Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Development of an Improved Titanate-Based Sorbent for Strontium and Actinide Separations under Strongly Alkaline Conditions

D. T. Hobbs[a]; T. B. Peters[a]; K. M. L. Taylor-Pashow[a]; S. D. Fink[a]
[a] Savannah River National Laboratory, Savannah River Nuclear Solutions LLC, Aiken, SC

To cite this Article Hobbs, D. T. , Peters, T. B. , Taylor-Pashow, K. M. L. and Fink, S. D.(2011) 'Development of an Improved Titanate-Based Sorbent for Strontium and Actinide Separations under Strongly Alkaline Conditions', Separation Science and Technology, 46: 1, 119 — 129

To link to this Article: DOI: 10.1080/01496395.2010.492772

URL: http://dx.doi.org/10.1080/01496395.2010.492772

Separation Science and Technology, 46: 119–129, 2011
Copyright © Savannah River Nuclear Solutions LLC (SRNS)
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.492772

Development of an Improved Titanate-Based Sorbent for Strontium and Actinide Separations under Strongly Alkaline Conditions

D. T. Hobbs, T. B. Peters, K. M. L. Taylor-Pashow, and S. D. Fink
Savannah River National Laboratory, Savannah River Nuclear Solutions LLC, Aiken, SC

High-level nuclear waste produced from fuel reprocessing operations at the Savannah River Site (SRS) requires pretreatment to remove ^{134,137}Cs, ^{90}Sr, and alpha-emitting radionuclides (i.e., actinides) prior to disposal onsite as low level waste. The separation processes at SRS include the sorption of ^{90}Sr and alpha-emitting radionuclides onto monosodium titanate (MST) and caustic side solvent extraction of ^{137}Cs. The MST and separated ^{137}Cs is encapsulated along with the sludge fraction of high-level waste (HLW) into a borosilicate glass waste form for eventual entombment at a federal repository. The predominant alpha-emitting radionuclides in the highly alkaline waste solutions include plutonium isotopes ^{238}Pu, ^{239}Pu, and ^{240}Pu; ^{237}Np; and uranium isotopes, ^{235}U and ^{238}U. This article describes recent results evaluating the performance of an improved sodium titanate material that exhibits increased removal kinetics and capacity for ^{90}Sr and alpha-emitting radionuclides compared to the current baseline material, MST.

Keywords alkaline waste; ion exchange; ionic strength; neptunium; peroxotitanate; plutonium; temperature; uranium

INTRODUCTION

Monosodium titanate (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. This material currently serves as the baseline sorbent for the removal of ^{90}Sr and alpha-emitting radionuclides from HLW at the Savannah River Site (SRS) (1–5). Deployment of this material occurs by a batch adsorption process in which the MST is added at a concentration of $0.4\,\mathrm{g\,L^{-1}}$ to waste solution and mixed for 24 hours. The MST solids and any entrained sludge solids are separated from the waste solution by ultrafiltration. The filtrate moves on to the cesium separation process. The MST solids are washed to reduce the soluble salt content in the interstitial liquid and then are transferred to the Defense Waste Processing Facility (DWPF) for incorporation into a highly durable borosilicate glass wasteform.

The performance of MST to efficiently and rapidly remove alpha-emitting radionuclides serves as the limiting factor in operational throughput for the pretreatment facilities. Higher alpha activities are projected for the Salt Waste Processing Facility (SWPF) and Actinide Removal Process (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 (6). Thus, acceleration of waste disposal at SRS requires materials that exhibit increased loading capacities and removal kinetics for ^{90}Sr and alpha-emitting radionuclides compared to the baseline material, MST.

Recent studies identified a promising new family of peroxotitanate materials with improved strontium and actinide removal characteristics (7). Compared to the baseline MST material, the new peroxotitanate materials, referred to as modified MST or mMST, exhibit higher batch capacities and kinetics for the separation of strontium and actinides from alkaline waste solutions (7–9). Consequently these materials offer the opportunity to reduce sorbent use and increase throughput in processing facilities. This article describes recent results from the ongoing development of this new material for strontium and actinide separations from the strongly alkaline SRS nuclear waste solutions.

EXPERIMENTAL

Preparation of MST and mMST

The MST used in these studies was prepared using a sol-gel process developed at the Savannah River National Laboratory (SRNL) and supplied by Optima Chemical Group LLC (Douglas, GA, Lot #00-QAB-417) as a 15 wt% suspension in water containing 0.10–0.15 M NaOH and 100–150 $\mathrm{mg\,L^{-1}}$ $NaNO_2$ (4). Modified monosodium titanate (mMST) used in these studies was prepared by the post-synthesis treatment of MST. The details of this procedure have been previously published (7). Bench-scale

---

Received 18 February 2010; accepted 10 May 2010.

Address correspondence to D. T. Hobbs, Savannah River Nuclear Solutions LLC, Aiken 29808, United States. E-mail: david.hobbs@srnl.doe.gov

quantities of the mMST were prepared using 25 grams of the Optima-supplied MST. Optima Chemical Group LLC (Douglas, GA) also produced a pilot-scale quantity (15 kg) of mMST, Lot #06-QAB-0139, as a 15 wt% suspension in water using the same conditions as used for the bench-scale preparations.

Preparation of Simulated Waste Solutions

All solutions were prepared using reagent grade chemicals and ultrapure water (MilliQ Element). Table 1 provides a summary of the compositions for the simulated waste solutions used in the performance testing. Prior to the addition of sodium carbonate to the simulated waste solution, the sodium carbonate was dissolved in ultrapure water and contacted with MST for a minimum of 48 hours to remove any tramp strontium. Radioactive components included ^{85}Sr and ^{137}Cs radiotracers (Perkin Elmer Life Sciences, Boston, MA), uranyl nitrate hexahydrate (Mallinckrodt, Phillipsburg, NJ), and nitric acid solutions of plutonium(IV) and neptunium(V), which derive from plutonium and neptunium production operations at the Savannah River Site. After assembling, the solutions were allowed to mix for 1–3 weeks at ambient room temperature using a magnetic stirrer. After this equilibration time, we filtered the solutions through a 0.45-micron nylon-membrane filter to remove any undissolved solids. The filtrates were stored in tightly-stoppered, high density polyethylene (HDPE) bottles at ambient laboratory temperature.

