vessel and heated in an oven at 200 ^oC for 7 days.

Synthesis of K-NbTS-P
A total of 0.34 g (1.25 mmol) of $NbCl_5$ (Aldrich) was mixed with 10 mL of DDI water and 1.4 g of titanium isopropoxide (TIP, Alfa Aesar) in a plastic beaker. Similar to the synthesis for K-TS-P, 5 ml of 30 wt % H_2O_2 was added under constant stirring followed by 10 mL of 10 M KOH solution and 20 ml of 1.06 M solution of silicic acid (Fisher Scientific Cat #A288-500) in 3 M KOH. The mixture was sealed and heated in an oven at 210 ^oC for 10 days.

Synthesis of K-GG-P
Pure germanium pharmacosiderite was synthesized by adding 0.41 g of GeO_2 (Alfa Aesar) to 10 mL of 5.4 M KF solution under constant stirring. To this mixture 6 mLl of 0.5 M urea solution was added. The resulting mixture was stirred for 15 minutes, sealed, and then placed in an oven at 200 ^oC for 4 days.

Products obtained after hydrothermal reaction in each of the above three syntheses were treated likewise: the pressure vessel was cooled to RT; the solid was separated by filtration, rinsed with DDI water and pure ethanol and dried in air at 55 ^oC.

3.3. Strontium and Actinide Removal Performance Testing

Testing of combined strontium and actinide removal performance occurred at the Savannah River National Laboratory (SRNL) using the simulated waste solution composition as shown in Table 1 including plutonium, uranium, and neptunium in addition to ^{85}Sr. Strontium and actinide removal testing occurred at 25 ± 2 °C at a MST solids concentration of 0.4 g/L. Sampling of the test bottles occurred at 4, 24 and 168 hours of contact. We filtered the samples through 0.45-micron syringe filters (nylon membrane) to remove MST solids. 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.

3.4 Sorbent Stability Testing

Short term sorbent stability tests featured contacting 0.1 grams of the sorbent with 10 mL of a simulated 5.6 M salt solution without radioactive materials. Bottles containing the sorbent and salt solution rotated on a Barnstead/Thermolyne LabQuake tumbler mixer at ambient laboratory temperature. After contacting the sorbents for 6 – 18 days, we filtered the mixture through a 0.45-micron Acrodisc® syringe filter. We collected the filtrate and analyzed for titanium and niobium content using inductively coupled plasma emission spectrometry (ICP-ES).

4.0 Results and Discussion

4.1 Preparation and Use of Dried MST

A comprehensive report detailing the experimental methods and results of testing dried MST materials was previously published.[9] We report in this section a brief summary of the findings and recommendations from that report. Savannah River Site experience with handling dry solids indicates that handling dried MST within the SWPF or ARP is feasible and could offer certain advantages if the dried material performed equivalently. This evaluation did not identify an operational reason that overwhelmingly supports introducing MST into the SWPF in either a slurry or dry chemical form. The current configuration of the ARP limits introduction of the MST only as a slurry form into the Alpha Sorption Tank. However, testing indicates that dried MST exhibits poorer strontium and alpha removal kinetics, which may adversely impact process cycle times and waste feed throughput. Thus, we recommend that these facilities not use dried MST.

4.2 Preparation, Characterization and Performance Testing of Modified Sorbent Materials

4.2.1 TSP Samples

Previous testing indicated that the titanosilicate materials having the pharmacosiderite structure (TSP) exhibit very good strontium and actinide removal characteristics.[10] The research group at TAMU prepared a series of TSP samples including niobium and germanium substituted materials. The TAMU group tested these samples for strontium removal characteristics using a simulated SRS waste simulant spiked with strontium.

Unlike previous TSP samples, these samples exhibited relatively poor strontium removal performance. In comparison with the SNT samples prepared in this project (see Section 4.2.2) the TSP samples exhibited approximately an order of magnitude lower strontium removal capacity. We do not have an explanation as to the cause of the poor performance of these TSP samples compared to previous samples. Because of the poor strontium removal performance the project team chose not to evaluate any of the TSP samples at SRNL for combined strontium and actinide removal performance and we stopped further study of this class of sorbents in this project.

4.2.2 TAMU SNT and SNT/TS Samples

SNT materials are prepared by a hydrothermal process in which a titanium reagent is combined with sodium hydroxide in water and heated under elevated temperature and pressure for a number of hours. Previous testing with a commercially prepared SNT samples offered by Fortum Engineering, Honeywell and those produced by the Clearfield group at Texas A&M University exhibited very good strontium removal, but generally poorer plutonium and neptunium removal performance than the baseline MST material.[11,12] The removal kinetics of the SNT materials proved slower than that exhibited by MST. A significant finding arising from the TAMU study indicates that improved removal performance correlated with decreasing crystallinity. In this project, the research aimed to investigate modifications to the SNT synthesis to increase removal kinetics and capacity.

We investigated synthetic modifications including the addition of templating reagents (e.g., hexylamine), conversion to the acid form and refluxing in isopropanol or sodium hydroxide solution. Table 2 provides a summary of the synthetic conditions used to prepare selected SNT and SNT/TS samples.

X-ray diffraction measurements indicated a range of crystallinity among these materials. Scanning electron microscopy reveals that the particles are flat rectangularly shaped solids. The addition of hexylamine changes the morphology slightly by reducing the rectangular dimensions of the particles.

The TAMU group measured strontium removal of the SNT and SNT-TS materials with the SRS simulant (see Table 1) prepared with strontium, but without any of the actinides. Figure 1 provides a plot of the strontium concentration versus time for a selected group of SNT and SNT-TS samples and a sample of the baseline MST (labeled as comm. MST). The H-SNT, Na-SNT and SNT-water exhibited greater strontium removal compared to the baseline MST material. The H-SNT sample exhibited particularly good removal kinetics and capacity. The SNT-TS material exhibited similar strontium capacity although the removal kinetics appeared somewhat slower than that of the baseline MST material.

Based on strontium removal performance testing at TAMU we tested four SNT samples at SRNL for combined strontium and actinide removal performance. Samples JD1-01-1A, JD1-01-1B and DM5-441-1 are pure SNT materials. Sample JD1-01-1B derived from JD1-01-1A by acid washing to provide a partial conversion into the proton form. Preparation of sample DM5-441-1 featured a post synthesis reflux of the SNT in NaOH solution for 8 hours. Sample DM5-50-2 is mixed material comprised on SNT and titanosilicate phases.

Table 2. Summary of synthetic conditions of SNT phases and their identifications

Sample ID	Phase ID	Temperature, °C	Heating Time, h	Remarks
DM4-43-1	c-SNT	175	72	*c* stands for crystalline
DM4-45-1	c-SNT-w	175	72	w stands for washing
DM4-45-2	SNT-amine	175	72	Ti:amine=1:2
JD1-01-1A	Na-SNT	175	21	pH=12
JD1-01-1B	H-SNT	From Na-SNT	n/a	pH=6
DM5-44-2	SNT-IP	80, reflux	32	24 h reflux in isopropanol, 8 h in NaOH solution
DM5-441-1	SNT-water	80, reflux	19	19 h reflux in NaOH solution
DM5-50-2	SNT-TS	200	10	Hydrothermal reaction

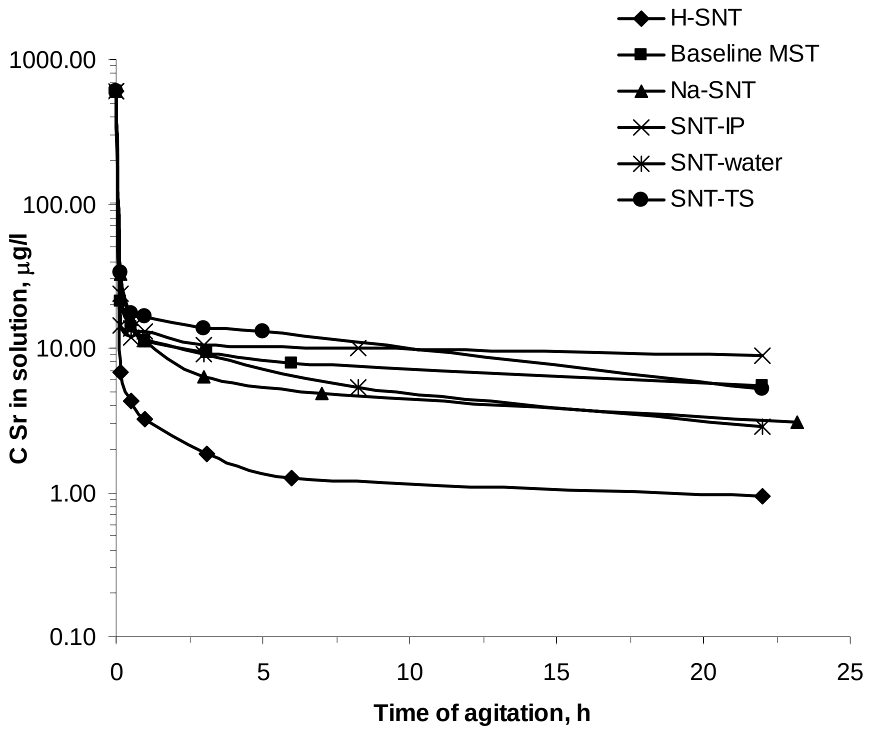

Figure 1. Plot of strontium concentration versus time upon contact with simulated SRS waste solution with SNT, SNT-TS and baseline MST materials.

Figures 2 – 4 provide plots of the ^{85}Sr, ^{237}Np and Pu concentrations, respectively, versus time upon contact of the simulated SRS waste solution with each of the four TAMU prepared samples. Of the three SNT samples, the acid washed sample JD1-01-1B (H-SNT) was the only material that performed as good as or better than the baseline MST. The H-SNT sample exhibited better strontium removal performance at all sampling times than the baseline MST samples. However, the H-SNT exhibited poorer removal kinetics, yet higher capacity, for plutonium and neptunium.

