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Testing and Characterization of Engineered Forms of Monosodium Titanate (MST)

K. M. L. Taylor-Pashow
C. A. Nash
D. T. Hobbs

May 2012

Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
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Prepared for the U.S. Department of Energy under
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DISCLAIMER

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REVIEWS AND APPROVALS

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EXECUTIVE SUMMARY

Engineered forms of MST and mMST were prepared at ORNL using an internal gelation process. Samples of these two materials were characterized at SRNL to examine particle size and morphology, peroxide content, tapped densities, and Na, Ti, and C content. Batch contact tests were also performed to examine the performance of the materials. The ^{E}mMST material was found to contain less than 10% of the peroxide found in a freshly prepared batch of mMST. This was also evidenced in batch contact testing with both simulated and actual waste, where little difference in performance was seen between the two engineered materials, ^{E}MST and ^{E}mMST.

Based on these results, attempts were made to increase the peroxide content of the materials by post-treatment with hydrogen peroxide. The peroxide treatment resulted in a slight (~10%) increase in peroxide content; however, the peroxide:Ti molar ratio was still much lower (~0.1 X) than what is seen in a freshly prepared batch of mMST. Testing with simulated waste showed the performance of the peroxide treated materials was improved.

Batch contact tests were also performed with an earlier (2003) prepared lot of ^{E}MST to examine the effect of ionic strength on the performance of the material. In general the results showed a decrease in removal performance with increasing ionic strength, which is consistent with previous testing with MST. A Sr loading isotherm was also determined, and the ^{E}MST material was found to reach a Sr loading as high as 13.2 wt % after 100 days of contact at a phase ratio of 20000 mL/g. At the typical MST phase ratio of 2500 mL/g (0.4 g/L), a Sr loading of 2.64 wt % was reached after 506 hours of contact.

Samples of ^{E}MST and the post-peroxide treated ^{E}mMST were also tested in a column configuration using simulated waste solution. The breakthrough curves along with analysis of the sorbent beds at the conclusion of the experiments showed that the peroxide treated ^{E}mMST has a higher Sr and Np capacity, but that both materials have similar Pu capacities. The ^{E}MST removed a larger percentage of U than the peroxide treated ^{E}mMST, which is consistent with previous testing which showed that mMST has little affinity for U under these conditions.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
CST	crystalline silicotitanate
DF	decontamination factor
DWPF	Defense Waste Processing Facility
^{E}MST	engineered monosodium titanate
^{E}mMST	engineered modified monosodium titanate
ICP-ES	inductively coupled plasma – emission spectroscopy
ICP-MS	inductively coupled plasma – mass spectroscopy
MST	monosodium titanate
mMST	modified monosodium titanate
ORNL	Oak Ridge National Laboratory
PuTTA	plutonium thenoyltrifluoroacetone scintillation
PVDF	polyvinylidene fluoride
PXRD	powder X-ray diffraction
SCIX	small column ion exchange
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TGA	Thermogravimetric Analysis
TIC/TOC	total organic carbon/total inorganic carbon
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

The Department of Energy – Office of Environmental Management is funding development of At Tank or Near Tank HLW treatment processes for use at the Hanford Site and the Savannah River Site (SRS). The primary objective is to accelerate waste processing by maximizing the available compliant tank space to efficiently support permanent waste disposal including vitrification and to treat problematic waste prior to transfer to the either the Waste Treatment and Immobilization Plant (WTP) or Salt Waste Processing Facility (SWPF). This technology will also assist in the alignment of the salt and sludge processing life cycle at SRS, thereby eliminating the 7-year salt only campaign at the Defense Waste Processing Facility (DWPF).

Transformational acceleration of waste pretreatment will be realized by combining all radiochemical separations into a single unit operation within waste tanks. Combined radiochemical separations can be achieved using a combined ion-exchange and sorption process within a waste tank. The ion-exchange portion of this concept is currently being developed for cesium removal and is referred to as small column ion exchange (SCIX). However, the SCIX process as currently planned uses the ion-exchanger crystalline silicotitanate (CST). This material is very effective for removal of cesium and, to a lesser degree, strontium. However, this material has no affinity for the actinide elements and, thus, an additional treatment step would be needed to remove the alpha activity in the waste. The purpose of this work is to develop a sorption material for deployment in a column configuration in combination with an ion-exchange material.

The proposed process would add an engineered form of monosodium titanate (^{E}MST) or peroxide-modified monosodium titanate (^{E}mMST) that could be deployed in a SCIX column. The ^{E}MST and ^{E}mMST could be utilized in a separate column or mixed with CST to provide a mixed ion-exchange bed in the SCIX column. Earlier work identified an internal gelation process as an efficient method for producing an engineered form of MST.[1] In the current work, limited quantities of engineered forms of both MST and mMST (^{E}MST and ^{E}mMST) were produced using the internal gelation process. These materials have been extensively characterized, and their Sr and actinide removal performance has been tested through batch contact testing with both simulated and actual waste, and also in a small column using a simulated waste solution.

2.0 Experimental Procedure

2.1 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} $NaNO_2$.[2] 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.[3] A quantity of the mMST (LS-10) was prepared using 25 grams of the Optima-supplied MST.

The engineered forms of MST and mMST (^{E}MST and ^{E}mMST) were prepared by researchers at Oak Ridge National Laboratory (ORNL) using an internal gelation process to incorporate the MST or mMST into a hydrous titanium oxide matrix.[1] The first samples of ^{E}MST were prepared by ORNL in 2003. These materials were prepared by incorporating either 32 wt % or 50 wt % MST. The MST used for this material was from Optima, Lot # 00-QAB-417. Additional samples of both ^{E}MST and ^{E}mMST were prepared by ORNL in 2010 using the same method.

These samples incorporated 45 wt % of the MST or mMST. For the 2010 material, SRNL provided ORNL with MST from Harrell Industries, along with a laboratory prepared sample of mMST. The mMST was prepared by treatment of the same Harrell MST with H_2O_2 following the previously published procedure.[3]

Samples of the 2010 ^{E}MST and ^{E}mMST were also post-treated with H_2O_2, in an attempt to improve the performance of the materials. For this process, a similar procedure to that used to prepare mMST from MST was used. Samples of ^{E}MST and ^{E}mMST were suspended in water, and the pH of the suspensions was adjusted to 7. Hydrogen peroxide (30 wt %) was then added dropwise, while mixing. The amount of H_2O_2 added was the amount needed to provide a 3:1 H_2O_2:Ti mole ratio. The moles of Ti was based on the total Ti content of the material, including Ti from the binder. After the addition was complete, the reactions were mixed at 25 °C for 24 hours. The products were then isolated and washed 6 times with distilled water. After the washing was complete, the products were suspended in water, and the pH of the suspension was adjusted to 4. The products were then collected by filtration, washed again with distilled water, and then dried in a vacuum oven at 50 °C. The peroxide treatment resulted in the formation of some fines; however, these were removed during the washing sequence.

2.2 Material Characterization

Samples of the ^{E}MST and ^{E}mMST, along with the peroxide treated versions, were characterized using a number of methods. Samples of each material were submitted for powder X-ray diffraction (PXRD), particle size analysis, and total organic carbon/total inorganic carbon (TIC/TOC) analysis. Thermogravimetric analysis (TGA) was also performed for 2010 ORNL prepared materials. Photos of the materials were obtained using an optical microscope (Leica MZ Apo).

Samples of the ^{E}MST and ^{E}mMST were digested and submitted for inductively coupled plasma – emission spectroscopy (ICP-ES). For the digestion, samples of approximately 50 mg were placed in a small glass beaker. Distilled water (2 mL) and concentrated sulfuric acid (2 mL) were then added to the particles. The mixture was then heated on a hot-plate, with stirring, until the solids had dissolved. Once dissolved, the solution was transferred to a 50-mL volumetric flask, and diluted to volume with distilled water. Samples of this solution were then submitted for ICP-ES analysis.

The tap densities of the ^{E}MST and ^{E}mMST were also determined. For these measurements, a 10-mL graduated cylinder was loosely filled to the 10-mL mark with either ^{E}MST or ^{E}mMST. The mass was then determined. The graduated cylinder was then gently tapped until the volume of the beads was no longer changing. This volume was then recorded. The tap density was then determined by dividing the mass by the final tapped volume, giving the density in g/mL. The measurements were performed in triplicate.

The peroxide contents of the materials were also measured using an iodometric titration method. The general procedure for the titrations involved first performing the reaction between sodium iodide and peroxide to form iodine, which was then titrated with sodium thiosulfate using starch as an indicator. See reactions 1 and 2 below.

$$H_2O_2 + 2\,I^- + 2H^+ \rightarrow I_2 + 2\,H_2O \qquad (1)$$

$$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI \qquad (2)$$

Samples of the engineered materials were first ground using a mortar and pestle to reduce the particle size of the material. Samples of each material (~0.77 – 0.80 g) were then placed in 25-mL volumetric flasks. The particles were suspended in approximately 15-20 mL of distilled water. Next, 0.42 mL aliquots of 18 M sulfuric acid were added to the suspensions, and the samples were then diluted to the 25-mL mark with additional distilled water. The suspensions were then transferred to glass vessels containing stir bars, and 20 mL aliquots of a 0.27 M solution of sodium iodide were added. These reactions were then stirred at room temperature for ~24 hours. Aliquots of the reaction mixture were then removed and titrated with a 0.1 M solution of sodium thiosulfate, using starch as an indicator. All titrations were performed in triplicate.

2.3 Batch Contact Testing with Simulant

A series of batch contact tests were performed with simulated waste solutions to examine the uptake of Sr and actinides by the engineered materials. Testing of the materials included both the 2003 prepared ORNL sample of ^{E}MST with a 50 wt % MST loading, and the 2010 prepared ORNL samples of ^{E}MST and ^{E}mMST with 45 wt % loadings of MST and mMST. The first set of tests performed (ET 1-14) examine the performance of the 2003 ^{E}MST in simulants with varying ionic strength. The target sodium concentrations of the simulants ranged from 5.6 M to 8.0 M. The composition of the simulants is provided in Table 2-1. A sample of the Optima MST (00-QAB-417) was also tested at the lowest and highest ionic strengths for comparison. The sorption tests were performed as follows. Fifty milliliters of the appropriate simulant was placed into each of 14 125-mL polyethylene bottles. ^{E}MST or MST was then added to the appropriate test bottles, at an MST concentration of 0.4 g/L. The amount of ^{E}MST added was based on the 50 wt % reported loading of MST. The bottles were then placed in a temperature controlled waterbath shaker, and were mixed at 25 °C. Samples were removed after 6, 30, 120, and 191 hours. At each sampling event, the bottle was removed from the waterbath and manually shaken for 30 seconds to ensure the solids were homogeneously suspended. A sample was then removed and filtered through a 0.1-µm polyvinylidene fluoride (PVDF) syringe filter to remove the solids. An aliquot of the filtrate (3 mL) was acidified with 5 M nitric acid (6 mL) and submitted for inductively coupled plasma – mass spectroscopy (ICP-MS), gamma scan, and plutonium thenoyltrifluoroacetone scintillation (PuTTA) analyses.

Table 2-1. Composition of Simulants Used in Tests ET 1-14 (Varying Ionic Strength).

Component	SWS-7-2010-1		SWS-7-2010-2		SWS-7-2010-3	
	Target	**Measured**	**Target**	**Measured**	**Target**	**Measured**
$NaNO_3$	2.03 M	1.98 M	2.18 M	2.05 M	2.36 M	1.94 M
NaOH	2.21 M	2.01 M	2.37 M	2.20 M	2.57 M	1.88 M
Na_2SO_4	0.140 M	0.127 M	0.150 M	0.134 M	0.163 M	0.125 M
$NaAl(OH)_4$	0.280 M	0.278 M	0.300 M	0.289 M	0.325 M	0.303 M
$NaNO_2$	0.500 M	0.496 M	0.536 M	0.513 M	0.580 M	0.489 M
Na_2CO_3	0.150 M	0.160 M	0.161 M	0.162 M	0.174 M	0.184 M
Total Na	5.6 M	5.39 M	6.00 M	5.65 M	6.50 M	5.79 M
K^+	0.007 M	NM	0.007 M	NM	0.007 M	NM
Total Sr	2.0 mg/L	1.68 mg/L	2.0 mg/L	2.67 mg/L	2.0 mg/L	2.21 mg/L
^{85}Sr	30,000 dpm/mL	2.77E+04 dpm/mL	30,000 dpm/mL	1.99E+04 dpm/mL	30,000 dpm/mL	3.56E+04 dpm/mL
Total Pu	200 µg/L	114 µg/L	200 µg/L	143 µg/L	200 µg/L	167 µg/L
^{237}Np	500 µg/L	457 µg/L	500 µg/L	402 µg/L	500 µg/L	497 µg/L
Total U	10,000 µg/L	9,260 µg/L	10,000 µg/L	9,600 µg/L	10,000 µg/L	9,290 µg/L
^{137}Cs	30,000 dpm/mL	1.05E+05 dpm/mL	30,000 dpm/mL	2.14E+05 dpm/mL	30,000 dpm/mL	2.11E+05 dpm/mL
Component	**SWS-7-2010-4**		**SWS-7-2010-5**		**SWS-7-2010-6**	
	Target	**Measured**	**Target**	**Measured**	**Target**	**Measured**
$NaNO_3$	2.54 M	2.40 M	2.72 M	2.61 M	2.90 M	2.71 M
NaOH	2.76 M	2.48 M	2.96 M	1.91 M	3.16 M	2.14 M
Na_2SO_4	0.175 M	0.112 M	0.188 M	0.119 M	0.200 M	0.129 M
$NaAl(OH)_4$	0.350 M	0.311 M	0.375 M	0.388 M	0.400 M	0.358 M
$NaNO_2$	0.625 M	0.522 M	0.670 M	0.565 M	0.714 M	0.604 M
Na_2CO_3	0.188 M	0.191 M	0.201 M	0.207 M	0.214 M	0.220 M
Total Na	7.00 M	5.92 M	7.50 M	6.44 M	8.00 M	6.83
K^+	0.007 M	NM	0.007 M	NM	0.007 M	NM
Total Sr	2.0 mg/L	1.37 mg/L	2.0 mg/L	2.82 mg/L	2.0 mg/L	2.42 mg/L
^{85}Sr	30,000 dpm/mL	3.37E+04 dpm/mL	30,000 dpm/mL	3.15E+04 dpm/mL	30,000 dpm/mL	3.12E+04 dpm/mL
Total Pu	200 µg/L	160 µg/L	200 µg/L	168 µg/L	200 µg/L	142 µg/L
^{237}Np	500 µg/L	482 µg/L	500 µg/L	475 µg/L	500 µg/L	487 µg/L
Total U	10,000 µg/L	10,300 µg/L	10,000 µg/L	8,170 µg/L	10,000 µg/L	4,010 µg/L
^{137}Cs	30,000 dpm/mL	2.10E+05 dpm/mL	30,000 dpm/mL	1.14E+05 dpm/mL	30,000 dpm/mL	1.06E+05 dpm/mL

The second set of tests (ET 15-21) was performed to determine the Sr loading isotherm of the ^{E}MST. For these tests, samples of the 2003 prepared ^{E}MST were contacted with a non-rad simulant having a Sr concentration of 5.5 mg/L. The composition of the simulant is provided in Table 2-2. Samples of the ^{E}MST (0.040 g each) were placed in polyethylene bottles. Aliquots of the simulant were then added to provide liquid:solid ratios of 20000 (duplicate), 5000 (duplicate), 2500 and 1250 mL/g. The test bottles were then placed in a 25 °C shaker oven, and were shaken at a speed of 200 rpm. Samples were removed after 24, 168, 336, 504, and 2400 hours. The test bottles with liquid:solid ratios of 2500 and 1250 were only sampled once at the 504 hour time point. For each sampling event, the shaking was stopped and the bottles were left to stand undisturbed for 1 hour. A sample of the supernate was then removed and filtered through a 0.1-µm PVDF syringe filter and submitted for Sr analysis.

Table 2-2. Composition of Simulant Used for Sr Loading Isotherm Testing (ET 15-21).

Component	SWS-10-2010	
	Target	Measured
Free NaOH	1.33 M	1.11 M
$NaNO_3$	2.60 M	2.54 M
$NaAl(OH)_4$	0.429 M	0.413 M
$NaNO_2$	0.134 M	0.134 M
Na_2SO_4	0.521 M	0.496 M
Na_2CO_3	0.026 M	0.042 M
Total Na	5.6 M	5.68 M
Total Sr	5.5 mg/L	5.64 mg/L

The third set of tests (ET 24-28) examined the performance of the 2010 ORNL prepared materials, both ^{E}MST and ^{E}mMST. The performance of these materials was compared to samples of non-engineered MST and mMST. The composition of the simulant used in this testing is provided in Table 2-3. For these tests, samples of sorbent were placed in 50-mL centrifuge tubes. The amounts added corresponded to 0.4 g/L. The amounts of ^{E}MST and ^{E}mMST added were based on the 45 wt % reported loading of MST or mMST. Forty mL of SWS-5-2009 was then added to each tube, and the tubes were rotated at a speed of 8 rpm on a LabQuake tumbler at ambient laboratory temperature. The tests were sampled after 1, 4, and 24 hours of mixing. At each sampling event, the tube was removed from the tumbler and manually shaken for 10-15 seconds to ensure the solids were homogeneously suspended. A sample was then removed and filtered through a 0.1-µm PVDF syringe filter to remove the solids. An aliquot of the filtrate (3 mL) was acidified with 5 M nitric acid (6 mL) and submitted for ICP-MS, gamma scan, and PuTTA analyses.

Table 2-3. Composition of Simulant Used for Tests ET 24-37 (SWS-5-2009).

Component	Target	Measured
Free NaOH	1.33 M	1.37 M
Total $NaNO_3$	2.60 M	2.13 M
$NaAl(OH)_4$	0.429 M	0.404 M
$NaNO_2$	0.134 M	0.133 M
Na_2SO_4	0.521 M	0.483 M
Na_2CO_3	0.0260 M	0.0298 M
Total Na	5.6 M	5.05 M
^{85}Sr	30,000 dpm/mL	spiked before each set of tests
Total Sr	0.60 mg/L	0.521 mg/L
^{137}Cs	30,000 dpm/mL	96,300 dpm/mL
Total Cs	1.40×10^{-4} M	1.26×10^{-4} M
Pu	200 µg/L	220 µg/L
Np	500 µg/L	460 µg/L
U	10,000 µg/L	10,700 µg/L

Tests ET 29-37 followed a similar procedure, and used the same simulant (SWS-5-2009) as tests ET 24-28. Tests ET 29-33 examined the performance of the 2010 ORNL prepared materials, ^{E}MST and ^{E}mMST, along with the non-engineered forms of MST and mMST. For these tests MST and ^{E}MST were added at an MST concentration of 0.4 g/L, while mMST and ^{E}mMST were added at an mMST concentration of 0.1 g/L. Again, the amounts of ^{E}MST and ^{E}mMST added were based on the 45 wt % reported loading of MST or mMST. These tests were sampled after 6, 24, 48, and 168 hours of mixing, following the same sampling procedure used for Tests ET 24-28. Tests ET 34-37 examined the performance of the two post-peroxide treated samples of the engineered materials. The non-engineered MST was also included in this test set for comparison. In these tests, MST was added at a concentration of 0.4 g/L, while the two peroxide treated engineered materials were added at an equivalent MST concentration of 0.1 g/L. These tests were sampled after 24 and 168 hours of mixing, following the same sampling procedure used for the previous tests.

Table 2-4. Summary of Simulant Batch Contact Tests

Test Group	Purpose of Tests	Material Used
ET 1-14	Effect of ionic strength	2003 prepared ^{E}MST, baseline MST
ET 15-21	Sr loading isotherm	2003 prepared ^{E}MST
ET 24-28	Performance of 2010 ORNL prepared ^{E}MST and ^{E}mMST	2010 prepared ^{E}MST and ^{E}mMST, baseline MST and mMST
ET 29-33	Performance of 2010 ORNL prepared ^{E}MST and ^{E}mMST using lower concentrations of sorbent	2010 prepared ^{E}MST and ^{E}mMST, baseline MST and mMST
ET 34-34	Performance of post-peroxide treated ^{E}MST and ^{E}mMST	Peroxide treated ^{E}MST and ^{E}mMST, and baseline MST

2.4 Batch Contact Testing with Real Waste

Tests were performed using a sample of Tank 49H supernate. The sample of Tank 49H was made up of samples taken from December 2010 to February 2011. Thirteen ~3 L samples taken during this time period were combined into a 50-L carboy, and a 400-mL aliquot of the solution was removed and used for this testing. The details of the origin of this sample are given in Table 2-5, and the measured composition is given in Table 2-6. The supernate was contacted with 4 different sorbents: MST, mMST, and the 2010 ORNL prepared engineered forms of MST and mMST (^{E}MST and ^{E}mMST). The MST and ^{E}MST were added at equivalent MST concentrations of 0.4 g/L, while the mMST and ^{E}mMST were added at equivalent mMST concentrations of 0.2 g/L. A reduced amount of the modified versions is used due to the increased performance of the modified material compared to the baseline MST. Each test used 80 mL of Tank 49 supernate. The contact tests were carried out in a temperature controlled waterbath-stirrer at 25 °C for 24 hours, with stirring. Samples were removed after 2, 6, 12, and 24 hours of contact. The test bottle was shaken by hand before removing each sample. The sample was then filtered through a 0.1-µm syringe filter to remove the solids. An aliquot of the filtrate was then acidified with an equal volume of 5 M nitric acid. The samples were analyzed for ^{90}Sr, Pu, Np, and U concentrations using ^{90}Sr, PuTTA, and ICP-MS analyses.

