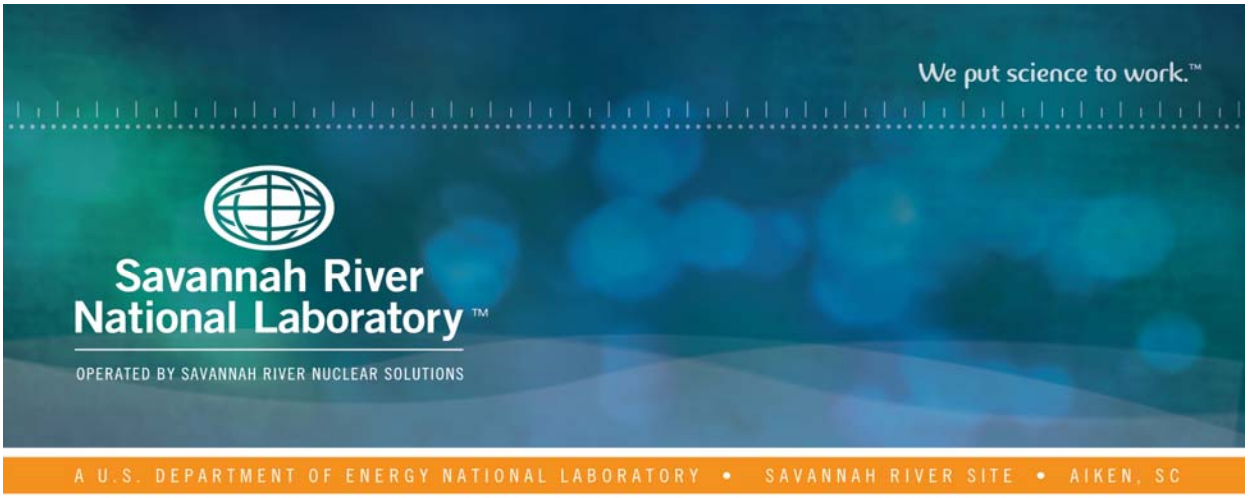

Results of Routine Strip Effluent Hold Tank, Decontaminated Salt Solution Hold Tank, Caustic Wash Tank and Caustic Storage Tank Samples from Modular Caustic-Side Solvent Extraction Unit during Macrobatch 6 Operations

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EXECUTIVE SUMMARY

Strip Effluent Hold Tank (SEHT), Decontaminated Salt Solution Hold Tank (DSSHT), Caustic Wash Tank (CWT) and Caustic Storage Tank (CST) samples from the Interim Salt Disposition Project (ISDP) Salt Batch ("Macrobatch") 6 have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, and by Inductively Coupled Plasma Emission Spectroscopy (ICPES).

The Pu, Sr, and Cs results from the current Macrobatch 6 samples are similar to those from comparable samples in previous Macrobatch 5. In addition the SEHT and DSSHT heel samples (i.e. 'preliminary') have been analyzed and reported to meet NGS Demonstration Plan requirements.

From a bulk chemical point of view, the ICPES results do not vary considerably between this and the previous samples. The titanium results in the DSSHT samples continue to indicate the presence of Ti, when the feed material does not have detectable levels. This most likely indicates that leaching of Ti from MST has increased in ARP at the higher free hydroxide concentrations in the current feed.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
CF	Concentration Factor
CST	Caustic Storage Tank
CWT	Caustic Wash Tank
DF	Decontamination Factor
DSS	Decontaminated Salt Solution
DSSHT	Decontaminated Salt Solution Hold Tank
ICPES	inductively-coupled plasma emission spectroscopy
ISDP	Interim Salt Disposition Project
MCU	Modular Caustic-Side Solvent Extraction Unit
MST	Monosodium Titanate
MCU	Modular Caustic-Side Solvent Extraction Unit
SE	Strip Effluent
SEHT	Strip Effluent Hold Tank
SHT	Solvent Hold Tank
SRNL	Savannah River National Laboratory
WAC	Waste Acceptance Criteria

