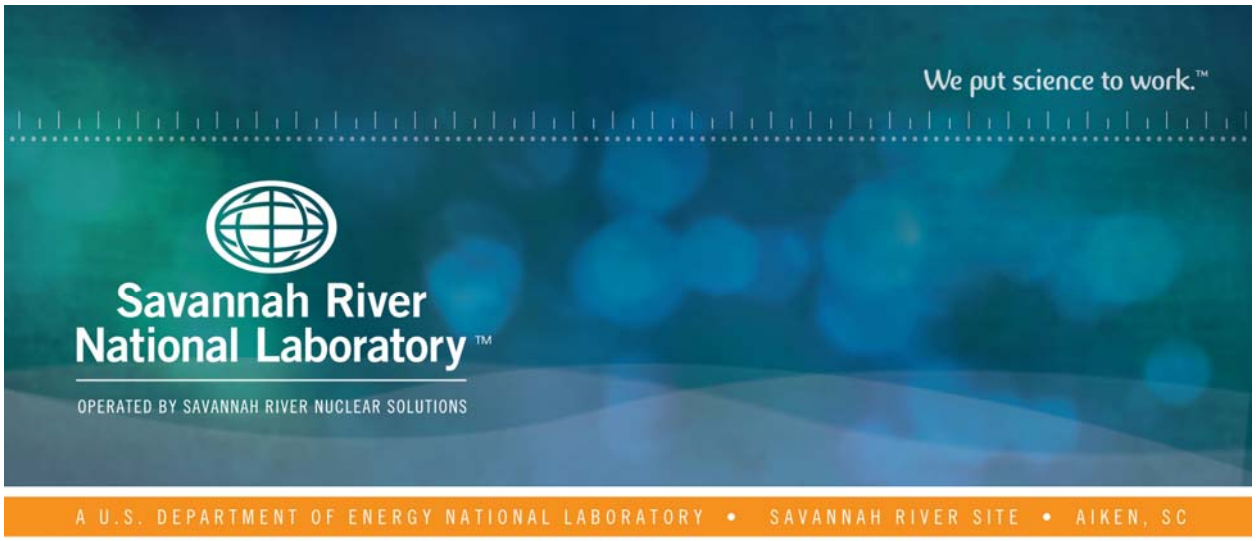

Sample Results from Routine Samples After the NGS Changeover

T. B. Peters

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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") 6D and 7B have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, and by Inductively Coupled Plasma Emission Spectroscopy (ICPES).

The results from the current microbatch samples are similar to those from earlier samples from Macrobatch 6, up to the point where MCU experienced the outages due to solids, in April 2014. The solids problems initially experienced in April 2014 had an obvious effect on some of the sample results. The Pu and Sr results in the DSSHT samples were unaffected, but the solids caused poor solvent behavior, resulting in reduced cesium removal. For the SEHT samples, the Pu and Sr increased due to the carryover of feed into the strip contactor, and the cesium declined due to poor solvent performance. However, even with that handicap, the new solvent system still managed significantly better cesium decontamination than with the old solvent formulation.

LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
DF	Decontamination Factor
DSS	Decontaminated Salt Solution
DSSHT	Decontaminated Salt Solution Hold Tank
IC-A	Ion chromatography - anions
ICPES	inductively-coupled plasma emission spectroscopy
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	monosodium titanate
SE	Strip Effluent
SEHT	Strip Effluent Hold Tank
SHT	Solvent Hold Tank
SRNL	Savannah River National Laboratory

Table of Contents

List of Tables

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 ~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 Decontaminated Salt Solution Hold Tank (DSSHT) and Strip Effluent Hold Tank (SEHT) in the MCU process. The MCU sample plan[i] requires that batches be sampled and analyzed for plutonium and strontium content by Savannah River National Lab (SRNL) to determine MST effectiveness. The cesium measurement is used to monitor cesium removal effectiveness and the inductively coupled plasma emission spectroscopy (ICPES) is used to monitor inorganic carryover.

A previous report provided the results of several sets of sample results from earlier Macrobatch 6 operations.[ii] Since that report, SRNL analyzed a series of samples used in the changeover to a new solvent formulation (NGS blend) ending in January.[iii] Thereafter, SRNL received subsequent SEHT and DSSHT samples from both Macrobatch 6D (1/2014 to 5/2014) and Macrobatch 7B (7/2014 to 8/2014). No samples from Macrobatch 7A were received because the processing volume under Macrobatch 7A was limited and samples pulled monthly.

