Further Development of Modified Monosodium Titanate, an Improved Sorbent for Pretreatment of High Level Nuclear Waste at the Savannah River Site – 11215

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ABSTRACT

High-level nuclear waste produced from fuel reprocessing operations at the Savannah River Site (SRS) requires pretreatment to remove Cs-137, Sr-90, and alpha-emitting radionuclides (i.e., actinides) prior to disposal onsite as low level waste. Separation processes planned at SRS include caustic side solvent extraction, for Cs-137 removal, and sorption of Sr-90 and alpha-emitting radionuclides onto monosodium titanate (MST). The predominant alpha-emitting radionuclides in the highly alkaline waste solutions include plutonium isotopes Pu-238, Pu-239, and Pu-240. This paper describes recent results from the development of an improved titanate material that exhibits increased removal kinetics and effective capacity for Sr-90 and alpha-emitting radionuclides compared to the baseline MST material.

INTRODUCTION

Approximately 140 million liters of high-level nuclear waste (HLW) are presently stored in 49 underground carbon steel tanks at the Savannah River Site (SRS). Approximately 9 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 50% 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 and is comprised of principally Cs-134 and Cs-137 with smaller amounts of Sr-90 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 faster removal kinetics for Sr-90 and alpha-emitting radionuclides compared to the baseline material, monosodium titanate (MST). Increased effective loading capacity and faster removal kinetics offer decreased facility footprint and increased throughput for this stage of the pretreatment facility. Deployment opportunities for this improved material include both the operating Actinide Removal Process and the Salt Waste Process Facility, under construction, at SRS.

The baseline material for Sr-90 and alpha-emitting radionuclide removal at SRS is monosodium titanate, $NaTi_2O_5H$, which is produced by a sol-gel process.[1-5] Testing funded by the Department of Energy, Office of Environmental Management, evaluated modifications to the synthesis of MST that would provide a material with improved sorption capacity and kinetics. It was found that addition of hydrogen peroxide during or after the synthesis of the MST produces materials with significantly improved performance characteristics for the removal of strontium,

plutonium, and neptunium.[6] Interestingly, the peroxide-modified materials exhibit reduced affinity for uranium compared to the baseline MST material.

The improved performance for strontium and plutonium removal will allow pretreatment facilities to use markedly less sorbent and shorten the contact time for this stage of the process, which should result in a significant increase in throughput for the processing facilities. Furthermore, reduction in the amount of sorbent used reduces risk and amount of residual solids in the processing tanks. Earlier testing evaluated performance of the modified MST (mMST) with both simulated and actual tank waste, including testing of a vendor prepared pilot scale batch (15 kg) along with filtration characteristics of the material.[7-9] Recent work, presented in this paper, included examination of the performance of the material under varying conditions, evaluation of sorbate desorption, and further characterization of the material including evaluation of the post-synthesis gas release, examination of the solids settling characteristics, characterization of the peroxide content, and the effect of age on the performance of the material.

EXPERIMENTAL

Materials

The baseline 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 mg L^{-1} NaNO$_2$.[5] Modified monosodium titanate (mMST) used in these studies was prepared by the post-synthesis treatment of MST with hydrogen peroxide. The details of this procedure have been previously published.[6] Bench-scale 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.

Effect of Radiation on MST Performance

To determine if irradiation of the MST or modified MST (mMST) would have an effect on the sorption of strontium and actinides, the materials were irradiated in a gamma source, and the performance was tested. The total dose the materials received was 3.95 x 10^6 R, which corresponds to the dose the material may receive after the accumulation of 50 batches in the Actinide Removal Process (ARP). This value also bounds the total dose the material may receive in the Salt Waste Processing Facility (SWPF). The materials were irradiated in two different media, the as-received aqueous suspension and in a non-radioactive simulated waste solution (SWS).

Performance tests were carried out using a simulated waste solution (SWS-5-2009), having the composition shown in Table I. The experiments were carried out in a waterbath-shaker at 25 °C, with an agitation speed of 175 rpm. All MST experiments were performed with a sorbent loading of 0.4 g/L, and the mMST experiments were performed at a loading of 0.2 g/L. Samples

were removed and filtered after 6, 12, and 24 hours of contact, and were analyzed for Sr, U, Np, and Pu content.

Table I. Composition of Simulated Waste Solutions.