1.0 Introduction

During operation of the Interim Salt Disposition Process (ISDP), quantities of salt waste are processed through the Actinide Removal Process (ARP) and Modular Caustic-Side Solvent Extraction Unit (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 Macrobatch 6 operations.[ii] Since that report, SRNL received subsequent SEHT and DSSHT samples from Macrobatch 6 (6/2013 to 8/2013) as well as the preliminary samples from the Next Generation Solvent (NGS) changeover Demonstration.[iii]

The work performed in this document is described in a TTR[iv] and TTQAP.[v]

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 sent for analysis without dilution or filtration. SEHT samples were sent with dilution 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. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

The radiochemical results from the DSSHT and SEHT analyses are listed in Table 1. Values in parentheses are analytical uncertainties. Under normal operations, there is only one transfer from Tank 21H to Tank 49H in each macrobatch. In order to improve operational efficiency, there have been a total of 4 transfers to Tank 49H. This in turn generates 4 slightly different batches of material; labeled 6-A, 6-B, 6-C, and 6-D. The ^{238}Pu, ^{90}Sr and ^{137}Cs content in each

batch varies by ~6% or less. Therefore, entries in the "Source Material" column are averages of all four batches.[vi,vii,viii] The batches are detailed in Appendix A.

Table 1. Radiochemical Results for the DSSHT and SEHT Results

Sample ID	Sample Date	^{238}Pu (dpm/mL)	^{90}Sr (dpm/mL)	^{137}Cs (dpm/mL)
DSSHT Samples				
MCU-13-842	6/3/2013	1.03E+03 (6.42%)	2.91E+03 (9.52%)	9.33E+05 (5.00%)
MCU-13-993	6/27/2013	1.51E+02 (7.66%)	2.99E+03 (11.3%)	9.11E+05 (5.00%)
MCU-13-1162	7/22/2013	1.08E+03 (7.65%)	9.70E+02 (11.2%)	1.14E+06 (5.00%)
MCU-13-1361	8/24/2013	8.26E+02 (7.14%)	9.28E+02 (10.6%)	7.65E+05 (5.00%)
DSSHT preliminary	9/18/2013	6.09E+02 (5.52%)	5.37E+03 (14.1%)	NA
SEHT Samples				
MCU-13-863	6/3/2013	<4.77E+01	9.10E+02 (12.5%)	1.33E+09 (5.00%)
MCU-13-997	6/27/2013	<1.71E+01	2.11E+03 (11.4%)	1.71E+09 (5.00%)
MCU-13-1166	7/22/2013	<2.32E+01	1.70E+03 (12.1%)	1.69E+09 (5.00%)
MCU-13-1360	8/24/2013	<4.34E+01	4.99E+02 (16.8%)	1.78E+09 (5.00%)
SEHT preliminary	9/19/2013	<6.74E+00	5.35E+01 (31.1%)	NA
Source Material (average of 6-A, 6-B, 6-C and 6-D)		2.91E+04	4.14E+05	1.30E+08

Compared to the previous Macrobatch 6 samples, the Pu behavior is roughly similar, barring the single unusually low result for MCU-13-993. The Sr and Cs behavior is also roughly similar to those from Macrobatch 5. One exception to this is the unusually low ^{90}Sr result for the SEHT Preliminary sample. The preliminary samples represent the material remaining in the DSSHT and SEHT heel. Prior to the preliminary samples the MCU Facility performed flushes through the seal pot flushes to prepare MCU for the NGS flowsheet. The SEHT was pumped to the heel, then filled with strip chemicals. This was repeated three times for the SEHT. The DSSHT had ~1700 gallons in it prior to the two flushes. The DSSHT was not pumped out between flushes; therefore an additional 440 gallons of scrub chemicals was added to the DSS prior to pumping the tank to the heel. This correlates to ~20% dilution. After the addition of the flush the tanks were pumped back to the heel. Therefore, the preliminary samples are significantly diluted.

