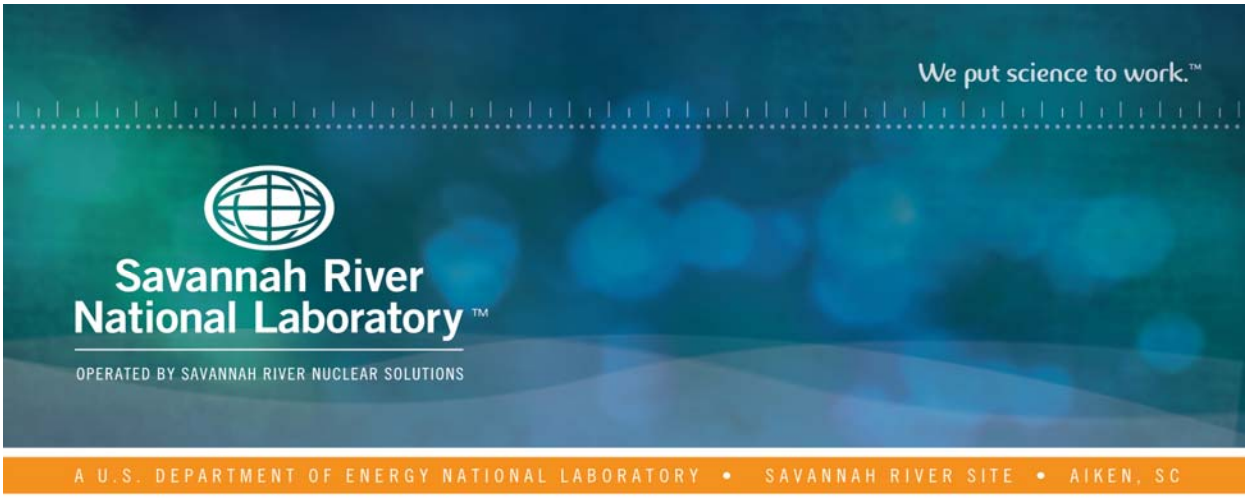

Sample Results from the Interim Salt Disposition Program Macrobatch 7 Tank 21H Qualification MST Solids Sample

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) performed experiments on qualification material for use in the Interim Salt Disposition Program (ISDP) Batch 7 processing. The Marcrobatch 7 material was received with visible fine particulate solids, atypical for these samples. The as received material was allowed to settle for a period greater than 24 hours. The supernatant was then decanted and utilized as our clarified feed material. As part of this qualification work, SRNL performed an Actinide Removal Process (ARP) test using the clarified feed material. From this test, the residual monosodium titanate (MST) was analyzed for radionuclide uptake after filtration from H-Tank Farm (HTF) feed salt solution. The results of these analyses are reported and are within historical precedent.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Project
ESS	Extraction, Strip, Scrub
HTF	H-Tank Farm
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ICPMS	Inductively Coupled Plasma Mass Spectroscopy
ISDP	Integrated Salt Disposition Program
MST	Monosodium Titanate
% RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

This report details the results of the analysis of MST solids recovered from the ARP test. Results of supernate analysis for Salt Batch 7 qualification are previously reported. Previous documents cover initial and subsequent characterization, which include analytical results on the supernate.[1,2,3] This work was specified by Task Technical Request (TTR) [4] and by Task Technical and Quality Assurance Plan (TTQAP) in section 4.4.[5]

Details for the work are contained in a controlled laboratory notebook.[6]

For this macrobatch, Tank 21H is used as the blend and preparation tank. This material will be transferred to Tank 49H where it will be combined with the heel from Macrobatch 6. In this qualification effort for Macrobatch 7, only samples from Tank 21H have been analyzed. In this campaign, the qualification and tank strategy indicates that analysis of Tank 49H is not needed as the material was qualified for Macrobatch 5.[7] The goal for MST and ESS testing is to simulate a single MST strike.

