SRNL-STI-2011-00061
Revision 1

Keywords: *MCU, ARP, ISDP*

Retention: *Permanent*

Sample Results from the Integrated Salt Disposition Program Macrobatch 4 Tank 21H Qualification Samples

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June 2011

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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Prepared for
U.S. Department of Energy

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed samples from Tank 21H to qualify them for use in the Integrated Salt Disposition Program (ISDP) Batch 4 processing. All sample results agree with expectations based on prior analyses where available. No issues with the projected Salt Batch 4 strategy are identified.

This revision includes additional data points that were not available in the original issue of the document, such as additional plutonium results, the results of the monosodium titanate (MST) sorption test and the extraction, scrub strip (ESS) test.

LIST OF ABBREVIATIONS

AA – Atomic Absoption
AD – Analytical Development
AMP – ammonium molybdophosphate
ARP – Actinide Removal Project
CVHg – Cold Vapor Mercury
ESS – extraction, scrub, strip
IC – Ion Chromatography
ICPES – Inductively Coupled Plasma Emission Spectroscopy
ICPMS – Inductively Coupled Plasma Mass Spectroscopy
ISDP – Integrated Salt Disposition Program
MST – monosodium titanate
PODD – Performance Objectives Demonstration Document
PuTTa – Plutonium thenoyl trifluoroacetone scintillation
SRNL – Savannah River National Laboratory
SRR – Savannah River Remediation
TIC-TOC – Total Inorganic Carbon-Total Organic Carbon
TTQAP - Task Technical and Quality Assurance Plan
TTR – Technical Task Request
WAC – Waste Acceptance Criteria
% RSD – percent relative standard deviation

1.0 Introduction

This report covers the revision to the Tank 21H qualification sample results[1] for Macrobatch (Salt Batch) 4 of the Integrated Salt Disposition Program (ISDP).[▽] A previous document covers initial characterization which includes results for a number of non-radiological analytes.[2] These results were used to perform aluminum solubility modeling to determine the hydroxide needs for Salt Batch 4 to prevent the precipitation of solids. Sodium hydroxide was then added to Tank 21 and additional samples were pulled for the analyses discussed in this report. This work was specified by Task Technical Request [3] and by Task Technical and Quality Assurance Plan (TTQAP).[4]

Details for the work are contained in controlled laboratory notebooks.[5]

2.0 Experimental Procedure

On September 23, 2010, five samples were pulled from Tank 21H at three different depths. The Tank 21H material arrived at SRNL in five bottles (HTF-21-10-126, HTF-21-10-127, HTF-21-10-128, HTF-21-10-129, HTF-21-10-130). These samples were pulled after addition of sodium hydroxide to that tank.

For this macrobatch, Tank 21H is used as the blend/preparation tank. This material will be transferred to Tank 49H where it will be combined with the heel from Macrobatch 3. In this qualification effort for Macrobatch 4, only samples from Tank 21H have been analyzed. In this campaign, the qualification and tank strategy [6] indicates that analysis of Tank 49H is not needed as the material was qualified for Macrobatch 3. As long as the Tank 21H material is qualified, and the qualified Tank 49H material has not changed, then the blend of these two tanks will provide a usable composite.

All of the samples were optically clear, with no visible solids present. The researchers measured the density of the solution in each bottle to make sure that the samples pulled from each depth were relatively homogenous. Samples were well shaken before measuring. The results are listed in Table 1. Results in parentheses are the percent relative standard deviation (% RSD). The density measurements were made at 25 ºC. The analytical uncertainty is typically <1% for density measurements. Once the density was measured, the five samples were composited.

[▽] This revision includes extensive changes and hence revision bars are not included.

Table 1. Sample Density Measurements (25 ºC)

Sample	Measured Density (g/mL)	Sample Depth from Bottom (“)
HTF-21-10-126	1.293	220
HTF-21-10-127	1.278	161
HTF-21-10-128	1.281	62
HTF-21-10-129	1.281	62
HTF-21-10-130	1.288	62
Average (%RSD)	1.284 (0.48%)	

In the previous report on the Tank 21H samples,[2] SRNL reported a measured density of 1.279 g/mL, which is excellent agreement with this current measurement (the values are not normalized to each other, so it is expected some drift upwards due to the caustic addition and evaporation).

2.1 MST Sorption Test

For the MST Sorption Test, technicians generated ~210 mL of the ISDP4 composite. The composite was not filtered, nor was the turbidity measured; gross formation of solids was not observed. The composition of the composite is described in Table 2. The composition mimics the projected blend.

Table 2. Constituents of the ISDP4 Composite

Component	Mass Added (g)
Tank 21H	225.18
Tank 49H	45.10

Technicians placed 150 mL of this solution into the experimental bottle, and the remainder (~65 mL) into the control bottle. Both bottles had magnetic stir bars added to provide mixing. 0.4 g/L of MST solids (from an archived batch of material from Blue Grass Chemical Specialties, lot # MST-2753[7]) was added to the experiment bottle at time = 0 hours. Throughout the course of the experiment, the bottles were agitated using a magnetic stir plate and stir bars. Temperature control (to 25±3 ºC) was provided by an actively controlled water bath.