Table 2 lists the average Decontamination Factor (DF) values for ^{238}Pu, ^{90}Sr and ^{137}Cs for both Macrobatch 5 and 6.[Π] The values in parentheses are the % relative standard deviation. The values in Table 2 were derived from all Salt Batch 6 samples; the ones in this report as well as the previous report.[ii] For the ^{238}Pu value, the result from the MCU-13-993 sample was not used as this result is obviously an outlier.

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

Table 2. Average DF Values from Macrobatch 5 and 6

Isotope	Average Macrobatch 6 DF	Average Macrobatch 5 DF
^{238}Pu	28.4 (41.4%)	35.6 (44.4%)
^{90}Sr	189 (70.0%)	184 (41.7%)
^{137}Cs	148 (15.7%)	289 (33.1%)

The purpose in comparing the two 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, some variation in the DF values is expected. For example, the numerically large difference in the DF values for ^{137}Cs should not be taken as Macrobatch 6 necessarily being much less efficient in cesium removal.[1] The high %RSD also makes it problematic to make direct comparisons. Furthermore, during Macrobatch 5 operations before October 2012, ARP was using a larger MST strike and time, which biases part of the DF values for Pu and Sr higher for Macrobatch 5. It would appear that the decreased quantity of MST is not affecting the overall MST performance.

Figure 1 shows the graph of the ^{238}Pu results in the DSSHT for all of the Macrobatch 6 DSSHT samples (from this and the previous report). Figure 2 shows the same for ^{90}Sr. Figure 3 shows the similar ^{137}Cs data, but also includes the SEHT sample results. Figure 4 shows the concentration factor (CF) over time.

The Waste Acceptance Criteria (WAC) limits are from X-SD-Z-00001.[ix] The feed values are from the Tank Farm blend calculations.[vi,vii,viii]

[1] The apparently large difference in DF is somewhat deceptive. While the Macrobatch 5 DF of 289 corresponds to a removal of 99.65% of the cesium, the Macrobatch 6 DF of 148 corresponds to a removal of 99.32%.

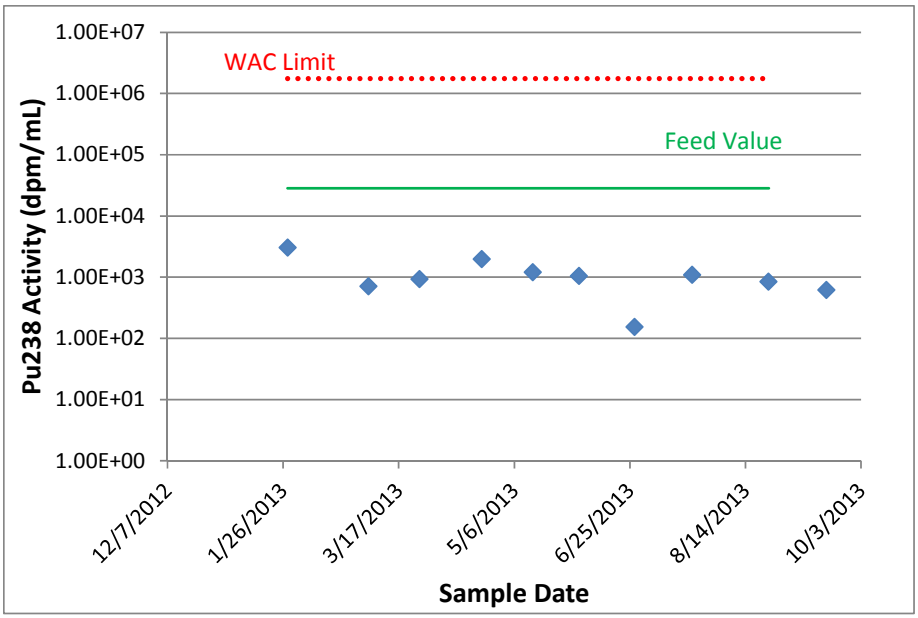

Figure 1. ^{238}Pu Data for all Macrobatch 6 DSSHT Samples

While the graph of the Pu and Sr data can show the overall trend, it is also important to consider the flow rates as recorded in the facility, as well as the periodicity of the removal of the MST filter cake.

