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Results of Short-Term Analyses of the Salt (Macro) Batch 5 Tank 41H Qualification Sample (Resample)

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed samples from Tank 41H in November 2021 in support of qualification of Salt Waste Processing Facility (SWPF) Salt Batch 5. This document reports the short-term results of the analyses of samples of Tank 41H. Analysis of the Tank 41H Salt Batch 5 sample indicates that the material does not display any unusual characteristics or observations, such as floating solids, the presence of large amounts of solids, or unusual colors. Further sample results will be reported in a future document. This report satisfies part of Deliverable 3 of the Technical Task Request (TTR).

After a data review it was found that the original results reported in the revision 0 of this document were actually from Salt Batch 4 (Tank 21H). A new set of samples was sent for analysis to satisfy deliverable 3 of the TTR. The results from the original analyses have been replaced with the recent analyses of the actual Salt Batch 5 sample.

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LIST OF ABBREVIATIONS

ACSM	Analytical Characterization and Sample Management
IC	Ion Chromatography
ICPES	Inductively-Coupled Plasma Emission Spectroscopy
%RSD	Percent Relative Standard Deviation
SRNL	Savannah River National Laboratory
SRMC	Savannah River Mission Completion
TIC/TOC	Total Inorganic Carbon/Total Organic Carbon
TTR	Technical Task Request
TTQAP	Task Technical and Quality Assurance Plan
WAC	Waste Acceptance Criteria

List of Revisions

Revision Number	Summary of Changes	Date
0	Initial Issue	1/6/2022
1	Deleted original data and replaced with new analytical data	8/17/2022

1.0 Introduction

This report provides initial analytical laboratory results of SWPF Salt Batch 5 samples from Tank 41H. These results will be used by Savannah River Mission Completion (SRMC) to show compliance with downstream facilities. This work was specified by a TTR[i] and Task Technical and Quality Assurance Plan (TTQAP).[ii] Details for the work are contained in controlled laboratory notebooks.[iii]

2.0 Experimental Procedure

A single 3L Tank 41H sample (HTF-41-21-124) was pulled and delivered to SRNL on November 29, 2021. The sample was a variable depth sample obtained approximately 32" from the bottom of the tank (transfer pump suction). Tank 41H was mixed at full speed for approximately 12 hours on 11/23/2021 before the sample was pulled; the sample was pulled approximately 5 days after pump shutdown. The sample was a visually clear solution with no apparent solids.

Due to a sample transfer error, the HTF-41-21-124 material was not sampled during the original evolution in December 2021. The results of that sample are detailed in a previous report.[iv]

Once the error was discovered in July 2022, a rapid effort to definitively locate and sample the correct material (HTF-41-21-124) was undertaken. Results from this July sampling are detailed in this report.

The densities of a filtered (using a 0.45 μm nylon syringe filter) and an unfiltered solution collected from the original sample were each measured twice and are reported in Table 1. Filtered sub-samples (using a 0.45 μm syringe filter) were sent to Analytical Characterization and Sample Management (ACSM) for analysis. Exceptions to this sample handling method are labeled below as (unfiltered). In this case, well-mixed samples from the sample bottle were removed for analysis with no filtration. The samples were not diluted before delivery to ACSM, with the exception of the total mercury and the methyl mercury sub-samples which were diluted with HCl in order to preserve the ratios of the various mercury species. The dilutions are accounted for in the reported values provided. For the wt% insoluble solids measurements, we used ~100 mL of sample for each measurement.

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. The customer requested that a Functional Classification of Safety Class apply to this work.[i] Thus, a Design Verification technical review was performed via a document review according to the applicable elements detailed in Section 5.3.1 'Design Verification by Document Review' of E7 2.60. Data collection and analysis methods used in this work comply with this requirement as detailed in the TTQAP. Results from this report are not RW-0333P as per the TTR.

3.0 Results and Discussion

The results of the density measurements are listed in Table 1. Values in parentheses are the percent relative standard deviation (%RSD) values.

Table 1. Sample Density Measurements (28.8 ºC)

Sample	Measured Density (g/mL)
HTF-41-21-124 (filtered)	1.306 (0.27%)
HTF-41-21-124 (unfiltered)	1.315 (0.48%)

The analytical uncertainty is typically <3% for density measurements. The results are typical for dissolved saltcake of this type. For comparison, the average density of the SWPF Salt Batch 4 solution was 1.26 g/mL (filtered, 28.0 ˚C) and 1.26 g/mL (unfiltered, 28.0 C).[v]

The results of the Inductively-Coupled Plasma Emission Spectroscopy (ICPES) analysis are listed in Table 2. The values in the parentheses are the %RSD.