Batch Contact Tests with Simulated Waste Solutions

Strontium and actinide removal testing with the simulant occurred at 25 ± 2°C with sorbent concentrations ranging from 0.1 g L^{-1} to 0.8 g L^{-1}. Test bottles were shaken at 175 rpm in an orbital shaker/waterbath. Sampling of the test bottles occurred at varying times of contact. Prior to sampling the test bottles, the bottles were manually agitated to obtain a representative sub-sample of both the solids and solutions. The samples were filtered through 0.45-μm nylon, 0.10-μm polyvinylidene fluoride (PVDF), or 0.10-μm polytetrafluoroethylene (PTFE) membrane syringe filters to remove MST solids. A measured amount of the filtrate was acidified with an equal volume of 5 M nitric acid solution, mixed well, and allowed to stand with occasional mixing for a minimum of 2 hours (typically overnight) before radiochemical analyses. Gamma spectroscopy measured the ^{85}Sr and ^{237}Np content while alpha spectroscopy measured the total alpha activity. The ^{238,239,240}Pu content was analyzed by radiochemical separation of the plutonium followed by alpha counting of the extracted plutonium. Selected isotopes including ^{86,88}Sr, ^{237}Np, ^{239,240}Pu, and ^{235,238}U were also measured by inductively coupled plasma mass spectrometry (ICP-MS).

Testing was also performed with simulated waste solution at different temperatures and ionic strengths. The compositions of these simulants are shown in Table 1. The effect of temperature testing used Simulant

TABLE 1
Composition of simulants used in mMST performance testing

Solution ID Component	Simulant A (4.5 M Na)		Simulant B (5.6 M Na)		Simulant C (6.5 M Na)		Simulant D (5.6 M Na)	
	Measured	Uncertainty	Measured	Uncertainty	Measured	Uncertainty	Measured	Uncertainty
^{137}Cs (dpm/mL)	7.22E+04	1.03E+03	7.48E+04	1.33E+03	7.66E+04	2.48E+03	7.48E+04	1.33E+03
^{85}Sr (dpm/mL)	1.84E+05	2.94E+03	7.01E+04	1.29E+03	1.59E+05	5.36E+02	7.01E+04	1.29E+03
Sr (μg/L) (ICP-MS)	1.16E+03	7.51E+01	1.03E+03	1.13E+02	6.59E+02	1.09E+02	9.66E+03	1.13E+02
Pu (μg/L) (PuTTA)	2.96E+02	6.75E+00	2.31E+02	9.66E+00	3.34E+02	2.77E+01	7.26E+01	9.66E+00
^{237}Np (μg/L) (ICP-MS)	4.65E+02	9.24E+00	4.99E+02	1.70E+01	4.67E+02	9.02E+00	1.24E+02	2.48E+01
U (μg/L) (ICP-MS)	1.11E+04	1.21E+02	1.02E+04	2.71E+02	1.02E+04	1.40E+02	1.31E+04	2.61E+03
Al(M) (ICP-ES)	3.60E-01	3.60E-02	nd	–	5.30E-01	5.30E-02	nd	–
Al(M) (titration)	3.91E-01	3.91E-02	5.13E-01	5.13E-02	5.58E-01	5.58E-02	5.13E-01	5.13E-02
Free OH (M)	1.08E+00	1.08E-01	1.30E+00	1.30E-01	1.54E+00	1.54E-01	1.30E+00	1.30E-01
CO_3 (M)	2.37E-02	2.37E-03	3.50E-02	1.75E-02	3.18E-02	3.18E-03	3.50E-02	1.75E-02
NO_2 (M)	1.16E-01	1.16E-02	1.39E-01	1.39E-02	1.65E-01	1.65E-02	1.39E-01	1.39E-02
NO_3 (M)	2.18E+00	2.18E-01	2.58E+00	2.58E-01	3.11E+00	3.11E-01	2.58E+00	2.58E-01
SO_4 (M)	4.01E-01	4.01E-02	5.15E-01	5.15E-02	5.99E-01	5.99E-02	5.15E-01	5.15E-02
Na (M) (ICP-ES)	4.92E+00	4.92E-01	4.57E+00	5.94E-01	7.13E+00	7.13E-01	4.57E+00	5.94E-01
Calculated Na (M)	4.58E+00	4.60E-01	5.63E+00	5.90E-01	6.61E+00	6.60E-01	5.63E+00	5.90E-01
Ionic Strength (M)	5.01E+00	–	6.18E+00	–	7.24E+00	–	6.18E+00	–

nd = not determined.

B, which has a nominal sodium concentration of 5.6 M and an ionic strength (Z) of 6.18 M. The ionic strength testing used three simulants, Simulant A, Simulant B, and Simulant C. These simulants had sodium concentrations of 4.5 M, 5.6 M, and 6.5 M, respectively.

Prior to use in the effect-of-temperature experiments, Simulant B was spiked with additional ^{85}Sr radiotracer to bring the ^{85}Sr activity to approximately 1.2E + 05 dpm/mL. Tests were carried out by placing 60 mL of the simulant into each of the three clean HDPE bottles. The bottles were tightly stoppered, and were placed in a waterbath-shaker set to the appropriate temperature of 26, 45, or 66°C. After incubating the sample bottles overnight at the preset temperature, measured amounts of the mMST suspension were added to two of the bottles. The quantity of suspension added provided an mMST concentration of $0.2\,g\,L^{-1}$. The third bottle served as a control with no added sorbent. The bottles were returned to the waterbath and were agitated at 175 rpm for a total of 24 hours at the set temperature.

Aliquots from each test bottle were removed after approximately 6, 12, and 24 hours following the mMST addition. The aliquots were filtered through a 0.1-μm PTFE membrane syringe filter, collecting the filtrate in a clean HDPE sample bottle. Acidified samples from each aliquot were prepared for radiochemical analysis.

A similar procedure was used to conduct the effect of ionic strength experiments using three of the simulants described in Table 1. These experiments were carried out at a constanttemperature of 25.9 ± 0.1°C. Each simulant was tested with both mMST (in duplicate) and baseline MST, along with a control (no sorbent). The sorbent concentrations were $0.2\,g\,L^{-1}$ and $0.4\,g\,L^{-1}$ for mMST and MST, respectively.

Batch Contact Tests with Actual Waste Solution

For testing with the actual waste, 100 mL of the filtered and spiked tank waste (Table 2) was poured into test bottles equipped with magnetic stirring bars. The test bottles were placed into a temperature controlled waterbath (25 ± 3°C) and incubated overnight. Each bottle was then removed from the waterbath, a pre-weighed amount of the appropriate sorbent was added, and the test bottle was returned to the waterbath. At the desired sampling time, a 3-mL aliquot was removed from each test bottle, filtered through a 0.1-μm PVDF membrane syringe filter, and the filtrate was collected in a clean sample bottle. Portions (1.00 mL) of the filtered sample were then pipetted into a second set of sample bottles containing 19 mL of 2 M nitric acid. The acidified samples were shaken for approximately 15 seconds and then allowed to equilibrate with occasional mixing for a minimum of 2 hours (typically overnight) prior to analysis. The acidified samples were analyzed to determine the following: ^{238,239,240}Pu, ^{86,88,90}Sr, and actinides.