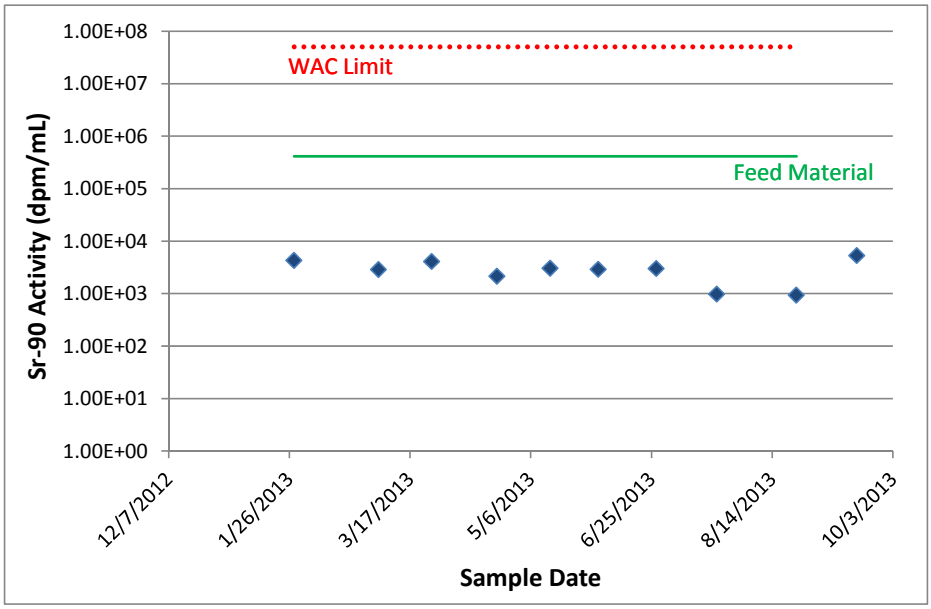

Figure 2. ^{90}Sr Data for all Macrobatch 6 DSSHT Samples

For the ^{137}Cs results, both the DSSHT and SEHT results are shown in Figure 3. The DSSHT samples are all well below the WAC limit, and the SEHT samples give an average concentration factor of 13.3 (10.8% RSD)[∇] as illustrated in Figure 4.