2.0 Experimental Procedure

Three 21H samples including two 80 mL variable depth samples and one 1L cask were pulled and arrived to SRNL on May 16, 2013. The samples contained visible quantities of fine dark solids, atypical for these samples. A well-mixed composite sample from all three bottles was allowed to settle and the supernatant was decanted from the top layer and utilized as feed material for the Actinide Removal Process (ARP)/Extraction Strip and Scrub (ESS) testing. This sampling method was chosen based on its similarity to the plant process as well as similar densities to a filtered sample. Researchers measured the density of each of the solutions including both settled and filtered samples (see Table 1). A discussion on the density measurements has been previously reported.[2]

Table 1 Sample Density Measurements (25 ºC)

Sample	Measured Density (g/mL)
HTF-21-13-79 (settled)	1.293
HTF-21-13-80 (settled)	1.260
HTF-21-13-81 (settled)	1.262
HTF-21-13-79 (filtered)	1.248
HTF-21-13-80 (filtered)	1.229
HTF-21-13-81 (filtered)	1.256
Average, settled (%RSD)	1.272 (1.45%)
Average, filtered (%RSD)	1.244 (1.11%)

As part of the salt batch qualification, SRNL performed an ESS test and an ARP test on the settled material. These results are reported separately.[3] From the ARP test, SRNL isolated the MST solids from two separate 200 mL solutions using filtration at temperature (25 ± 3 °C). The solids were immediately removed after 8 hours to ensure subsequent absorption did not occur.

However, ARP processes will have most solids contacting for more than 8 hours and will adsorb over multiple strikes due to the MST cake that is built up on the filter. This MST experiment was run in duplicate single MST strike and subsequent filtration.

2.1 Analysis of MST Solids

The MST addition and adsorption was performed in two identical contact experiments. The purpose of performing duplicate adsorptions was to provide enough material to test for additional analytes (^{14}C, ^{129}I, and ^{3}H) and to provide enough material for four ESS tests. After the MST test completed, the MST solids were collected using unwashed filtration in two separate filter cups while the liquid was combined to serve as the feed for the ESS testing. Personnel digested the retained MST solids (aqua regia/microwave) in one filter cup and retained the solids for the other and sent them to Analytical Development for analysis. As it is problematic to attempt to isolate only the MST solids, SRNL digested the collected slurry and normalized all the results to titanium, giving a result in "pCi analyte/gram of titanium." To do this, the researcher divided the analyte result in pCi by the grams of titanium from the digestate. Inductively Coupled Plasma Mass Spectroscopy (ICPMS), Inductively Coupled Plasma Emission Spectroscopy (ICPES), and various radio-counting methods were used for analysis.

The analyses for ^{14}C and ^{129}I were completed using solid samples with other preparations outside of aqua regia/microwave dissolution. The filter containing both the MST and some salt solution was washed gently with water to remove as much of the salt solution as possible. Assuming the equal distribution of material, the filter was segmented into four sections. Two sections were utilized for the analysis of ^{129}I, one section was used for measuring ^{14}C, and the final section was saved in case re-analysis was required. For ^{129}I, the filter material was digested in a solution of nitric acid to which some potassium iodide was added. The iodide was subsequently precipitated using silver to form silver iodide (AgI). The activity of the ^{129}I was then determined by beta/gamma counting. The AgI precipitate was then neutron activated to measure the recovery of the original added iodide.

For the ^{14}C analysis, the filter material was processed using a combustion wet-ashing technique oxidizing the carbon in the sample to carbon dioxide. The carbon dioxide was captured in a capture agent and analyzed by liquid scintillation counting for ^{14}C.

3.0 Results

As there are very few sludge solids in the feed material after settling, the solids digestion data reflects the MST solids, and whatever adsorbs to the MST, as well as entrained/interstitial salt solution. However, through investigating the activity of ^{137}Cs, ^{129}I, and ^{99}Tc as examples of a salt soluble analytes in the qualification material and MST solids, only ~1% or less of the material is present as an interstitial salt solution.