We attribute the better performance of the H-SNT in part to the partial exchange of the sodium with protons during the acid washing. Proton exchange is well known to be faster than sodium exchange. However, given the very high sodium concentration (5.6 M) in the simulated waste solution, this effect is most likely mitigated by competing exchange reactions (e.g., Na^+ for H^+ versus Sr^{2+} for H^+).

The mixed phase sample, DM5-50-2 (SNT-TS) represents a novel material comprised of two sorbent materials, SNT and a titanosilicate with the structure of the crystalline silicotitanate (CST) ion exchange material. This sample exhibited slower strontium removal kinetics compared to the other pure SNT and MST samples. Plutonium and neptunium removal characteristics were similar to those of the other SNT materials, which is remarkable. Previous testing with commercially prepared CST materials showed that this sorbent exhibits very little affinity for actinides. Given the reduced SNT content in the SNT-TS material, the relatively good plutonium and neptunium removal performance reflects either increased actinide removal characteristics of the SNT or the CST phase.

Overall, the performance of the H-SNT and the SNT-TS samples showed evidence of enhanced affinities for strontium and actinides and increased strontium removal kinetics for the H-SNT sample. However, the overall characteristics were not significantly improved compared to the baseline MST samples. Thus, we chose not to continue development of these materials in Phase 1 of this project. We believe that the SNT-TS mixed phase material exhibits promise for one-step treatment process to remove cesium, strontium and actinides from HLW solutions. We plan to pursue further development of this material under the EMSP project #81949.[13]

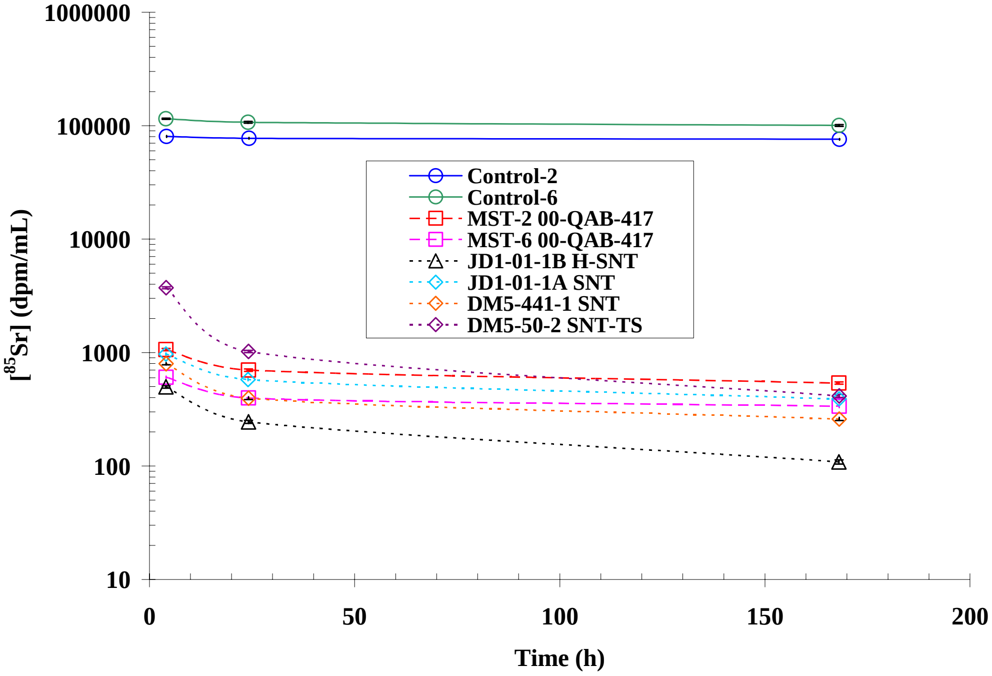

Figure 2. Plot of ^{85}Sr activity versus time upon contact of TAMU prepared SNT and SNT-TS materials with simulated SRS waste solution.

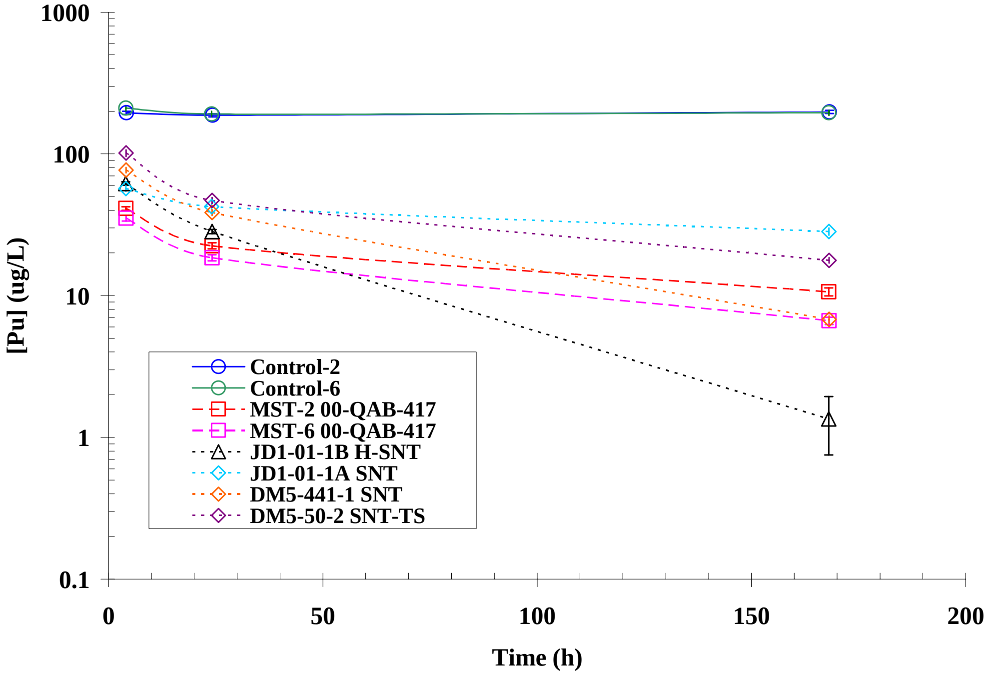

Figure 3. Plot of plutonium concentration versus time upon contact of TAMU prepared SNT and SNT-TS materials with simulated SRS waste solution.

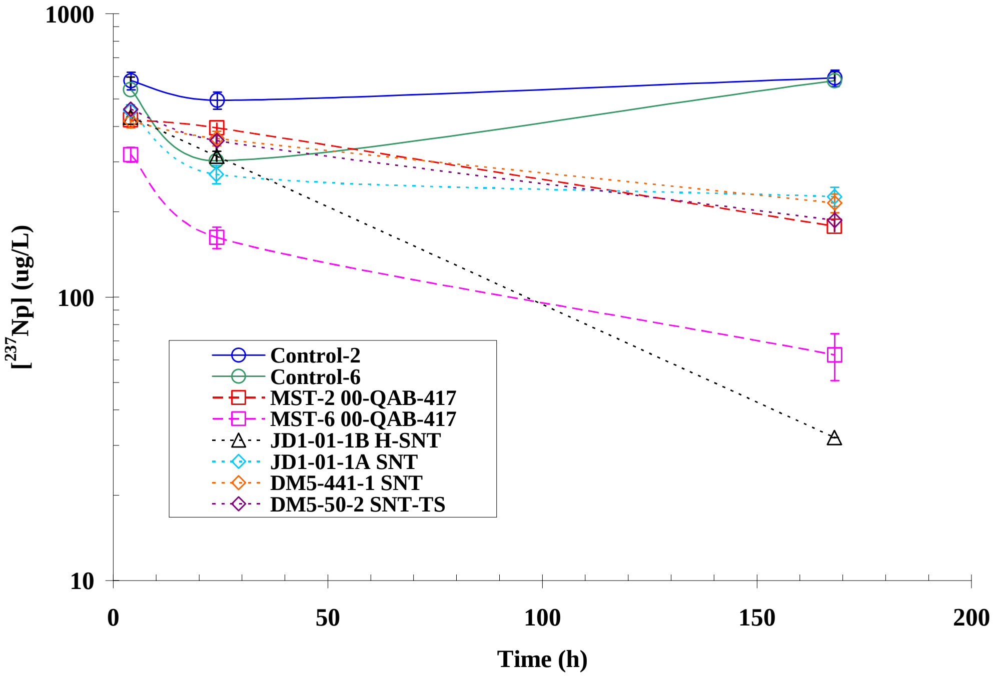

Figure 4. Plot of ^{237}Np concentration versus time upon contact of TAMU prepared SNT and SNT-TS materials with simulated SRS waste solution.

4.2.3 TAMU MST Samples

TAMU investigated the use of templating reagents to modify the morphology of the MST particle for improved strontium and actinide removal performance. The templating reagent was added during the synthesis of the MST. TAMU tested two templating reagents, hexylamine (HA) and tetraethylene glycol (TEG).

Table 3 provides a summary table of the template reagent, BET and microporous surface area (SA) measurements and strontium distribution constants for selected MST samples prepared using templating reagents and the baseline MST sample supplied by SRNL (Optima # 00-QAB-417).

Table 3. Identification and properties of selected MST samples prepared using templating reagents including the baseline MST sample.

Sample ID	Phase ID	Template	Slurry pH	BET Surface Area, m^2/g	Microporous Surface Area, m^2/g	Sr K$_d$, mL/g (contact time)
DM4-46-1	MST-amine	HA	9.23	232	204	917,000 (23.2 h)
DM5-261-1	MST-TEG-1.0	TEG	9.53	288	143	301,000 (24 h)
DM5-27-1	MST	none	9.26	458	178	336,000 (24 h)
DM5-271-1	MST-TEG-0.3	TEG	10.08	219	97	308,000 (21.5h)
DM5-28-1	MST-TEG-0.29	TEG	9.924	292	163	294,000 (24 h)
DM5-281-1	MST-TEG-0.58	TEG	11.60	16	0	332,000 (21.5 h)
00-QAB-417	MST	None*	11.87	141	0	260,000 (22 h)

* sample of MST prepared by Optima Chemical Company, Inc. (Lot #00-QAB-417).

