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Strontium and Actinides Removal from Savannah River Site Actual Waste Samples by Freshly Precipitated Manganese Oxide

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1.0 Summary

The authors investigated the performance of freshly precipitated manganese oxide and monosodium titanate (MST) for the removal of strontium (Sr) and actinides from actual high-level waste. Manganese oxide precipitation occurs upon addition of a reductant such as formate (HCO_2^-) or peroxide (H_2O_2) to a waste solution containing permanganate (MnO_4^-). An addition of non-radioactive strontium typically precedes the MnO_4^- and reductant addition, which serves primarily to isotopically dilute the strontium-90 (^{90}Sr) present in the waste. Tests utilized a Tank 37H/44F composite waste solution. Personnel significantly increased the concentration of actinides in the waste by the addition of acidic americium/curium solution (F-Canyon Tank 17.1 solution), which contained a significant quantity of plutonium (Pu), and neptunium-237 (^{237}Np) stock solution. Initial tests examined three manganese oxide treatment options.

- Nominal Manganese: sequential addition of 0.01 M non-radioactive Sr, 0.01 M MnO_4^-, and 0.045 M HCO_2^-
- Low Manganese: sequential addition of 0.01 M non-radioactive Sr, 0.002 M MnO_4^-, and 0.009 M HCO_2^- to yield a lower solids concentration
- Manganese without Strontium: sequential addition of 0.01 M MnO_4^- and 0.045 M HCO_2^- only

Results indicated the following.

- All three manganese oxide treatment options reduced the ^{90}Sr concentration below the Saltstone Waste Acceptance Criteria (WAC). After 24 hours of reaction, 99% of the initial level of 154 nCi/g of Sr was removed from solution. In these tests, the use of non-radioactive Sr to provide isotopic dilution provided no significant advantage in kinetics or ultimate capacity for Sr removal in the treatment of actual wastes.
- Comparison MST tests also reduced the ^{90}Sr concentration below the Saltstone WAC. After 24 hours of reaction, 90% of the initial level of 154 nCi/g of Sr was removed from solution.
- Under the conditions tested (i.e., high Pu concentration), all three manganese oxide treatment options proved unsuccessful in reducing the Pu (sum of ^{238}Pu, ^{239}Pu, and ^{240}Pu) activity below the Saltstone WAC. After 24 hours of reaction, only 23% of the initial level of 303 nCi/g of Pu was removed from solution. The Nominal Manganese option provided the best level of decontamination within 24 hours of treatment (i.e., 41% of the initial level of 303 nCi/g of Pu removed from solution).
- The addition of non-radioactive Sr for isotopic dilution of Sr appeared to enhance Pu removal (41% of the initial level of 303 nCi/g of Pu was removed with the addition of Sr and none, 0%, of the Pu was removed without Sr addition). The data set is not sufficient to fully evaluate this observation.
- The MST tests, like manganese oxide, also proved unsuccessful in decontaminating Pu to the required concentration (after 24 hours of reaction, 58% of the initial level of 303 nCi/g of Pu was removed from solution). Under the conditions tested, MST proved slightly more effective than manganese oxide in reducing the Pu concentration.

- Neptunium decontamination appeared roughly equivalent for both treatment methods (after 24 hours of reaction, both the Nominal Manganese treatment and MST treatment removed 47% of the initial level of 0.0877 nCi/g of Np) with both methods failing to achieve the required removal efficiency.
- The poor decontamination performance observed in both manganese oxide and MST treatments likely resulted due to the increased concentrations of Pu present in the waste. Increased levels of either MST or MnO_4^- are required to achieve the required level of decontamination.

Personnel conducted additional tests based upon a recommendation from these findings. These tests examined both MST and manganese oxide treatment options. Freshly precipitated manganese oxide tests varied the amount of MnO_4^- added, the reductant used (i.e., H_2O_2 versus HCO_2^-), and removal of the insoluble actinides present in the initial phase of testing. Results and conclusions obtained from the additional tests include the following.

- Increasing the amount of MnO_4^- added led to an increase in the quantity of Pu and Np removed. Uranium (U) did not behave with the same correlation.
- Co-precipitation (and not adsorption) seems the predominate mechanism for Pu and Np removal in freshly precipitated manganese oxide tests.
- The removal of Np in manganese oxide tests may correlate with the addition of Sr at the start of the tests. The data is less conclusive for Pu.
- The use of H_2O_2, rather than HCO_2Na, as a reductant did not significantly improve the ultimate removal of actinides in the manganese oxide tests but did complete the reaction much faster.
- Plutonium and neptunium removal via MST appears to follow classical adsorption theory (i.e., the quantity removed depends upon the starting solution concentration). Insufficient data exists to ascertain the adsorption model that best fits the data.

Analysis of the data continues. The authors will compare the data from these tests with those from earlier experiments using simulated wastes to provide insights as to consistency of performance and the removal mechanism for each treatment option. Such analysis begins the effort to develop a predictive model for the process efficiency at removing the targeted radionuclides. Recommendations for additional testing will result from that comparison.

2.0 Introduction

The baseline flowsheet for the Salt Waste Processing Facility (SWPF) at the Savannah River Site uses monosodium titanate (MST) for the removal of radioactive strontium (Sr), plutonium (Pu) and neptunium (Np). Hobbs and Walker[1] studied the adsorption of Pu and uranium (U) onto MST in alkaline solutions. These tests showed that MST would remove the targeted radionuclides from simulated alkaline waste. Continued testing indicates that Pu removal kinetics and Np capacity of the MST material impacts the size of equipment and waste blending plans for the SWPF. Additionally, calculations suggest the baseline MST process may not achieve the desired decontamination in wastes containing elevated concentrations of Pu and Np.[2] Consequently, the Department of Energy (DOE) requested that Savannah River Technology Center (SRTC) personnel investigate the ability of freshly precipitated manganese oxide to remove Sr and actinides from high-level waste. Manganese oxide precipitation occurs by addition of a reductant (e.g., sodium formate, HCO_2Na) to a solution containing sodium permanganate ($NaMnO_4$). Isotopic dilution, by the addition of non-radioactive Sr, typically precedes the reduction step. This approach follows similar studies performed for Hanford waste.[3] If successful, this process offers increased throughput resulting in decreased equipment size. The DOE also requested that SRTC conduct tests to evaluate the capability of MST in actual high-level waste that contained elevated concentrations of Pu and Np as a means of comparison to the manganese oxide treatment.

Previously, research identified the adsorption kinetics of actinides and Sr onto MST as a technical risk. Hobbs' MST tests examined the extent and rate of adsorption of Sr, U, Np and Pu as a function of temperature, MST concentration, and the concentrations of sodium (Na) and adsorbing species (Sr, Pu, Np and U).[4] Analysis of the testing indicated the need to perform additional kinetic testing with radioactive Savannah River Site (SRS) tank waste and with simulants at lower ionic strength and MST concentrations. Subsequent radioactive waste tests utilized a composite material prepared from archive samples from over twenty SRS tanks. Results indicated that the extent and rate of Sr, Pu, Np and U removal with MST in radioactive waste agree with that previously measured with simulants.[5,6] Additional tests with simulated waste solutions measured the extent and rate of Sr, Pu, Np and U removal at 25 °C in the presence of 0.2 and 0.4 g/L MST at 4.5 and 7.5 M Na concentration. More recent testing measured removal characteristics of the MST testing using a simulated salt solution with a Na concentration of 5.6 M. Results indicated lower sorbate removal with increased Na ion concentration.[7] Tests described in this document address the capability of manganese oxide treatment to remove Sr, Pu, and Np from actual high-level waste containing elevated concentrations of Pu. Additionally, the tests investigate MST (using two unique batches) performance with the same waste for direct comparison to the manganese oxide performance.

3.0 Experimental

The investigation consisted of two phases of testing. In the initial phase, 10 tests evaluated the performance of either manganese oxide or MST for the removal of ^{90}Sr and alpha-emitting radionuclides from actual high-level waste. Table 1 provides a summary of the test parameters. Six of the 10 tests used MnO_4^- at three different conditions in duplicate. Three of the 10 tests used MST. A single control test contained neither MnO_4^- nor MST. Nine of the tests used the same actual high-level waste stock solution containing elevated concentrations of Pu. One test used a similar, yet more dilute salt waste that omitted the additional Pu. Researchers performed this last test as a comparison to previous experiment with actual high-level waste, sodium tetraphenylborate, and MST in a continuous addition mode.[8] In the second phase of testing, referred to as the Second Generation test phase, we subjected residual material from 8 of the 10 initial phase tests to further manganese oxide or MST treatments at varying conditions.

Table 1. Actual high-level waste test design

Test	**Description**	**Salt Waste**	**Sr**	**$MnO4^-$**	HCO_2^-	**MST**
1	Control	5.6 M Na^+	not added	not added	Not added	not added
2A	Nominal Manganese	5.6 M Na^+	0.01 M	0.01 M	0.045 M	not added
2B	Nominal Manganese	5.6 M Na^+	0.01 M	0.01 M	0.045 M	not added
3A	Low Manganese	5.6 M Na^+	0.01 M	0.002 M	0.009 M	not added
3B	Low Manganese	5.6 M Na^+	0.01 M	0.002 M	0.009 M	not added
4A	Manganese w/out Sr	5.6 M Na^+	not added	0.01 M	0.045 M	not added
4B	Manganese w/out Sr	5.6 M Na^+	not added	0.01 M	0.045 M	not added
5A	MST: Lot 33180	5.6 M Na^+	not added	not added	not added	0.4 g/L
5B	MST: Lot TNX	5.6 M Na^+	not added	not added	not added	0.4 g/L
6	MST: Lot TNX	4.7 M Na^+	not added	not added	not added	0.4 g/L

3.1 Preparation of Salt Solutions for Initial Phase Testing

The actual high-level waste solutions used in these tests came from archived waste samples. The waste solution identified as 5.6 M Na^+ in this report originated from supernate samples taken from Tanks 37H and 44F. D. D. Walker prepared a composite of these samples for use in a solvent extraction demonstration.[9] Researchers prepared the waste for this testing by analyzing the received Tank 37H/44F Composite waste solution for Na. Once analyzed, they then diluted the waste with 1.6 M NaOH to the desired Na concentration of 5.8 M. This permitted adding small aqueous aliquots of the treatment additives so that the final test solutions would contain 5.6 M Na^+. Two dilutions and analyses occurred to achieve the desired sodium concentration. The resulting solution volume equaled 1000 mL. Researchers then added 6 mL of acidic Americium/Curium solution (Tank 17.1 solution obtained from T. B. Peters[10]) and 66 µg (contained in 1 mL of 5 M HNO_3) of ^{237}Np (from D. T. Hobbs' 2.68 mg/mL ^{237}Np stock solution) to the diluted waste solution. Operators shook the solution to mix and allowed it to equilibrate over 1 week. We did not filter the solution prior to use. Filtered and unfiltered aliquots received analysis by titration, atomic adsorption (AA), ion chromatography (IC), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-emission spectroscopy (ICP-ES), gamma radiolysis, and Pu triphenyltrifluoroacetone scintillation analysis (PuTTA). Appendix 1 contains the final diluted composition of the waste solution. Table 2 shows specific components of relevance.

Table 2. Components of interest in actual high-level waste 5.6 Na$^+$ salt solution

Component	Unit	Target	Soluble Concentration	Total Concentration	Process Limit
Na	M	5.6	5.8	5.8	None
OH$^-$	M	as received	3.7	not measured	None
^{90}Sr	nCi/g	as received	154	626	40
^{237}Np	nCi/g	0.06	0.0877	0.118	0.03
Total U	µg/L	as received	7820	8110	None
^{238}Pu	nCi/g	882	235	828	18
$^{239/240}$Pu	nCi/g		68	235	18
Total Pu	nCi/g		303	1063	18

(The specific activities of ^{90}Sr, ^{237}Np, ^{238}Pu, ^{239}Pu, and ^{240}Pu are 137.1, 0.000705, 17.12, 0.0614, and 0.228 Ci/g, respectively.)

The waste solution identified as 4.7 M Na$^+$ came from T. B. Peters. It consisted of the same Tank 37H/44F Composite previously described along with a small fraction of waste solution composited from several residual waste tank samples (i.e., this mixture has been referred to as the multi-tank composite in prior testing by Peters[8]). This Tank 37H/44F/Multi-Tank Composite solution remained from the previous actual waste Small Tank Tetraphenylborate Continuously Stirred Tank Reactor (CSTR) demonstration.[8] As with the other waste solution, researchers prepared this waste for testing by analyzing the received waste solution for Na. Once analyzed, they diluted the waste with 1.6 M NaOH to the desired endpoint of 4.7 M. Again, personnel used two dilutions and analyses to achieve the desired concentration. Unlike the previous waste solution, personnel did not add other radionuclides to the diluted waste solution. They shook the solution to mix and allowed it to equilibrate over 2 weeks. We did not filter the solution prior to use. Personnel analyzed filtered and unfiltered aliquots by titration, AA, IC, ICP-MS, ICP-ES, gamma radiolysis, and PuTTA. Appendix 2 contains the final diluted composition of the waste solution. Table 3 shows specific components of relevance.