Component	Measured Concentrations		
	SWS-5-2009	SWS-9-2009	SWS-10-2007
$NaNO_3$	2.13 ± 0.21 M	2.35 ± 0.18 M	2.42 ± 0.24 M
NaOH	1.37 ± 0.14 M	1.27 ± 0.13 M	1.36 ± 0.14 M
Na_2SO_4	0.483 ± 0.048 M	0.531 ± 0.040 M	0.562 ± 0.056 M
$NaAl(OH)_4$	0.484 ± 0.048 M	0.389 ± 0.039 M	0.419 ± 0.042 M
$NaNO_2$	0.133 ± 0.013 M	0.127 ± 0.010 M	0.141 ± 0.014 M
$NaCO_3$	0.0298 ± 0.0030	0.0302 ± 0.0030	0.0266 ± 0.0027
Total Na	5.05 ± 0.01 M	5.05 ± 0.01 M	5.52 ± 0.72 M
Total Sr	0.521 ± 0.052 mg/L	0.676 ± 0.026 mg/L	0.318 ± 0.106 mg/L
Sr-85	189,000 dmp/mL	12,000 dmp/mL	189,000 dmp/mL
Total Pu	0.216 ± 0.019 mg/L	0.17 ± 0.033 mg/L	0.235 ± 0.007 mg/L
Np-237	0.392 ± 0.92 mg/L	0.463 ± 0.026 mg/L	0.450 ± 0.098 mg/L
Total U	10.7 ± 0.13 mg/L	10.1 ± 0.36 mg/L	11.3 ± 0.38 mg/L
Cs-137	102,000 ± 1910 dpm/mL	123,000 ± 6130 dpm/mL	86,900 ± 577 dpm/mL

Effect of Age on mMST Performance

Iodometric titration analyses indicated that the peroxide content of mMST samples decreases linearly with age. Strontium and actinide sorption tests were performed with several lab prepared batches of mMST of varying age (see Table II). Performance tests were conducted with a simulated waste solution (SWS-9-2009) having the composition shown in Table I. The experiments were performed in a waterbath-shaker at 25 °C, with an agitation speed of 175 rpm and an mMST concentration of 0.2 g/L. Samples were removed after 6, 12, and 24 hours of contact, and were filtered through a 0.1 μm PVDF syringe filter. The samples were then acidified before being submitted for analysis of Sr, U, Np, and Pu content.

Table II. Age of mMST Samples.

Sample	Age at Time of Testing
LS-2	4.70 y
LS-7	0.30 y
LS-8[a]	0.19 y
LS-9	0.09 y

(a) Sample LS-8 was exposed to elevated temperature (49 °C) causing accelerated aging.

Desorption of Sr, Pu, and Np from mMST

A series of desorption experiments were performed to determine if any of the strontium or actinides that are loaded onto the mMST solids during the contact period will desorb during the washing sequence performed before sending the mMST to the DWPF for vitrification. The

mMST samples were first loaded by contacting 0.2 g of mMST (Optima Batch 06-QAB-0139) with 1.0 L of simulated salt solution (SWS-10-2007) having the composition shown in Table I. Three samples were loaded in this fashion using contact times of 504, 672, and 720 hours. The mMST solids were then isolated and placed into clean centrifuge tubes. The decontaminated salt solutions from each test were then diluted with ultrapure water to provide three dilutions having target Na concentrations of 2.8, 1.0, and 0.5 M. These concentrations represent dilution factors of 2, 5.6 and 11.2, and represent the intermediate and final stages of the washing sequence. Then 4 mL of these diluted salt solutions were added to the isolated mMST samples, which still contained some entrained undiluted decontaminated salt solution. These samples were then mixed in a waterbath-shaker at 25 °C for 24 hours. The solids were then separated from the diluted salt solutions by centrifugation. The salt solutions were filtered through 0.1 μm PVDF filters, and were submitted for analysis of Cs, Sr, U, Np, and Pu content.

Results from the initial tests indicated that the dilutions did not reach the conditions expected in the final wash stage (i.e. [Na] of 0.5 M), due to higher than anticipated residual interstitial supernate. Additional desorption experiments were performed with more dilute samples of the decontaminated salt solution. The samples of decontaminated salt solution were diluted to dilution factors of 10.9, 20.7, and 47.7. An 8.5-mL aliquot of each diluted solution was added to the 0.2 g of the isolated mMST solids which had been previously loaded with sorbates. The samples were then mixed in a waterbath-shaker at 25 °C for 24 hours. The solids were then separated from the diluted salt solutions by centrifugation. The salt solutions were filtered through 0.1 μm PVDF filters, and were submitted for analysis of Cs, Sr, U, Np, and Pu content.

RESULTS AND DISCUSSION

Effect of Radiation on MST Performance

Similar removal kinetics were seen for the irradiated samples when compared to the unirradiated controls. The decontamination factors are summarized in Table III. There is no general trend for the effect of radiation on the material performance. For the majority of the samples, the DF values for the irradiated samples are within 2 sigma uncertainty of the unirradiated samples, with a few exceptions. In two cases the DF values are slightly higher for the irradiated samples when compared to the unirradiated samples. For Sr, the 24-h DF value for the mMST irradiated in the as-received suspension is slightly higher than the 24-h DF for the unirradiated mMST. For Np, the 24-h DF value for the MST irradiated in the as-received suspension is higher than the DF for the unirradiated MST. The only adverse effect of irradiation was seen for Pu, where the 6-h DF for the mMST irradiated in the SWS was slightly lower than the DF for the unirradiated MST. At later time points, 12 and 24 hours, the DF values come within 2 sigma uncertainty of the unirradiated material.

