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Investigation of Savannah River Site High Level Waste Solutions for Evidence of Colloidal Plutonium

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List of Abbreviations:
MW molecular weight
MST monosodium titanate ($NaTi_2O_5$)
mL milliliter

1.0 Executive Summary

Reseachers examined samples from different waste tanks (7F, 13H, 26F, and 35H) for evidence of colloidal plutonium by filtrations through increasingly smaller pore sized membranes. The data from these filtrations indicates either the absence of colloidal plutonium or that any colloids are sufficiently small enough to pass through the finest filter tested (10,000 MW, or ~1.5 nm).

Keywords: plutonium, colloidal, filter

2.0 Introduction

The Savannah River Site (SRS) selected an amorphous sodium titanate material, referred to as monosodium titanate, to remove strontium from supernatant high-level wastes as part of the In-Tank Precipitation (ITP) process.[1] This material is of a class of hydrous metal oxides originally developed by R. Dosch and coworkers at the Sandia National Laboratory in the 1970s.[2] Synthesis of these amorphous materials uses a sol-gel process that yields solids with a high

surface area. Testing indicated that these materials remove a number of other species from alkaline solution including the actinides.[2,3]

Actinide removal characteristics of the MST came under increasing scrutiny in early 1990s to ensure that the MST would not sorb sufficient fissile isotopes from the waste to pose a nuclear criticality hazard.[4,5] Research also investigated whether the decontaminated liquid waste from the ITP process would meet Z-Area limits for total alpha activity.[6] Generally, plutonium isotopes represent the largest contribution to total alpha activity in SRS waste solutions. Parallel activities investigated the solubility of plutonium in high ionic strength alkaline solutions. The solubility studies indicated higher plutonium solubilities than previously estimated. Consequently, the concentration of plutonium in waste solutions became an increasingly significant factor in determining the quantity of MST required in the pretreatment.

Under acidic and neutral pH conditions, plutonium exhibits multiple oxidation states with differing solubilities. Plutonium can also polymerize during hydrolysis forming stable colloids.[7] Only limited studies exist regarding plutonium chemistry in highly alkaline and high ionic strength salt solutions. Thus, colloidal plutonium may exist under the highly alkaline conditions in SRS high-level waste (HLW) tanks.

Testing to date indicates that the relatively slow rate of plutonium removal with MST determines equipment size for the strontium and alpha removal stage of the SRS Salt Waste Processing Facility.[8] In addition to removal kinetics, the quantity of a removal agent required to remove alpha activity may decrease significantly if the plutonium exists as colloidal material. The baseline crossflow filtration process would likely remove colloidal plutonium, resulting in decreased demand for removal by contacting with MST, another sorbent or by an alternate removal method. Previous HLW samples analyzed for plutonium activity did not attempt to separate colloidal plutonium from the sample. Thus, the reported plutonium activity included that present from dissolved plutonium, undissolved plutonium, and in select cases – as fine solids. To reduce the uncertainty over the presence and possible impacts of colloidal plutonium on salt processing, SRTC initiated testing to determine if colloidal plutonium exists in SRS high-level waste solutions.[9]

3.0 Experimental

Testing used archived samples from Tanks 7F, 13H, 26F, and 35H.[11] These samples remained stored in polyethylene bottles at ambient cell conditions from archival time until used in this testing.

3.1 Method of Filtration

The authors selected centrifugal filtration to perform the evaluation as this method easily adapts for use in the shielded cells at SRTC. In addition to a relatively wide range of filter pore sizes, the filters offer reduced likelihood for cross contamination of the samples. The filter design requires small amounts of liquids, which also minimizes generation of waste. The combination of centrifugation, easy separation and recovery of the filtrate and small size makes this system ideal for use in a remotely handled operation.

Figure 1 shows a photograph of a centrifugal filter with the filter-reservoir installed.