During the experiment, personnel collected samples from each of the two bottles at 0, 2, 4, 6, 12, and 24 hours. For the sample at 0 hours, sampling occurred immediately prior to

MST addition. Technicians filtered the samples using 0.45 μm Versapor ™ syringe filters, removed the samples from the cells for analysis, and analyzed for plutonium (PuTTA), ^{90}Sr (beta scintillation), and ^{238}U (ICPMS). Samples were sent to Analytical Development (AD) with moderate dilution, and those dilutions are accounted for in the results section. Other than the extra sampling times at 2 and 4 hours, this test uses the same protocol as used in the previous Macrobatch testing.[8]

2.2 ESS Test Conditions

For the ESS Demonstration Test, material from the MST Sorption Test was used. For this test, the researchers used a nominal starting volume of 90 mL of aqueous feed and 30 mL of fresh, unused solvent (S2-D1-YESBOB-T-WI).[ϒ] This test uses the same protocol as used in the previous Macrobatch testing.[8]

3.0 Results and Discussion

In a previous document[2], ICPES, IC and TIC/TOC results were reported for a Tank 21H sample prior to sodium hydroxide addition. In this document, SRNL reports analysis results for samples taken from Tank 21H following sodium hydroxide addition (HTF-21-10-126 to HTF-10-130). These results will be used for the qualification of Salt Batch 4.

3.1 Tank 21H Qualification Analyses

The tank samples were analyzed by Analytical Development (AD) by the listed non-radiological methods (Table 3) and radiological (Table 4) methods. Samples were performed in duplicate unless otherwise noted by blue shading in the table cell. Duplicate samples show the averages of the individual results, with the percent relative standard deviation in parentheses.

Results shaded in light green are calculated values.

[ϒ] This batch of solvent was originally prepared with no extractant as S2-NOBOB-T-WI (see WSRC-NB-2005-00060). The extractant was added later on (see WSRC-NB-2007-00054).

Table 3. Non-Radiological Analyses

Method	Analyte
ICPES	Ag, Al, B, Be, Ba, Ca, Cd, Co, Cr, Cu, Fe, Gd, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Si, Sn, Ti, Zn, Zr
IC Anions	F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, $C_2O_4^{2-}HCO_2^-$
IC Cations	NH_4^+
TIC	total inorganic carbon
TOC	total organic carbon
AA-As	As
AA-Se	Se
CV-Hg	Hg
HPLC	tetraphenylborate, phenol
SVOA	tributylphosphate
VOA	isopropanol, iso/butanol

Table 4. Radiological Analyses

Method	Analyte
Tritium	^{3}H
^{14}C	^{14}C
gamma scan, Cs-removed	^{60}Co, ^{106}Ru, ^{125}Sb, ^{125m}Te, ^{137m}Ba, ^{144}Ce, ^{154}Eu, ^{155}Eu, ^{241}Am, ^{226}Ra, emitters outside of ^{137}Cs and ^{134}Cs
^{90}Sr	^{90}Sr
^{129}I	^{129}I
gamma scan	^{137}Cs, ^{134}Cs
^{232}U	^{232}U
PuTTa (filtered and unfiltered) (Plutonium thenoyl trifluoroacetone scintillation)	^{238}Pu, $^{239/40}Pu$
Am/Cm	^{241}Am, ^{243}Am, ^{244}Cm, ^{245}Cm
$^{59/63}Ni$	$^{59/63}Ni$
^{99}Tc	^{99}Tc
$^{147}Pr/^{151}Sm$	$^{147}Pr/^{151}Sm$
Rad ICPMS (Inductively Coupled Plasma Mass Spectroscopy)	isotopes from mass number 81 to 209 and 230 to 252, incl. ^{233}U and above, ^{237}Np, ^{230}Th, ^{232}Th
Liquid Scintillation Counting	total alpha, total beta

3.2 Tank 21H Qualification Results (non-radiological analytes)

The results of the ICPES analysis are listed in Table 5. The results in Table 5 reflect an additional sample being measured since the previous report revision, resulting in new averages.

Results from the IC Anions, Free Hydroxide, and TIC/TOC are listed in Table 6. The analytical uncertainty for each of these methods is 10%.

The TIC and TOC results are in terms of mg/L of carbon. If we assume that the entire TIC result is carbonate, this translates to a carbonate concentration of 0.257 M.

The results for the weight percent insoluble solids, phenol, tetraphenylborate, tributyl phosphate, isopropanol, methanol, isobutanol/butanol, ammonium, arsenic, mercury, and selenium are listed in Table 7. The analytical uncertainty for the organics is 20%, and 20% for As, Hg, and Se.

Table 5. ICPES Results (mg/L)

Analyte	Result	Analyte	Result
Ag	<2.14	Mn	<0.2
Al	3900 (0.36%)	Mo	6.89 (2.98%)
B	70.7 (1.40%)	Na	155500 (5.00%)
Ba	<0.13	Ni	<2.35
Be	<0.11	P	190 (0.74%)
Ca	1.35 (10%) [℘]	Pb	<7.31
Cd	1.54 (2.30%)	S	2340 (1.21%)
Ce	<6.6	Sb	<6.88
Co	<1.19	Si	60.6 (4.43%)
Cr	51.9 (2.72%)	Sn	<4.29
Cu	1.48 (10%) [℘]	Sr	<0.07
Fe	3.93 (8.64%)	Th	<8.91
Gd	<1.36	Ti	<0.17
K	446.5 (21.1%)	U	<44.5
La	<1.08	V	<0.52
Li	22.8 (7.77%)	Zn	6.37 (5.99%)
Mg	<0.25	Zr	<0.47

[℘] Sample was analyzed in duplicate with one result below detection. Only the measured value is given.

