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Key Words:
MST
Actinides
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Demonstration of MST Efficacy on Removal of Actinides and Strontium in "Bounding Alpha" Waste

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List of Abbreviations

ADS	Analytical Development Section
AMP	Ammonium Molybdophosphate
DF	Decontamination Factor (= starting concentration/ending concentration)
DL	Detection Limit
DU	Depleted Uranium
HLW	High Level Waste
MnO_4^-	Permanganate
MST	Monosodium Titanate
Np	Neptunium
Pu	Plutonium
PuTTa	Plutonium triphenoyltrifluoroacetone extraction
RADICPMS	Radiological inductively coupled plasma mass spectrometry
SRTC	Savannah River Technology Center
SWPF	Salt Waste Processing Facility
U	Uranium
WAC	Waste Acceptance Criteria
WPTS	Waste Processing Technology Section

1.0 Executive Summary

Previous work at SRS identified five macrobatches of waste projected to fail to meet removal requirements for total alpha after treatment with monosodium titanate (MST) at the baseline conditions proposed for the Salt Waste Processing Facility (SWPF). This document describes an experimental demonstration that examined removal of strontium and alpha emitting radionuclides from a composite of several tanks present in the most limiting macrobatches. The work investigated the amount of MST needed to treat this "bounding alpha" macrobatch composite such that the separated liquid can meet the Salt Waste Processing Facility limits. The experiments show the following results.

- Plutonium removal behavior gives Decontamination Factor (DF) that agreed well with pre-test expectations.

- Plutonium removal to meet current SWPF requirements for this "bounding" waste requires 1.2 g/L (i.e., 3X the baseline) MST.

- Alpha decontamination using 1.2 g/L of MST would meet the proposed new Saltstone Waste Acceptance Criteria (WAC).

- Strontium removal met the current SWPF specification with the baseline treatment using 0.4 g/L MST.

- Neptunium was sufficiently removed to meet the SWPF requirement using 0.4 g/L MST.

- Uranium removal increased with increasing MST concentration. Uranium removal is not a factor in meeting the SWPF limits on total alpha.

2.0 Introduction

In the last 10 years, SRTC personnel studied the ability of MST to sorb a variety of elements, such as Sr, Np, U, and Pu. Previous work at SRTC examined the specifics of MST sorption.[1,2,3,4,5,6,7,8,9,10] During FY01, personnel developed the projected blending plan for the facility defining 67 macrobatches and estimated MST performance for removing Sr and Pu from these batches.[11] The projections identified five batches – SPT-002, SPT-008, SPT-065, SPT-066, and SPT-067 – for which a single addition of MST at 0.4 g/L may not meet process objectives at the proposed operating conditions. The two most limiting macrobatches, SPT-008 and SPT-066, consist of waste blended from Tanks 21H, 26F, 33F, and 39H. The customer requested that SRTC experimentally determine

whether or not MST could meet performance requirements with these bounding wastes.[12,13]

Personnel obtained and analyzed samples from these four tanks. Analyses for macrobatch SPT-008 did not prove the most limiting as shown in the following section. Hence, the management team opted to proceed with a demonstration using a composite of all the samples. To this composite, researchers added MST at three intervals and monitored removal of strontium and actinides as a function of time.

3.0 Experimental Detail

We received salt solution from Tanks 21H, 26F, 33F, and 39H. We analyzed each of these tank wastes for the pertinent radioisotopes (Appendix 1). After analyses, the researchers consulted with the management team. The team, along with the consent of the customer, decided to combine all four of the salt solutions (except for archival samples) into a single composite. From the measurements of the individual tank samples, the composite was estimated to be at 5.6 M sodium; no dilution or concentration was required. At the time, activity estimates of the composite indicated that the composite would prove more challenging than the most limiting macrobatch, SPT-008. After combining the salt solutions, the researchers analyzed the composite at two times over a period of two weeks ("Composite 1 week" and "Composite 2 week") to ensure that the actinides and strontium equilibrated after mixing. Although the results between the two different times differed somewhat, the researchers judged that the actinides and strontium had equilibrated. Table 1 lists the activities of the macrobatches and the composites.

Table 1. Radioisotope Concentration in Each of the Salt Solutions.