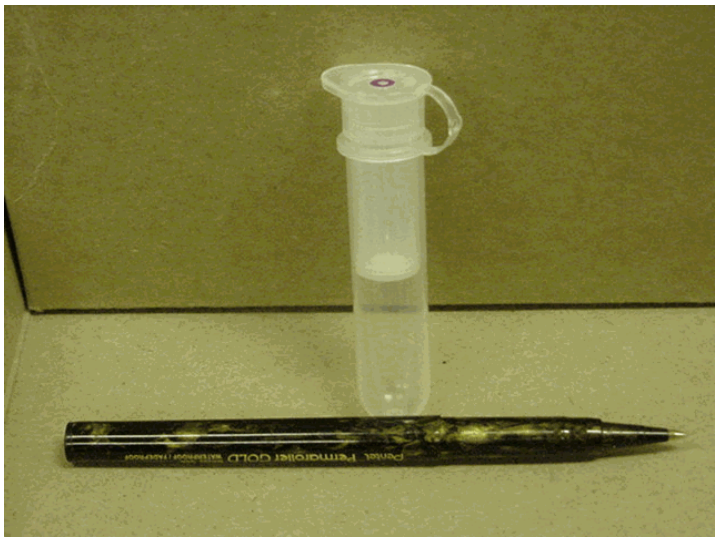

Figure 1. Millipore Centrifugal Filtration Unit

Each filter is about 5 inches in length and fits into a 15 mL centrifugal tube holder. The filter-reservoir holds about 2 mL of liquid. The filters are made from a variety of materials and porosities. We tested filters that featured polysulfone membranes in three different pore sizes; 0.45 mm (Millipore part #UFC40DV25), 100,000 MW (5 nm, Millipore part #UFC4THK25) and 10,000 MW (~1.5 nm, Millipore part #UFC4TGC25).

Figure 2 shows the filtering unit with the filter-reservoir removed.

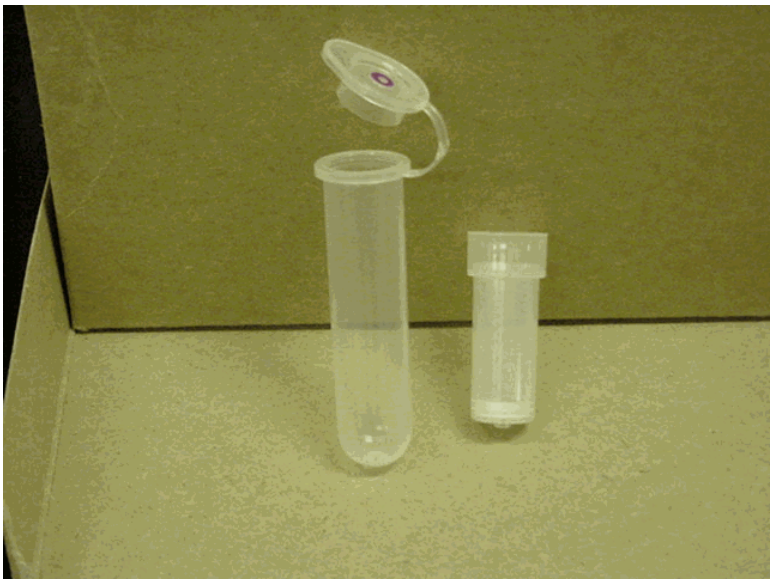

Figure 2. A Centrifugal Filter with the Reservoir Removed.

3.1 Procedure

3.1.1 Simulant Testing

Before trying real waste we performed a limited series of filtrations using a simulant and the three filter membranes. Personnel filtered samples of the simulant to see whether the filters would pass a salt solution. Each of the filters successfully passed the salt solutions without visual degradation of the filter material within a period of 2 hours.