Table 3. Specific components of interest in actual high-level waste 4.7 M Na$^+$ solution

Component	Unit	Target	Soluble Concentration	Total Concentration	Process Limit
Na	M	4.7	4.8	4.8	None
OH$^-$	M	as received	3.5	3.5	None
^{90}Sr	nCi/g	as received	569	634	40
^{237}Np	nCi/g	as received	< 0.010	< 0.016	0.03
Total U	µg/L	as received	1800	1800	None
^{238}Pu	nCi/g	as received	3.4	3.4	18
$^{239/240}$Pu	nCi/g	as received	< 0.4	< 0.6	18
Total Pu	nCi/g	as received	< 4	< 4	18

(The specific activities of ^{90}Sr, ^{237}Np, ^{238}Pu, ^{239}Pu, and ^{240}Pu are 137.1, 0.000705, 17.12, 0.0614, and 0.228 Ci/g, respectively.)

3.2 Initial Phase Sr and Actinides Removal Tests

Researchers performed testing with the radioactive waste solutions in the SRTC Shielded Cells Facility. All tests used 250-mL polyethylene (PE) bottles fitted with a cap. Researchers prepared each test by placing 114 mL of the appropriate waste solution in the bottle. The MST tests initiated with the addition of a pre-dosed aliquot of 0.048 g MST (contained in a 6 mL aqueous slurry). The MST used in the tests came from two different batches. One batch, Lot 33180, represents a "qualified" batch of MST. The other source, TNX MST, consisted of residual MST from the prior demonstrations with actual waste.[8,9] This material was from a composite of MST drums located at the former SRS TNX site.

Freshly precipitated manganese oxide tests initiated with addition of 2 mL pre-dosed aliquots of 0.60 M $Sr(NO_3)_2$ to each test that required Sr addition. Note that personnel added a 2 mL aliquot of water to the Manganese without Strontium tests as well as the control to maintain the same level of dilution. Operators shook the bottles (by manipulator) to mix. Approximately, 30 minutes later – timing varied slightly from test to test as determined by amount of time required to perform additions to all tests – personnel added pre-dosed 2 mL aliquots of $NaMnO_4$ to each test. The Nominal Manganese and Manganese without Strontium tests used 0.60 M stock $NaMnO_4$ solution while the Low Manganese tests used 0.12 M stock $NaMnO_4$ solution. The control received 2 mL of water. After each addition, operators shook the test bottles. Approximately 30 minutes later, personnel added pre-dosed 2 mL aliquots of HCO_2Na to each test; the Nominal Manganese and Manganese without Strontium tests used 2.72 M stock HCO_2Na solution while the Low Manganese tests used 0.54 M stock HCO_2Na solution. The control received 2 mL of water. This completed initiation of the tests.

Researchers placed the test bottles on a shaker table at ambient temperature (21 °C) and agitated continuously at a rate capable of suspending solid materials as visually observed. Sampling occurred 2, 5, 24, 96, and 168 hours after addition of the MST or Sr aliquots. Sampling involved removing a test bottle from the shaker, manually shaking to produce a homogeneous mixture, and pulling approximately 4.5 mL of the test mixture into a disposable 10-mL syringe. Personnel filtered the sample mixture through a 0.45-µm nylon syringe filter disk and into a PE sample bottle. They capped the original test bottle and replaced in the shaker, typically within 5 minutes from the start of sampling. After sampling all tests, the operator pipetted 1-mL portions of each filtered sample into a second set of pre-weighed, PE sample bottles containing ~49.5 mL of 2 M nitric acid. They weighed the diluted samples to determine the mass of sample transferred into each bottle. They shook the diluted samples and submitted for analysis by ICP-MS, PuTTA, and radiochemistry for U (sum of ^{234}U, ^{235}U, ^{236}U, and ^{238}U), ^{237}Np, Pu (sum of ^{238}Pu, ^{239}Pu, and ^{240}Pu), and ^{90}Sr concentrations.

3.3 Second Generation Tests

We performed additional actinide removal treatments on residual material from eight of the 10 Initial Phase tests. Testing examined a number of parameters. These included the reductant added (HCO_2^- vs. H_2O_2), removal of solids (in particular insoluble actinides), and the quantity of MnO_4^- or MST added. Table 4 contains a synopsis of the individual additive concentrations and filtration utilized in the respective tests.

The Second Generation tests used the residual material in their original test containers (except for the Tests 2A and 2B which we filtered using 0.45-µm disposable nylon filters and the filtrate transferred to new 250-mL PE bottles). Just prior to the start of these tests, technicians sampled the residual material from each of the involved tests for soluble actinides. Table 5 contain the analytical results. Additionally, personnel conducted scouting tests for identifying necessary techniques for the use of H_2O_2 as a reductant. We obtained the following reaction guidelines from these tests.

- Magnetic stirring provided the best reduction of MnO_4^-.
- Peroxide addition onto the surface of the solution proved acceptable as long as good mixing occurred.
- Complete reduction of the MnO_4^- occurred within 5 minutes of the H_2O_2 addition. (Formate takes as long as 24 hours to complete the reduction.)
- The percent excess of H_2O_2 required proved half that of HCO_2^-.
- Dilute (6 wt %) H_2O_2 in water appeared sufficiently stable for use in the tests. Personnel prepared fresh solution on the morning of testing and assured its stability by testing it with simulated waste just prior to its use in the cells.

The addition and sampling sequence varied depending upon the additives involved. Table 6 provides the addition and sampling sequence employed. We used three strikes for MST, while using only two MnO_4^- strikes in the remaining tests. Note that filtrates for Tests 3A and 2B remained dark purple in color after all the required strikes of MnO_4^- and H_2O_2. Technicians combined additional H_2O_2 to each test until the filtrate from each solution turned colorless. Test 3A required 3 additional strikes of 0.045 M H_2O_2 and Test 2B required 1 additional strike of 0.045 M H_2O_2 to completely reduce the MnO_4^-.

Table 4. Planned Second Generation test parameters

Treatment	Test	Number of Strikes[a]	MST (g/L)[b]	MnO_4^- (M)[b]	H_2O_2 (M)[b]	HCO_2^- (M)[b]	Filtered
Manganese Oxide	4B	2		0.01		0.045	no
	3B	2		0.02		0.09	no
	4A	2		0.01	0.0225		no
	3A	2		0.02	0.045		no
	2A	2		0.01	0.0225		yes
	2B	2		0.02	0.045		yes
MST	5A	3	0.2				no
	5B	3	0.2				no

[a] Number of strikes refers to the planned number of strikes of each additive (e.g., 2 strikes for Test 4A would equate to 2 strikes of MnO_4^-, followed by 2 strikes of H_2O_2).
[b] Values shown for MST, MnO_4^-, H_2O_2, and HCO_2^- represent concentrations added during each strike.

Table 5. Soluble actinide concentrations at the end of the Initial Phase and after 4 months of storage

Test	Pu (nCi/g)		^{237}Np (nCi/g)		U (µg/L)	
	Initial[a]	4 Months[b]	Initial[a]	4 Months[b]	Initial[a]	4 Months[b]
2A	328	288	0.0633	0.0473	(7200)[c]	8222
2B	255	304	0.0430	0.0550	7221	8026
3A	327	370	0.0556	0.0657	7116	8079
3B	328	390	0.0609	0.0619	7986	8317
4A	366	341	0.0648	0.0693	7800	8553
4B	391	374	0.0630	0.0617	7824	8395
5A	129	119	0.0464	0.0315	6402	7501
5B	98	102	0.0428	0.0294	6632	7100

[a] Initial refers to samples taken at the end of the Initial Phase.

[b] Samples taken prior to the start of Second Generation testing, ~ 4 months after the Initial Phase testing.

[c] Value in parentheses reflects an estimate based upon prior samples from the test. We believe the actual measured value of the test (11,256 ug/L) to be inaccurate.

Table 6. Addition and sampling sequence for MST and manganese oxide Second Generation tests

MST	MnO_4^- with HCO_2^-	MnO_4^- with H_2O_2
Add MST	Add MnO_4^- then HCO_2^-	Add MnO_4^- then H_2O_2
Sample 24 h later then add MST	Sample 24 h later then add MnO_4^- and HCO_2^-	Sample ~ 2.5 h later then add MnO_4^- and H_2O_2
Sample 24 h later then add MST	Sample 24 h later	Sample ~ 2.5 h later (stop if sample is colorless)
Sample 24 h later		Add H_2O_2 then sample (repeat until colorless)

Technicians delivered the additives by pouring from prepared, pre-dosed bottles into the test vessels, followed by rinsing of the additive bottles with test solution. During the additions, the test solutions were magnetically stirred to ensure adequate mixing. The MST used in two tests came from Lot 33180. Personnel did not add Sr to any of the tests. After approximately 3 minutes of stirring, operators shook the bottles (by manipulator) to mix. Approximately, 30 minutes later – timing varied slightly from test to test as determined by amount of time required to perform additions to all test - researchers placed the test bottles on a shaker table at ambient temperature and agitated continuously at a rate capable of suspending solid materials as visually observed. Sampling occurred as noted in Table 6. Sampling involved removing a test bottle from the shaker, manually shaking to produce a homogeneous mixture, and pulling approximately 4 mL of the test mixture into a disposable 10-mL syringe. Personnel filtered the sample mixture through a 0.45-µm, nylon syringe filter disk and into a PE sample bottle. They capped the original test bottle and replaced in the shaker, typically within 5 minutes from the start of sampling. After sampling all tests, the operator pipetted 1-mL portions of each filtered sample into a second set of pre-weighed, PE sample bottles containing 49 mL of 2 M nitric acid. They weighed the diluted samples to determine the mass of sample transferred into each bottle. They shook the diluted samples and submitted them for analysis by ICP-MS and PuTTA for soluble U, Np, and Pu concentrations.

4.0 Results and Discussion

4.1 Initial Phase Tests

4.1.1 Manganese Oxide Treatment

Figures 1 - 4 present the results of manganese oxide tests with respect to each sorbate (i.e., ^{90}Sr, total Pu, ^{237}Np, and total U). Appendix 3 contains the numerical data. Table 7 provides a summary of average decontamination factors (DFs) for each of the sorbates after 5 and 24 h of reaction. The table also provides data previously reported by M. C. Duff for comparison.[11] Note that the Duff data came from simulated waste tests with significant differences in the initial sorbate concentrations. A comparison of the actual waste and Duff's simulant test solutions is shown in Table 8. Numerical kinetics data from the Duff test (referred to as Test #24 in Reference 13) is contained at the end of Appendix 3.

4.1.1.1 Strontium Removal

All three manganese oxide test variations reduced the ^{90}Sr concentration below the Saltstone WAC (40 nCi/g). Examination of the Sr data indicates that the bulk of decontamination occurred within 2 h. This observation mimics that observed in prior studies using manganese oxide to treat Hanford high-level waste.[3] The data indicate that the Manganese without Strontium tests proved the most rapid and the Nominal Manganese tests proved the slowest of all test sets. However, no conclusions on the rates of decontamination should be made given the small number of samples and the minor differences in data. Ultimately, all three manganese oxide test variations yielded nearly the same level of decontamination by the end of one week (see Appendix 3).