Table 2-5. Origin of Tank 49H Sample

Source	Tank 49H
Date Sampled	Dec. 2010 to Feb. 2011
Tank Farm Identification	HTF-49-10-167, -175 HTF-49-11-9, -11, -12, -15, -16, -17, -18, -19, -20, -21, -22
Date Received at SRNL	Dec. 2010 to Feb. 2011
Approximate Volume (L)	39

Table 2-6. Composition of the Tank 49H Sample

Analyte	Concentration (mg/L)	Method % Uncertainty
Na^+	150,000	10
K^+	505	10
Rb^+	0.476	20
Cs^+	2.09	20
Free OH	2.65 (M)	10
NO_3^-	188,000	10
NO_2^-	4160	10
Al^{3+}	5110	10
SO_4^{2-}	6490	10
PO_4^{3-}	874	10
CO_3^{2-}	0.239 (M)	10
F^-	< 100	10
Cl^-	373	10
oxalate	175	10
formate	919	10
^{137}Cs	1.44E+08 (dpm/mL)	5.00
^{90}Sr	3.57E+05 (dpm/mL)	9.41
^{238}Pu	6.76E+04 (dpm/mL)	5.64
$^{239/240}Pu$	1.27E+04 (dpm/mL)	5.67
Mass-235	0.183 µg/L	20
Mass-238	26.1	20
Density	1.269 g/mL	10

2.5 Column Testing with Simulant

Two small scale ion-exchange column experiments were performed using samples of the 2010 ORNL prepared ^{E}MST and the peroxide treated ^{E}mMST. A total of 30-L of simulant was prepared (15-L per column), having the composition shown in Table 2-7. A schematic of the column is shown in Figure 2-1, and arrangement of the equipment is shown in Figure 2-2. The glass columns had an internal diameter of 11 mm, and had 1 mm fine graduations on the glass. The pumps used to supply feed to each column were Fluid Metering Inc (FMI) pumps possessing a QG20 motor with a Q0 stainless steel piston, 1/8" diameter. The samples of ^{E}MST and peroxide treated ^{E}mMST were pre-soaked in a non-rad, sorbate free salt solution prior to loading in the columns. The composition of this solution is provided in Table 2-8. The salt solution was treated with MST prior to use to remove any tramp Sr. Specifically, 1.80775 g of ^{E}MST and 1.80162 g of peroxide treated ^{E}mMST were placed in glass vials. Aliquots (10-mL) of the salt solution were then added and the materials were left to soak for several days before the start of the column experiment. During this soaking period, it was observed that the ^{E}MST material swelled considerably, compared to the peroxide treated ^{E}mMST, which did not appear to swell.

Table 2-7. Composition of Simulant Used for Column Testing.

Component	Target	Measured
Free NaOH	2.21 M	1.90 M
Total $NaNO_3$	2.03 M	2.05 M
$NaAl(OH)_4$	0.280 M	0.275 M
$NaNO_2$	0.500 M	0.548 M
Na_2SO_4	0.140 M	0.131 M
Na_2CO_3	0.150 M	0.151 M
Total Na	5.6 M	5.38 M
^{85}Sr	30,000 dpm/mL	7,180 dpm/mL
Total Sr	6.00 mg/L	0.603 mg/L
^{137}Cs	30,000 dpm/mL	39,400 dpm/mL
Total Cs	18.6 mg/L	16.8 mg/L
Pu	200 μg/L	162 μg/L
Np	500 μg/L	500 μg/L
U	10,000 μg/L	4,320 μg/L

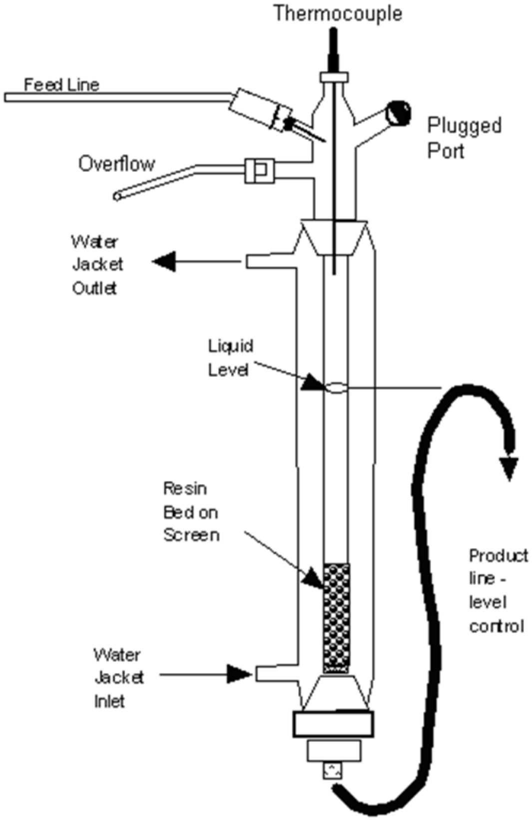

Figure 2-1. Ion-Exchange Column Design.

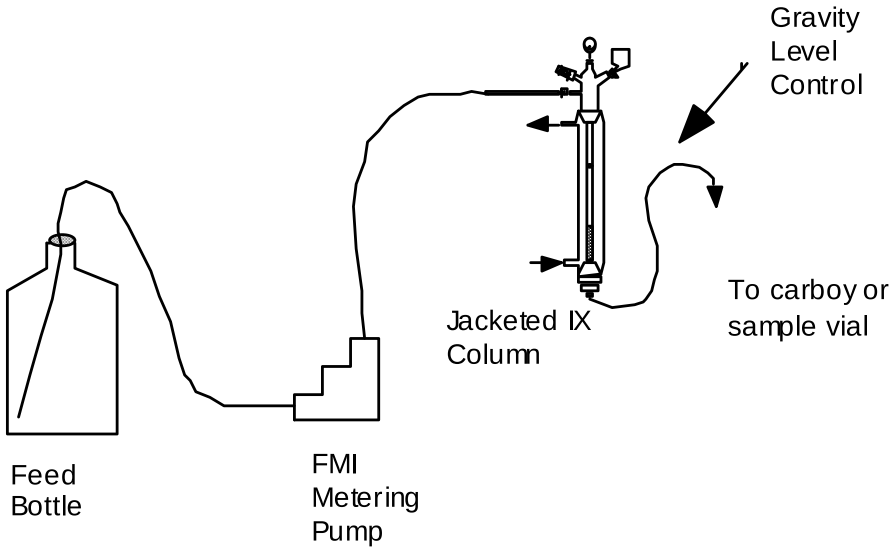

Figure 2-2. Schematic of Column Set-Up.

Table 2-8. Composition of Salt Solution Used for Pre-Soaking Materials for Column (SWS-1-2010).

Component	Target Concentration
Free NaOH	1.33 M
$NaNO_3$	2.90 M
$NaNO_2$	0.149 M
Na_2SO_4	0.581 M
Na_2CO_3	0.029 M
Total Na	5.6 M

The soaked materials were then transferred into the columns along with the salt solution. The 15-L of simulant (per column) was then passed through the column at a flow rate of approximately 0.5 mL/min. The temperature of the columns was controlled throughout the experiment using a temperature controlled recirculating waterbath set at 25 °C to circulate water through the column jacket. Samples were collected throughout the experiment. Each sample was collected over a period of approximately 10 minutes. The sample size was determined by the difference in the vial mass before and after collecting the sample. Sample collections were timed, and this information was also used to calculate the current flow rate, to insure there was no drift. Samples were then acidified by the addition of 6 mL of 5 M nitric acid. The precise amount of acid added was also determined by the difference in mass. The acidified samples were then submitted for ICP-MS, gamma scan, and PuTTA analyses.

After the column experiment was complete the resin beads were removed from the columns and representative samples were digested for analysis. Approximately 0.05 g of the air dried material from each column was placed into a 50-mL glass beaker. Two mL of distilled water and 2 mL of concentrated sulfuric acid were then added to each beaker. The mixtures were placed on a stirring hot plate, and were stirred and heated until all of the solids dissolved. The solutions were allowed to cool, and were then transferred to 25-mL volumetric flasks and diluted to volume with distilled water. Samples of these solutions were then submitted for gamma scan, PuTTA, ICP-MS, and ICP-ES analyses.

3.0 Results and Discussion

3.1 Characterization of Materials

3.1.1 *Photographs*

Photos of the ^{E}MST and ^{E}mMST samples were acquired at higher magnification using an optical microscope equipped with a still camera. Images in Figures 3-1 through 3-4 show the particles are generally spherical, although there are some irregular shaped particles. Post-treatment of the materials with H_2O_2 did not affect the size and morphology of the particles.

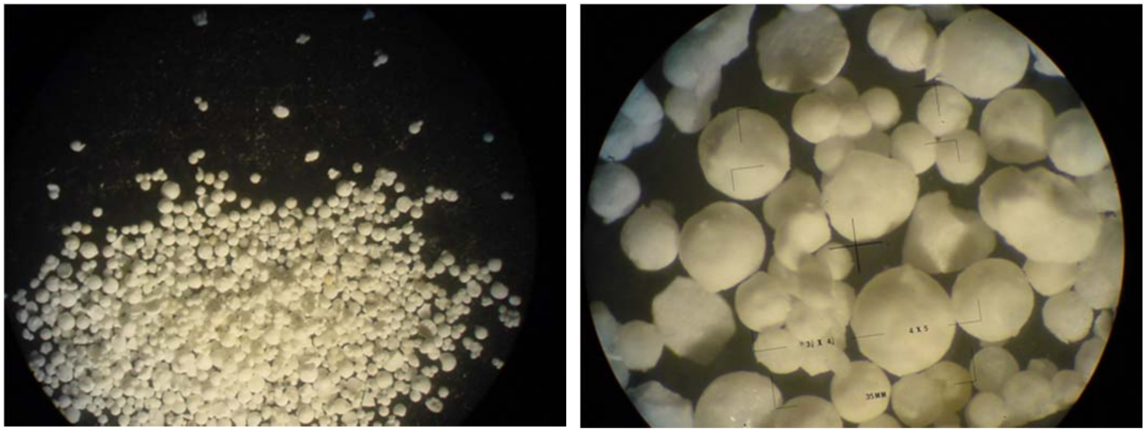

Figure 3-1. Photos of 2010 ORNL prepared ^{E}MST at 10x (left) and 55x (right) magnification.

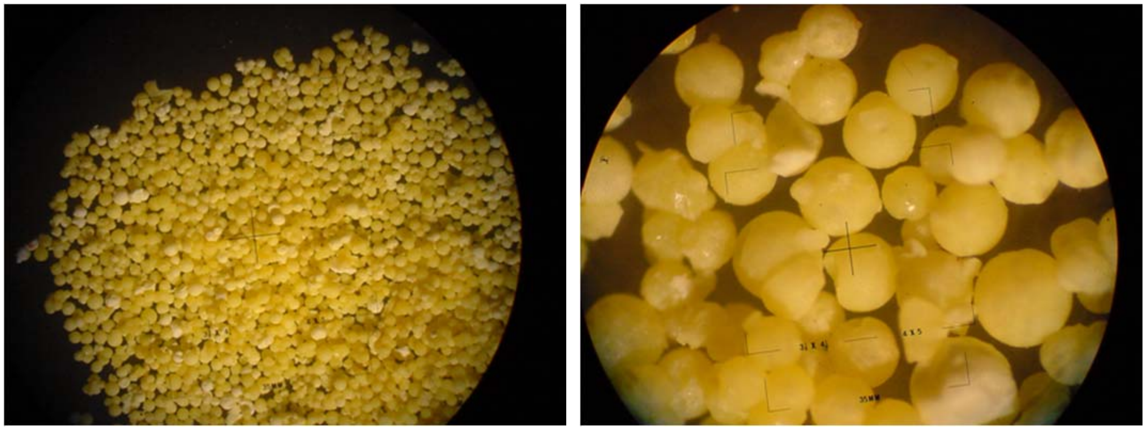

Figure 3-2. Photos of 2010 ORNL prepared ^{E}mMST at 10x (left) and 55x (right) magnification.

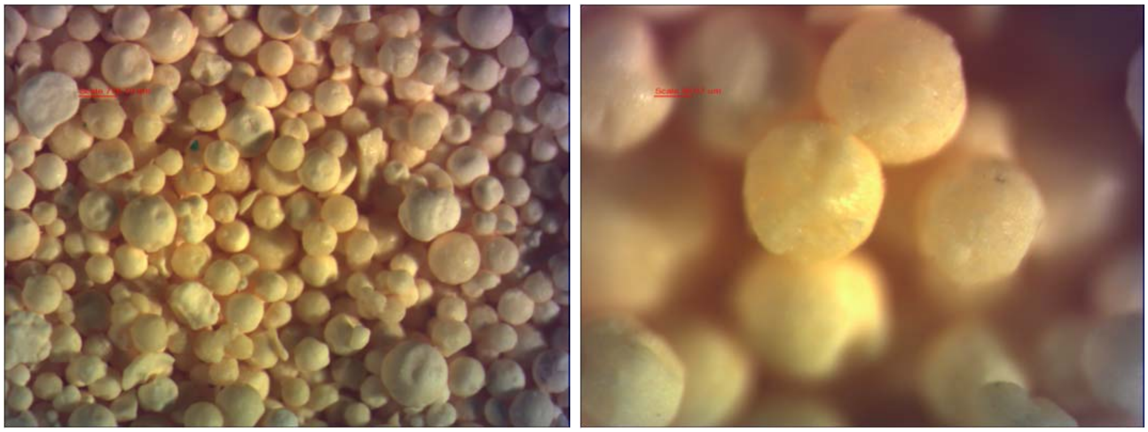

Figure 3-3. Photos of peroxide treated ^{E}MST at 16x (left) and 63x (right) magnification.

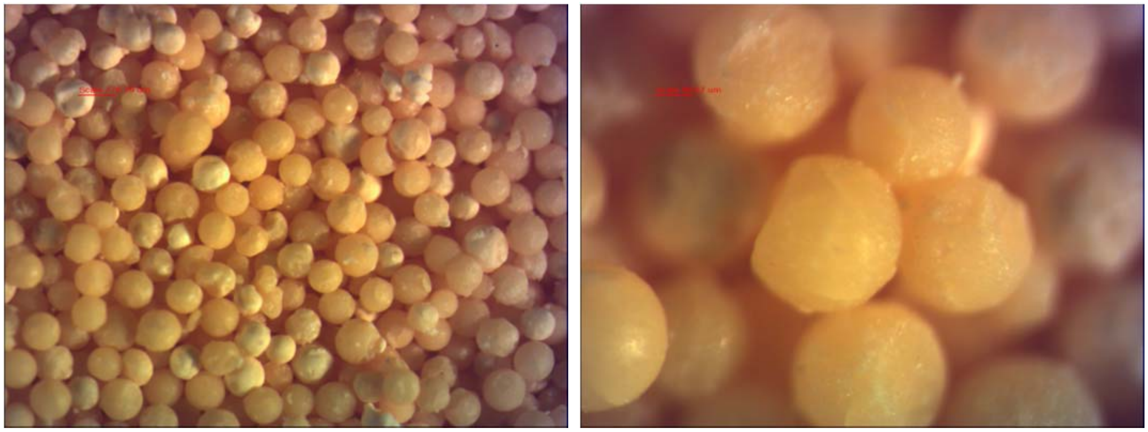

Figure 3-4. Photos of peroxide treated ^{E}mMST at 16x (left) and 63x (right) magnifications.

3.1.2 *Powder X-ray Diffraction*

Samples of the 2010 ORNL prepared ^{E}MST and ^{E}mMST and the peroxide treated versions of both materials were analyzed using PXRD. Figure 3-5 compares the diffraction pattern of the ^{E}MST to a sample of non-engineered MST. The peak at 8.7 two theta in the non-engineered MST was slightly shifted to a two theta value of 9.2 in the engineered form. This shift is consistent with a decrease in d-spacing, indicating a decrease in spacing between the layers likely due to dehydration. Comparison of ^{E}mMST to non-engineered mMST (Figure 3-6) indicated that the engineered material is more amorphous than the non-engineered mMST. Post treatment of the materials with peroxide did not result in changes to the diffraction patterns for either material (Figures 3-7 and 3-8).

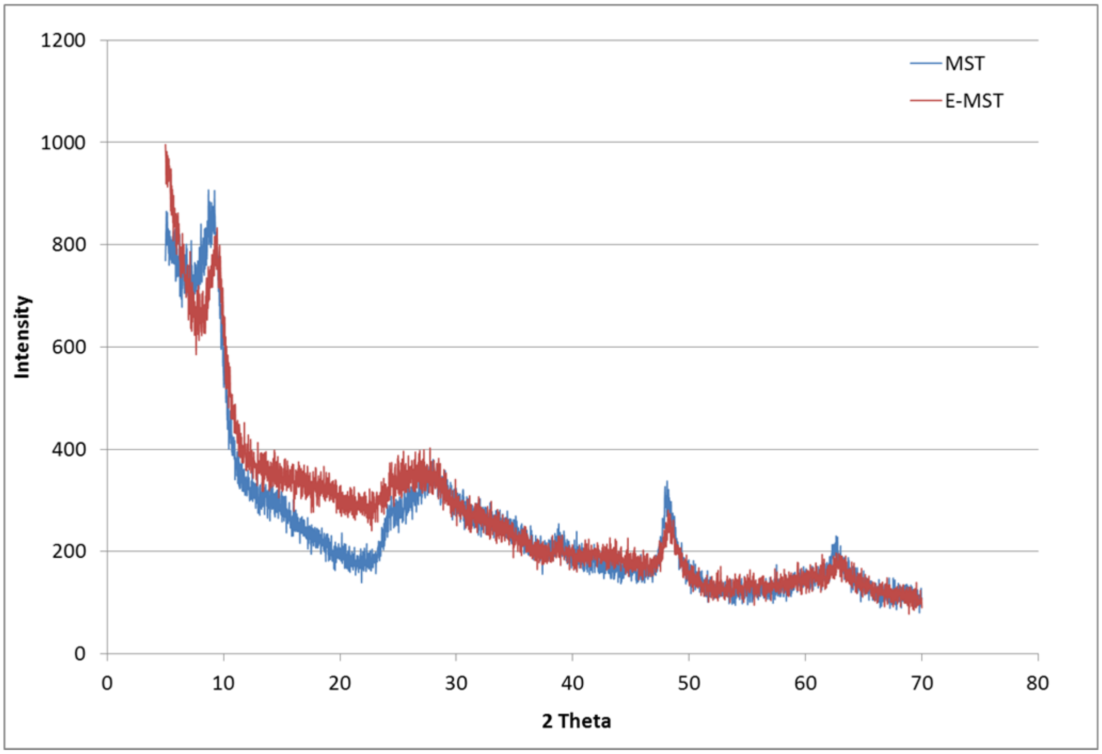

Figure 3-5. PXRD of MST and ^{E}MST.

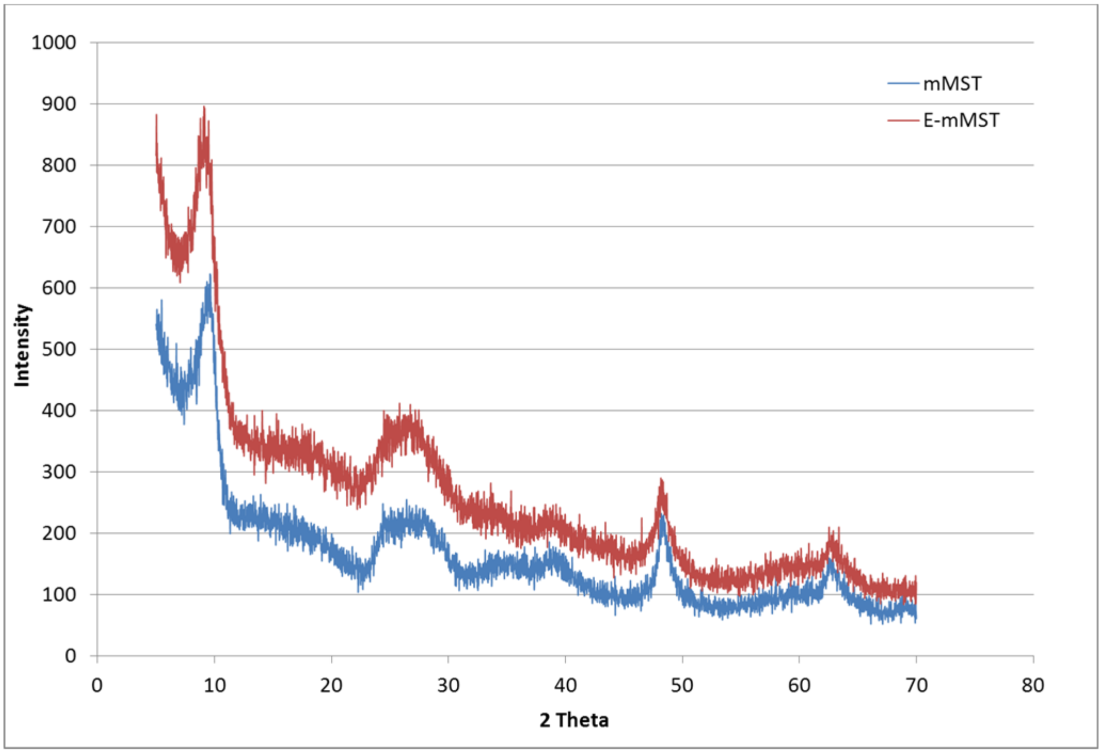

Figure 3-6. PXRD of mMST and ^{E}mMST.

