Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1) warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2) representation that such use or results of such use would not infringe privately owned rights; or
3) endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

We put science to work.™

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Analytical Results from Routine DSSHT and SEHT Monthly Samples

T. B. Peters

August 2016

SRNL-STI-2016-00384, Revision 0

SRNL.DOE.GOV

DISCLAIMER

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U.S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied:

1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or
2. representation that such use or results of such use would not infringe privately owned rights; or
3. endorsement or recommendation of any specifically identified commercial product, process, or service.

Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.

Printed in the United States of America

Prepared for
U.S. Department of Energy

Keywords: *MCU*

Retention: *Permanent*

Analytical Results from Routine DSSHT and SEHT Monthly Samples

T. B. Peters

August 2016

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

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

T. B. Peters, Advanced Characterization and Processing Date

TECHNICAL REVIEW:

L. Magwood Jr., Advanced Characterization and Processing,
Reviewed per E7 2.60 Date

APPROVAL:

B. J. Wiedenman, Manager Date
Advanced Characterization and Processing

D. E. Dooley, Manager Date
Environmental & Chemical Process Technology Research Programs

E. A. Brass, Manager Date
MCU & Salt/Sludge Engineering

EXECUTIVE SUMMARY

Strip Effluent Hold Tank (SEHT) and Decontaminated Salt Solution Hold Tank (DSSHT) samples from several of the "microbatches" of Integrated Salt Disposition Project (ISDP) Salt Batch ("Macrobatch") 8B have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, cations (Inductively Coupled Plasma Emission Spectroscopy - ICPES), and anions (Ion Chromatography Anions - IC-A).

The analytical results from the current microbatch samples are similar to those from previous macrobatch samples. The Actinide Removal Process (ARP) and the Modular Caustic-Side Solvent Extraction Unit (MCU) continue to show more than adequate Pu and Sr removal for times when monosodium titanate (MST) is used. Even with no MST strike being performed there exists some small Pu and Sr removal, likely from filtration of fines containing these elements.

The Cs removal continues to be excellent, with decontamination factors (DF) averaging 16,400.

The bulk chemistry of the DSSHT and SEHT samples do not show any signs of unusual behavior.

SRNL recommends that a sample of the strip feed be analyzed for cation and anion content if a further decline in boron concentration is noted in future SEHT samples.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ABBREVIATIONS

AD	Analytical Development
ARP	Actinide Removal Process
CF	Concentration Factor
DF	Decontamination Factor
DSS	Decontaminated Salt Solution
DSSHT	Decontaminated Salt Solution Hold Tank
IC-A	Ion chromatography - anions
ICPES	Inductively-coupled plasma emission spectroscopy
ISDP	Interim Salt Disposition Project
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	Monosodium titanate
NGS	Next Generation Solvent
RSD	Relative standard deviation
SE	Strip Effluent
SEHT	Strip Effluent Hold Tank
SRNL	Savannah River National Laboratory
SSFT	Salt Solution Feed Tank
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

During operation of the ISDP, quantities of salt waste are processed through ARP and MCU in batches of ~3,800 gallons. MST is used in ARP to adsorb actinides and strontium from the salt waste, then the waste slurry is filtered prior to sending the clarified salt solution to MCU. The MCU uses solvent extraction technology to extract cesium from salt waste and concentrate cesium in an acidic aqueous stream (Strip Effluent – SE), leaving a decontaminated caustic salt aqueous stream (Decontaminated Salt Solution – DSS). Sampling occurs in the DSSHT and SEHT in the MCU process. The MCU sample plan requires that batches be sampled and analyzed on a quarterly frequency for plutonium and strontium content by SRNL to determine MST effectiveness.[i] A Task Technical and Quality Assurance Plan (TTQAP) was prepared to cover routine analyses.[ii] The cesium measurement is used to monitor cesium removal effectiveness while the ICPES and IC-anions are used to monitor inorganic carryover. More recently, SRNL has been requested to monitor the mercury content in the samples, and most of these samples have been analyzed accordingly.

A previous report provided the results of several sets of sample results from Macrobatch 7 operations.[iii] Since that report, SRNL analyzed a series of samples from December 2015 through April 2016. The sample results described in this report are from Macrobatch 8B as no samples were pulled from Macrobatch 8A.