Table 7. Comparison of average decontamination factors (DFs) for each manganese oxide test

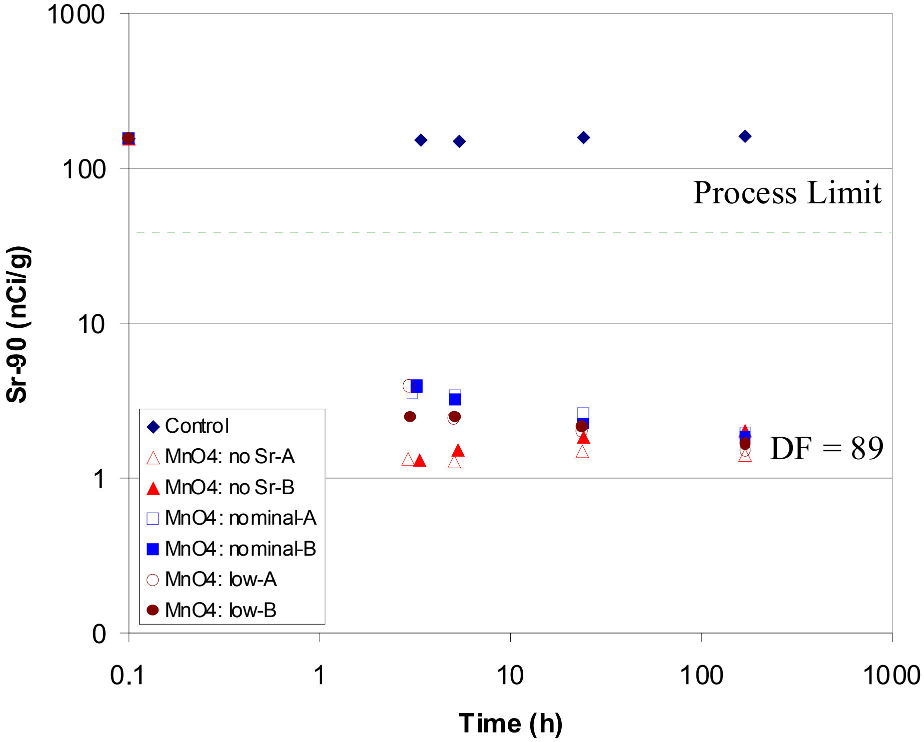
	^{90}Sr DF		**Pu DF**		**^{237}Np DF**		**U DF**	
Test	**5 h**	**24 h**	**5 h**	**24 h**	**5 h**	**24 h**	**5 h**	**24 h**
Control	1.0	1.0	1.1	1.0	1.3	1.0	1.1	1.0
Nominal Manganese	47	64	1.6	1.7	0.9	1.9	1.0	1.1
Low Manganese	62	74	1.0	1.3	0.9	1.2	1.0	1.1
Manganese without Sr	110	94	1.0	0.9	0.8	1.2	1.0	1.0
Duff's Test #24[11]	14	78	4.2	3.5	1.2	1.2	1.2	1.3

Table 8. Comparison of test solution compositions used in the current actual waste tests and Duff's simulant Test # 24

Component	Duff's Test #24	Current Testing[a]
Na^+ (M)	5.6	5.8
OH^- (M)	1.33	3.7
NO_3^- (M)	2.6	0.86
NO_2^- (M)	0.34	0.58
$Al(OH)_4^-$ (M)	0.43	<0.2
SO_4^{-2} (M)	0.52	0.004
CO_3^{-2} (M)	0.026	<0.2
Sr (µg/L)	660	1.4 (5.6)[b]
^{237}Np (µg/L)	423	153 (all soluble)
$^{239/240}Pu$ (µg/L)	181	1185 (4100)
^{238}U (µg/L)	10880	7820 (8110)

[a] Values shown in parentheses represent the total concentration of the analyte.
[b] Actual waste test values shown are for ^{90}Sr. Non-radioactive Sr was below detection.

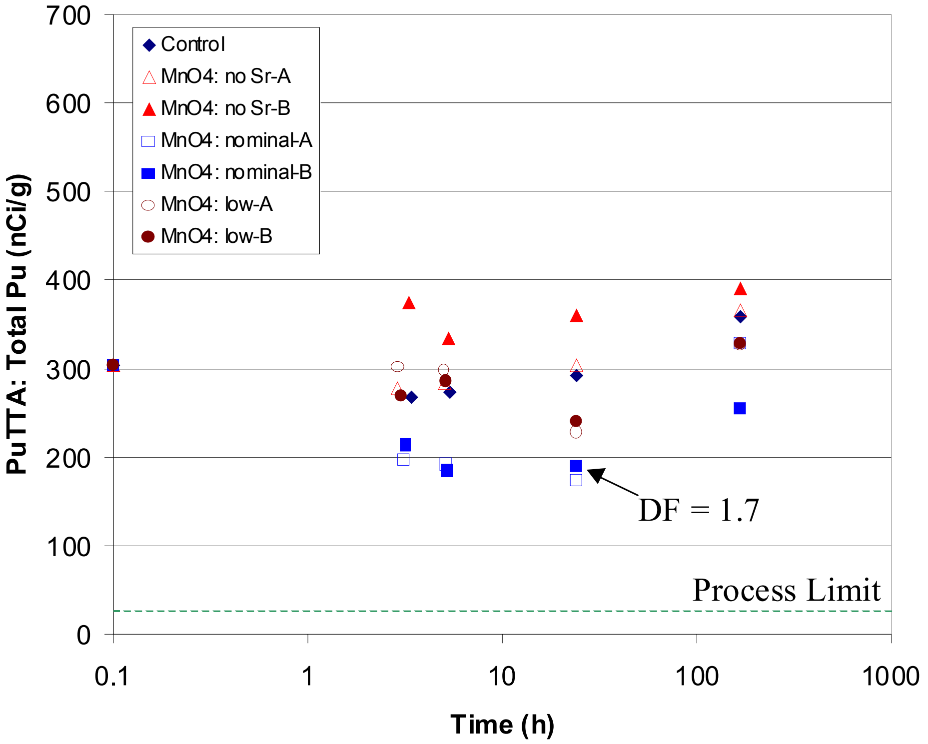
Figure 1. Concentration of ^{90}Sr during the manganese oxide tests



4.1.1.2 Plutonium Removal

Plutonium behaved differently than Sr. Figure 2 and Table 7 show that only the Nominal Manganese tests showed significant decontamination within the planned 24-hour process cycle. In all cases, the extent of removal peaked within 5 hours and then declined over

Figure 2. Concentration of Pu during the manganese oxide tests



the remaining test period. All of the tests failed to reduce the Pu concentration below the Saltstone WAC (total alpha = 18 nCi/g). Duff's Test #24 showed similar kinetics (i.e., removal maximized very early in the test). As expected, Duff's test showed better DFs for simulant. This can be attributed to the significantly lower Pu concentration in her solution (approximately 4% as much Pu as in these actual waste tests). Additionally, all Pu stayed soluble in Duff's test while only 29% of the Pu in the current tests remained soluble.

4.1.1.3 Neptunium Removal

Figure 3 and Table 7 provide Np behavior for the conditions tested. The Np concentration data suggests that addition of MnO_4^- resulted in dissolution of some Np solids present in the sludge solids. This may occur since MnO_4^- is a strong oxidizer. Generally, higher oxidation states of actinides exhibit higher solubilities. The oxidation potential for MnO_4^- under alkaline conditions is sufficiently high to oxidize Np(V) to Np(VI). Thus it is possible that the higher Np concentration may reflect oxidation of Np(V) to Np(VI). If true, this effect might produce a delay in Np removal, as observed with this data set. Given the complexity of the tests due to the changing systems, comparison of the tests is difficult. The data do not indicate which condition offers the best decontamination. None of the tests achieved the required level of decontamination (Np = 0.03 nCi/g).

Figure 3. Concentration of ^{237}Np during the manganese oxide tests

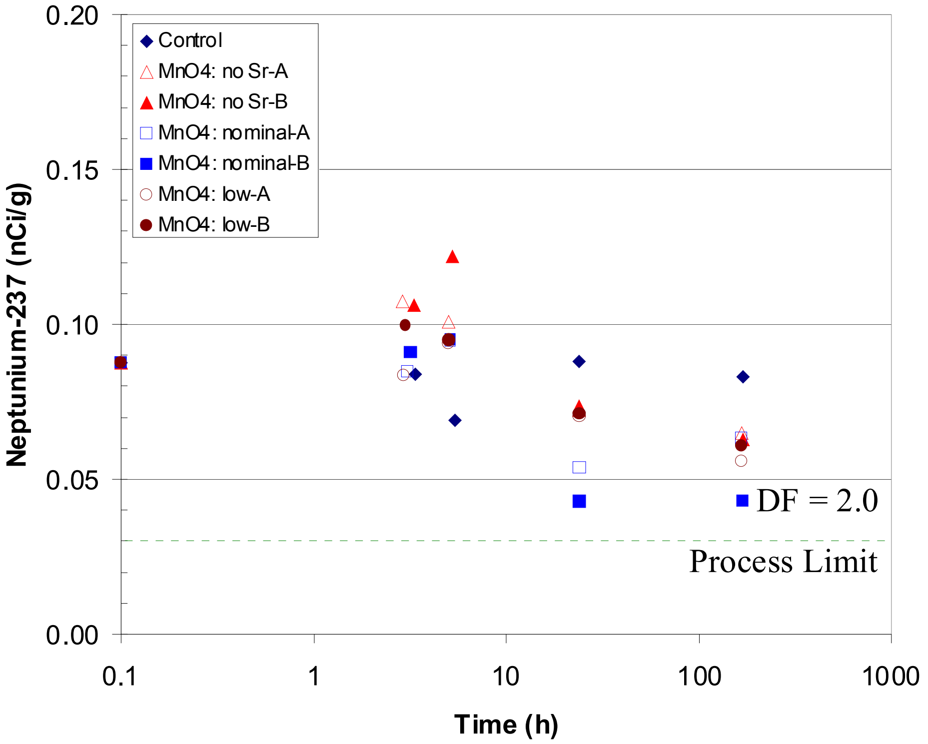
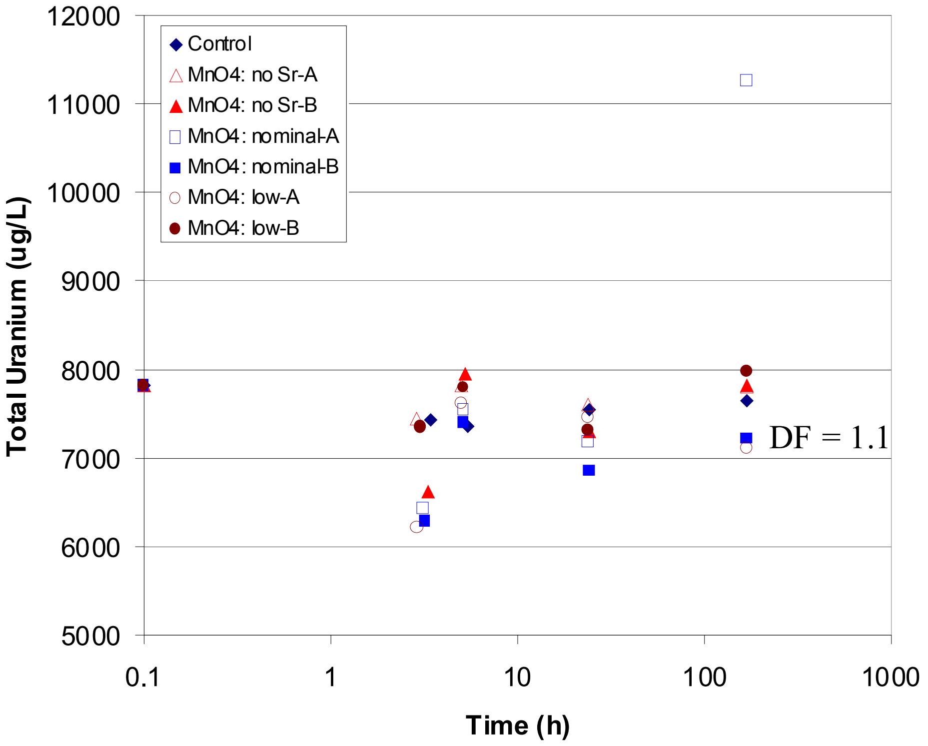


Figure 4. Concentration of U during the manganese oxide tests



4.1.1.4 Uranium Removal

Figure 4 and Table 7 provide the data for U removal by manganese oxide treatment. Uranium behaved similarly to that reported by Duff.[11] Less than 10% of the U was removed in any of the tests within 24 or 168 hours. Note that the waste does not require U removal. However, we monitored its removal efficiency since it competes with the other sorbates in MST pre-treatment and is removed in the manganese oxide treatment process (based on simulant tests). None of the tests were distinguishable from the others. The low DF values indicate little removal of U in these tests (actually removal was high on a per g basis, there is just a lot more U than Pu in the tests).

4.1.2 MST Treatment of 5.6 M Na^+ Solution

Figures 5 - 8 present MST removal data for ^{90}Sr, total Pu, ^{237}Np, and total U, respectively. Appendix 3 contains numerical test data. Table 9 provides a summary of DFs for each of the sorbates, with respect to each MST lot, after 24 and 168 h of reaction. The table also provides data previously reported by K. M. Marshall for comparison.[12] This data came from a simulant test with the same batch of MST and with a similar salt composition (see Table 10 for the solution comparison).