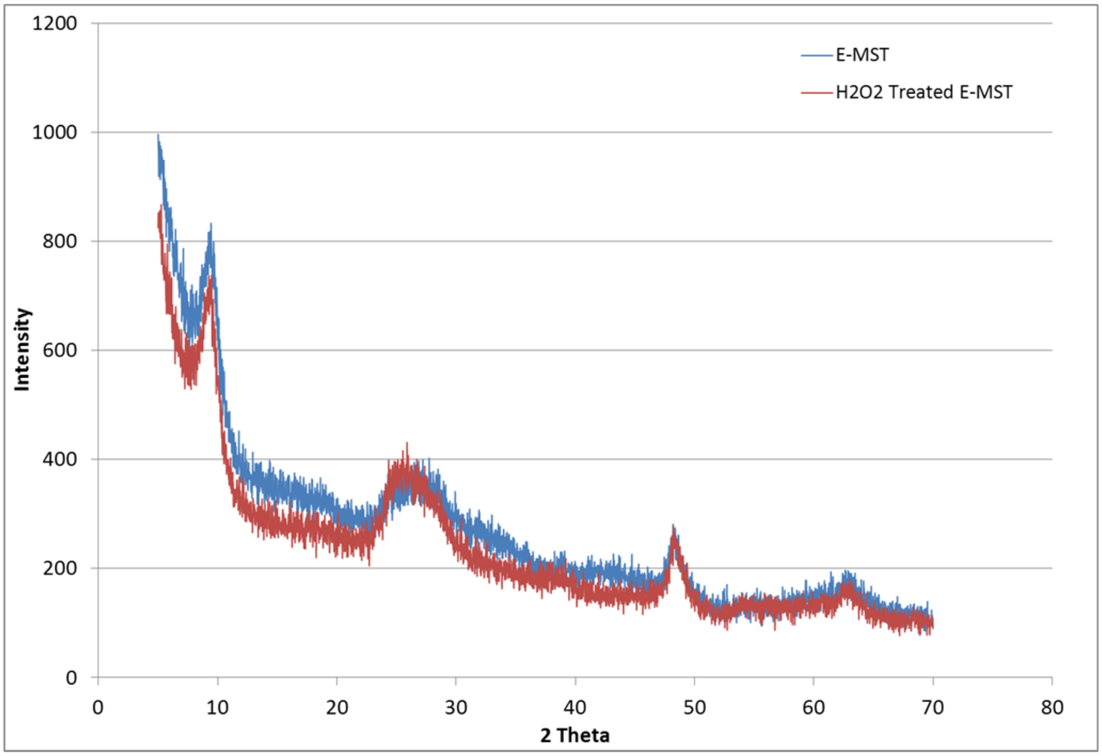

Figure 3-7. PXRD of ^{E}MST before and after peroxide treatment.

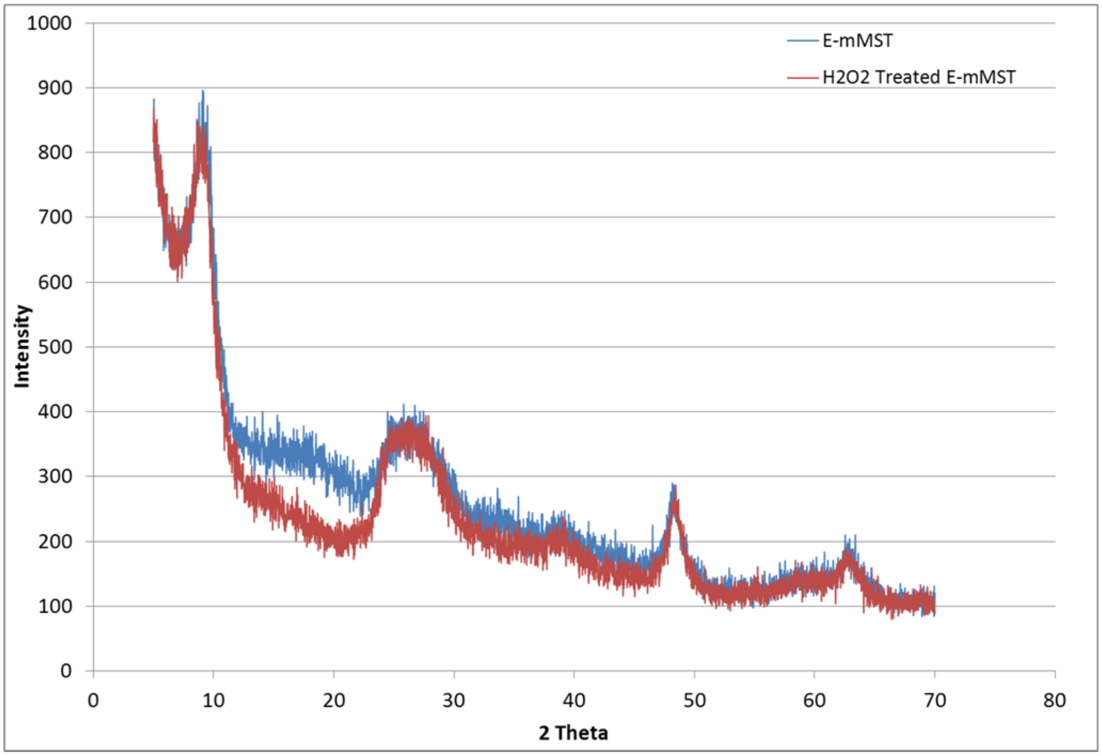

Figure 3-8. PXRD of ^{E}mMST before and after peroxide treatment.

3.1.3 *Particle Size Analysis*

Samples of the 2010 ORNL prepared ^{E}MST and ^{E}mMST were analyzed for both number and volume particle size distributions. The results are shown in Figures 3-9 (number) and 3-10 (volume). The number distributions were centered around 500 µm for both the ^{E}MST and the ^{E}mMST and the majority of particles are in the range of 200 – 800 µm. The volume distributions were centered around 550 µm for both materials. Samples of the peroxide treated materials were also analyzed for particle size distributions, and as shown in Figures 3-9 and 3-10, the particle size distributions shifted to slightly smaller particle size after the peroxide treatment.

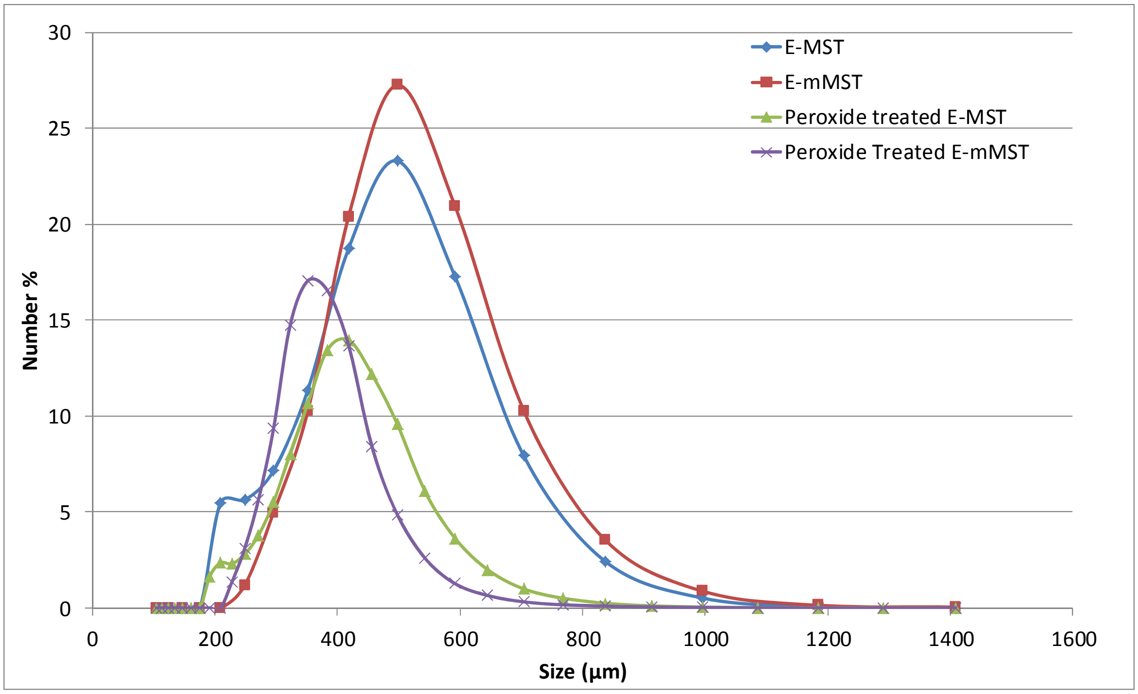

Figure 3-9. Number based particle size distribution of ^{E}MST, ^{E}mMST, and the peroxide treated versions of both.

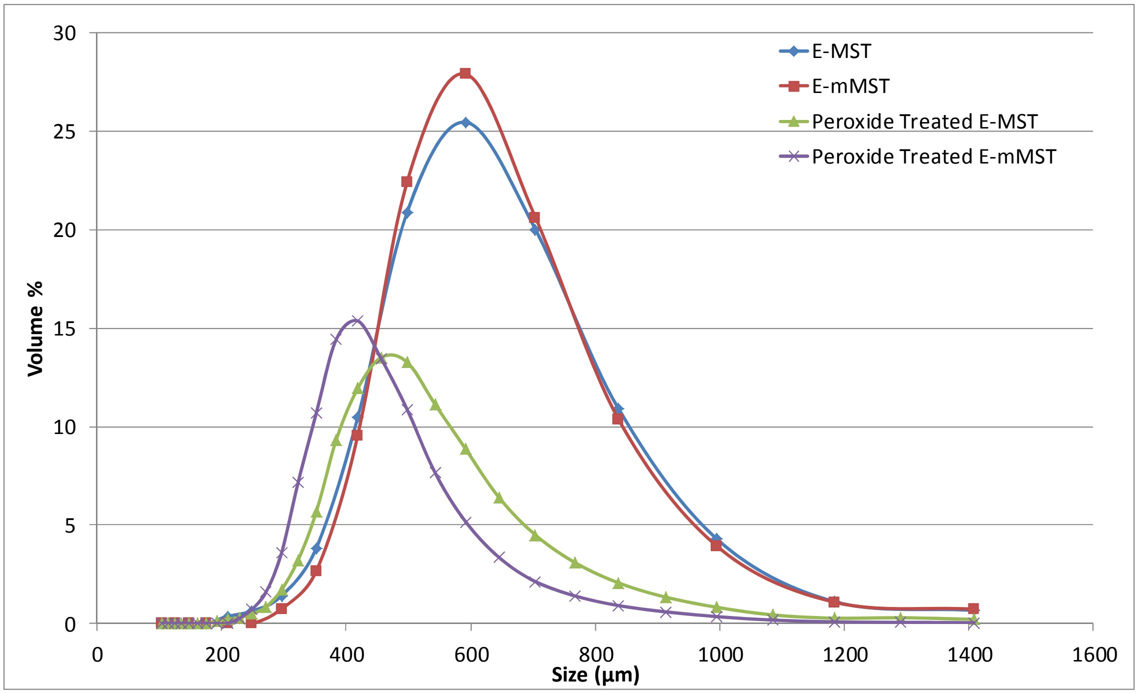

Figure 3-10. Volume based particle size distribution of ^{E}MST, ^{E}mMST, and the peroxide treated versions of both.

3.1.4 *Thermogravimetric Analysis (TGA)*

Samples of the 2010 ORNL prepared ^{E}MST and ^{E}mMST were analyzed using TGA. The samples were heated from room temperature to 600 °C at a rate of 5 °C per minute. The results are shown in Figure 3-11. The results show both the loss of water and organic material.

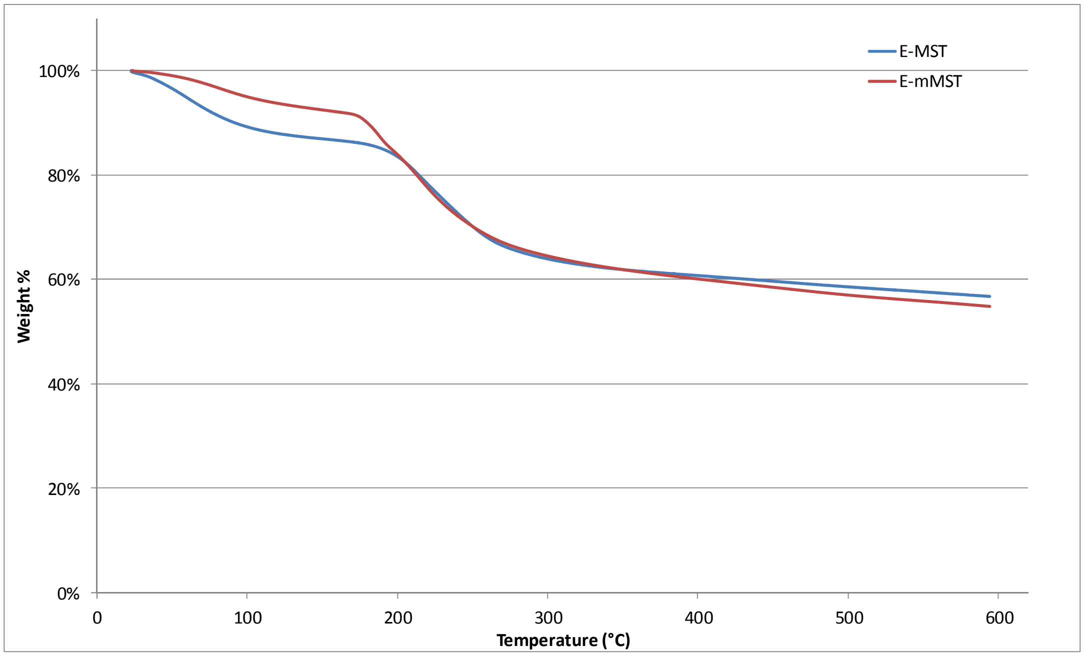

Figure 3-11. TGA of 2010 ORNL Prepared Samples of ^{E}MST and ^{E}mMST.

3.1.5 *Tap Densities*

The tap densities of the 2010 ORNL prepared were measured using the procedure described in Section 2.2. The results are provided in Table 3-1. The ^{E}mMST was found to have a higher tapped density (1.108 g/mL) than the ^{E}MST (0.941 g/mL).

Table 3-1. Tap Densities of ^{E}MST and ^{E}mMST.

	^{E}MST	^{E}mMST
Trial 1	0.930 g/mL	1.106 g/mL
Trial 2	0.958 g/mL	1.107 g/mL
Trial 3	0.935 g/mL	1.110 g/mL
Average	**0.941 g/mL**	**1.108 g/mL**
Standard Deviation	0.0151 g/mL	0.0023 g/mL

3.1.6 *Elemental Analysis*

Samples of the 2010 ORNL prepared ^{E}MST and ^{E}mMST were digested as described in Section 2.2 and the solutions were submitted for ICP-ES and TIC/TOC analyses. Results of the analysis are provided in Table 3-2. Analysis showed that the two materials had similar Ti contents, 29.58 wt % and 28.50 wt % for ^{E}MST and ^{E}mMST, respectively. The materials had very low Na contents, with the Na content for the ^{E}mMST being below the detection limit. The theoretical Ti:Na ratio for MST is 2. Higher Ti:Na ratios were expected in the engineered material due to additional Ti from the hydrous $TiO_x•H_2O$ binder. In addition, the MST is likely in the protonated form due to the internal gelation process. Modified MST is expected to have a higher Ti:Na ratio than MST as the mMST is adjusted to a pH of 4 after synthesis before storage as 15 wt % slurry. The materials also had a higher organic content than expected. The ^{E}MST contained 0.40 wt % C, while the ^{E}mMST contained 0.84 wt % C. The presence of organic material is due to the internal gelation process used to prepare the materials.

Table 3-2. Results from ICP-ES and TIC/TOC analyses of ^{E}MST and ^{E}mMST.

	Na (mg/L) (%RSD)	Ti (mg/L) (%RSD)	wt % Ti	Ti:Na Molar Ratio	TIC (µg/g)	TOC (µg/g)	wt % Total C
^{E}MST-1	6.1 (20.2%)	295 (10.3%)	28.62	23.2	26.2	4016	0.40 wt %
^{E}MST-2	6.24 (53%)	306 (11.3%)	30.55	23.4	-	-	-
Ave. ^{E}MST	6.17	300	29.58	23.3	26.2	4016	0.40 wt %
^{E}mMST-1	< 5.6	277 (10.2%)	27.65	> 23.8	118	8260	0.84 wt %
^{E}mMST-2	< 5.6	297 (10.7%)	29.34	> 25.5	-	-	-
Ave. ^{E}mMST	< 5.6	287	28.50	> 24.6	118	8260	0.84 wt %

3.1.7 *Iodometric Titrations*

Samples of both the 2010 ORNL prepared ^{E}MST and ^{E}mMST and the peroxide treated versions of each were analyzed using the iodometric titration method to determine the amount of peroxide in the materials. The ^{E}mMST material had a much lower (6.6%) H_2O_2:Ti ratio than what is seen for freshly prepared mMST, and the peroxide content increased only slightly (~10%) after the additional peroxide treatment. The ^{E}MST material contained little to no peroxide, as expected, and the peroxide treatment was able to incorporate some peroxide; however, the H_2O_2:Ti ratio was still less than that of the ^{E}mMST. The results from these measurements are summarized in Table 3-3.

Table 3-3. Results of Iodometric Titratons.

	Peroxide:Ti Molar Ratio (Std. Dev.)
^{E}MST Trial 1	< 0.001
^{E}MST Trial 2	< 0.001
^{E}MST Trial 3	< 0.003
Average ^{E}MST	< 0.002 (0.001)
^{E}mMST Trial 1	0.021
^{E}mMST Trial 2	0.023
^{E}mMST Trial 3	0.021
Average ^{E}mMST	0.022 (0.001)
H_2O_2 Treated ^{E}MST Trial 1	0.012
H_2O_2 Treated ^{E}MST Trial 2	0.016 (not included in average, overshot endpoint)
H_2O_2 Treated ^{E}MST Trial 3	0.014
Average H_2O_2 Treated ^{E}MST	0.013 (0.001)
H_2O_2 Treated ^{E}mMST Trial 1	0.024
H_2O_2 Treated ^{E}mMST Trial 2	0.024
H_2O_2 Treated ^{E}mMST Trial 3	0.024
Average H_2O_2 Treated ^{E}mMST	0.024 (0.000)
mMST (LS-10) at age 0.22 years	0.327 (0.003)

3.2 Batch Contact Testing – Effect of Ionic Strength

Tests ET-1 through ET-14 examined the performance of the 2003 prepared ^{E}MST in a series of simulated waste solutions with varying ionic strength. A sample of non-engineered MST was also tested in the highest and lowest ionic strength solutions. Six simulant solutions were prepared with target Na concentrations of 5.6, 6.0, 6.5, 7.0, 7.5, and 8.0 M; however, analysis of the simulants showed that the actual Na concentrations were 5.39, 5.65, 5.79, 5.92, 6.44, and 6.83, respectively. In general the decontamination factors (DFs) were found to decrease upon an increase in ionic strength, which is the expected trend and is consistent with prior testing of MST in various ionic strength solutions.

Figure 3-12 provides a plot of the ^{85}Sr DFs versus the sodium concentration of the simulant. There is a large decrease in the DF upon increasing the Na concentration from 5.39 to 5.65, especially at the later time points. The difference in DF obtained in solutions with Na concentrations ranging from 5.79 to 6.83 does not appear to be significant. A similar trend was seen for Pu, where the greatest effect on DF is upon increasing the Na concentration from 5.39 to 5.65 (Figure 3-13).