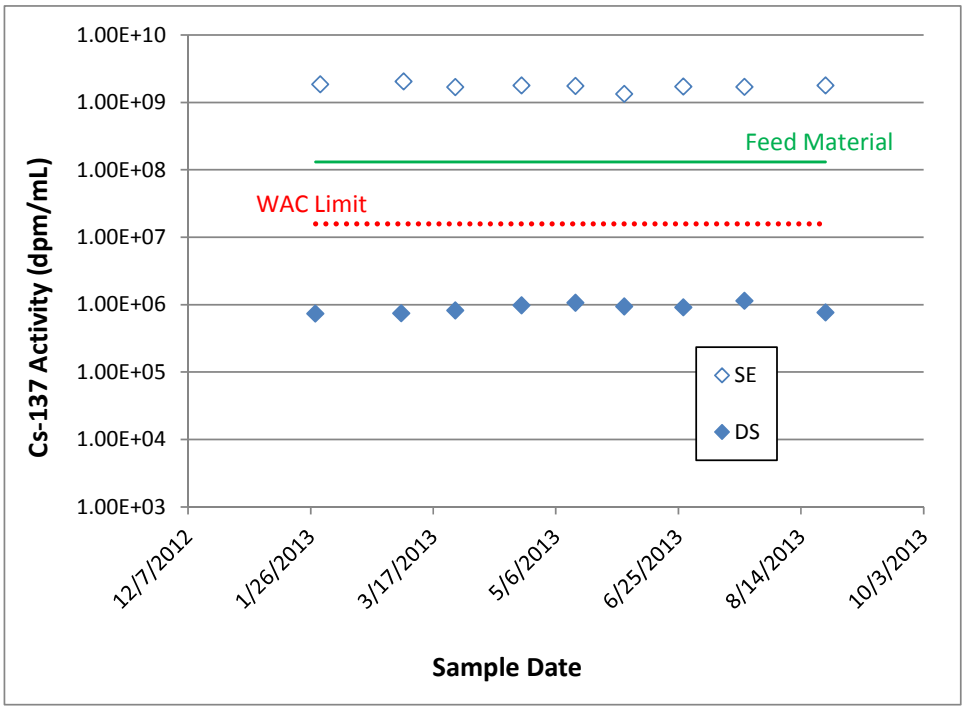

Figure 3. ^{137}Cs Data for all Macrobatch 6 DSSHT and SEHT Samples

The average CF value for macrobatch 6 is very close (within the RSD uncertainty) to that from Macrobatch 5, which averaged 12.9 (10.9% RSD).

[∇] The concentration factor (CF) is defined as the SEHT value divided by the feed value.

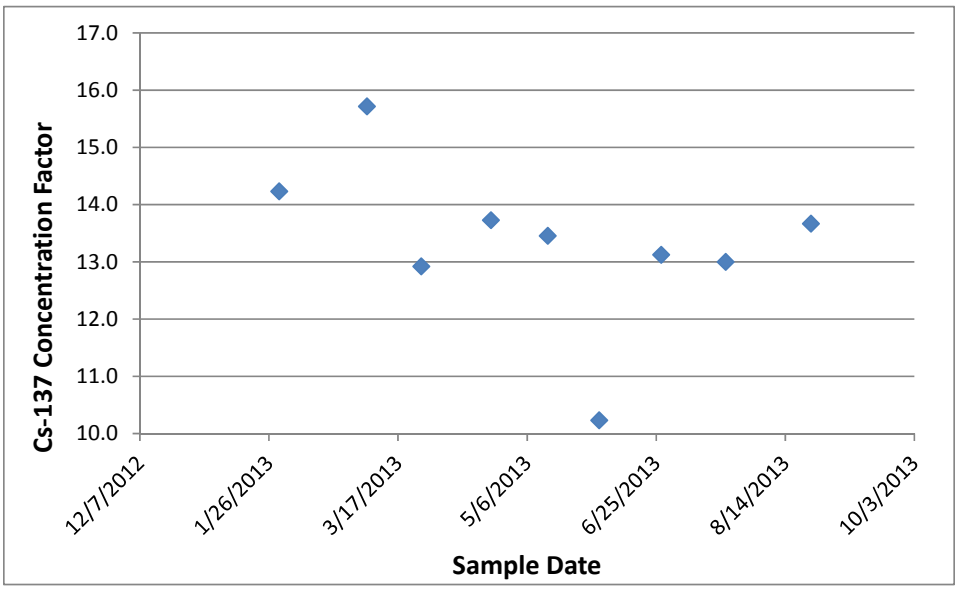

Figure 4. ^{137}Cs Concentration Factor For Macrobatch 6 Samples

The CF value from the second data point in the series is slightly higher than the other samples which are due to the slightly higher SE result. Similarly, the CF value from the sixth data point in the series is lower than the other samples which is due to a lower SE result.

The meaningful (present in non-trace quantities) ICPES results for the all the quarterly DSSHT and SEHT samples except the preliminary NGS samples are listed in Table 3 and Table 4 respectively. As there are four different sub-batches (6-A, 6-B, 6-C, 6-D), the average dilution, across the four sub-batches, is recorded in the right most column. Titanium is introduced to the system via MST leaching at ARP. Note that material from Tank 49H undergoes a ~17 vol % dilution from ARP and MCU.[y] Therefore, direct comparisons between the source material and the DSSHT sample results should take this into account. We note that a comparison of several of the more concentrated analytes (Al, B, Cr, K, Na, P, and S) gives an average dilution to ~88%, indicating that additional sources of dilution have largely been avoided. The initial DSSHT samples (MCU-13-158)[ii] give consistently lower analyte concentrations than the later samples, and this may be an indication that this first sample of Salt batch 6 had some residual water flush or other material, such as heel from Salt Batch 5. In general, the ICPES results are similar to what was seen for the Macrobatch 5 samples.