Table 9. Comparison of DFs for each MST test with 5.6 M Na^+ solution

Test	^{90}Sr DF		Pu DF		^{237}Np DF		U DF	
	24 h	**168 h**	**24 h**	**168 h**	**24 h**	**168 h**	**24 h**	**168 h**
Control	1.0	1.0	1.0	0.8	1.0	1.1	1.0	1.0
MST: Lot 33180	10	10	2.4	3.1	2.0	2.1	1.2	1.2
MST: TNX	11	12	2.5	2.4	1.9	1.9	1.2	1.2
K. Marshall's data[12]	123	155	4.1	9.1	1.5	2.0	1.4	1.6

Table 10. Comparison of test solution compositions for actual waste used in current testing and simulant used by Marshall[12]

Component	Marshall[12]	Current Testing[a]
Na^+ (M)	5.6	5.8
OH^- (M)	3.0	3.7
NO_3^- (M)	1.0	0.86
NO_2^- (M)	0.50	0.58
$Al(OH)_4^-$ (M)	0.10	<0.2
SO_4^{-2} (M)	0.49	0.004
CO_3^{-2} (M)	0.02	<0.2
Sr (µg/L)	621	1.4 (5.6)[b]
^{237}Np (µg/L)	241	153 (all soluble)
$^{239/240}Pu$ (µg/L)	231	1185 (4100)
^{238}U (µg/L)	7050	7820 (8110)

[a] Values shown in parentheses represent the total concentration of the analyte.
[b] Values shown are for ^{90}Sr. Non-radioactive Sr was below detection.

Treatment of the radioactive waste with MST reduced the concentration of ^{90}Sr below the WAC of 40 nCi/g. Both lots of MST exhibited very similar removal characteristics. Note that the measured DF's with the radioactive wastes were well below those reported recently by Marshall.[12] The lower DF's may reflect higher total strontium concentration in the radioactive waste compared to that in the simulated waste solution. In the simulant test, the initial total strontium concentration measured 621 μg/L. The total strontium concentration in the radioactive waste was indeterminate due to the high dilution factor employed to prepare the sample for ICP-MS analysis. Based on the ICP-MS detection limit, the total strontium concentration in the waste solution could be as high as 2000 μg/L. The removal performance of the MST is dependent on the total mass concentrations of the strontium, the actinides and any other species that adsorbs onto the MST. Given that the waste solution measured about 10% higher in soluble uranium to that in the simulant, a lower DF value for strontium would be expected if the total strontium concentration in the waste was close to 2000 μg/L.

Figure 5. Concentration of ^{90}Sr during the MST test with 5.6 M Na$^+$ solution

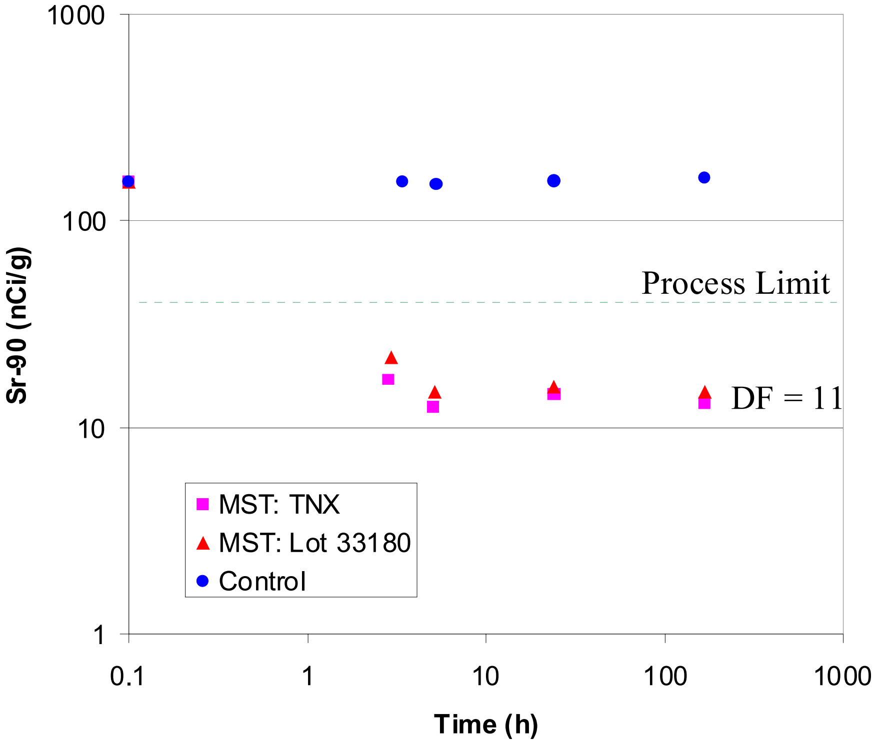


Figure 6. Concentration of Pu during the MST test with 5.6 M Na$^+$ solution

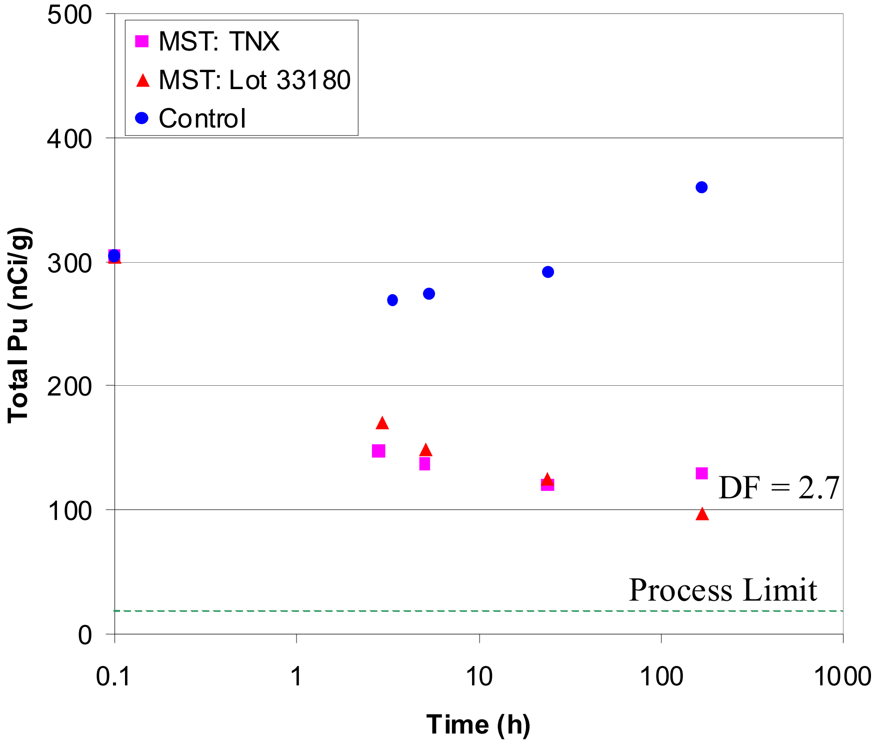


Figure 7. Concentration of ^{237}Np during the MST test with 5.6 M Na$^+$ solution

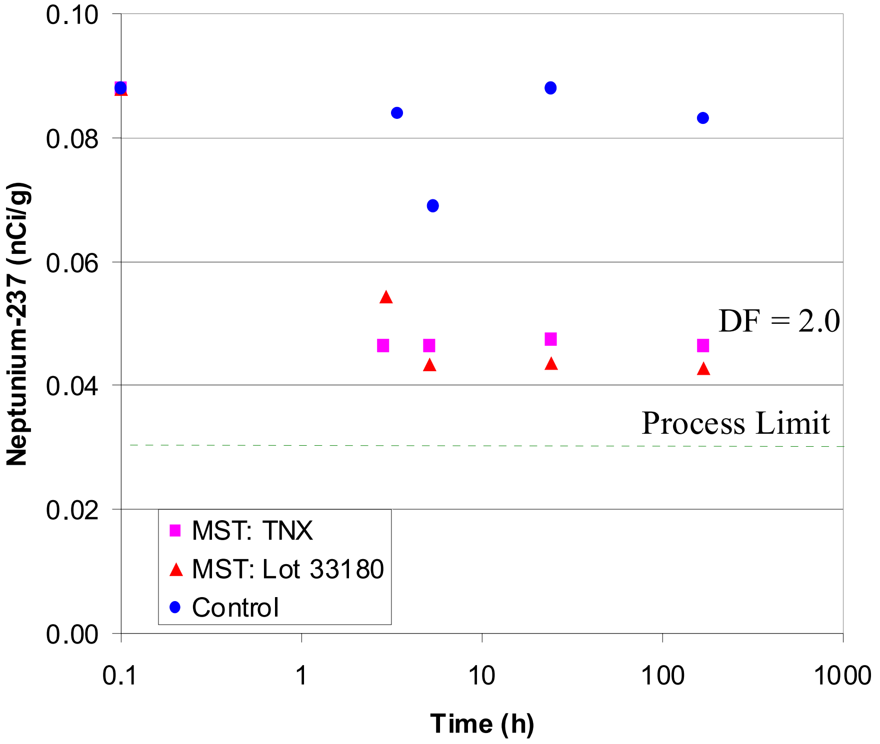
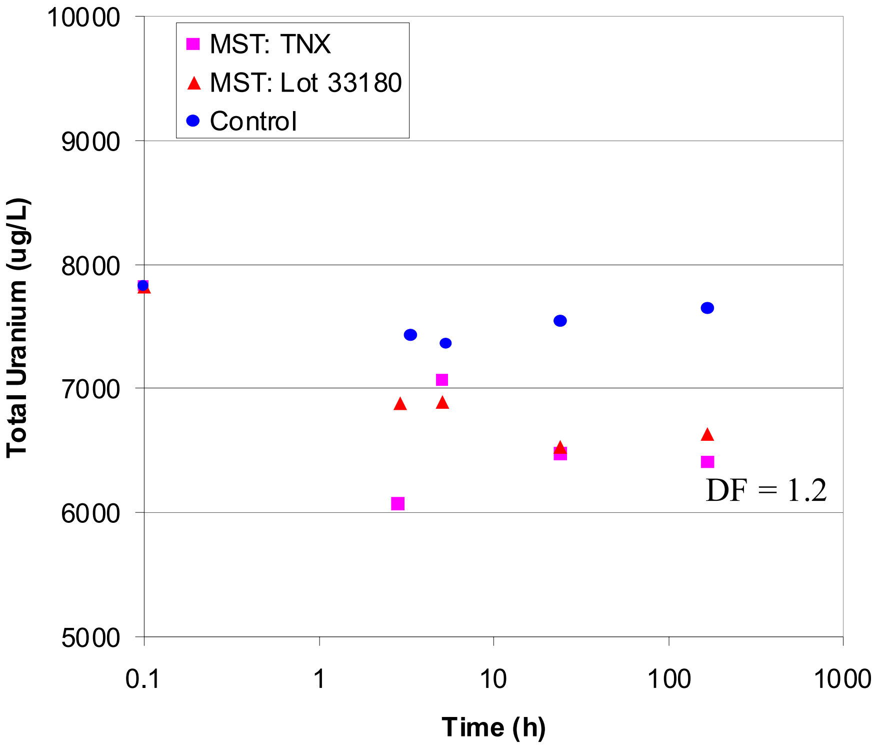


Figure 8. Concentration of U during the MST test with 5.6 M Na^+ solution



4.1.3 MST Treatment of 4.7 M Na^+ Solution

The purpose of this test was to provide a measure of the effect of mixing on MST treatment. Minimal information is available to assess the influence of mixing on sorbtion behavior. Comparison of the solvent extraction[9] and tetraphenylborate CSTR[8] demonstrations with actual waste showed a marked loss in efficiency as mixing performance decreased. Hence, we added this test to provide a more reliable examination of the influence of mixing.