For the ^{E}MST, the Np DF values also decrease upon increasing Na concentration up to a Na concentration of 5.92, after which the DF appears to rise with increasing Na concentration (Figure 3-14). However, for the non-engineered MST the Np DF was found to increase when the Na concentration was increased from 5.39 to 6.83 M. The U DFs for the ^{E}MST followed a similar trend to the Sr DFs, where the most drastic decrease in DF was seen when the Na concentration was increased from 5.39 to 5.65 M, with less effect over the remaining Na concentration range (Figure 3-15). However, for the non-engineered MST there was no significant difference in the DFs measured in the 5.39 and 6.83 M Na simulants. A summary of the DFs for all tests is provided in Appendix A (Table A-1).

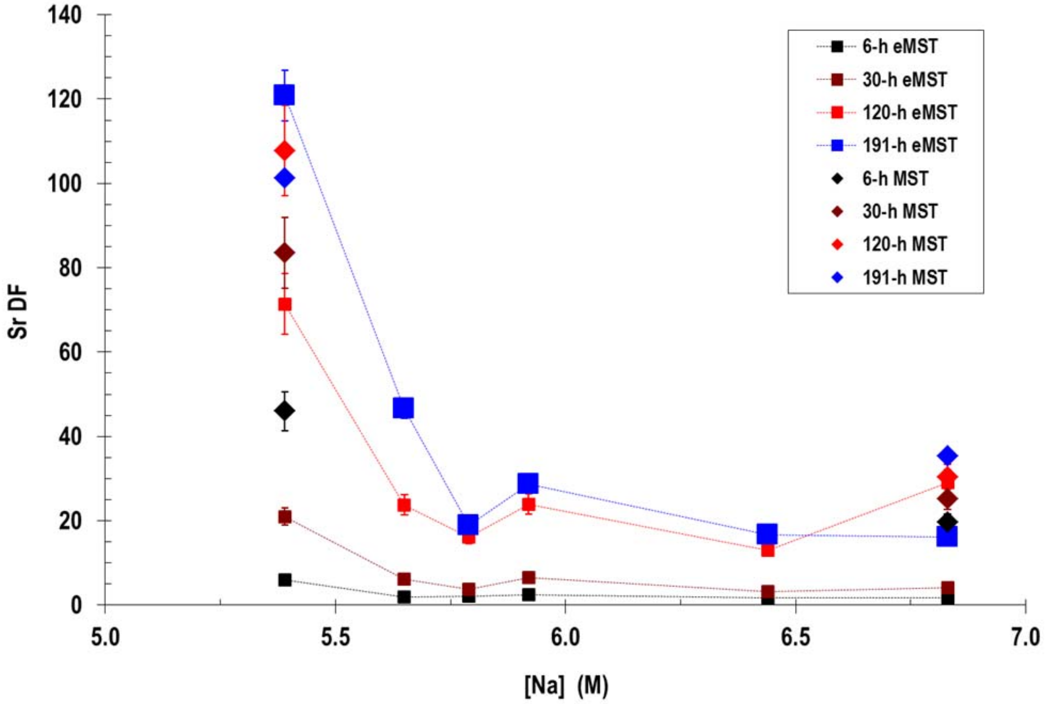

Figure 3-12. ^{85}Sr DF values versus Na concentration of the simulant for ^{E}MST and MST.

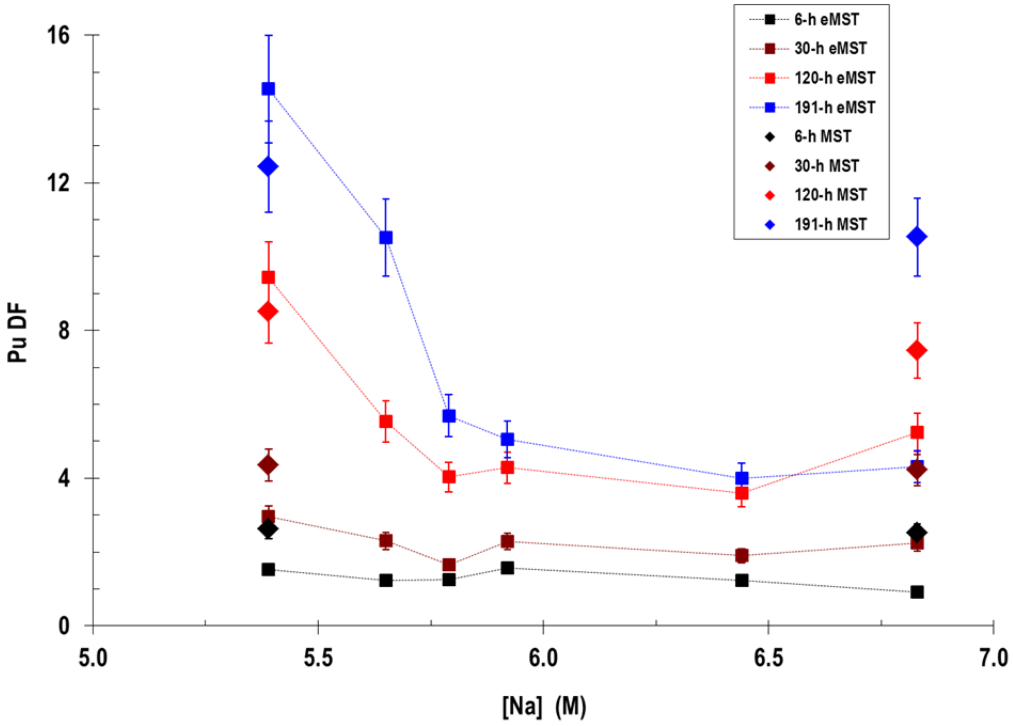

Figure 3-13. Pu DF values versus Na concentration of the simulant for ^{E}MST and MST.

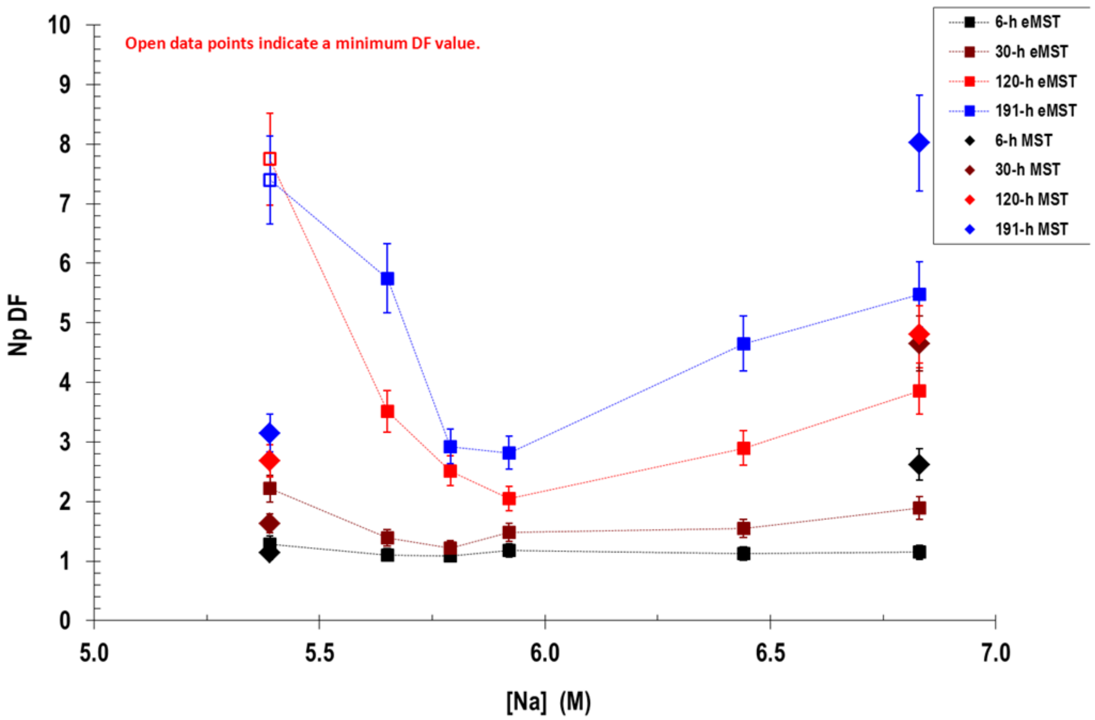

Figure 3-14. Np DF values versus Na concentration of the simulant for ^{E}MST and MST.

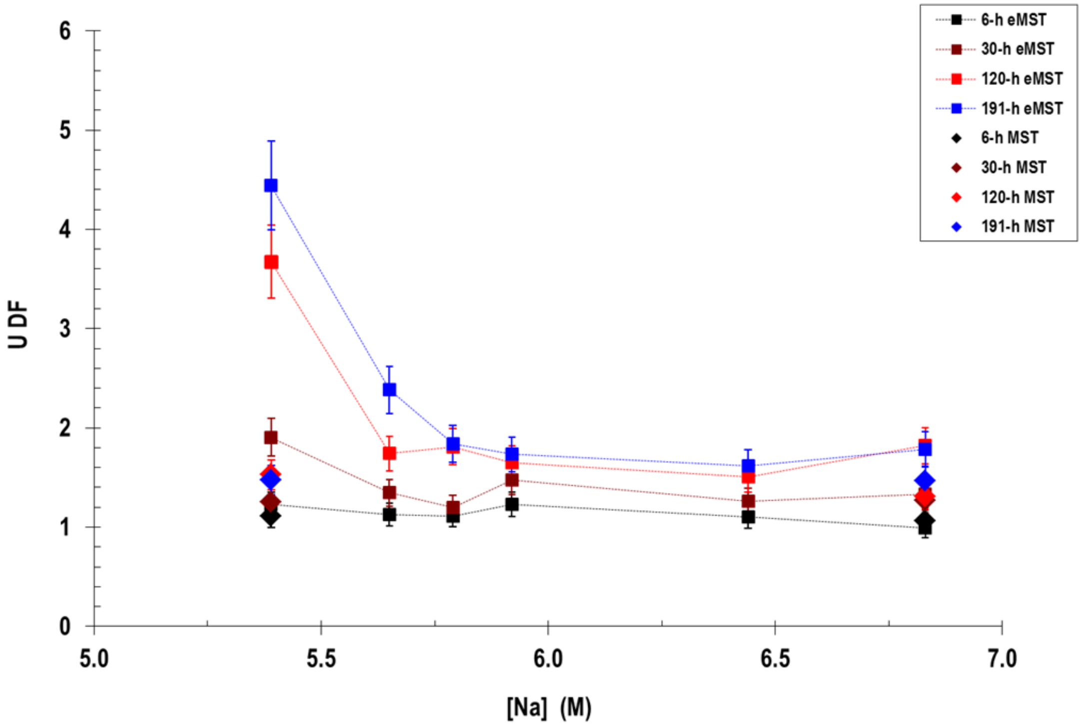

Figure 3-15. U DF values versus Na concentration of the simulant for ^{E}MST and MST.

3.3 Sr Loading Isotherm

A series of experiments were performed to examine the Sr loading isotherm of samples of the 2003 ORNL prepared ^{E}MST at various phase ratios. Samples of the ^{E}MST were contacted with a non-radioactive simulated salt solution containing 5.5 mg/L of Sr at liquid:solid phase ratios of 20000, 5000, 2500, and 1250 mL/g. The Sr loading results (on a per gram of MST basis) are shown in Figure 3-16. The 2500 and 1250 phase ratio samples were only sampled once, at the 504 hour time point. The 20000 and 5000 mL/g experiments were performed in duplicate. The 1250 mL/g phase ratio represents the typical concentration of MST used in sorption testing and in the Actinide Removal Process (ARP), 0.4 g/L (0.8 g/L of 50 wt % MST).

The two lowest phase ratio experiments, 1250 and 2500 mL/g, reached Sr loadings of 1.34 and 2.64 wt % after 506 hours of contact based on the mass of MST using the reported 50 wt % loading of MST in this lot of ^{E}MST. The duplicate experiments at 5000 mL/g appeared to reach their maximum loadings after 506 hours, as no additional Sr sorption was seen at the later time point of 2402 hours. These experiments reached Sr loadings of 4.93 and 4.86 wt % after 506 hours on a per gram of MST basis. The highest phase ratio experiments continued to sorb additional Sr over the entire test period, reaching maximum Sr loadings of 13.2 and 12.2 wt % after 2402 hours, again based on the mass of MST. These values show an increase in wt% Sr loaded of 4.69 and 3.11 wt % over the values at 506 hours, respectively.

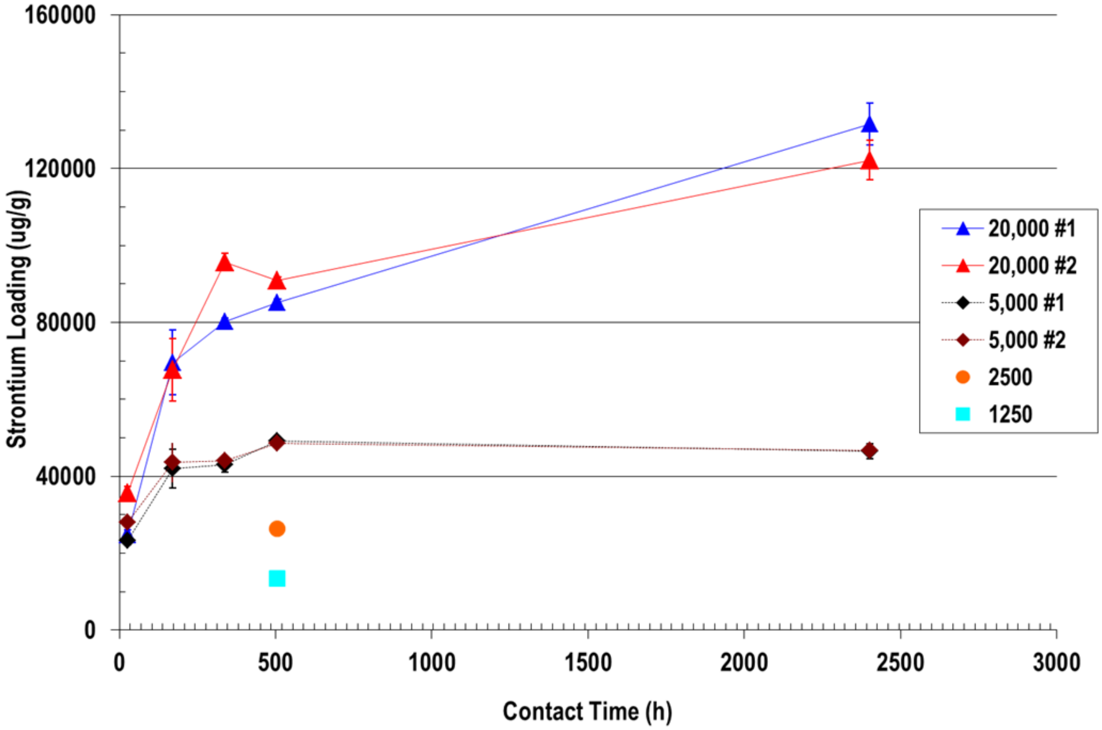

Figure 3-16. Sr loading isotherms for ^{E}MST (per g of MST basis) at various liquid:solid phase ratios. Phase ratios given in units of mL/g.

3.4 Batch Contact Testing with Simulant

A series of batch contact tests were performed using simulated waste solution (SWS-5-2009) to examine the performance of the 2010 ORNL prepared ^{E}MST and ^{E}mMST samples. The performance of these materials was compared to the non-engineered forms of MST and mMST.

The procedure used is described in Section 2.3 (Tests ET 24 – 33). In all tests MST and ^{E}MST were added at an equivalent MST concentration of 0.4 g/L. The modified samples, mMST and ^{E}mMST, were also added at 0.4 g/L for Tests ET 24-28, but were only added at concentrations of 0.1 g/L for Tests ET 29-33.

A summary of the DFs obtained is provided in Table 3-4. Plots of sorbate concentration versus time and DF versus time are provided in Appendix A (Figures A-1 – A-8). Comparison of the results from Tests ET-25 and ET-30 and from Tests ET-26 and ET-32 showed that the performance of MST and ^{E}MST is consistent over the two sets of test data where the MST and ^{E}MST were added at the same concentrations for both sets of tests. This data also shows that the MST outperforms the ^{E}MST for Sr and Pu removal at these time scales. This is likely a kinetic effect due to the slower mass transfer in the larger engineered particles.

The Np and U removal was similar for the MST and ^{E}MST. Similar effects are seen when comparing the results from Tests ET-27 and ET-28 and the results from Tests ET-31 and ET-33. In both of these sets of data the non-engineered mMST greatly outperforms the ^{E}mMST for Sr and Pu removal when added at the same equivalent mMST concentration. Again, this is likely due to kinetic effects from the slower mass transfer in the larger particles. There was not a large difference in Np and U removal when comparing the mMST and ^{E}mMST.

Comparison of the results from Tests ET-26 and 32 with the results from Test ET-28, showed that the performance of ^{E}MST and ^{E}mMST was similar, indicating the improved performance normally seen for mMST over MST was lost in the engineered forms of the material. It was hypothesized that this loss in performance for the ^{E}mMST was due to the loss of the peroxide functionality during the internal gelation process used to produce the engineered materials. This hypothesis was somewhat confirmed by iodometric titrations, which showed that although the ^{E}mMST contained more peroxide than the ^{E}MST, the H_2O_2:Ti ratio was less than 10% of the value for a freshly prepared batch of mMST (Table 3-3). Based on these results, attempts were made to restore the improved performance by treating samples of the ^{E}MST and ^{E}mMST with peroxide to increase the peroxide content (See Section 2.1 for procedure).

Iodometric titration of the post-peroxide-treated materials showed a slight increase in the peroxide content of the materials. The peroxide content of the H_2O_2 treated ^{E}MST was still lower than that of the ^{E}mMST. The post peroxide treatment increased the peroxide content of the ^{E}mMST by approximately 10% (See Table 3-3). Batch contact testing was then performed using these peroxide-treated materials to determine if the performance had been improved. A summary of the DFs obtained with the peroxide-treated materials is provided in Table 3-5, compared to the materials before peroxide treatment.

Comparing the results from tests ET-32 and ET-36 show increased removal of Sr, Pu, and Np by the peroxide treated ^{E}MST compared to the ^{E}MST even at one quarter of the concentration (168 h results). Comparison of the results from Tests ET-33 and ET-37 show a similar trend, where the peroxide-treated ^{E}mMST outperforms the as-received ^{E}mMST. The results from the 24 hour sample from ET-37 indicated an error in the sampling; therefore these results should be disregarded. Comparison of two peroxide-treated materials (ET-36 and ET-37) shows that the peroxide-treated ^{E}mMST slightly outperforms the peroxide-treated ^{E}MST. This is consistent with the slightly higher peroxide content measured in the peroxide-treated ^{E}mMST.

Table 3-4. Summary of DFs for Batch Contact Testing with Simulant.

	^{85}Sr DF (Unc.)							
Test ID	**ET-25**	**ET-30**	**ET-26**	**ET-32**	**ET-27**	**ET-31**	**ET-28**	**ET-33**
Sorbent	**MST**	**MST**	**^{E}MST**	**^{E}MST**	**mMST**	**mMST**	**^{E}mMST**	**^{E}mMST**
Conc. (g/L)	**0.4**	**0.4**	**0.4**	**0.4**	**0.4**	**0.1**	**0.4**	**0.1**
4 h	53.7 (5.37)		1.46 (0.146)		273 (31.5)		2.20 (0.220)	
6 h		54.4 (5.44)		3.12 (0.312)		40.0 (4.00)		1.13 (0.113)
24 h	68.6 (6.86)	66.3 (5.98)	8.48 (0.848)	6.46 (0.583)	435 (43.5)	43.1 (3.89)	8.79 (0.879)	1.22 (0.110)
48 h		74.0 (7.40)		5.45 (0.545)		53.4 (5.34)		1.46 (0.146)
168 h		86.3 (9.55)		10.6 (1.06)		54.8 (5.48)		1.86 (0.186)
	Pu DF (Unc.)							
Test ID	**ET-25**	**ET-30**	**ET-26**	**ET-32**	**ET-27**	**ET-31**	**ET-28**	**ET-33**
Sorbent	**MST**	**MST**	**^{E}MST**	**^{E}MST**	**mMST**	**mMST**	**^{E}mMST**	**^{E}mMST**
Conc. (g/L)	**0.4**	**0.4**	**0.4**	**0.4**	**0.4**	**0.1**	**0.4**	**0.1**
4 h	3.98 (0.394)		0.902 (0.0930)		185 (26.7)		1.43 (0.149)	
6 h		4.68 (0.427)		1.43 (0.132)		23.2 (2.27)		1.07 (0.0961)
24 h	6.47 (0.641)	6.86 (0.596)	2.65 (0.237)	1.82 (0.178)	751 (146)	94.8 (11.3)	3.11 (0.278)	1.08 (0.103)
48 h		9.66 (1.01)		1.87 (0.204)		152 (22.6)		1.22 (0.128)
168 h		18.2 (1.77)		3.12 (0.284)		291 (40.3)		1.48 (0.141)
	NpDF (Unc.)							
Test ID	**ET-25**	**ET-30**	**ET-26**	**ET-32**	**ET-27**	**ET-31**	**ET-28**	**ET-33**
Sorbent	**MST**	**MST**	**^{E}MST**	**^{E}MST**	**mMST**	**mMST**	**^{E}mMST**	**^{E}mMST**
Conc. (g/L)	**0.4**	**0.4**	**0.4**	**0.4**	**0.4**	**0.1**	**0.4**	**0.1**
4 h	0.936 (0.374)		0.682 (0.273)		1.35 (0.541)		1.27 (0.508)	
6 h		1.54 (0.615)		1.73 (0.692)		1.73 (0.692)		1.10 (0.442)
24 h	1.28 (0.512)	1.38 (0.550)	1.22 (0.639)	1.20 (0.478)	2.82 (1.13)	1.20 (0.508)	1.99 (0.890)	1.01 (0.405)
48 h		2.40 (0.961)		2.04 (0.817)		1.27 (0.509)		0.944 (0.378)
168 h		2.33 (0.933)		2.04 (0.817)		1.62 (0.647)		1.27 (0.509)
	U DF (Unc.)							
Test ID	**ET-25**	**ET-30**	**ET-26**	**ET-32**	**ET-27**	**ET-31**	**ET-28**	**ET-33**
Sorbent	**MST**	**MST**	**^{E}MST**	**^{E}MST**	**mMST**	**mMST**	**^{E}mMST**	**^{E}mMST**
Conc. (g/L)	**0.4**	**0.4**	**0.4**	**0.4**	**0.4**	**0.1**	**0.4**	**0.1**
4 h	1.16 (0.465)		0.751 (0.300)		1.05 (0.421)		1.06 (0.423)	
6 h		1.12 (0.447)		1.14 (0.455)		1.09 (0.436)		1.05 (0.418)
24 h	1.21 (0.484)	1.03 (0.412)	1.47 (0.588)	1.26 (0.502)	1.05 (0.419)	0.899 (0.360)	1.06 (0.424)	0.991 (0.396)
48 h		1.27 (0.510)		1.24 (0.497)		0.989 (0.395)		0.864 (0.346)
168 h		1.35 (0.541)		1.42 (0.569)		1.01 (0.402)		1.06 (0.425)

Table 3-5. Comparison of DFs for ^{E}MST and ^{E}mMST before and after peroxide treatment.

