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Analytical Results from Salt Batch 9 Routine DSSHT and SEHT Monthly Samples

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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") 9 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 Cs removal continues to be acceptable, with decontamination factors (DF) averaging 25700 (107% RSD).

The bulk chemistry of the DSSHT and SEHT samples do not show any signs of unusual behavior, other than lacking the anticipated degree of dilution that is calculated to occur during Modular Caustic-Side Solvent Extraction Unit (MCU) processing.

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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 the Actinide Removal Process (ARP) and MCU in batches of ~3,800 gallons. Until recently, Monosodium Titanate (MST) was 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. 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 the Savannah River National Laboratory (SRNL) to determine MST effectiveness.[i] A Task Technical and Quality Assurance Plan (TTQAP) were prepared to cover routine analyses.[ii] The cesium measurement is used to monitor cesium removal effectiveness while the ICPES and IC-A are used to monitor inorganic carryover.

A previous report provided the results of several sets of sample results from, and ending Macrobatch 8B operations.[iii] The sample results described in this report are from Macrobatch 9.

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-A). 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-A4571-00084-29.

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. Values in parentheses are the 1 sigma analytical uncertainties as provided by Analytical Development (AD). The source material (Tank 49H) entries were derived from customer blend documents for Salt Batch 9, 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-16-1244/5/6	8/22/2016	7.15E+04 (7.0%)	5.84E+05 (23%)	8.20E+03 (5.0%)
MCU-16-1350/1/2	11/15/2016	2.76E+04 (5.0%)	7.38E+05 (13%)	4.93E+05 (5.0%)
MCU-16-1613/4/5	12/18/2016	6.94E+04 (6.6%)	9.42E+05 (16%)	1.96E+04 (5.0%)
MCU-17-95/6/7	2/8/2017	5.11E+04 (8.9%)	6.40E+05 (17%)	4.56E+04 (5.0%)
SEHT Samples				
MCU-16-1241/2/3	8/22/2016	<3.81E+02	2.23E+04 (21%)	7.25E+09 (5.0%)
MCU-16-1356/7/8	11/15/2016	<1.91E+02	<1.97E+03	6.42E+09 (5.0%)
MCU-16-1606/7/8	12/18/2016	6.60E+01 (70%)	<2.93E+03	7.57E+09 (5.0%)
MCU-17-98/99/100	2/8/2017	<9.52E+01	<8.09E+01	3.91E+09 (5.0%)
Source Material (9) [v]		9.63E+04	9.70E+05	5.22E+08

Previously, ARP stopped striking with MST. All the sample results for the Macrobatch reflect the lack of MST use. This explains the relatively small decrease in ^{238}Pu and ^{90}Sr results for the DSSHT samples. The small decline indicates some small amount of removal from residual fines and/or dilution effects. The lack of 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 generally near the theoretical maximum of ~7.8E+09 dpm/mL with the exception of the February 2017 sample. Due to customer recirculation of DSS material, this sample is expected to be noticeably diluted compared to typical results.

For Cs, the relevant comparison is between the Macrobatch 8B operations with the Next Generation Solvent (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 8B	Average 9
^{137}Cs	22100 (114%)	25700 (107%)

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 with 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.

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 Salt Batch 9 samples, the average CF is 12.1 (26% RSD), which is lower than the average CF of all Salt Batch 8B samples of 14.2 (8.40% RSD).[◊] The Salt Batch 9 sample average does include the February SEHT sample, which is known to be diluted, and thus biases the average CF value low. Without the February sample, the average CF is 13.6 (8.4% RSD)

The use of the NGS blend does not affect the performance of the Pu and Sr removal. Table 3 lists the average DF values for ^{238}Pu and ^{90}Sr for Macrobatch 8B and Macrobatch 9.[Π] The purpose in comparing the two macrobatches is to establish that the average decontamination of these two 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 (no MST) from Macrobatches 8B and 9

Isotope	Average Macrobatch 8B DF	Average Macrobatch 9 DF
^{238}Pu	1.33 (18%)	2.03 (50%)
^{90}Sr	1.81 (20%)	1.38 (20%)

It is interesting to note that for these samples which were 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 and/or dilution effects on the feed as it passes through the ARP and MCU system.

