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Development of Improved Sorbents for Radiochemical Separations at the Savannah River Site

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Abstract

High-level nuclear waste produced from fuel reprocessing operations at the Savannah River Site (SRS) requires pretreatment to remove ^{137}Cs, ^{90}Sr and alpha-emitting radionuclides (i.e., actinides) prior to disposal. Separation processes planned at SRS include caustic side solvent extraction, for ^{137}Cs removal, and ion exchange/sorption of ^{90}Sr and alpha-emitting radionuclides with monosodium titanate (MST). The predominant alpha-emitting radionuclides in the highly alkaline waste solutions include plutonium isotopes ^{238}Pu, ^{239}Pu and ^{240}Pu. This paper describes results from a project to produce sorbents that exhibit increased removal kinetics and capacity for ^{90}Sr and alpha-emitting radionuclides versus that of the baseline MST material. Testing indicated that MST samples prepared in the presence of organic-based templating agents showed limited improvements in performance compared to the baseline MST. We observed significantly improved plutonium and neptunium removal performance with MST samples prepared upon the addition of a proprietary reagent. The modified MST offers the possibility of increased throughput and reduced solids handling in waste processing facilities at the SRS.

Introduction

Approximately 140 million liters of high-level nuclear wastes (HLW) are presently stored in 48 underground carbon steel tanks at the Savannah River Site (SRS). Approximately 8 vol % of the waste consists of precipitated metal oxides and hydroxides resulting from caustic additions to acidic waste solutions produced from fuel reprocessing and other operations at the site. The precipitated solids, referred to as sludge, contain about 60% of the radioactivity and settle to the bottom of the HLW storage tanks. The remaining volume of HLW is stored as concentrated liquid and saltcake produced from evaporation of the waste solutions. The radioactivity in this fraction of the HLW is comprised of principally ^{134,137}Cs with smaller amounts of ^{90}Sr and alpha-emitting isotopes of uranium, plutonium, neptunium and other actinide elements.

Cost effective disposal of the large quantities of high-level radioactive waste solutions requires reducing the radioactive material to the smallest possible volume for incorporation into durable long-term waste forms such as borosilicate glass. 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. Increased loading capacity and removal kinetics would result in decreased facility footprint and increased throughput for this stage of the pretreatment facility.

Experimental

Synthesis of Monosodium Titanate Materials

We prepared monosodium titanate samples using a modified sol-gel procedure reported by Lynch, et al.,[1] The modified procedure developed at SRNL produces a material with controlled particle size distribution and low alcohol content. The SRNL procedure combines 0.5-mL of a solution (Solution #2) containing isopropanol (87.5 vol %) and water (12.5 vol%) followed by 2.0-mL of a solution (Solution #1) containing isopropanol (65.3 vol%), sodium methylate (9.7 vol %) and tetraisopropyl titanate (25.0 vol %) in 47.5 mL of isopropanol with vigorous mixing. After mixing for a minimum of 10 minutes, we simultaneously add 118 mL of Solution #2 at a flowrate of 4.0 mL/min and 32 mL of Solution #1 at a flowrate of 1.0 mL/min. After addition of both solutions is complete, we heat the reaction slurry to boiling and distill off the alcohol. We replace the distilled alcohol with water to maintain a constant slurry volume during the distillation step.

We investigated the influence of templating reagents, hexylamine ($C_6H_{13}NH_2$, HA), and tetraethylene glycol ($C_8H_{18}O_5$, TEG). In these tests we added the templating reagent at several different levels ranging from a Ti:reagent ratio of 1:0.28 to 1:2. After each synthesis we washed the MST solids thoroughly with deionized water to remove excess templating reagent.

We also prepared modified MST samples using a proprietary chemical (PC). This chemical was added either during the original synthesis of the MST solids or added to a slurry of MST suspended in water. We removed excess PC by thoroughly washing the MST solids with deionized water.