Table 6. IC Anions, Free Hydroxide and TIC/TOC Results

Analyte	Result (mg/L)
F^-	<100
Cl^-	122 (4.53%)
Br^-	<100
Formate	961 (4.78%)
Nitrite	40933 (0.86%)
Nitrate	202667 (24.08%)
Phosphate	418 (17.41%)
Sulfate	6493 (13.12%)
Oxalate	200[∅]
TIC	3087 (1.21%)
TOC	322 (1.76%)
Carbonate	0.257 M
Free Hydroxide	2.622 M

Table 7. Miscellaneous Results

Analyte	Result (mg/L)
wt % insol. solids	<0.250 wt%
phenol	<10
tetraphenylborate	<5
tributylphosphate	<1
isopropanol	<0.25
iso/butanol	<0.5
methanol	0
NH_4^+	<10
As	0.274 (8.26%)
Hg	42.0 (3.70%)
Se	0.244 (1.16%)

The oxalate concentration is <500 mg/L, and the formate result is 982 mg/L. The formate result is converted to the equivalent carbon result of 393 mg/L. Subtracting this result from the TOC result gives a remainder of 0 mg/L of carbon (-71 mg/L, which is impossible, assume the organic carbon is zeroed out), which leaves no organic carbon in

[∅] Three analyzes were performed, of which two of the results returned as below the detection limit values. Only the measured value is reported.

the form of methanol. This methanol result should be considered a rough result as no direct analytical method for methanol exists. The carbonate result is calculated from the TIC result and assumes all of the inorganic carbon is in the form of carbonate.

3.3 Tank 21H Qualification Results (radiological analytes)

The results of the radiological analysis are listed in Table 8. The analytical uncertainty for RADICPMS samples are 20%. Other analytical methods have varying uncertainties, typically 5-10% and are noted for single sample results. The $^{239/40}$Pu value was not previously reported; all other results are the same as in the previous revision.

Table 8. Radiological Results of Tank 21H Analyses for Macrobatch 4 (pCi/mL unless otherwise noted)

Analyte	Average Result	Analyte	Average Result
^{3}H	6.36E+02 (18.5%) ∅	^{155}Eu	< 2.53E+01
^{14}C	7.55E+02 (25.8%)	^{232}Th	<3.30E-03
^{59}Ni	< 9.50E-01	^{233}U	< 1.94E+02
^{63}Ni	< 1.54E+01	^{234}U	< 1.25E+02
^{60}Co	< 2.11E+00	^{235}U	3.72E-01 (12.33%)
^{90}Sr	1.88E+05 (0.34%)	^{236}U	< 1.29E+00
^{90}Y	1.88E+05 (0.34%)	^{238}U	9.16E+00 (0.26%)
^{94}Nb	< 3.02E+00	^{237}Np	1.45E+01 (20.0%) ∅
^{99}Tc	2.06E+04 (6.96%)	^{238}Pu (soluble)	1.17E+04 (6.81%)
^{106}Ru	< 5.23E+01	^{238}Pu (total) ϒ	1.26E+04 (4.79%)
^{106}Rh	< 5.23E+01	$^{239/40}$Pu	2.74E+03 (6.16%)
^{125}Sb	< 3.77E+01	^{241}Pu	<8.20E+03
^{126}Sn	1.37E+02 (3.03%)	^{242}Pu	< 7.64E+01
^{129}I	1.91E+01 (10.03%)	^{244}Pu	< 3.54E-01
^{134}Cs	< 7.07E+03	^{241}Am	< 1.72E+01
^{135}Cs	2.97E+02 (3.99%)	^{243}Am	< 2.22E+00
^{137}Cs	5.27E+07 (13.3%)	^{244}Cm	3.48E+00 (22.87%)
^{137m}Ba	4.99E+07 (13.3%)	^{245}Cm	< 5.77E+00
^{144}Ce	< 5.27E+01	Total Alpha	< 1.68E+04
^{144}Pr	< 5.27E+01	Total Beta	6.89E+07 (9.24%)
^{147}Pm	< 1.61E+02	Total Gamma	5.27E+07
^{151}Sm	< 8.51E+01	Total Sol. Pu (mg/L)	3.88E-02 ℨ
^{154}Eu	< 9.73E+00	Total Sol. U (mg/L)	27.4 Σ
^{226}Ra	< 1.91E+02		

∅ Sample was analyzed in duplicate with one result below detection. Only the measured value is given.
ϒ The Waste Acceptance Criteria (Tank 50 WAC) limit is for total ^{238}Pu. There is an Actinide Removal Process (ARP) limit of 7.93E+05 pCi/mL for soluble ^{238}Pu. Unlike most samples, this one was deliberately not filtered before analysis..
ℨ For this calculation, only the measured values above the detection limits are used.
Σ For this calculation, only the measured values above the detection limits are used.

^{90}Y is calculated as equal to the ^{90}Sr result. ^{106}Rh is calculated as equal to the ^{106}Ru result. ^{137m}Ba is calculated as 94.7% of the ^{137}Cs result.[9] ^{144}Pr is calculated as equal to the ^{144}Ce result. The ^{135}Cs result assumes that all of mass 135 from the ICPMS result is ^{135}Cs. The Total Alpha value is calculated by adding all the alpha results together and treating the less-than results as real values. Thus, this value is biased high. Total gamma is calculated as the sum of the ^{137}Cs, ^{134}Cs, ^{135}Cs, ^{60}Co, ^{94}Nb, ^{106}Ru, ^{125}Sb, ^{126}Sn, ^{144}Ce, ^{144}Pr, ^{154}Eu, ^{155}Eu, and ^{226}Ra. The ^{238}Pu (soluble or total) and $^{239/40}$Pu results are from radiocounting, while the other Pu results are from ICPMS.

The Total Soluble Plutonium value is calculated by adding all the plutonium results together and treating the measurements less-than the method detection limits as equal to the method detection limit. Thus, this value is conservative. The Total Soluble Uranium value is calculated by adding all the uranium results together and treating the values reported as less-than the method detection limits as equal to the method detection limit. Thus, this value is conservative.