Table III. Summary of Decontamination Factors (DF). Uncertainty (Unc.) column represents one sigma uncertainty.

Sr DF												
Contact Time (h)	mMST						MST					
	Unirradiated		Irr. As Rec.		Irr. In SWS		Unirradiated		Irr. As Rec.		Irr. In SWS	
	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.
6	141	9.94	160	11.3	122	8.66	60.5	4.28	61.1	4.32	43.5	3.08
12	173	12.3	193	13.6	169	12.0	67.0	4.74	67.7	4.79	48.8	3.45
24	190	13.5	253	17.9	194	13.7	73.7	5.21	72.7	5.14	60.3	4.26
U DF												
Contact Time (h)	mMST						MST					
	Unirradiated		Irr. As Rec.		Irr. In SWS		Unirradiated		Irr. As Rec.		Irr. In SWS	
	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.
6	0.995	0.0144	1.03	0.0270	1.03	0.0336	1.16	0.0491	1.20	0.0589	1.17	0.0139
12	1.02	0.0453	1.04	0.0208	1.05	0.0211	1.21	0.0235	1.22	0.0828	1.17	0.0240
24	0.932	0.0182	0.924	0.0161	0.924	0.0176	1.15	0.0245	1.13	0.0304	1.08	0.0232
Np DF												
Contact Time (h)	mMST						MST					
	Unirradiated		Irr. As Rec.		Irr. In SWS		Unirradiated		Irr. As Rec.		Irr. In SWS	
	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.
6	1.95	0.123	2.11	0.0434	1.82	0.117	2.96	0.141	3.29	0.173	3.12	0.226
12	2.21	0.125	2.29	0.0682	1.94	0.0562	4.23	0.197	4.97	0.459	4.24	0.121
24	2.56	0.120	2.53	0.237	2.22	0.172	5.64	0.226	8.07	0.523	5.99	0.172
Pu DF												
Contact Time (h)	mMST						MST					
	Unirradiated		Irr. As Rec.		Irr. In SWS		Unirradiated		Irr. As Rec.		Irr. In SWS	
	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.	DF	Unc.
6	67.2	8.06	72.1	7.91	34.6	3.20	6.12	0.512	6.08	0.508	4.71	0.423
12	151	19.7	160	21.8	103	13.3	9.71	0.789	9.90	0.837	8.49	0.722
24	193	22.1	291	60.2	145	15.7	11.6	0.950	13.2	1.30	11.4	0.942

Desorption of Sr, Pu, and Np from mMST

Results from the initial set of desorption experiments showed no measurable desorption of sorbates. Table IV compares the calculated concentration of each sorbate based upon the mixture of the diluted, decontaminated salt solution and the residual interstitial liquid with the measured concentration of each sorbate after the desorption test period of 24 hours. Desorption would be evidenced by a higher measured than calculated concentration. There is some indication of additional sorption of sorbates, including Pu, Np-237, and U, as evidenced by the measured solution concentrations being well below the calculated values. This is likely due to the much higher sorbent concentration in these experiments (28-34 g/L) compared to the initial loading condition (0.2 g/L).

Table IV. Results from Initial Set of Desorption Tests.

[Na] of soln (M)		3.7		2.7		2.8	
Analyte	Unit	Calc.[a]	Measured	Calc.[a]	Measured	Calc.[a]	Measured
Cs-137	dpm/mL	5.62E+04	5.62E+04	3.86E+04	3.86E+04	4.10E+04	4.10E+04
Sr-85	dpm/mL	5.35E+01	< 3.65E+01	3.88E+01	3.78E+01	4.92E+01	5.13E+01
Pu	µg/L	1.30E+00	5.33E-01	1.10E+00	2.76E-01	8.78E-01	1.57E-01
Np-237	µg/L	1.04E+02	6.26E+01	6.30E+01	3.56E+01	7.41E+01	4.61E+01
U	µg/L	5.26E+03	1.73E+03	3.81E+03	1.31E+03	4.33E+03	1.31E+03

(a) Calculated values are based on the measured volume of diluted decontaminated salt solution and estimated volume of interstitial final filtrate without any desorption.

Since the initial tests did not reach the Na concentration expected in the final stages of washing, additional tests were conducted by further diluting the decontaminated salt solution to reduce the Na concentration to a level of approximately 0.5 M, the expected Na concentration at the end of the washing cycle. Again, Table V compares the calculated and measured sorbate concentrations in the solution. The calculated and measured concentrations for Sr-85, Pu, and U for all three diluted solutions are very similar and indicate no measurable desorption at the more dilute sodium concentrations. For Np-237 the measured and calculated concentrations were similar for the two diluted solutions having Na concentrations of 0.39 M and 0.56 M, respectively. The Np-237 concentration in the 0.88 M Na concentration solution measured 57.6 µg/L compared to the calculated concentration of 16.8 µg/L. This result may indicate that a small amount of Np-237 desorbed at this solution concentration. However, no measurable desorption occurred in either of the two solutions which were more dilute than the 0.88 M Na solution. One would expect desorption, if any, to increase in the more diluted sodium solutions. Since that is not the case with Np-237 (or any of the other sorbates), we suspect that the Np-237 concentration in the 0.88 M Na solution may be due to experimental error.

