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Strontium and Actinide Separations from High Level Nuclear Waste Solutions Using Monosodium Titanate 2. Actual Waste Testing

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Abstract: Pretreatment processes at the Savannah River Site will separate ^{90}Sr, alpha-emitting and radionuclides (i.e., actinides) and ^{137}Cs prior to disposal of the high-level nuclear waste. Separation of ^{90}Sr and alpha-emitting radionuclides occurs by ion exchange/adsorption using an inorganic material, monosodium titanate (MST). Previously reported testing with simulants indicates that the MST exhibits high selectivity for strontium and actinides in high ionic strength and strongly alkaline salt solutions. This paper provides a summary of data acquired to measure the performance of MST to remove strontium and actinides from actual waste solutions. These tests evaluated the effects of ionic strength, mixing, elevated alpha activities, and multiple contacts of the waste with MST. Tests also provided confirmation that MST performs well at much larger laboratory scales (300 – 700 times larger) and exhibits little affinity for desorption of strontium and plutonium during washing.

Keywords: Sorption, ion exchange, strontium, plutonium, neptunium, uranium

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INTRODUCTION

Monosodium titanate (MST), $NaTi_2O_5HxH_2O$, is an amorphous white solid that exhibits high selectivity for the ion exchange/adsorption of many metallic ions in both acidic and alkaline waste solutions (1). Interestingly, MST exhibits high selectivity for strontium and several actinides in highly alkaline solutions making the material an attractive candidate to treat high level nuclear waste solutions produced from fuel reprocessing operations (2, 3). The Savannah River Site contractor selected MST for use in the In-Tank Precipitation (ITP) Process in the early 1980s.

Savannah River National Laboratory (SRNL) personnel developed a slightly modified synthesis of MST that produced a material tailored for deployment in the ITP process (4). A recent study using high resolution transmission electron microscopy of the SRNL-developed MST revealed a spherically-shaped particle that featured an amorphous glass-like core and outer fibrous region. Analysis of the strontium-sorbed MST located the strontium only in the outer fibrous region of the particle suggesting that the inner glasslike region is not readily accessible for sorption/ion exchange (5).

After abandoning the In-Tank Precipitation Process for waste pretreatment in 1998, the SRS went through a lengthy technology selection process and once again selected MST as the preferred method for strontium and actinide separations (6). Pretreatment facilities planned for the Savannah River Site that will use MST include the Actinide Removal Process (ARP) and the Salt Waste Processing Facility (SWPF). The ARP facility is scheduled to begin operations in FY07 and SWPF beginning in FY09.

SRNL conducted a number of tests on the performance of MST to remove strontium and actinides in support of the design of these facilities. These studies focused on the effects of ionic strength, temperature, mixing, and solution composition. A recent publication provides a summary of the key findings from these studies using simulated waste solutions (4). This paper provides a summary of research data acquired on the performance of MST using actual tank wastes. Tank waste solutions are much more complex chemical mixtures than the simulants and include trace components such as transition and main group metal ions and lanthanides. These trace components as well as minor chemical components such as phosphates, silicates, halides and organics may influence sorption/ion exchange of the strontium and actinides with the MST.

EXPERIMENTAL

Monosodium Titanate (MST)

All testing used one of three batches of MST prepared by Optima Chemical Group, LLC (Douglas, GA). The preparation of the MST follows a laboratory procedure developed by the Savannah River National Laboratory (SRNL) (4). Batch numbers for the MST samples included 95-QAB-451, 96-QAB-281 and 00-QAB-417. MST Batch #00-QAB-417 derives from Batch # 95-QAB-451. WSRC returned a portion of Batch #95-QAB-451 material to Optima Chemicals, Inc. in 2000 for repackaging in new drums. The MST is supplied as aqueous slurry containing approximately 15 wt% MST solids, $0.10 - 0.15$ M NaOH and $100 - 150\ \mathrm{mg/L_{-1}NaNO_2}$.

Actual Waste Samples

The Closure Business Unit of the Washington Savannah River Company provided all of the waste samples used in these studies. For small samples (0.1 L), the tank sampling method consisted of lowering a stainless steel bottle into the waste. After filling the sample bottle, the bottle was capped and transported to SRNL in a shielded container. For larger samples (38L), a specially designed sampler was lowered into the tank in an open configuration to allow waste to fill the container. After filling, the sampler was closed, the sampler lifted out of the waste and the external surfaces sprayed with water to remove external contamination. The sampler was then lifted from the tank, placed in a shielded container and transported to SRNL.

Sample bottles were removed from the shipping containers and placed into the Shielded Cells Facility (SCF) at SRNL. We opened the small sample bottles transferred the liquid samples into plastic bottles. We transferred the contents of the 38-L sampler into stainless steel tanks. In some cases we combined the contents of several sample bottles from a single tank or from multiple tanks to provide sufficient volume of waste for testing. As necessary, we also diluted the tank samples with deionized distilled (DDI) water or 1.66 M sodium hydroxide solution to the appropriate concentration for testing. Aliquots were taken from each storage bottle or tank and analyzed for radiochemical and chemical composition. Table 1 provides a summary of the sodium, strontium, and actinide concentrations for each of the seven tank waste solutions used in the following tests.

Batch Ion Exchange/Adsorption Tests at Different Ionic Strengths

These tests used a composite of tank wastes from more than twenty SRS waste tanks. We treated the composite material with two separate additions of 0.55 M sodium tetraphenylborate solution (0.147 L and 0.035 L, respectively) seventeen days apart to remove radio-cesium. Removal of the radio-cesium decreased the gamma activity in the material to a very low level allowing contact handling of the material. After mixing for additional 10-days, we filtered the mixture through 0.45-μm filter. We collected the filtrate into a clean plastic bottle and transferred the bottle from the SCF to a radio-hood.