Table 2. ICPES Results[ɣ]

Analyte	Result (mg/L)	WAC Requirement (mg/L)	Analyte	Result (mg/L)	WAC Requirement (mg/L)
Ag	<0.165	NA	Mn	< 0.385	NA
Al	7230 (0.20%)	<6740	Mo	32.3 (0.22%)	NA
B	61.5 (0.58%)	NA	Na	6.93 M (1.3%)	5.6-7.0 M
Ba	<0.768	NA	Ni	<0.466	NA
Be	<0.103	NA	P	227 (0.62%)	NA
Ca	<4.06	NA	Pb	<5.59	NA
Cd	<0.135	NA	S	4920 (0.43%)	NA
Ce	<2.66	NA	Sb	<1.98	NA
Co	<0.295	NA	Si	<20.6	<842
Cr	114 (0.62%)	NA	Sn	< 8.13	NA
Cu	<1.06	NA	Sr	< 0.140	NA
Fe	6.60 (0.43%)	NA	Th	< 1.99	NA
Gd	<0.371	NA	Ti	< 1.42	NA
K	912 (0.0%)	<2240	U	< 5.16	NA
La	< 0.274	NA	V	< 1.95	NA
Li	< 14.6	NA	Zn	6.13 (3.7%)	NA
Mg	< 0.481	NA	Zr	< 0.199	NA

[ɣ] While many of the analytes listed in Table 2 were not requested in the TTR, they have been included for the sake of completeness.

ICPES analytical uncertainty is 10%, except for sodium which was run with the new "high precision" method with an uncertainty of 5%. We will note that the Al values is above the WAC limits.

The ICPES results do not vary greatly from historical data. The sodium concentration of 159,500 mg/L (6.93 M) is within the range of past salt batch samples.

Results from the Ion Chromatography (IC) Anions, Volatile Organic Analysis (VOA), Semi-volatile Organic Analysis (SVOA), Total Mercury, Free Hydroxide Titration, and Total Inorganic Carbon (TIC)/Total Organic Carbon (TOC) analyses are listed in Table 3. The values in the parentheses are the %RSD. Values in italics indicate that one of the two replicates was less-than, and not used.

Table 3. IC Anions, VOA, SVOA, Total-Hg, Free Hydroxide Titration, and TIC/TOC Results ♦

Analyte	Result (mg/L)	WAC Requirement (mg/L)
F^-	<100	<4070
Cl^-	182 (0.78%)	<7950
Br^-	<500	NA
Formate	<100	<4500
Nitrite	32400 (1.7%)	≤2.14E+05
Nitrate	147000 (0.48%)	≤4.37E+05
Phosphate	<100	<3.14E+04
Sulfate	15100 (0.47%)	<5.69E+04
Oxalate	209 (1.0%)	<2.72E+04
TIC	3910 (2.7%)	<1.20E+05
TOC	138 (2.6%)	<4500
Free Hydroxide	4.68E+04 (4.4%)	(3.91-7.82)E+04
Total Hg (unfiltered)	73.6 (1.5%)	<325
general VOA scan	<0.2	NA
butanol	<0.2	NA
general SVOA scan	<2	NA
tributylphosphate	<2	NA
Insoluble solids	*131*	<1200

The analytical uncertainties for IC, and Free Hydroxide results are 10%, and 14% for TIC/TOC.

♦ While the bromide analyte listed in Table 3 was not requested in the TTR, it has been included for the sake of completeness.

The oxalate value of 209 mg/L is typical of the salt batches prepared to date.

The TIC and TOC results are in terms of mg/L of carbon. Assuming the entire TIC result is carbonate, this translates to a carbonate concentration of 0.325 M, or 1.95E+04 mg/L (RSD = 2.7%).

The cation/anion ratio is 98.6%, showing excellent agreement.

Radiochemical results are reported in Table 4. The values in the parentheses are the %RSD. Unfiltered results include the dilution from sample digestion.

