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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, Inductively Coupled Plasma Emission Spectroscopy (ICPES), and Ion Chromatography Anions (IC-A).

The results from the current microbatch samples are similar to those from earlier samples from this and previous macrobatches. 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, due to the use of the Next Generation Solvent (NGS). The Savannah River National Laboratory (SRNL) notes that historically, most measured Concentration Factor (CF) values during salt processing have been in the 12-14 range. However, recent processing gives CF values closer to 11. This observation does not indicate that the solvent performance is suffering, as the Decontamination Factor (DF) has still maintained consistently high values. Nevertheless, SRNL will continue to monitor for indications of process upsets.

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

LIST OF ABBREVIATIONS

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

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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 and the waste slurry is then 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[1] requires that batches be sampled and analyzed for plutonium and strontium content by SRNL to determine MST effectiveness. A Task Technical and Quality Assurance Plan (TTQAP) was prepared to cover this sort of analyses.[2] 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 6 and 7 operations.[3] Since that report, SRNL analyzed a series of samples from September 2014 and later.

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 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 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.[4]

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 nominally monthly samples, with no regular monthly samples taken during October, due to equipment outages. Values in parentheses are analytical uncertainties. 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.[5] Entries shaded in grey are previously reported results,[3] but are included for comparison.

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-14-499/500	7/23/2014	4.97E+02 (5.92%)	6.17E+03 (16.6%)	3.07E+05 (5.00%)
MCU-14-662	8/24/2014	3.52E+03 (6.29%)	7.53E+03 (15.9%)	5.50E+03 (5.45%)
MCU-14-845	9/22/2014	1.37E+03 (6.40%)	5.85E+03 (14.6%)	3.22E+03 (5.08%)
MCU-14-906	10/6/2014	NA	NA	1.20E+05 (5.00%)
MCU-14-1023/1024	11/28/2014	4.54E+02 (4.97%)	4.93E+03 (20.0%)	1.57E+05 (5.00%)
MCU-14-1166/1167	12/30/2014	5.80E+02 (5.65%)	6.18E+03 (22.1%)	2.41E+04 (5.00%)
MCU-15-46	1/16/2015	1.04E+03 (9.47%)	8.43E+03 (16.9%)	2.16E+03 (5.00%)
SEHT Samples				
MCU-14-496/507	7/24/2014	3.52E+01 (13.0%)	3.66E+02 (18.6%)	1.78E+09 (5.00%)
MCU-14-666	8/25/2014	<3.86E+00	1.11E+02 (20.2%)	1.84E+09 (5.00%)
MCU-14-844	9/21/2014	<2.13E+00	4.25E+02 (21.3%)	1.57E+09 (5.00%)
MCU-14-1029	11/29/2014	4.89E+02 (6.75%)	1.13E+02 (23.8%)	1.24E+09 (5.00%)
MCU-14-1171	12/30/2014	1.76E+01 (21.3%)	<3.11E+03	1.44E+09 (5.00%)
MCU-15-47	1/16/2015	<2.84E+00	<2.96E+02	9.12E+08 (5.00%)
Source Material (7B)		2.66E+04	5.17E+05	1.13E+08

The ^{137}Cs in the DSSHT has dropped to an all new low. The previous set of DSSHT samples from processing with the previous BOBCalixC6 solvent formulation were typically in the low ~E+06 dpm/mL. With NGS, the values are being driven down to as low as ~E+03 dpm/mL. The January SEHT sample (MCU-15-47) shows radiochemical results lower than the body of the other SEHT results. This is likely due to having restarted MCU on DSSHT on January 14.

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). 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%)	16400 (125%)

The large standard deviations associated with the cesium removal are due to the large fluctuations in the DSSHT sample values. The October sample (MCU-14-906) was much higher than the previous sample, and not until January (MCU-15-46) does the ^{137}Cs activity in the DSSHT drop to desired levels. A review of MCU operational records shows that DSSHT samples with high ^{137}Cs activity were taken shortly after operational restarts with untreated Salt Solution Feed Tank (SSFT) feed versus starting the MCU process with the DSSHT material. Therefore, the high ^{137}Cs activity DSSHT samples do not correspond to poor solvent behavior, but are temporary artifacts due to operational methods. Thus, average DF results reported here are lower than typical results seen during processing, which can range as high as 40,000+ for periods of operations.

CF is a unit less value defined as the ^{137}Cs in the SE divided by the ^{137}Cs in the feed. Historically, most CF values during salt processing have been in the 12-14 range. However, recent processing gives CF values closer to 11. A survey of all MCU sample outputs indicates that since September 2014, the CF values, the free hydroxide, the sodium and aluminum values have shown a subtle downward trend. The magnitude of the downward trend is small but fairly consistent for those analytes. It is possible that these are indicators that the salt feed is undergoing some small changes, with a lower sodium, aluminum and free hydroxide content, while maintaining or even increasing cesium concentrations. If the contents of Tank 49H are somewhat stratified, this may be one possible explanation; however, we do not have concrete evidence of this.