Table 1. Sodium and sorbate concentrations in the tank waste solutions

		Waste solution identification						
		1	2	3	4	5	6	7
Test description	Unit	Effect of ionic strength	Effect of ionic strength	Large scale demonstrations	Large scale demonstrations	Hydraulically scaled reactor	Elevated alpha activity	Elevated alpha activity
Sodium	M	7.5 (0.75)	4.5 (0.45)	5.6 (0.56)	6.2 (0.62)	6.2 (0.62)	5.6 (0.56)	5.6 (0.56)
Strontium	ug L^{-1}	41.0 (2.0)	24.6 (0.74)	<75	<980	175 (44)	3.70 (0.59)	174 (8.0)
Plutonium	ug L^{-1}	13.5 (1.0)	8.22 (0.22)	1.94 (0.14)	3.31 (0.23)	3.66 (0.16)	251 (13)	411 (39)
Neptunium	ug L^{-1}	389 (95.5)	174 (22.7)	<0.00192	<0.019	320 (80)	105 (26)	136 (2.8)
Uranium	ug L^{-1}	11,500 (876)	5860 (319)	5360 (1340)	727 (182)	12,500 (3120)	9810 (2450)	4690 (51.7)

*Values in parenthesis are single standard deviation of the reported concentrations.

We added 75-μL of ^{85}Sr radiotracer (Perkin-Elmer Life Sciences, specific activity = 7.992 Ci L^{-1}) and 100-μL of ^{237}Np (0.671 mg L^{-1} in 0.1 M nitric acid) to the composite waste solution. After mixing overnight, we filtered the waste solution through a 0.45-μm filter and collected the filtrate in a plastic bottle. The sodium concentration of the waste solution measured 7.5 M (Waste Solution 1). We diluted a portion of the 7.5 M waste solution with DDI water to decrease the sodium concentration to 4.5 M (Waste Solution 2). After mixing the diluted waste solution for 2 days, we filtered the diluted solution through a 0.45-μm filter and collected the filtrate in a plastic bottle.

We placed 120-mL of each of two waste solutions into 250-mL plastic bottles. After incubating at 25 ± 3°C overnight in a Lab Line shaking waterbath (Cole Parmer Catalog #E-01290-20), we added the appropriate amount of MST slurry (#95-QAB-451) to provide a MST concentration of 0.2 g L^{-1}. Aliquots of each test bottle were taken after 0.25, 0.50, 0.75, 1.0, 1.5, 2, 4, 8, 24, 96, and 168-hours after the MST addition. Each aliquot was filtered through a 0.45-μm syringe filter. We collected the filtrate in a plastic sample bottle.

We prepared samples of the filtrates for radiochemical analysis by pipetting 4-mL of the filtrates slowly into 4-mL of 5 M nitric acid solution. We gently mixed the acidified samples and allowed the samples to stand with occasional mixing for a minimum of 2 hours to produce a clear colorless solution for analysis. The ^{85}Sr activity was measured by gamma pulse height spectroscopy. We determined concentrations of ^{237}Np, ^{238}U, ^{239}Pu and ^{240}Pu by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis. The $^{239/240}$Pu and ^{238}Pu activity determination relied on alpha spectroscopy after chemically separating the plutonium from uranium and neptunium.

Large Scale Demonstrations

Large scale demonstrations used supernate samples from each tank farm that were obtained using 38-liter samplers. The first demonstration used a solution formed by mixing supernates from two waste tanks. We diluted the composite solution to a sodium concentration of 5.6 M using 1.66 M sodium hydroxide solution and stored the diluted solution at ambient cell temperature (Waste Solution 3). The second demonstration featured supernate from a single tank diluted to a sodium concentration of 6.2 M (Waste Solution 4).

We conducted the large scale demonstrations in a 100-L stainless steel cylindrical tank equipped with an air-driven mixer. We placed approximately 66-L of the waste solution into the reactor. With mixing we added sufficient MST slurry (#95-QAB-281) to provide a MST concentration of 0.5 g L^{-1}. The mixing speed was adjusted to provide a surface vortex of about 1 – 3 inches compared to a total waste height of about 23-inches. Aliquots were taken from the reactor 1, 2, 3, 8, 12, 24, and 30-hours after the addition of the MST. We prepared the samples for analysis as described above except we performed a 100-fold dilution into 0.2 M nitric acid. The larger dilution reduced personnel exposure from the high gamma activity in the waste solutions.

Hydraulically Scaled Reactor (HSR) Testing

This test examined the efficacy of MST in actinide and strontium removal using conditions similar to those planned for the ARP. We fabricated a 30-L working volume reactor to provide equivalent mixing conditions (i.e., tip speeds and geometrical similarity) to the 17,700-L reactor installed in the ARP facility. The mixing energy of the ARP agitator in the ARP Facility ensured turbulent conditions and, hence, will likely resemble that planned for the SWPF, which features a batch reactor having a working volume of 340,000 liters. In addition to the 90° baffles, the 30-L reactor had the same sloping bottom as that in the ARP Facility reactor. The 30-L reactor did not contain heating and cooling coils that the ARP reactor features.

This test featured the same composite waste solution from the second large scale demonstration (Waste Solution 4) to which we added ^{85}Sr, $^{239/240}$Pu, ^{237}Np, depleted U, non-radioactive cesium and non-radioactive strontium to produce Waste Solution 5 (see Table 1). We added the actinides as a carbonate solution to reduce the chance of sudden precipitation of these components when added to the strongly alkaline waste solution. We detected no visible evidence of solids formation upon the addition of any of the added components. The solution was equilibrated by mixing at ambient laboratory temperature for three weeks.

