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Sample Results from the Interim Salt Disposition Program Macrobatch 9 Tank 21H Qualification Samples

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed samples from Tank 21H in support of qualification of Macrobatch (Salt Batch) 9 for the Interim Salt Disposition Program (ISDP). This document reports characterization data on the samples of Tank 21H. Extensive analysis of the samples shows the following general characteristics:

- The density and color are typical of salt solution samples from Tank 21H.
- While the weight percent (wt%) insoluble solids content is higher than the previous salt batch sample, the value is still quite low. The color of the solids suggests that they are not largely composed of sludge materials. In order to better understand the solids present in the Tank 21H sample, SRNL recommends analyzing the solids for bulk chemical makeup.
- The bulk chemical composition (e.g., OH, Na, Al, nitrate, nitrite) is roughly similar to previous salt batch samples, with typical variations of <20%.
- The radionuclide concentrations are also similar to previous salt batch samples, although the ^{137}Cs concentration is slightly higher for this batch.
- The plutonium and ^{90}Sr results indicate that a monosodium titanate (MST) strike will not be needed for qualification.
- The low levels of mercury in the sample indicate that off-site speciation is not required.

Further work will report the results of the Extraction-Scrub-Strip (ESS) testing using the Tank 21H material.

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LIST OF ABBREVIATIONS

AA	Atomic Absorption
AD	Analytical Development
CV-Hg	Cold Vapor Mercury
ESS	Extraction-Scrub-Strip
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ICPMS	Inductively Coupled Plasma Mass Spectroscopy
ISDP	Interim Salt Disposition Program
MST	Monosodium titanate
PuTTa	plutonium thenoyl trifluoroacetone
% RSD	Percent relative standard deviation
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SVOA	Semi Volatile Organic Analysis
TBP	tributylphosphate
TIC/TOC	Total Inorganic Carbon-Total Organic Carbon
TPB	tetraphenylborate
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
VOA	Volatile Organic Analysis
Wt%	Weight percent

1.0 Introduction

This report provides the Tank 21H qualification sample results for ISDP Macrobatch (Salt Batch) 9. A previous document covered initial characterization which included results for a number of radiological and non-radiological analytes[i]; these analyses are also included in this report for completeness. This work was specified in a Technical Task Request (TTR) [ii] and in a Task Technical and Quality Assurance Plan (TTQAP).[iii] Details of the work are contained in controlled laboratory notebooks.[iv]

2.0 Experimental Procedure

Two 200 mL Tank 21H samples (HTF-21-15-106 and -107) and a single 1L Tank 21H sample (HTF-21-15-108) were collected and delivered to SRNL on September 1, 2015. The two 200 mL samples were surface samples and the 1L sample was a variable depth sample obtained approximately 62" from the bottom of the tank (transfer pump suction). The contents of Tank 21H were mixed at full speed for approximately 15 hours with one pump before the samples were collected; the samples were collected approximately 28 hours after pump shutdown. All the samples had the same visual appearance, clear solutions with no apparent solids.

The density of filtered solution (using a 0.45 μm syringe filter) from each sample was measured twice. Averages of the individual results, with percent relative standard deviation (%RSD)[℘] in parentheses, are reported in Table 1. With Savannah River Remediation (SRR) concurrence, the contents of the three sample bottles were then combined and mixed. After compositing and allowing the contents of the composite bottle to sit for several days, it was found that a thin layer of fine off-white solids had settled to the bottom of the composite bottle.

Table 1. Sample Density Measurements (24.9º C)

Sample	Measured Density (g/mL)
HTF-21-15-106	1.251 (0.25%)
HTF-21-15-107	1.246 (0.99%)
HTF-21-15-108	1.254 (0.17%)
Average (%RSD)	1.250 (0.32%)

The analytical uncertainty is typically <1% for density measurements.

[℘] %RSD is defined as the standard deviation of the array, divided by the average of the array, expressed in % terms.

Duplicate filtered samples (using a 0.45 μm syringe filter) were sent to Analytical Development (AD) for analysis. The two exceptions are the unfiltered Hg result, and the wt% insoluble solids result in Table 4. In these cases, a well-mixed sample from the composite bottle was removed for analysis with no filtration. None of the samples were diluted before delivery to AD.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 Procedure 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. Results from this report are not RW-0333P (enhanced quality assurance requirements) as per the TTR. For this document, an additional person was used as a design check to ensure coverage during the document editing.

3.0 Results and Discussion

The tank samples were analyzed by AD using listed non-radiological methods (Table 2) and radiological methods (Table 3). Analyses were performed in duplicate. Averages of the individual results, with %RSD in parentheses, are reported in Tables 4 and 5.