2.0 Experimental Procedure

The samples were contained in 10-mL P-nut vials. SEHT samples were delivered in doorstops for shielding purposes, while the DSSHT samples were delivered in “thief” holders. Samples of the same type were each composited into a single bottle. The SEHT samples were analyzed for ^{137}Cs, ^{238}Pu, $^{239/40}$Pu and ^{90}Sr content, as well as for cation content (ICPES). The DSSHT samples were also analyzed for anion content (IC-Anions). The DSSHT samples were sent for analysis without dilution or filtration. SEHT samples were sent for analysis with dilution using deionized water only when necessary, but without filtration.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. For SRNL documents, the extent and type of review using the SRNL Technical Report Design Checklist is outlined in WSRC-IM-2002-00011, Rev. 2.[iv] Records for this work are contained in an electronic notebook ELN-A4571-00084-26.

3.0 Results and Discussion

3.1 Results from DSSHT and SEHT Samples

The ^{137}Cs, ^{90}Sr, and ^{238}Pu results from the DSSHT and SEHT radiochemical analyses are listed in Table 1. These samples were roughly monthly samples, with no regular monthly samples taken during February, due to outages. Values in parentheses are the 1 sigma analytical uncertainties as provided by Analytical Development (AD). The source material (Tank 49H material that has been processed through ARP) entries were derived from customer blend documents for Salt Batch 8B, and are used for comparison.[v]

Table 1. Radiochemical Results for the DSSHT and SEHT Samples

Sample ID	Sample Date	^{238}Pu (dpm/mL)	^{90}Sr (dpm/mL)	^{137}Cs (dpm/mL)
DSSHT Samples				
MCU-15-924/925/926	Dec 2015	6.06E+03 (6.3%)	6.77E+03 (26%)	1.81E+04 (5.0%)
MCU-16-52/102/103	Jan 2016	8.36E+04 (8.8%)	4.89E+05 (28%)	3.94E+04 (5.0%)
MCU-16-345/346/347	Mar 2016	9.46E+04 (7.7%)	9.75E+05 (22%)	1.76E+04 (5.5%)
MCU-16-578/579/580	Apr 2016	1.17E+05 (6.9%)	4.87E+05 (24%)	7.24E+04 (5.0%)
SEHT Samples				
MCU-15-921/922/923	Dec 2015	<5.37E+01	1.97E+03 (26%)	5.17E+09 (5.0%)
MCU-16-69/107/108	Jan 2016	<2.23E+01	6.27E+03 (23%)	1.50E+10 (5.0%)
MCU-16-339/340/341	Mar 2016	2.84E+01	1.94E+03 (30%)	6.41E+09 (5.0%)
MCU-16-593/594/595	Apr 2016	<1.47E+02	1.47E+03 (36%)	6.10E+09 (5.0%)
Source Material (8B)		1.15E+05	1.03E+06	4.35E+08

Between the December and January sample, the plant stopped striking with MST. This explains the large increase in ^{238}Pu and ^{90}Sr results for the DSSHT samples starting in January. The change in MST use does not affect the ^{137}Cs removal and the values in the DSSHT are typical. The ^{137}Cs values in the SEHT are increasing towards the theoretical maximum of ~7.1E+09 dpm/mL. The January 2016 sample results for ^{90}Sr and ^{137}Cs are suggestive of either sample contamination in the cells or loss of the diluent before sample dilution (the ^{137}Cs result for the January sample is higher than physically possible). As a point of comparison, the closest comparable SEHT sample run at F/H lab for January 2016 gave a result of 6.15E+09 dpm/mL.

Historically, the concentration factor (^{137}Cs in the strip effluent divided by the ^{137}Cs in the Tank 49H feed - CF) of MCU has been in the 12-14 range. For these samples of Salt Batch 8B, the average CF is 13.5, which is comparable to the previous reported CF value for 7B.[iii] The exception to this is the value for the January sample, which is 34.5, which is not physically feasible.

For Cs, the relevant comparison is between the Macrobatch 7B operations with the NGS (Table 2).[iii] The values in parentheses are the % relative standard deviation.

Table 2. Average Cs DF Values from Macrobatch 7B and 8B

Isotope	Average 7B	Average 8B
^{137}Cs	20900 (111%)	16400 (58%)

The large standard deviations associated with the cesium removal are due to the large fluctuations in the DSSHT sample values. Proper cesium removal behavior at steady state operations can routinely achieve DF in the 30,000+ range. On the other hand, startup on untreated Salt Solution Feed Tank (SSFT) feed versus starting the MCU process with the DSSHT material can cause an increase in the DSSHT ^{137}Cs values.