^{85}Sr, ^{237}Np and uranium concentrations remained unchanged over the 3-week period. We observed a significant decrease in the ^{239,240}Pu concentrations between the 14-day and 21-day samples. The cause of the significant change in plutonium concentration is not known. After the 3-week equilibration time, we added sufficient MST slurry (#96-QAB-281) to provide a MST concentration of 0.4 g L^{-1}. We sampled the reactor 2, 4, 12, 18, 24, and 30 hours after the MST addition.

In parallel, we carried out batch ion exchange/adsorption tests using the same testing protocol as described for the ionic strength tests. This provides for a comparison of Sr/actinide separations between the hydraulically-scaled reactor (30-L) and that in waterbath shaker (0.12-L). Sampling and radiochemical analyses for these tests featured the same experimental and analytical protocols as described previously.

Elevated Alpha Activity and Multiple Strike Tests

The initial set of tests featured a composite material composed of supernate samples from four different waste tanks to provide waste solution with elevated alpha activity principally from plutonium and elevated ^{90}Sr activity (Waste Solution 6). The combined composite sample was calculated to have a sodium concentration of 5.6 M based on the measured sodium concentrations and volumes used to prepare the composite from the four waste tank samples. After allowing the composite to equilibrate for two weeks we conducted batch contact tests in duplicate. For these tests we made three separate additions of MST (#95-QAB-451) at a concentration of 0.4 g L^{-1}. MST additions occurred at time 0, 30 and 54 hours. Sampling of the test bottles occurred at 0, 4, 24, 30, 54, and 78 hours. The samples at 0, 30, and 54 hours occurred immediately before the addition of the MST.

The second set of multiple strike tests featured a supernate sample from a single waste tank diluted to 5.6 M with 1.66 M sodium hydroxide solution (Waste Solution 7). The 5.6 M Na waste solution equilibrated for 12 weeks. After the equilibration time, we conducted five tests using the test protocols shown in Table 2. For each test we placed 120-mL of the equilibrated waste solution into a 250-mL polyethylene bottle fitted with a cap. We then added the desired amount of MST (#00-QAB-417) at the appropriate time. Test bottles were continuously stirred (magnetically) in a water bath at a constant temperature of 25 ± 4°C.

For Tests E and H involving intermediate filtration, the bulk test solutions (post-sampling) were filtered through 0.1-μm polyether sulfone membrane disposable cup filters. For Test H, the test solution was centrifuged prior to filtration to collect the first strike MST solids for desorption testing. Sampling involved removing a test bottle from the waterbath, manually shaking to produce a homogeneous mixture, pulling approximately 7-mL of the test mixture into a disposable 10-mL syringe, and filtering the sample

Table 2. Multiple strike tests conditions

Test ID	Description
A	Addition of 0.4 g/L MST with sample analysis at 0, 6, 12, 24, 48, and 168 h.
B	Addition of 0.8 g/L MST with sample analysis at 0, 6, 12, 24, 48, and 168 h.
E	Add 0.4 g/L MST (incrementally) at 0, 6, and 12 h with filtration (0.1 μm) prior to the second and third MST strikes and with sample analysis at 0, 6, 12, 24, 36, 48, and 168 h (prior to filtrations and incremental additions at 6 and 12 h).
G	Control – no addition of MST with sample analysis at 0, 6, 12, 24, and 168 h.
H	Add 0.2 g/L MST (incrementally) at 0, 6, and 12 h with filtration (0.1 μm) prior to the second and third MST strikes and with sample analysis at 0, 6, 12, 24, and 168 h (prior to filtrations and incremental additions at 6 and 12 h).

mixture through a 0.1-μm polyvinylidene fluoride syringe filter disk and into a sample bottle. Five milliliter portions of each filtered sample were pipetted into a second sample bottle containing 20 mL of 2 M nitric acid. The diluted, acidified samples were manually shaken for approximately 15 seconds and allowed to equilibrate for a minimum of 2 hours before subsampling for specific radiochemical analyses.

Desorption Tests

Desorption tests used the residual MST solids from Test A and those from the first strike of Test H (see Table 2). In the case of Test H, the solids were held in 3-mL sample of its waste solution until after all adsorption tests completed. The tests were conducted by concentrating the residual MST solids using a centrifuge. After centrifuging the test mixtures, we decanted as much supernate as possible off the settled solids and added the desired volume of supernate back to the solids to provide a 2 wt% solids concentration. The mass of solids present was calculated assuming the centrifuged volume of test solution contained the target concentration of MST added during the adsorption tests (i.e., if 0.4 $g\,L^{-1}$ MST was added in the adsorption test, then the residual adsorption test volume contained 0.4 $g\,L^{-1}$ MST solids).

The residual test solutions and centrifuged solids were held for a period of 1 to 2 weeks between the adsorption and desorption tests. The decanted residual supernate from each test was sampled and analyzed to determine both the amount of strontium and plutonium loaded onto the MST during its adsorption testing as well as the residual soluble concentration added back to the centrifuged MST solids. The residual solids and supernate were transferred to a custom-built glass vessel and diluted with distilled, deionized water to simulate washing of the solids. The exact level of dilution was based upon the amount of water calculated to reduce the measured sodium concentration (5.6 M) of the residual supernate to a final sodium concentration of 0.5 M (i.e., approximately 11-fold dilution). After dilution, we continuously stirred (magnetically) the suspension at a constant temperature of $25 \pm 3^\circ C$ in the same apparatus as used in the adsorption tests. We sampled the tests at 4, 8, 12, and 24-hours using the same methodology as reported above for the adsorption tests.