In a previous document,[i] density (at 24.9 °C), Inductively Coupled Plasma Emission Spectroscopy (ICPES), Ion Chromatography (IC), Total Inorganic Carbon/Total Organic Carbon (TIC/TOC), Hg (filtered and unfiltered), and Free Hydroxide were reported for the Tank 21H composite sample. These results are also reported here for completeness and are reported with other non-radiological results in Table 4. In that same document, selected radiochemical results were also reported for the Tank 21H composite sample. For completeness, those are contained with the other radiochemical results in Table 5.

Table 2. Non-Radiological Analyses

Method	Analyte
IC Cations	ammonium cation
IC Anions	fluoride, chloride, bromide, formate, nitrite, nitrate, sulfate, phosphate, oxalate
ICPES	Ag, Al, B, Ba, Be, Ca, Ce, Cd, Cr, Cu, Fe, Gd, K, La, Li, Mg, Mo, Mn, Na, Ni, P, Pb, S, Sb, Si, Sn, Sr, Th, Ti, U, V, Zn, Zr
TIC	total inorganic carbon (carbonate)
TOC	total organic carbon
Atomic Absorption (AA)-As	As
AA-Se	Se
Cold Vapor-Hg (CV-Hg)	Hg
High Performance Liquid Chromatography (HPLC)	Tetraphenylborate (TPB)
Semi-Volatile Organic Analysis (SVOA)	Tributylphosphate (TBP), phenol, Isopar L ™
Volatile Organic Analysis (VOA)	isopropanol, butanol, isobutanol
pH	pH
titration	Free Hydroxide
density tube	density
total insoluble solids	Wt% insoluble solids

Table 3. Radiological Analyses

Method	Analyte
Tritium	^{3}H
^{14}C	^{14}C
gamma scan, Cs-removed[⊕]	^{60}Co, ^{106}Ru, ^{125}Sb, ^{126}Sn, ^{144}Ce, ^{154}Eu, ^{155}Eu
Individual radio count method for each isotope: ^{90}Sr, ^{94}Nb, ^{129}I, ^{99}Tc , ^{135}Cs, ^{226}Ra	^{90}Sr, ^{94}Nb, ^{129}I, ^{99}Tc , ^{135}Cs, ^{226}Ra
gamma scan	^{134}Cs, ^{137}Cs (from ^{137m}Ba)
^{232}U	^{232}U
$^{238-241}Pu$ (Plutonium thenoyl trifluoroacetone scintillation - PuTTa)	^{238}Pu, $^{239/40}Pu$, ^{241}Pu
Am/Cm	^{241}Am, ^{243}Am, ^{244}Cm, ^{245}Cm
$^{59/63}Ni$	$^{59/63}Ni$
$^{147}Pm/^{151}Sm$	$^{147}Pm/^{151}Sm$
Inductively Coupled Plasma Mass Spectroscopy (ICPMS)	isotopes from mass number 81 to 209 and 230 to 252, incl. ^{233}U and above, ^{237}Np, ^{242}Pu, ^{244}Pu
Liquid Scintillation Counting	total alpha, total beta

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

Non-radiological results are listed in Table 4. Results are in mg/L unless otherwise noted. The analytical uncertainties for all results are 10% except as noted. The analytical uncertainty for the pH measurement is typically 0.5 pH units. The analytical uncertainties for the As, Se, and Hg results are 20%. Values in parentheses are %RSD. The values shaded in green are calculated results.

[⊕] For these isotopes, the cesium must be removed in order to resolve these species.