The MST sample prepared at TAMU in the absence of a templating reagent (DM5-27-1) exhibited the highest BET surface area. Note that most of the surface area in this sample is due to mesopores and not micropores. The Optima # 00-QAB-417 sample of MST exhibited a much lower surface area than the laboratory prepared sample and no pore structure. The MST-amine sample exhibited lower BET SA, but very high fraction of surface area from micropores (under 20 Å). This sample exhibited the highest strontium distribution constant. Samples prepared with TEG exhibited reduced pore structure compared to the one MST-amine sample and lower Sr K_d values. Note that Sr K_d value did not correlate with either of the surface area measurements.

Figure 5 provides a plot of the strontium concentration versus time for the MST-amine, MST-TEG-0.58 and baseline MST samples measured at TAMU. Both of the template-modified MST samples exhibited faster removal kinetics. The MST-amine sample exhibited a higher strontium capacity compared to the MST-TEG sample, which exhibited a similar strontium capacity to that of the baseline MST sample.

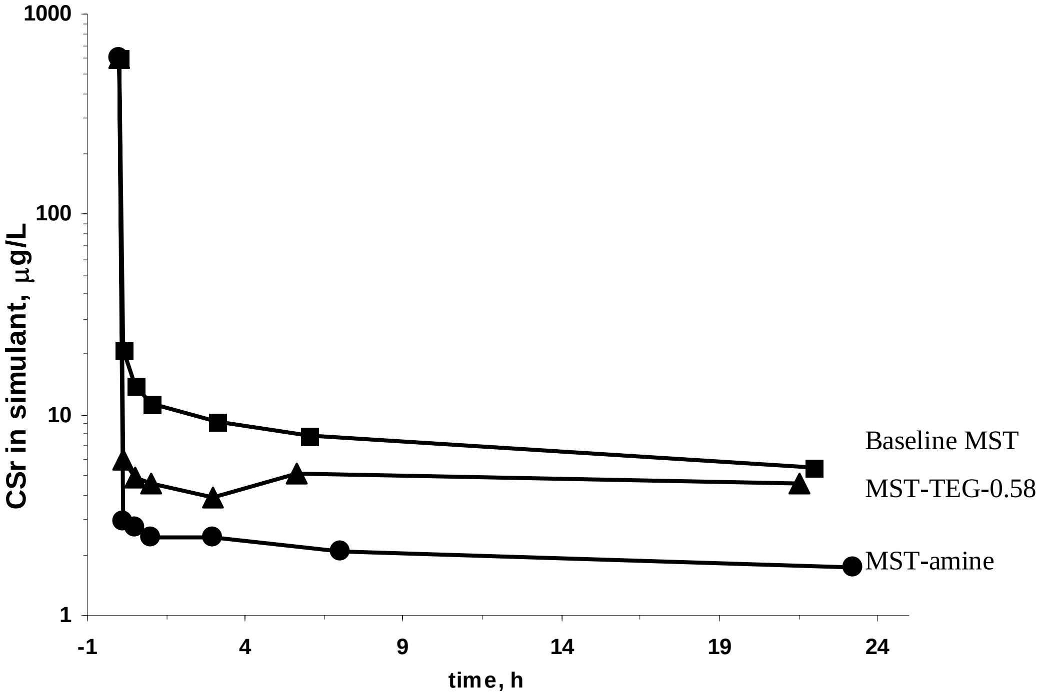

Figure 5 Strontium concentration versus time for MST-amine, MST-TEG-0.58 and baseline MST samples.

TAMU provided three samples of MST for combined strontium and actinide removal testing at SRNL. Samples tested included DM4-46-1 (MST-amine), DM5-28-1 (MST-TEG-0.58) and MST (no template). Figures 6 – 8 provide graphs of the ^{85}Sr, total Pu and ^{237}Np concentrations versus time upon contact of the TAMU prepared MST samples and a baseline MST sample with a simulated SRS waste solution.

Testing used the same simulated SRS waste solution. We evaluated the MST-amine sample in Test Set #2 and the MST and TEG-modified MST samples Test Set #6. Between Test Set #2 and Test Set #6 we added an additional aliquot of ^{85}Sr radiotracer to increase the activity in the simulant. This is apparent by the higher ^{85}Sr in Control-6 samples versus that in the Control-2 samples (see Figure 4.2.3-2).

Testing results indicated that the MST-amine sample performed poorer than the baseline MST sample for strontium, plutonium and neptunium removal. The MST-TEG sample exhibited very similar strontium removal performance and slightly better plutonium and neptunium removal performance compared to the baseline MST sample. Note that the MST sample prepared at TAMU in the absence of a templating reagent exhibited very similar sorbate removal characteristics compared to the TEG-modified MST sample. This suggests that the addition of TEG exerts little enhancement in removal efficiency for the MST.

The templated synthesis method has the potential to introduce a much higher organic content into the MST than the current production method. Increased organic content in the MST may have significant downstream impacts. Given that the HA-modified sample exhibited poorer performance and the TEG-modified materials exhibited only a marginal improvement in performance versus the baseline MST and no improvement compared to the TAMU MST, we stopped additional development of modified MST materials using organic-based templating reagents.

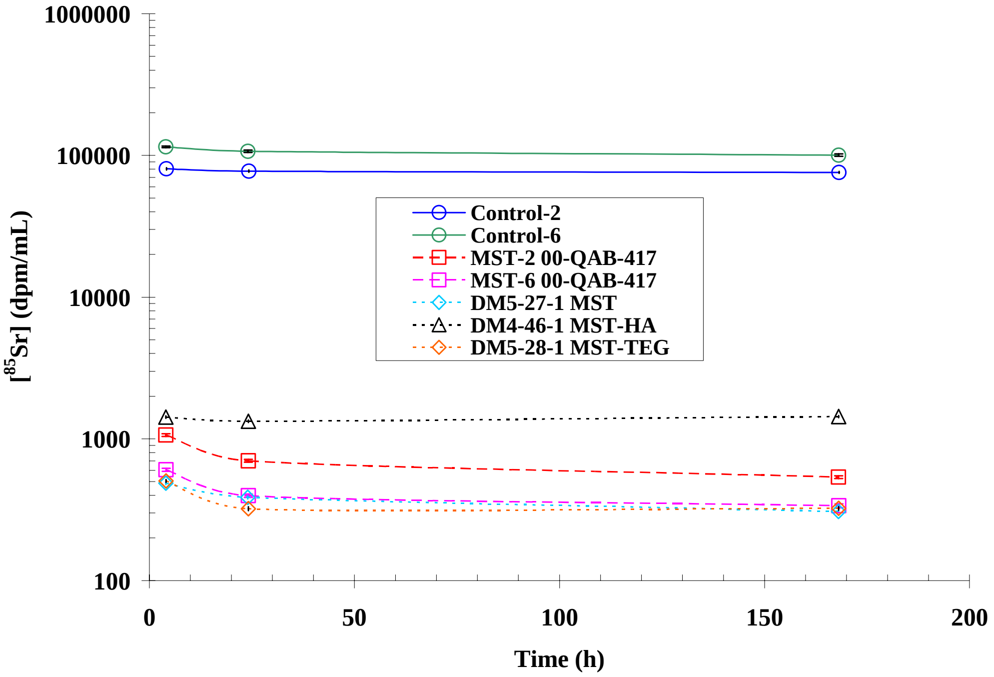

Figure 6. Plot of ^{85}Sr activity versus time upon contact of TAMU prepared MST, templated-MST and baseline MST materials with simulated SRS waste solution

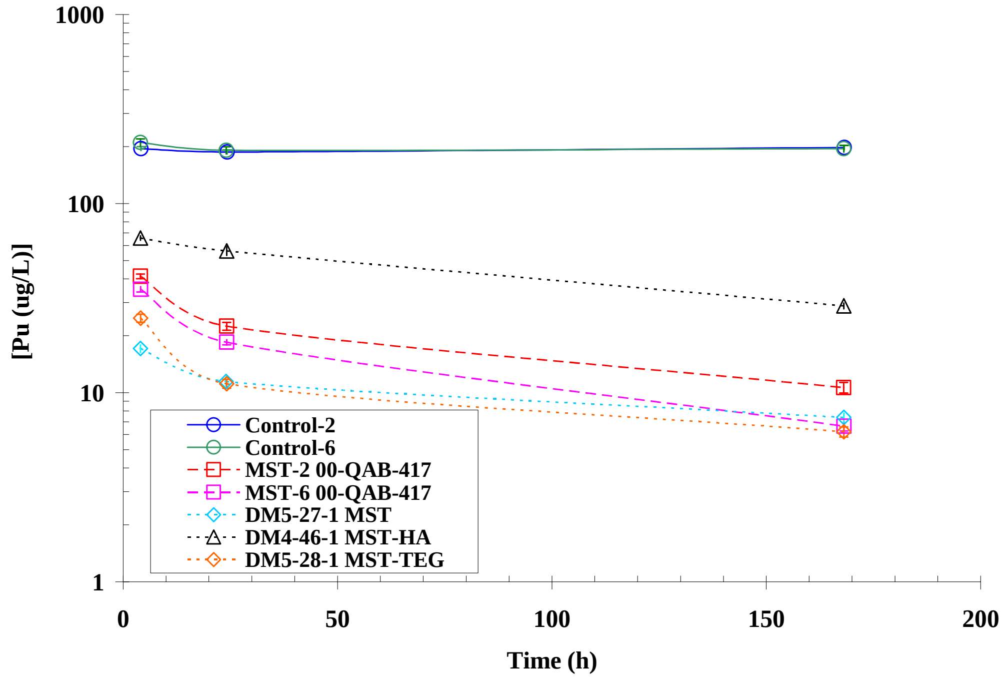

Figure 7. Plot of plutonium concentration versus time upon contact of TAMU prepared MST, templated-MST and baseline MST materials with simulated SRS waste solution