Table V. Results from Additional Desorption Tests with More Dilute Solutions.

| [Na] of soln (M)		0.88		0.39		0.56	
Analyte	Unit	Calc.[a]	Measured	Calc.[a]	Measured	Calc.[a]	Measured
Cs-137	dpm/mL	1.30E+04	1.23E+04	5.61E+03	4.76E+03	8.19E+03	7.46E+03
Sr-85	dpm/mL	1.29E+01	1.11E+01	1.13E+01	1.02E+01	1.89E+01	1.33E+01
Pu	µg/L	1.42E-01	< 5.82E-01	7.53E-02	< 8.12E-02	< 7.47E-02	< 1.76E-01
Np-237	µg/L	1.68E+01	5.76E+01	<8.20E+00	<5.00E+00	<9.54E+00	<5.00E+00
U	µg/L	9.60E+02	1.04E+03	3.12E+02	7.58E+01	5.40E+02	9.90E+01

(a) Calculated values are based on the measured volume of diluted decontaminated salt solution and estimated volume of interstitial final filtrate without any desorption.

Gas Release from mMST

The mMST material releases oxygen during the synthesis, and continues to offgas after the synthesis at a rapidly diminishing rate until below a measurable rate after 4 months. Several experiments were performed to measure the gas release rate under different conditions during the first month after synthesis. For each experiment a 25-g batch of mMST was synthesized, and

after the work-up was immediately transferred to the gas release apparatus to begin measurements.

Figure 1 compares the gas release rate of five batches of mMST. Samples LS-5 and LS-9 were synthesized using the standard procedures, and LS-6 and LS-7 materials were washed with acidic or alkaline solutions, respectively, during the synthesis work-up. Sample LS-8 was also synthesized using the standard procedures, but the gas release measurements were performed at 49 °C to simulate conditions the material may be exposed to during shipping and storage during the summer months. Initially the release rate measured approximately 0.15 mL min^{-1} (per 125 g of 15 wt % slurry) for LS-5 and rapidly decreased by an order of magnitude within 2 days and two orders of magnitude after about 20 days. Four weeks after the preparation of the mMST, the gas release rate on a slurry volume basis is approximately 14 mL per day per L of 15 wt % slurry. The initial gas release rate for LS-7 is lower than LS-9 indicating some effect from the alkaline wash; however, at the later time points the gas release rate for LS-7 becomes more similar to LS-9. The gas release rate at elevated temperature (LS-8) is consistently higher than the measured rates at room temperature, and calculations using the trend lines, predict this will remain true until the decomposition is complete. At one year after the synthesis, the calculated rate at 49 °C is still approximately twice the release rate at room temperature. After one year of storage at 49 °C approximately 28% of the peroxide groups will have decomposed versus approximately 12% after storage at room temperature for one year.
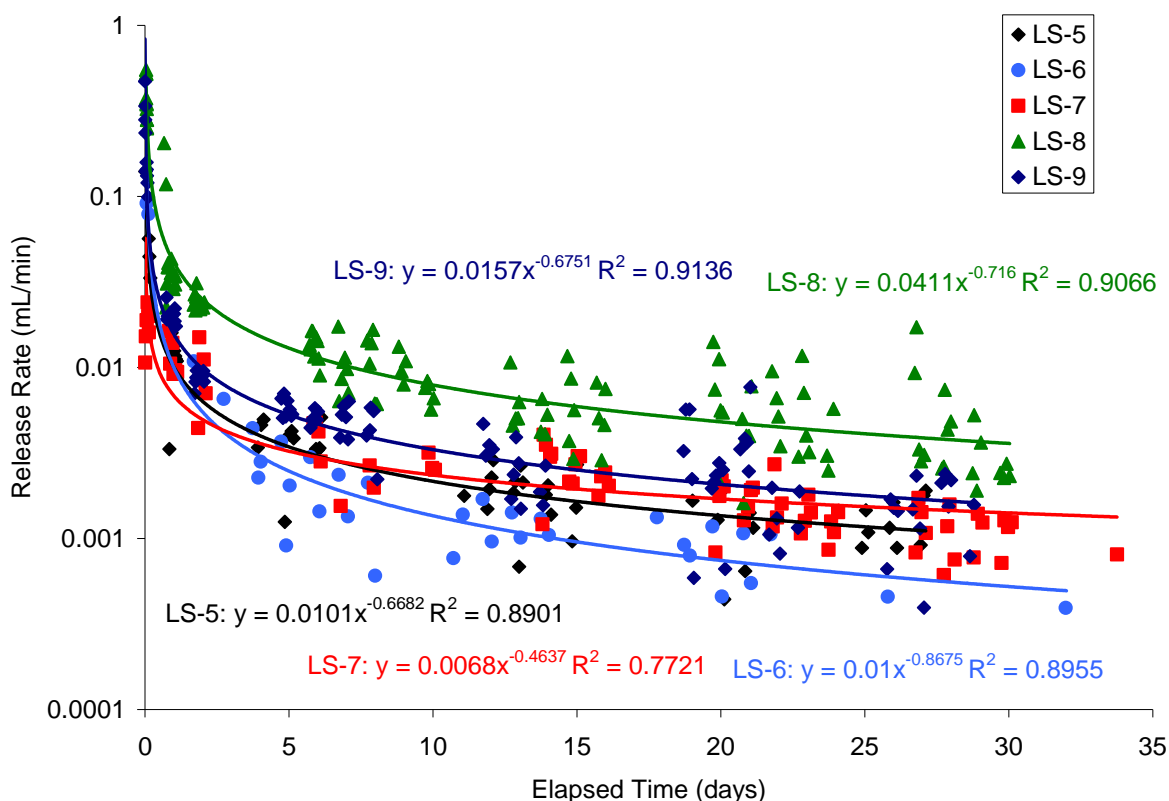
Figure 1. Comparison of gas release rates from LS-5, LS-6, LS-7, LS-8, and LS-9.