RESULTS

Effect of Ionic Strength

Figures 1 and 2 provide plots of the strontium concentration and plutonium activity in solution, respectively, as a function of time upon addition of 0.2 $g\,L^{-1}$ MST to tank waste supernates diluted to sodium concentrations

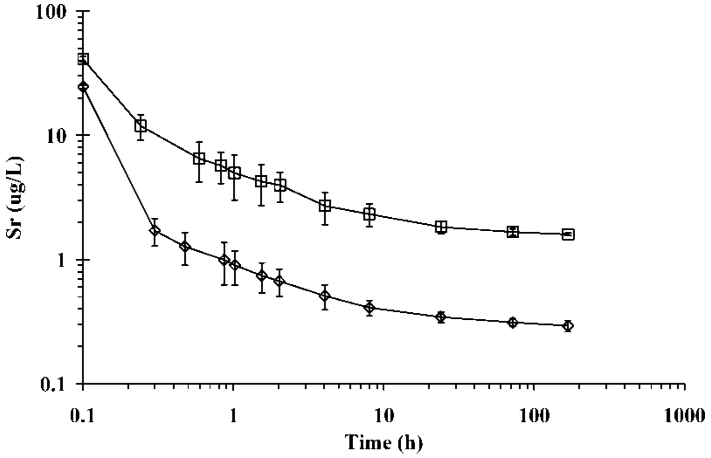

Figure 1. Concentration of strontium versus time in waste solutions at different sodium concentrations: ○ = 4.5 M and □ = 7.5 M.

of 4.5 M and 7.5 M. A plot of the ^{237}Np concentration with time exhibited a similar shape to that of plutonium. Uranium removal proved in determinant for both ionic strength solutions given the combination of the low MST concentration (0.2 g L^{-1}) and high uranium concentration in the waste solution.

Strontium removal proceeded rapidly at both ionic strengths and approached equilibrium within 24 hours (Fig. 1). Removal of the actinides proved slower than strontium and had not reached equilibrium at the final sampling time (168-hours) for plutonium and neptunium. Plutonium and

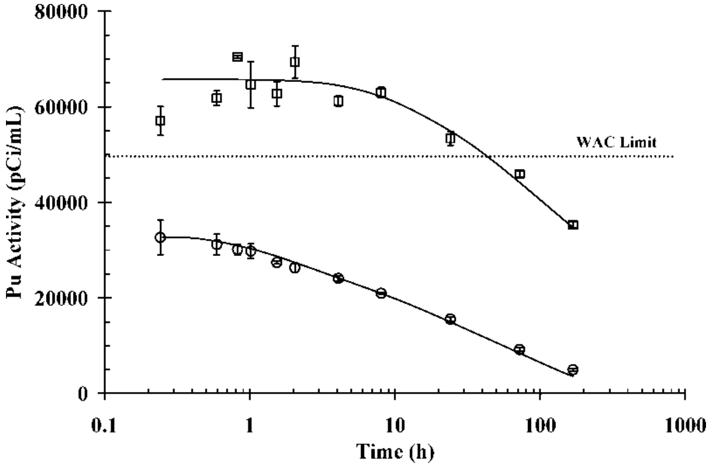

Figure 2. Concentration of plutonium versus time in waste solutions at different sodium concentrations: ○ = 4.5 M and □ = 7.5 M.

Table 3. Batch distribution constants for tests at different ionic strengths

[Na], M	K_d (mL g^{-1})[a] Strontium	 Plutonium	 Neptunium
4.5	4.12E + 05	4.35E + 04	1.37E + 04
	(4.37E + 04)	(2.24E + 03)	(1.00E + 01)
7.5	1.20E + 05	5.95E + 03	9.05E + 03
	(2.99E + 03)	(1.08E + 02)	(1.65E + 03)

[a]Tank waste supernate contacted with 0.2 g L^{-1} MST at 25°C for 168-hours. Numbers in parenthesis are single standard deviation.

neptunium removal in the higher ionic strength supernate (7.5 M sodium) were not discernible until the 24-hour sampling time (Fig. 2).

Table 3 provides the calculated batch distribution constants (K_d) measured after 168-hours of contact. The K_d values decrease in the order, Sr $>$ Pu $>$ Np at 4.5 M sodium concentration and Sr $>$ Np $>$ Pu at 7.5 M sodium concentration. K_d values for strontium and plutonium decreased by factors of 3.4 and 7.3, respectively, upon an increase in the sodium concentration from 4.5 M to 7.5 M. Note that the K_d values for neptunium were not statistically different at the two different ionic strengths.

Large Scale Demonstrations

These tests featured waste supernates treated with MST supplied by Optima Chemicals, Inc. (Lot #96-QAB-281). The first test used a composite of supernate samples from two waste tanks treated with 0.5 g L^{-1} MST (Waste Solution 3). The second test treated a supernate sample (Waste Solution 4) from a single waste tank contacted with 0.4 g L^{-1} MST. Table 4 provides the calculated batch distribution constants determined

Table 4. Batch distribution constants for large scale demonstrations

		K_d (mL g^{-1})[a]	
Waste solution	[MST] (g L^{-1})	Strontium	Plutonium
3	0.5	8.0E + 03	1.0E + 04
		(1.2E + 03)	(1.0E + 03)
4	0.4	3.5E + 03	4.8E + 03
		5.2E + 02)	(1.2E + 03)

[a]Values measured after 24 hours of contact with MST. Numbers in parenthesis are single standard deviation.

from the measurement of ^{90}Sr and plutonium concentrations after 24-hours of contact with the MST. At the time of these tests, both the ARP and SWPF flowsheets set a contact time of 24-hours for each batch of waste processed in these facilities.

Hydraulically Scaled Reactor Testing

This test used Waste Solution 5 recovered from the second Large Scale Demonstration and spiked with stable cesium and strontium, ^{85}Sr, depleted uranium, ^{237}Np and plutonium. We contacted this waste with 0.4 g L^{-1} MST (Optima Chemical Group, LLC Lot #96-QAB-281) at ambient laboratory temperature. Concurrently with the HSR test we carried out a test with this waste at the 0.1-L scale using a waterbath shaker operating at 175 rpm and temperature maintained at 25 ± 3°C. The waterbath shaker serves as the standard method for mixing and controlling temperature during small scale laboratory batch contact tests evaluating strontium and actinide removal performance.