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 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]

3.0 Results and Discussion

3.1 Results from DSSHT, SEHT and CDT 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 sample taken during June. MCU was in a solids recovery outage and therefore did not process salt from April 6th 2014 to July 8th, 2014. Values in parentheses are analytical uncertainties. The source material entries were derived from customer blend documents for Salt Batch 6D and 7B, and are used for comparison.[v,vi]

The DSSHT and SEHT data for the January samples were at the close of the NGS micro batch Demonstration of the new solvent, but are also considered to be the January routine monthly samples. While those data points were previously reported, they are also included here for clarity.[vii]

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-14-29/31/32	1/17/2014 (6D)	1.30E+03 (4.97%)	1.63E+03 (16.3%)	8.47E+04 (5.00%)
MCU-14-128	2/20/2014 (6D)	1.20E+03 (6.13%)	1.85E+03 (15.8%)	1.67E+04 (5.00%)
MCU-14-213	3/20/2014 (6D)	2.35E+02 (7.88%)	2.16E+03 (14.9%)	2.10E+04 (5.00%)
MCU-14-290	4/28/2014 (6D)	3.17E+02 (5.33%)	<1.47E+03	1.58E+05 (5.00%)
MCU-14-313/314	5/16/2014 (6D)	2.48E+02 (6.10%)	1.74E+03 (15.1%)	1.64E+05 (5.00%)
MCU-14-499/500	7/23/2014 (7B)	4.97E+02 (5.92%)	6.17E+03 (16.6%)	3.07E+05 (5.00%)
MCU-14-662	8/24/2014 (7B)	3.52E+03 (6.29%)	7.53E+03 (15.9%)	5.50E+03 (5.45%)
SEHT Samples				
MCU-14-56/57/58	1/17/2014 (6D)	<2.70E+00	<4.00E+01	1.65E+09 (5.00%)
MCU-14-132	2/20/2014 (6D)	<1.74E+00	<1.08E+02	1.57E+09 (5.00%)
MCU-14-212	3/19/2014 (6D)	<1.30E+00	2.75E+02 (18.7%)	1.42E+09 (5.00%)
MCU-14-283/284	4/26/2014 (6D)	3.81E+02 (6.45%)	2.78E+03 (15.4%)	4.61E+08 (5.00%)
MCU-14-311/312	5/16/2014 (6D)	2.22E+02 (6.38%)	2.69E+03 (15.4%)	4.61E+08 (5.00%)
MCU-14-496/507	7/24/2014 (7B)	3.52E+01 (13.0%)	3.66E+02 (18.6%)	1.78E+09 (5.00%)
MCU-14-666	8/25/2014 (7B)	<3.86E+00	1.11E+02 (20.2%)	1.84E+09 (5.00%)
Source Material (6D)		2.82E+04	4.11E+05	1.30E+08
Source Material (7B)		2.66E+04	5.17E+05	1.13E+08

The data set points to a significant change starting with the April samples, which coincides with the known solids problems at MCU that started on April 6th, 2014. These samples reflect the performance issues caused by the solids. While the April DSSHT samples do not show much change in the Pu and Sr, this is not surprising given that the removal of these elements happens upstream at the Actinide Removal Process (ARP). The ^{137}Cs in the DSSHT shows a significant increase, by ~5-10 fold. In the SEHT sample, the ^{238}Pu value dramatically increases, while there is an increase in the ^{90}Sr, too. At the same time, the ^{137}Cs in the SEHT dropped significantly. These are all symptoms of the disruption at MCU, when, due to the solids, there was some cross contamination of liquid streams, in particular the transfer of feed or DSSHT into the SEHT.[viii] However, the last sample in the sequence (August) indicates that steady operations have resumed. The ^{137}Cs in the DSSHT has dropped to an all new low. The data also gives positive indications that the NGS blend solvent is producing superior Cs removal. The previous set of DSSHT samples from Salt Batch 6 processing were typically in the low ~E+06 dpm/mL. With the new solvent, the values are being driven down to as low as ~E+03 dpm/mL.