None of these observations indicates that the solvent performance is suffering, as the DF has still maintained consistently high values. Nevertheless, SRNL will continue to monitor for indications of process upsets.

While the use of the NGS 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) .

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

The purpose in comparing the three macrobatches is to establish that the average decontamination of these three isotopes are 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%)	35.1 (58.4%)
^{90}Sr	184 (41.7%)	197 (59.1%)	81.1 (18.7%)

At this time, the effect of the ARP cleaning cycles still needs to be correlated to the Pu and Sr removal to see if we can discern a pattern. 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. Furthermore, use of oxalic acid during cleaning may in turn liberate otherwise insoluble Pu and Sr solids.

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.[6] 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.[5,7] In Table 4, the Average Dilution row is the average of three element's percentage value of their concentration in Salt Batch 7B feed. For example, for the MCU-14-845 sample, the boron, chromium and sodium are on average 82.3% 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 16-24% dilution is reasonable. Furthermore, the variation of the dilution is small, indicating the DSSHT stream was not subject to large changes in dilution.

Table 4. ICPES Results for the DSSHT Samples

Sample date	MCU-14/15-xxx Sample ID				
	Feed 7-B	MCU-14-845	MCU-14-1023/1024	MCU-14-1166/1167	MCU-15-46
	NA	9/22/2014	11/28/2014	12/30/14	1/16/2015
Al	4450	3390	2710	2490	3220
B	50.4	45.1	47.4	42.0	49.1
Cr	40.0	33.0	30.6	28.8	34.3
K	327	328	276	223	244
Na	143000	107000	107000	105000	121000
P	165	160	170	156	183
S	3260	2760	2750	2670	2630
Ti	<0.58 [ϒ]	5.13	4.42	3.84	2.62
Zn	4.83	3.84	4.59	3.07	5.04
% of feed concentration	NA	82.3%	81.8%	76.3%	89.2%

The analytical uncertainty for the ICPES analysis is 10%.

The analytes in the DSSHT are relatively stable over all the samples, given the differences between the two salt batch feeds. The low aluminum concentrations are likely due to solubility issues. The effects of the cyclic oxalic acid cleanings still need to be investigated.

Table 5. ICPES Results for the SEHT Samples

	MCU-14/15-xxx Sample ID			
	MCU-14-844	MCU-14-1029	MCU-14-1171	MCU-15-47
Sample date	9/21/2014	11/29/2014	12/30/14	1/16/2015
B	101	93.3	96.4	95.6
K	19	28.5	27.5	25.7
Na	33.2	38.8	34.3	33.4

The analytical uncertainty for the ICPES analysis is 10%.

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

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 initially seem to stay at 20-30 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

	MCU-14/15-xxx Sample ID					
	7-B Feed	MCU-14-845	MCU-14-906	MCU-14-1023/1024	MCU-14-1166/1167	MCU-15-46
Sample date	NA	9/22/2014	10/6/2014	11/28/2014	12/30/14	1/16/2015
F	82.5	<100	<100	<100	<100	<100
Formate	467	459	435	474	460	530
Cl	277	200	184	207	196	364
Nitrite	29400	24200	22300	25200	24100	28200
Br	NA	<500	<500	<500	<500	<500
Nitrate	151000	124000	108000	116000	101000	124000
Phosphate	509	435	412	429	348	457
Sulfate	8220	6270	5960	6680	6070	7040
oxalate	359	287	391	296	446	305

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 – with the exception that the MCU-15-46 sample. This last sample shows a general moderate increase in anion and cation content. This may be due to faster processing rates at MCU which result in a lower overall dilution. The oxalate in the last sample declined, which may be due to solubility issues caused by moderate changes in the overall composition.

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 is indicative of the varying amount of MST residing in the ARP system, but shows approximately the same behavior as previous samples. 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 BOBCalix based solvent.

SRNL will continue to monitor the oxalate content in future DSSHT samples.

5.0 References

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

[2] 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.

[3] T. B. Peters, "Sample Results from Routine Samples after the NGS Changeover", SRNL-STI-2014-00479, November 2014.

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

[5] D. L. McWhorter, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 7-B July 2014", X-ESR-H-00691, July 23, 2014.

[6] A. R. Shafer, "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, December 11, 2014.

[7] T. B. Peters, A. L. Washington II, "Sample Results from the Interim Salt Disposition Program Macrobatch 7 Tank 21H Qualification Samples", SRNL-STI-2013-00437, August 2013.

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