Figure 3 provides a plot of the ^{85}Sr and plutonium concentrations versus time in the HSR (30-L) and the waterbath (0.1-L). The results indicate rapid removal of both strontium and plutonium from the waste solution in the HSR such that the system appeared to reach equilibrium within 2 hours of contact with the MST (see Fig. 3). We observed similar behavior for neptunium and uranium (not shown). We also observed good agreement between the measured solution concentrations for both ^{85}Sr and plutonium, as well as ^{237}Np and uranium (not shown), in the waste solutions treated at both the 30-L and 0.1-L scales.

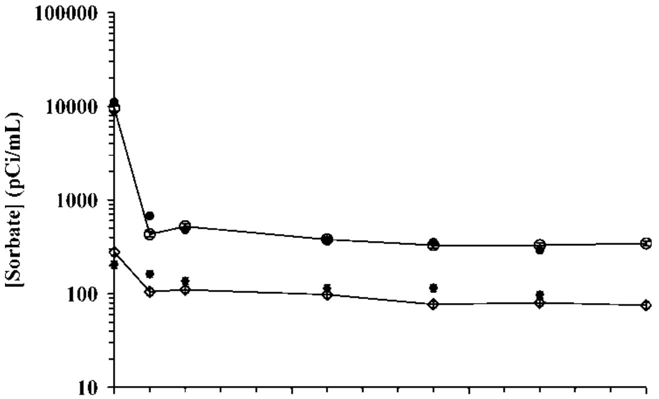

Figure 3. ^{90}Sr and plutonium activities versus time upon contact with MST: ○ = ^{85}Sr in hydraulically scale reactor, ● = ^{85}Sr in waterbath shaker, △ = Pu in Hydraulically Scale Reactor, and ▲ = Pu in waterbath shaker.

Table 5. Radioisotope activities in elevated alpha activity tests

Time (h)	^{90}Sr (pCi mL^{-1})	^{237}Np (pCi mL^{-1})	Total Pu (pCi mL^{-1})
0	519,000 (130,000)	73.8 (18.4)	612,500 (20,800)
4	23,300 (8,130)	32.8 (0.71)	166,000 (884)
24	14,900 (972)	21.7 (5.39)	97,800 (1,860)
30	60,100 (31,000)	19.6 (2.39)	97,400 (1,330)
54	7,690 (7,680)	$<$18.1	31,000 (1,860)
78	26,300 (23,000)	$<$20.9	19,600 (1,400)
WAC	50,000	37.5	22,500

Numbers in parenthesis are single standard deviation. WAC = Waste Acceptance Limit.

Elevated Alpha Activity Testing and Multiple Strike Testing

The initial elevated alpha activity test featured three consecutive additions of 0.4 g L^{-1} MST at time 0, 30 and 54-hours to a waste supernate diluted to 5.6 M in sodium concentration (Waste Solution 6). This test used a MST sample supplied by Optima Chemical Group, LLC and identified as Lot #95-QAB-451. The waste supernate featured elevated concentrations of both plutonium, ^{90}Sr and ^{237}Np compared to previous actual waste tests (see Table 1).

Table 5 provides a summary of the solution concentrations versus time for ^{90}Sr, ^{237}Np and plutonium in addition to the WAC limits for each of these radioactive components in this test. Figure 4 provides a plot of the plutonium concentration versus time over the course of the experiment. Results indicated that a single strike of MST at a concentration of 0.4 g L^{-1} and contact time of 4-hours was sufficient to reduce ^{90}Sr and ^{237}Np concentrations below the target WAC limit.[i] For plutonium, three strikes of 0.4 g L^{-1} MST were required to reduce the plutonium activity to below the WAC limit for alpha activity.

The second set of elevated alpha activity tests featured consecutive additions of 0.2 g L^{-1} and 0.4 g L^{-1} MST at time 0, 6 and 12-hours with intermediate filtration between the second and third additions and single additions of 0.4 and 0.8 g L^{-1} MST. For these tests we used a MST sample supplied by Optima Chemical Group, LLC and identified as Lot #00-QAB-417. The shorter contact times in this test compared to the earlier actual waste tests reflect a change in 2004 for the planned contact times in the SWPF. The reduced contact time was adopted to increase facility throughput.

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[i] WAC Limits as of 2002. New WAC limits are under development with the Nuclear Regulatory Commission in response to new legislation governing the disposal of high level waste produced from fuel reprocessing operations within the Department of Energy.

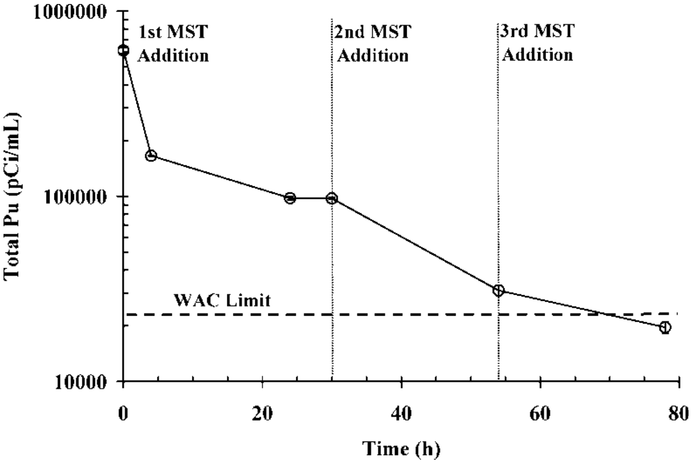

Figure 4. Plutonium activity versus time in elevated alpha activity test #1.

