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Sample Results from Routine Salt Batch 7 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") 7B 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, and there is a distinct positive trend in Cs removal (increasing cesium decontamination), due to the use of the Next Generation Solvent (NGS).

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

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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 ARP and MCU in batches of ~3800 gallons. Monosodium titanate (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 this sort of analyses.[ii] The cesium measurement is used to monitor cesium removal effectiveness and the ICPES is used to monitor inorganic carryover.

A previous report provided the results of several sets of sample results from earlier Macrobatch 7 operations.[iii] Since that report, SRNL analyzed a series of samples from February 2015 until the end of Salt Batch 7 operations.

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 were removed from the holders. 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 then sent for analysis without dilution or filtration. SEHT samples were sent for analysis with dilution using 3M nitric acid only when necessary, but without filtration.

2.1 <u>Quality Assurance</u>

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-A4571-00084-5.

3.0 Results and Discussion

3.1 <u>Results from DSSHT and SEHT Samples</u>

The ^{137}Cs, ^{90}Sr, and ^{238}Pu results from the DSSHT and SEHT radiochemical analyses are listed in Table 1. These samples were nominally monthly samples, with no regular monthly samples taken during April and May, 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 7B, 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-15-381	2/23/2015	8.29E+02 (6.2%)	5.49E+03 (13%)	1.24E+04 (5.0%)
MCU-15-565/566/567	3/16/2015	1.60E+03 (5.9%)	4.76E+03 (13%)	1.94E+03 (5.0%)
MCU-15-707/707/708	6/15/2015	7.39E+02 (7.0%)	1.33E+04 (19%)	4.77E+05 (5.0%)
SEHT Samples				
MCU-15-382	2/25/2015	1.52E+01 (20%)	2.73+02 (21%)	1.35E+09 (5.0%)
MCU-15-562/563/564	3/16/2015	<1.41E+01	5.49E+02 (24%)	1.64E+09 (5.0%)
MCU-15-719/720/721	6/15/2015	8.61E+01 (24%)	<3.90E+02	1.01E+09 (5.0%)
Source Material (7B)		2.66E+04	5.13E+05	1.13E+08

The ^{137}Cs in the DSSHT has dropped to an all new low, evidenced in the March sample (MCU-15-565/566/567). With the NGS blend solvent, the values are being driven down to as low as ~E+03 dpm/mL. However, the June sample (MCU-15-707/708/709) shows an increase in ^{137}Cs compared to the previous data point. ^{137}Cs samples analyzed at F/H lab at the same time showed similar results. This should not be taken as an indication of a general failure in the capability of the NGS blend solvent. The high ^{137}Cs data point is more indicative of MCU restarting on salt feed as opposed to the more typical restart using decontaminated material.

For Cs, the relevant comparison is between the Macrobatch 6 average during operations with the previous BOBCalixC6 solvent, and 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 BOBCalixC6 Solvent and NGS

Isotope	Average BOBCalixC6 Solvent	Average NGS
^{137}Cs	148 (15.7%)	20900 (111%)

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.

Therefore, the high ^{137}Cs activity DSSHT samples do not correspond to poor solvent behavior, but are temporary artifacts due to operational methods. Nevertheless, SRNL will continue to monitor for indications of process upsets.

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 last three samples of Salt Batch 7B, the average CF is 11.8, which is comparable to the previous reported CF value for 7B.[iii]

While the use of the NGS blend does not affect the performance of the Pu and Sr removal, analysis of the DSSHT samples provides an indication to the removal efficiency of the MST at ARP. Table 3 lists the average DF values for ^{238}Pu and ^{90}Sr for Macrobatch 5, Macrobatch 6 and Macrobatch 7B.[Π] The Macrobatch 5 and 6 averages are for all of the Macrobatch 5 and 6 samples (each), regardless of the solvent that was used at MCU, with the exception of the April and May 2014 samples for Macrobatch 6 (the exclusion of these samples was due to the process upset generating atypical conditions and results).[iii]

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 5, 6 and 7B

Isotope	Average Macrobatch 5 DF	Average Macrobatch 6 DF	Average Macrobatch 7B DF
^{238}Pu	35.6 (44.4%)	46.7 (107%)	32.8 (53%)
^{90}Sr	184 (41.7%)	197 (59.1%)	80.7 (27%)

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. While the variations in the ^{238}Pu results are consistent with historical precedent, the ^{90}Sr performance does seem to have dropped somewhat in 7B (although still entirely acceptable). As the ^{238}Pu results do not show discernably poorer removal, a drop in Sr removal is unlikely due to poor MST performance. Possible reasons for poorer Sr removal may include different, less removable forms of Sr compounds, or effects of the oxalic acid cleaning schedules at 512-S.