While the use of the NGS blend does not affect the performance of the Pu and Sr removal, sample analysis from the DSSHT provides an indication of the removal efficiency due to the incorporation of MST in the ARP. Table 3 lists the average DF values for ^{238}Pu and ^{90}Sr for Macrobatch 7B and Macrobatch 8B.[Π] Only one sample (December 2015) in Macrobatch 8B was pulled during the period when MST was in use ("w/MST"). Also provided are the DF values for samples pulled after the discontinuation of the MST strike ("no MST"). The purpose in comparing the three macrobatches is to establish that the average decontamination of these three isotopes is approximately the same. Given the differences in the feed and in operating conditions, variations in the DF values are expected. The high percent relative standard deviation (%RSD) also makes it problematic to make direct comparisons. The differences between the Macrobatches are not unusual.

Table 3. Average Pu and Sr DF Values from Macrobatches 7B and 8B

Isotope	Average Macrobatch 7B DF	Average Macrobatch 8B DF (w/MST)	Average Macrobatch 8B DF (no MST)
^{238}Pu	32.8 (53%)	19.1	1.19 (17%)
^{90}Sr	80.7 (27%)	152	1.77 (34%)

At this time, the effect of the 512-S Filter cleaning cycles still needs to be correlated to the Pu and Sr removal to see if a pattern can be discerned. In theory, as MST cake builds up at ARP, the removal efficiencies of Pu and Sr should improve, which would result in lower Pu and Sr values in the DSSHT.

[Π] Recall that DF is defined as the feed value divided by the DSSHT sample value.

It is interesting to note that for those samples pulled after discontinuation of the MST strike, there is still a slight, but consistent removal of Pu and Sr. This is likely due to filtration at 512-S removing Pu and Sr-containing fines.

The meaningful (present in non-trace quantities) ICPES results for the DSSHT samples are listed in Table 4 and the meaningful ICPES results for the SEHT samples are listed in Table 5. The analytes in the DSSHT are relatively stable over all the samples, with the exceptions of analytes that are potentially subject to solubility swings. The low Al in several samples indicates potential precipitation, for example.

Note that material from Tank 49H undergoes a ~13 to 17 vol % dilution from ARP and MCU while MST is in full use.[vi] Therefore, direct comparisons between the source material and the DSSHT sample results should take this into account. Of the reported elements in Table 4, boron, chromium and sodium are elements that are only subject to dilution effects in the ARP/MCU system – they are not affected by the MST strike, solvent extraction, nor are they subject to solubility changes. In Table 4, the "% decline from feed concentration" row is the average of three element's percentage decline compared to the value of their concentration in Salt Batch 8B feed. For example, for the MCU-15-924/5/6 sample, the boron, chromium and sodium are on average 91.2% of their respective concentrations in the Salt Batch 8B feed.

Table 4. ICPES Results for the DSSHT Samples

Analyte	MCU-15/16-xxx Sample ID (mg/L)				
	Feed 8B [v,vii]	15-924/5/6	16-52/102/3	16-345/6/7	16-578/9/580
Al	5260	4210	4110	4940	4200
B	64.0	65.7	64.0	70.6	66.3
Cr	69.0	62.3	60.4	66.6	62.8
K	605	498	492	544	461
Na	145000	117000	127000	127000	129000
P	175	207	193	251	230
S	2570	1810	1860	3150	2660
Si	57.3	114	71.4	132	78.6
Ti	<0.93	<9.35	<9.35	<17.1	<8.96
Zn	4.65	4.86	6.49	7.64	5.19
% decline from feed concentration	NA	8.8%	8.3%	1.9%	5.5%

The analytical uncertainty for the ICPES analysis is 10%.

The small effective dilution itself is declining due to the discontinuation of the MST strike. While theoretically the decline from feed concentration should be 13-17%,[vi] the measured values are of a smaller magnitude. This is because the Salt Batch 8B feed values are calculated values, and deviate slightly from the concentrations in the actual feed. This theory is supported by data from a recent SSFT sample, for which a report is in preparation.

Table 5. ICPES Results for the SEHT Samples

Analyte	MCU-15/16-xxx Sample ID (mg/L)			
	15-921/2/3	16-69/107/8	16-339/340/1	16-593/4/5
B	88.1	83.4	87.9	84.6
K	46.4	58.6	35.4	16.3
Na	39.9	50.5	37.2	30.7

The analytical uncertainty for the ICPES analysis is 10%.

For the ICPES data from the SEHT samples, there are few analytes (boron, potassium and sodium) that consistently appear in concentrations above the detection limit. Boron should consistently be at 108 mg/L since the SEHT is a solution of 0.01 M boric acid. While the boron value indicates the boric acid concentration is low, it is within acceptable procurement specifications. Sodium and potassium concentrations are consistent with previous data.