Sample	^{238}Pu nCi/g	$^{239/240}$Pu nCi/g	^{90}Sr nCi/g	^{237}Np nCi/g	$^{235/238}$U nCi/g	Total Alpha nCi/g
Est .Macrobatch SPT-008	8.29	1.20	2.29E+02	< 8.98E-02	0.00330	9.49
Est. Macrobatch SPT-066	6.67E+02	1.27E+01	1.14E+03	< 4.73E-01	3.70E-03	679
Est. Composite	3.87E+02	8.03E+00	7.59E+02	< 3.01E-01	3.95E-03	395
Composite 1 week	6.37E+02	9.13E+00	2.11E+03	< 3.95E-01	4.70E-03	646
Composite 2 week	3.72E+02	3.85E+00	3.85E+02	< 3.99E-01	2.91E-03	376
Time 0 Control	4.78E+02	1.22E+01	4.15E+02	5.90E-02	3.90E-03	490

We measured the activities in each case, except in the "macrobatch" entries. In that case, we calculated the activities using our measured values where available, and measured values from the High Level Waste System Plan.[15] See Appendix 2 for details.

The SRTC estimates of the activities of each of the radioisotopes in the composite turned out to be reasonably close to the measured values by the time of the third (Time = 0 Control) sample. Differences were most likely due to complex actinide and strontium chemistry (dissolution and precipitation during mixing and equilibrium) occurring between soluble and insoluble species.

After preparing the composite, technicians dispensed 100 mL each into three 125-mL polyethylene bottles. We used two of the bottles to conduct the MST experiments, while one bottle served as a control. We added 0.4 g/L of MST (from lot 33180) to the two reaction bottles at intervals of 0, 30, and 54 hours. During the experiment, personnel collected samples from each of the three bottles at 0, 4, 24, 30, 54, and 78 hours. (For samples at 0, 30, and 54 hours, sampling occurred immediately prior to MST addition.) Throughout the course of the experiment, the bottles were agitated using a magnetic stir plate and stir bars.

Technicians filtered the samples using 0.45 μm syringe filters, diluted them with acid, removed them from the cells for analysis, and analyzed for uranium, neptunium (RADICPMS), plutonium (PuTTa), and strontium (Beta scintillation).

4.0 Results of Investigations

4.1 Plutonium Results

Researchers analyzed the filtered solutions for total plutonium ($^{238}Pu + {}^{239/240}Pu$). Table 2 shows these plutonium results while Figure 1 shows the graphical results.

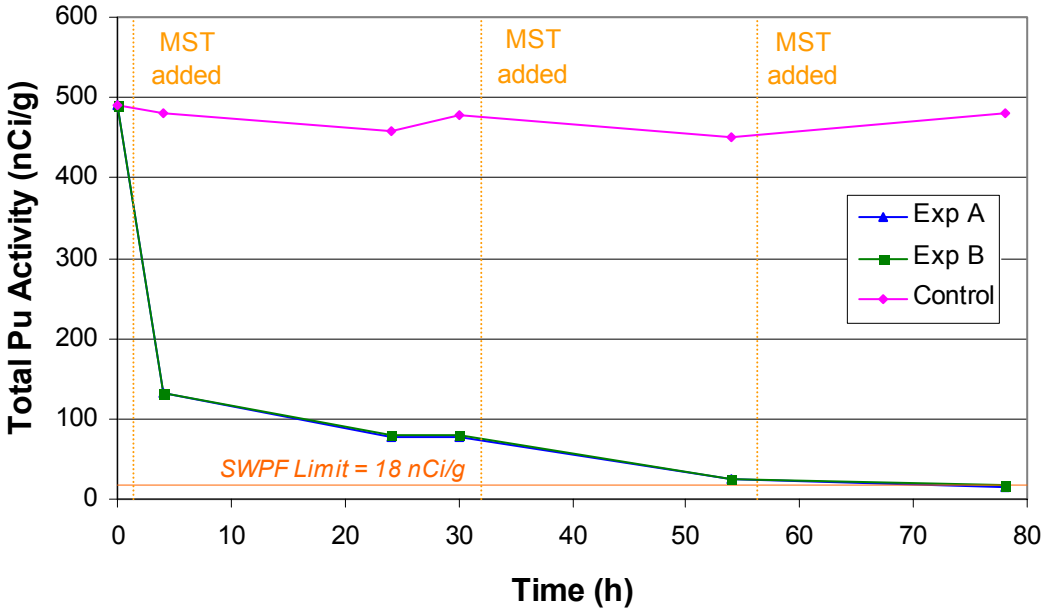
Table 2. Total Plutonium concentrations In the Filtrate.