The titanium results in the DSSHT samples are notable. In all cases, we have greater than detectable levels of Ti in the samples, where there is less-than detectable amounts in the feed material. This is important, as the only possible source of Ti is from the MST used at ARP. In fact, SRNL has found evidence of Ti-containing solids in the DSSHT coalescer and pre-filters.[x]

[y] Each 3715 gallon batch of Tank 49H material is mixed with 105 gallons of MST slurry, and is then combined with 1 volume of scrub acid for each 15 volumes of salt solution, and further caustic wash. This dilutes each 3715 gallons to 4332 gallons, or ~17 vol % increase in volume.

Testing at SRNL has shown that Ti leaching from MST increases at higher free hydroxide concentration in the waste solution; this is suspected as a contributor to the Ti component in the MCU samples.[xi]

Table 3. ICPES Results for the DSSHT Samples (mg/L)

Analyte	MCU-13-842	MCU-13-993	MCU-13-1162	MCU-13-1361
Al	4380	4290	4420	4320
B	43.4	44.0	43.8	45.0
Cr	38.1	36.9	37.4	37.3
K	287	303	302	272
Na	124000	122000	125000	121000
P	155	150	148	153
S	2210	2400	2250	2660
Ti	3.06	1.83	1.85	2.67
Zn	5.39	4.70	4.31	4.21

The analytical uncertainty for the ICPES samples is 10%.

Table 4. ICPES Results for the SEHT Samples (mg/L)

Analyte	MCU-13-863	MCU-13-997	MCU-13-1166	MCU-13-1360
Al	<0.985	<1.03	<1.02	<2.38
B	<0.121	<0.126	<0.125	<6.04
Ca	0.549	1.03	0.842	0.653
Cr	<0.468	<0.490	<0.483	<0.502
Fe	<0.649	0.731	<0.670	1.12
K	<11.3	<11.8	<11.7	<16.0
Mg	0.121	0.466	0.191	<2.968
Na	36.5	65.3	40.9	49.6
P	<10.2	<5.47	<5.40	<24.0
S	<230	<241	<237	<462
Ti	<0.198	<0.208	<0.205	<1.29
Zn	<0.57	1.12	0.789	<0.61

The analytical uncertainty for the ICPES samples is 10%.

The SEHT samples follow the general trends observed for the previous sample results most analytes are below detection limits. [ii]

3.1 Comparison to F/H Lab Results

During the sample period, F/H Laboratory was analyzing DSSHT and SEHT samples for ^{137}Cs content. Figure 5 shows the comparison of results between SRNL and F/H Lab.

On average, SRNL and F/H Lab results were ~7% different for the DSSHT samples, and ~11% different for the SE samples.