Table 4. Radiochemistry Results

Analyte	Filtered Result (pCi/mL)	Unfiltered Result (pCi/mL)	WAC Requirement (pCi/mL)
^{137}Cs	2.51E+08 (1.1%)	2.67E+08 (0.16%)	<5.28E+08 [a]
^{137m}Ba /total gamma	2.37E+08 (1.1%)	2.53E+08 (0.16%)	<4.99E+08
^{238}Pu	8.39E+04 (1.1%)	9.14E+04 (1.4%)	<6.67E+04 [b]
^{239}Pu	1.15E+03 (0.28%)	1.26E+03 (1.0%)	<6.67E+04 [b]
^{240}Pu	7.07E+02 (0.90%)	<9.58E+02	<6.67E+04 [b]
^{242}Pu	<9.99E+00	<1.67E+01	NA [c]
^{244}Pu	<4.64E-02	<7.75E-02	NA [c]
^{233}U	3.60E+01 (1.1%)	3.52E+01 (8.4%)	<1.13E+04
^{234}U	1.84E+02 (1.0%)	1.83E+02 (0.69%)	<4630
^{235}U	2.08E-01 (1.1%)	2.07E-01 (0.61%)	<113
^{236}U	2.09E+00 (0.46%)	2.05E+00 (1.2%)	<4630
^{238}U	1.37E+00 (0.00%)	1.37E+00 (1.2%)	<3120 [d]
^{90}Sr	7.04E+05 (5.0%)	6.19E+05 (15%)	<1.38E+06/2.91E+07
^{90}Y	7.04E+05 (5.0%)	6.19E+05 (15%)	<2.62E+06
Total alpha, Cs-removed	<6.57E+04	<5.33E+04	<2.13E+05
Total beta, Cs-removed	1.32E+06 (4.1%)	1.65E+06 (4.3%)	NA
Total beta	2.96E+08 (2.4%)	2.88E+08 (6.7%)	NA

[a] This WAC value is from ref.i and may be different from the current WAC.
[b] for SWPF, these values are report only, for Saltstone the targets are 6.67E+04 pCi/mL each
[c] Needed for total Pu criticality limit (2.5 mg/L)
[d] Report-only for SWPF, listed value is for Saltstone

For the ^{90}Sr WAC, the number after the slash is the total (unfiltered) result, while the value before the slash is the soluble (filtered) value. The ^{137}Cs result is higher than SWPF Salt Batch 4 (1.52 E+08 pCi/mL and 1.39E+08 pCi/mL for filtered and unfiltered respectively). The ^{137}Cs result for SWPF Salt Batch 5 converts to 0.950 Ci Cs/gal (filtered) and 1.01 Ci/gal (unfiltered). ^{137m}Ba is 94.6% of the ^{137}Cs value and is the same as the total gamma. The ^{90}Y is equal to the ^{90}Sr. Other radiochemical results are typical of previous salt batches. We note that the ^{238}Pu value alone is above the Pu targets. The total alpha measurement is a gross semi-quantitative analysis and has poor precision compared to the sum of the quantitative radiochemical analyses results for the various actinides. The plutonium isotopes ^{238}Pu, ^{239}Pu and ^{240}Pu are the major contributors to the alpha activity in SRS Salt Batch Feed samples.

4.0 Conclusions

Analysis of the Tank 41H SWPF Salt Batch 5 sample indicates that the material does not display any unusual characteristics or observations, such as floating solids, the presence of large amounts of solids, or unusual colors. The analytical results received thus far are typical of previous salt batches. The concentration of Na^+ (the major cation) is 6.93 M. The primary anion concentrations included 2.76 M OH^-, 2.36 M NO_3^-, 0.704 M NO_2^-, 0.325 M CO_3^{2-}, and 0.268 M AlO_2^-. The gamma/beta activities associated with the $^{137}Cs/^{137m}Ba$ decay series (primary radionuclides) ranged from 2.51E+08 to 2.67E+08 pCi/mL, which is higher than the previous salt batch. Further sample results will be reported in a future document. This report satisfies part of Deliverable 3 of the Technical Task Request (TTR).

5.0 References

[i] A. Samadi-Dezfouli, "Salt Batch Qualification for Feed to Salt Waste Processing Facility", X-TTR-H-00090, Rev. 3, June 21, 2021.

[ii] T. B. Peters and D. H. Jones, "Task Technical and Quality Assurance Plan for SWPF Feed Batch Qualification Testing", SRNL-RP-2019-00582, Rev. 2, May 2021.

[iii] T. B. Peters, "Salt Batch 5 Qualification", ELN, A4571-00527-02.

[iv] T. B. Peters, "Results of Short-Term Analyses of the Salt (Macro) Batch 5 Tank 41H Qualification Sample", SRNL-STI-2021-00684, rev.0, January 2021.

[v] Automated LIMS report for LW-AD-PROJ-210624-2, samples LW22787, 22788, 22789, 22790.

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