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Solids Settling Characteristics

Results from the gravity settling tests for MST and mMST in salt solutions with varying sodium concentrations (4.6, 5.6, and 6.6 M) are shown in Figure 2. The rates were determined by measuring the height of the clear supernate at the top of the graduated cylinder over time. As can be seen from the graph, the mMST settling rate is much slower than the MST settling rate, indicating the mMST contains a larger fraction of fine particles. For MST, there did not appear to be a measurable effect of the sodium concentration on the settling rate. For mMST the settling rate was slightly lower in the highest sodium concentration solution. This is the expected trend, as the viscosity of the solution increases with increasing ionic strength. The apparent increase in settling rate for mMST at times > 20 hours is attributed to the fact that mMST adheres to the walls of the graduated cylinder to a much greater extent than MST, making the measurement of the clear supernate at the top of the cylinder difficult. When this was taken into account the height of the clear supernate appeared to increase rapidly over a short period of time, which was likely not the case.
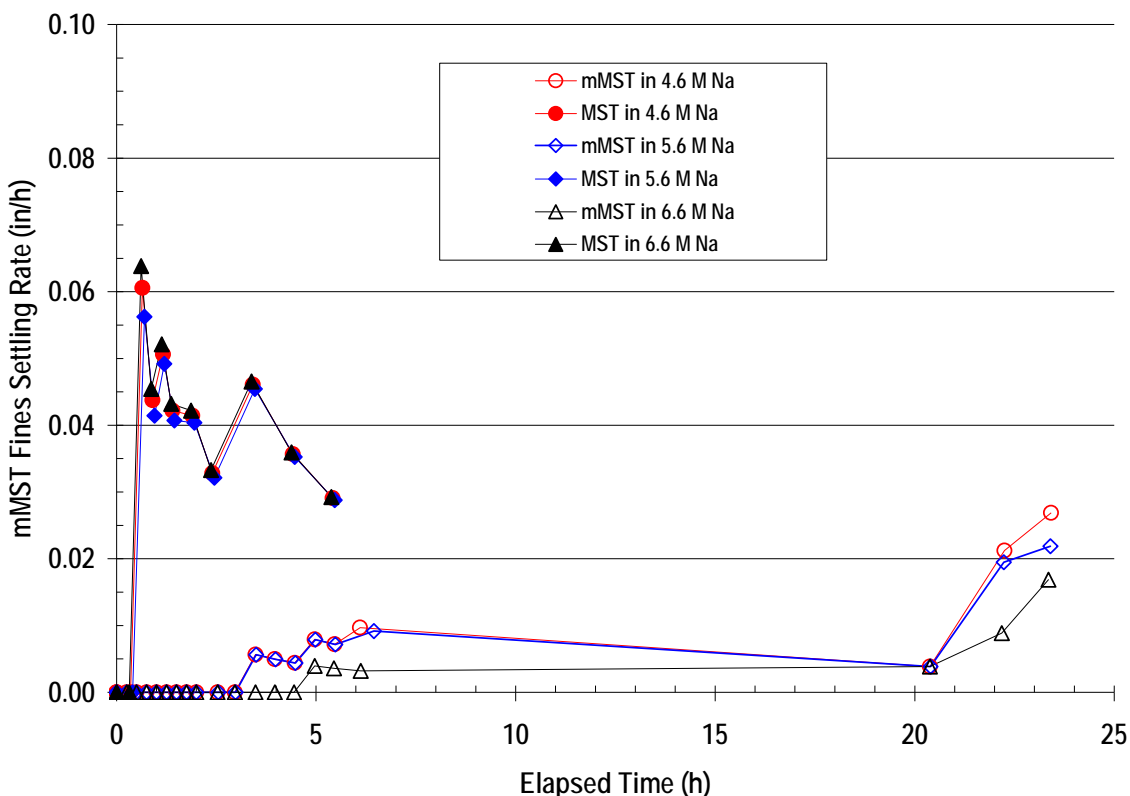
Figure 2. MST and mMST fines settling rates vs. time.