Characterization of MST Samples

We determined surface areas of the MST samples by nitrogen adsorption using a Quantachrome Autosorb-6 automated nitrogen gas adsorption unit. Prior to surface area measurements, we filtered the MST suspension, washed the solids with deionized distilled water and alcohol and dried in air at 55 ˚C. We then preheated the dried solids (0.2 – 0.6 g) to 120 ˚C and outgassed at 100 ˚C and pressure of 0.002 torr. We collected the isotherms at 77 ˚C and analyzed by the BET method. We determined the micropore volume by the DeBoer t-plot method and the micropore distribution by the MP method. We measured particle size distribution of MST samples using a Microtrac Model #S3000 instrument with the sample solids suspended in water.

Evaluation of Sr and Actinide Removal Performance

We evaluated strontium and actinide removal performance by contacting a simulated waste solution with a measured quantity of the modified MST sample. Table 1 provides the composition of the simulated waste solution. For the MST samples prepared with the organic-based templating reagents, we measured strontium removal performance in a simulant with no added actinides. Two of the template-produced MST samples were evaluated for combined strontium and actinide removal performance using the simulant with added actinides.

We performed the batch contacts at 25 ± 2 °C. We sample each test bottle after 4, 24 and 168 hours of contact. All samples were filtered through 0.45-μm nylon-membrane filters to remove MST solids. Measured aliquots of the filtrate were then diluted with an equal volume of 5 M nitric acid. Gamma spectroscopy measured the ^{85}Sr and neptunium content. We measured the ^{238,239,240}Pu content by radiochemical separation of the plutonium followed by alpha counting of the extracted plutonium.

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 mg L^{-1}
$NaNO_2$	0.134 M		
Na_2CO_3	0.0260 M	Total Na	5.6 M

Results and Discussion

MST samples prepared with and without templating reagents exhibited surface areas ranging from 16 m^2/g to 242 m^2/g (see Table 2). In general the affinity for strontium as measured by the batch distribution constant, K_d, increased with increasing BET surface area. Unlike the baseline and MST-TEG samples, a large fraction of the MST-HA surface area is due to mesopores. This sample also exhibited the largest K_d, for strontium (see Table 2). The MST-TEG sample exhibited the lowest strontium K_d value. Note, however, that the K_d value for the MST-TEG sample is excellent for the removal of strontium in the high sodium solution.

Table 2. Surface Area (SA) and Batch Distribution Constants (K_d) for MST Samples

Sample ID	BET SA m^2/g	Microporous SA[a] m^2/g	K_d [b] mL/g
Baseline MST[c]	141	0	3.32E+05
MST-HA[d]	232	204	9.17E+05
MST-TEG[e]	16	0	2.60E+05

[a] Determined the micropore volume by the DeBoer t-plot method and the micropore distribution by the MP method.

[b] Determined in simulated waste solution having only strontium.

[c] MST supplied by Optima Chemical Company, Inc., Duluth, GA, Lot #00-QAB-417.

[d] MST prepared in the presence of hexylamine (HA).

[e] MST prepared in the presence of tetraethylene glycol (TEG).

Given the high strontium affinities for the MST samples, we conducted tests to determine the affinity of these samples for strontium, plutonium and neptunium with a simulant containing these three sorbates and uranium (see Table 1). Table 3 provides a summary of the K_d values for the baseline MST, MST-HA and MST-TEG samples for each sorbate and at each sampling time. Figure 1 provides a graph of the plutonium concentration versus contact time for these tree samples as well. Unlike the initial testing in a strontium-only simulant, test results in the more complex simulant indicated that the MST-HA sample performed poorer and the MST-TEG sample slightly better than the baseline MST sample for strontium removal. This trend also holds for these materials for plutonium and neptunium removal. Thus, we conclude that sorbate affinity does not correlate with surface area of this series of samples.