Test ID	**ET-32**	**ET-36**	**ET-33**	**ET-37**
Sorbent	**^{E}MST**	**H_2O_2 treated ^{E}MST**	**^{E}mMST**	**H_2O_2 treated ^{E}mMST**
Conc. (g/L)	**0.4**	**0.1**	**0.1**	**0.1**
24 h ^{85}Sr DF (Unc.)	6.46 (0.646)	2.51 (0.251)	1.22 (0.122)	> 1936*
168 h ^{85}Sr DF (Unc.)	10.65 (1.06)	12.8 (1.28)	1.86 (0.186)	15.6 (1.56)
24 h Pu DF (Unc.)	1.82 (0.178)	1.89 (0.197)	1.08 (0.103)	> 839*
168 h Pu DF (Unc.)	3.12 (0.284)	10.4 (0.943)	1.48 (0.141)	23.3 (2.35)
24 h Np DF (Unc.)	1.27 (0.510)	1.18 (0.472)	1.01 (0.410)	> 1.75*
168 h Np DF (Unc.)	1.62 (0.650)	> 1.97	1.27 (0.510)	> 1.97
24 h U DF (Unc.)	1.26 (0.500)	1.10 (0.441)	0.991 (0.400)	> 31.6*
168 h U DF (Unc.)	1.42 (0.570)	1.10 (0.440)	1.06 (0.430)	1.01 (0.406)

*Results indicated an error in sampling, these results should be disregarded.

3.5 Batch Contact Testing with Real Waste

A series of batch contact tests were also performed using a sample of Tank 49 supernate. The 2010 prepared ORNL ^{E}MST and ^{E}mMST were contacted with the waste, along with samples of the non-engineered forms of MST and mMST. The MST and ^{E}MST were added at a concentration of 0.4 g/L, while the mMST and ^{E}mMST were added at a concentration of 0.2 g/L.

A summary of the DFs is provided in Table 3-6 and plots of sorbate concentration and DF versus time are provided in Appendix A (Figures A-9 – A-16). Overall, mMST showed the greatest Sr and Pu removal performance, while MST showed greater removal of Np and U. The engineered materials did not perform as well as the non-engineered materials, and this is likely due to the slower mass transfer as a result of the larger particle size of the engineered forms. When only comparing the engineered forms, there did not appear to be an increase in performance of the modified material compared to the baseline engineered MST. As discussed above, it is possible that the peroxide functionality of the mMST was decomposed during the internal gelation process used to produce the engineered materials.

Table 3-6. Summary of DF values from real waste testing. (Number in parentheses represents 1 sigma uncertainty).

Time	^{90}Sr DF (Unc.)			
	MST	**mMST**	**^{E}MST**	**^{E}mMST**
2-h	33.3 (3.98)	27.9 (3.43)	1.04 (0.132)	1.02 (0.127)
6-h	43.8 (5.01)	41.2 (4.92)	1.26 (0.147)	1.02 (0.117)
12-h	60.2 (7.30)	64.2 (7.87)	2.05 (0.242)	1.36 (0.168)
24-h	58.2 (7.07)	92.6 (10.9)	2.38 (0.286)	1.44 (0.176)
Time	**Pu DF (Unc.)**			
	MST	**mMST**	**^{E}MST**	**^{E}mMST**
2-h	1.65 (0.108)	1.64 (0.112)	1.04 (0.0691)	1.07 (0.0673)
6-h	1.86 (0.123)	2.12 (0.146)	1.11 (0.0761)	0.973 (0.0669)
12-h	2.19 (0.149)	3.49 (0.239)	1.25 (0.0888)	1.01 (0.0732)
24-h	2.19 (0.157)	4.45 (0.305)	1.19 (0.0866)	1.08 (0.0779)
Time	**Np DF (Unc.)**			
	MST	**mMST**	**^{E}MST**	**^{E}mMST**
2-h	1.20 (0.434)	1.28 (0.456)	1.10 (0.357)	1.08 (0.304)
6-h	1.39 (0.403)	0.932 (0.270)	1.21 (0.351)	0.912 (0.264)
12-h	> 1.83	1.24 (0.351)	1.58 (0.448)	1.49 (0.421)
24-h	> 1.49	1.25 (0.621)	0.945 (0.267)	0.961 (0.272)
Time	**U DF (Unc.)**			
	MST	**mMST**	**^{E}MST**	**^{E}mMST**
2-h	1.11 (0.314)	1.07 (0.302)	1.10 (0.312)	1.06 (0.300)
6-h	1.08 (0.306)	1.03 (0.291)	1.05 (0.297)	1.01 (0.285)
12-h	1.10 (0.310)	1.02 (0.289)	1.11 (0.313)	1.02 (0.289)
24-h	1.10 (0.311)	0.987 (0.279)	1.12 (0.315)	1.01 (0.287)

3.6 Column Testing

Two ion-exchange columns were used, one with the 2010 ORNL prepared ^{E}MST and the other with the peroxide treated ^{E}mMST material. Approximately 1.8 g of each material was pre-soaked in a salt solution, and then loaded into the columns. Each column processed ~15 L of simulated waste solution at a flow rate of ~0.5 mL/min, and samples of the effluent were collected throughout the experiment. During the soaking, the ^{E}MST material was found to swell dramatically (~114%) compared to the peroxide treated ^{E}mMST, which only swelled ~23%. Photos of the columns are provided in Figures 3-17 and 3-18. Additional swelling studies showed that both the ^{E}MST and ^{E}mMST swell upon contact with salt solution, whereas neither of the peroxide treated materials swelled significantly.

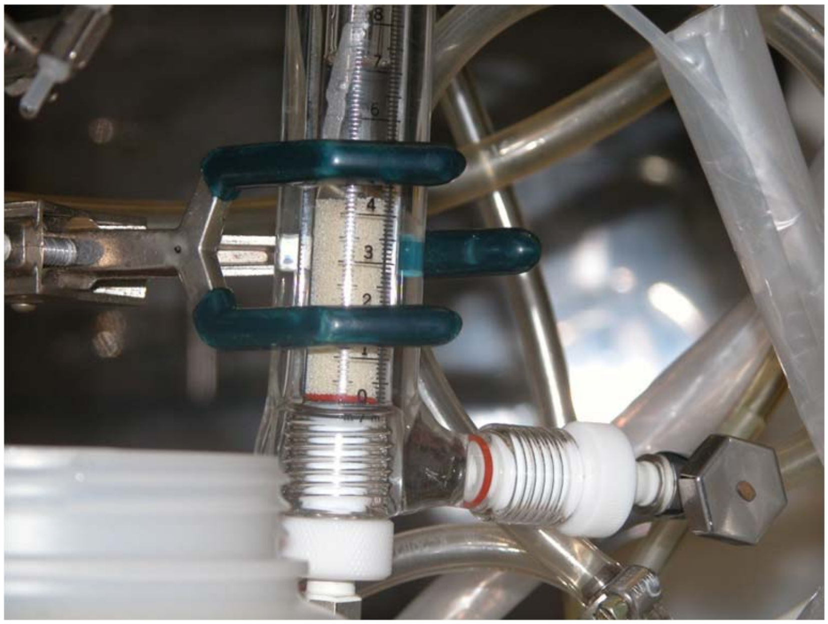

Figure 3-17. Photo of ^{E}MST Column.

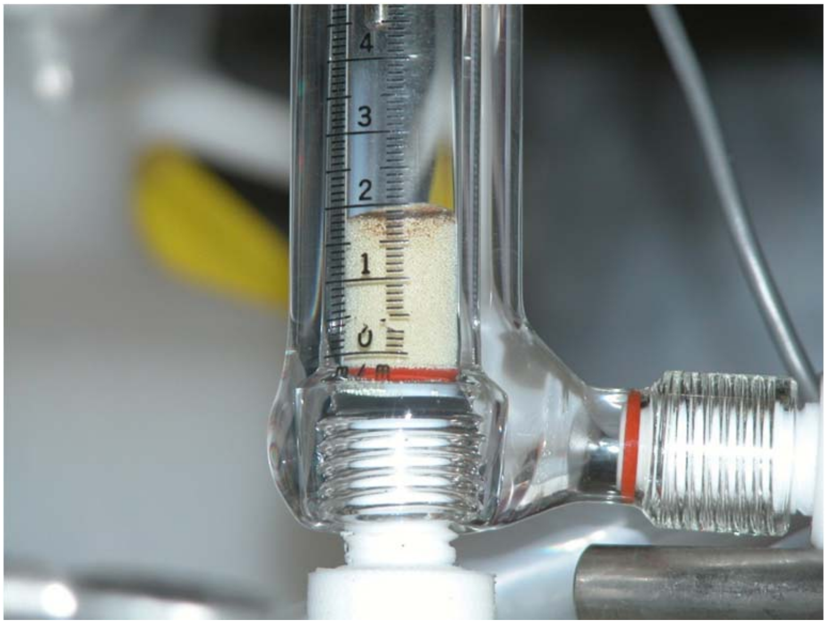

Figure 3-18. Photo of Peroxide Treated ^{E}mMST Column.

A summary of the flow rates and samples collected is provided in Appendix B. Column 1 (^{E}MST) processed a total of 3578 bed volumes, while Column 2 (peroxide treated ^{E}mMST) processed a total of 6934 bed volumes. The large difference in the number of bed volumes processed is due to the variable amounts of swelling. The bed volume of Column 1 was much greater than that of Column 2, due to the increased swelling of the ^{E}MST material. For Column 1, a sample was analyzed about every 500 bed volumes, and for Column 2, a sample was analyzed about every 1000 bed volumes. Note that both tests used the same mass quantity of ion exchanger.

The breakthrough curves for ^{85}Sr are shown in Figure 3-19. This data shows that the peroxide treated ^{E}mMST out-performs the ^{E}MST on a bed volume basis. Although 50% breakthrough was not reached for ^{85}Sr, the curves indicate that a larger number of bed volumes can be processed through the peroxide treated ^{E}mMST column before reaching 50% breakthrough, indicating a higher capacity. The breakthrough curve for the ^{E}MST is sharper, and this is likely due to the swollen bed, which reduces the bed volumes per hour rate to about half of the other column.

The breakthrough curves for Pu are shown in Figure 3-20. Unlike the ^{85}Sr curves, which started near 0% breakthrough, these curves show ~20% breakthrough after only about 1000 bed volumes. At the end of the tests breakthroughs of ~50-60% were reached for both columns. From this data and from analysis of the sorbent beds (see below) there does not appear to be a large difference in Pu capacity between the two materials.

Figure 3-21 shows the Np breakthrough curves for both columns. Again, similarly to the Pu curves, there is a significant amount of breakthrough early in the test, and the peroxide treated ^{E}mMST actually reaches 100% breakthrough before the end of the column test. There does not appear to be a large difference in the capacities of the two materials, estimated by the number of bed volumes passed when 50% breakthrough is reached. The U breakthrough curves are shown in Figure 3-22. Both columns reached 100% breakthrough prior to the end of the column experiment.

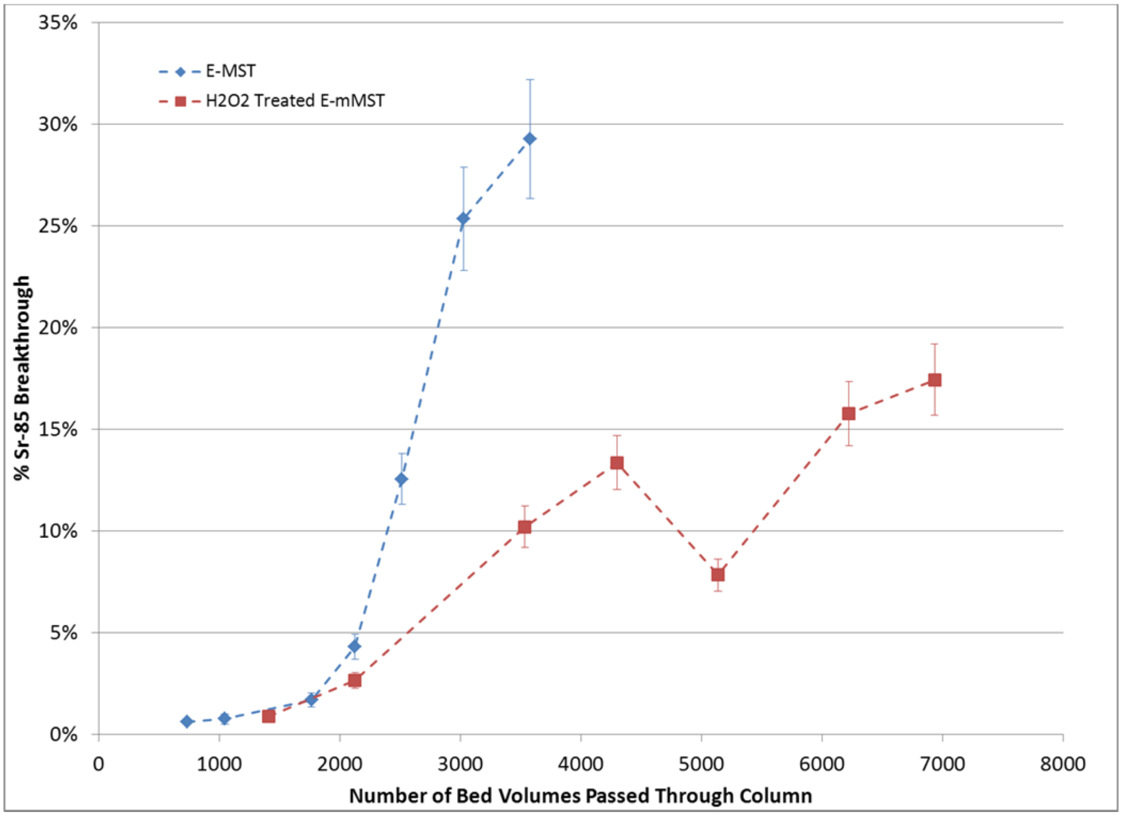

Figure 3-19. ^{85}Sr breakthrough curves for the ^{E}MST and peroxide treated ^{E}mMST columns.

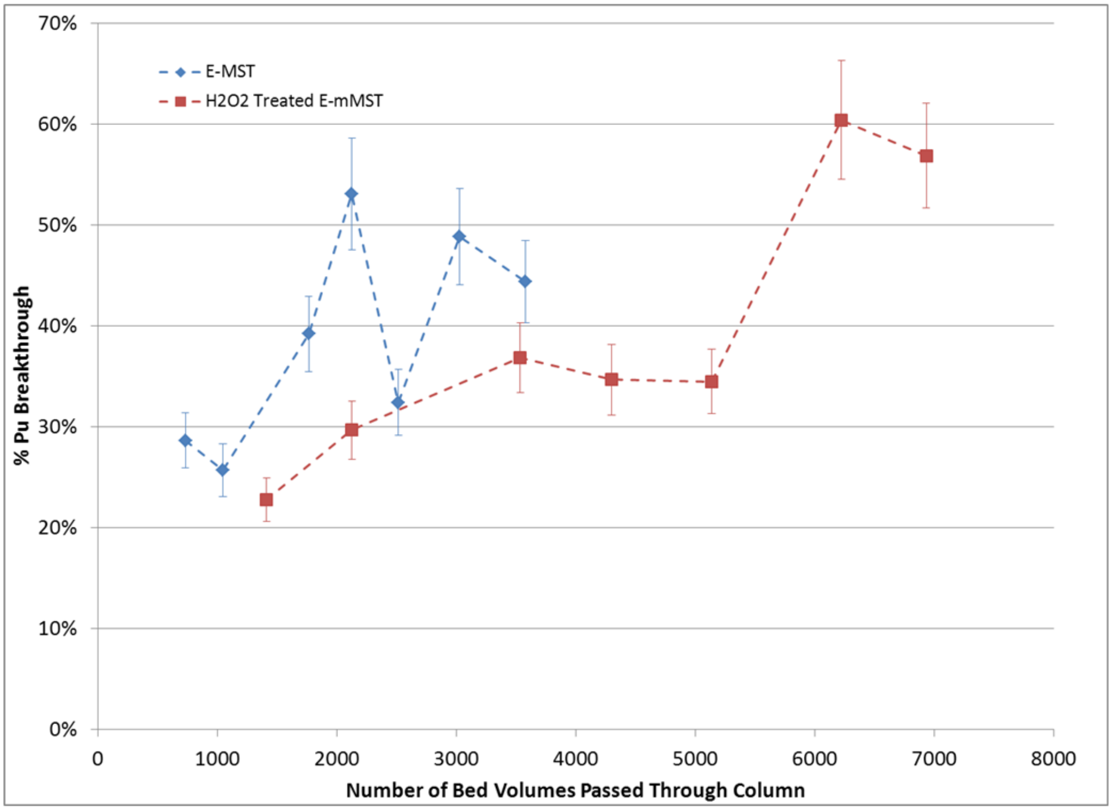

Figure 3-20. Pu breakthrough curves for the ^{E}MST and peroxide treated ^{E}mMST columns.

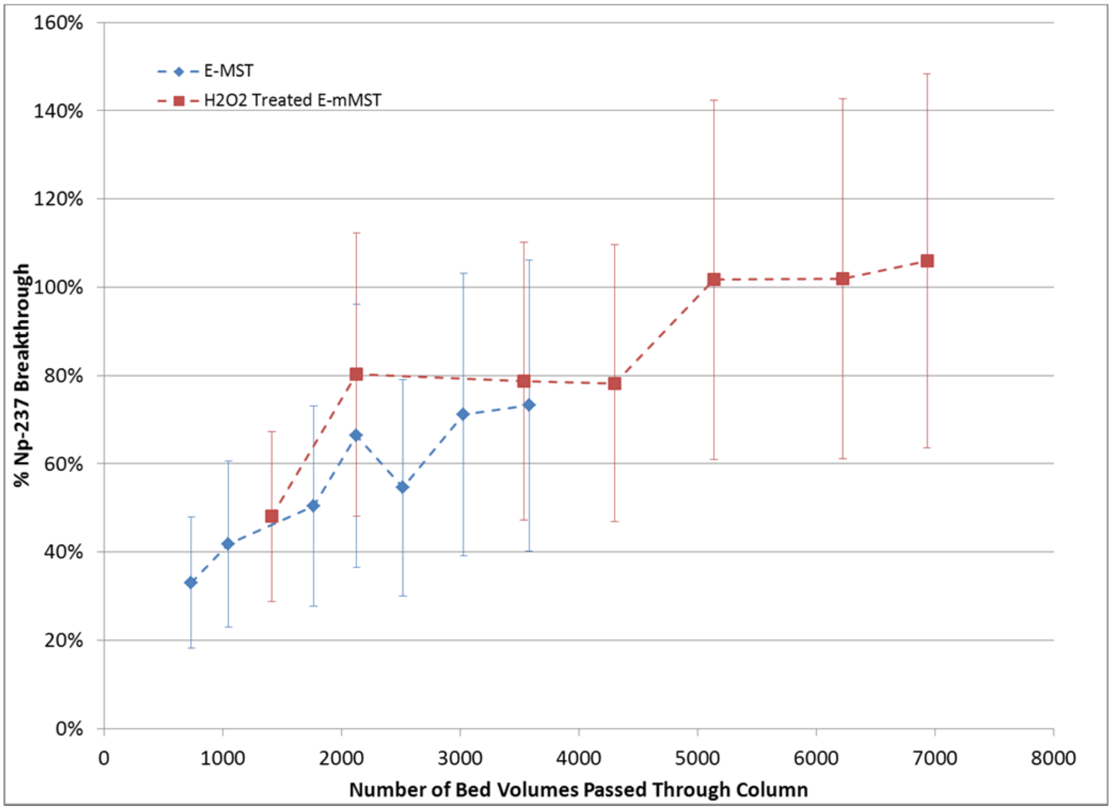

Figure 3-21. Np breakthrough curves for the ^{E}MST and peroxide treated ^{E}mMST columns.