3.4 Performance Objectives Demonstration Document (PODD) Sample Analyses

The same stock of Tank 21H material was analyzed for the PODD radionuclide analysis.[10] In this case, a special sample preparation was utilized to get the best detection limit possible. Using 100 mL of the Tank 21H solution, the researchers acidified the sample with concentrated nitric acid, until the pH registered 1 or less. To this acidified solution, the researchers added ~1g of ammonium molybdophosphate (AMP). After stirring for a few minutes, the yellow AMP solids were removed by filtration. This procedure was repeated twice more with fresh quantities of AMP. The final filtrate from this procedure was sent in its entirety to AD for analysis. The dilution caused by the procedure was taken into account when reporting the results. See Table 9. A previous document indicates there is no effect of AMP on U and Pu.[11] From a literature search, SRNL concludes that it is unlikely the other PODD elements would have an affinity for AMP.[12]

As the ^{239}Pu, ^{240}Pu and ^{241}Pu results have high detection limits from the ICPMS analytical method, SRNL derived an additional set of data for these analytes from the PODD sample. See Table 9. As all the sample results are from the same material, the results that are better detection limits or real values can be used.

While several of the desired PODD detection limits were not met, tightening the detection limits would require further analytical method development.

Table 9. Nuclides Requiring Lower Detection Limits in Tank 21H for the PODD Analyses

Analyte	Result (pCi/mL)	Requested Detection Limit (pCi/mL)
^{59}Ni	< 7.06E+00	2.00E+01
^{94}Nb	< 1.44E+00	4.38E-01
^{135}Cs	2.49E+02 (10.0%)	*
^{144}Ce	< 2.36E+01	1.03E+01
^{144}Pr	< 2.36E+01	1.03E+01
^{226}Ra	< 6.53E+01	4.08E+01
^{232}U	1.41E+00 (20.0%)	*
^{233}U	< 1.94E+02	*
^{243}Am	< 8.78E+00	*
^{244}Pu	< 1.71E-02	***
^{245}Cm	< 1.21E+01	***
^{251}Cf	< 1.24E+01	9.01E+01

* Measured above detection limits for Tank 50H.

** The ^{239}Pu, ^{240}Pu and ^{241}Pu values are single calculated results from a combination of radiocounting and RADICPMS.

*** Detection limit should be as low as reasonably achievable

Some of the PODD detection limits were higher than the same results from the radiochemical sample results in Table 8. As the results are for the same sample material, the lower of the two values can be used. The ^{135}Cs is from ICPMS analysis, and we conservatively assume that all of mass-135 is due to ^{135}Cs, which is not necessarily true (^{135}Ba interferes). ^{144}Pr is calculated as equal to the ^{144}Ce result.

3.5 Results from the MST Sorption Test

For the MST Sorption Test, technicians used ~210 mL of a composite made from Tank 21H and Tank 49H samples (see section 2.1). The composite was not filtered and we did not observe gross formation of solids. The turbidity was not measured.

During the experiment, personnel collected samples from each of the two bottles at 0, 2, 4, 6, 12, and 24 hours. For the sample at 0 hours, sampling occurred immediately prior to MST addition. Technicians filtered the samples using 0.45 μm Versapor ™ syringe filters, removed the samples from the cells for analysis, and analyzed for plutonium (PuTTA), ^{90}Sr (beta scintillation), and ^{238}U (ICPMS). Samples were sent to Analytical Development (AD) with moderate dilution, and those dilutions are accounted for in the results section.

3.5.1 Plutonium Results

Researchers analyzed the filtered samples for ^{238}Pu. Table 10 shows the plutonium results while Figure 1 shows the graphical results for ^{238}Pu. The ^{238}Pu data is more useful than the $^{239/40}$Pu as the former is not limited by detection limit values. The uncertainty in Table 10 is the analytical uncertainty associated with the measurement and does not include any contribution to uncertainty due to experimental and sampling methods.

Table 10. ^{238}Pu Concentrations in the MST Strike Filtrates

Time (hours)	Experiment	Control
	^{238}Pu (pCi/mL)	^{238}Pu (pCi/mL)
0*	1.26E+04 (4.46%)	1.26E+04 (4.46%)
2	4.32E+03 (4.73%)	1.25E+04 (4.81%)
4	4.05E+03 (4.65%)	1.23E+04 (4.82%)
6	3.70E+03 (4.80%)	1.30E+04 (4.48%)
12	3.17E+03 (5.77%)	1.23E+04 (5.36%)
24	2.61E+03 (5.76%)	1.28E+04 (5.76%)