Actinides and strontium adsorb to MST and the analysis of the MST provides relevant data for those species. Additionally, elements including Eu, Co, and Am, have the potential to adsorb depending on the alkalinity of the solution and solubility. However, the other results for materials that have limited affinity for MST are a function of material in the feed solution. Therefore, the values reported in Table 2 should all be considered upper bounds. Additionally, the high upper limit total alpha value is shown as a detection limit value (<). This can be attributed

to the extremely high beta value (~100 fold greater) where some of the beta counts actually leak into the alpha counter.

The researchers have observed some discrepancies between the qualification and the MST solids. Most notably the ^{238}U, ^{154}Eu, ^{60}Co, ^{241}Am, and ^{244}Cm analytes are shown with significant activity that excludes the possibility of a concentration effect in the solids. The researchers have postulated this to be attributed to non-visible solids collecting on the filter along with the MST. This assertion was confirmed by checking back with the Macrobatch 6 qualification[3] and MST solids[8] reports where the qualification material was filtered and the MST solids were decanted (unfiltered). Unlike the Macrobatch 7 material which contained visible solids upon arrival, the Macrobatch 6 material was not observed to have solid material, yet similar results are shown between filtered and decanted/settled material.

Results for these elements encompass the MST solids, non-visible solids present in the settled solution, and the material from interstitial or entrained salt solution due to hydration in the absence of washing during the experiment. As there are no experimental data for many of these analytes (all except Sr, Pu, Np, Co, Eu, and Am which are directly adsorbed by MST) as to whether or not they adsorb to MST under our conditions without a washing step, SRNL cannot conclusively determine if the real values for an analyte result are from MST solids adsorption or interstitial liquid entrainment.

All results were single results as there was not enough material to analyze duplicates. However, there is a blank generated to ensure instrument calibration. The blank does not show any cross contamination from any analyte. Values in parentheses are the analytical uncertainty. The exception to this is the ^{241}Am result, which is the average of two different analyses that both provided a result. In this case, the value in parenthesis is the % RSD.

Table 2 Tank 21H MST Solids Radiological Results

Analyte	Result (pCi per gram of Ti)	Analyte	Result (pCi per gram of Ti)
^{233}U	<8.57E+04	^{147}Pm	<4.58E+07
^{234}U	6.19E+04 (23.9%)	^{151}Sm	<5.65E+07
^{235}U	5.33E+02 (2.36%)	^{134}Cs	<2.19E+06
^{99}Tc	2.18E+06 (7.13%)	^{137}Cs	3.57E+09 (5.00%)
^{237}Np	6.43E+04 (4.53%)	^{144}Ce	<1.86E+05
^{238}Pu	1.55E+07 (5.48%)	^{154}Eu	2.68E+06 (5.00%)
$^{239/40}$Pu	1.24E+06 (9.58%)	^{155}Eu	<4.34E+05
^{241}Pu	3.73E+06 (15.1%)	^{226}Ra	<4.90E+05
^{242}Pu	<3.38E+04	^{238}U	9.66E+03 (5.52%)
^{244}Pu	<1.57E+02	^{241}Am*	9.92E+06 (5.00%)
Total Alpha	<2.09E+08	^{242m}Am	5.54E+04 (10.8%)
Total Beta	1.86E+10 (10.0%)	^{243}Am	6.73E+05 (11.7%)
^{60}Co	2.88E+05 (5.00%)	^{242}Cm	4.58E+04 (10.8%)
^{90}Sr	5.54E+09 (11.3%)	^{243}Cm	<3.54E+06
^{94}Nb	<1.17E+04	^{244}Cm	3.50E+07 (5.10%)
^{106}Ru	<9.60E+04	^{245}Cm	<3.60E+05
^{125}Sb	<6.65E+04	^{247}Cm	<1.03E+05
^{126}Sb	<1.49E+04	^{249}Cf	<1.15E+05
^{126}Sn	<7.92E+04	^{251}Cf	<9.32E+04
^{14}C	<1.15E+05	^{129}I	3.15E+03 (6.18%)
^{3}H	<8.80E+05		

* Denotes the data shown is an average or two analytical methods

Additionally, the ICPES data provides metallic information from the digested sample in grams of analyte per gram of Ti. This information is shown in Table 3 below. The value in parenthesis is the % RSD. As a note, only the analytes present in solution are shown as relevant material.