TABLE 2
Composition of the tank waste supernate sample

Analyte	Unit	Concentration	Standard Deviation
^{137}Cs	pCi/mL	2.26E+08	0
^{90}Sr	pCi/mL	2.75E+04	2.8E+03
Total Sr	μg/L	1.58E+03	3.2E+02
Total Pu (PuTTA)	μg/L	2.54E+02	1.4E+01
Total Pu (ICP-MS)	μg/L	2.06E+02	4.1E+01
^{237}Np	μg/L	1.29E+02	2.6E+01
Total U	μg/L	1.02E+04	2.05E+03
Na	M	5.48E+00	3.67E-01
OH^-	M	2.10E+00	7.00E-02
NO_3^-	M	2.47E+00	1.51E-01
NO_2^-	M	6.48E-01	6.33E-03
$Al(OH)_4^-$	M	4.23E-01	6.79E-03
CO_3^{2-}	M	5.66E-01	7.85E-03
SO_4^{2-}	M	5.18E-02	1.01E-03
PO_4^{3-}	M	2.17E-03	4.23E-05
F^-	M	bdl	–
Cl^-	M	bdl	–

bdl = below method detection level.

Reuse and Double Strike Testing

Reuse testing—i.e., tests involving multiple contacts of a single aliquot of mMST with different solutions—were carried out using Simulant D having the targeted chemical composition and sorbate concentrations shown in Table 1. Reuse and double strike tests were also performed using actual waste supernate from a SRS waste tank. Analytical results revealed that the tank waste sample was much lower in ^{90}Sr and alpha activity than expected given past studies involving tank samples. Therefore, the composition of the tank waste solution was adjusted to increase the plutonium and strontium content to provide a more challenging matrix for evaluating the MST performance characteristics consistent with prior studies. Table 2 provides the measured composition of the tank sample after spiking with strontium and plutonium.

RESULTS AND DISCUSSION

Performance Testing of mMST for Strontium and Actinide Removal

Effect of Temperature

Testing to evaluate the effect of temperature over the range of 26–66°C on the removal of strontium, plutonium, neptunium, and uranium by $0.2\,g\,L^{-1}$ of mMST was conducted. The testing featured a simulated waste solution having a 5.6 M sodium concentration (Simulant B) as

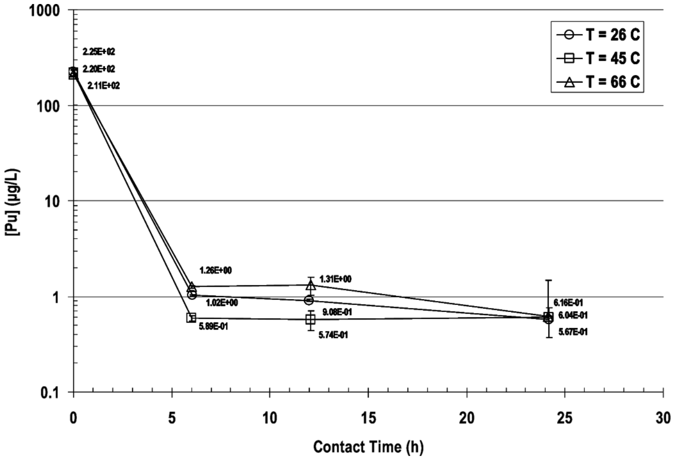

FIG. 1. Plutonium concentration versus time upon contact of a simulated waste solution with $0.2\,\mathrm{g\,L^{-1}}$ of mMST at 26°C (circles), 45°C (squares), and 66°C (triangles).

shown in Table 1. Figures 1 and 2 provide the average plutonium and ^{237}Np concentrations, respectively, versus time at each of the three temperatures. Table 3 provides a summary of the average decontamination factors (DF) for each sorbate at each temperature from duplicate tests. The DF value is calculated by dividing the initial sorbate concentration by the sorbate concentration upon contact with the sorbent for a period of time.

As previously reported for tests at 25°C, strontium, plutonium, and neptunium removal proceeds rapidly, and is more than 95% complete by the first sampling event at six hours (8–10). Generally, small increases in sorbate removal occurred in the latter two sampling events at 12 and 24 hours compared to that measured at 6 hours. The most noticeable exception to this trend occurred with neptunium in the 66°C test. In this test, the neptunium concentration increased with sampling time after 6 hours.

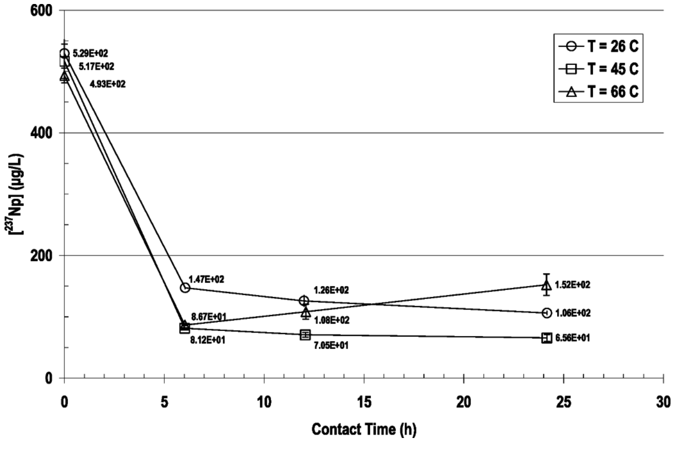

FIG. 2. ^{237}Np concentration versus time upon contact of a simulated waste solution with $0.2\,\mathrm{g\,L^{-1}}$ of mMST at 26°C (circles), 45°C (squares), and 66°C (triangles).

In general, the DF values for strontium, plutonium, and neptunium increased upon an increase in the temperature from 26 to 45°C, followed by a decrease upon raising the temperature to 66°C (see Table 3). The non-linear response in DF with temperature suggests that temperature is influencing more than one factor involved with the adsorption of strontium, plutonium, and neptunium onto the mMST. For example, the temperature could be affecting both the sorbent (mMST) as well as the chemical potential of the solution phase sorbate species.

The magnitude of the change in the quantities of the strontium and plutonium removed is generally small over the range of temperatures and sampling times. For example, the percent sorbate removed over the range of temperatures (26°C to 66°C) and contact time (6–24 hours) was as follows: 95.2–98.1% for strontium and 98.7–99.9% for plutonium. The range for neptunium removal proved larger at 60.0–89.1%. Previous testing with the baseline MST material indicated that the strontium DF values decreased with increasing temperature (11). However, quantitative comparison of the results of this study and the earlier one with MST is difficult due to large differences in the initial strontium concentrations ($11.6\,\mu\mathrm{mol\,L^{-1}}$ in this study versus 0.06–$1.2\,\mu\mathrm{mol\,L^{-1}}$ in the earlier study). Nevertheless, the small effect of temperature on the strontium decontamination by mMST indicates that rigorous temperature control during a batch contact process is not required to achieve very good strontium DF values.