	Experiment A	Experiment B	Exp. A/B	Control
Time (hours)	Total Pu (nCi/g)	Total Pu (nCi/g)	Standard Dev.	Total Pu (nCi/g)
0*	490	490	NA	490
4	132	133	0.489	481
24	77.2	79.3	1.50	458
30	77.2	78.7	1.05	478
54	23.8	< 25.9	NA	451
78	14.9	< 16.5	NA	481

*The time = 0 data are the same data point.

The data from the duplicate reactions compared quite well**.** Figure 1 plots the total plutonium data for the two duplicate experiments and the control over time. Figure 1 also shows the Salt Waste Processing Facility process requirement for total alpha

Figure 1. Total Plutonium in Solution Over Time.



removal (18 nCi/g). As this experiment involved three MST consecutive strikes, we can calculate a stepwise DF value for each addition. Table 3 lists the DF values after each strike. As one would expect, increasing MST addition brings diminishing returns.

Table 3. Total Plutonium Decontamination Factors After Each MST Addition.

Time After MST addition	Total Hours	DF Value, Exp. A	DF Value, Exp. B	Average DF
30	30	6.3	6.2	6.2
24	54	3.0	2.9	2.9
24	78	1.7	1.6	1.6

From the plutonium data we note that by 24 hours after the third MST strike, the total plutonium in solution fell below the SWPF total alpha limits of 18 nCi/g. If regulatory approval occurs for the proposed new Saltstone WAC the total alpha limit will increase to 99 nCi/g. If this is the case, our data shows that within 24 hours of a single MST strike, the total alpha would fall within the revised WAC limits.

4.2 Strontium Results

Researchers analyzed the filtered solutions for strontium-90. Table 4 shows the numerical values while Figure 2 shows the graphical results.

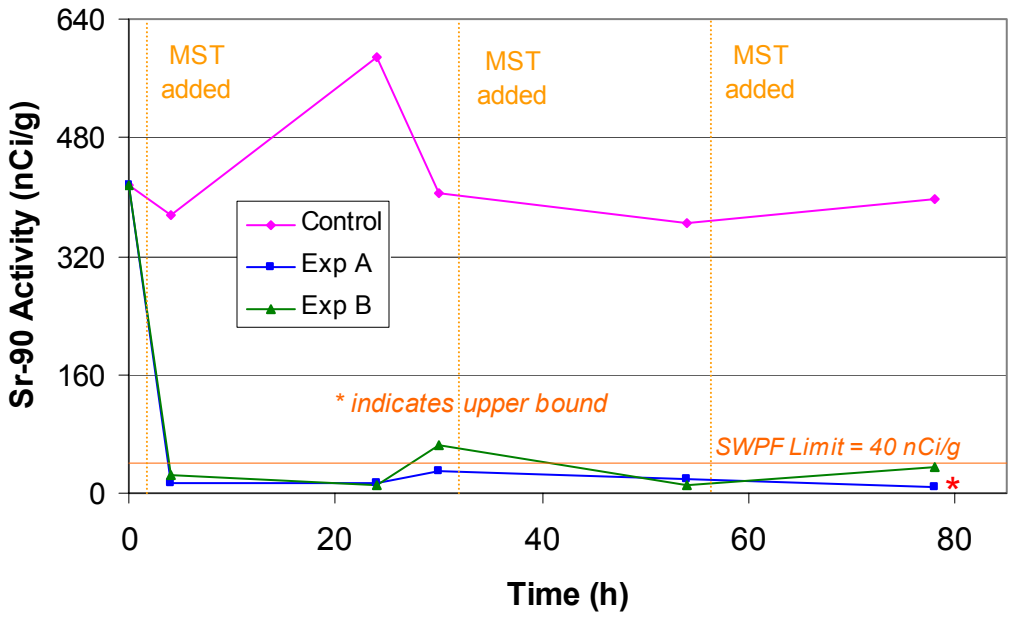
Table 4. Strontium-90 Concentrations in the Filtrate.