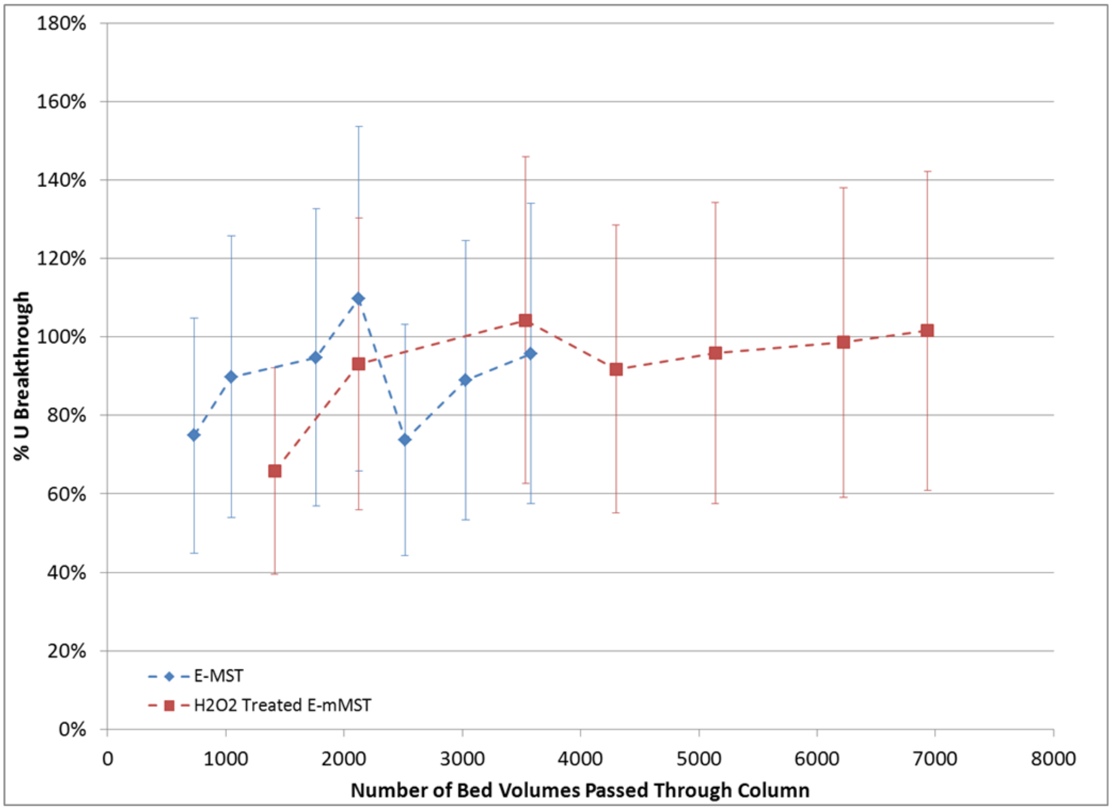

Figure 3-22. U breakthrough curves for the ^{E}MST and peroxide treated ^{E}mMST columns.

In addition to analyzing samples of the effluent collected throughout the test, at the end of the experiment, samples of the bed materials were digested and analyzed for sorbate concentrations. Table 3-7 provides a summary of the sobent loadings determined from these measurements. As can be seen from the data, the peroxide treated ^{E}mMST sorbed a higher percentage of each sorbate than the ^{E}MST, with the exception of U and Pu. The Pu uptake by both materials was similar, 57.9% and 58.1%, for ^{E}MST and peroxide treated ^{E}mMST, respectively.

Table 3-7. Sorbate loadings on ^{E}MST and peroxide treated ^{E}mMST at the end of the column runs. The values in parenthesis indicate the percentage of the feed that was sorbed.

	^{E}MST	H_2O_2 Treated ^{E}mMST
^{85}Sr (dpm/g) (gamma)	3.38 E+07 ± 1.69 E+06 (54.4%)	3.81 E+07 ± 1.91 E+06 (74.0%)
Total Sr (µg/g) (ICP-MS)	2,880 ± 579 (62.1%)	3,600 ± 719 (73.7%)
^{237}Np (µg/g) (gamma)	1,170 ± 58.6 (28.0%)	1,260 ± 63.0 (34.6%)
^{237}Np (µg/g) (ICP-MS)	1,060 ± 212 (22.9%)	1,190 ± 238 (36.0%)
^{137}Cs (dpm/g) (gamma)	54,500 ± 2,730 (0.02%)	233,000 ± 11,600 (0.08%)
Cs (µg/g) (ICP-MS)	39.3 ± 7.85 (0.03%)	118 ± 23.6 (0.09%)
Pu (µg/g) (PuTTA)	715 ± 35.4 (57.9%)	769 ± 38.4 (58.1%)
U (µg/g) (ICP-MS)	3,470 ± 693 (9.83%)	1,900 ± 379 (5.73%)

4.0 Conclusions

Bench scale quantities of ^{E}MST and ^{E}mMST were successfully prepared at ORNL using an internal gelation process. Characterization of these materials showed that they are generally spherical with some irregular shaped particles, and have an average diameter of 450 – 550 µm. The majority of the particles were found to be in the range of 200 – 800 µm. Iodometric titration was used to determine the peroxide content of the materials, and the ^{E}mMST was found to contain less than 10% of the peroxide found in a freshly prepared batch of mMST. This was also evidenced in batch contact testing with both simulated and actual waste, where little difference in performance was seen between the two engineered materials, ^{E}MST and ^{E}mMST.

Based on these results, attempts were made to increase the peroxide content of the materials by post-treatment with hydrogen peroxide. The peroxide treatment resulted in a slight (~10%) increase in peroxide content, however the peroxide:Ti molar ratio was still much lower (~0.1 X) than what is seen in a freshly prepared batch of mMST. Performance testing with simulated waste showed the performance of the peroxide treated materials was improved.

A series of batch contact tests were also performed with an earlier (2003) prepared lot of ^{E}MST to examine the effect of ionic strength on the performance of the material. In general the results showed a decrease in removal performance with increasing ionic strength, which is consistent with previous ionic strength testing with MST. For Sr, Pu, and U, the most drastic decrease in DF was observed upon increasing the Na concentration from 5.39 to 5.65 M, with less of an effect over the remaining Na concentration range (up to 6.83 M). For Np, the performance was also found to decrease upon increasing Na concentration up to 5.92 M, after which the DF appeared to rise with increasing ionic strength. For the non-engineered MST, the Np DF was found to increase when the Na concentration was increased from 5.39 to 6.83 M.

Results from the Sr loading isotherm testing showed that the ^{E}MST material can reach a Sr loading as high as 13.2 wt % after 100 days of contact at a phase ratio of 20000 mL/g. At the typical MST phase ratio of 2500 mL/g (0.4 g/L), a Sr loading of 2.64 wt % was reached after 506 hours of contact.

Samples of ^{E}MST and peroxide-treated ^{E}mMST were also tested in a column configuration using simulated waste solution. Each column processed a total of approximately 15 L of simulated waste over a period of approximately 3 weeks. The ^{E}MST material was found to swell dramatically (~114%) compared to the peroxide treated ^{E}mMST, which swelled only slightly (~23%). This difference in swelling resulted in a difference in the total number of bed volumes processed, even though similar volumes were processed. The breakthrough curves along with analysis of the sorbent beds at the conclusion of the experiments showed that the peroxide treated ^{E}mMST has a higher Sr and Np capacity, but that both materials have similar Pu capacities. The ^{E}MST removed a larger percentage of U than the peroxide-treated ^{E}mMST, which is consistent with previous testing which showed that mMST has little affinity for U under these conditions.

5.0 Recommendations

We recommend additional testing be performed to optimize the material. Additional experiments should be performed to determine the optimal conditions for the internal gelation process forming the particles, particularly optimizing conditions affecting the porosity of the particles to provide the best possible mass transport. Additional experiments should also be performed to optimize the post-peroxide treatment of the material to increase the peroxide content. Optimization of both of these processes will result in increased performance of the material for strontium and actinide separations.

6.0 References

1. C. A. Nash, D. T. Hobbs, K. Adu-Wusu, and E. C. Buck, "Phase I Technical Report for the Engineering of Monosodium Titanate." WSRC-TR-2004-00286, Rev. 0, July 30, 2004.
2. D. T. Hobbs, M. J. Barnes, R. L. Pulmano, K. M. Marshall, T. B. Edwards, M. G. Bronikowski, and S. D. Fink, (2005) "Strontium and Actinide Separations from High Level Nuclear Waste Solutions Using Monosodium Titanate 1. Simulant Testing." Separation Science and Technology, 40 (15): 3093.
3. M. Nyman, and D. T. Hobbs, (2006) "A Family of Peroxo-titanate Materials Tailored for Optimal Strontium and Actinide Sorption." Chem. Mater. 18 (26): 6425.

Appendix A. Batch Contact Testing Results

Table A-1. Summary of DFs obtained in varying ionic strength simulants.

Test ID	ET-2	ET-5	ET-7	ET-9	ET-11	ET-13	ET-3	ET-14
Sorbent	^{E}MST	^{E}MST	^{E}MST	^{E}MST	^{E}MST	^{E}MST	MST	MST
Target [Na] (M)	5.6	6.0	6.5	7.0	7.5	8.0	5.6	8.0
Measured [Na] (M)	5.39	5.65	5.79	5.92	6.44	6.83	5.39	6.83
	^{85}Sr DF							
6-h	6.05	1.84	2.03	2.55	1.74	1.65	46.0	19.6
30-h	21.0	6.12	3.70	6.50	3.14	4.19	83.5	25.2
120-h	71.4	23.7	16.1	23.9	13.0	29.1	108	30.4
191-h	121	46.7	18.9	28.6	16.7	16.2	101	35.3
	Pu DF							
6-h	1.53	1.24	1.25	1.56	1.22	0.918	2.62	2.51
30-h	2.96	2.30	1.65	2.29	1.90	2.24	4.36	4.22
120-h	9.45	5.54	4.03	4.28	3.59	5.24	8.51	7.46
191-h	14.5	10.5	5.69	5.05	4.00	4.32	12.4	10.5
	Np DF							
6-h	1.29	1.10	1.09	1.18	1.12	1.15	1.14	2.62
30-h	2.22	1.38	1.22	1.48	1.55	1.89	1.63	4.65
120-h	> 7.75	3.51	2.51	2.04	2.90	3.86	2.69	4.80
191-h	> 7.40	5.75	2.92	2.82	4.65	5.47	3.15	8.02
	U DF							
6-h	1.23	1.13	1.11	1.23	1.10	0.991	1.11	1.06
30-h	1.90	1.35	1.20	1.47	1.26	1.33	1.25	1.27
120-h	3.67	1.74	1.81	1.65	1.50	1.82	1.53	1.31
191-h	4.44	2.38	1.84	1.73	1.62	1.78	1.47	1.47

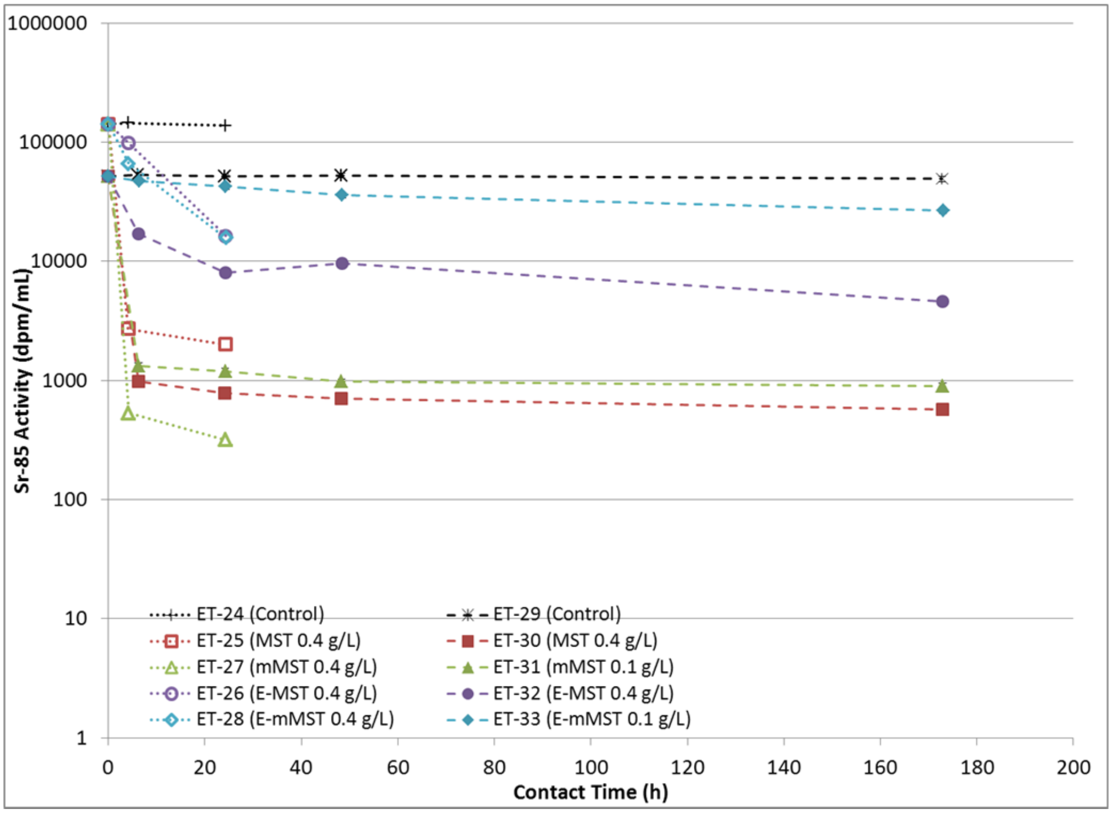

Figure A-1. ^{85}**Sr activity versus contact time for Tests ET-24 through ET-33.**

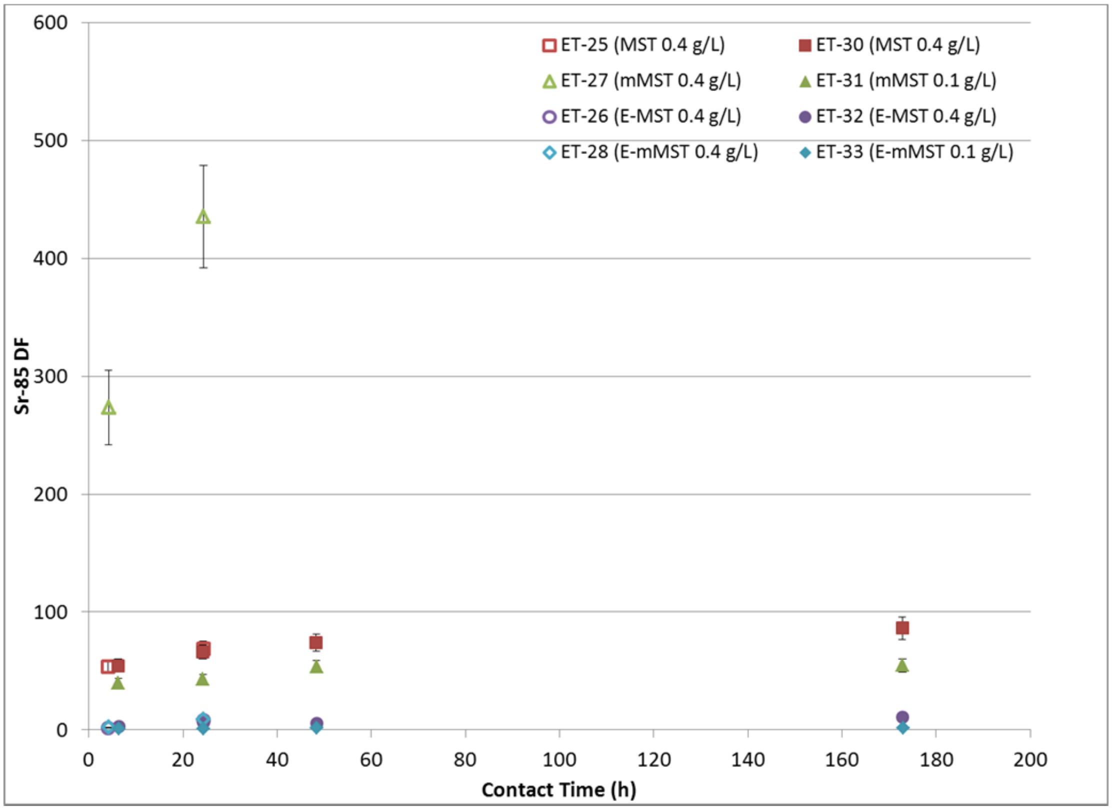

Figure A-2. ^{85}**Sr DF versus contact time for Tests ET-25 through ET-33.**

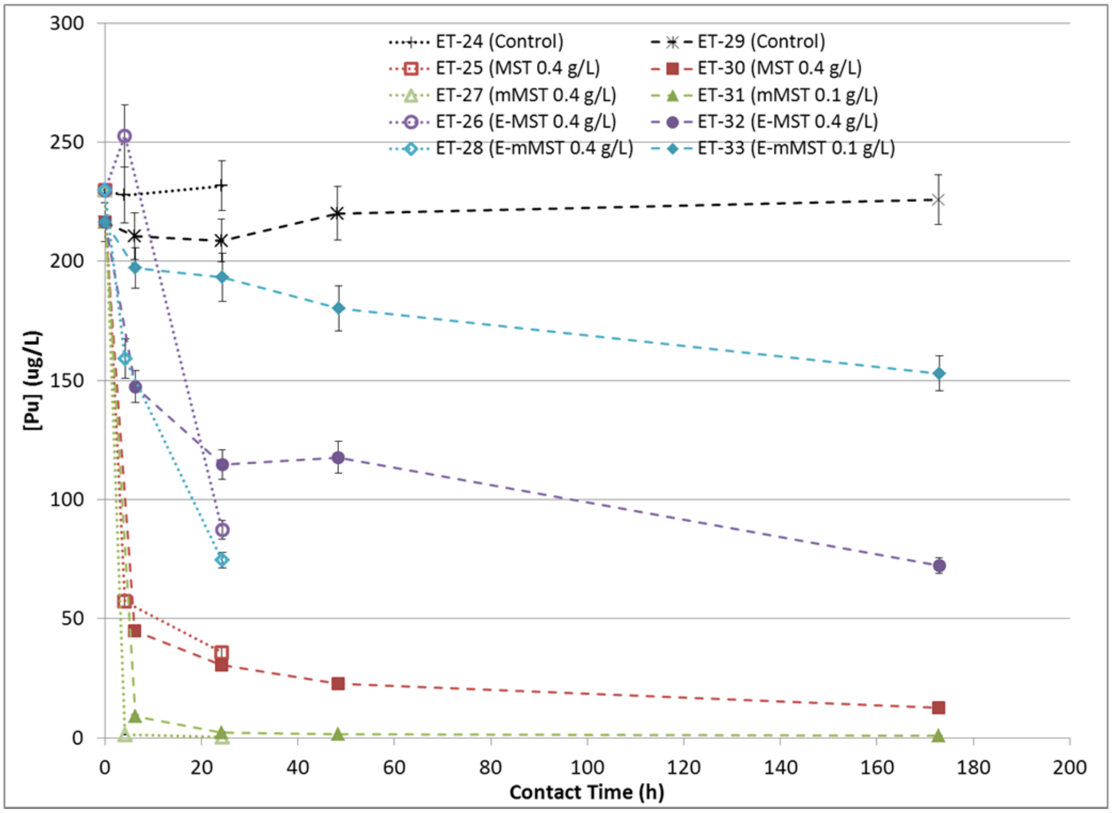

Figure A-3. Pu concentration versus contact time for Tests ET-24 through ET-33.