The DSSHT samples were also analyzed by IC-A, see Table 6. In the table, the “% decline from feed concentration” is the average of percentage decline of three anions (nitrate nitrite, sulfate) compared to the value of their concentration in Salt Batch 8B feed. The same conclusions for the anion content are noted in the cation content (Table 4).

Table 6. IC-Anions Results for the DSSHT Samples

Analyte	MCU-15/16-xxx Sample ID (mg/L)				
	8B Feed [v]	15-924/5/6	16-52/102/3	16-345/6/7	16-578/9/580
F	97.3	<100	<100	<250	<250
Formate	468	296	328	<250	<250
Cl	385	317	364	402	397
Nitrite	37100	33200	33400	34823	34867
Nitrate	124000	94100	96400	98200	101000
Phosphate	537	414	435	514	498
Sulfate	5530	4870	5160	5698	5759
oxalate	203	149	126	248	245
% decline from feed concentration	NA	15.5%	13.0%	7.97%	6.81%

The analytical uncertainty for the IC-A analysis is 10%.

As with the ICPES results, the IC-Anions results for the DSSHT sample are typical of this type of material and show only moderate variations.

4.0 Conclusions

SEHT and DSSHT samples from several of the "microbatches" of ISDP Salt Batch ("Macrobatch") 8B have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, cations (ICPES), and anions (IC-A).

The analytical results from the current microbatch samples are similar to those from previous macrobatch samples. ARP continues to show more than adequate Pu and Sr removal for times when a MST strike is used. Even with no MST strike being performed there exists some small Pu and Sr removal, likely from filtration of fines containing these elements.

In MCU the Cs removal continues to be excellent, with decontamination factors averaging 16,400.

The bulk chemistry of the DSSHT and SEHT samples do not show any signs of unusual behavior.

SRNL recommends that a sample of the strip feed be analyzed for cation and anion content if a further decline in boron concentration is noted in future SEHT samples.

5.0 References

[i] M. W. Geeting, "Interim Salt Disposition Project (ISDP) Sample Plan", U-ESR-H-00068, Revision 5, April 28, 2009.

[ii] T. B. Peters, A. L. Washington II, F. F. Fondeur, "Task Technical and Quality Assurance Plan for Routine Samples in Support of ARP and MCU", SRNL-RP-2013-00536, September 2013.

[iii] T. B. Peters, "Sample Results from Routine Salt Batch 7 Samples", SRNL-STI-2015-00674, January 2016.

[iv] Savannah River National Laboratory, "Technical Report Design Check Guidelines", WSRC-IM-2002-00011, Rev. 2.

[v] D. L. McWhorter, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 8-B August 2015", X-ESR-H-00769, August 4, 2015.

[vi] A. G. Garrison, "Evaluation of Interim Salt Disposition Project (ISDP) Macrobatch Dilution Bases Experienced at Actinide Removal Process and Modular Caustic Solvent Extraction Unit (ARP/MCU)", X-ESR-H-00724, rev. 1, May 28, 2015.

[vii] T. B. Peters, A. L. Washington II, "Sample Results from the Interim Salt Disposition Program Macrobatch 8 Tank 21H Qualification Samples" SRNL-STI-2014-00561, January 2015.

Distribution:

T. B. Brown, 773-A
M. E. Cercy, 773-42A
D. A. Crowley, 773-43A
D. E. Dooley, 773-A
A. P. Fellinger. 773-42A
S. D. Fink, 773-A
C. C. Herman, 773-A
D. T. Hobbs, 773-A
E. N. Hoffman, 999-W
J. E. Hyatt, 773-A
K. M. Kostelnik, 773-42A
B. B. Looney, 773-42A
D. A. McGuire, 773-42A
T. O. Oliver, 773-42A
F. M. Pennebaker, 773-42A
G. N. Smoland, 773-42A
B. J. Wiedenman, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)
P. R. Jackson, DOE-SR, 703-46A
J. A. Crenshaw, 703-46A
E. A. Brass, 241-121H
C. K. Chiu, 704-30S
E. J. Freed, 704-S
A. G. Garrison, 241-121H
B. A. Gifford, 704-56H
V. Jain, 766-H
R. T. McNew, 766-H
M. A. Rios-Armstrong, 766-H
A. R. Shafer, 766-H
C. M. Santos, 241-152H
P. E. Fogelman, 241-121H
K. M. Marra, 241-120H
T. C. Demeter, 704-25S
A. Samadi-Dezfouli, 707-4E
M. A. Rios-Armstrong, 766-H
C. Sudduth, 707-7E
A. W. Wiggins, 241-168H
T. L. Fellinger, 766-H