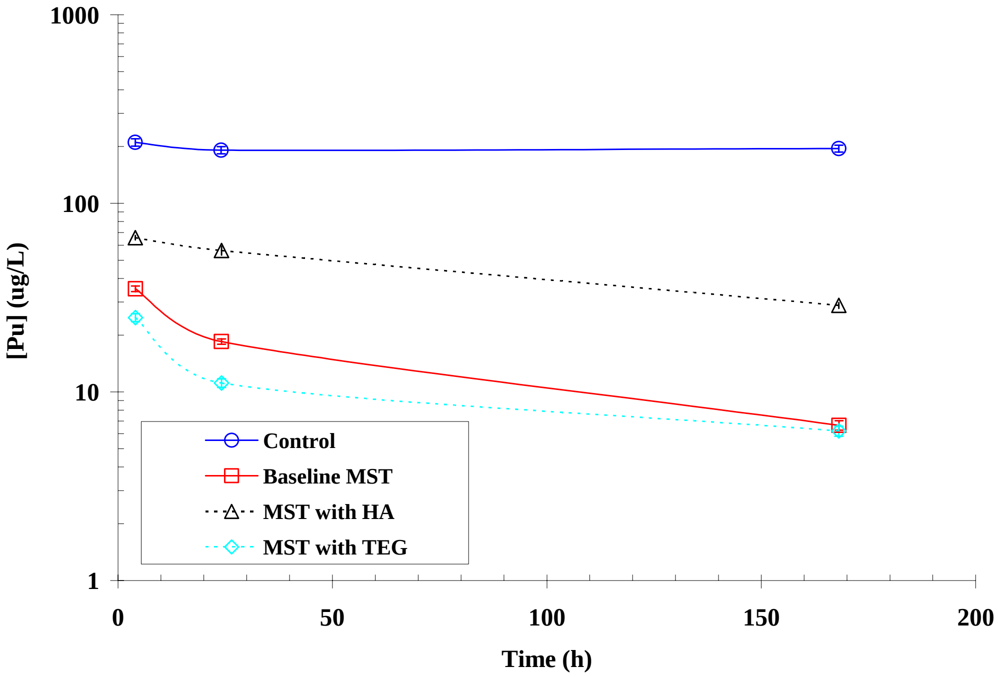
The templated synthesis method has the potential to introduce a much higher organic content into the MST than the current production method. Increased organic content in the MST may have significant downstream impacts. Given that the HA-modified sample exhibited poorer performance and the TEG-modified sample exhibited only a marginal improvement in performance versus the baseline MST, we decided not to pursue further use of organic-based templating reagents for the production of improved MST materials.

Table 3. Batch Distribution Constants for MST Samples Prepared in the Presence of Organic Templating Reagents

		K_d (mL/g)		
Time (h)	**Sorbate**	**Baseline MST**	**MST-HA**	**MST-TEG**
4	Sr	4.74(12)E+05	1.39(4)E+05	5.69(15)E+05
24	Sr	6.73(22)E+05	1.43(4)E+05	8.32(33)E+05
168	Sr	>7.45E+05	1.29(3)E+05	>7.76E+05
4	Pu	>1.25E+04	4.93(18)E+03	>1.88E+04
24	Pu	2.34(8)E+04	5.86(36)E+03	4.05(28)E+04
168	Pu	7.16(16)E+04	1.47(7)E+04	7.63(56)E+04
4	Np	1.74(22)E+03	nd	1.23(15)E+03
24	Np	2.17(53)E+03	3.50(28)E+02	4.52(11)E+03
168	Np	2.08(42)E+04	1.64(13)E+03	>1.44E+05

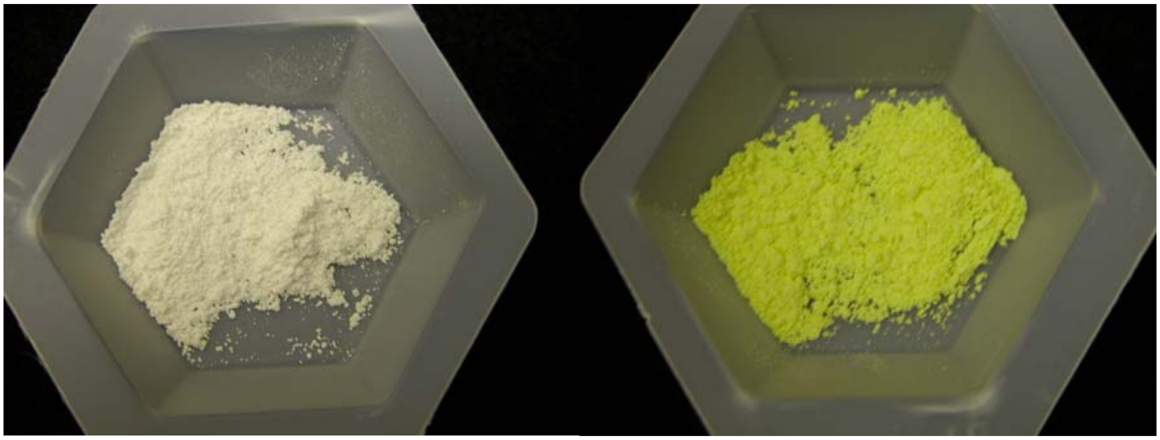
Numbers in parenthesis are single standard deviation.
nd = not determined