For plutonium, the range of DF values spanned by the 95% confidence interval is large for all three temperatures (Table 3). The wide range of values is due to the combination of achieving very low mass concentrations upon contact with mMST and the relatively high uncertainty in the low mass concentrations given that these concentrations are close to the quantifiable limit for the analytical method. Given the extensive overlap in DF values for each sampling event and each temperature, we concluded that temperature did not exhibit a strong influence on plutonium adsorption for this data set. Previous testing with the baseline MST material indicated plutonium DF values increase with increasing temperature (11).

For neptunium, the DF values increased with contact time and upon a change in the temperature from 26 to 45°C. The DF values decreased upon raising the temperature from 45 to 66°C. However, there is overlap for each sampling event at the lower two temperatures suggesting that the influence of temperature is small. Note, however, that the confidence interval at 66°C for the 24-hour sampling event does not overlap with and is lower than that measured at the earlier sampling events (6 and 12 hours). This suggests that neptunium adsorption is being lost with time at 66°C. Consequently, the percentage of neptunium

TABLE 3
Summary of measured decontamination factors for strontium, plutonium, neptunium, and uranium at 26, 45, and 66°C with 0.2 g L^{-1} mMST

	Strontium				**Plutonium**		
Temperature (°C)	25.8	44.9	66.1	**Temperature (°C)**	25.8	44.9	66.1
Contact Time (h)	6.05	6.03	6.03	**Contact Time (h)**	6.05	6.03	6.03
Sr DF (gamma)	24.8	37.7	32.6	**Pu DF (alpha)**	212	389	185
uncertainty	3.43	0.687	0.112	**uncertainty**	4.28	28.1	5.28
Contact Time (h)	12.00	12.07	12.08	**Contact Time (h)**	12.00	12.07	12.08
Sr DF (gamma)	28.8	45.2	35.6	**Pu DF (alpha)**	260	414	165
uncertainty	3.32	1.41	1.66	**uncertainty**	6.46	98.3	35.8
Contact Time (h)	24.16	24.17	24.14	**Contact Time (h)**	24.16	24.17	24.14
Sr DF (gamma)	35.3	49.6	41.5	**Pu DF (alpha)**	414	332	137
uncertainty	2.35	0.063	3.78	**uncertainty**	145	484	22.6

	Neptunium				**Uranium**		
Temperature (°C)	25.8	44.9	66.1	**Temperature (°C)**	25.8	44.9	66.1
Contact Time (h)	6.05	6.03	6.03	**Contact Time (h)**	6.05	6.03	6.03
Np DF (ICP-MS)	3.47	6.03	5.72	**U DF (ICP-MS)**	0.988	0.997	1.11
uncertainty	0.030	0.042	0.0653	**uncertainty**	0.027	0.0138	0.0313
Contact Time (h)	12.00	12.07	12.08	**Contact Time (h)**	12.00	12.07	12.08
Np DF (ICP-MS)	4.41	7.76	4.68	**U DF (ICP-MS)**	1.03	1.09	1.05
uncertainty	0.312	0.420	0.532	**uncertainty**	0.0322	0.00018	0.0209
Contact Time (h)	24.16	24.17	24.14	**Contact Time (h)**	24.16	24.17	24.14
Np DF (ICP-MS)	4.94	7.86	3.17	**U DF (ICP-MS)**	1.04	1.04	1.00
uncertainty	0.125	0.678	0.362	**uncertainty**	0.0153	0.0177	0.0903

removed after 24 hours of contact by mMST ranges from 60–70% at 66°C versus 76–89% at 26 and 45°C. Previous testing with MST indicated that DF values for neptunium decrease with increasing temperature over the same temperature range (11). Based on the results in this dataset, we concluded that the temperature of the batch contact process should not exceed 45°C to maximize neptunium removal when using mMST.

There appeared to be no measurable removal of uranium by mMST at 26 and 45°C and for the 12 and 24-hour sampling events at 66°C (see Table 3). The 6-h DF value for uranium at 66°C is greater than unity at the 3-sigma interval suggesting a small amount of uranium removal. However, the later sampling events (12 and 24-hours) exhibited no measurable removal. Therefore, the apparent removal of a small amount of uranium at the 6-h sampling event likely reflects errors associated in sampling and analysis. The low affinity of mMST for the adsorption of uranium as measured in these tests at 26, 45, and 66°C is consistent with that reported previously in tests at 25°C (9).

To evaluate if temperature was influencing the adsorption kinetics, we plotted the negative logarithm of the adsorption rate for each sorbate (−log k) against the inverse of temperature (K^{-1}). The adsorption rate in mole L^{-1} s^{-1} was estimated by calculating the change in the sorbate concentration at the start of the test and that after six hours of contact. This is the time interval exhibiting the greatest concentration change. Figure 3 provides the Arrhenius plots for strontium, plutonium, and neptunium. For each sorbate, the adsorption rate did not change with temperature. Thus, it can be concluded that temperature is not influencing the rate of adsorption by the mMST in the temperature range of 26–66°C. Note that the reaction rates followed the order Sr > Np > Pu. This order follows that of the initial sorbate concentration for the simulated waste solution, strontium at $11.6 \pm 0.5\ \mu mol\ L^{-1}$, neptunium at $2.17 \pm 0.08\ \mu mol\ L^{-1}$, and plutonium at $0.914 \pm 0.028\ \mu mol\ L^{-1}$.

Effect of Ionic Strength

The effect of ionic strength on the strontium and actinide removal performance was evaluated using three simulated waste solutions which varied in ionic strength (Z) from 5.01 to 7.24 M, which corresponds to sodium concentrations of 4.58 to 6.61 M (See Table 1). The compositions of the simulated waste solutions were targeted in such a manner so as to fix the relative concentrations over the range of ionic strengths while maintaining the same sorbate concentrations. As can be seen from Table 1, the neptunium (500 $\mu g\ L^{-1}$) and uranium (10,000 $\mu g\ L^{-1}$)

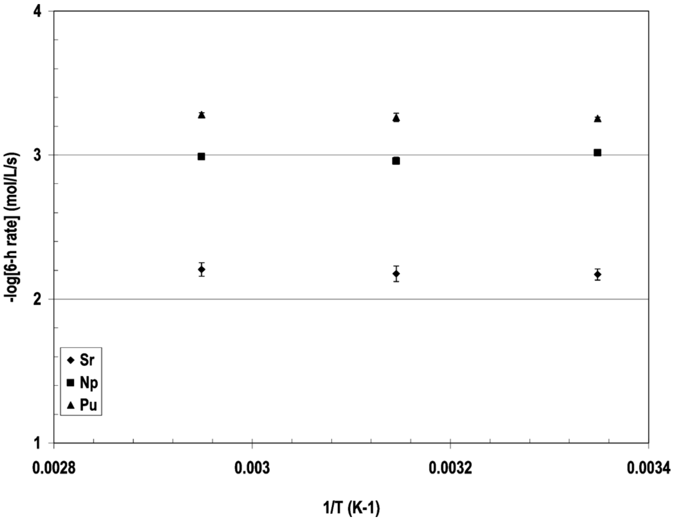

FIG. 3. Arrhenius plot of 6-h reaction rates versus 1/T for the removal of strontium, plutonium, and neptunium by mMST.