As a rough comparison, the decontamination factors (DF) for Pu and Sr are calculated. Table 2 lists the average Decontamination Factor (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 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, in operating conditions, and the very small Macrobatch 7B data set (two points) variation in the DF values are expected. The high %RSD also makes it problematic to make direct comparisons. The differences between the Macrobatches are not unusual.

Table 2. 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%)	30.5 (106%)
^{90}Sr	184 (41.7%)	197 (59.1%)	75.6 (14.0%)

For Cs, the relevant comparison is between the Macrobatch 6 average during operations with the old solvent, and the Macrobatch 6D/7B operations with the new solvent (Table 3), less the April and May 2014 samples. The values in parentheses are the % relative standard deviation.

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

Table 3. Average Cs DF Values from Old Solvent and New Solvent

Isotope	Average Old Solvent	Average New Solvent
^{137}Cs	148 (15.7%)	7280 (110%)

The large standard deviations associated with the new solvent DF are due to the startup of the new solvent. However, the Cs DF is noticeably higher than with the old solvent. It is anticipated that under steady state operations, the Cs DF will continue to climb.

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 ~14 to 24 vol % dilution from ARP and MCU.[Y] Therefore, direct comparisons between the source material and the DSSHT sample results should take this into account. The feed materials for 6D and 7B are very similar, with the noticeable difference being that 6D is higher in Al and potassium, while 7B is higher in sulfur (sulfate).

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. 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-29/31/32 sample, the boron, chromium and sodium are on average 91.5% of their respective concentrations in the Salt Batch 6D or 7B feed. This is from the system dilution that occurs in APR/MCU and when compared to the calculated 17% dilution is reasonable. Furthermore, the variation of the dilution is small, indicating the DSSHT stream was not subject to large changes in dilution even during the period of solids problems.

[Y] Each 3715 gallon batch of Tank 49H material is mixed with 105 gallons of MST slurry, and is then combined with ~255 gallons of scrub and ~525 gallons of caustic wash at 4.0 GPM. This dilutes each 3715 gallons to ~4600 gallons, or ~24 vol % increase in volume. At 8.5 GPM, ~247 gallons of caustic wash is added, thus a ~14 vol % increase occurs.

Table 4. ICPES Results for the DSSHT Samples

[redacted]	MCU-14-xxx Sample ID						
	29/31/32	128	213	290	313/314	499/500	662
Salt Batch	Salt Batch 6D					Salt batch 7B	
Sample date	1/17/14	2/20/14	3/20/14	4/28/14	5/16/14	7/23/14	8/24/14
Al	4580	4530	5100	4200	4340	3370	4350
B	44.2	47.3	41.3	44.4	44.6	42.7	44.5
Cr	37.6	37.2	38.6	34.9	36	39.1	38.8
K	233	243	245	242	443	334	319
Na	119000	116000	122000	127000	117000	123000	123000
P	155	151	172	141	144	163	158
S	<3000	2650	<3000	2400	2230	2110	2760
Ti	<8.4	<4.2	<8.4	3.55	2.76	4.24	6.17
Zn	5.23	4.84	4.61	4.89	4.96	5.22	4.9
Average dilution	91.6%	93.1%	90.6%	91.4%	90.2%	89.5%	90.4%

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 variation in the aluminum is likely due to solubility issues and the variability in the potassium in the May sample may be a function of the solids problem.

Table 5. ICPES Results for the SEHT Samples

	MCU-14-xxx Sample ID						
	Salt batch 6D					Salt Batch 7B	
	56/57/58	132	212	283/284	311/312	496/507	666
Sample date	1/17/14	2/20/14	3/19/14	4/26/14	5/16/14	7/24/14	8/25/14
B	99.9	105	98.9	73.3	77.4	103	101
K	50.7	38	28	37.8	49.2	19.3	16
Na	43.9	45.3	30.7	6970	8120	41.2	26.6

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 as the SEHT is a solution of 0.01 M boric acid. Sodium and potassium are initially seems to stay at 40-50 mg/L but have trended downward over time.
Over time the potassium values vary by a factor of ~3. It is difficult to determine the reason for this, given that the largest decrease occurred in July and August, after the solids problem had

occurred, and the Salt Batch 7B feed was used. On the other hand, both the boron and sodium results point to disruptions in the MCU operations. The boron can only be lowered due to dilution of the SEHT, and the dramatic increase in the sodium values can only indicate incursion of feed or DSSHT into the SEHT stream.