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

Figure 1. ^{238}Pu in Solution Over Time for the MST Sorption Test

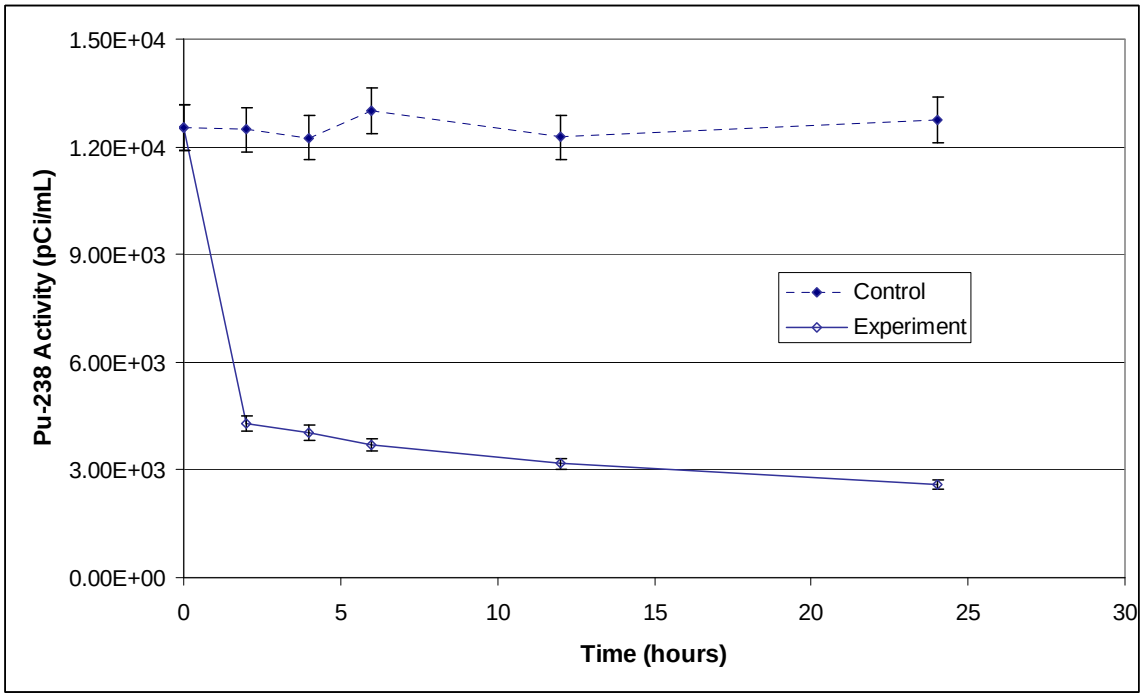

Table 11 lists the decontamination factors (DF) after the MST strike.

Table 11. ^{238}Pu Decontamination Factors (DF) Over Time

Time (hours)	Experiment	Control
	DF	DF
2	2.91	1.01
4	3.11	1.02
6	3.40	0.96
12	3.96	1.02
24	4.82	0.98

3.5.2 Strontium Results

Researchers analyzed the filtered samples for ^{90}Sr. Table 12 shows the plutonium results while Figure 2 shows the graphical results for ^{90}Sr. The uncertainty in Table 12 is the analytical uncertainty associated with the measurement and does not include any contribution to uncertainty due to experimental and sampling methods.

Table 12. ^{90}Sr Concentrations in the MST Strike Filtrates

Time (hours)	Experiment	Control
	^{90}Sr (pCi/mL)	^{90}Sr (pCi/mL)
0*	2.19E+05 (7.99%)	2.19E+05 (7.99%)
2	2.96E+03 (12.0%)	2.11E+05 (8.10%)
4	4.07E+03 (10.9%)	2.41E+05 (8.87%)
6	3.80E+03 (11.3%)	2.56E+05 (9.19%)
12	5.77E+03 (10.0%)	1.96E+05 (7.13%)
24	5.38E+03 (10.2%)	2.79E+05 (8.11%)

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

Figure 2. ^{90}Sr in Solution Over Time for the MST Sorption Test

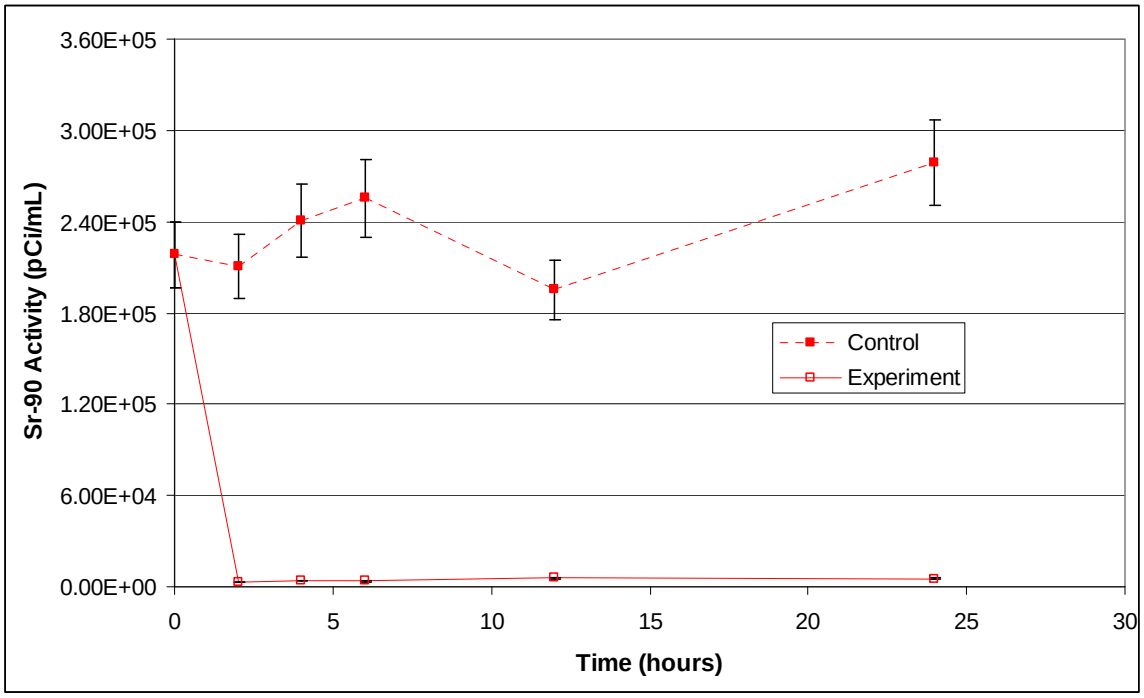

Table 13 lists the decontamination factors (DF) after the MST strike.