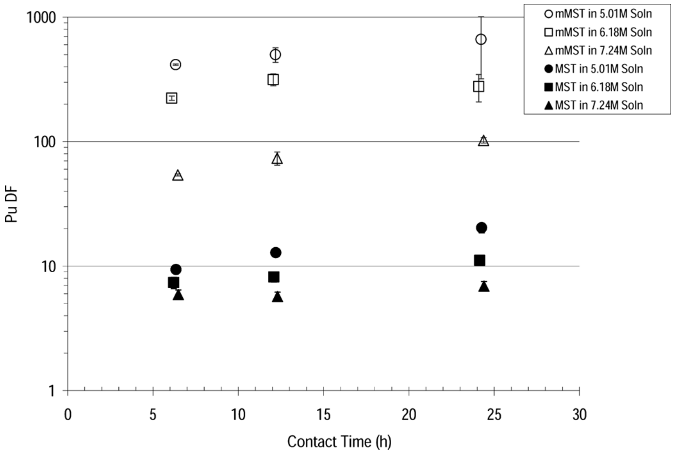

FIG. 5. Plutonium DF values versus contact time upon addition of $0.2\,g\,L^{-1}$ mMST (open) and $0.4\,g\,L^{-1}$ MST (filled) to solutions of varying ionic strengths, 5.01 (circles), 6.18 (squares), and 7.24 (triangles).

concentrations measured close to the target values amongst all three simulants. There was a greater variance among the simulants in the stable strontium and plutonium concentrations.

Figures 4–6 provide plots of the DF values for ^{85}Sr, plutonium and ^{237}Np as a function of contact time upon addition of $0.2\,g\,L^{-1}$ mMST and $0.4\,g\,L^{-1}$ MST. The sorbate concentrations for the control samples (i.e., no added sorbent) exhibited no changes with time confirming that sorption onto bottle walls or filters, or precipitation of the sorbates did not occur during any stage of the testing and sampling events.

Inspection of Fig. 4 revealed that the addition of the mMST ($0.2\,g\,L^{-1}$) at one-half the concentration of the MST ($0.4\,g\,L^{-1}$) achieved greater removal of strontium than MST over the range of ionic strengths tested. This finding is consistent with previous testing, which showed more effective strontium removal by mMST compared to MST (7,9,10). The strontium DF values decreased for both mMST and MST upon an increased ionic strength from 4.93 to 6.18 M, and then increased in the highest ionic strength simulant (Z = 7.24 M) to values similar to those measured for the lowest ionic strength simulant (Z = 5.01 M). The decrease in strontium removal upon an increase in the ionic strength is the expected trend and reflects the higher sodium concentration driving the ion exchange reaction to the left as shown in Eq. (1).

$$Sr(OH)^+ + NaHTi_2O_5 \leftrightarrow Sr(OH)(HTi_2O_5) + Na^+ \quad (1)$$

The increase in strontium DF values for both mMST and MST in the highest ionic strength simulant

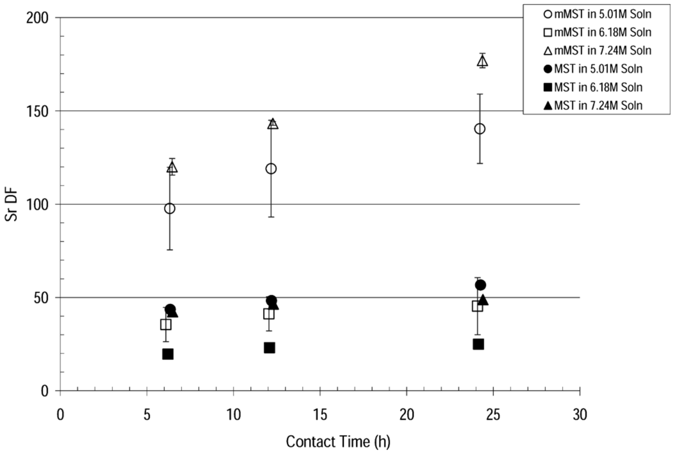

FIG. 4. Strontium DF values versus contact time upon addition of $0.2\,g\,L^{-1}$ mMST (open) and $0.4\,g\,L^{-1}$ MST (filled) to solutions of varying ionic strengths, 5.01 (circles), 6.18 (squares), and 7.24 M (triangles).

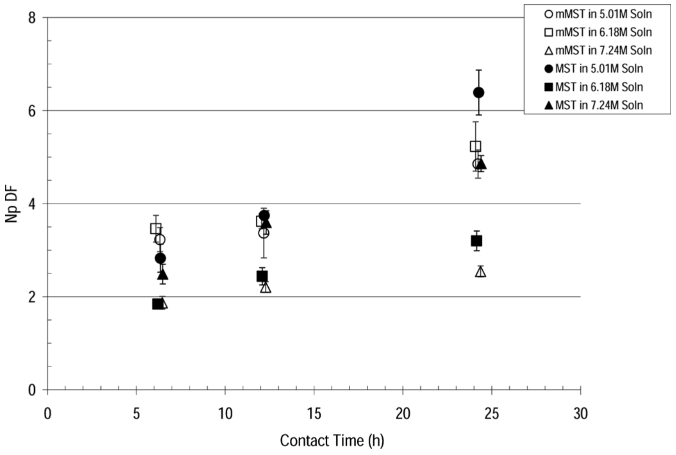

FIG. 6. Neptunium DF values versus contact time upon addition of $0.2\,g\,L^{-1}$ mMST (open) and $0.4\,g\,L^{-1}$ MST (filled) to solutions of varying ionic strengths, 5.01 (circles), 6.18 (squares), and 7.24 (triangles).

(Z = 7.24 M) can be attributed to the lower total strontium concentration in this simulant compared to the other (lower ionic strength) simulants. The average and single standard deviation of the total strontium concentrations in the control samples measured 1160 ± 75.1, 1030 ± 113, and 659 ± 109 μg/L by ICP-MS analysis for the 5.01 M, 6.18 M, and 7.24 M simulants, respectively. The total strontium concentrations for the lowest and intermediate ionic strength simulants are identical within analytical uncertainty and are about 66% higher on a mass basis than that in the highest ionic strength simulant. Given that the test conditions did not approach the total ion exchange capacity of the titanate samples, both mMST and MST achieved good strontium removal in the highest ionic strength simulant resulting in DF values similar to those measured at a much higher initial strontium concentration in the lowest ionic strength solution.