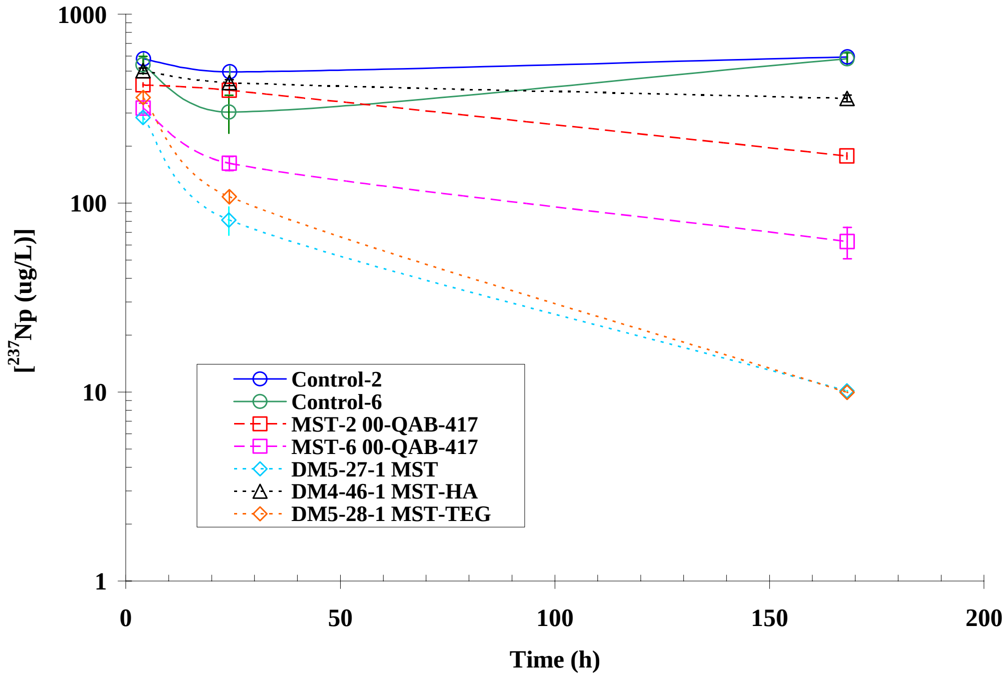

Figure 8. Plot of ^{237}Np activity versus time upon contact of prepared MST, templated-MST and baseline MST materials with simulated SRS waste solution

4.2.4 pH-Adjusted MST Samples

Given the preliminary findings of improved strontium removal upon converting SNT from the sodium form to the acid form, we tried a similar treatment with MST slurry at the SRNL. The acid treatment at TAMU featured a pH of 6. We chose to perform the pH adjustment of the MST slurry at two conditions, pH 4 and pH 7. Note that the pH of the baseline MST slurry used in these studies measures about 11.6 at ambient laboratory temperatures. We observed that the pH-adjusted MST samples settled at different rates than observed with the as-received MST sample.

We measured the particle size distribution (PSD) of the baseline MST, the two pH adjusted MST samples and an unadjusted MST sample that went through the same sequence of operations that the pH adjusted samples did, but without any acid addition. The baseline MST and unadjusted samples should be identical unless the physical manipulations produced an unexpected change. Figure 9 provides a plot of the particle size distribution (PSD) of the four MST materials measured using a Microtrac S3000 instrument. We measured the PSD of the baseline MST sample in November 2003, whereas the measurement of the PSD for the other three MST samples occurred in March 2004.

The PSD of the baseline MST and the unadjusted MST samples are nearly identical indicating that the operational steps (i.e., dilution with water, filtration, brief rinsing with water and air drying followed by dilution to known volume with water) did not physically alter the PSD of the MST. For the two pH adjusted samples we observed a shift in the PSD to smaller sizes. This trend is not unexpected since adjustment to pH 7 and below would be expected to alter the surface charge on the MST particles. Reversing the surface charge could disperse aggregates that are present at the highly alkaline pH of the original slurry and could result in different gravity settling characteristics.

The greater shift in the PSD occurred for the pH 7 sample. Compared to the PSD of the pH 7 sample, the PSD of the pH 4 sample is shifted to slightly larger particle sizes suggesting that aggregation of a fraction of the MST particles occurs at the lower pH. This small increase may reflect aggregation of particles at the lower pH, which is further away from the expected isoelectric point or point of zero charge for MST. For metal oxides, isoelectric points typically occur in the pH range of 7 – 9.[14]

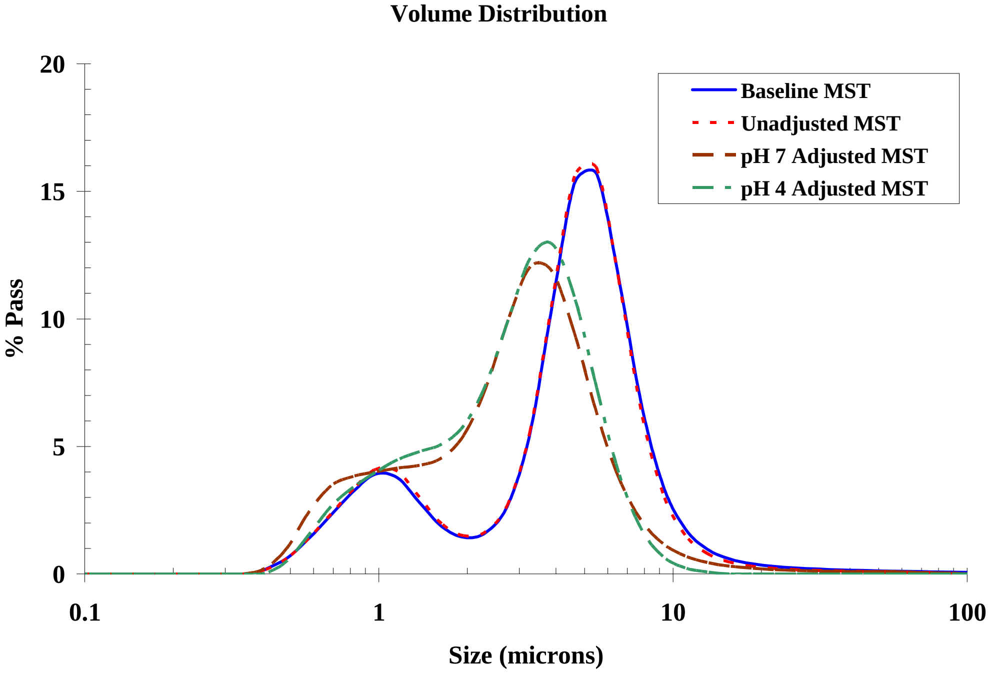

Figure 9. Particle size distribution of baseline, unadjusted and pH-adjusted MST samples.

We tested the two pH adjusted as well as the unadjusted and baseline MST materials for strontium and actinide removal performance using the simulated SRS waste solution. Figures 10 – 12 provide plots of the ^{85}Sr, Pu and ^{237}Np concentrations versus time upon contact of the simulant with 0.4 g/L of the pH-adjusted and unadjusted MST materials. Table 4 provides a summary of the calculated distribution constants for each sorbate at each sampling time. The distribution constants values derive from equation 1.

$$K_d\ (\text{mL g}^{-1}) = (\text{DF} - 1)/[\text{S}] \qquad (1)$$

where, DF = decontamination factor = $[C]_o/[C]_t$,
$[C]_o$ = concentration or activity of sorbate at time zero,
$[C]_t$ = concentration or activity of sorbate at sampling time, and
[S] = sorbent concentration (g mL^{-1}).

From a review of the graphs in Figures 10 – 12 and the K_d values presented in Table 4 we conclude that the pH adjustment did not alter the characteristics of the MST to significantly change the removal of strontium, plutonium and neptunium. Given these results we terminated this line of investigation to produce an improved MST material.

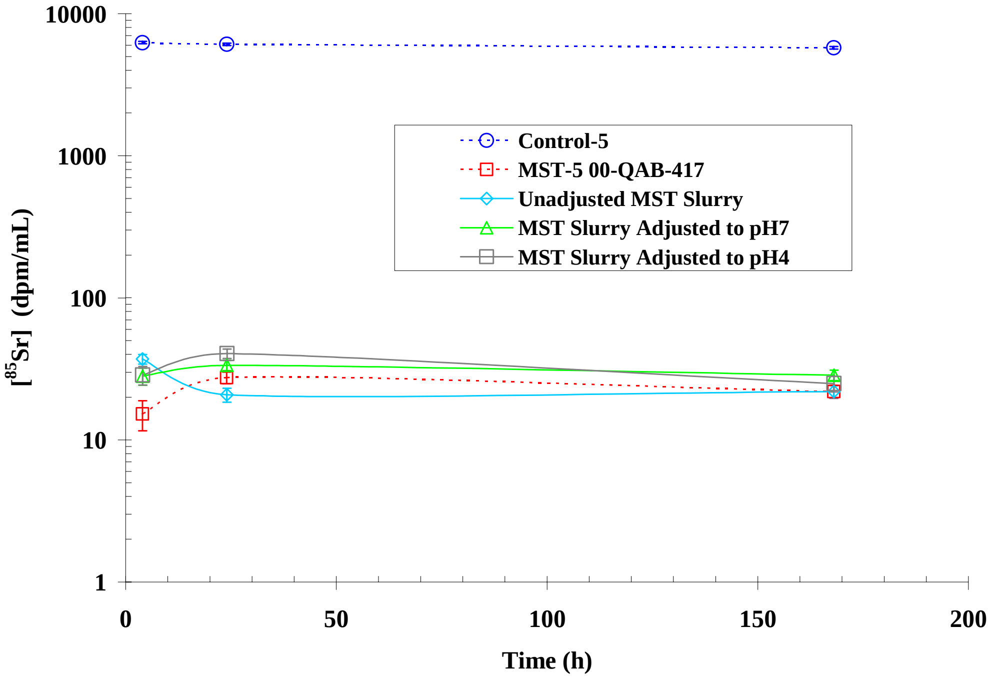

Figure 10. Plot of ^{85}Sr activity versus time upon contact of pH-adjusted and unadjusted MST materials with simulated SRS waste solution.