Figures 9 - 12 provide the removal efficiency data for ^{90}Sr, total Pu, ^{237}Np, and total U, respectively, obtained by contacting with MST in a 4.7 M Na^+ solution. Appendix 3 contains numerical test data. Table 11 provides a summary of DFs for each of the

Table 11. Batch and continuous reaction DFs for MST with 4.7 M Na^+ solution

Test	^{90}Sr DF		Pu DF		^{237}Np DF		U DF	
	24 h	**168 h**	**24 h**	**168 h**	**24 h**	**168 h**	**24 h**	**168 h**
MST: TNX - Batch	23	39	7.1	5.9	> 1.5	4.1	1.5	1.5
MST: TNX - CSTR Demo[8] (steady state values)	46		155		not measured		2.4	

Figure 9. Concentration of ^{90}Sr during the MST test with 4.7 M Na$^+$ solution

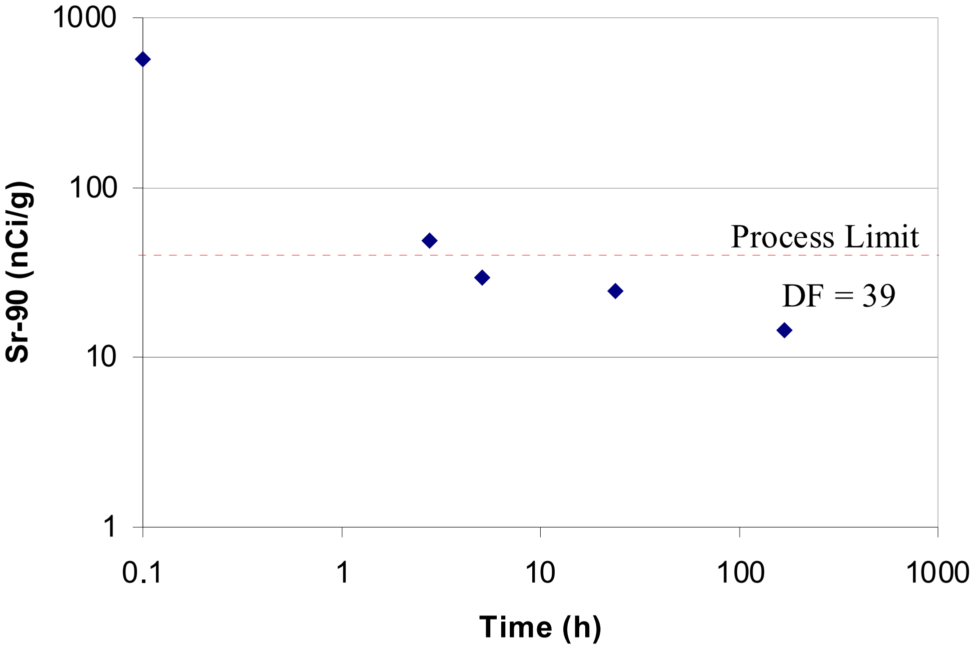


Figure 10. Concentration of Pu during the MST test with 4.7 M Na$^+$ solution

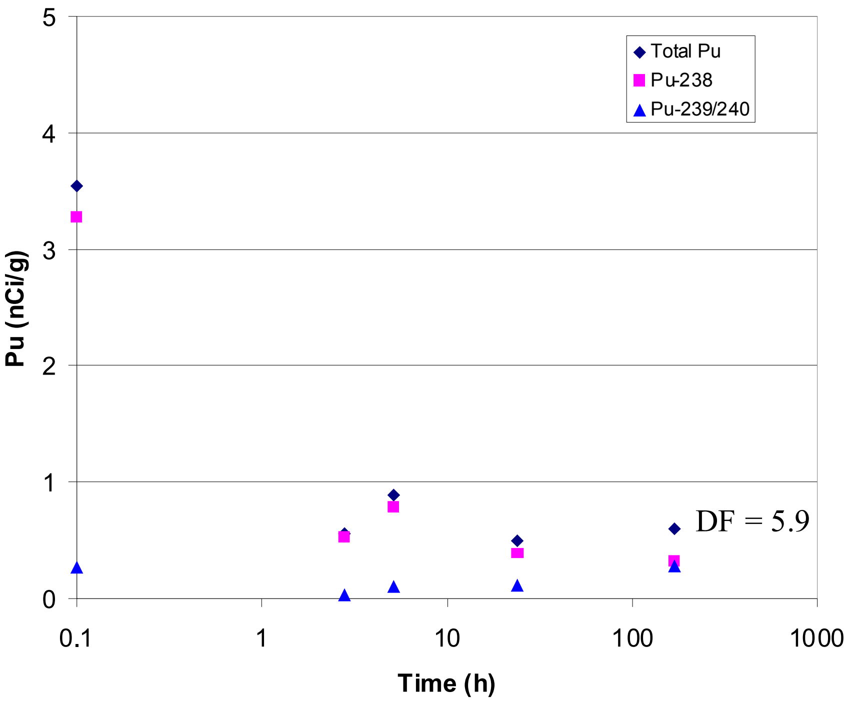


Figure 11. Concentration of ^{237}Np during the MST test with 4.7 M Na$^+$ solution

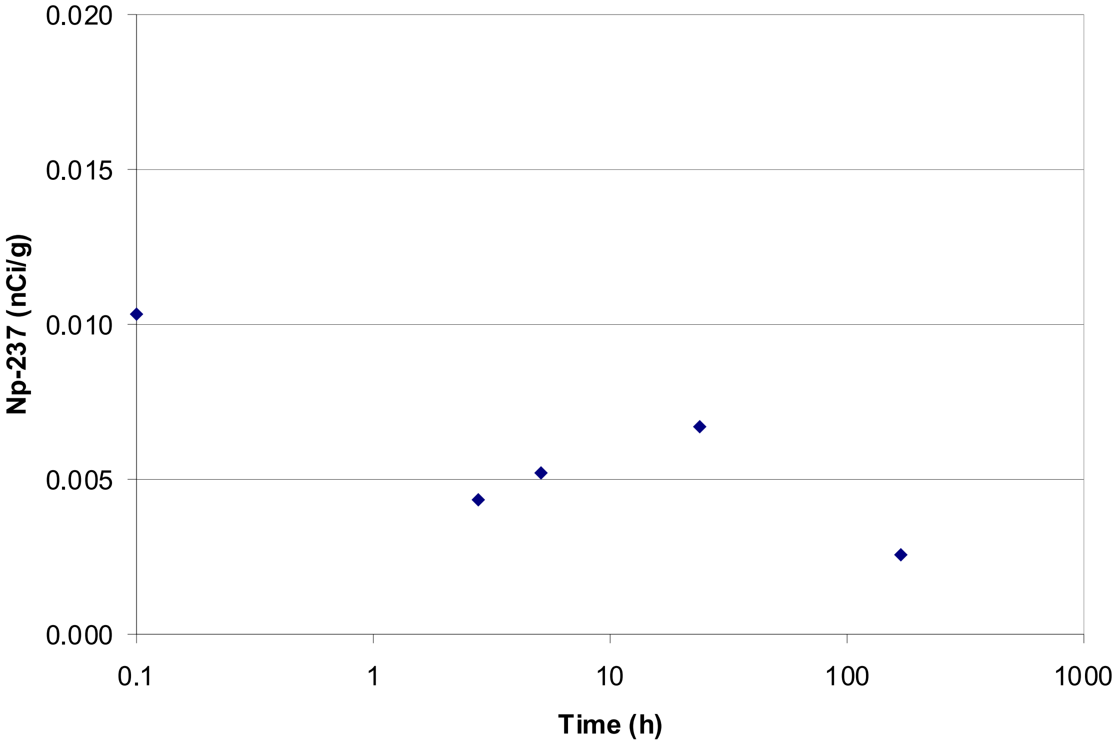
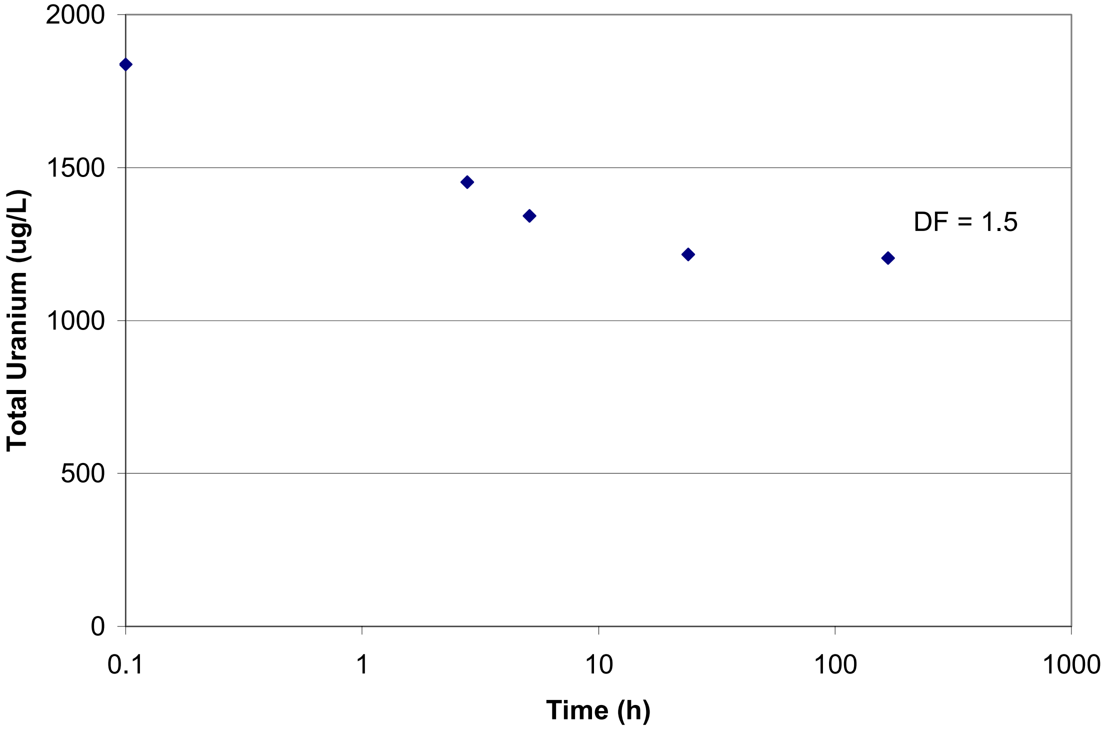


Figure 12. Concentration of U during the MST test with 4.7 M Na$^+$ solution



sorbates after 24 and 168 h of reaction. The table also provides data previously obtained from the Small Tank Tetraphenylborate Precipitation Actual Waste demonstration for comparison. Testing, in both cases, used the same waste salt solution.

Strontium decontamination in the current test satisfied the Saltstone WAC. The observed DF after 168 hours closely matched the steady state DF obtained in the CSTR demonstration. Plutonium and neptunium concentrations fell below the Saltstone WAC prior to the start of testing. The CSTR demonstration achieved significantly better Pu decontamination than observed in the current test. The earlier demonstration did not track Np removal efficiency. Uranium DF in the current test proved slightly poorer than observed in the continuous test. The data suggest that the different levels of agitation between the continuous precipitation process and that of the orbital shakers used in the current batch tests provided similar decontamination results (i.e., use of the orbital mixer in the current tests provided an adequate level of mixing).

4.1.4 Comparison of Treatment Options

The primary objective of this test program was to investigate the ability of freshly precipitated manganese oxide treatment to remove Sr, Pu, and Np to satisfactory levels. The performance of manganese oxide treatment relative to the current baseline process, MST adsorption, provides the most direct assessment. Table 12 compares the average DFs obtained from the Nominal Manganese tests with that of the two MST tests. Both test sets used the same waste solution, thereby negating concentration effects. The table contrasts the 24-h DFs since that sampling time matches the cycle time in the proposed facility. The comparison shows that Nominal Manganese provided superior ^{90}Sr decontamination while MST gave better Pu decontamination. Neptunium and uranium DFs proved nearly identical in both test sets. Since, neither MST nor manganese oxide treatments successfully achieved Pu and Np decontamination, we recommend further tests to determine the amount of added sorbent required in each process option to successfully treat this waste.

Table 12. Comparison of average 24 hour DFs for Nominal Manganese and MST with 5.6 M Na$^+$ solution

Test	^{90}Sr 24-h DF	Pu 24-h DF	^{237}Np 24-h DF	U 24-h DF
Nominal Manganese	64	1.7	1.9	1.1
MST	10.2	2.5	1.9	1.2

4.2 Second Generation Tests

4.2.1 MST Treatment

We conducted duplicate tests of MST treatment of actual waste. The tests consisted of three successive additions of 0.2 g/L MST to the waste. Appendix 4 and Figures 13 and 14 contain the concentration data obtained from the tests. The tests show good agreement between the data sets with both approaching the required level of decontamination for Saltstone disposal. The graphs also show DFs for the individual contacts. Table 13 contains the overall DF measurements. Even though the tests did not reach equilibrium, the DFs proved slightly better than those observed in the Initial Phase tests. The slightly increased DFs may be attributed to differences in starting concentration between the Initial Phase and Second Generation tests. A better comparative method for the two phases of testing would assess their loadings (i.e., µmole sorbate/g MST) versus the resulting solution concentration of the sorbate. Table 14 contains the loadings for both tests from both test phases. The behavior of both Pu and Np appears to follow classical adsorption theory (i.e., loading concentration is directly proportional with solution concentration). Insufficient data exists for uranium to assess whether it follows classical adsorption behavior.