As in the case with strontium, the addition of the mMST ($0.2\,\mathrm{g\,L^{-1}}$) at one-half the concentration of MST ($0.4\,\mathrm{g\,L^{-1}}$) achieved greater removal of plutonium than MST over the range of ionic strengths tested (Fig. 5). Typically, the DF values for mMST measured about 30 times greater than those for MST. The plutonium DF values decreased for both mMST and MST materials with increased ionic strength over the range of Z = 5.01–7.24 M. For example, the 24-h DF values for mMST measured 663 ± 344, 277 ± 68.7, and 102 ± 5.08, for the Z = 5.01, 6.18, and 7.24 M simulants, respectively. Note that the measured DF values for the lowest ionic strength simulant are based on analytical results for samples close to the quantifiable limit for the analytical method and, therefore, have much higher experimental uncertainty. Nevertheless, the testing indicates excellent removal of plutonium ($\geq$99%) by mMST in simulants over a wide range of ionic strengths.

The closeness in plutonium DF values between the lowest (Z = 5.01 M) and intermediate (Z = 6.18 M) simulants compared to those in the highest ionic strength simulant (Z = 7.24 M) is likely due to the differences in initial plutonium concentrations among the three simulants. For example, the average and single standard deviation of plutonium concentrations in the control samples measured 296 ± 6.75, 231 ± 9.66, and $334 \pm 27.7\,\mu\mathrm{g\,L^{-1}}$ by alpha spectroscopy (PuTTA) for the 5.01 M, 6.18 M, and 7.24 M simulants, respectively, over the three sampling events (6, 12, and 24 hours). Thus, the approximately 22% lower concentration of plutonium in the intermediate ionic strength simulant results in a higher plutonium removal than would be expected if the plutonium concentration had been equal to that of the lower ionic strength solution (i.e., $296 \pm 6.75\,\mu\mathrm{g\,L^{-1}}$).

Neptunium removal performance is provided in Fig. 6. For mMST added at $0.2\,\mathrm{g\,L^{-1}}$, there was no difference in neptunium removal in the two lower ionic strength solutions. After 24 hours of contact, $0.2\,\mathrm{g\,L^{-1}}$ mMST removed about 80% of the neptunium in these two simulants (Z = 5.01 M and 6.13 M, [Na] = 4.5 M and 5.6 M). Neptunium removal was lower in the highest ionic strength simulant (Z = 7.24 M, [Na] = 6.5 M) achieving about 60% removal of the neptunium after 24 hours. The baseline MST material, added at the higher concentration of $0.4\,\mathrm{g\,L^{-1}}$, exhibited very similar neptunium DF values as the mMST material added at $0.2\,\mathrm{g\,L^{-1}}$.

Under these test conditions, no measurable removal of uranium by mMST was observed when added at a concentration of $0.2\,\mathrm{g\,L^{-1}}$, which is consistent with previous testing (9). The addition of $0.4\,\mathrm{g\,L^{-1}}$ MST did result in measurable removal of uranium in each of the three simulants. Within the experimental variance defined as the interval calculated from the average and ± two times the standard deviation, the results indicated between 20–25% of the initial uranium was removed after 24 hours of contact with MST. Furthermore, the extent of uranium removal by MST did not change significantly among the three different ionic strength solutions.

In summary, an increase in ionic strength of the simulated waste solution resulted in a general decrease in the removal of strontium and plutonium by mMST. Furthermore, the testing results indicated that neptunium removal by mMST was unaffected by the change in ionic strength at the two lower values, and the highest ionic strength simulant resulted in a slightly decreased neptunium removal. Finally, the influence of ionic strength on uranium removal proved indeterminate given the low affinity of mMST for uranium.

Reuse and Double Strike Testing

A reuse test was conducted with the vendor-prepared mMST using Stimulant D (Table 1). The reuse test consisted of contacting the mMST with the simulated waste solution at asorbent concentration of $0.2\,\mathrm{g\,L^{-1}}$ for six hours at ambient laboratory temperature, separating the solids from the solution by filtration and adding fresh mMST solids ($0.2\,\mathrm{g\,L^{-1}}$) to the filtrate from the first contact. After mixing for six hours the test suspension was again filtered to isolate the solids and filtrate. The partially-loaded solids from the second contact were then added to fresh simulated waste solution, contacted for six hours and then filtered to separate the solids and simulated waste solution (Contact #3). The solids from the first contact and third contacts were isolated and the amounts of strontium and actinides adsorbed onto the solids were determined. Samples of each of the filtrates were also analyzed to determine sorbate concentrations.

Table 4 provides a summary of the measured DF values for this test and those previously reported for the baseline MST (12). The measured DF values follow the expected trends. As previously observed, the mMST exhibits greater

TABLE 4
Average decontamination factors for mMST and MST measured in the reuse tests

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

ND = not determined; Blank entry (–) indicates not measured.

strontium and plutonium removal than the baseline MST. For example, the strontium DF value for the mMST measured about 4 times that of the baseline MST in Contact #1 even at one-half the sorbent concentration ($0.2\,\mathrm{g\,L^{-1}}$ vs. $0.4\,\mathrm{g\,L^{-1}}$). The plutonium DF value of 244 for mMST represents 99.6% removal of the plutonium compared to a DF value of 10.1 or 90.1% removal of the plutonium by MST.

Given the greater strontium removal by mMST during Contact #1, the strontium DF values between the materials cannot be compared for Contact #2 (see Table 4). The lower plutonium DF value for the mMST (4.24) compared to the baseline MST (11.5) in Contact #2 reflects the lower initial plutonium concentration for the solution used in Contact #2 for the mMST test compared to the MST test (filtrate from Contact #1). Strontium and plutonium DF values for the mMST in Contact #3 are much lower than those in Contact #1. Note that the neptunium DF values for the mMST appear similar to that of the baseline MST. Solution analyses for uranium indicated that within analytical uncertainty, no measurable removal of uranium occurred in any of the contacts with the mMST.

Table 5 provides the measured and calculated sorbent loadings for each of the sorbates for single use (Contact #1) and after reuse (solids after Contacts #2 and #3). Very good agreement was observed between the measured and calculated loadings except for uranium after the reuse test. The low calculated value for uranium in the reuse test ($85.5 \pm 3.83\,\mu\mathrm{g\,g^{-1}}$) reflects no measurable removal based on the solution analyses. The measured uranium loadings (ca. 2,270 and $2{,}790\,\mu\mathrm{g\,g^{-1}}$) after single contact and two contacts, respectively, represents the first data indicating sorption of uranium by mMST at a concentration of $0.2\,\mathrm{g\,L^{-1}}$. Note that these values are about a factor of 2.8 lower than the baseline MST, which was added at twice the concentration as the mMST.