Table 13. ^{90}Sr Decontamination Factors (DF) Over Time

Time (hours)	Experiment	Control
	DF	DF
2	73.8	1.04
4	53.7	0.91
6	57.6	0.85
12	37.9	1.12
24	40.7	0.78

3.5.3 Uranium Results

Researchers analyzed the filtered samples for ^{238}U. Table 14 shows the uranium results while Figure 3 shows the graphical results for ^{238}U. The uncertainty in Table 14 is the analytical uncertainty associated with the measurement and does not include any contribution to uncertainty due to experimental and sampling methods.

Table 14. ^{238}U Concentrations in the MST Strike Filtrates

Time (hours)	Experiment ^{238}U (pCi/mL)	Control ^{238}U (pCi/mL)
0*	9.52E+00 (20.0%)	9.52E+00 (20.0%)
2	8.89E+00 (20.0%)	9.51E+00 (20.0%)
4	8.80E+00 (20.0%)	9.31E+00 (20.0%)
6	9.17E+00 (20.0%)	9.41E+00 (20.0%)
12	9.50E+00 (20.0%)	9.60E+00 (20.0%)
24	8.59E+00 (20.0%)	9.57E+00 (20.0%)

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

Figure 3. ^{238}U in Solution Over Time for the MST Sorption Test

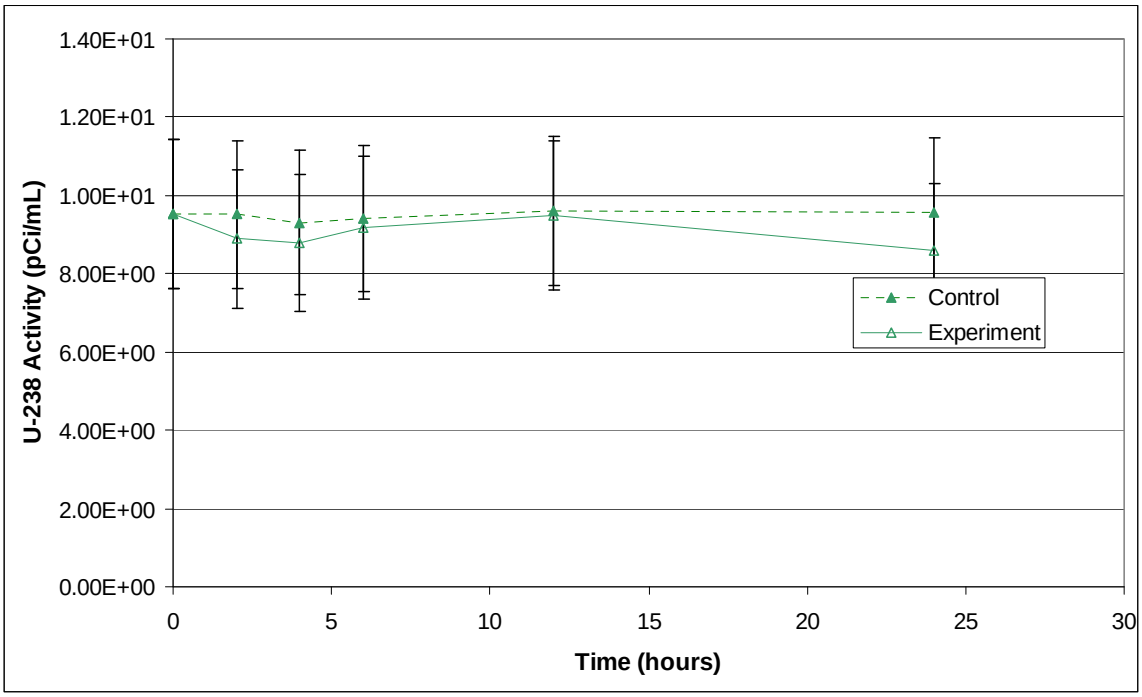

Table 15 lists the DF after the first MST strike.

Table 15. ^{238}U Decontamination Factors (DF) Over Time

Time (hours)	Experiment	Control
	DF	DF
2	1.07	1.00
4	1.08	1.02
6	1.04	1.01
12	1.00	0.99
24	1.11	0.99

3.5.4 Neptunium and Americium Results

There was insufficient ^{237}Np and ^{243}Am in the feed solution to determine any decontamination effects of MST.

3.5.5 Consideration of DF Values

The DF values for plutonium and strontium are lower than observed for the previous three macrobatches.[8,13,14] See Table 16.

Table 16. Pu and Sr 24-Hour DF Values for All 4 Macrobatches

Macrobatch	Pu DF	Sr DF
1	14.0	59.4
2	5.64	70.9
3	9.30	70.6
4	4.82	40.7

There is nothing in the experimental setup or execution (temperature, stirring, source tanks, starting Pu and Sr concentrations, etc) that would be expected to give lower DF values.

A previous study investigated the effects on DF by the concentrations of the six most common anions in salt solutions (NO_3^-, OH^-, NO_2^-, $Al(OH)_4^-$, CO_3^{2-} and SO_4^{2-}).[15] That study, and predicted DFs from those correlations do not corroborate the decline in DFs for the Pu and Sr in Macrobatch 4.

Finally, there is a fairly large difference in the mass concentration of plutonium between the two macrobatches. Macrobatch 3 has ~6 μg/L of Pu, while Macrobatch 4 has ~28 μg/L of Pu.

While the removal efficiency is still within acceptable parameters, SRNL is considering the possible reasons for the lower removal efficiency for Pu and Sr.

3.5.6 Analysis of MST Solids

After the MST test completed, personnel digested the retained MST solids (aqua regia/microwave) and sent them to AD for analysis. Table 17 shows the results of the titanium analysis.