Figure 5 provides a plot of plutonium concentration versus time for the single and multiple strike tests according to the testing protocols identified in Table 1 (Tests A, B, E, and H). As expected single additions of 0.4 and 0.8 g L^{-1} MST failed to remove sufficient plutonium to achieve the WAC limit within 24-hours. Note that the 0.8 g L^{-1} strike did achieve the WAC limit sometime between the 24-hour and 168-hour sampling times. Three

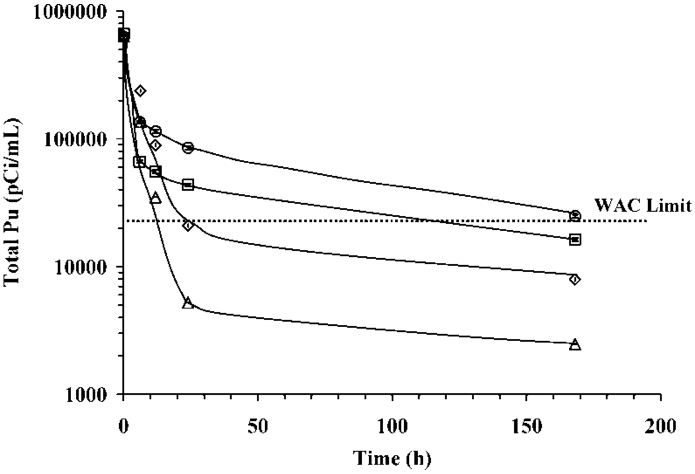

Figure 5. Plutonium activity versus time in elevated alpha activity test #2: ○ = 0.4 g L^{-1} MST, □ = 0.8 g L^{-1} MST, ◇ = 3 additions of 0.2 g L^{-1} MST with intermediate filtration, and △ = 3 additions of 0.4 g L^{-1} MST with intermediate filtration.

additions of 0.2 or 0.4 g L^{-1} MST with intermediate filtration resulted in sufficient plutonium removal so that the treated solution meets the WAC total alpha limit after 24-hours. The larger addition test (3 × 0.4 g L^{-1} MST) exhibited an overall DF at 24-hours of 120 compared to that for the smaller addition test (3 × 0.2 g L^{-1} MST) of 33. Both are higher than the single strike tests, which measured 7.8 and 15 at 0.4 and 0.8 g L^{-1} MST, respectively (see Table 6).

Results for ^{90}Sr, ^{237}Np and uranium show similar trends reported for plutonium above. Table 6 provides the 24-hour decontamination factors (DF) values determined for each of the sorbates. The DF values decrease with increasing initial cation equivalents concentration. For example, DF values for strontium measured in the single strike tests are about a factor of 7 higher than those for plutonium and a factor of 47 higher than those for uranium. The total cation equivalents for strontium, plutonium, and uranium in this waste measured 3.96 ± 0.18 for strontium, 6.88 ± 0.64 for plutonium and 39.6 ± 0.44 for uranium. Note that even though the decontamination factor for uranium is low (1.3 – 2.3) compared to strontium and plutonium, the total quantity of uranium sorbed by the MST is larger on a mass basis than that of strontium and plutonium combined.

Desorption Tests

MST solids from two of the 2nd set of multiple strike tests (Tests A and H in Table 1) were recovered from the test bottles tested for desorption under washing conditions. Table 7 provides a summary of the test results as well calculated theoretical maximum values assuming complete desorption of ^{90}Sr and plutonium from the MST solids. For both tests, the measured ^{90}Sr, ^{238}Pu and ^{239,240}Pu activities proved very low and often below the detection limit for the analytical method. The 24-hour samples showed some evidence of desorption of ^{90}Sr and ^{238}Pu. However, the amount of activity in these samples measured 3—4 orders of magnitude below the theoretical maximum value suggesting that very little desorption occurred within the 24-hour time period.

Table 6. 24-hour decontamination factors measured in multiple strike tests

		24-hour decontamination factor			
Test ID	MST additions (g L^{-1})	Sr	Pu	Np	U
A	0.4	55	7.8	>2.2	1.3
B	0.8	98	15	>2.2	1.9
E	3 × 0.2	660	33	>2.2	1.5
H	3 × 0.4	260	120	>2.2	2.3

Table 7. ^{90}Sr, ^{238}Pu, and ^{239,240}Pu activities in diluted supernate from MST desorption tests

		Concentration (pCi/mL)					
Test ID	Reaction time (h)	Sr-90	±	Pu-238	±	Pu-239/240	±
A	0	235	20	<103	DL	33	8.2
A	4	184	51	<37	DL	<120	DL
A	8	<143	DL	<585	DL	<38	DL
A	12	<122	DL	86	17	<156	DL
A	24	347	61	235	47	<91	DL
	Theoretical maximum	5.7E + 05		3.5E + 06		1.6E + 05	
H	0	418	41	<2410	DL	<114	DL
H	4	<112	DL	<293	DL	<69	DL
H	8	306	61	<106	DL	<37	DL
H	12	173	51	252	50	<551	DL
H	20	275	51	560	639	<65	DL
	Theoretical maximum	1.6E + 06		7.0E + 06		3.2E + 05	
Blank	4	214	61	<36	DL	<148	DL
Blank	12	143	51	66	13	<65	DL

± values are single standard deviation.
DL = below minimum detection level of the analytical method.
Theoretical maximum assumes complete desorption of ^{90}Sr and Pu.

DISCUSSION

Tests conducted with actual tank supernates at two different ionic strengths as measured by sodium concentrations indicated decreased sorption of strontium and plutonium with increasing ionic strength. In addition to reduced sorption as measured by batch K_d values (see Table 2), the rate of sorption decreased significantly for plutonium. These results confirm trends previously observed with simulated waste solutions (4). Based on these results, flowsheets developed for the planned ARP and SWPF adopted an intermediate sodium concentration of 5.6 M as the baseline sodium concentration for the waste processed through these facilities.