Figure 13. Concentration of Pu during the Second Generation MST tests

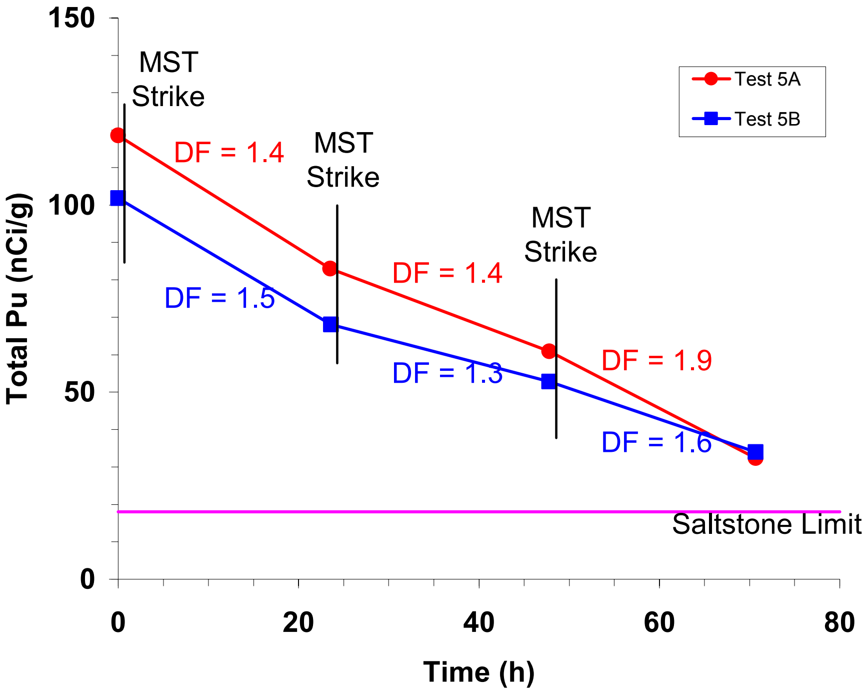


Figure 14. Concentration of Np during the Second Generation MST tests

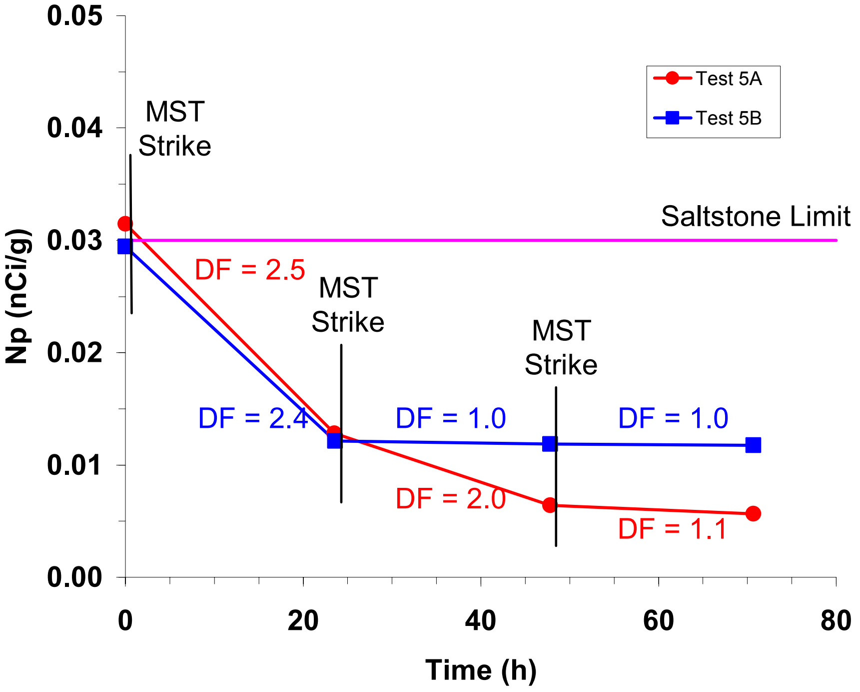


Table 13. DFs from Second Generation tests with MST

Test	Pu DF	^{237}Np DF	U DF
5A	3.7	3.6	1.1
5B	3.0	2.5	1.5

DF values were calculated from changes in concentration between the pre-test sample, T= 0 h, and the last sample obtained from each test.

Table 14. Actinide loadings on MST from both Second Generation and Initial Phase tests with MST

Test	Pu Loading[a] (µmole Pu/g MST)	^{237}Np Loading[a] (µmole Np/g MST)	U Loading[a] (µmole U/g MST)
5A – Initial Phase	2.44 (0.682)[b]	0.759 (0.341)	14.9 (26.9)
5B – Initial Phase	2.77 (0.551)	0.127 (0.315)	12.5 (27.9)
5A - 2nd Generation	0.725 (0.179)	0.317 (0.042)	2.51 (30.0)
5B - 2nd Generation	0.640 (0.165)	0.217 (0.0865)	16.8 (19.7)

[a] Loading values were obtained from changes in concentration between the pre-test sample, T= 0 h, and the last sample obtained from each test.

[b] Values in parentheses are the corresponding soluble actinide concentration (µmole/L). For the Second Generation tests, the values are not considered to be at equilibrium.

4.2.2 Manganese Oxide Treatment

We used residual material from the six Initial Phase manganese oxide tests for additional manganese oxide tests. Second Generation testing examined the reductant added (HCO_2^- vs. H_2O_2), removal of solids (in particular insoluble actinides), and the quantity of MnO_4^- or MST added. Appendix 4 contains actinide concentration data from the tests. Table 15 provide the overall DFs for Pu, Np, and U in each test. Again, DF is a concentration dependent measure best utilized for comparing test solutions with nearly identical composition and concentration. In these tests, the compositions and actinide concentrations remained similar, but not identical. Therefore, a comparison of DF permits some level of comparison but it should not be considered an exact judge of test effectiveness. The tests behaved as expected. Tests utilizing 0.02 M MnO_4^- produced the largest DFs for both Pu and Np, as shown graphically in Figures 15 - 18. Testing did not demonstrate the same behavior for U. As a whole, little difference existed in the DF for those tests comparing H_2O_2 to HCO_2^- as the reductant. Removal of insoluble actinides by filtration did not significantly increase the resulting solution DF values.

Table 15. DFs from Second Generation manganese oxide tests

Test	Pu DF	^{237}Np DF	U DF	Test Parameters MnO_4^- (M)	Type of Reductant	Filtered
2A	1.5	0.8	1.1	0.01	H_2O_2	yes
2B	4.9	1.4	0.9	0.02	H_2O_2	yes
3A	2.6	1.3	0.9	0.02	H_2O_2	no
3B	2.9	1.6	1.2	0.02	HCO_2^-	no
4A	1.3	1.1	1.1	0.01	H_2O_2	no
4B	1.5	1.0	1.2	0.01	HCO_2^-	no

DF values were calculated from changes in concentration between the pre-test sample, T= 0 h, and the last sample obtained from each test.

Table 16 presents relevant actinide data from both the Initial and Second Generation Phase manganese oxide tests. Figures 19 – 21 graphically display the data with the tests identified as either having or not having Sr added. All Second Generation tests as well as two of the six Initial Phase tests occurred without adding Sr. For Pu, a trend appears showing increasing Pu removed with increased MnO_4^- addition. Whether the addition of Sr affects the amount removed remains uncertain given the scatter in the data. Figure 20 appears to demonstrate that Np removal depends upon the addition of Sr, although the data shows significant scatter. Figure 21 indicates minimal, if any, removal of U upon MnO_4^- addition regardless of whether we added Sr. Freshly precipitated manganese oxide may remove actinides from solution by one or more mechanisms. Presumably, the two most viable pathways are co-precipitation or adsorption, with the former being most likely under the conditions employed in these tests (i.e., significantly greater concentration of MnO_4^- relative to the actinide concentrations and fairly rapid reduction, especially in the cases using H_2O_2). The quantity of actinide removed should increase with increasing added MnO_4^- (or manganese solids formed from the MnO_4^- upon reduction) if co-precipitation occurs.

Figure 15. Concentration of Pu during Second Generation manganese oxide tests with HCO_2^- as the reductant

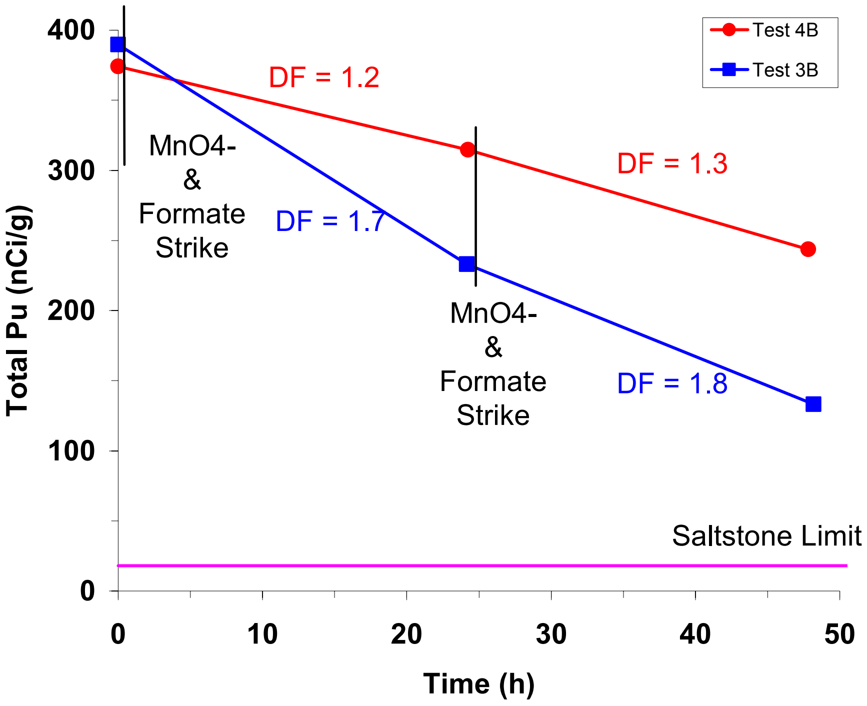


Figure 16. Concentration of Np during Second Generation manganese oxide tests with HCO_2^- as the reductant

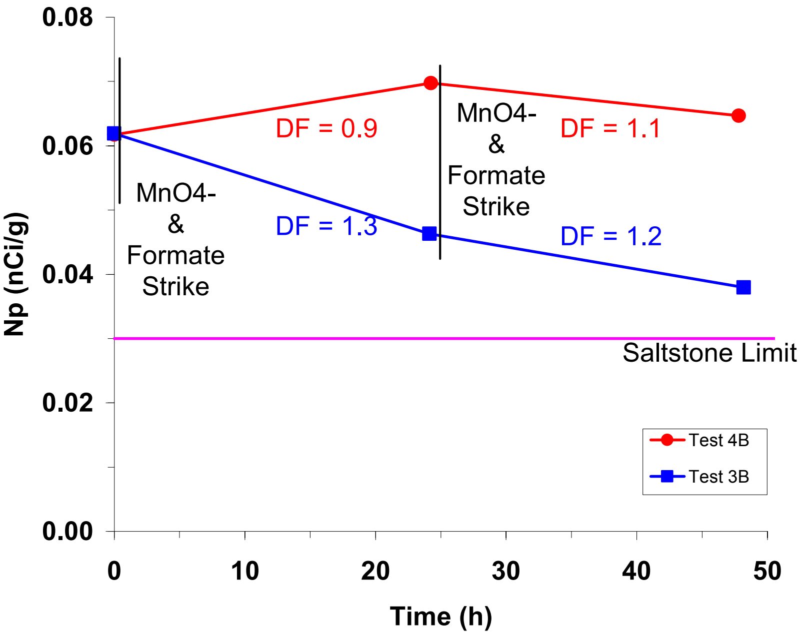


Figure 17. Concentration of Pu during Second Generation manganese oxide tests with filtered waste and H_2O_2 as the reductant

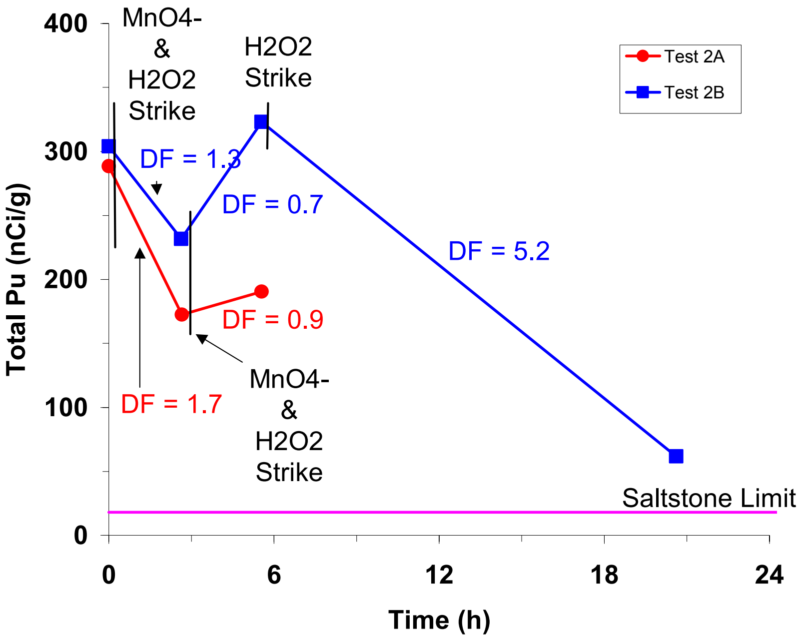


Figure 18. Concentration of Np during Second Generation manganese oxide tests with filtered waste and H_2O_2 as the reductant