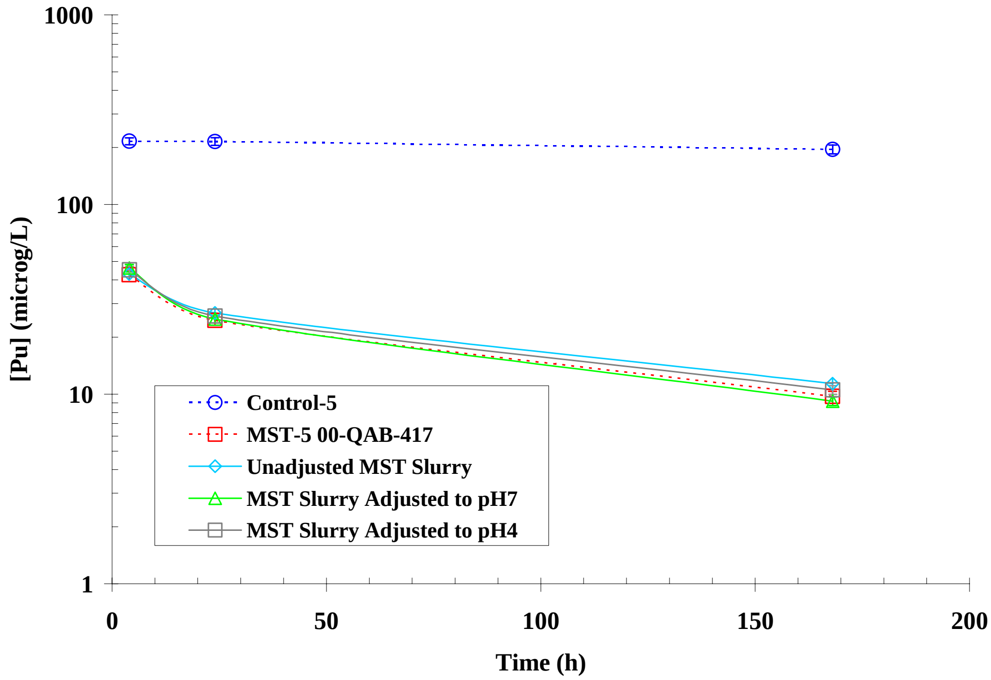

Figure 11. Plot of plutonium concentration versus time upon contact of pH-adjusted and unadjusted MST materials with simulated SRS waste solution.

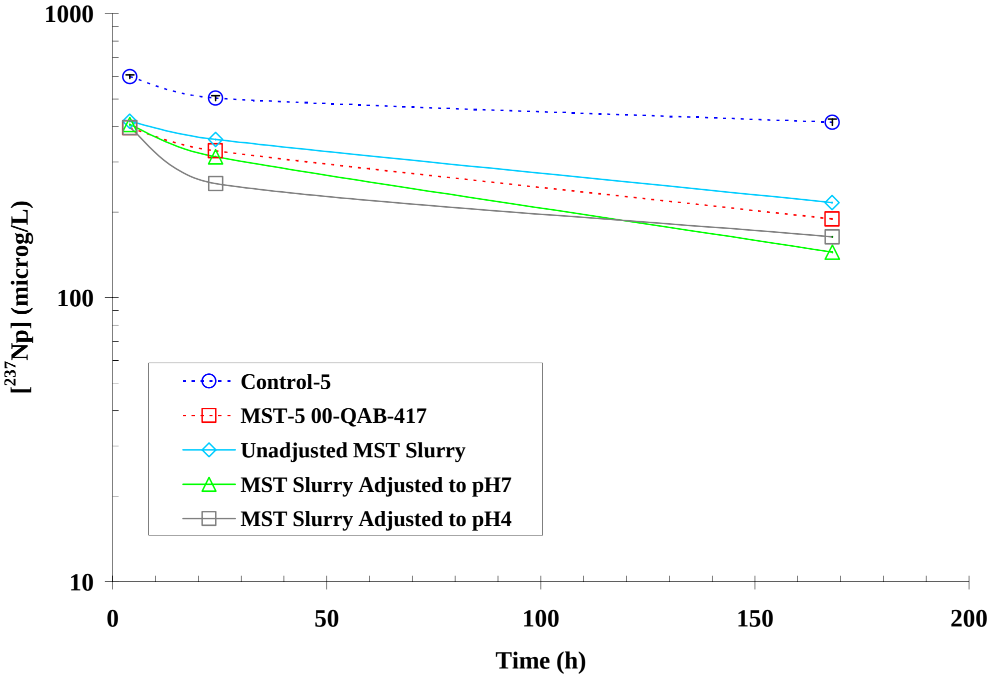

Figure12. Plot of ^{237}Np concentration versus time upon contact of pH-adjusted and unadjusted MST materials with simulated SRS waste solution.

Table 4. Calculated distribution constants for baseline, acid-adjusted and unadjusted MST samples.

		Strontium K_d (mL g^{-1})	
Sample	**4-hour**	**24-hour**	**168-hour**
MST-5	1,030,000 (247,000)	554,000 (53,200)	657,000 (68,900)
Unadjusted MST Slurry	419,000 (33,600)	731,000 (83,800)	655,000 (67,100)
MST Adjusted to pH 7	554,000 (77,800)	454,000 (38,600)	503,000 (43,700)
MST Adjusted to pH 4	543,000 (82,300)	374,000 (29,300)	575,000 (73,400)

		Plutonium K_d (mL g^{-1})	
Sample	**4-hour**	**24-hour**	**168-hour**
MST-5	10,200 (634)	19,500 (1,250)	47,800 (3,940)
Unadjusted MST Slurry	10,000 (617)	17,500 (1,140)	40,500 (3,430)
MST Adjusted to pH 7	9190 (566)	19,100 (1,270)	50,800 (3,770)
MST Adjusted to pH 4	9430 (581)	18,300 (1,330)	43,800 (3,260)

		Neptunium K_d (mL g^{-1})	
Sample	**4-hour**	**24-hour**	**168-hour**
MST-5	846 (65.7)	1490 (138)	2720 (233)
Unadjusted MST Slurry	669 (52.4)	1130 (100)	2070 (173)
MST Adjusted to pH 7	761 (61.3)	1680 (163)	4340 (528)
MST Adjusted to pH 4	843 (67.4)	2690 (220)	3530 (440)

values in parentheses are single standard deviation

4.2.5 Chemically Modified MST

The project team investigated the modification of MST using a proprietary chemical and conditions to improve strontium and actinide removal performance. These modified MST samples exhibited similar particle morphology as the baseline MST and also exhibited excellent strontium removal performance in preliminary testing. Thus we tested selected samples for strontium and actinide removal performance using the simulated SRS waste solution at SRNL.

Figures13 – 15 provide plots of the ^{85}Sr, Pu, and ^{237}Np concentrations, respectively, versus time upon contact of the simulated SRS waste solution with each of four of the modified MST samples as well as the baseline MST sample. The control sample represents the simulated waste solution with no added sorbent. Table 5 provides the distribution constants for each of the tested materials at the each of the sampling times.

Testing results indicated that the modified MST materials behaved similarly to that of the baseline MST material in terms of strontium removal capacity and kinetics. For example K_d values for strontium fall within the range bounded by the two MST samples. The SRNL prepared sample (SRTC-1) may be exhibiting slightly improved removal kinetics than the other modified MST and baseline MST materials. However, the overall small data set and large uncertainties in some of the sample results prevents a definitive determination of increased removal kinetics for strontium for the SRTC-1 sample.

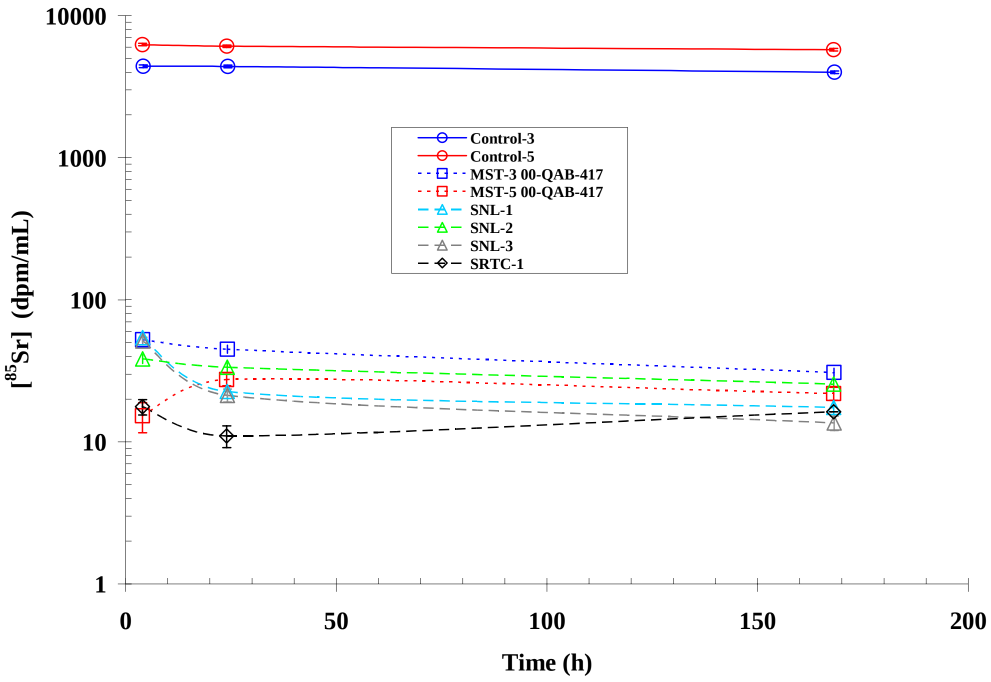

Figure 13. Plot of ^{85}Sr activity versus time upon contact of modified MST and baseline MST materials with simulated SRS waste solution.