The meaningful (present in non-trace quantities) ICPES (B, Cr, Na) and IC-A (nitrite, nitrate, sulfate) 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.

The material from Tank 49H undergoes a ~13 vol % dilution from ARP and MCU while no MST is in use.[vi] Therefore, direct comparisons between the source material and the DSSHT sample results should take this into account. Of the reported analytes in Table 4, B, Cr, Na, nitrite, nitrate, and sulfate are analytes that are only subject to dilution effects in the ARP/MCU system – they are not affected by the solvent extraction, nor are they subject to solubility changes.

◊ The average CF of all the Salt Batch 8B samples does not include the January 2016 result which was physically impossible.
Π Recall that DF is defined as the feed value divided by the DSSHT sample value.

These analytes are shaded in Table 4. In Table 4, the "% decline from feed concentration" row is the average of six analytes percentage decline compared to the value of their concentration in Salt Batch 9 feed. For example, for the MCU-16-1244/5/6 sample, the six analytes are an average of 88% of their respective concentrations in the Salt Batch 9 feed.

Table 4. ICPES Results for the DSSHT Samples

Analyte	MCU-16/17-xxx Sample ID (mg/L)				
	Salt Batch 9 [v]	16-1244/5/6	16-1350/1/2	16-1613/4/5	17-95/6/7
Al	5860	5000	5590	5630	5600
B	52.3	53	51.3	43.7	53.8
Cr	67.5	58.7	58.7	57.5	53.6
K	566	527	<1310	<1310	564
Na	144000	127000	123000	126000	127000
Si	21.0	83.2	<172	<172	151
Zn	12.2	<0.592	<11.1	<11.1	5.66
F	97.3	<100	<100	<100	<100
Formate	468	<100	<100	<100	126
Cl	385	584	511	481	631
Nitrite	37100	31100	26600	24500	30300
Nitrate	124000	95300	94500	88600	99900
Phosphate	537	420	275	246	361
Sulfate	5530	5020	4430	4180	5210
oxalate	203	391	343	331	378
% decline from feed concentration	NA	12.0%	17.0%	21.8%	12.2%

The analytical uncertainty for the ICPES and IC-A analyses is 10%.

The measured % decline in concentrations are roughly similar to what is predicted from knowing that the feed is diluted from addition of used scrub (~13% dilution).

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, with the previously noted exception of the February 2016 (MCU-17-98/99/100) samples. Boron should consistently be at 108 mg/L since the SEHT is a solution of 0.01 M boric acid. The initial boron result for this sample was so low, a second ICPES analysis was performed, giving a similar result. The boron value for this sample is an average of two results with the %RSD in parnethesis. The February sample is simply low in boron content, for reasons unknown.

While the boron values for the other samples indicate the boric acid concentrations are low, they are within acceptable procurement specifications. Sodium and potassium concentrations are consistent with previous data.

Table 5. ICPES Results for the SEHT Samples

Analyte	MCU-16/17-xxx Sample ID (mg/L)			
	16-1241/2/3	16-1356/7/8	16-1606/7/8	17-98/99/100
B	86.8	95.3	101	46.1 (23%)
K	<31.5	46.1	61.6	<86.4
Na	<26.1	51.3	64.6	42.7

The analytical uncertainty for the ICPES analysis is 10%.

4.0 Conclusions

SEHT and DSSHT samples from several of the “microbatches” of ISDP Salt Batch (“Macrobatch”) 9 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. 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 acceptable, with decontamination factors for Cs averaging 25700 (107% RSD).

The bulk chemistry of the DSSHT and SEHT samples do not show any signs of unusual behavior, other than the average degree of dilution being slightly higher than what is calculated to occur during MCU processing.

The low boron result in the February sample is how the sample arrived at SRNL. Conversations with the customer have come to no firm conclusion as to why the boron could be this low, and the feedstock material has been consumed. SRNL recommends examining the recent certificates of analyses from the customer and consideration should be given to analyzing the next strip feed lot delivered to tank farm.

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, rev. 1, May 2014.

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[v] C. I. Aponte, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 9", X-ESR-H-00844, October 11, 2016.

[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.

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