4.0 Results and Discussion

Personnel obtained opproximately 15 mL samples each of Tanks 7F, 13H, 26F, and 35H from archived samples stored

in the shielded cells. We marked each of needed filters and bottles uniquely to prevent mixing different solutions. Researchers then filtered each sample of a waste solution only once; no sequential filtrations occurred. To increase our measurement base we decided to filter each of the tank samples in duplicate; each waste sample was filtered separately twice for each filter size. After filtering, we collected ~0.5 mL of the filtrate and recorded the weight. We next mixed the filtrate into a bottle pre-filled with 49.5 mL of a 2 M HNO_3 acid solution, giving a 100:1 dilution. The 100:1 dilution ensured the radionuclide content of the analyzed samples fell below the dose limits. The acidified samples received analysis for plutonium activity by alpha counting (PuTTA) after extraction with triphenyltrifluoroacetone.[10] Appendix 1 describes the identity and conditions of each sample.

Table 1 lists the data from the 0.45 mm filtrations normalized to 0.5 g of waste.

Note the large variances in the measurements for Tank 26F.

Table 1. Data From 0.45 mm Filtrations, Adjusted for Sample Weight

Sample ID (LIMS)	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)
Tank **7F** Waste	8.99E+01	8.99E+00
	1.48E+02	1.66E+01
Tank **13H** Waste	8.33E+02	5.09E+01
	9.95E+02	6.03E+01
Tank **26F** Waste	9.59E+01	2.60E+01
	1.28E+02	1.84E+00
Tank **35H** Waste	3.15E+03	6.19E+01
	3.21E+03	5.60E+01

Appendix 2 lists these values with uncertainties and the averages.

Table 2 lists the data for from 100,000 MW (5 nm) filtrations normalized to 0.5 g of waste. Tanks 13H and 35 H showed large variances.

Table 2. Data From 100,000 MW (5nm) Filtrations, Adjusted for Sample Weight

Sample ID (LIMS)	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)
Tank **7F** Waste	6.74E+01	4.88E+00
	1.37E+02	1.50E+01
Tank **13H** Waste	1.30E+03	5.26E+01
	8.69E+02	1.03E+01
Tank **26F** Waste	4.71E+02	9.77E+01

	2.00E+02	5.41E+01
Tank **35H** Waste	2.96E+03	7.02E+01
	2.15E+02	5.67E+00

Appendix 3 lists these values with uncertainties and the averages.

Table 3 lists the data for from 10,000 MW (~1.5 nm) filtrations, normalized to 0.5 g of waste. Large differences occurred in the measurements for Tanks 7F and 13 H.

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Table 3. Data From 10,000 MW (~1.5 nm) Filtrations, Adjusted for Sample Weight

Sample ID (LIMS)	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)
Tank **7F** Waste	1.40E+02	2.43E+01
	1.88E+02	3.86E+02
Tank **13H** Waste	2.68E+03	1.42E+00
	1.93E+03	5.11E+01
Tank **26F** Waste	1.88E+02	4.14E+01
	1.74E+02	1.04E+02
Tank **35H** Waste	3.58E+03	3.55E+01
	3.61E+03	5.72E+01

Appendix 4 lists these values with uncertainties and the averages.

Table 4 compares the normalized averages of each filtration. The table denotes the measurements that exhibited large variances.

Table 4. Averages of Each Filtration for Each Waste

Sample ID (LIMS)	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)
Real Waste, 0.45 um		
Average of Tank **7F** Waste	1.19E+02	1.28E+01
Average of Tank **13H** Waste	9.14E+02	5.56E+01
Average of Tank **26F** Waste	1.12E+02	1.39E+01 (lrg sample diff)

Average of Tank **35H** Waste	3.18E+03	5.90E+01
Real Waste, 100,000 MW		
Average of Tank **7F** Waste	1.02E+02	9.94E+00
Average of Tank **13H** Waste	1.08E+03	3.15E+01 (lrg sample diff)
Average of Tank **26F** Waste	3.36E+02	7.59E+01
Average of Tank **35H** Waste	1.59E+03 (lrg sample diff)	3.79E+01 (lrg sample diff)
Real Waste, 10,000 MW		
Average of Tank **7F** Waste	1.64E+02	2.05E+02 (lrg sample diff)
Average of Tank **13H** Waste	2.31E+03	2.63E+01 (lrg sample diff)
Average of Tank **26F** Waste	1.81E+02	7.27E+01
Average of Tank **35H** Waste	3.60E+03	4.64E+01

"lrg sample diff" denotes a factor of 5 difference or greater between the averages of the duplicate samples.