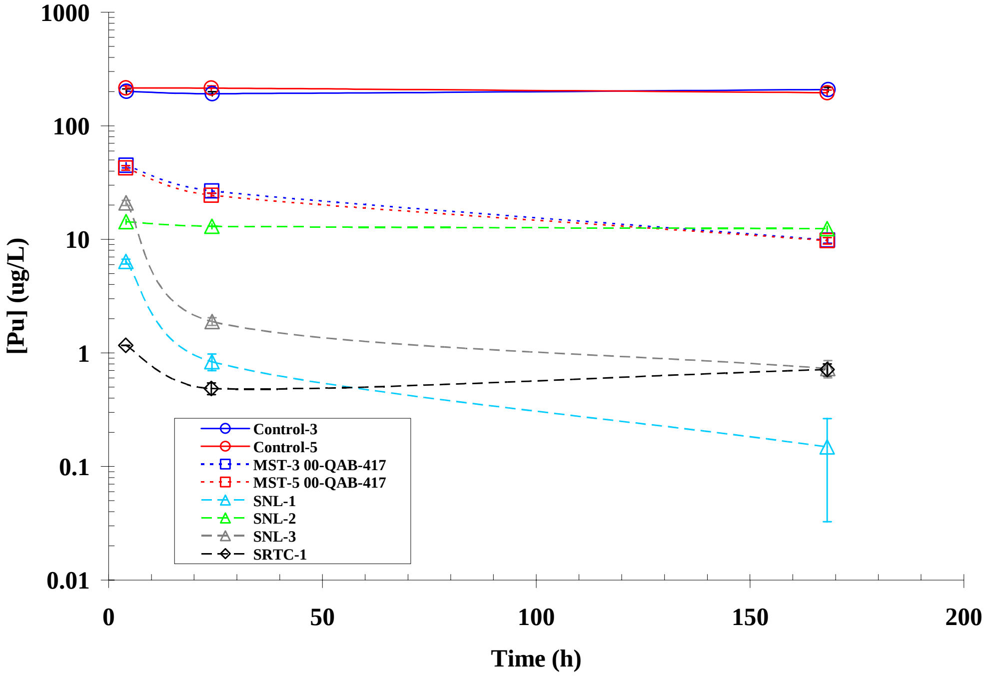

Figure 14. Plot of plutonium concentration versus time upon contact of modified MST and baseline MST materials with simulated SRS waste solution.

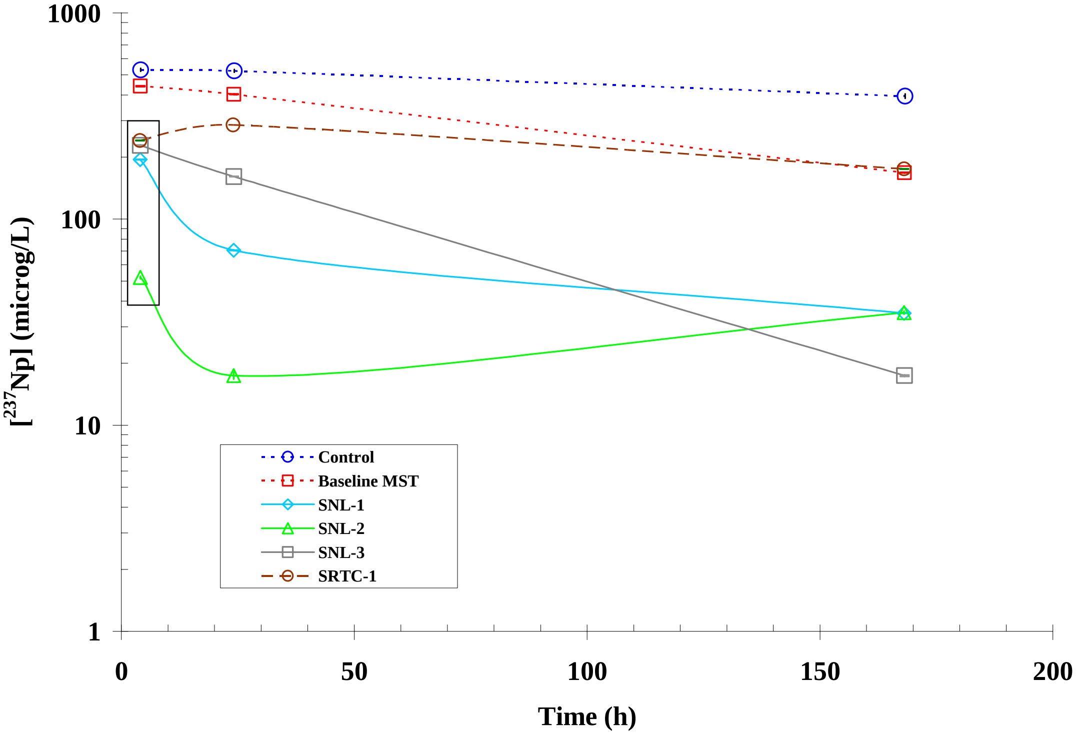

Figure 15. Plot of ^{237}Np concentration versus time upon contact of modified MST and baseline MST materials with simulated SRS waste solution.

Table 5. Calculated distribution constants for chemically modified MST samples.

	Strontium K_d (mL g^{-1})		
Sample	**4-hour**	**24-hour**	**168-hour**
MST-3	207,000 (13,400)	242,000 (16,500)	321,000 (23,900)
MST-5	1,030,000 (247,000)	554,000 (53,200)	657,000 (68,900)
SNL-1	200,000 (12,500)	481,000 (51,000)	567,000 (58,000)
SNL-2	285,000 (21,300)	325,000 (25,900)	388,000 (31,400)
SNL-3	211,000 (13,700)	511,000 (54,800)	729,000 (86,200)
SRTC-1	878,000 (109,000)	1,370,000 (242,000)	>877,000 (nd)

	Plutonium K_d (mL g^{-1})		
Sample	**4-hour**	**24-hour**	**168-hour**
MST-3	8720 (600)	15,400 (1,010)	50,300 (3,840)
MST-5	10,200 (634)	19,500 (1,250)	47,800 (3,940)
SNL-1	76,200 (5,070)	566,000 (98,100)	3,490,000 (272,0000)
SNL-2	32,800 (2,200)	34,200 (2,290)	39,400 (2,830)
SNL-3	21,500 (1,480)	249,000 ((21,800)	707,000 (127,000)
SRTC-1	>485000 (nd)	1100000 (138000)	679000 (91300)

	Neptunium K_d (mL g^{-1})		
Sample	**4-hour**	**24-hour**	**168-hour**
MST-3	501 (37.3)	745 (57.6)	3,370 (343)
MST-5	846 (65.7)	1,490 (138)	2,720 (233)
SNL-1	4,300 (317)	16,000 (3,020)	25,600 (6,660)
SNL-2	22,900 (3,120)	72,700 (4,020)	25,500 (4,200)
SNL-3	3,300 (305)	5,600 (667)	54,000 (3,280)
SRTC-1	3,000 (223)	1890 (181)	3,400 (293)

nd = not determinable
values in parentheses are single standard deviation

The chemically modified MST samples exhibit significantly improved plutonium and neptunium removal capacity and kinetics. The four reported modified MST samples measured between approximately 2 and 50 times higher plutonium and neptunium removal than the baseline MST samples at the 4-h and 24-h sampling times. Plutonium and neptunium removal proved faster with the modified MST samples compared to the baseline MST samples. For example, plutonium and neptunium concentrations in the treated simulated waste solutions after 4 hours of contact with the modified-MST samples are less than those measured after 24 hours of contact with the baseline MST (see Figures 14 and 15).

The excellent strontium and actinide removal characteristics exhibited by these modified MST materials may have significant impact on SWPF and ARP operations. The higher actinide removal capacities and removal kinetics suggest that these facilities may require less MST and shorter contact times to affect the necessary decontamination factors. Thus we recommend continued development to confirm the promising results.

4.3 Sorbent Stability Testing

This project originally targeted three sorbents for development that would provide a material that exhibited improved performance versus the baseline monosodium titanate (MST) material. The three materials include modified MST, sodium nonatitanate (SNT) with and without niobium substitution (Nb-SNT), and a titanosilicate material that exhibits a pharmacosiderite structure (TSP). MST and SNT have good chemical stability in alkaline salt solutions. Chemical stability of the Nb-SNT and TSP sorbents in alkaline waste solutions has not been previously studied. Thus, we conducted short duration tests in which we contacted each of the sorbents with a simulated waste solution (of the same composition as that in Table 1, but without radionuclides) and measured liquid phase samples for titanium and niobium content after a contact period of 6 – 18 days. We also visually inspected the solids.

We observed no visible signs of change in the sorbent materials after the contact period. However, solution analyses indicate that a variable percentage of the titanium and niobium in the sorbents dissolved into the salt solution. The Nb-SNT sorbent exhibited the greater dissolution. After 6 days of contact, 2.05 ± 0.042 % of the titanium and 4.84 ± 0.056 % of the niobium in the Nb-SNT dissolved. In contrast only 0.081 ± 0.018 % of the titanium in the TSP sorbent dissolved after 18 days of contact.

Based on these limited short term stability testing results, we conclude that the TSP material, but not the Nb-SNT material, exhibits good stability in alkaline salt solutions. The dissolution of between 2 and 5% of the sorbent after 6 days of contact for the Nb-SNT may have adverse impacts on SWPF, ARP and downstream processing operations as discussed in the following sections. Although we observed very little dissolution of titanium from the TSP material in this test, we recommend additional stability testing be performed in the event that a TSP material with superior sorption characteristics is developed. TSP does contain silicon and under prolonged contact with the alkaline waste solution could undergo leaching of the silicon and post precipitation of aluminosilicate phases such as that observed with the related crystalline silicotitanate (CST) sorbent.

4.4 Impacts to SWPF and ARP operations

MST and SNT exhibit good chemical stability in alkaline waste solutions. Thus, little, if any, of the MST or SNT would decompose and release chemical components into the waste solution and then transfer into the caustic side solvent extraction (CSSX) operation in the SWPF. Modified MST and SNT would likely exhibit excellent chemical stability in the strongly alkaline waste solutions and, thus, not release any chemical components that would transfer to CSSX. Given the good chemical stability in short term tests, we believe that TSP materials will not exhibit adverse impacts on operations within SWPF and ARP facilities.