The reduced affinity of the mMST for uranium is also evident when one compares the molar ratios of strontium to the actinides in the simulant and the sorbent solids. Table 5 also provides the molar ratios of Sr:Pu, Sr:Np, and Sr:U for the simulants and mMST. For plutonium and neptunium the affinity index (i.e., molar ratio in the solids divided by that in the simulant) are near unity for both single and two contacts suggesting that the mMST has the same relative affinity for strontium, plutonium and neptunium. Uranium exhibits an index of about 30 indicating much more strontium adsorbed onto the solids than uranium. Thus, it can be concluded that the mMST exhibits lower affinity for uranium compared to the other sorbates.

We also evaluated the performance of mMST in both double-strike and reuse configurations with actual tank waste at 25°C. Seven tests in all were conducted in two stages. Tests S-2 and S-3 are double-strike tests conducted by filtering the test solutions approximately 6 hours after first contacting with mMST and then adding fresh mMST to the filtrate. Tests S-2 and S-3 added $0.1\,\mathrm{g\,L^{-1}}$ and $0.2\,\mathrm{g\,L^{-1}}$ mMST, respectively, in each strike. Tests S-4 and S-5 used filtered, composited, residual tank waste solution remaining from previous tests. These reuse tests filtered the decontaminated test solutions approximately 6 hours after first contacting with mMST and then added the collected mMST solids to fresh tank waste solution. Tests S-4 and S-5 used $0.1\,\mathrm{g\,L^{-1}}$ and $0.2\,\mathrm{g\,L^{-1}}$ mMST, respectively. This test design mimics the proposed operations in the Alpha Finishing Process of the SWPF.

Figures 7 and 8 provide plots of strontium concentration and plutonium activity, respectively, versus time for the single and double strike tests with mMST and MST. Good agreement in the measured strontium concentrations is observed between the 2 and 4-h sample results in the single-strike tests and that for the first strike of the

TABLE 5
Sorbent loadings and affinity index for mMST and MST

	Sorbent Loading (µg/g)				
	mMST - Single Contact		mMST - After Reuse		MST - After Reuse
Sorbate	Measured	Calculated	Measured	Calculated	Measured
Sr	44,700 ± 7,240	49,800 ± 2,550	29,200 ± 4,570	27,300 ± 3,790	39,500 ± 866
Pu	411 ± 53.1	394 ± 34.3	338 ± 67.6	296 ± 47.1	171 ± 2.83
Np	496 ± 134	503 ± 57.5	599 ± 134	426 ± 79.2	>84
U	2,270 ± 198	3,550 ± 59.6	2,790 ± 334	85.5 ± 3.83	7,240 ± 2,440

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

double-strike tests. Unfortunately, the first sample after the second mMST addition resulted in the total strontium falling below the analytical method detection limit. Thus, we cannot quantitatively assess the magnitude of the strontium removal upon the second strike of mMST.

Good agreement was also observed between the 2 and 4-h sample results for the single strike tests and that for the first strike of the double strike tests with respect to plutonium activity. Upon the addition of the second strike of mMST, the plutonium activity decreased to a value well below the total alpha activity waste acceptance criteria (WAC) limit at both MST concentrations (see Fig. 8). The 30-h result for the double-strike test indicates a higher plutonium concentration than the previous two samples and the 170-h sample which is below the method detection limit. We believe this value is in error, most likely the result of cross contamination during sample handling with other materials in the highly shielded cells used for these experiments.

Table 6 provides a summary of the measured DF values for strontium, plutonium, and neptunium in the double strike tests. Greater than values are given when the measured concentration for a sorbate is below the analytical method detection limit. Uncertainties for the single replicate tests are determined from the analytical uncertainties. Strontium, plutonium, and neptunium DFs for the

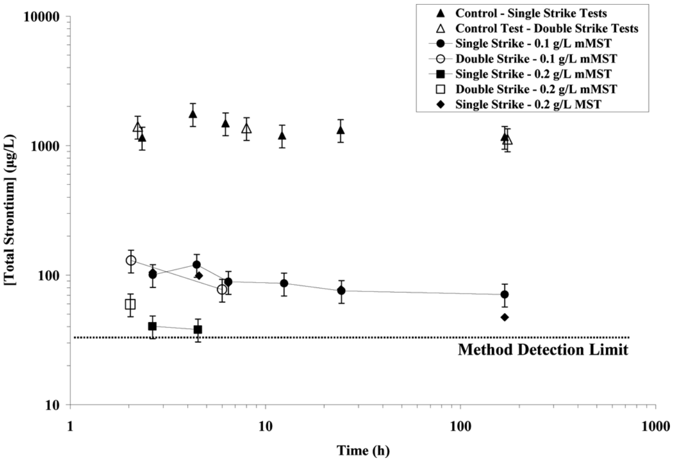

FIG. 7. Total strontium concentration versus time for the single and double strike tests with actual tank waste.

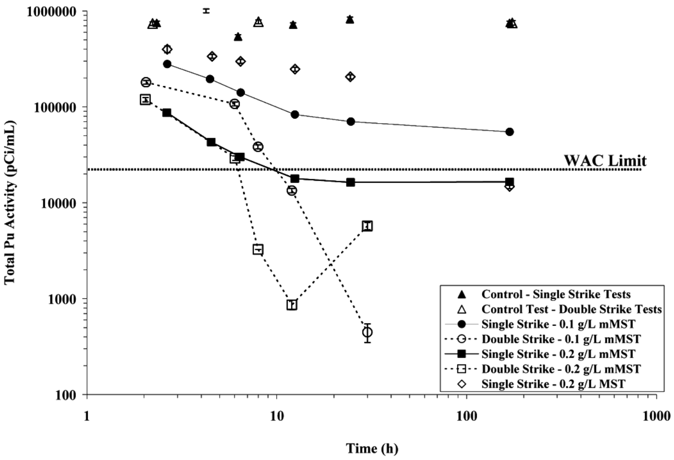

FIG. 8. Total plutonium activity versus time for the single and double strike tests with actual tank waste.

TABLE 6
Strontium, plutonium and neptunium decontamination factors measured in double strike actual waste tests

		Decontamination Factors (DF)					
		Total Sr		Total Pu*		^{237}Np	
Test Description	Time (h)	Value	Uncertainty	Value	Uncertainty	Value	Uncertainty
Supplemental Test S-2 Double-strike Test with 0.1 g/L mMST	2.1	10.0	2.83	4.18	0.278	1.40	0.395
	6.0	16.8	4.74	7.02	0.477	1.55	0.437
	8.0	>2.49		19.7	1.36	1.86	0.527
	12.0	>2.62		56.3	3.99	1.96	0.553
	30.0	>2.66		1690	383	2.21	0.624
	174	>8.12		>104		2.41	0.682
Supplemental Test S-3 Double-strike test with 0.2 g/L mMST	2.0	21.8	6.17	6.31	0.448	1.34	0.379
	6.0	>24.3		25.9	1.87	1.50	0.423
	8.0	>26.4		>231		2.60	0.735
	12.0	22.0	6.24	871	106	2.79	0.789
	30.0	>26.4		131	13.4	3.29	0.929
	174	>80.6		>761		4.62	1.31

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

two double-strike tests (S-2 and S-3) exhibit the expected increase with time. The large increase in DF between the 6 and 8-hour sampling time resulted from the removal of the mMST solids from the first strike and addition of fresh mMST.