5.0 Conclusions

A review of the data indicates no particular pattern or trend can be discerned in the activities of the different waste solutions after filtering. Figure 3 shows the ^{238}Pu activities, and illustrates the lack of a clear trend. This conclusion is somewhat tenuous due to only having six data points per waste solution. Furthermore, some samples exhibited a large variance in the results of duplicate testing. At this point we cannot explain why, other than the low plutonium concentrations may approach the lower detection limit.

The authors recommend additional measurements. We propose repeating measurements for samples from Tanks 13H and 35H which showed the largest number of large variations between measurements of the duplicate samples. Additionally, one of the waste solutions will undergo a sequential filtration; 0.45 mm-->100,000 MW (5 nm) -->10,000 MW (~1.5 nm) using the same sample to check for any different behavior.

Finally we propose that additional tank samples in the form of waste solutions from dissolved saltcake be added to this study.

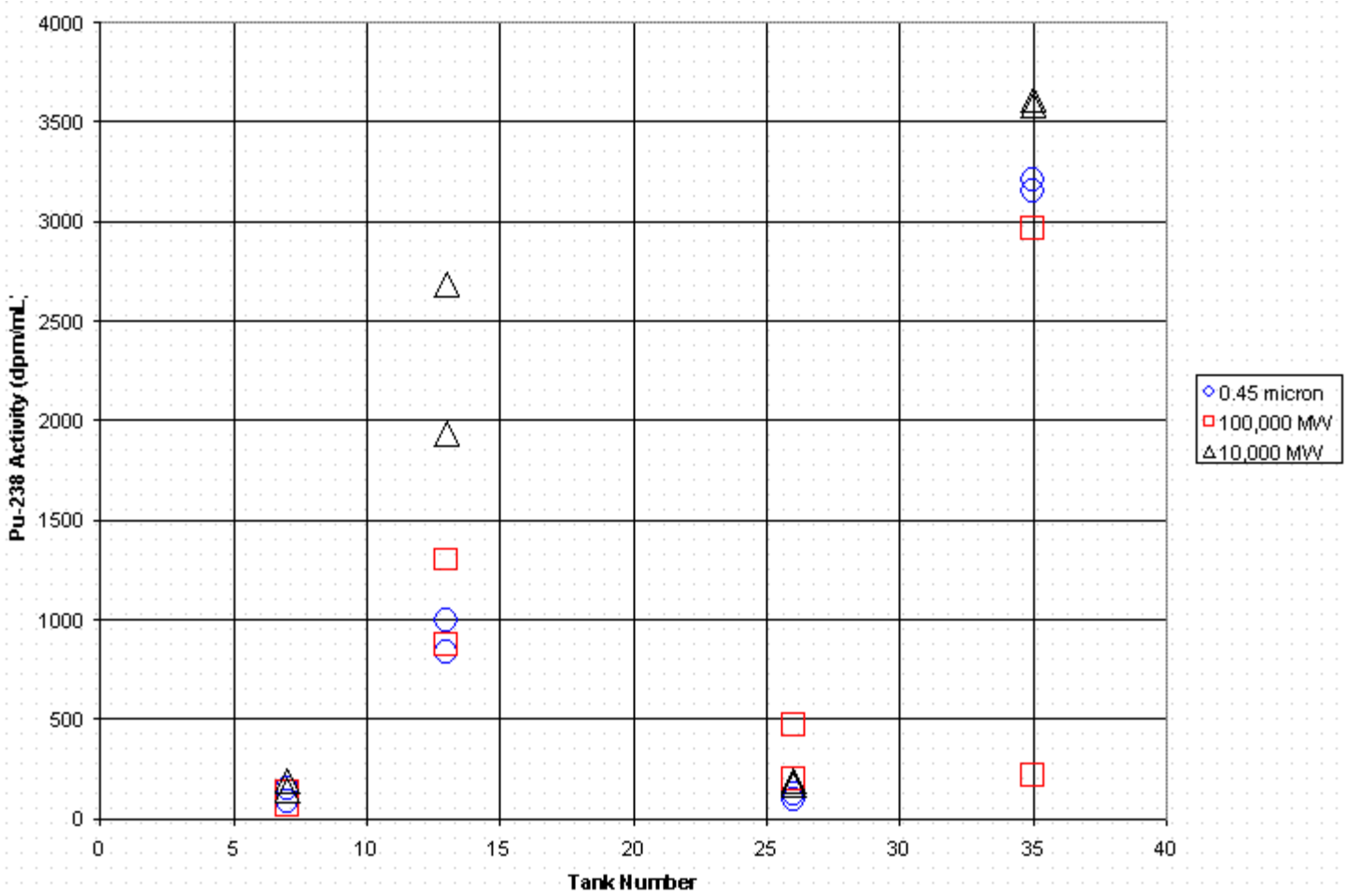

Figure 3. Plot of 238Pu activity vs. Tank Number

6.0 References

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11. The 7F, 13H, 26F, and 35H samples were derived from samples KMB-7F-001, KMB-13H-001, KMB-26F-001, and KMB-35H-001 respectively. See WSRC-NB-2000-00125, pg 8.

Appendix 1. Sample Identity, Filter Used, and Weight of Filtered Samples Acidified for Plutonium Measurements.

Filter Type	Tank Source	Sample I.D.	Filtrate Weight (g)
0.45 mm	7F	D-3	0.623
0.45 mm	13H	D-4	0.690
0.45 mm	26F	D-5	0.610
0.45 mm	35H	D-6	0.623
0.45 mm	7F	D-7	0.627