Dissolution of the sorbent at or above the levels measured for the Nb-SNT material could adversely impact crossflow filter performance in either the SWPF or ARP facility. Dissolution of the sorbent will reduce the size of the solid particles, which could fill filter pores and reduce filter flux or allow particles of the Nb-SNT to pass through to the filtrate and reduce the filtrate quality. We did not measure the particle size distribution or perform filtration tests with the Nb-SNT materials after contacting with the simulated waste solution to determine if the dissolution of the sorbent significantly altered the particle size distribution or filtration characteristics. Since the Nb-SNT materials exhibited Sr/actinide removal performance well below that of the MST and SNT materials, we did not pursue further studies on particle size distribution and filtration characteristics.

Concentrations of the titanium and niobium in the simulated waste solution from the sorbent stability tests measured at 1.9 – 55 mg/L for titanium and 120 – 140 mg/L for niobium. A possible impact of these dissolved metals would be in the CSSX stage during the extraction of cesium from the waste solution. Effects of titanium (Ti^{4+}) and niobium (Nb^{5+}) in the CSSX operation have not been studied. However, since these metals would be present as the respective Ti(IV) and Nb(V) hydroxyl complexes, neither metal would be expected to interact with the solvent or the cesium and decrease the effectiveness of the extraction stage.

One possible impact for TSP would be post precipitation of aluminosilicate solids upon leaching of silicon from the TSP sorbent and reaction with aluminate present in the waste solution. The precipitation of aluminosilicate solids post filtration in the Sr/actinide removal stage of the SWPF would adversely impact hydraulic performance of the centrifugal contactors in the CSSX stage of the SWPF and result in the accumulation of solids in product tanks and transfer lines within the SWPF and ARP facilities. Thus we recommend additional stability testing be performed in the event that a TSP material with superior sorption characteristics to MST is developed.

Precipitation of the dissolved niobium and titanium from the Nb-SNT could adversely impact solvent extraction in the SWPF if the precipitation occurs post filtration of the sorbent solids in the Sr/actinide removal stage. If solids precipitation occurs after solvent extraction, the impacts would be limited to possible accumulation of solids in holding tanks and transfer lines.

For the modified MST sorbent we assumed that the modification does not change the empirical formula for MST, which is written as $NaTi_2O_5H$. Sodium nonatitanate (SNT) has the empirical formula $Na_4Ti_9O_{20}\cdot xH_2O$. May Nyman has synthesized SNT derivatives in which niobium substitutes for titanium in the framework.[15] The degree of substitution can range up to as much as 50% of the titanium. For this evaluation we assumed that the Nb-SNT sorbent has the following empirical formula, $Na_4Nb_2Ti_9O_{25}\cdot 4H_2O$. We selected the potassium form of the TSP sorbent for evaluation in this study. The empirical formula for this sorbent is $K_3HTi_4Si_3O_{16}\cdot 4H_2O$.

The baseline process for waste solution treatment specifies the addition of 0.4 g/L MST for the treatment of HLW solutions in the SWPF and ARP.[16] To allow for batches of salt solutions higher in alpha activity, DOE provided guidance to the Engineering, Procurement and Construction (EPC) vendors for the SWPF to assume that 80% of the feed solution can be satisfactorily treated with 0.4 g/L MST and 20% treated with 0.8 g/L. Using these MST concentrations at an annual processing rate[17] of 2.7E+07 L y^{-1} for waste solution diluted to 5.6M in sodium, we calculated the annual usage of MST at 1.1E+04 kg y^{-1}. Quantities of the alternate sorbents, Nb-SNT and TSP, were determined using the same assumptions for MST and the theoretical equivalents of the respective sorbent.

Table 6 provides a list of the quantities of the three sorbents estimated for use on an annual basis in the SWPF. Baseline quantities refer to amounts estimated using the EPC guidance above. We derived the usage quantities for the Nb-SNT and TSP derived from consideration of the theoretical exchange capacity versus performance comparison with MST at equivalent total titanium levels. Using this methodology the baseline annual usage of Nb-SNT and TSP materials are 16,000 and 13,000 kg y^{-1}. These estimated baseline quantities represent an increase in solids of 45% and 18% for the Nb-SNT and TSP materials compared to MST. The higher solids would adversely impact filtration throughput in the SWPF and ARP operations. However, the baseline quantities of the alternate sorbents provide significant decreases in the quantity of titanium processed in the DWPF versus that for MST (17% for Nb-SNT and 21% TSP).

Substitution of a new sorbent material for the baseline MST material is unlikely unless the new material exhibits a significant change in performance. The optimized case provides the quantities of sorbents used in the SWPF assuming a fourfold increase in sorption capacity versus that measured for the currently available MST. As discussed in Section 4.2.5, we produced modified MST samples that exhibit significantly improved strontium and actinide removal performance. Based on K_d values these modified materials would allow decreased quantities of MST and shorter contact times to effect the necessary strontium and actinide removal factors. A conservative estimate is that the MST concentration could be lowered by a factor of 4 (i.e., 0.1 g L^{-1}) and batch contact times reduced to about 4 hours.

Table 6. Estimated Annual Use of Selected Sorbents in the SWPF and Equivalent Quantities of Titanium

	Baseline Case (kg y^{-1})		Optimized Case (kg y^{-1})	
Sorbent	Sorbent Quantity	Ti Quantity	Sorbent Quantity	Ti Quantity
MST	11,000	5,300	2,800	1,300
Nb-SnT	16,000	4,400	4,000	1,100
TSP	13,000	3,400	3,300	880

S. Subosits recently provided preliminary calculations on the impact of reduced MST usage and shorter contact time on planned operations in the 512-S and 96-H facilities.[18] Tables 7 and 8 provide a summary of the results from the preliminary calculations. His calculations indicate that a decrease in MST usage of 0.4 to 0.1 g L^{-1} provides a very small increase in throughput for either facility. A much more significant increase in throughout occurs with a shorter contact time. The shorter contact time allows for a significantly shorter overall cycle time. The magnitude of the increase is dependent on the filter flux since this operation is not the throughput limiting operation.

In the 512-S facility the throughput increases from 1.27 gallons per minute (gpm) with a 0.5-micron pore size crossflow filter media or 1.60 gpm with a 0.1-micron pore size filter to 2.36 and 3.96 gpm, respectively. Thus, the salt waste throughput of the 512-S increases by a factor of between 1.6 and 3.1. For the 96-H facility the throughput increases from 3.17 gpm to 6.64 gpm, which represents an increase of greater than two times in the throughput.

We have not estimated throughput impacts for the SWPF. However, we believe that the lower quantities and contact times would provide similar increases in throughput in the SWPF facility. The reduced contact times may also allow the incorporation of smaller batch contact reactors. If smaller batch contact equipment (e.g., small alpha strike tank) is possible, this could result in a smaller footprint for the SWPF. A smaller footprint for the strontium/actinide separation process would provide significant capital and operating cost savings. We recommend that a more detailed cost evaluation be carried out on the impact of optimized MST use in the SWPF.

Table 7. Preliminary calculations of the impact of decreased MST usage and shorter MST contact time on 512-S ARP throughput.

Processing Option		Filter Media	Waste Solution
([MST], g L^{-1}	Contact Time, h	Size, µm	Throughput, gal min^{-1}
0.4	24	0.5	1.27
0.1	24	0.5	1.28
0.4	24	0.1	1.60
0.1	24	0.1	1.62
0.4	4	0.5	2.36
0.1	4	0.5	2.40
0.4	4	0.1	3.84
0.1	4	0.1	3.96

Table 8. Preliminary calculations of the impact of decreased MST usage and shorter MST contact time on 241-96H ARP throughput.

Processing Option		Filter Media	Waste Solution
([MST], g L^{-1}	Contact Time, h	Size, µm	Throughput, gal min^{-1}
0.4	24 or 4	0.5	3.17
0.1	24 or 4	0.5	3.26
0.4	24	0.1	3.36
0.1	24	0.1	3.46
0.4	4	0.1	6.57
0.1	4	0.1	6.97

4.5 Impacts to Tank Farm Facilities and Operations

Direct release of the sorbents into tank farm facilities will occur only in the event of an off-normal operation such as an inadvertent transfer. The release of these sorbents into a HLW tank other than those associated with Salt Processing would not be expected to adversely impact operations in these facilities. These sorbents have sufficient density that each would gravity settle similar to that of sludge solids. In the event that the solids transfer into a HLW evaporator, we expect that the solids would exhibit behavior similar to that exhibited by entrained sludge solids exhibit.

Some additional sorption of strontium and actinide elements may occur depending on the available sites on the sorbent and the chemical potential of the waste solution in the receiving tank. The quantity of sorbed material is not sufficient to be criticality concern. None of these sorbents are oxidizing agents, react with alkaline waste solutions to release large quantities of heat or produce hydrogen or other flammable gas generation in the event they transferred into other tank farm facilities. Thus the off-normal release of these sorbents into tank farm facilities does not present a safety concern.

4.6 Impacts on DWPF Operations

Herman, Edwards and Peeler recently conducted a detailed study of the impacts of the introduction of MST into DWPF operations.[19] This study evaluated the use of MST in the DWPF at two concentrations, 0.4 g L^{-1} (baseline) and 0.1 g L^{-1} (optimized) in addition to the use of alternate sorbent materials and methods including engineered MST and In-Situ Mixed Iron Oxide.

Based on the assessment, the authors concluded that the use of MST at the baseline or optimized quantities is plausible from a DWPF Chemical Processing Cell (CPC) and glass formulation perspectives. The authors concluded that the use of MST at either the baseline (11,000 kg y^{-1}) or optimized levels (2,800 kg y^{-1}) would have minimal impact on the acid demand in the CPC. However, they recommended that testing should be conducted to determine the effects, if any, that introduction of MST has on slurry rheology, antifoam effectiveness, potential generation of hydrogen and processing time in the CPC. With respect to projected operating windows, the MST baseline and optimized MST cases had calculated maximum waste loadings at 43 and 42%, respectively. Projections regarding the total number of glass canisters indicated 308 canisters per year for the baseline MST case and 306 canisters per year for the optimized MST case.