Single tests (S-4 at 0.1 g L^{-1} and S-5 at 0.2 g L^{-1}) evaluated the performance of the mMST upon reuse. In these tests the mMST was first contacted with a filtered composite of the residuals from an earlier set of tests, which had a reduced radioactivity compared to the initial waste. After approximately six hours, the mMST solids were recovered from the waste solution, and were added to a fresh batch of the tank waste solution at the original spiked concentrations. Figure 9 provides a plot of the total plutonium activity as a function of total test time for the reuse tests. Included in Fig. 9 are the curves measured for plutonium removal in the single-strike tests allowing for a 6-hour offset from the beginning of the experiment.

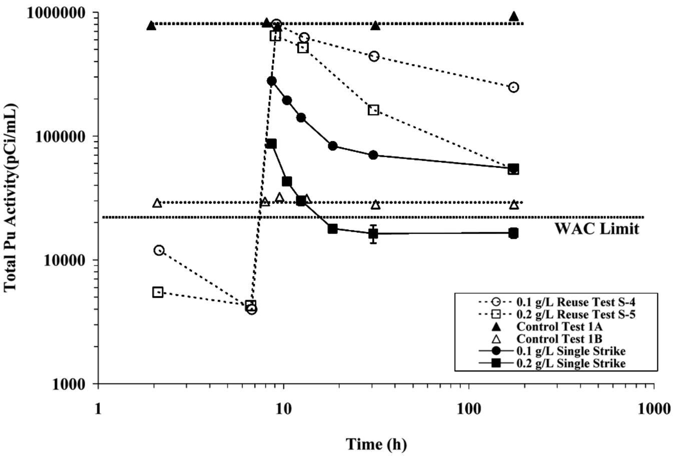

FIG. 9. Total plutonium activity versus time in the mMST reuse tests.

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

A comparison of the plutonium activity changes with time in the reuse and single strike tests indicates that less removal of plutonium occurs in the reuse test. Generally, the plutonium activity is about a factor of 10 higher in the tests with the reused mMST compared to a single strike of fresh mMST. A similar trend was also observed for strontium. These results indicate that a higher mMST concentration is required in the SWPF strike tanks to affect the necessary radionuclide removal if the mMST is first used in the Alpha Finishing Process and then returned to the SWPF.

CONCLUSIONS

mMST exhibits excellent performance for the removal of strontium, plutonium, and neptunium from simulated and actual tank waste solutions. In general, mMST is much more effective than MST in removing strontium, plutonium, and neptunium from strongly alkaline salt solutions. Unlike MST, mMST exhibits very little affinity for uranium. mMST adsorption characteristics were largely unaffected over the temperature range, 26–66°C. Generally, an increase in the ionic strength of the solution resulted in reduced removal of strontium, plutonium, and neptunium by the mMST.

ACKNOWLEDGEMENTS

We thank the U.S. Department of Energy for funding this work through the Office of Waste Processing in the Office of Environmental Management. The authors thank the technical staff at the Savannah River National Laboratory for their assistance in completing the experimental work including Mona Blume, Kim Wyszynksi, and D. Burckhalter, as well as the contributions of David Diprete, CeCi Diprete, Curtis Johnson, and Mark Jones in completing the many radiochemical and elemental analyses.

REFERENCES

1. Lynch, R.; Dosch, R.; Kenna, B.; Johnstone, J.; 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. (1976) Sandia Solidification Process Cumulative Report. Technical Report SAND-76-0105, Sandia Laboratories, Albuquerque, NM, January 1976.
3. Dosch, R.G. (1978) The Use of Titanates in Decontamination of Defense Wastes. Technical Report SAND-78-0710, Sandia Laboratories, Albuquerque, NM, June 1978.
4. Hobbs, D.T.; Barnes, M.J.; Pulmano, R.L.; Marshall, K.M.; Edwards, T.B.; Bronikowski, M.G.; 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.
5. Peters, T.B.; Barnes, M.J.; Hobbs, D.T.; Walker, D.D.; Fondeur, F.F.; Norato, M.A.; Fink, S.D.; Pulmano, R.L. (2006) Strontium and actinide separations from high level nuclear waste solutions using monosodium titanate 2. actual waste testing. *Separation Science and Technology*, 41 (11): 2409.
6. Lorier, T.H.; Jantzen, C.M. (2003) Evaluation of the TiO2 Limit for DWPF Glass. Technical Report WSRC-TR-2003-00396, Revision 0, Washington Savannah River Company, Aiken, SC, October 30, 2003.
7. Nyman, M.; Hobbs, D.T. (2006) A family of peroxo-titanate materials tailored for optimal strontium and actinide sorption. *Chem. Mater.*, 18 (26): 6425.
8. Hobbs, D.T.; Nyman, M.D.; Tripathi, A.; Medvedev, D.; Clearfield, A. (2005) Development of Improved Sorbents for Radiochemical Separations at the Savannah River Site. Proceedings of the Symposium on Waste Management, Tucson, AZ, February 27–March 3, 2005.
9. Hobbs, D.T.; Nyman, M.D.; Poirier, M.R.; Barnes, M.J.; Stallings, M.E. (2006) Development of an improved sodium titanate for the pretreatment of nuclear waste at the Savannah River Site. Proceedings of the Symposium on Waste Management, Tucson, AZ, February 26–March 2, 2006.
10. Hobbs, D.T.; Poirier, M.R.; Barnes, M.J.; Peters, T.B.; Fondeur, F.F.; Thompson, M.E.; Fink, S.D. (2008) Development of an Improved Sodium Titanate for the Pretreatment of Nuclear Waste at the Savannah River Site. Proceedings of the Symposium on Waste Management, Tucson, AZ, February 24–28, 2008.
11. Hobbs, D.T.; Bronikowski, M.G.; Edwards, T.B.; Pulmano, R.L. (1999) Final Report on Phase III Testing of Monosodium Titanate Adsorption Kinetics. Technical Report WSRC-TR-99-00134, Rev. 0, Washington Savannah River Company, Aiken, SC, May 28, 1999.
12. Peters, T.B.; Hobbs, D.T.; Fink, S.D. (2006) Results of Supplemental MST Studies, Technical Report WSRC-STI-2006-00012, Rev. 0, Washington Savannah River Company, Aiken, SC, July 24, 2006.