Figure 1. Plutonium Removal with MST Samples Prepared in the Presence of Templating Reagents



We also pursued an alternate, proprietary method for the production of modified MST materials with improved strontium and actinide removal performance. In this synthetic route the modified MST can be produced either during the initial sol-gel synthesis or by post-synthesis treatment of MST solids. The modified MST exhibits a yellow color compared to a white color for the baseline MST (see Figure 2). Particle size measurements indicate similar particle size for the modified MST samples compared to baseline MST samples. Thus, we would expect the modified MST to exhibit similar filtration characteristics to that of the baseline MST material.

Figure 2. Photographs of the Baseline and Modified MST Samples



Baseline MST **Modified MST**

We tested the strontium and actinide removal performance of several modified MST samples. Table 5 provides a comparison of the K_d values for strontium, plutonium and neptunium with the baseline and modified MST samples. The two baseline MST samples represent the same batch of the baseline MST tested at two different times spanning the test sets in which we tested the performance of the four modified MST samples. Figure 3 shows a graph of the solution phase plutonium concentrations versus time upon contact of the baseline and modified MST samples with the simulated waste solution.

Strontium removal performance of the modified MST samples mirrored that of the baseline MST samples. Thus, the chemical modification of the MST did not significantly affect the removal of strontium. In contrast to strontium, the modified MST samples exhibited much improved removal characteristics for plutonium and uranium. For example, the batch distribution constants for plutonium and neptunium with the modified MST samples measured as much as fifty times higher than those of the baseline MST samples (see Table 5).

Table 5. Distribution Constants (K_d) for Modified MST Samples.

		Strontium K_d (mL g^{-1})	
Sample	**4-hour**	**24-hour**	**168-hour**
Baseline MST-1	2.07(13)E+05	2.42(16)E+05	3.21(24)E+05
Baseline MST-2	1.03(25)E+06	5.54(53)E+05	6.57(69)E+05
MMST-1	2.00(12)E+05	4.81(51)E+05	5.67(58)E+05
MMST-2	2.85(21)E+05	3.25(26)E+05	3.88(31)E+05
MMST-3	2.11(14)E+05	5.11(55)E+05	7.29(86)E+05
MMST-4	8.78(1.09)E+05	1.37(24)E+06	>8.77E+05

		Plutonium K_d (mL g^{-1})	
Sample	**4-hour**	**24-hour**	**168-hour**
Baseline MST-1	8.72(60)E+03	1.54(10)E+04	5.03(38)E+04
Baseline MST-2	1.02(63)E+04	1.95(12)E+04	4.78(39)E+04
MMST-1	7.62(51)E+04	5.66(98)E+05	3.49(27)E+06
MMST-2	3.28(22)E+04	3.42(23)E+04	3.94(28)E+04
MMST-3	2.15(15)E+04	2.49(22)E+05	7.07(1.27)E+05
MMST-4	>4.85E+05	1.10(14)E+06	6.79(91)E+05