Table 3 Tank 21H ICP-ES data for MST Solids

Analyte	Result (g per gram of Ti)
Al	3.33E-01 (10.1 %)
B	4.56E-03 (10.1 %)
Ba	6.49E-04 (10.9 %)
Ca	3.16E-02 (10 %)
Cd	2.60E-03 (10.3 %)
Cr	3.73E-03 (10.2 %)
Fe	1.24E-01 (10 %)
K	2.65E-02 (11.3 %)
Li	1.15E-02 (10.1 %)
Mg	9.82E-03 (10 %)
Mn	2.66E-02 (10 %)
Na	9.20E+00 (10 %)
Ni	5.91E-03 (10 %)
Si	4.44E-02 (10.2 %)
Sr	4.29E-04 (16.9 %)
Th	2.31E-03 (12.7%)
Ti	1.00E+00 (10 %)
U	2.96E-02 (10.9%)
Zn	1.50E-03 (10.5 %)
Zr	9.38E-04 (10.1 %)

3.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This task was performed under RW-0333P as identified in the TTQAP and TTR. Personnel qualified for RW-0333P have performed and reviewed this work.

4.0 Conclusions

Despite the optical clarity of the settled slurry, analysis of the Tank 21H sample indicates that the additional solids present in the HTF Macrobatch 7 sample increases the activity by approximately one order of magnitude in various species including Am, Cm, Co, and Eu over the Macrobatch 6 MST solid samples.[3] This conclusion is confirmed by the absence of this analytes in the Macrobatch 7 qualification report due to sample filtration.[2] Apart from this additional activity, there are close similarities with these analytes and those mentioned with the previous Macrobatch 6 report.[8]

5.0 References

[1] T. B. Peters, A. L. Washington, II, "Results of Initial Analyses of the Macrobatch 7 Tank 21H Qualification Samples," SRNL-STI-2013-00346, Rev. 0, June 2013.

[2] T. B. Peters and A. L. Washington, II, "Sample Results from the Interim Salt Disposition Program Macrobatch 7 Tank 21H Qualification Samples," SRNL-STI-2013-00437, Rev. 0, August 2013.

[3] A. L. Washington II, T. B. Peters, S. D. Fink, "Sample Results from the Integrated Salt Disposition Program Macrobatch 6 Tank 21H Qualification MST and ESS Samples", SRNL-STI-2013-00034, February 2013.

[4] S. E. Campbell and J. W. Ray, "Technical Task Request – Qualification of ISDP Salt Batch 7," HLW-DWPF-TTR-2013-0043, Rev. 1, June 20, 2013.

[5] T. B. Peters and A. L. Washington, II, "Task Technical and Quality Assurance Plan for ISDP Salt Batch 7 Sample Qualification", SRNL-RP-2013-00283, Rev. 1, August, 2013.

[6] SRNL-NB-2012-00107, T. B. Peters, October 25, 2012.

[7] S. E. Campbell, "Qualification and Sampling Strategy for ISDP Batch 5 to Obtain Compliance to 512-S, DWPF, Tank Farm, and Saltstone Waste Acceptance Criteria", X-ESR-H-00347, November 17, 2011.

[8] T.B. Peters and F.M. Pennebaker, "Sample Results from the Integrated Salt Disposition Program Macrobatch 6 Tank 21H Qualification MST Solids Sample", SRNL-STI-2013-00065, Rev. 0, February 2013.