Time (hours)	Exp. A	Exp. B	Exp. A/B	Control
	^{90}Sr (nCi/g)	^{90}Sr (nCi/g)	Standard Dev.	^{90}Sr (nCi/g)
0*	4.15E+02	4.15E+02	NA	4.15E+02
4	1.40E+01	2.32E+01	6.47	3.76E+02
24	1.25E+01	1.14E+01	0.790	5.88E+02
30	3.05E+01	6.56E+01	24.9	4.06E+02
54	1.81E+01	1.05E+01	5.37	3.66E+02
78	< 8.04E+00	3.41E+01	NA	3.98E+02

* The time = 0 data are the same data point.

The data points from the duplicate reactions showed fair amount of deviation, notably at Time = 30. The control showed a single large deviation for the 24-hour samples but otherwise behaved reasonably well. This may be due to contamination in the cells. We cannot determine a standard deviation from the Time = 78 data points as one of them fell below detection limits. This data point is marked with an "*" on the graph to indicate they represent upper bounds.

Figure 2. Strontium in Solution Over Time.



The data shows that with a single MST addition, the strontium in solution drops below the Salt Waste Processing Facility requirement of 40 nCi/g.[14] As this experiment involved three MST consecutive strikes, we can calculate a stepwise DF value for each addition. Table 5 lists the DF values after each strike. In the case of Experiment A, the 78 hour data point fell below the detection limit, so we can only calculate a minimal DF value.

Table 5. Strontium Decontamination Factors After Each MST Addition.

Time After MST addition	Total Hours	DF Value, Exp. A	DF Value, Exp. B	Average DF
30	30	13.6	6.33	9.97
24	54	1.69	6.25	3.97
24	78	> 2.25	0.31	NA

We also analyzed the solution for non-radioactive strontium. To detect the small amounts of cold strontium, we struck a sample of the bounding waste composite with AMP (ammonium molybdophosphate - a cesium removal agent) so we could avoid having to dilute the sample for ALARA reasons. The analysis showed that the bounding waste composite had cold strontium at 90.2 ppb (compared to the mass of ^{90}Sr of 3.82 ppb). Therefore we can conclude that even in the face of a large excess of cold strontium, the MST was still effective in removing the radioactive strontium.

4.3 Neptunium Results

Researchers analyzed the filtered solutions for neptunium-237. Table 6 shows the numerical values while Figure 3 shows the graphical results.

Table 6. Neptunium-237 Concentrations in the Filtrate.

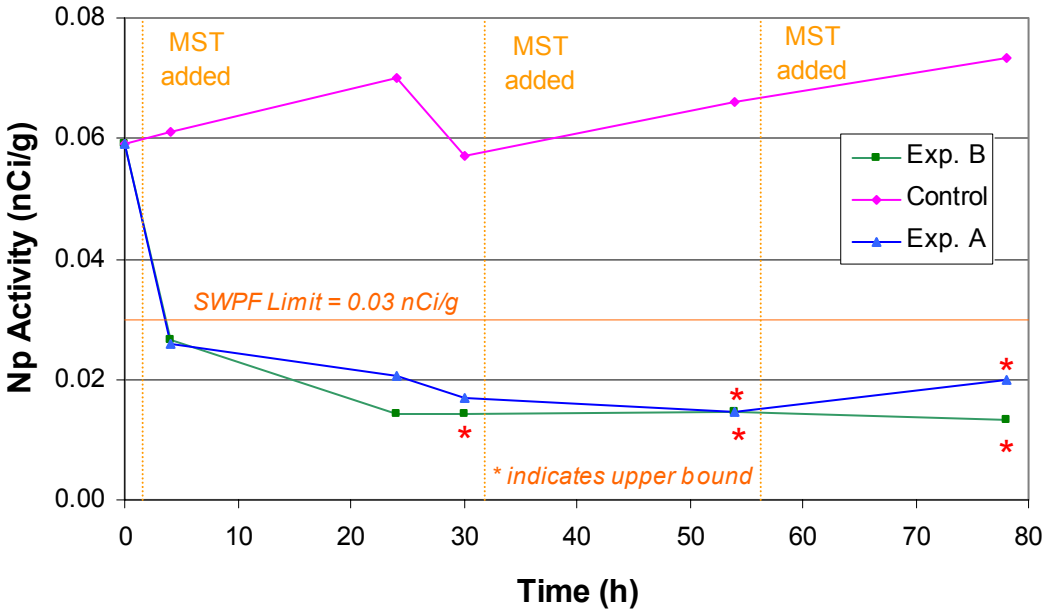
Time (hours)	Exp. A	Exp. B	Exp. A/B	Control
	^{237}Np (nCi/g)	^{237}Np (nCi/g)	Standard Dev.	^{237}Np (nCi/g)
0*	5.90E-02	5.90E-02	NA	5.90E-02
4	2.58E-02	2.66E-02	5.07E-04	6.11E-02
24	2.04E-02	<1.43E-02	NA	6.99E-02
30	1.70E-02	1.43E-02	1.92E-03	5.72E-02
54	<1.45E-02	<1.44E-02	NA	6.59E-02
78	<2.01E-02	<1.34E-02	NA	7.33E-02