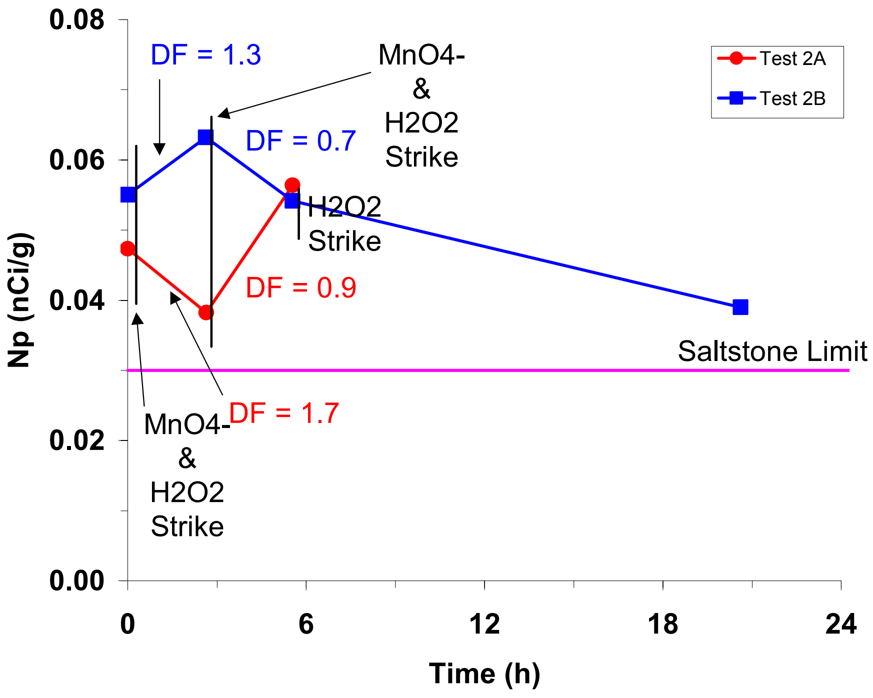


Table 16. Total actinides removed from both Initial Phase and Second Generation manganese oxide tests

Test	Theoretical MnO_2 Solid Formed (g)	Pu Removed (µmole Pu)	^{237}Np Removed (µmole Np)	U Removed (µmole U)
2A – Initial Phase	0.1043	0.087	0.030	0.322
2B – Initial Phase	0.1043	0.075	0.040	0.479
3A – Initial Phase	0.0209	0.047	0.015	0.180
3B – Initial Phase	0.0209	0.042	0.015	0.256
4A – Initial Phase	0.1043	0.000	0.014	0.109
4B – Initial Phase	0.1043	-0.039	0.012	0.263
2A - 2nd Generation	0.1374	0.039	-0.005	0.200
2B - 2nd Generation	0.2573	0.104	0.009	-0.321
3A - 2nd Generation	0.2747	0.098	0.008	-0.415
3B - 2nd Generation	0.2678	0.111	0.014	0.402
4A - 2nd Generation	0.1269	0.051	0.003	0.306
4B - 2nd Generation	0.1391	0.068	-0.002	0.412

Values were obtained from changes in concentration between the pre-test samples, T= 0 h, and the last sample obtained from each test (in the case of the second generation) or the 24 h sample (in the case of the Initial Phase tests).

Figure 19. Total Pu removed from both Initial Phase and Second Generation manganese oxide tests

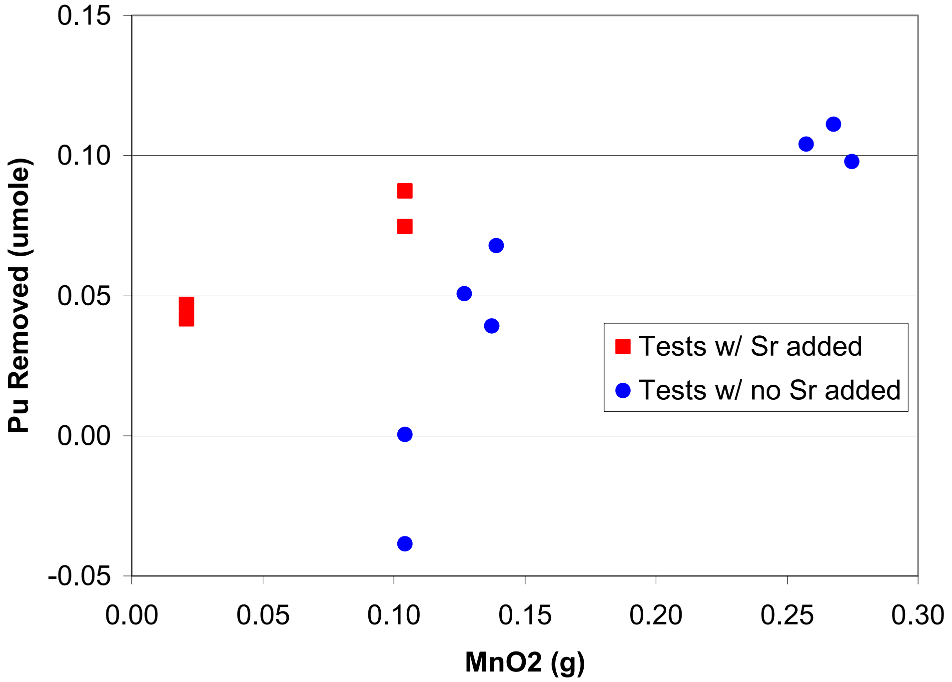


Figure 20. Total Np removed from both Initial Phase and Second Generation manganese oxide tests

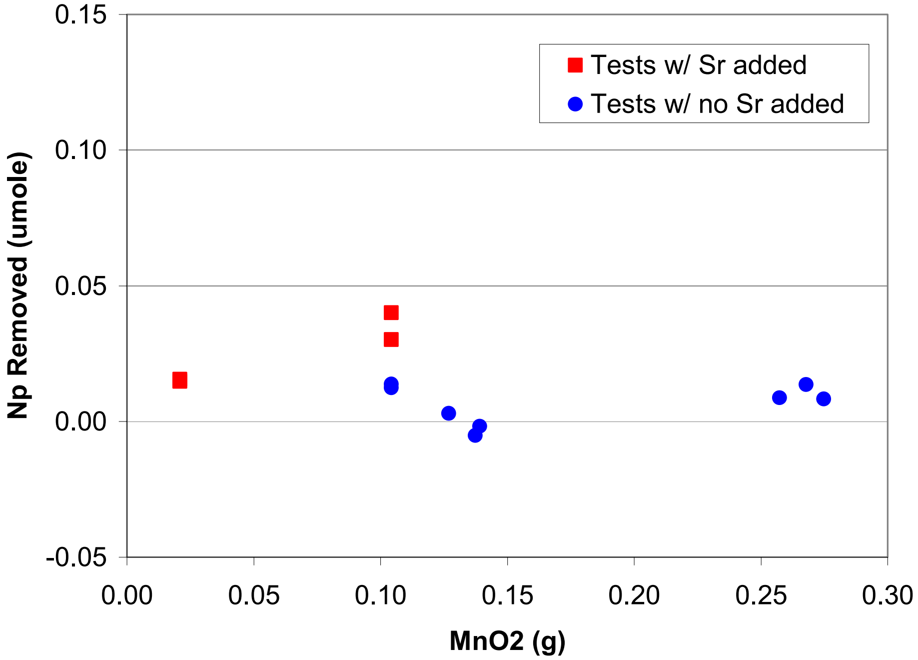
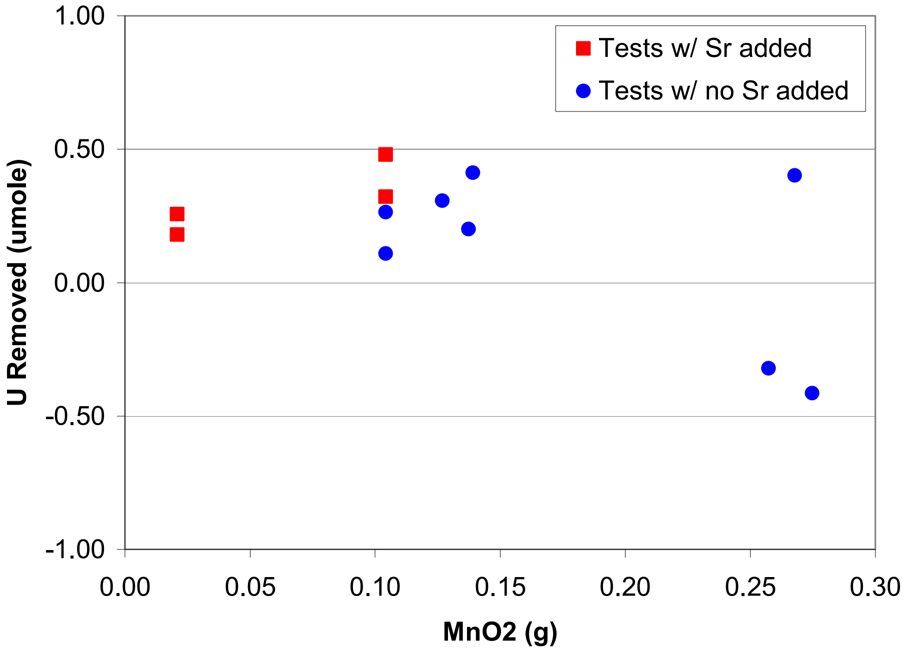


Figure 21. Total U removed from both Initial Phase and Second Generation manganese oxide tests



The data and its analysis presented in the section on Second Generation testing requires further comparison with other existing data sets and additional testing to adequately understand the behavior of the actinide species with these treatment methods. That work continues at this time.

5.0 Conclusions and Recommendations

The authors investigated the performance of freshly precipitated manganese oxide and MST for the removal of Sr and actinides from actual high-level waste. Testing occurred in two phases. Initial Phase tests examined three manganese oxide treatment options: Nominal Manganese (sequential addition of 0.01 M non-radioactive Sr, 0.01 M MnO_4^-, and 0.045 M HCO_2^-), Low Manganese (sequential addition of 0.01 M non-radioactive Sr, 0.002 M MnO_4^-, and 0.009 M HCO_2^- to yield a lower solids concentration), and Manganese without Strontium (sequential addition of 0.01 M MnO_4^- and 0.045 M HCO_2^- only). Results indicated the following.

- All three manganese oxide treatment options reduced the ^{90}Sr concentration below the Saltstone Waste Acceptance Criteria (WAC). In these tests, the use of non-radioactive Sr to provide isotopic dilution provided no significant advantage in kinetics or ultimate capacity for Sr removal in the treatment of actual wastes.
- Comparison MST tests also reduced the ^{90}Sr concentration below the Saltstone WAC.
- Under the conditions tested (i.e., high Pu concentration), all three manganese oxide treatment options proved unsuccessful in reducing the Pu activity below the Saltstone WAC. The Nominal Manganese option provided the best level of decontamination within 24 hours of treatment.
- The addition of non-radioactive Sr for isotopic dilution of Sr appeared to enhance Pu removal. The data set is not sufficient to fully evaluate this observation.
- The MST tests, like manganese oxide, also proved unsuccessful in decontaminating Pu to the required concentration. Under the conditions tested, MST proved slightly more effective than manganese oxide in reducing the Pu concentration.
- Neptunium decontamination appeared roughly equivalent for both treatment methods with both methods failing to achieve the WAC.
- The poor decontamination performance observed in both manganese oxide and MST treatments likely resulted due to the increased concentrations of Pu present in the waste. Increased levels of either MST or MnO_4^- are required to achieve the required level of decontamination.

Personnel conducted the Second Generation phase tests based upon a recommendation from the Initial Phase test findings. These tests again examined both MST and manganese oxide treatment options. Freshly precipitated manganese oxide tests varied the amount of MnO_4^- added, the reductant used (i.e., H_2O_2 versus HCO_2^-), and removal of the insoluble actinides present in the initial phase of testing. Results and conclusions obtained from the additional tests include the following.

- Increasing the amount of MnO_4^- added led to an increase in the quantity of Pu and Np removed. Uranium did not behave with the same correlation.

- Co-precipitation (and not adsorption) seems the predominate mechanism for Pu and Np removal in freshly precipitated manganese oxide tests.
- The removal of Np in manganese oxide tests may correlate with the addition of Sr at the start of the tests. The data is less conclusive for Pu.
- The use of H_2O_2, rather than HCO_2Na, as a reductant did not significantly improve the ultimate removal of actinides in the manganese oxide tests but did complete the reaction much faster.
- Plutonium and neptunium removal via MST appears to follow classical adsorption theory. Insufficient data exists to ascertain the adsorption model that best fits the data.