4.7 Impacts to Saltstone Facility

Possible impacts from the use of MST, Nb-SNT and TSP sorbents include the release of titanium and niobium into the decontaminated waste solution transferred to the Saltstone Facility. Titanium and niobium are not listed as hazardous metals by the EPA and are not listed in the current Saltstone WAC. Note that the Saltstone WAC does limit the concentration of ^{94}Nb. ^{94}Nb is a daughter product of uranium fissioning. The release of niobium from Nb-SNT materials would add ^{93}Nb, which is the naturally occurring isotope of niobium, but not ^{94}Nb. Therefore, transfer of these elements into the Saltstone Facility via the decontaminated salt solution would not impact the operating permit for this facility.

Release of titanium and niobium into the decontaminated waste solution could affect grout curing. The effects of these elements in grout curing have not been evaluated. Concentrations of the titanium and niobium in the decontaminated waste solution measured from about 1 mg/L to 140 mg/L in the alkaline salt solutions. These concentrations are sufficiently low to limit affects of these elements on grout curing. Thus, we conclude that the use of MST, Nb-SNT and TSP in the treatment of HLW solutions will have minimal impact to operations in the Saltstone Facility.

5.0 Conclusions and Recommendations

Based on the results of Phase 1 activities of the project, we offer the following conclusions and recommendations.

- Dried MST exhibited poorer strontium and alpha removal kinetics, which may adversely impact process cycle times and waste feed throughput. Thus, we recommend that pretreatment facilities not use dried MST.
- Samples of TSP, SNT, templated-MST and pH-adjusted MST materials did not exhibit significantly improved strontium and actinide removal performance compared to the baseline MST. Thus, we halted further development of these materials.
- Chemically modified MST samples exhibited significantly increased actinide removal performance compared to the baseline MST. Testing results indicate that the modified MST offers the possibility of reduced MST concentrations and shorter contact times compared to the baseline MST.
- Nb-SNT exhibited evidence of chemical instability upon contact with strongly alkaline salt solutions for several days. The chemical instability could have significant impacts on downstream operations in the SWPF and DWPF.
- Evaluation of the impacts of MST and TSP materials determined that the use of these materials showed no significant impacts on the SWPF and the Saltstone Facility.
- Preliminary calculations indicate that the use of the chemically modified MST sorbent will provide significantly increased waste throughput in the ARP facilities should shorter batch contact times and reduced MST concentrations be realized. The maximum throughput increases are realized using a 0.1-micron pore-size filter media in these facilities.
- Evaluation of the impacts of incorporation of MST into DWPF operations indicates that both the baseline MST and optimized MST (4X decrease) quantities can be accommodated from CPC and glass formulation perspectives. The evaluation recommended that the MST materials be tested to determine the effects, if any, that introduction of MST has as slurry rheology, antifoam effectiveness, potential generation of hydrogen and processing time in the CPC.
- Based on the promising enhanced actinide removal performance of the chemically modified MST samples, which could have significant positive impacts on the SWPF, ARP and perhaps an in-tank deployment for Sr/actinide removal, we recommend that the Department of Energy continue funding to develop chemically modified MST materials.

6.0 Acknowledgements

The authors thank Dmitri Medvedev and Akhilesh Tripathi of Texas A&M University and Steve Thoma, Linnah Neidel, Leslie Lybarger and Art Sanchez of the Sandia National Laboratory for performing many of the syntheses and characterizations of samples prepared in this project. We also thank Mona Blume and Lin Thacker of SRNL for performing the strontium and actinide removal performance testing as well as David DiPrete and Ceci DiPrete of SRNL for the radiochemical measurements. Finally we thank David Peeler, Tommy Edwards and Connie Herman of the SRNL for performing the engineering evaluation of impacts of the use of optimized MST on DWPF operations as well as Steve Subosits and Eric Harrison of the Westinghouse Savannah River Site Closure Business Unit for preliminary calculations on the impacts to ARP facilities.

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8.0 Attachment

Laboratory Procedure for the Synthesis of Monosodium Titanate

Stoichiometry:

	$2Ti(OC_3H_7)_4$ tetraisopropyl titanate (TPT)	+	$NaOCH_3$ sodium methylate	+	$5H_2O$ water	=	$NaTi_2O_5H$ monosodium titanate (MST)	+	CH_3OH methanol	+	$8C_3H_7OH$ isopropyl alcohol (IPA)
CAS #:	546-68-9		124-41-4								67-63-0
MW:	288.25		54.02		18.02		199.76		32.04		60.10
Sp. G. (g/cc):	0.955		0.95 25% Soln (4.4M)		1.00		1.03-1.10				

Basis: 66.7 gm 15 wt % Monosodium Titanate (MST) slurry
(10.0 gm MST solids)

Equipment: 300 mL 3-neck Reaction Flask with agitator,
Condenser,
Heating mantle,
3 - Variable Speed Pumps
3 – Flowmeters,
4 – 150mL Graduated Cylinders

Chemicals:

tetraisopropyl titanate (TPT)	30.0 mL
isopropyl alcohol,	154.3 mL
25 wt % (4.4M) sodium methylate	11.6 mL
deionized water for reaction	4.05 mL
deionized water for final wt % adjustment	~ 55-57 mL

Procedure:

1. Prepare 120 mL of Solution #1 by mixing the chemicals as listed below in the order shown.
   Solution #1 Mix (v/v): 65.3% IPA
   9.7% sodium methylate ($NaOCH_3$)
   25.0% TPT
2. Prepare 32.5 mL of Solution #2 by mixing the chemicals as listed below in the order shown.
   Solution #2 Mix (v/v): 87.5% IPA
   12.5% water
3. Charge 47.5 mL IPA into the reaction flask.
4. With agitation, charge 0.5 mL of Solution #2 followed by 2.0 mL of Solution #1 below liquid level in to the reaction flask to initiate precipitation.
5. Agitate reaction mix for a minimum of ten minutes to initiate precipitation of monosodium titanate (MST) solids.
6. With agitation, charge simultaneously and below liquid level remaining 118 mL of Solution #1 at a flow rate of 4.0 mL/minute and 32 mL of Solution #2 at a flow rate of 1.0 mL/minute. Adjust the flow rate of solutions as necessary to maintain constant conductivity or good particle morphology as viewed under the microscope.
7. After addition of both solutions is complete, heat the reaction slurry to boiling (ca. 82 °C) and distill off the alcohol to a maximum alcohol concentration in the liquid phase of <500-ppm. If necessary alcohol can be removed by successive decantations and additions of deionized water.
8. After alcohol removal is complete, cool the slurry to ambient temperature and add sufficient quantity of deionized water to adjust the MST solids level to 15 wt %. Check the slurry pH, and adjust if necessary to pH ≥10 with aqueous caustic soda (NaOH) solution.
9. Package and store the final slurry in a sealed polyethylene container. Do not let the solids dry out. In the absence of dehydration, the product shelf life may be indefinite.

9.0 References

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[1] Lynch, R. W.; Dosch, R. G.; Kenna, B. T.; Johnstone, J. K.; Nowak, E. J.; Sandia Solification 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. and 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, TH and CM Jantzen. “Evaluation of the TiO_2 Limit for DWPF Glass”, WSRC-TR-2003-00396, Revision 0, October 30, 2003.

[8] Hobbs, D. T., Nyman, M. and 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. and Nyman, M. D., “Preparation and Use of Dried Monosodium Titanate,” WSRC-TR-2003-00546, January 2004.

[10] Barnes, M. J., Edwards, T. B., Hobbs, D. T. and Marshall, K. M., “Strontium and Actinide Removal Testing with Monosodium Titanate and Other Sorbents,” WSRC-TR-2001-00436, Rev. 0, October 2001.

[11] Hobbs, D. T., Blume, M. S. and Thacker, H. L., “Screening Evaluation of Sodium Nonatitanate for Strontium and Actinide Removal from Alkaline Salt Solution,” WSRC-TR-2000-00361, Rev. 0, October 2000.

[12] Hobbs, D. T., Blume, M. S. and Thacker, H. L., “Screening Evaluation of Alternate Sorbents and Methods for Strontium and Actinide Removal from Alkaline Salt Solution,” WSRC-TR-2001-00072, Rev. 0, February 2001.

[13] Hobbs, D. T. and Nyman, M. D., “Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides,” Proposal submitted to the Environmental Management Science Program, Program Announcement LAB 01-16, March 2001.

[14] Nelson, R. D.; *Dispersing Powders in Liquids*, Handbook of Powder Technology Volume 7, Elsevier, Amsterdam, 1988, 199.

[15] Hobbs, D. T., “FY03 Annual Report for Environmental Management Science Program - Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides,” WSRC-RP-2003-00475, June 2003.

[16] Dimenna, R. A., Elder, H. H., Fowler, J. R., Fowler, R. C., Gregory, M. V., Hang, T., Jacobs, R. A., Paul, P. K., Pike, J. A., Rutland, P. L., Smith, III, F. G., Subosits, S. G., Taylor, G. A., Campbell, S. G., Washburn, F. A., “Bases, Assumptions, and Results of the Flowsheet Calculations for the Decision Phase Salt Disposition Alternatives,” WSRC-RP-99-00006, May 2001.

[17] W. Brasel, personal communication to D. T. Hobbs, November 14, 2003, recorded in laboratory notebook, WSRC-NB-2003-00238, page 8.

[18] Subosits, S. G., personal communication to E. Harrison, “Throughput Tables for Optimized MST Scenarios,” April 21, 2004 recorded in laboratory notebook WSRC-NB-2004, pages 167-168.

[19] Herman, C. C., Edwards, T. B. and Peeler, D.K., “The impact of alternative sorbents as compared to monosodium titanate on the Defense Waste Processing Facility,” WSRC-TR-2004-00200, May 2004.