Table 17. Tank 21H MST Solids Analyses Chemical Results

Analyte	Method	Result (mg/L)	% Uncertainty
Ti	ICPES	298	10%

While in principle a known amount of MST (380 mg) is added, we do not know the mass of the MST that is filtered off at the end of the MST strike experiment; the mass is small to begin with and contains an unknown amount of interstitial salt solution. Due to this fact, we have to ratio the results of the MST solids analysis to the Ti result from the ICPES analyses. The MST solids were digested into a 50mL liquid sample, with a density of ~1 g/mL. With a Ti result of 298 mg/L, this means our sample had 14.9 mg of titanium. The analytes were from the 50 mL sample, so the raw result is multiplied by 50 mL to get the amount of analyte in the MST solids sample, after converting to pCi. The pCi result is then divided by the mass of Ti in grams, to get the final result of "pCi analyte per g of Ti", which is reported in Table 18.

As there are no, or virtually no sludge solids in the feed material, the solids digestion data reflects the MST solids, and whatever adsorbs to the MST, as well as entrained salt solution. Actinides and strontium adsorb to MST and the analysis of the MST provides relevant data for those species. However, the other results for materials that have no affinity for MST are a function of material in the feed solution. Results for these elements are from interstitial or entrained salt solution. As there is no experimental data for many of these analytes as to whether or not they adsorb to MST under our conditions, SRNL cannot conclusively determine if the real values for an analyte result is from MST sorption or interstitial liquid entrainment. Therefore, the values reported in Table 18 should all be considered upper bounds.

The ^{134}Cs result was calculated from the supernate $^{137}Cs/^{134}Cs$ ratio and the ^{137}Cs result. As MST does not have an affinity for cesium, the $^{137}Cs/^{134}Cs$ ratio will be the same as in the supernate. All other results were single results as there was not enough material to analyze duplicates.

Table 18. Tank 49H MST Solids Radiological Results

Analyte	Result (pCi per gram of Ti)	Analyte	Result (pCi per gram of Ti)
^{233}U	<6.54E+04	^{151}Sm	<1.06E+05
^{234}U	1.24E+05 (20.0%)	^{134}Cs	<1.08E+06
^{235}U	6.56E+02 (20.0%)	^{137}Cs	7.56E+09 (5.00%)
^{99}Tc	3.79E+06 (5.89%)	^{144}Ce	<2.68E+05
^{237}Np	5.56E+04 (20.0%)	^{147}Pm	<4.75E+04
^{238}Pu	7.03E+07 (4.79%)	^{151}Sm	<1.06E+05
$^{239/40}Pu$	1.45E+07 (4.80%)	^{154}Eu	<2.62E+04
^{241}Pu	<2.39E+07	^{155}Eu	<1.38E+05
^{242}Pu	<2.56E+04	^{226}Ra	<7.32E+05
Total Alpha	<1.01E+08	^{241}Am	1.18E+05 (26.7%)
Total beta	1.28E+10 (10.0%)	^{242m}Am	<8.99E+02
^{60}Co	<8.69E+03	^{243}Am	<2.75E+04
^{90}Sr	1.27E+09 (7.24%)	^{242}Cm	<7.44E+02
^{94}Nb	<1.13E+04	^{243}Cm	<8.63E+04
^{99}Tc	3.79E+06 (5.89%)	^{244}Cm	3.73E+05 (11.3%)
^{106}Ru	<1.48E+05	^{245}Cm	<7.09E+04
^{125}Sb	<9.31E+04	^{247}Cm	<1.25E+05
^{126}Sb	1.13E+04 (15.8%)	^{249}Cf	<1.28E+5
^{126}Sn	1.13E+04 (15.8%)	^{251}Cf	<8.00E+04
^{147}Pm	<4.75E+04	^{90}Sr	1.27E+09 (7.24%)

3.6 Results from the ESS Test

For the ESS Test, filtrate from the MST Sorption Test was used. For this test, the researchers used a nominal starting volume of 90 mL of aqueous feed and 30 mL of fresh, unused solvent (S2-D1-YESBOB-T-WI).[ϒ]

Table 19 shows the results from the ESS Test, corrected to the normal process operating temperatures (i.e., 23 ºC for extraction and 33 ºC for scrubbing and stripping). As a comparison, the results from the previous macrobatch qualification ESS test (using the same solvent) in 2010 are displayed.[8]

[ϒ] This batch of solvent was originally prepared with no extractant as S2-NOBOB-T-WI (see WSRC-NB-2005-00060). The extractant was added later on (see WSRC-NB-2007-00054).

Table 19. Cesium Distribution Values for the ESS Test

Material	Extraction	Scrub#1	Scrub#2	Strip#1	Strip#2	Strip#3
Acceptable Range	>8	>0.6, <2	>0.6, <2	<0.2	<0.16	<0.16
S2-D1-YES BOB-T-WI, ISDP 3 (previous test)	16.37	1.80	2.58	0.12	0.037	0.036
S2-D1-YES BOB-T-WI, ISDP 4 (current test)	12.33	1.69	0.892	0.0434	0.057	0.019

The current test shows acceptable values for all steps. From the bulk chemistry of the solution, an extraction DF of ~12.7 is predicted.[16]

3.6.1 Strip Effluent and DSS Results

During, and at the end of the ESS test, the gamma activity in the strip effluent and the decontaminated salt solution (DSS) was measured. The results are shown in Table 20.