Shelf-Life Testing

Several batches of mMST of different ages, prepared both in our lab and by the vendor, were analyzed using an iodometric titration method to determine the amount of peroxide present in the material. The amount of peroxide was found to decrease linearly with the age of the sample

(Table VI, Figure 3). There was one exception to this trend, Sample LS-8. This lab prepared sample had been held at 49 °C for one month (for gas release measurements), whereas the other samples had not been exposed to elevated temperatures. Sample LS-8 contained approximately one-half the amount of peroxide of a slightly older sample, LS-7, that was stored at ambient laboratory temperature.

Table VI. mMST Samples, Age and Peroxide Content

Sample	Age (y)	Peroxide/Ti Molar Ratio	St. Dev.	Sample Notes
LS-1	4.72	0.142	0.0017	Lab Prepared
LS-2	4.61	0.140	0.0026	Lab Prepared
LS-3	4.70	0.131	0.0066	Lab Prepared
LS-4A	4.37	0.173	0.0011	Lab Prepared
LS-4B	4.37	0.171	0.0034	Left on filter for 4 days during work-up
LS-5	3.16	0.208	0.0017	Lab Prepared
06-QAB-0139	3.56	0.202	0.0018	Vendor Prepared
LS-6	1.33	0.263	0.0006	Acid wash during synthesis work-up
LS-7	0.27	0.333	0.0093	Alkaline wash during synthesis work-up
LS-8	0.16	0.206	0.0011	Held at 49 °C for 30 days
LS-10	0.22	0.328	0.0061	Lab Prepared
3:1 Small Batch	0.02	0.327	0.0030	Small scale batch

The linear regression shown is $y = -0.0399x + 0.3332$, $R^2 = 0.9806$.
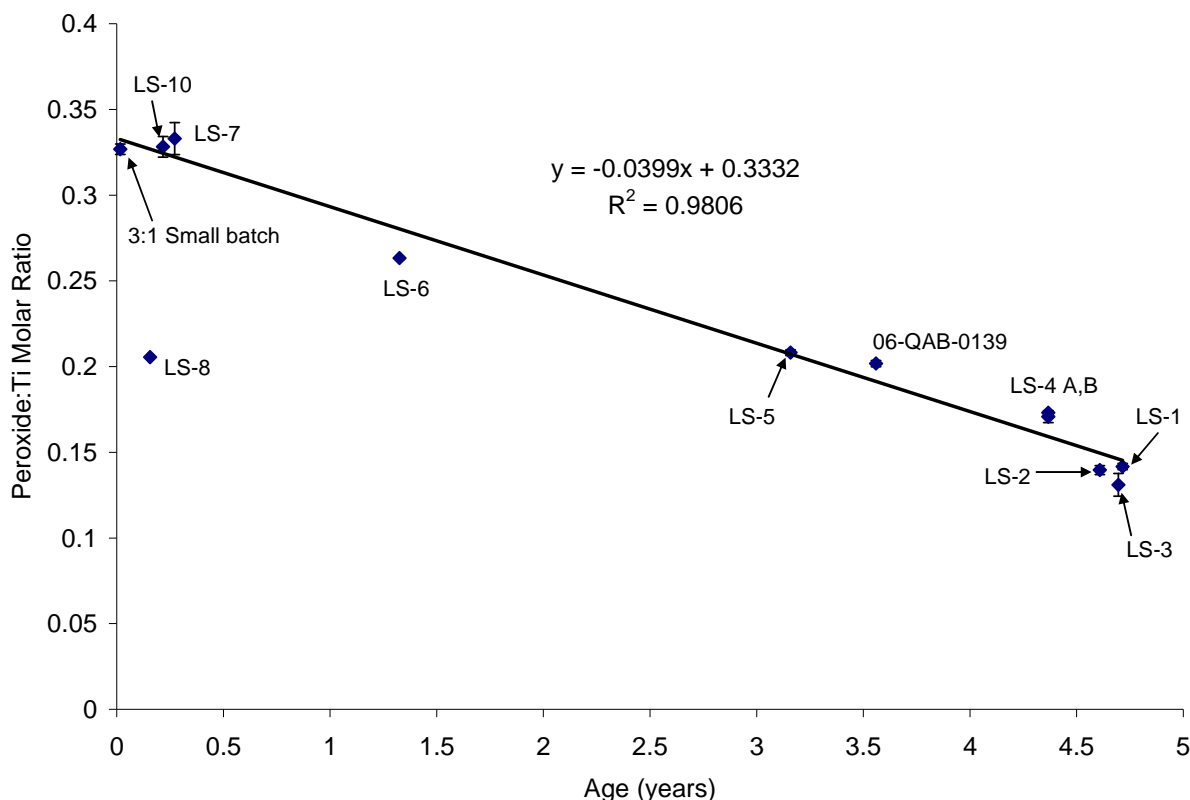
Figure 3. Peroxide content of mMST samples vs. age. (LS-8 is excluded from the linear regression.)