0.45 mm	13H	D-8	0.578
0.45 mm	26F	D-9	0.385
0.45 mm	35H	D-10	0.610
100,000 MW	7F	D-11	0.631
100,000 MW	13H	D-12	0.706
100,000 MW	26F	D-13	0.732
100,000 MW	35H	D-14	0.586
100,000 MW	7F	D-15	0.761
100,000 MW	13H	D-16	0.696
100,000 MW	26F	D-17	0.629
100,000 MW	35H	D-18	0.585
10,000 MW			

	7F	D-19	0.630
10,000 MW	13H	D-20	0.355
10,000 MW	26F	D-21	0.617
10,000 MW	35H	D-22	0.580
10,000 MW	7F	D-23	0.626
10,000 MW	13H	D-24	0.472
10,000 MW	26F	D-25	0.636
10,000 MW	35H	D-26	0.606

The vendor labels each of the filter types by a color marking on the filter; red for 0.45 mm, purple for 100,000 MW (5nm), and blue for 10,000 MW (~1.5 nm).

Appendix 2. Data From 0.45 mm Filtrations

Sample ID (LIMS)	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)
Real Waste, 0.45 um		
(300152553) **7F**	8.99E+01 (unc. = 10.07%)	8.99E+00 (unc. = 91.44%)
(300152568) **13H**	8.33E+02 (unc. = 3.21%)	5.09E+01 (unc. = 13.56%)
(300152569) **26F**	9.59E+01 (unc. = 8.98%)	2.60E+01 (unc. = 30.33%)
(300152570) **35H**	3.15E+03 (unc. = 2.75%)	6.19E+01 (unc. = 28.85%)
(300152571) **7F**	1.48E+02 (unc. = 7.13%)	1.66E+01 (unc. = 75.51%)
(300152572) **13H**	9.95E+02 (unc. = 3.95%)	6.03E+01 (unc. = 17.48%)
(300152573) **26F**	1.28E+02 (unc. = 12.22%)	1.84E+00 (unc. = 428.30%)
(300152574) **35H**	3.21E+03 (unc. = 2.74%)	5.60E+01 (unc. = 31.70%)
Average of Tank **7F** Waste	1.19E+02	1.28E+01
Average of Tank **13H** Waste	9.14E+02	5.56E+01

Average of Tank **26F** Waste	1.12E+02	1.39E+01 (lrg sample diff)
Average of Tank **35H** Waste	3.18E+03	5.90E+01

Sample notations marked "lrg sample diff" indicate that there was at least a factor of 5x difference between the measurements of the duplicate samples of a waste.