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

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. Note that material from Tank 49H undergoes a ~16 to 26 vol % dilution from ARP and MCU.[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 MST, are not affected by the solvent extraction, and are not subject to solubility changes.[vii] 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 7B feed. For example, for the MCU-15-381 sample, the boron, chromium and sodium are on average 79.1% of their respective concentrations in the Salt Batch 7B feed. This is from the system dilution that occurs in ARP/MCU and when compared to the calculated 12-21% dilution is reasonable. Historically, for all Salt Batch 7 samples, the dilution has ranged from 10-24%.[iii,viii]

Table 4. ICPES Results for the DSSHT Samples

Analyte	MCU-15-xxx Sample ID (mg/L)			
	Feed 7-B [v]	381	565/566/567	706/707/708
Al	4450	2600	3120	693
B	50.4	42.9	47.6	47.7
Cr	40.0	29	32.7	32.3
K	327	190	254	240
Na	143000	114000	125000	120000
P	165	150	175	187
S	3260	2800	2930	2600
Si	61.2	56.9	55.0	64.4
Ti	<0.58 [ϒ]	3.71	5.37	3.7
Zn	4.83	3.09	4.31	4.56
% decline from feed concentration	NA	21%	12%	14%

The analytical uncertainty for the ICPES analysis is 10%.

The analytes in the DSSHT are relatively stable over all the samples, with the notable exception of Al. The low aluminum concentration in the 706/707/708 samples are likely due to solubility issues leading to Al compound precipitation.

[ϒ] While most data points in the feed column are from reference 5, the Ti data point is from reference 6.

Table 5. ICPES Results for the SEHT Samples

Analyte	MCU-15-xxx Sample ID (mg/L)		
	382	562/563/564	719/720/721
B	96.3	86.7	95.2
K	32.2	<58.3	10.4
Na	31.0	<46.6	26.7

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. Sodium and potassium concentrations seem to stay at 25-35 mg/L but vary slightly over time.

The DSSHT samples were also analyzed by IC-A. See Table 6.

Table 6. IC-Anions Results for the DSSHT Samples

Analyte	MCU-15-xxx Sample ID (mg/L)			
	7-B Feed [v]	381	565/566/567	706/707/708
F	82.5	<10	<100	<100
Formate	467	463	562	572
Cl	277	208	220	<227
Nitrite	29400	24600	27100	24500
Br	NA	<50	<500	<100
Nitrate	151000	103000	120000	113000
Phosphate	509	425	463	<100
Sulfate	8220	6120	7140	6700
oxalate	359	433	303	419
% decline from feed concentration	NA	25%	14%	20%

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. The phosphate result for the -706/707/708 sample is an exception and is likely due to analytical instrument troubles and should not be taken to indicate a sudden selective decline in the phosphate anion.

In Table 6, the “% decline from feed concentration” row is the average of three anions (nitrate nitrite, sulfate) percentage decline compared to the value of their concentration in Salt Batch 7B feed. The same trends in the anion content are noted in the cation content (Table 4).

4.0 Conclusions

The routine monthly samples from MCU are used as an indicator of Pu and Sr removal at ARP, and Cs removal at MCU. The variation in the Pu and Sr results are indicative of the varying amount of MST residing in the ARP system, but show approximately the same Pu removal behavior as previous samples. The Sr removal has declined somewhat, for unknown reasons, but is still entirely acceptable. The Cs removal is a function of the MCU solvent type, and in this case NGS is showing far better removal than with the previous BOBCalixC6 based solvent.

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