Table 20. Strip Effluent and DSS Results

Sample	^{137}Cs activity (pCi/mL)	pH
Strip Effluent #1	1.33E+08	4
Strip Effluent #2	4.82E+07	5
Strip Effluent #3	3.32E+07	4
DSS	1.16E+06	14

The analytical uncertainty on the ^{137}Cs activity is 10% and ±1 pH unit for the pH measurement.

4.0 Conclusions

Analysis of the Tank 21H sample indicates that the material does not display any unusual characteristics. In conjunction with the previous report,[1] the Tank 21H material, when combined with the Tank 49H heel is acceptable for processing in the ISDP process.

This report also covers the MST sorption and ESS results for the ISDP Salt Batch 4 feed sample. The following observations are made from the work.

- A demonstration of the monosodium titanate removal of strontium and actinides provided acceptable 12 hour decontamination values for Pu and Sr of 3.96 and 37.9, respectively. These DF values are slightly lower than previous tests, but not enough to warrant a high degree of concern.

- A demonstration of cesium extraction, scrubbing and stripping cesium mass transfer – intended to partially mimic the MCU operations – yielded behavior within acceptable norms. The measured distribution values are: 12.33, 1.69, 0.892, 0.0434, 0.057, and 0.019 for Extraction, Scrub #1, Scrub #2, Strip #1, Strip #2, and Strip #3, respectively. The values indicate the cesium removal should be comparable to prior batches in MCU.

5.0 References

[1] T. B. Peters, S. D. Fink, "Sample Results from the Integrated Salt Disposition Program Macrobatch 4 Tank 21H Qualification Samples", SRNL-STI-2011-00061, Rev.0, March 2011.
[2] T. B. Peters, F. F. Fondeur, S. D. Fink, "Results from Tank 21H Initial Samples for Integrated Salt Disposition Process Macrobatch 4", SRNL-STI-2010-00472, September 2010.
[3] HLW-DWPF-TTR-2010-0035, "Qualification of ISDP Salt Batch 4", September 2010.
[4] T. B. Peters, S. D. Fink, "Task Technical and Quality Assurance Plan for ISDP Salt Batch 4 Sample Qualification", SRNL-RP-2010-0-1433, November 30, 2010.
[5] T. B. Peters, "ISDP4", SRNL-NB-2011-00027
[6] S. E. Campbell, "Qualification and Sampling Strategy for ISDP Batch 4 to Obtain Compliance to 512-S, DWPF, Tank Farm, and Saltstone Waste Acceptance Criteria", X-ESR-H-00234, August 19, 2010.
[7] D. T. Hobbs, Characterization of Monosodium Titanate Sample Supplied by Blue Grass Chemical Specialties", WSRC-RP-2003-01084, November 20, 2003.
[8] T. B. Peters, S. D. Fink, "Results from Monosodium Titanate (MST) and Extraction-Scrub-Strip (ESS) Testing of ISDP Macrobatch 3 Blend", SRNL-STI-2010-00290, May, 2010.
[9] http://www.nndc.bnl.gov, E. Browne, J. K. Tuli Citation: Nuclear Data Sheets 108, 2173 (2007)
[10] K. H. Rosenberger, B. C. Rogers, and R. K. Cauthen, "Saltstone Performance Objective Demonstration Document", CBU-PIT-2005-00146, Rev. 0, June 2005.
[11] M. J. Barnes D. P. DiPrete D. T. Hobbs T. B. Peters M. E. Stallings S. D. Fink, "Effects of Ammonium Molybdophosphate (AMP) on Strontium, Actinides, and RCRA Metals in SRS Simulated Waste", WSRC-TR-2003-00572, Rev. 0, January 27, 2004.
[12] S. F. Marsh, Z. V. Svitra, and S. M. Bowen, "Distribution of 14 Elements on 63 Absorbers from Three Simulant Solutions (Acid-Dissolved Sludge, Acidified Supernate, and Alkaline Supernate) for Hanford HLW Tank 102-SY", LA-12654, Rev. August 1994.
[13] C. A. Nash, T. B. Peters, S. D. Fink, "TANK 49H SALT BATCH SUPERNATE QUALIFICATION FOR ARP/MCU"WSRC-TR-2008-00117, Rev. 0", August 25, 2008.
[14] T. B. Peters,C. A. Nash, S. D. Fink, "ISDP SALT BATCH #2 SUPERNATE QUALIFICATION", WSRC-TR-2008-00446, Rev. 1", January 5, 2009.
[15] M. J. Barnes, T. B. Edwards, D. T. Hobbs, K. M. Marshall, "Strontium and Actinide Removal Testing with Monosodium Titanate and Other Sorbents", WSRC-TR-2001-00436, Rev.0, October 29, 2001.
[16] L. H. Delmau, D. A. Bostick, T. J. Haverlock, B. A. Moyer, "Caustic-Side Solvent Extraction: Extended Equilibrium Modeling of Cesium and Potassium Distribution Behavior", ORNL/TM-2002/116, May 2002.

Distribution:

A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A

E. J. Freed, 704-56H
D. J. Martin, 241-152H
M. W. Geeting, 241-152H
S. P. McLeskey, 241-152H
B. A. Gifford, 704-56H
S. E. Campbell, 241-152H
A. W. Wiggins, 704-60H
E. W. Harrison, 704-60H
C. E. Duffey, 704-61H
T. T. Le, 704-61H
J. E. Occhipinti, 704-S
D. C. Sherburne, 704-S
J. W. Ray, 704-S
A. R. Shafer, 704-27S
C. K. Chiu, 704-27S
H. H. Elder, 704-24S
P. R. Jackson, 703-46A

T. B. Peters, 773-42A
C. A. Nash, 773-42A
M. R. Poirier, 773-42A
F. F. Fondeur, 773-A