Analysis of the data continues. The authors will compare the data from these tests with those from earlier experiments using simulated wastes to provide insights as to consistency of performance and the removal mechanism for each treatment option. Such analysis begins the effort to develop a predictive model for the process efficiency at removing the targeted radionuclides. Recommendations for additional testing will result from that comparison.

6.0 Quality Assurance

Personnel prepared non-radioactive solutions from reagent grade chemicals using calibrated balances checked daily before use.[13] The weights used for balance checks received calibration by the SRTC Standards Laboratory. Personnel verified the accuracy of glassware and pipettes used to measure volumes by gravimetric methods using water as a standard.[14] All measurement and test equipment (M&TE) used in this task received calibration or verification for accuracy prior to their use. The Analytical Development Section performed all chemical and radiochemical analyses per approved analytical methods.[15]

The following documents govern the work reported in this document.

- D. T. Hobbs, T. B. Peters, M. J. Barnes, M. C. Duff and K. M. Marshall, “Task Technical and Quality Assurance Plan for FY01 Strontium and Actinide Removal Testing,” WSRC-RP-2001-00188, Rev. 1, July 31, 2001.

- Savannah River Site Salt Processing Project Research and Development Program Plan, PNNL-13253, Rev. 1, November 2000.

- Notebook WSRC-NB-2001-00168 (M. J. Barnes) contains the experimental data obtained from this work.

7.0 References

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[1] D. T. Hobbs and D. D. Walker, “Plutonium and Uranium Adsorption on Monosodium Titanate (U),” WSRC-RP-92-93, August 13, 1992.

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Appendix 1. Composition of diluted 5.6 M Na^+ actual high-level waste

Analytical Method	Analyte	Units	Soluble Concentration	Total Concentration
Titration	hydroxide	M	3.7	Not measured
IC	nitrate	M	0.864	Not measured
IC	nitrite	M	0.584	Not measured
IC	sulfate	M	0.004	Not measured
IC	chloride	M	0.005	Not measured
IC	formate	M	< 0.03	Not measured
IC	oxalate	M	< 0.01	Not measured
Titration	carbonate	M	< 0.2	Not measured
Titration	aluminate	M	< 0.2	Not measured
AA	sodium	M	5.38	Not measured
AA	potassium	M	0.041	Not measured
ICP-ES	Al	mg/L	6069	6054
ICP-ES	B	mg/L	78.9	78.5
ICP-ES	Cr	mg/L	104	102
ICP-ES	Fe	mg/L	17	56.7
ICP-ES	Mg	mg/L	< 2	< 2
ICP-ES	Mn	mg/L	< 2	2.31
ICP-ES	Mo	mg/L	88.8	91.6
ICP-ES	Na	M	5.79	5.77
ICP-ES	P	mg/L	233	211
ICP-ES	Si	mg/L	156	137
ICP-ES	Zn	mg/L	9.68	10.3
Gamma	^{137}Cs	dpm/mL	1.89E+09	Not measured
PuTTA	^{238}Pu	dpm/mL	6.43E+05	2.26E+06
PuTTA	$^{239/240}Pu$	dpm/mL	1.85E+05	6.41E+05
^{90}Sr	^{90}Sr	dpm/mL	4.20E+05	1.71E+06
ICP-MS	Mass 232	ug/L	217.6	158.6
ICP-MS	Mass 234	ug/L	38.10	44.77
ICP-MS	Mass 235	ug/L	84.65	105.7
ICP-MS	Mass 236	ug/L	44.43	42.76
ICP-MS	Mass 237	ug/L	153.0	137.4
ICP-MS	Mass 238	ug/L	7653	7961
ICP-MS	Mass 239	ug/L	< 18	40.94
ICP-MS	Mass 240	ug/L	371.5	1088
ICP-MS	Mass 241	ug/L	< 18	154.46
ICP-MS	Mass 242	ug/L	< 18	70.57
ICP-MS	Mass 243	ug/L	30.44	3236
ICP-MS	Mass 244	ug/L	< 18	676.8
ICP-MS	Mass 245	ug/L	< 18	42.29
ICP-MS	Mass 246	ug/L	< 18	39.23

Appendix 2. Composition of diluted 4.7 M Na^+ actual high-level waste

Analytical Method	Analyte	Units	Soluble Concentration	Total Concentration
Titration	Hydroxide	Molar	3.5	not measured
IC	Nitrate	mg/L	0.854	not measured
IC	Nitrite	mg/L	0.605	not measured
IC	Sulfate	mg/L	0.006	not measured
IC	Halides	mg/L	0.003	not measured
IC	Formate	mg/L	< 0.03	not measured
IC	Oxalate	mg/L	< 0.01	not measured
Titration	Carbonate	Molar	< 0.2	not measured
Titration	Aluminate	Molar	< 0.2	not measured
AA	Sodium	Molar	4.96	not measured
AA	Potassium	Molar	0.031	not measured
ICP-ES	Al	mg/L	6672	6661
ICP-ES	B	mg/L	69.1	73.2
ICP-ES	Cr	mg/L	134	137
ICP-ES	Fe	mg/L	31.7	19.4
ICP-ES	Mg	mg/L	< 2	< 2
ICP-ES	Mn	mg/L	< 2	< 2
ICP-ES	Mo	mg/L	95.6	106
ICP-ES	Na	M	4.86	4.75
ICP-ES	P	mg/L	234	243
ICP-ES	Si	mg/L	158	177
ICP-ES	Zn	mg/L	5.85	6.26
Gamma	^{137}Cs	dpm/mL	2.53E+09	not measured
PuTTA	^{238}Pu	dpm/mL	8.72E+03	8.18E+03
PuTTA	$^{239/240}Pu$	dpm/mL	7.07E+02	4.83E+03
^{90}Sr	^{90}Sr	dpm/mL	1.52E+06	1.69E+06
ICP-MS	Mass 232	ug/L	93.48	62.60
ICP-MS	Mass 234	ug/L	29.35	31.65
ICP-MS	Mass 235	ug/L	86.47	119.0
ICP-MS	Mass 236	ug/L	48.66	64.77
ICP-MS	Mass 237	ug/L	< 18	< 28
ICP-MS	Mass 238	ug/L	1673	1581
ICP-MS	Mass 239	ug/L	< 18	< 28
ICP-MS	Mass 240	ug/L	< 18	73.92
ICP-MS	Mass 241	ug/L	< 18	< 28
ICP-MS	Mass 242	ug/L	< 18	< 28
ICP-MS	Mass 243	ug/L	< 18	< 28
ICP-MS	Mass 244	ug/L	< 18	< 28
ICP-MS	Mass 245	ug/L	< 18	< 28
ICP-MS	Mass 246	ug/L	< 18	< 28

Appendix 3. Initial Phase testing sorbate data tables

Test 1: Control

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
3.4	208.6	59.6	268.20	153.3	0.08389	7430
5.4	211.2	62.4	273.57	148.8	0.06901	7354
24.0	226.9	64.6	291.53	156.7	0.08788	7546
168.3	279.7	79.6	359.34	160.1	0.08298	7642

Test 2A: Nominal Manganese

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
3.1	154.5	41.8	196.27	3.5	0.08490	6428
5.2	147.3	44.8	192.08	3.4	0.09464	7550
24.0	135.5	38.1	173.65	2.6	0.05363	7181
168.2	257.3	70.8	328.11	1.9	0.06326	11256

Test 2B: Nominal Manganese

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
3.2	162.7	51.3	213.99	4.0	0.09091	6287
5.2	143.7	41.6	185.28	3.2	0.09518	7395
24.0	147.4	42.5	189.84	2.3	0.04242	6869
168.3	196.9	58.1	255.05	1.9	0.04304	7221

Test 3A: Low Manganese

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
2.9	235.2	67.1	302.28	4.0	0.08368	6208
5.0	235.7	62.5	298.23	2.5	0.09382	7618
23.9	177.0	52.0	229.02	2.0	0.07016	7463
168.1	248.9	77.9	326.75	1.5	0.05560	7116

Test 3B: Low Manganese

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
3.0	213.9	54.7	268.64	2.5	0.09950	7356
5.1	223.9	63.1	287.03	2.5	0.09448	7806
23.9	186.6	53.7	240.29	2.1	0.07109	7312
168.1	257.5	70.3	327.80	1.7	0.06086	7986

Test 4A: Manganese without Strontium

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
2.9	215.8	61.8	277.60	1.3	0.10728	7449
5.0	219.8	64.0	283.72	1.3	0.10102	7815
23.9	235.7	67.7	303.43	1.5	0.07221	7604
168.0	280.2	85.9	366.12	1.4	0.06483	7800

Test 4B: Manganese without Strontium

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
3.3	291.4	82.9	374.26	1.3	0.10620	6622
5.3	261.8	72.2	334.01	1.5	0.12186	7955
24.0	278.8	81.0	359.83	1.8	0.07374	7298
168.3	306.9	83.7	390.61	2.0	0.06299	7824

Test 5A: MST: Lot TNX

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
2.9	111.5	35.8	147.30	17.0	0.04619	6067
5.1	106.0	31.7	137.70	12.5	0.04637	7070
24.0	92.9	26.9	119.76	14.4	0.04729	6480
168.1	101.2	27.8	128.99	13.1	0.04635	6402

Test 5B: MST: Lot 33180

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	235.4	67.9	303.27	153.7	0.08771	7820
2.9	134.5	36.4	170.94	21.7	0.05430	6878
5.1	115.1	33.4	148.52	14.8	0.04332	6892
24.0	98.2	27.2	125.39	15.8	0.04360	6524
168.1	75.0	22.6	97.57	14.9	0.04276	6632

Test 6: MST: Lot TNX (4.7 M Na^+)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{90}Sr (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0	3.28	0.27	3.54	569.2	0.01031	1837
2.8	0.53	0.03	0.56	48.7	0.00434	1452
5.1	0.79	0.11	0.89	29.4	0.00519	1343
24.0	0.38	0.12	0.50	24.6	0.00670	1216
168.0	0.32	0.28	0.60	14.5	0.00254	1204

Duff's Manganese Oxide Test #2[11]

Time (h)	$^{239/240}$Pu (ug/L)	^{85}Sr (ng/L)	^{237}Np (ug/L)	Total U (ug/L)
0	181	1.108	423	10880
4.6	43.2	0.082	365	8952
24.7	52.1	0.014	359	8545
166.1	19.7	0.009	303	9244

Appendix 4. Second Generation testing sorbate data tables

Test 2A: 0.01 M MnO_4^- with H_2O_2 (filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	226.1	62.2	288.4	0.0473	8222
2.6	134.8	37.5	172.3	0.0382	7977
5.5	148.4	42.1	190.5	0.0564	7620

Test 2B: 0.02 M MnO_4^- with H_2O_2 (filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	233.4	70.6	304.0	0.0550	8026
2.6	180.2	51.5	231.6	0.0632	10009
5.6	247.7	75.4	323.0	0.0541	7658
20.6	48.6	13.0	61.6	0.0390	9059

Test 3A: 0.02 M MnO_4^- with H_2O_2 (not filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	287.7	82.3	370.1	0.0657	8079
2.3	319.6	87.7	407.3	0.0830	7888
5.5	407.3	110.3	517.6	0.0872	7219
20.3	442.8	136.2	579.0	0.1424	10311
22.9	416.0	121.1	537.1	0.1223	9216
23.1	108.5	31.8	140.3	0.0516	9330

Test 3B: 0.02 M MnO_4^- with HCO_2^- (not filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	299.4	90.2	389.7	0.0619	8317
24.2	184.3	48.8	233.1	0.0463	9425
48.2	101.8	31.2	133.0	0.0380	7076

Test 4A: 0.01 M MnO_4^- with H_2O_2 (not filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	258.5	82.2	340.7	0.0693	8553
2.3	138.8	39.7	178.5	0.0409	7156
5.4	199.3	53.4	252.7	0.0637	7555

Test 4B: 0.01 M MnO_4^- with HCO_2^- (not filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	283.5	90.5	374.0	0.0617	8395
24.3	241.7	72.7	314.5	0.0697	7823
47.8	188.0	55.6	243.6	0.0647	7170

Test 5A: 0.2 g/L MST (not filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	93.6	25.0	118.6	0.0315	7501
23.5	62.4	20.6	83.0	0.0128	10546
47.8	47.7	13.1	60.9	0.0064	5966
70.7	25.0	7.3	32.3	0.0057	7142

Test 5B: 0.2 g/L MST (not filtered prior to testing)

Time (h)	^{238}Pu (nCi/g)	$^{239/240}$Pu (nCi/g)	Total Pu (nCi/g)	^{237}Np (nCi/g)	Total U (ug/L)
0.0	79.4	22.4	101.8	0.0294	7100
23.6	53.0	15.1	68.0	0.0121	6097
47.8	40.7	12.1	52.8	0.0119	5571
70.7	27.3	6.7	34.0	0.0117	4696