If the incursion into the SEHT is from DSSHT, then the sodium values lead to a conclusion that the SEHT was diluted ~7% by volume (using data from the MCU-14-311/312 sample).

A select few of the DSSHT and SEHT samples were also analyzed by Ion Chromatography Anions (IC-Anions). See Table 6. The feed materials for 6D and 7B are very similar, with no significant differences.

Table 6. IC-Anions Results for the DSSHT and SEHT Samples

Salt Batch	MCU-14-xxx Sample ID					
	6D	6D	6D	7B	7B	7B
Sample ID	283/284	290	313/314	499/500	496/507	662
Sample date	4/26/14	4/28/14	5/16/14	7/23/14	7/24/14	8/24/14
type	SEHT	DSSHT	DSSHT	DSSHT	SEHT	DSSHT
F	<10	<100	<100	<100	<10	<100
Formate	25	308	330	400	12	407
Cl	11	173	163	183	<10	181
Nitrite	1000	21600	21700	22400	10	23700
Br	<50	<500	<500	<500	<10	<500
Nitrate	17900	119000	132000	130000	<10	137000
Phosphate	<10	288	327	392	<10	386
Sulfate	371	5660	5890	6120	<10	5760
Oxalate	990	321	177	279	<10	220

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 of oxalate. Over the range of the three DSSHT samples, there is almost a 2× variation, which may be indicative of oxalate precipitation in the system.

For the SEHT samples, the MCU-14-283/284 sample was taken shortly after the solids problem was noticed, while the MCU-14-496/507 was taken after the problem was resolved. The difference in the two samples is illustrative. Under normal conditions, there should be virtually no anions detectable, as the SEHT is 0.01 M boric acid. The MCU-14-283/284 sample shows a wide variety of anions, some in relatively high concentration. The nitrate concentration is in the

same proportion as the sodium concentration in the same sample, giving further credence of ~7% volume carryover in that sample. The high oxalate concentration is another indication of a severe system disruption – there should be no oxalate in the SEHT samples.

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 solvent to remove Cs from the feed, and in this case the new solvent is showing far better removal than with the previous BOBCalix based solvent.

The solids problems initially experienced in April 2014 had an obvious effect on some of the sample results. The Pu and Sr results in the DSSHT samples were unaffected, but the solids caused poor solvent behavior, resulting in poorer cesium removal. For the SEHT samples, the Pu and Sr increased due to the carryover of feed into the strip contactor, and the cesium declined due to poor solvent performance. However, even with that handicap, the new solvent system still managed better DF than the average for the old solvent.

Finally, the later DSSHT samples are showing a significant decline in the oxalate values compared to the peak during the solids problems. SRNL will continue to monitor the oxalate content in future DSSHT 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] Peters, T. B., "Results of Routine Strip Effluent Hold Tank, Decontaminated Salt Solution Hold Tank, Caustic Wash Tank and Caustic Storage Tank Samples from Modular Caustic-Side Solvent Extraction Unit during Macrobatch 6 Operations" SRNL-STI-2013-00672, November, 2013.

[iii] T. B. Peters, F. F. Fondeur, K. M . Taylor-Pashow, "Results from the Salt Disposition Project (SDP) Next Generation Solvent (NGS) Demonstration Plan", SRNL-STI-2014-00101, April 2014.

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

[v] S. E. Campbell, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 6-D", X-ESR-H-00501, April 23, 2013.

[vi] D. L. McWhorter, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 7-A May 2014", X-ESR-H-00661, May 1, 2014.

[vii] T. B. Peters, F. F. Fondeur, K. M. L. Taylor-Pashow, "Results from the Salt Disposition Project (SDP) Next Generation Solvent (NGS) Demonstration Plan", SRNL-STI-2014-00101, April 2014.

[viii] T. B. Peters, A. L. Washington, II, L. N. Oji, C. J. Coleman, "Sample Results from MCU Solids Outage", SRNL-STI-2014-00336, September, 2014.

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