Strontium and actinide removal with MST was successfully demonstrated at a larger laboratory scale (66-L) using two different SRS tank waste materials. The treated waste solutions met the waste acceptance criteria for ^{90}Sr and alpha-emitting radionuclides. Batch K_d values in these demonstrations proved much smaller for strontium and slightly smaller for plutonium compared to the values measured in the ionic strength tests (cf. Tables 2 and 3). This is somewhat surprising given the higher MST concentration (0.4 – 0.5 g L^{-1} vs. 0.2 g L^{-1}). We attribute the lower strontium removal in the large scale demonstrations to the MST sample. The large demonstrations featured a MST material (#96-QAB-281) that exhibited a much lower affinity for strontium compared to the MST material (#95-QAB-451) used in the ionic strength tests.[ii]

MST is produced by a sol-gel synthetic method by mixing titanium(IV) isopropoxide, sodium methoxide and water in isopropanol. Samples prepared by researchers at Sandia National Laboratories typically exhibited irregular shapes (1–3). During the 1980s researchers at SRNL modified the synthesis conditions to produce more spherically-shaped particles (4). The SRNL synthesis has been successfully scaled up by several vendors and delivered as an aqueous slurry containing 100 – 150 g L^{-1} of MST solids.

Since MST is an amorphous solid, the exact structure of the material is not known. We believe it is a layered structure much like that reported for sodium nonatitanate (7). Tests with different commercially prepared batches of MST have exhibited a wide variance in adsorption characteristics, which interestingly does not correlate with particle size or surface area (8–10). Furthermore, we have observed that drying MST at 55 – 100°C reduces sorption kinetics, but not capacity, of the material (8). We attribute the slower sorption kinetics to removal of water which reduces the interlayer spacing and decreases the rate of exchange of sodium ions. With longer contact times (e.g. 168 hours), we observe similar removal performance between the as-received (slurry) and dried MST samples suggesting that the interlayer spacing recovers after prolonged contact with aqueous solutions to allow ion exchange to complete.

Recent high resolution transmission electron microscopy (HR-TEM) using the MST sample 95-QAB-451 revealed that the MST particle consists of a fibrous outer region and an amorphous glasslike inner core. Analysis of the strontium-sorbed MST located the strontium only in the outer fibrous region of the particle suggesting that the inner glasslike region is not readily accessible for sorption/ion exchange (5). The outer fibrous region represents about 45% of the total particle volume for this sample of MST. We did not perform HR-TEM measurements with MST sample 96-QAB-281. Perhaps the lower affinity for strontium and plutonium as exhibited by this sample results from a reduced outer fibrous region compared to that of the better performing material (95-QAB-451). Studies are in progress to determine if there exists a measurable difference in the extent of fibrous region among MST samples that exhibit varying sorption characteristics.

[ii] Unpublished product acceptance testing of MST samples conducted at SRNL measured strontium DF values of 179 ± 24, 186 ± 3, and 77.7 ± 5.1 for MST Batches 95-QAB-451, 00-QAB-417 and 96-QAB-281, respectively.

The HSR test represented a 300-fold increase in scale from that typically used in laboratory tests evaluating the performance of MST samples. The reactor design included features to provide mixing characteristics comparable to that which will occur in the batch contact reactor in the ARP facility. Comparison of the removal characteristics for tests in both the HSR and the waterbath shaker revealed very good agreement for strontium and the actinides (see Fig. 3). This finding confirms that removal characteristics measured in the laboratory successfully scaled by a factor of 300. Furthermore, we conclude that the rate of sorbate removal is not limited by the range of mixing conditions spanned by conditions in the waterbath shaker and the HSR. The test also provides confidence in that removal rates from strontium and actinides that are measured in laboratory equipment will translate to the large reactors planned in the ARP and SWPF.

Recent characterization of SRS waste supernates indicates increased concentrations of alpha-emitting radionuclides, particularly plutonium, in tank waste supernates (11). Consequently, there is increased importance that MST successfully remove increased quantities of plutonium. Extrapolation of the results with simulants at moderate plutonium activities to elevated plutonium activities suggested between two and three times as much MST would be required to achieve the required WAC limit for alpha activity.

Increasing the levels of MST by a factor of 2 or more has significant adverse impacts on the throughput in the ARP, SWPF and the Defense Waste Processing Facility (DWPF). Increased solids in ARP and SWPF operations result in increased filtration times and wash water volumes. The increased filtration times result in reduced facility throughput, which extends the operating lifetime of the facility and increases the overall lifecycle costs for disposal of the high level wastes.

DWPF throughput is adversely impacted by increased titanium in the feed to the melter. The current borosilicate glass formulation can accommodate up to 2 wt% titanium dioxide. Sustained use of MST quantities in the ARP and particularly the much larger SWPF above 0.4 g L^{-1} would result in titanium concentrations approaching and possibly exceeding the limit. To accommodate the higher titanium concentrations, DWPF would reduce the waste loading in the glass, which results in decreased throughput, increased number of glass canisters and, consequently, significantly higher lifetime operating costs.

Tests with waste solutions containing elevated plutonium activities confirmed that as much as 1.2 g L^{-1} of MST would be required to affect sufficient plutonium removal so that the decontaminated waste solution meets the WAC limit for alpha activity allowing disposal as a low-level radioactive waste in the Saltstone facility (see Fig. 4). Thus, the throughput of the ARP and SWPF and the downstream DWPF would be expected to decrease when processing tank wastes containing high alpha activities. The quantities of MST required to successfully remove elevated plutonium activities can be lowered by incorporating an intermediate filtration step (see Fig. 5). Multiple strikes with lower MST concentrations and intermediate filtration reduces the amount of MST sent forward to the DWPF. However, it does not improve throughput in the ARP and SWPF due to the additional filtration stages.