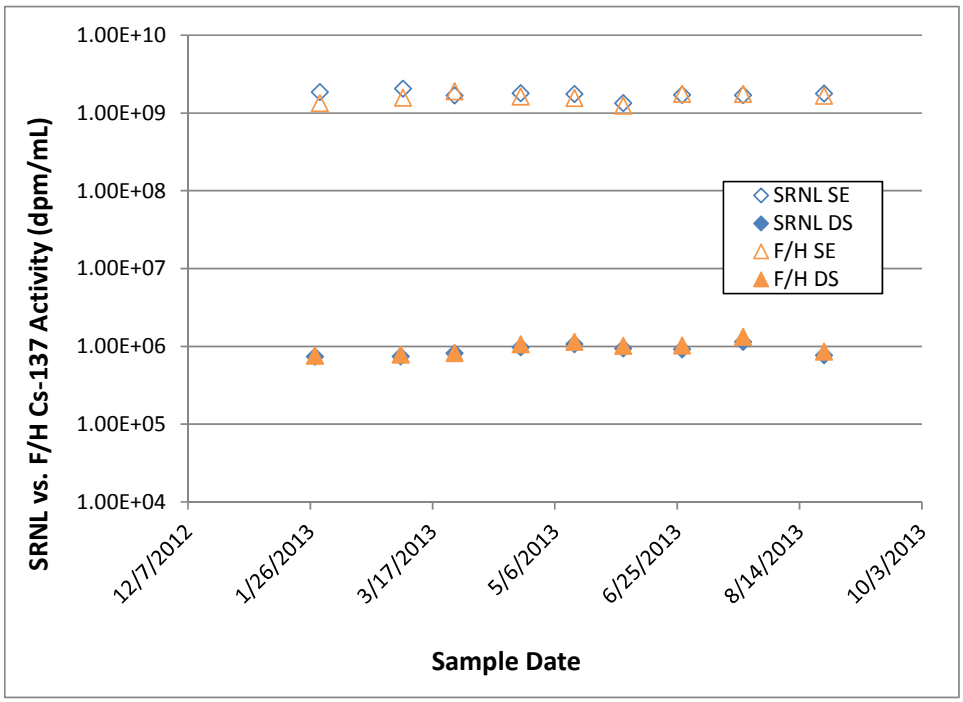

Figure 5. Comparison of SRNL and F/H Lab ^{137}Cs Sample Results

4.0 Conclusions

The results from the current set of samples are similar to those from comparable samples in Macrobatch 5. From a bulk chemical point of view, the ICPES results do not vary considerably between previous results and this macrobatch. The Cs, Pu and Sr results show there are no process upsets at ARP as the DSSHT continues to show acceptable decontamination.

The titanium results in the DSSHT samples continue to indicate the presence of Ti, when the feed material does not have detectable levels. This most likely indicates that leaching of Ti from MST has increased in ARP at the higher free hydroxide concentrations in the current feed.

Appendix A Analyte Concentrations in Each Feed Batch

During processing of Salt Batch 6 to date, there have been 3 additional transfers of Tank 21H (beyond the original one for Salt Batch 6) to Tank 49H. This has created subtle differences in the feed material to ARP and MCU. In order to compare the feeds to the ICPES data, Table 8 shows selected ICPES results for each of the 4 sub-batches to date (6-A,[vi] 6-B,[vi] 6-C,[vii] and 6-D[viii]).

Table 5. Selected ICPES Results for the 4 Sub-Batches (mg/L)

Analyte	6-A	6-B	6-C	6-D
Al	6510	6370	6260	6180
B	38.7	39.5	40.1	40.5
Ba	0.654	0.692	0.719	0.739
Cr	42.4	42.8	43.1	43.3
Fe	4.74	4.51	4.34	4.22
K	359	371	379	385
Na	151000	151000	151000	151000
P	146	144	141	140
S	2320	2300	2280	2270
Zn	4.60	4.66	4.70	4.73

The analytical uncertainty for the ICPES samples is 10%
NA = This value was not calculated

6.0 References

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

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[iii] T. E. Smith, "Technical Evaluation of Micro-Batchwise Next Generation Solvent Demonstration and Engineering Recommendations", X-ESR-H—00570, Rev. 0, September 1, 22013

[iv] Q. L. Nguyen, X-TTR-H-00026, July 22, 2013

[v] 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.

[vi] S. E. Campbell, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 6", X-ESR-H-00468, February 21, 2013.

[vii] S. E. Campbell, "Blend Evaluation for Tank 49 Feed for ISDP Salt Batch 6-C", X-ESR-H-00489, April 13, 2013.

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

[ix] X-SD-Z-00001, Rev. 12 "Waste Acceptance Criteria For Aqueous Waste Sent to the Z-Area Salt Stone Production Facility (U)," July 2013.

[x] T. B. Peters, F. F. Fondeur, S. D. Fink, "Results of Analyses of Macrobatch 3 Decontaminated Salt Solution (DSS) Coalescer and Pre-filters", SRNL-STI-2012-00513, June 2012.

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