* The time = 0 data are the same data point.

A number of the neptunium sample results fell below detection limits. For experiment A, the 54 and 78 hour data points fell below the detection level. For experiment B, the 24, 54, and 78 hour data points fell below the detection limit. These data points are marked

with a "*" on the graph to indicate they are upper bounds. For this same reason we could not calculate standard deviation for those points. For the two replicate values, the calculated standard deviation showed good agreement.

Figure 3. Neptunium in Solution Over Time.



As this experiment involved three MST consecutive strikes, we can calculate a stepwise DF value for each addition. Table 7 lists the DF values after each strike. In the case of both experiments, the 54 hour data points fell below the detection limit, so we can only calculate a minimal DF value in each case. Additionally, the 78 hour data points for both

Table 7. Neptunium Decontamination Factors After Each MST Addition.

Time After MST addition	Total Hours	DF Value, Exp. A	DF Value, Exp. B	Average DF
30	30	3.5	4.1	3.8
24	54	> 1.2	> 1.0	NA
24	78	NA	NA	NA

experiments fell below the detection limits, which prevents us from calculating a DF value. A total DF of ~4 occurred, reducing the neptunium levels to within Salt Waste Processing Facility requirements (< 0.03 nCi/g).

4.4 Uranium Results

Researchers analyzed the filtered solutions for uranium-235 and -238. Table 8 shows the numerical values while Figure 4 shows the graphical results. The time = 54 sample for Experiment A clearly represents a contamination of the archive sample in the cells. We reached this conclusion since reanalysis of the both the original samples as well as of

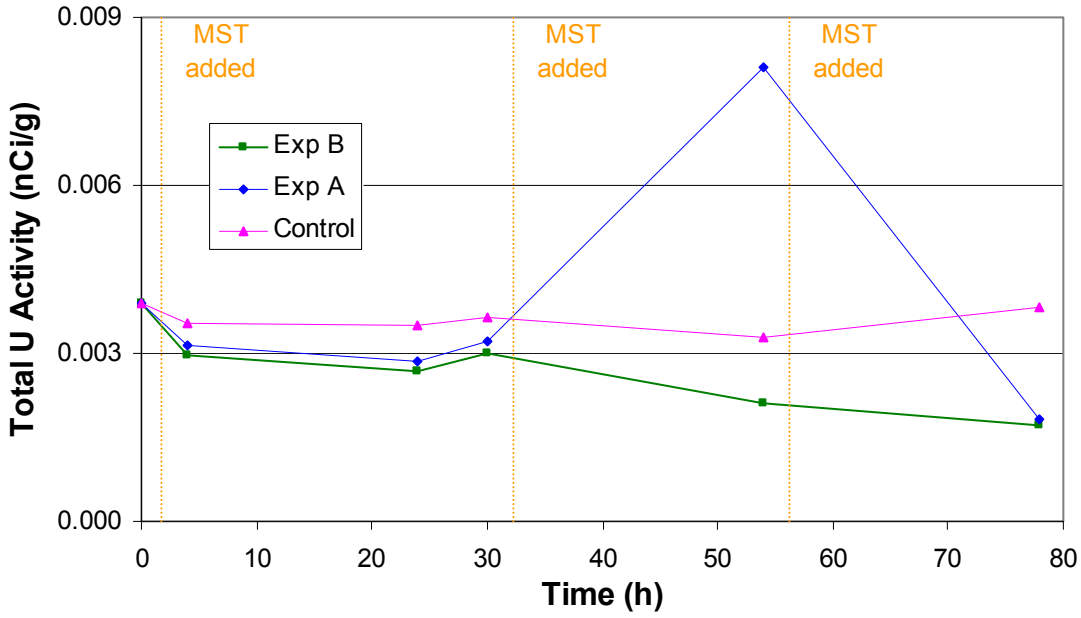
Table 8. Total Uranium (235+238) concentration in filtrate.