Table VII shows the decontamination factors (DFs) obtained for each of the samples of different ages (as listed in Table II). LS-8 has experienced accelerated aging due to exposure to elevated temperature, which is evident in the reduced peroxide content as measured by iodometric titration. As can be seen from the data, the Pu DF for the oldest sample (4.7 y, LS-2) is significantly lower than the Pu DF obtained with the other samples. Sample LS-8, which iodometric titration indicated had a reduced amount of peroxide, also shows a lower Pu DF. The Pu DF for samples of ages 0.30 y (LS-7) and 0.09 y (LS-9) are within error at the 6 and 24 hour sampling times. Samples from the 12 hour sampling time fell below the method detection limit, resulting in greater than values calculated for the DFs.

In the case of Np-237, LS-8, which has experienced accelerated aging due to exposure to elevated temperature, shows the highest Np-237 DF, whereas the DF for the other samples are not statistically different from each other. It is difficult to draw any conclusions regarding the Sr-85 removal, since many of the samples fell below the method detection limit, resulting in greater than values being obtained for the DFs. However, it does appear that the oldest sample (4.7 y, LS-2) resulted in the least Sr removal, as the results for all time points for this sample were above the method detection limit. At the 6-hour time point, the Sr DF for LS-2 is clearly lower than that obtained for LS-8 and LS-9; however at the later time points this conclusion cannot be drawn as the value falls within error of the minimum DF values for LS-8 and LS-9.

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There appears to be no effect of age on the uranium sorption of these materials as none of the samples appear to adsorb a measurable amount of uranium.

Earlier testing evaluated the performance of sample LS-2 over a time period of approximately 30 months with no measurable decrease in Pu DF. However, this testing at 56.4 months showed a significant decrease in Pu DF to a value only 18% of the Pu DF averaged over the earlier test dates (Table VIII and Figure 4). The Pu DF of this aged sample of mMST still exceeds the Pu DF obtained with the baseline MST at twice the concentration (i.e. 0.4 g/L vs. 0.2 g/L).

Table VII. Summary of Decontamination Factors (DF) from Shelf-Life Testing. Uncertainty (Unc.) column represents one sigma uncertainty.

Sr DF								
Sample	**LS-2**		**LS-7**		**LS-8**		**LS-9**	
Contact Time (h)	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**
6	38.0	5.25	39.5	7.76	> 106	5.29	> 73.7	3.69
12	45.3	10.5	62.4	15.2	> 47.5	2.37	> 62.3	3.12
24	50.2	8.22	> 64.6	3.23	> 64.5	3.22	> 56.4	2.82
U DF								
Sample	**LS-2**		**LS-7**		**LS-8**		**LS-9**	
Contact Time (h)	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**
6	0.953	0.0142	0.944	0.0319	1.00	0.0147	0.934	0.0407
12	1.03	0.0390	1.01	0.0479	1.00	0.0386	1.03	0.0547
24	0.962	0.0275	1.02	0.0253	0.990	0.0261	0.990	0.0256
Np DF								
Sample	**LS-2**		**LS-7**		**LS-8**		**LS-9**	
Contact Time (h)	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**
6	1.57	0.0597	1.34	0.0502	2.06	0.0769	1.62	0.149
12	1.68	0.118	1.45	0.0343	2.14	0.151	1.62	0.0946
24	1.85	0.0128	1.74	0.0235	2.44	0.0333	1.89	0.0637
Pu DF								
Sample	**LS-2**		**LS-7**		**LS-8**		**LS-9**	
Contact Time (h)	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**	**DF**	**Unc.**
6	14.0	1.46	93.3	12.0	40.1	6.08	122	15.9
12	26.9	2.19	> 137	7.54	> 65.0	3.58	> 251	13.8
24	57.9	7.93	281	88.6	166	25.6	386	146

Table VIII. Pu Decontamination Factor (DF) Over Time for mMST Sample LS-2.