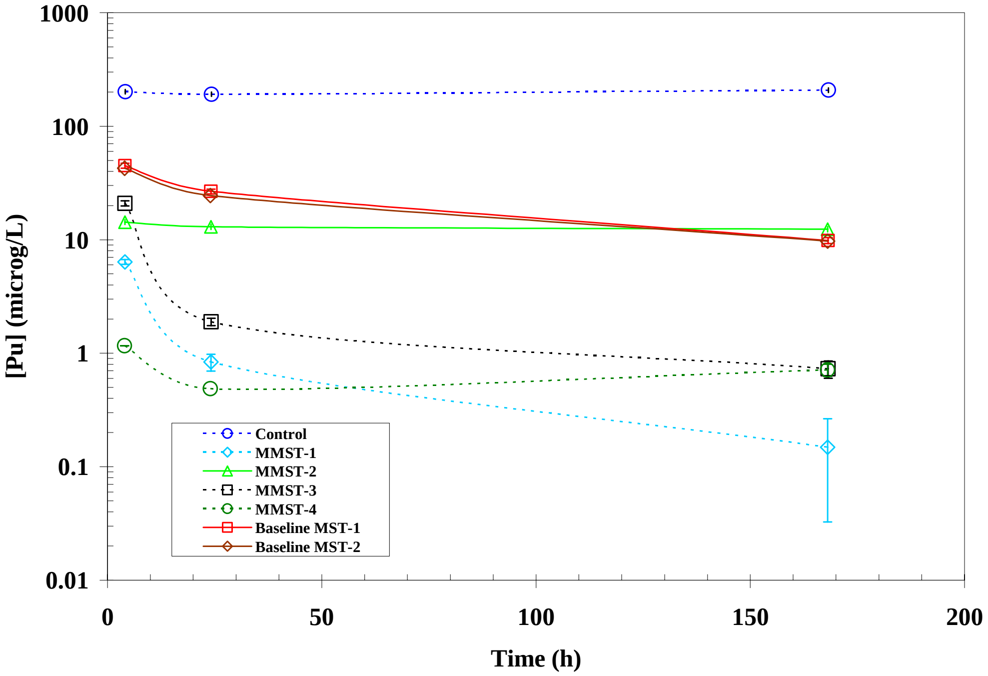
		Neptunium K_d (mL g^{-1})	
Sample	**4-hour**	**24-hour**	**168-hour**
Baseline MST-3	5.01(37)E+02	7.45(58)E+02	3.37(34)E+03
Baseline MST-5	8.46(66)E+02	1.49(14)E+03	2.72(23) E+03
MMST-1	4.30(32)E+03	1.60(30)E+04	2.56(67)E+04
MMST-2	2.29(31)E+04	7.27(40)E+04	2.55(42)E+04
MMST-3	3.30(30)E+03	5.60(67)E+03	5.40(33)E+04
MMST-4	3.00(22)E+03	1.89(18)E+03	3.40(29)E+03

Numbers in parenthesis are single standard deviation.

As evident in Figure 3, not only do the modified MST samples show increased actinide capacities, but the removal rates are also faster. The higher capacities indicate that less MST may be required to achieve the necessary separations. The faster removal rates also can have significant impact on throughput in the SWPF and ARP operations. Currently both of these facilities specify a contact time for the MST and waste solution of 24 hours. Compared to the baseline MST samples, the modified MST samples show removal rates that would allow much shorter contact times (e.g., 4 hours). Preliminary calculations indicate that operating these facilities with a 4-hour contact time increases throughput by as much as a factor of two. Thus, the modified MST materials appear promising for use in these facilities by reducing the amount of MST required and increasing throughput.

Reducing the amount of MST used in the SWPF and ARP facility has a positive impact on the Defense Waste Processing Facility (DWPF). The borosilicate glass used to immobilize the high level nuclear waste has a limited solubility for titanium. By reducing the amount of MST used in the pretreatment facilities, the quantity of titanium sent to the DWPF is reduced, which decreases the likelihood of sending an unacceptably high quantity of titanium to the melter for vitrification.

Figure 3. Plutonium Removal with MST Samples Produced with Proprietary Reagent



Conclusions

Results indicate that modified syntheses of MST with organic templates produced samples with increased strontium and actinide removal kinetics and capacities. However, the improved performance of these samples was not sufficient to warrant further development. In contrast, the addition of a proprietary chemical during the synthesis or as a post-synthesis treatment of MST provided samples that exhibit significantly improved performance for plutonium and neptunium removal. For example, batch distribution constants for plutonium and neptunium with the modified MST samples measured as much as 50 times higher than those for baseline MST samples. Plutonium and neptunium removal kinetics were also much improved. Strontium removal characteristics remained essentially unchanged upon modification of the MST. Based on these initial testing results, the modified MST offers the possibility of increased throughput and reduced solids handling in waste processing facilities at the Savannah River Site.

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.