Time (hours)	Exp. A	Exp. B	Exp. A/B	Control
	Total U (nCi/g)	Total U (nCi/g)	Standard Dev.	Total U (nCi/g)
0*	3.90E-03	3.90E-03	NA	3.90E-03
4	3.14E-03	2.95E-03	1.38E-04	3.55E-03
24	2.87E-03	2.68E-03	1.30E-04	3.49E-03
30	3.20E-03	3.01E-03	1.34E-04	3.63E-03
54	8.49E-03	2.09E-03	4.27E-03	3.30E-03
78	1.84E-03	1.71E-03	8.97E-05	3.82E-03

* The time = 0 data are the same data point.

new samples of the archived material show the same uranium values. Other than this data point, the duplicate experiments agreed well. The uranium concentration in the control remained constant throughout the time of the experiments.

Figure 4. Total Uranium (235+238) in Solution Over Time.



As this experiment involved three MST consecutive strikes, we can calculate a stepwise DF value for each addition. Table 9 lists the DF values after each strike. Due to the Time = 54 hour contaminated data point for Experiment A, we cannot calculate a DF value for either the second or third MST strike.

Table 9. Uranium Decontamination Factors After Each MST Addition.

Time After MST addition	Total Hours	DF Value, Exp. A	DF Value, Exp. B	Average DF
30	30	1.2	1.3	1.2
24	54	NA	1.4	NA
24	78	NA	1.2	NA

All the MST strikes proved effective in removing the uranium. The total DF of ~2 agrees with expectations from prior tests. The SWPF does not have a removal requirement for uranium.

5.0 Conclusions

- We prepared a "bounding alpha" waste composite from samples from Tanks 21H, 26F, 33F, and 39H that had high levels of plutonium, strontium, neptunium and uranium. After equilibrium, this composite proved more limiting than macrobatch SPT008, but not as limiting as macrobatch SPT066.

- Three MST strikes of 0.4 g/L each reduced the total plutonium to below the current SWPF process requirement of 18 nCi/g.

- A single MST strike reduced the strontium-90 activity to below the SWPF process requirement of 40 nCi/g.

- A single MST strike reduced the neptunium-237 activity to below the Salt Waste Processing Facility requirement of 0.03 nCi/g.

- The uranium behavior agreed with expectations from prior testing.

Appendix 1. Solution Composition of the Tank Samples and the Composite.