Table 4. Non-Radiological Results of Tank 21H Analyses for Macrobatch 9

Analyte	Result (mg/L)	Analyte	Result (mg/L)
Ag	<1.17	V	1.19 (1.8%)
Al	6010 (0.47%)	Zn	4.56 (0.62%)
B	48.7 (0.15%)	Zr	<0.412
Ba	0.12 (0.00%)	F^-	<100
Be	<0.106	Cl^-	696 (0.92%)
Ca	1.04 (20%)	Br^-	<500
Cd	<1.60	Formate	127 (0.56%)
Ce	<4.61	Nitrite	31700 (1.3%)
Cr	67.2 (0.11%)	Nitrate	106000 (1.3%)
Cu	<1.17	Phosphate	455 (0.93%)
Fe	4.21 (3.0%)	Sulfate	5660 (3.5%)
Gd	<1.44	Oxalate	453 (9.2%)
K	558 (1.6%)	TIC	2920 (0.24%)
La	1.12 (8.2%)	TOC	184 (1.2%)
Li	<8.86	pH	14 (0.00%)
Mg	<0.129	ammonium	<10
Mn	<0.419	Isopar-L	<11
Mo	25.7 (0.83%)	phenol	<10
Na	144000 (0.49%)	TPB	<5
Ni	<4.18	TBP	<1
P	198 (1.4%)	isopropanol	<0.25
Pb	<17.1	butanol	<0.75
S	1930 (0.73%)	isobutanol	<0.75
Sb	<34.8	methanol	72
Si	12.9 (1.1%)	As	0.381 (1.5%)
Sn	<22.1	Hg (unfiltered)	58.5 (12%)
Sr	<0.094	Hg (filtered)	62.8 (3.0%)
Th	<0.005[♦]	Se	0.265 (11%)
Ti	<9.35	wt % insoluble solids	0.0350 (61%) wt%
U	<51.3[◊]	Free Hydroxide	2.52 (0.00%) M

[♦] Previously, a result of <6.27 mg/L from ICPES was reported. However, it was found that a lower detection limit of <0.005 mg/L was obtained from ICPMS.
[◊] While the U value is provided by ICPES, a better total uranium value can be derived from the sum of the uranium isotopic results listed in Table 5 (10.7 mg/L).

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 0.243 M. The pH of the salt solution based on the measured free hydroxide is 14. The nickel (Ni) result converted into a concentration of $Ni(OH)_2$ is <6.60 mg/L.

The bulk chemical characteristics (e.g., OH, Al, Na, nitrate, nitrite) of this batch are roughly similar to that of Salt Batch 8, with typically <20% differences between the batches for the major components.

The wt% insoluble solids result is higher than the previous Salt Batch 8 sample (0.014 wt%). However, the magnitude of either result is small, and the presence of these quantities of solids should not present difficulties to processing. The high %RSD associated with this result is due to the small concentration of the solids being close to the method detection limit. SRNL believes that analyzing the solids for bulk chemical composition would be worthwhile in order to determine if the solids are primarily sludge solids or not.

SRNL also notes the Hg values are lower than in Salt Batch 8 (129 mg/L). The sample filtration had no effect on the mercury concentration given that the results are statistically the same.

Per Table 4, the oxalate concentration is 453 mg/L, and the formate concentration is 127 mg/L. The oxalate result is converted to the equivalent carbon result of 123 mg/L. The formate result is converted to the equivalent carbon result of 34 mg/L. Subtracting these results from the TOC result gives a remainder of 27 mg/L of carbon. If we assume all of this remainder carbon is in the form of methanol, this gives a calculated methanol result of 72 mg/L. This value is likely grossly conservative. No direct analytical method for methanol is available.

The wt% insoluble solids value is a value calculated from a wt% total solids and a wt% soluble solids measurements (insoluble = total – soluble).

3.2 Tank 21H Qualification Results (radiological analytes)

The results of the radiological analysis in pCi/mL are listed in Table 5. The analytical uncertainty for ICPMS samples is 20%. Other analytical methods have varying uncertainties, typically 5-15%. Values in parentheses are the %RSD. The values shaded in green are calculated results.

Table 5. Radiological Results of Tank 21H Analyses for Macrobatch 9 (pCi/mL)

Analyte	Result	Analyte	Result
^{3}H	1.79E+03 (0.40%)	^{155}Eu	<6.62E+01
^{14}C	8.66E+02 (14%)	^{226}Ra	<8.24E+00
^{59}Ni	<1.42E+01	^{232}U	2.12E+00 (15%)
^{63}Ni	<3.09E+01	^{233}U	1.71E+01 (1.5%)
^{60}Co	<6.93E+00	^{234}U	9.25E+01 (1.0%)
^{90}Sr	4.31E+05 (1.4%)	^{235}U	2.32E-01 (3.3%)
^{90}Y	4.31E+05 (1.4%)	^{236}U	1.41E+00 (1.3%)
^{94}Nb	<9.54E+00	^{238}U	3.55E+00 (0.67%)
^{99}Tc	6.28E+04 (8.6%)	^{237}Np	<3.53E+00
^{106}Ru	<9.27E+01	^{238}Pu	4.16E+04 (13%)
^{106}Rh	<9.27E+01	^{239}Pu	6.97E+02 (2.5%)
^{125}Sb	<6.98E+01	^{240}Pu	<1.14E+03
^{125m}Te	<6.98E+01	$^{239/40}$Pu	8.71E+02 (7.7%)
^{126}Sn	4.68E+02 (2.7%)	^{241}Pu	<1.70E+04
^{129}I	4.97E+01 (0.64%)	^{242}Pu	<1.91E+01
^{134}Cs	<3.37E+04	^{244}Pu	<8.85E-02
^{135}Cs	1.26E+03 (0.25%)	^{241}Am	<3.46E+00
^{137}Cs	2.44E+08 (0.26%)	^{243}Am	<3.65E+00
^{137m}Ba	2.31E+08 (0.26%)	^{244}Cm	1.94E+00 (32%)
^{144}Ce	<1.56E+02	^{245}Cm	<9.23E+00
^{144}Pr	<1.56E+02	Total Alpha (w/o cesium)	<3.43E+04
^{147}Pm	<1.53E+02	Total Beta (w/cesium)	2.65E+08 (0.84%)
^{151}Sm	<9.27E+01	Total Beta (w/o cesium)	8.96E+05 (0.71%)
^{154}Eu	<1.99E+01	Total Gamma	2.31E+08