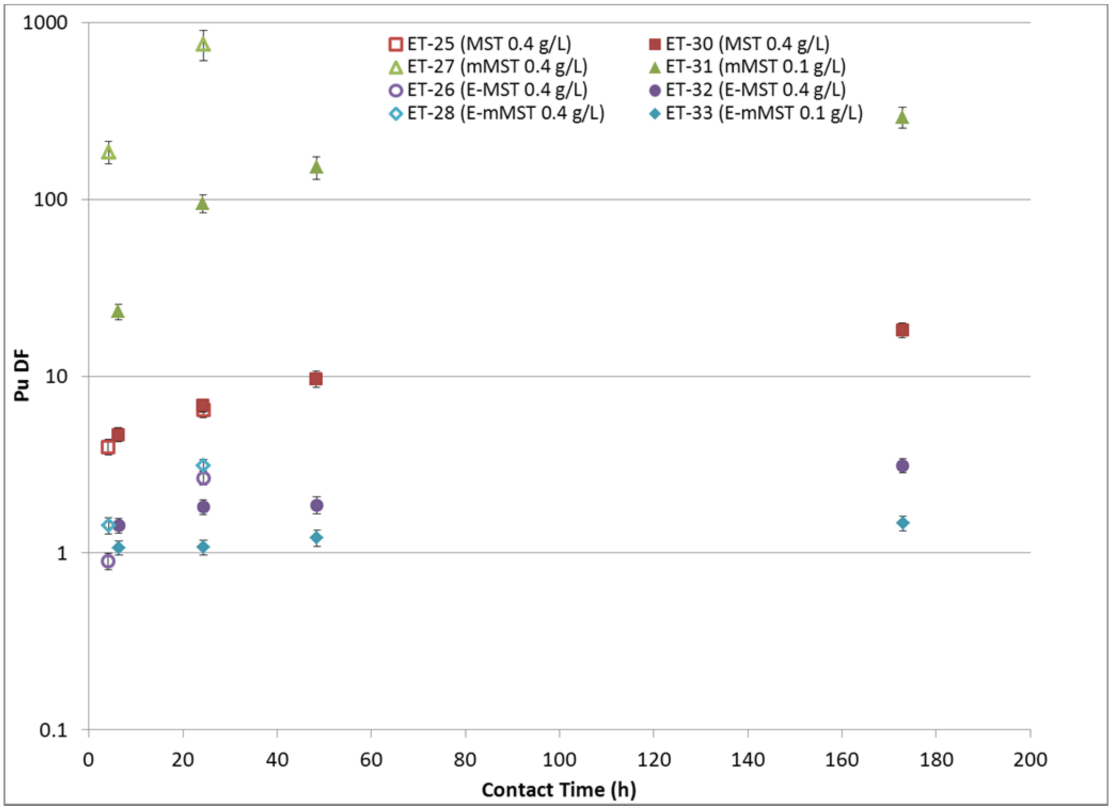

Figure A-4. Pu DF versus contact time for Tests ET-25 through ET-33.

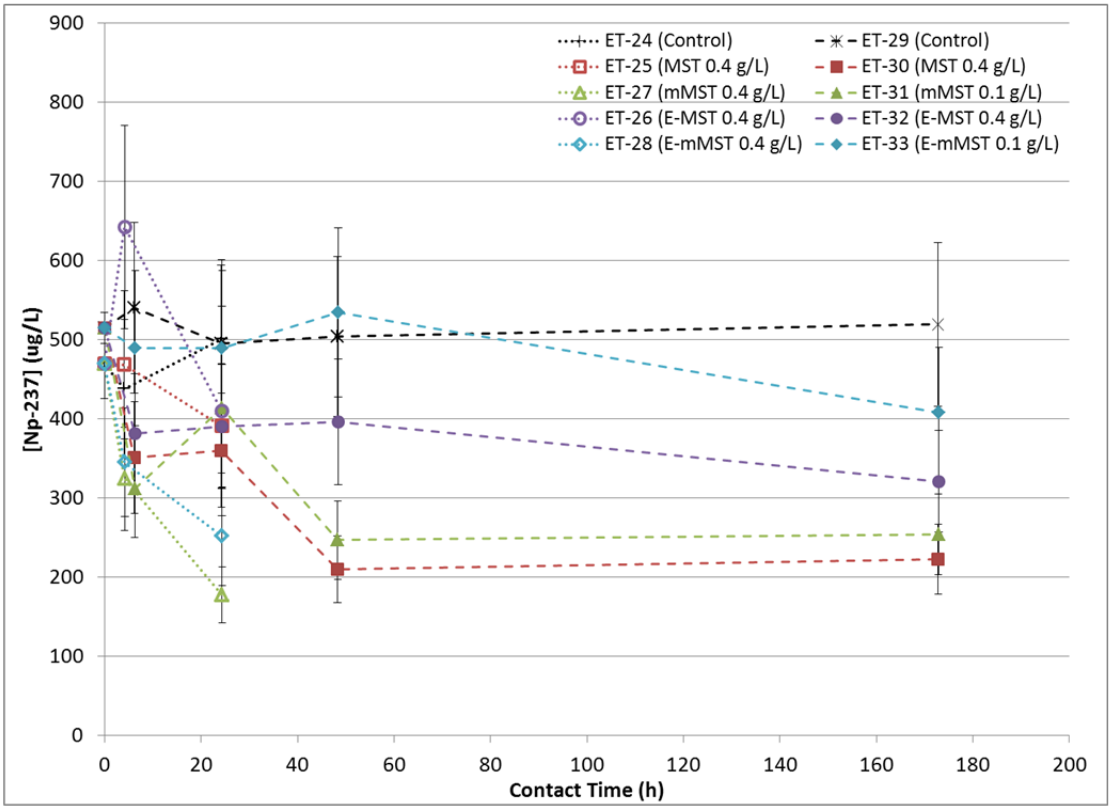

Figure A-5. ^{237}Np concentration versus contact time for Tests ET-24 through ET-33.

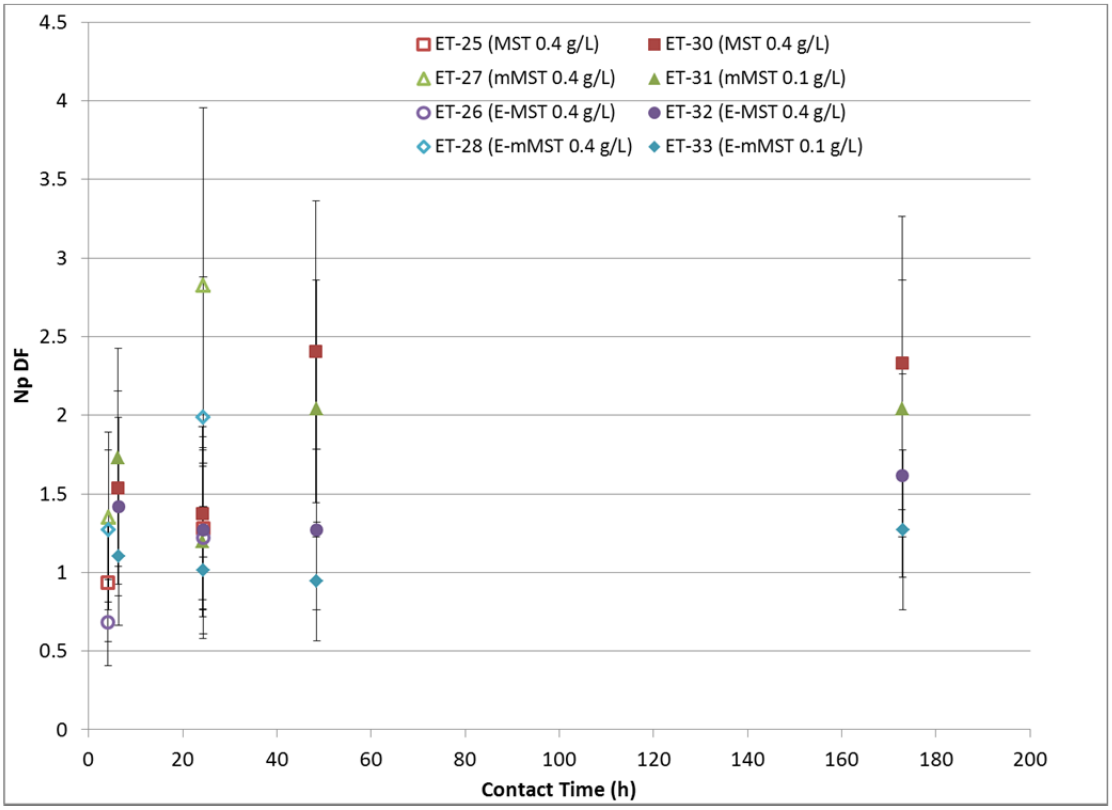

Figure A-6. ^{237}Np DF versus contact time for Tests ET-25 through ET-33.

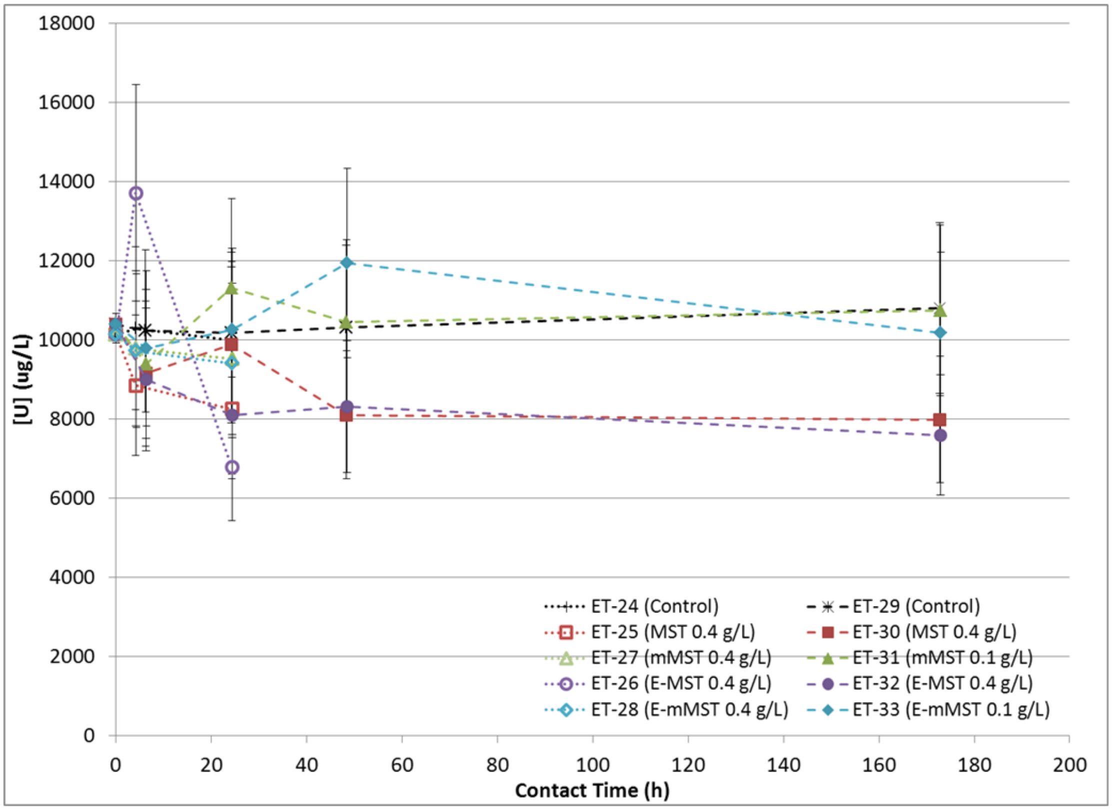

Figure A-7. U concentration versus contact time for Tests ET-24 through ET-33.

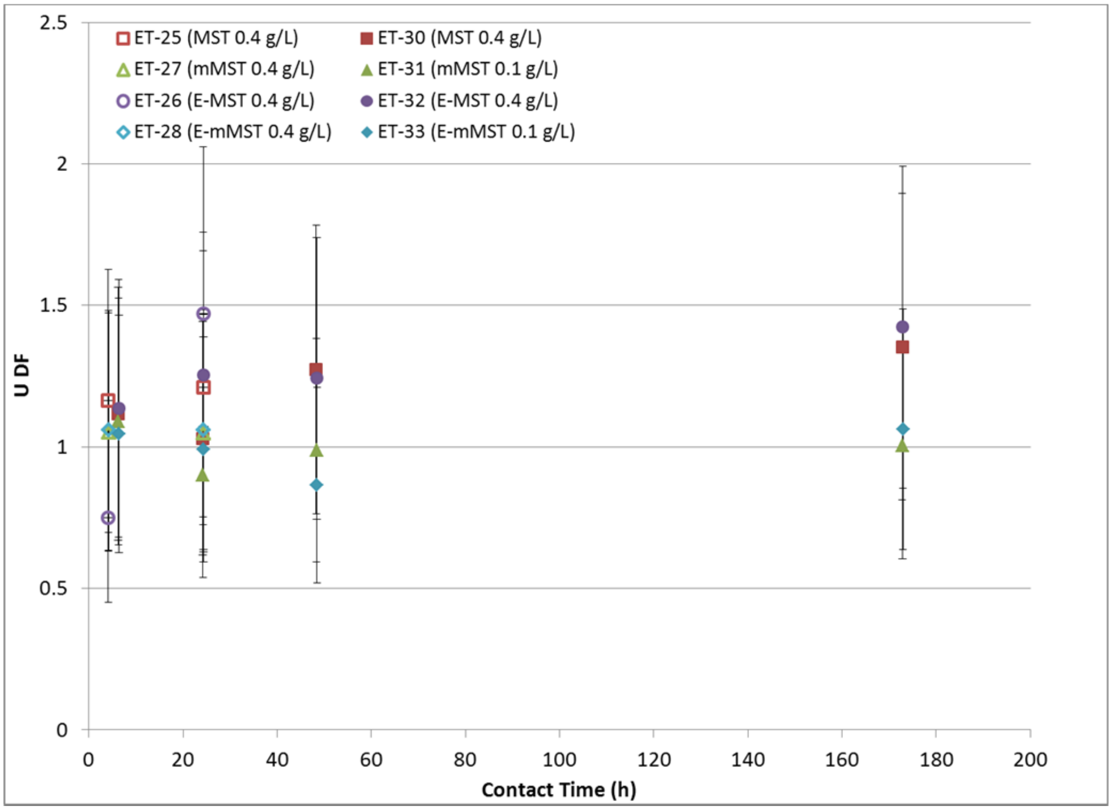

Figure A-8. U DF versus contact time for Tests ET-25 through ET-33.

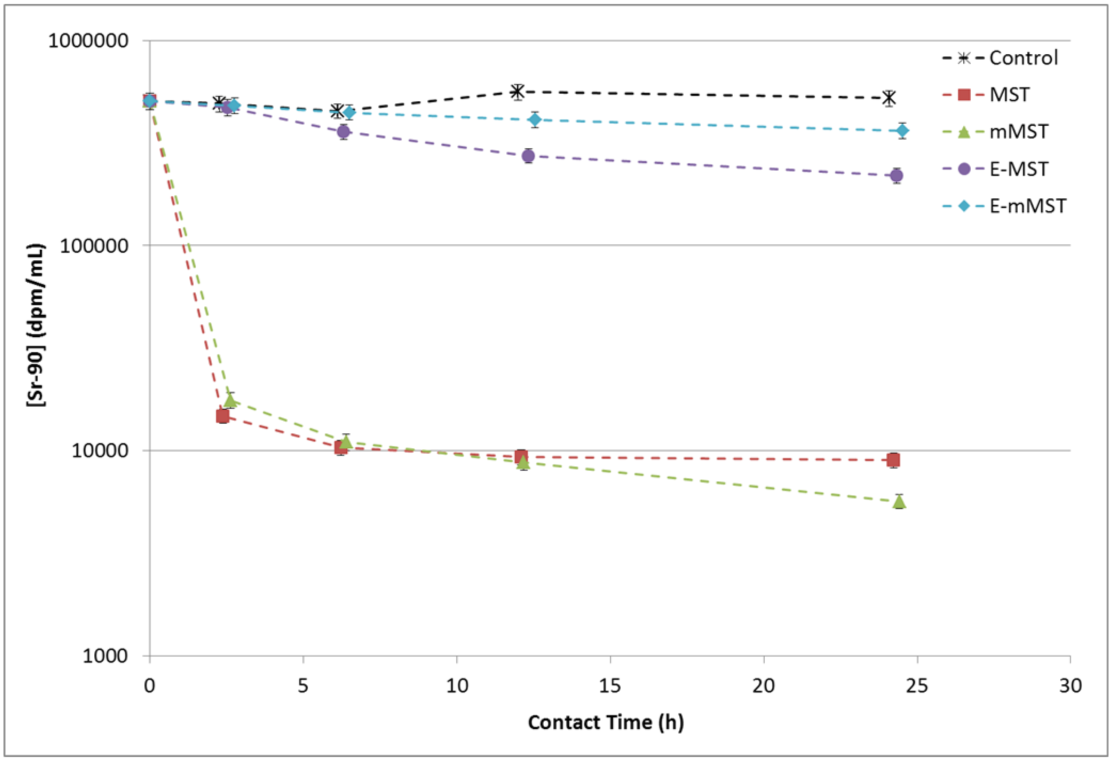

Figure A-9. ^{90}Sr activity versus contact time for real waste tests.

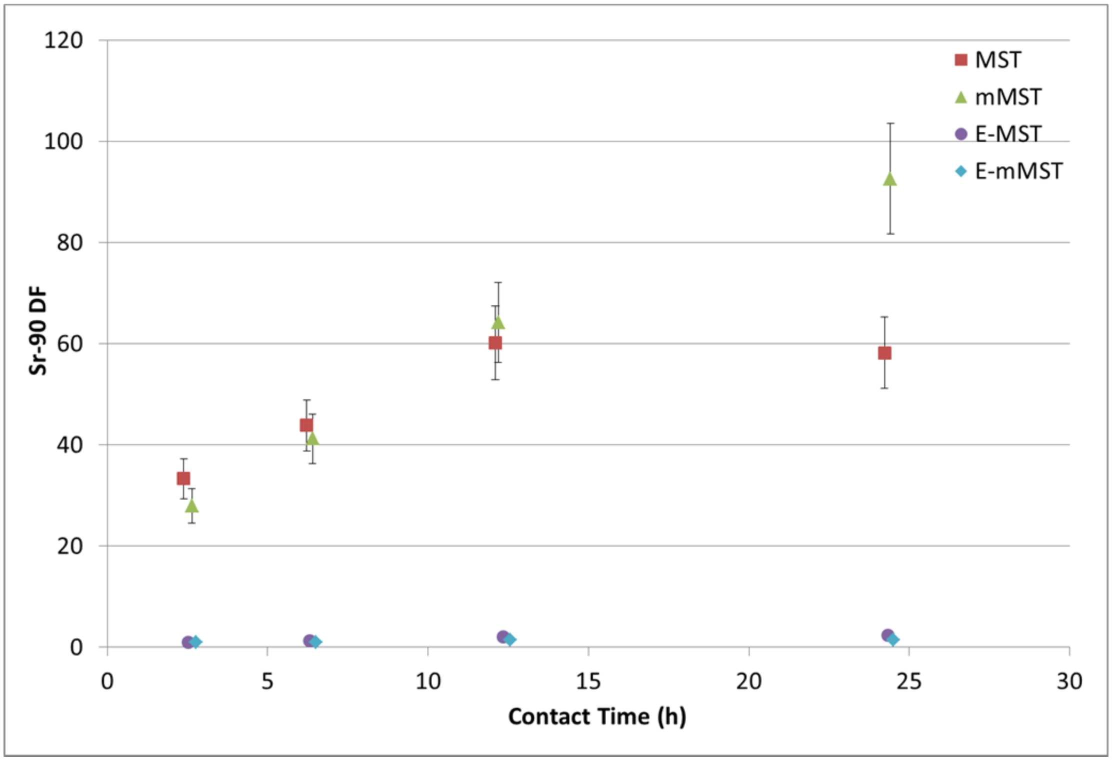

Figure A-10. ^{90}Sr DF versus contact time for real waste tests.