The improved removal of plutonium by incorporating an intermediate filtration state arises from the shape of the plutonium adsorption isotherm (12). At high initial plutonium concentrations, the resulting equilibrium concentration ($>0.2\ \mu M$) resides in a region where the adsorption isotherm exhibits an intermediate slope (see Fig. 1 in reference 12). Consequently, one achieves a lower equilibrium concentration upon two contacts with intermediate filtration versus a single contact with the same total quantity of MST that had been added over the course of two contacts. The adsorption isotherm exhibits a much steeper slope at lower final plutonium concentrations ($<0.2\ \mu M$). In this region, there is essentially no change in the equilibrium concentration between two contacts with intermediate filtration and a single contact with the same total MST quantity.

After concentrating the MST solids by crossflow filtration, the solids are washed with water to reduce the soluble salt content in the waste slurry sent forward to the DWPF for vitrification. During the washing cycle, the sodium content is reduced by approximately a factor of 11 from 5.6 M to 0.5 M. Given this large change in soluble salt composition, strontium and actinides sorbed onto the MST could desorb to some extent and dissolve back into the diluted waste solution. Desorption, if significant, would reduce the overall separation efficiency resulting in an overall increase in the amount of MST used during the operational life of the pretreatment facilities.

To assess the magnitude of desorption we carried out two tests with MST solids recovered from the test set in which MST additions contacted tank waste containing elevated alpha activities (Waste Solution 7). The solids would be expected to contain particularly high levels of strontium and plutonium. Thus, these solids would serve as good candidates for assessing the affinity for strontium and plutonium to desorb from the MST solids during washing. This test limited the total contact time to 24-hours, which is about a factor of three longer than the planned washing sequence in ARP and SWPF.

As shown in Table 6, very little, if any of the sorbed ^{90}Sr and plutonium desorbed from the MST solids in these tests. Thus, we conclude that desorption of strontium and plutonium is not rapid under the tested conditions and does not appear to be a risk with respect to overall removal efficiencies during normal operations. However, increased contact times (>24-hours) or contact with more dilute waste supernates, which could occur as a result of a process upset, may lead to increased desorption. Additional tests with longer contact times and more dilute waste supernates are needed to evaluate the degree of desorption in off-normal conditions.

REFERENCES

1. Lynch, R., Dosch, R., Kenna, B., Johnstone, J., and Nowak, E. (1976) The Sandia solidification process – a broad range aqueous solidification method. IAEA Symposium on the Management of Radioactive Waste, Vienna, Austria, 360–372.
2. Lynch, R.W. (Ed.) (1976) *Sandia Solidification Process Cumulative Report*; Technical Report SAND-76-0105, Ed., Sandia Laboratories: Albuquerque, NM.
3. Dosch, R.G. (1978) *The Use of Titanates in Decontamination of Defense Wastes*; Technical Report SAND-78-0710, Sandia Laboratories: Albuquerque, NM.
4. Hobbs, D.T., Barnes, M.J., Pulmano, R.L., Marshall, K.M., Edwards, T.B., Bronikowski, M.G., and Fink, S.D. (2005) Strontium and actinide separations from high level nuclear waste solutions using monosodium titanate 1. Simulant testing. *Separation Science and Technology*, 40 (15): 3093–3111.
5. Duff, M.C., Hunter, D.B., Hobbs, D.T., Fink, S.D., and Dai, Z. (2004) Mechanisms of strontium and uranium removal from high-level radioactive waste simulant solutions by the sorbent monosodium titanate. *Environ. Sci. Technol.*, 38: 5201–5207.
6. Harmon, H., Murphy, J., and Smalley, R. (2001) *Savannah River Site Salt Processing Project Down Selection Decision Analysis Summary Report*; Technical Report TFA-0106, Rev. 0, Pacific Northwest National Laboratory.
7. Stallings, M.E., Barnes, M.J., DiPrete, D.P., Peters, T.B., Fondeur, F.F., and Hobbs, D.T. (2005) Characterization of Savannah River Site high-level waste supernate samples, Abstracts of Papers, 229th ACS National Meeting, San Diego, CA.
8. Hobbs, D.T., Nyman, M.D., and Clearfield, A. (2004) *Tailoring Inorganic Sorbents for SRS Strontium and Actinide Separations: Optimized Monosodium Titanate and Pharmacosiderite Phase I Final Report*; Technical Report WSRC-TR-2004-00322, Rev. 0, Westinghouse Savannah River Company: Aiken, SC.
9. Hobbs, D.T., Peters, T.B., Duff, M.C., Barnes, M.J., Fink, S.D., and Walker, D.D. (2003) Radiochemical separations for the pretreatment of high-level nuclear waste solutions at the savannah river site. Proceedings of ICEM03; 9th International Conference on Environmental Remediation and Radioactive Waste Management, Oxford, England; ICEM03-4536, 1–6, ASME.
10. Hobbs, D.T., Nyman, M., Medvedev, D., Tripathi, A., and Clearfield, A. (2004) Evaluation of new inorganic sorbents for strontium and actinide removal from high-level nuclear waste solutions; Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC, USA. Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry, 44(1), 367–371.
11. Stallings, M.E., Barnes, M.J., DiPrete, D.P., Peters, T.B., Fondeur, F.F., and Hobbs, D.T. (2005) Characterization of Savannah River Site high-level waste supernate samples, Abstracts of Papers, 229th ACS National Meeting, San Diego, CA.
12. Clearfield, A. and Lehto, J. (1988)) Preparation, structure, and ion-exchange properties of $Na_4Ti_9O_{20}xH_2O$. *J. Solid State Chem.*, 73: 98–106.