^{90}Y is calculated as equal to the ^{90}Sr result. ^{106}Rh is calculated as equal to the ^{106}Ru result. ^{125m}Te is conservatively calculated as the ^{125}Sb result. ^{137m}Ba is calculated as 94.7% of the ^{137}Cs result.[v,∩] ^{144}Pr is calculated as equal to the ^{144}Ce result.[ϒ] Total gamma is calculated as the sum of the ^{60}Co, ^{94}Nb, ^{106}Rh, ^{125}Sb, ^{125m}Te, ^{126}Sn, ^{134}Cs, ^{137m}Ba, ^{144}Ce, ^{144}Pr, ^{154}Eu, ^{155}Eu, ^{226}Ra, ^{235}U, ^{237}Np, ^{241}Am, ^{243}Am, and ^{245}Cm results. The ^{238}Pu, $^{239/40}$Pu, and ^{241}Pu results are from radio-counting, while the ^{239}Pu, ^{240}Pu, ^{242}Pu, and ^{244}Pu results are from ICPMS. The radiochemical

∩ While the ^{137m}Ba result is calculated from the analytically provided ^{137}Cs result, in actuality the gamma of the ^{137m}Ba is measured and the ^{137}Cs is determined from that.
ϒ Nuclear decay transitions and values are generally taken from data from www.nndc.bnl.gov, NuDat 2.6.

$^{239/40}$Pu result cannot distinguish between the ^{239}Pu and ^{240}Pu. However, if a specific 239/240 isotopic breakdown from the tank is used, the individual ^{239}Pu and ^{240}Pu values can be calculated from this method. The total alpha result is from a sample with the cesium removed before analysis (failure to remove ^{137}Cs from the sample beforehand results in interference and a resulting higher minimum detection limit). The total alpha result is lower than the ^{238}Pu, which is the primary alpha emitter. The total alpha method is generally less precise than the individual method results. The ^{137}Cs result is slightly higher than the previous salt batch (2.13E+08 pCi/mL), and is the highest salt batch activity measured to date. Other major radiochemical results are typical of previous salt batches.

4.0 Conclusions and Recommendations

Results of the analyses of the Tank 21H samples from this report indicate that the material does not display any unusual characteristics nor is expected to pose any insurmountable problems for processing. However, the increasing ^{137}Cs dose in the salt batch feed will inevitably lead to increased dose for operating personnel. The plutonium and ^{90}Sr results indicate that an MST strike will not be needed for qualification. The low levels of mercury in the sample indicate that off-site speciation is not required.

Further work will report the results of the ESS testing using the Tank 21H material.

In order to better understand the solids present in the Tank 21H sample, SRNL recommends analyzing the solids for bulk chemical makeup.

5.0 References

[i] T. B. Peters, "Results of Initial Analyses of the Salt (Macro) 9 Tank 21H Qualification Samples", SRNL-STI-2015-00513, Rev. 1, October 2015.

[ii] M. A. Rios-Armstrong, TTR "Technical Task Request – Salt Batch Qualification for Feed to the Interim Salt Disposition Project (ISDP)", X-TTR-H-00059, Rev. 0, August 24, 2015.

[iii] T. B. Peters and D. H. Jones, "Task Technical and Quality Assurance Plan for Qualification of Salt Batches for Feed to ISDP", SRNL-RP-2015-00704, Rev. 0, September 2015.

[iv] T. B. Peters, "Salt Batch 9 Qualification", ELN, A4571-00084-23.

[v] Nuclear Data Sheets 108, 2173 (2007).

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