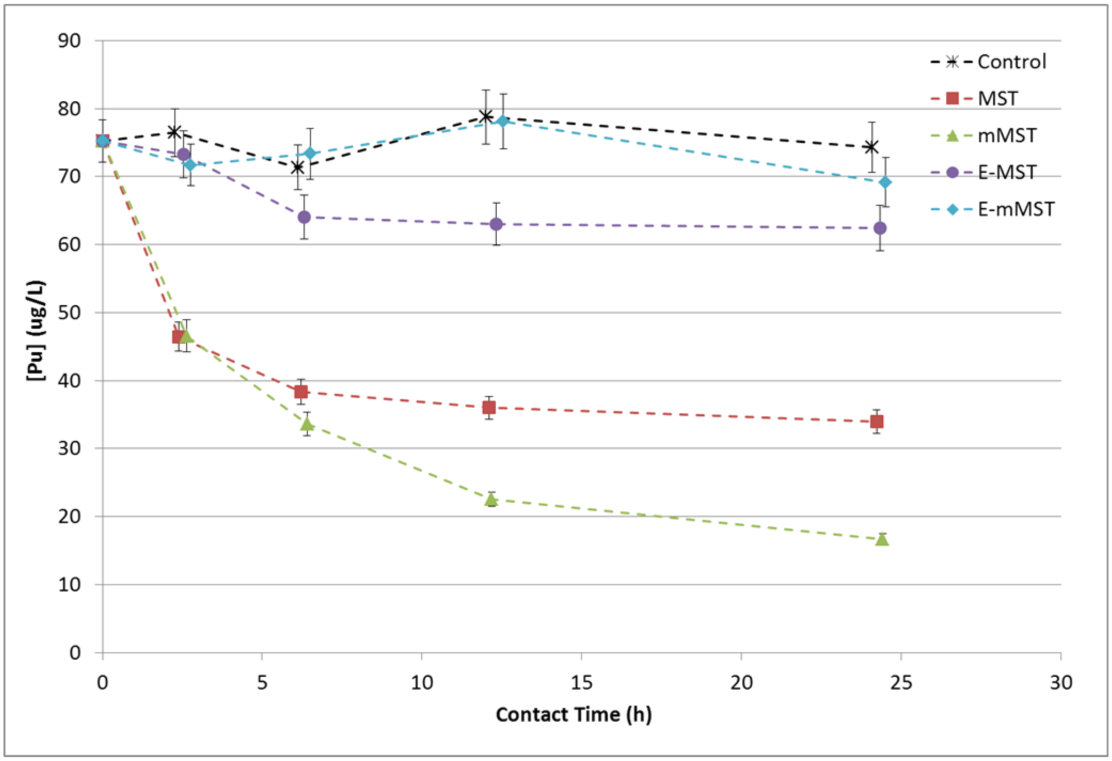

Figure A-11. Pu concentration versus contact time for real waste tests.

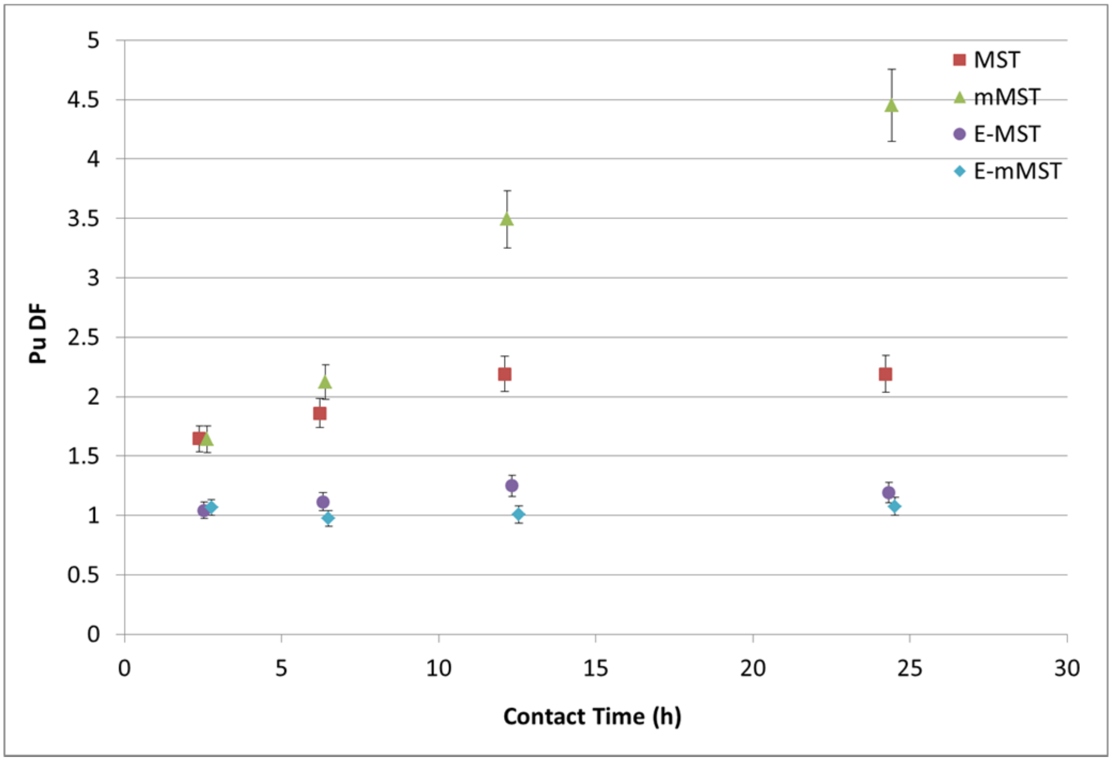

Figure A-12. Pu DF versus contact time for real waste tests.

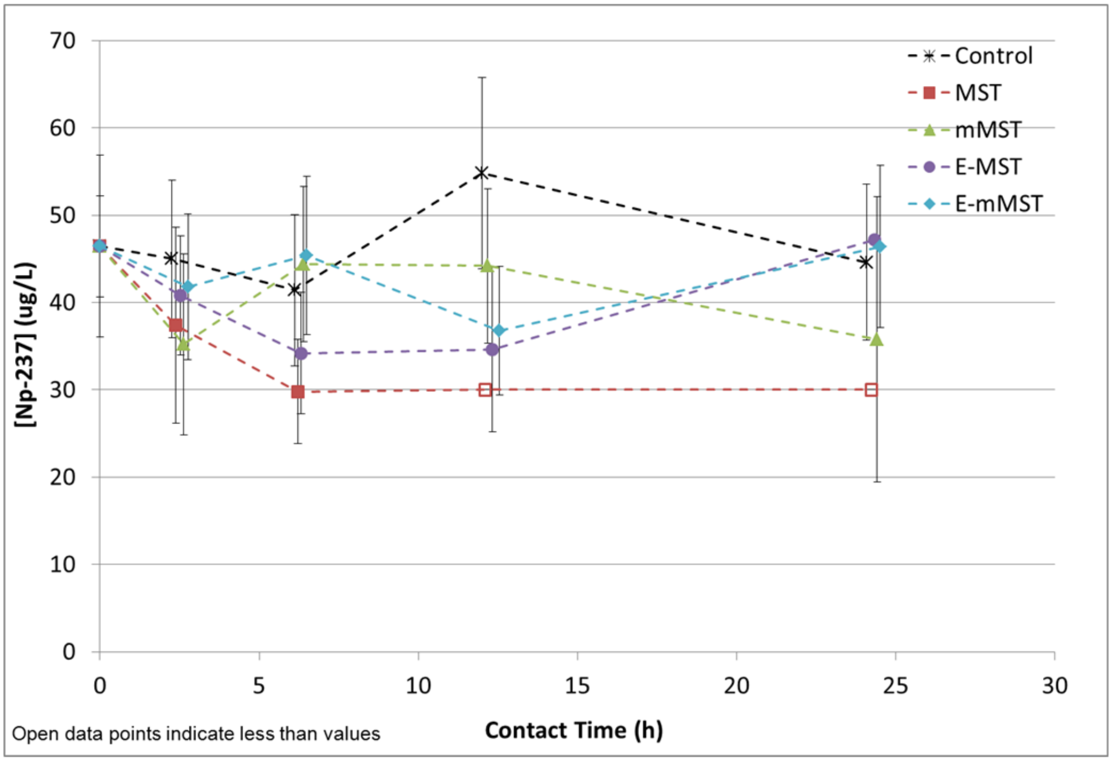

Figure A-13. ^{237}Np concentration versus contact time for real waste tests.

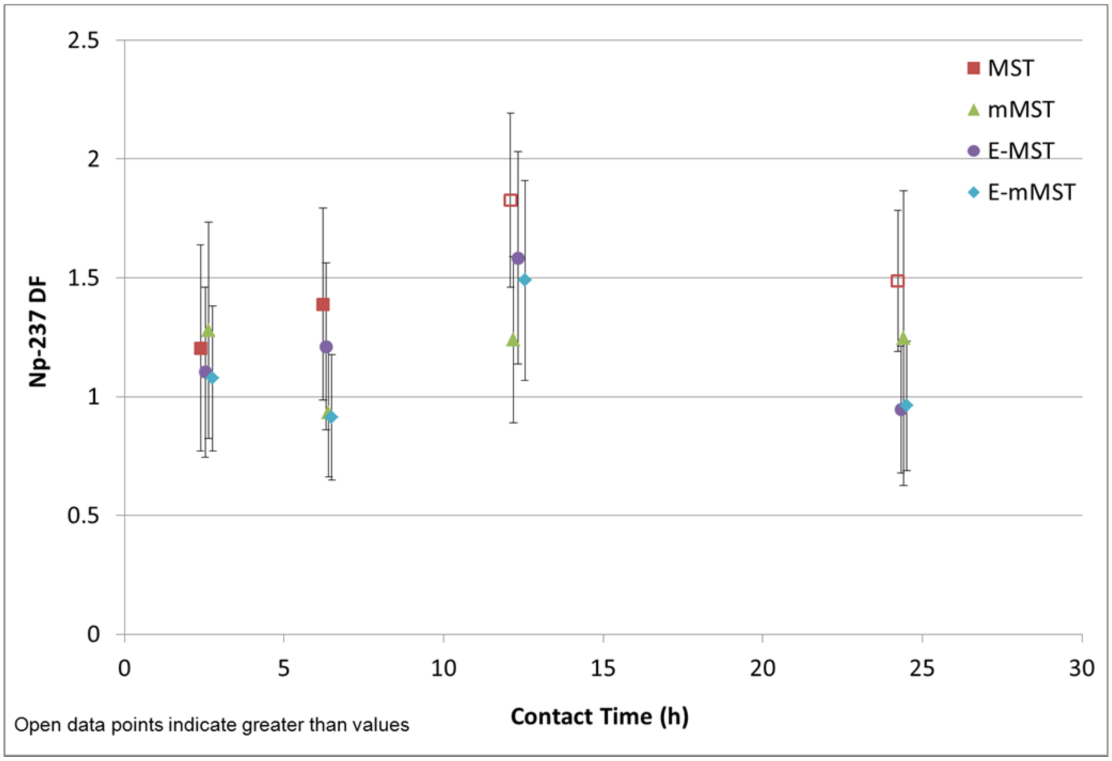

Figure A-14. ^{237}Np DF versus contact time for real waste tests.

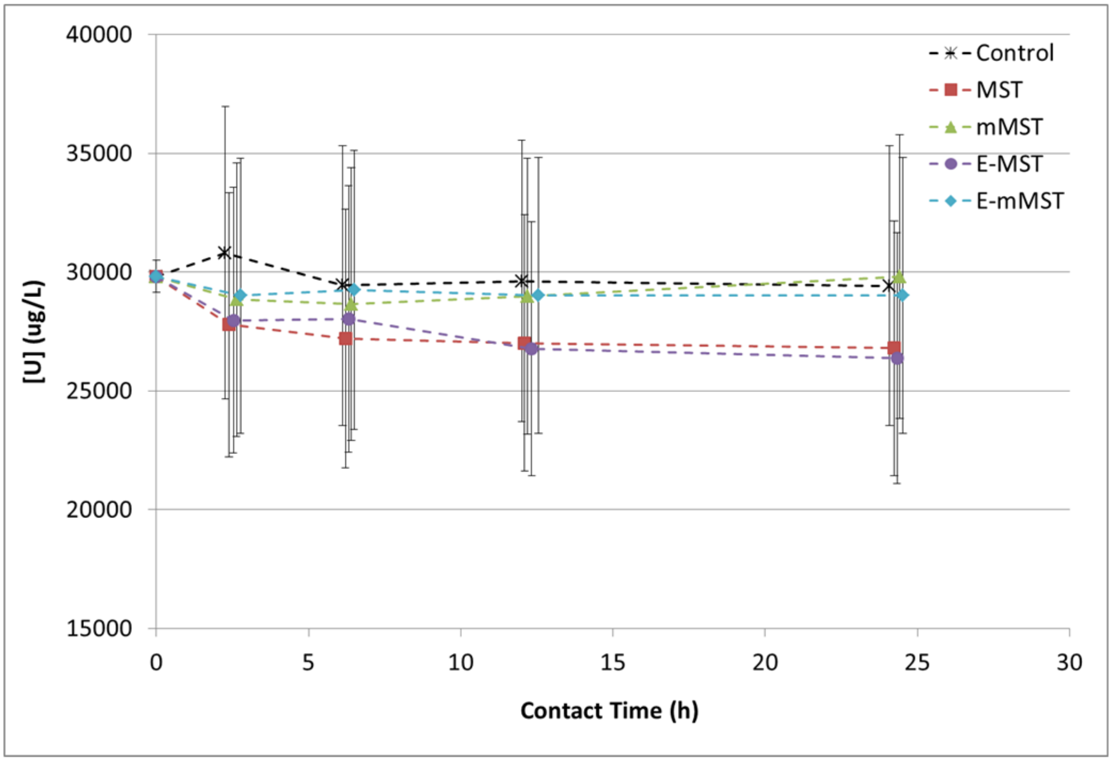

Figure A-15. U concentration versus contact time for real waste tests.

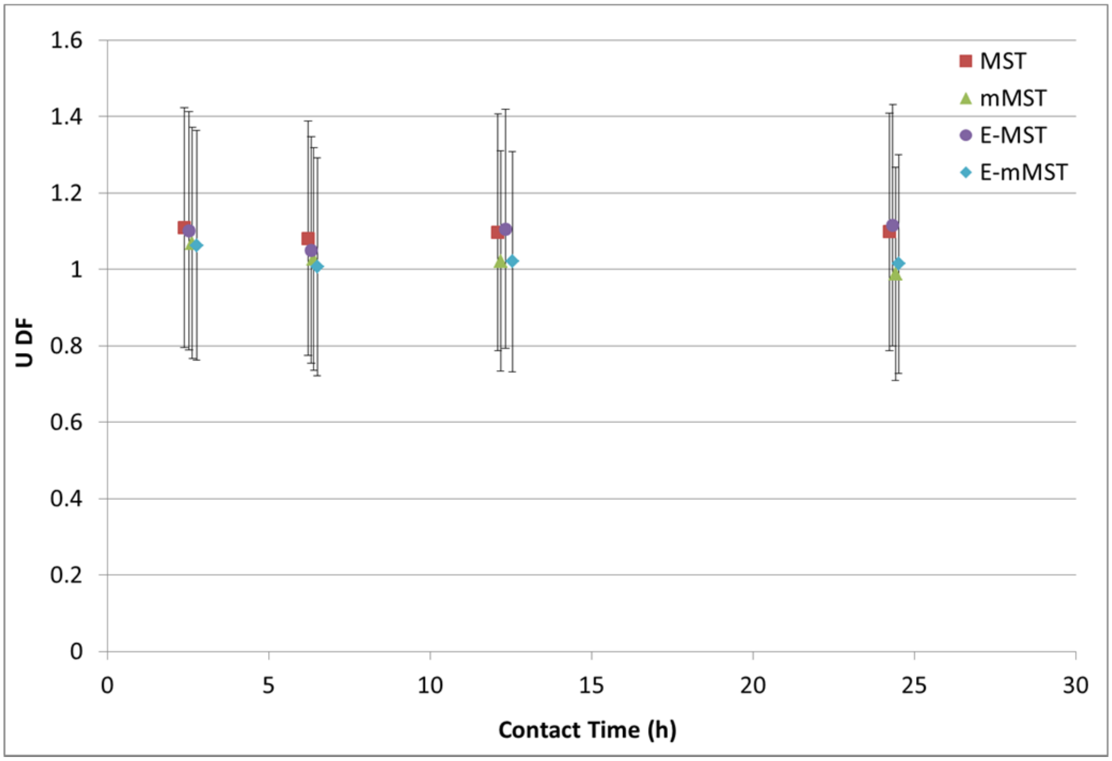

Figure A-16. U DF versus contact time for real waste tests.

Appendix B. Column Data

Table B-1. Data from Column 1 (^{E}MST).

Sample ID	Date/Time	Column Temp. (°C)	Ave. Flow Rate (mL/min)	Bed Volumes Passed	Volume Passed (mL)
Startup	9/2/11 13:15	25.5	n/a	0	0
Column 1 - 1A	9/6/11 10:05	26.8	0.474	690	2819
Column 1 - 1B	9/6/11 15:51	26.7	0.500	732	2991
Column 1 - 2A	9/7/11 9:36	-	0.510	864	3533
Column 1 - 2B	9/7/11 16:26	27.2	0.508	916	3743
Column 1 - 3A	9/8/11 9:56	26.4	0.509	1046	4276
Column 1 - 3B	9/8/11 14:55	26.9	0.510	1084	4430
Column 1 - 4A	9/9/11 9:19	26.4	0.512	1222	4993
Column 1 - 4B	9/9/11 14:20	27.0	0.513	1259	5147
Column 1 - 5A	9/12/11 9:27	27.0	0.512	1764	7207
Column 1 - 5B	9/12/11 14:44	25.2	0.510	1803	7369
Column 1 - 6A	9/13/11 10:48	26.6	0.508	1953	7982
Column 1 - 6B	9/13/11 15:47	29.7	0.506	1990	8133
Column 1 - 7A	9/14/11 9:55	26.2	0.509	2125	8685
Column 1 - 7B	9/14/11 14:50	29.5	0.507	2162	8835
Column 1 - 8A	9/15/11 9:39	30.2	0.507	2302	9407
Column 1 - 8B	9/15/11 15:16	30.9	0.503	2344	9578
Column 1 - 9A	9/16/11 8:47	27.3	0.510	2475	10114
Column 1 - 9B	9/16/11 14:16	25.1	0.497	2515	10278
Column 1 - 10A	9/19/11 9:21	24.3	0.520	3028	12373
Column 1 - 10B	9/19/11 14:59	24.5	0.521	3071	12548
Column 1 - 11A	9/20/11 9:14	25.0	0.508	3207	13103
Column 1 - 11B	9/20/11 14:51	27.6	0.519	3249	13278
Column 1 - 12A	9/21/11 10:35	25.8	0.508	3397	13880
Column 1 - 12B	9/21/11 15:01	27.2	0.501	3429	14013
Column 1 - 13A	9/22/11 10:01	25.1	0.413[*]	3545	14485
Column 1 - 13B	9/22/11 14:33	27.0	0.509	3578	14623
Average	n/a	**26.8**	**0.508**	n/a	n/a

[*] Column flow stopped sometime overnight due to low level in feed carboy (not included in average).

Table B-2. Data from Column 2 (H_2O_2 treated ^{E}mMST).

Sample ID	Date/Time	Column Temp. (°C)	Ave. Flow Rate (mL/min)	Bed Volumes Passed	Volume Passed (mL)
Startup	9/2/11 13:15	25.5	n/a	0	0
Column 2 - 1A	9/6/11 9:39	26.9	0.471	1411	2816
Column 2 - 1B	9/6/11 15:37	26.8	0.498	1498	2989
Column 2 - 2A	9/7/11 9:20	-	0.497	1762	3517
Column 2 - 2B	9/7/11 16:12	27.4	0.498	1866	3723
Column 2 - 3A	9/8/11 9:43	26.5	0.494	2126	4242
Column 2 - 3B	9/8/11 14:42	27.0	0.495	2200	4390
Column 2 - 4A	9/9/11 9:07	26.6	0.494	2473	4936
Column 2 - 4B	9/9/11 14:10	27.1	0.494	2548	5085
Column 2 - 5A	9/12/11 9:16	27.1	0.490	3535	7055
Column 2 - 5B	9/12/11 14:30	25.3	0.500	3615	7214
Column 2 - 6A	9/13/11 10:37	26.7	0.520	3929	7840
Column 2 - 6B	9/13/11 15:34	29.8	0.533	4008	7999
Column 2 - 7A	9/14/11 9:44	26.3	0.534	4299	8580
Column 2 - 7B	9/14/11 14:39	29.7	0.532	4378	8738
Column 2 - 8A	9/15/11 9:27	30.3	0.530	4677	9335
Column 2 - 8B	9/15/11 15:04	31.0	0.529	4767	9513
Column 2 - 9A	9/16/11 8:34	27.2	0.537	5048	10075
Column 2 - 9B	9/16/11 14:05	25.0	0.537	5138	10253
Column 2 - 10A	9/19/11 9:37	24.3	0.535	6224	12420
Column 2 - 10B	9/19/11 14:48	24.6	0.492	6300	12573
Column 2 - 11A	9/20/11 9:05	25.0	0.485	6566	13104
Column 2 - 11B	9/20/11 14:38	27.7	0.488	6648	13268
Column 2 - 12A	9/21/11 10:23	25.8	0.481	6934	13838
Average	n/a	**26.9**	**0.507**	n/a	n/a

Distribution:

K. M. Fox, 999-W
A. P. Fellinger, 773-41A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A

K. M. L. Taylor-Pashow, 773-A
C. A. Nash, 773-42A
D. T. Hobbs, 773-A
F. F. Fondeur, 773-A

M. T. Keefer, 766-H
J. W. Ray, 704-S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
A. V. Staub, 704-27S

P. R. Jackson, DOE-SR, 703-46A
K. H. Subramanian, 766-H

C. E. Duffey, 704-61H
D. J. Martin, 241-152H
K. L. Lang, 241-152H
E. J. Freed, 704-56H
M. W. Geeting, 241-152H
S. P. McLeskey, 704-27S
T. H. Huff, 707-13E
R. E. Edwards, 766-H
P. C. Suggs, 704-S
K. D. Harp, 766-H