Elapsed Time from Prep. To Performance Test (months)	Pu DF			
	6-hour Contact Time		12-hour Contact Time	
	Average	Std Dev	Average	Std Dev
0.44	9.57E+01	1.76E+01	1.72E+02	6.16E+00
6.16	6.38E+01	6.14E+00	1.43E+02	2.66E+01
11.7	6.82E+01	1.39E+01	1.24E+02	9.25E+00
13.4	7.85E+01	1.12E+01	1.48E+02	2.66E+01
29.9	9.52E+01	1.17E+01	1.22E+02	2.09E+01
56.4	1.40E+01	1.46E+00	2.69E+01	2.19E+00
Baseline MST (0.4 g/L)	6.93E+00	6.28E-01	1.02E+01	9.38E-01
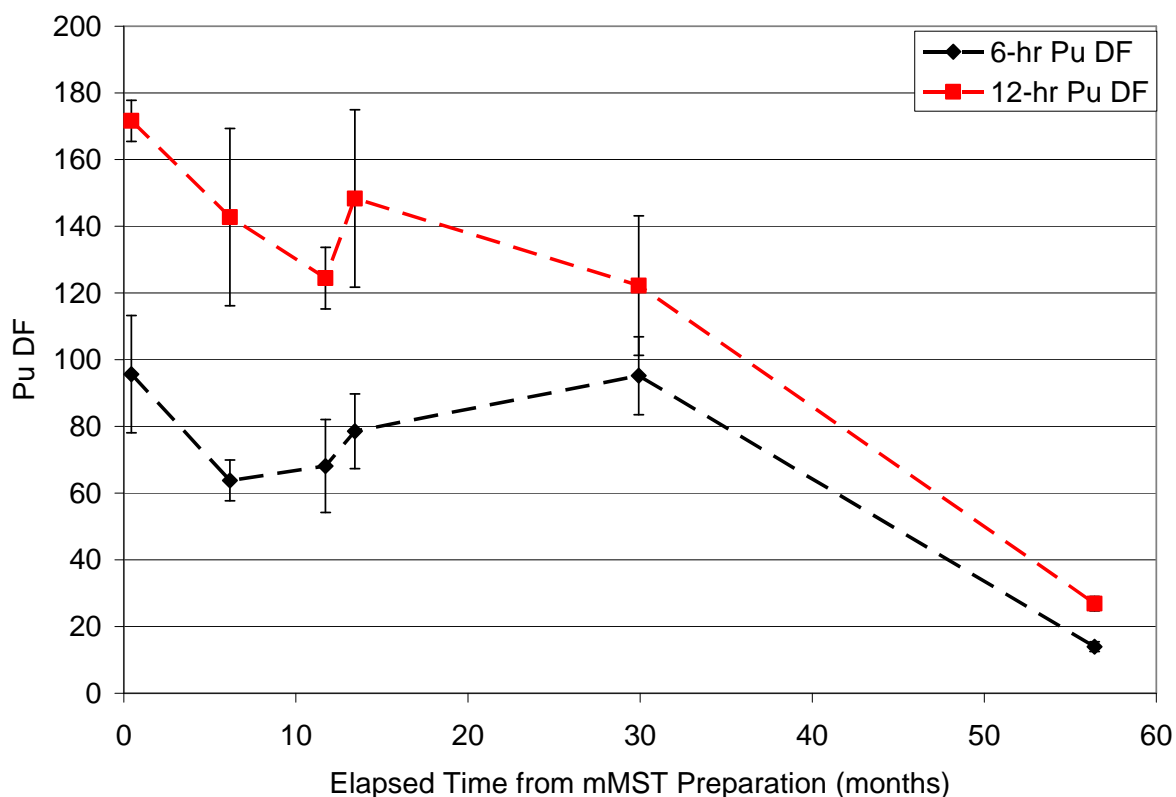
Figure 4. Pu DF for LS-2 as a function of elapsed time since preparation.

CONCLUSIONS

Recent testing of mMST focused on further characterization of the material including determination of peroxide content, evaluation of the post-synthesis gas release under different conditions, and evaluation of the performance of the material under varying conditions. Studies also focused on how the material changes with age. Iodometric titration was used to determine

the peroxide content of the mMST samples. Results from these tests indicated a loss of peroxide content with age or extended exposure to elevated temperatures.

Previous testing established that the mMST releases oxygen gas during the synthesis, and continues to off-gas at a rapidly diminishing rate after synthesis. Several modifications to the work-up of the material were evaluated to determine their effect on gas release after preparation. There appeared to be little effect of these modifications on the post-synthesis gas release rates. The alkaline wash did result in a slight decrease of the initial gas release rate; however after two days the gas release measurements are not statistically different among the different batches of mMST. Because the material may be exposed to elevated temperatures of up to 120 °F (49 °C) during shipping and storage, an experiment was performed to measure the rate of gas release at this elevated temperature. The gas release rate was found to be consistently higher than the rate measured at room temperature. The quantity of post-synthesis gas released from the mMST is sufficient under all conditions tested to require vented containers for the shipment and storage of large quantities of material.

A desorption test was designed to determine if any desorption of Sr, Pu, or Np occurred under conditions used to wash the mMST prior to transfer to the DWPF. Several dilutions of decontaminated salt solution were prepared. No loss of Sr, Np, or Pu was observed over the concentration range and contact times tested.

To determine the effect of gamma irradiation on the performance of the material, a performance test was completed using material that had been irradiated at a dose similar to what would be received in the ARP facility. Results from this testing indicated no adverse effects of irradiation on the performance of the material.

Performance tests were also completed with samples of varying age to determine if the loss of peroxide affects the Sr and actinide removal efficiency of the material. Testing did indicate some loss of Pu and Sr removal in the oldest sample tested (4.7 y). Previous testing with this sample indicated no loss in Pu removal up to an age of 30 months. The age of the sample did not appear to reduce the Np removal efficiency, and no measurable uptake of uranium was observed at this sorbent loading (0.2 g/L).

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