Analysis	Tank 21H (HTK-475)	Tank 26F (FTF-096, -102)	Tank 33F (FTF-107)	Tank 39H (HTF-E-146, -147, -148)	Composite
Pu-238 (nCi/g)	1.69E+01	5.55E+00	1.30E+01	8.38E+02	3.72E+02
Pu-239/240 (nCi/g)	1.68E+00	7.18E-01	2.19E+00	1.59E+01	3.85E+00
Sr-90 (nCi/g)	1.97E+02	3.44E+02	3.13E+01	1.43E+03	3.85E+02
Np-237 (nCi/g)	< 3.19E-03	< 1.46E-01	< 4.37E-03	< 5.92E-01	< 3.99E-01
U-235/238 (nCi/g)	3.27E-03	3.45E-03	3.38E-03	4.65E-03	2.93E-03
Total Alpha (nCi/g)	18.58	6.27	15.19	853.91	375.85
Cs-137 (nCi/g)	1.12E+03	9.44E+05	6.76E+03	6.66E+05	5.12E+05
Al (mg/L)	NA	NA	NA	NA	6894.4
OH^- (M)	NA	NA	NA	NA	2.23
CO_3^{2-} (M)	NA	NA	NA	NA	< 0.50
Ag (mg/L)	NA	NA	NA	NA	< 1.24
As (mg/L)	NA	NA	NA	NA	< 6.2
Ba (mg/L)	NA	NA	NA	NA	< 0.74
Cd (mg/L)	NA	NA	NA	NA	1.98
Cr (mg/L)	NA	NA	NA	NA	92.75
Hg (mg/L)	NA	NA	NA	NA	< 27.28
Na (mg/L)	20147	261023	69149	133504	118048
Pb (mg/L)	NA	NA	NA	NA	< 11.41
Se (mg/L)	NA	NA	NA	NA	< 6.20
Cl (mg/L)	NA	NA	NA	NA	223.2
F (mg/L)	NA	NA	NA	NA	< 496
formate (mg/L)	NA	NA	NA	NA	< 2480
nitrate (mg/L)	NA	NA	NA	NA	115816
nitrite (mg/L)	NA	NA	NA	NA	28024
oxalate (mg/L)	NA	NA	NA	NA	< 2480
phosphate (mg/L)	NA	NA	NA	NA	< 2480
sulfate (mg/L)	NA	NA	NA	NA	4216

NA = not analyzed for

Appendix 2. Macrobatch Activity Estimates.

To estimate the macrobatch activities, we referred to the HLW system plan[15] to find the composition of each macrobatch.

Macrobatch SPT-008

The plan identified Macrobatch SPT-008 as containing the most alpha emitters. Macrobatch SPT-008 has the estimated following composition in the HLW System Plan.

Tank	Volume (gallons)
Heel	20,434
21H	70,000
26F	730,000
33F	367,419
50H	20,000

Using these volume ratios and measured tank data, SRTC estimated the activity of each of the major radioisotopes of concern. Tank 21H, 26F, and 33F measured values came from our own recent measurements, while we used a measured value provided by HLW for the Tank 50H activity (zero for the listed species). We assumed the heel and inhibited water activities as zero for all radioisotopes.

	Activites in nCi/g					
	SRTC measured			HLW values		Macrobatch Activity
Isotope	Tank 21	Tank 26	Tank 33	Tank 50	heel	nCi/g
Pu-238	1.69E+01	5.55E+00	1.30E+01	0.00E+00	0.00E+00	8.29E+00
Pu-239/240	1.68E+00	7.18E-01	2.19E+00	0.00E+00	0.00E+00	1.20E+00
U-235/238	3.27E-03	3.45E-03	3.38E-03	0.00E+00	0.00E+00	3.30E-03
Np-237	3.19E-03	1.46E-01	4.37E-03	0.00E+00	0.00E+00	8.98E-02
Sr-90	1.97E+02	3.44E+02	3.13E+01	0.00E+00	0.00E+00	2.29E+02
volume (gal)	70000	730,000	367419	20000	20434	

The neptunium measurement is actually less than or equal to the value shown (detection limits).

Macrobatch SPT-066

The plan identified Macrobatch SPT-066 as containing the second most limiting alpha concentration. That batch has the estimated following composition.

Tank	Volume (gallons)
Heel	20,620
39H	980,000
Inhibited water	230,000

Using these volume ratios and measured tank data, SRTC estimated the activity of each of the major radioisotopes of concern. Tank 39H measured values came from our own recent measurements. We assume the heel and inhibited water activity as zero for all radioisotopes.

	Activites in nCi/g			
	SRTC measured	HLW values		Macrobatch Activity
Isotope	Tank 39H	inhib water	heel	nCi/g
Pu-238	8.38E+02	0.00E+00	0.00E+00	6.67E+02
Pu-239/240	1.59E+01	0.00E+00	0.00E+00	1.27E+01
U-235/238	4.65E-03	0.00E+00	0.00E+00	3.70E-03
Np-237	5.93E-01	0.00E+00	0.00E+00	4.73E-01
Sr-90	1.43E+03	0.00E+00	0.00E+00	1.14E+03
volume (gal)	980,000	230000	20620	

The neptunium measurement is actually less than or equal to the value shown (detection limits).

As it turns out, Macrobatch SPT-066 proves much more limiting than SPT-008.

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