"Unc" gives the analytical uncertainty associated with each result.

Appendix 3. Data From 100,000 MW (5nm) Filtrations, Adjusted for Sample Weight

Sample ID (LIMS)	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)
Real Waste, 100,000 MW		
(300152575) **7F**	6.74E+01 (unc. = 17.2%)	4.88E+00 (unc. = 111.42%)
(300152576) **13H**	1.30E+03 (unc. = 2.96%)	5.26E+01 (unc. = 30.06%)
(300152577) **26F**	4.71E+02 (unc. = 4.40%)	9.77E+01 (unc. = 10.03%)
(300152578) **35H**	2.96E+03 (unc. = 3.02%)	7.02E+01 (unc. = 21.92%)
(300152579) **7F**	1.37E+02 (unc. = 6.15%)	1.50E+01 (unc. = 34.32%)
(300152580) **13H**	8.69E+02 (unc. = 5.15%)	1.03E+01 (unc. = 142.60%)
(300152581) **26F**	2.00E+02 (unc. = 12.10%)	5.41E+01 (unc. = 15.41%)
(300152582) **35H**	2.15E+02 (unc. = 12.10%)	5.67E+00 (unc. = 25.45%)
Average of Tank **7F** Waste	1.02E+02	9.94E+00
Average of Tank **13H** Waste	1.08E+03	3.15E+01 (lrg sample diff)
Average of Tank **26F** Waste	3.36E+02	7.59E+01
Average of Tank **35H** Waste	1.59E+03 (lrg sample diff)	3.79E+01 (lrg sample diff)

Sample notations marked "lrg sample diff" indicate that there was at least a factor of 5x difference between the measurements of the duplicate samples of a waste.

"Unc" gives the analytical uncertainty associated with each result.

Appendix 4. Data From 10,000 MW (~1.5 nm)Filtrations, Adjusted for Sample Weight

Sample ID (LIMS)	Pu-238 (dpm/mL)	Pu-239/240 (dpm/mL)
Real Waste, 10,000 MW		

(300152584) **7F**	1.40E+02 (unc. = 10.48%)	2.43E+01 (unc. = 24.78%)
(300152588) **13H**	2.68E+03 (unc. = 3.33%)	1.42E+00 (unc. = 2228.75%)
(300152589) **26F**	1.88E+02 (unc. = 10.99%)	4.14E+01 (unc. = 21.98%)
(300152590) **35H**	3.58E+03 (unc. = 2.97%)	3.55E+01 (unc. = 98.26%)
(300152591) **7F**	1.88E+02 (unc. = 11.29%)	3.86E+02 (unc. = 26.85%)
(300152592) **13H**	1.93E+03 (unc. = 2.91%)	5.11E+01 (unc. = 25.24%)
(300152593) **26F**	1.74E+02 (unc. = 4.57%)	1.04E+02 (unc. = 13.38%)
(300152594) **35H**	3.61E+03 (unc. = 2.67%)	5.72E+01 (unc. = 48.18%)
Average of Tank **7F** Waste	1.64E+02	2.05E+02 (lrg sample diff)
Average of Tank **13H** Waste	2.31E+03	2.63E+01 (lrg sample diff)
Average of Tank **26F** Waste	1.81E+02	7.27E+01
Average of Tank **35H** Waste	3.60E+03	4.64E+01

Sample notations marked "lrg sample diff" indicate that there was at least a factor of 5x difference between the measurements of the duplicate samples of a waste.

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