Results of Routine Strip Effluent Hold Tank and Decontaminated Salt Solution Hold Tank Samples from Modular Caustic-Side Solvent Extraction Unit during Macrobatch 3 Operations

T. B. Peters
S. D. Fink

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REVIEWS AND APPROVALS

AUTHORS:

_____
T. B. Peters, Author, SRNL/SASP   Date

TECHNICAL REVIEW:

_____
C. A. Nash, Technical Reviewer, SRNL/ACP   Date

APPROVAL:

_____
S. D. Fink, SRNL/SASP, Manager   Date

_____
S. L. Marra, SRNL/E&CPT Research Programs, Manager   Date

_____
D. J. Martin, Manager, H Tank Farm Engineering   Date

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") 3 have been analyzed for ^{238}Pu, ^{90}Sr, ^{137}Cs, and by Inductively Coupled Plasma Emission Spectroscopy (ICPES). The results indicate good decontamination performance within process design expectations. While the data set is sparse, the results of this set and the previous set of results for Macrobatch 3 samples indicate consistent operations.

However, the Decontamination Factors for plutonium and strontium removal have declined in Macrobatch 3, compared to Macrobatch 2. This may be due to the differences in the Pu concentration or the bulk chemical concentrations in the feed material. SRNL is considering the possible reasons for this decline.

The DSSHT samples show continued presence of titanium, likely from leaching of the monosodium titanate in ARP.

LIST OF ABBREVIATIONS

ARP – Actinide Removal Process
DSS – Decontaminated Salt Solution
DSSHT – Decontaminated Salt Solution Hold Tank
ICPES – inductively-coupled plasma emission spectroscopy
MCU - Modular Caustic-Side Solvent Extraction Unit
MST – monosodium titanate
SE – Strip Effluent
SEHT – Strip Effluent Hold Tank
SRNL - Savannah River National Laboratory
SSRT – Salt Solution Receipt Tank

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[1] 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 the first three microbatches of Macrobatch 3 operations.[2]

Since that report, SRNL received subsequent SEHT and DSSHT samples from Macrobatch 3. Per customer direction, not all of these samples were analyzed. SRNL analyzed a limited subset of samples, as well as composites of some samples. Results for these samples are reported in this document and compared to prior trends.

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 and sent to Analytical Development. The DSSHT samples were not diluted or filtered. Some of the SEHT samples were diluted where necessary to reduce personnel exposure.

3.0 Results and Discussion

The radiochemical results from the DSSHT and SEHT analyses are listed in Table 1. Entries in the "Source Material" column that are shaded blue are from a report[3] that calculated the values from knowing the concentrations and blend volumes; other values are from direct measurement.[4]

Table 1. Radiochemical Results for the DSSHT and SEHT Results

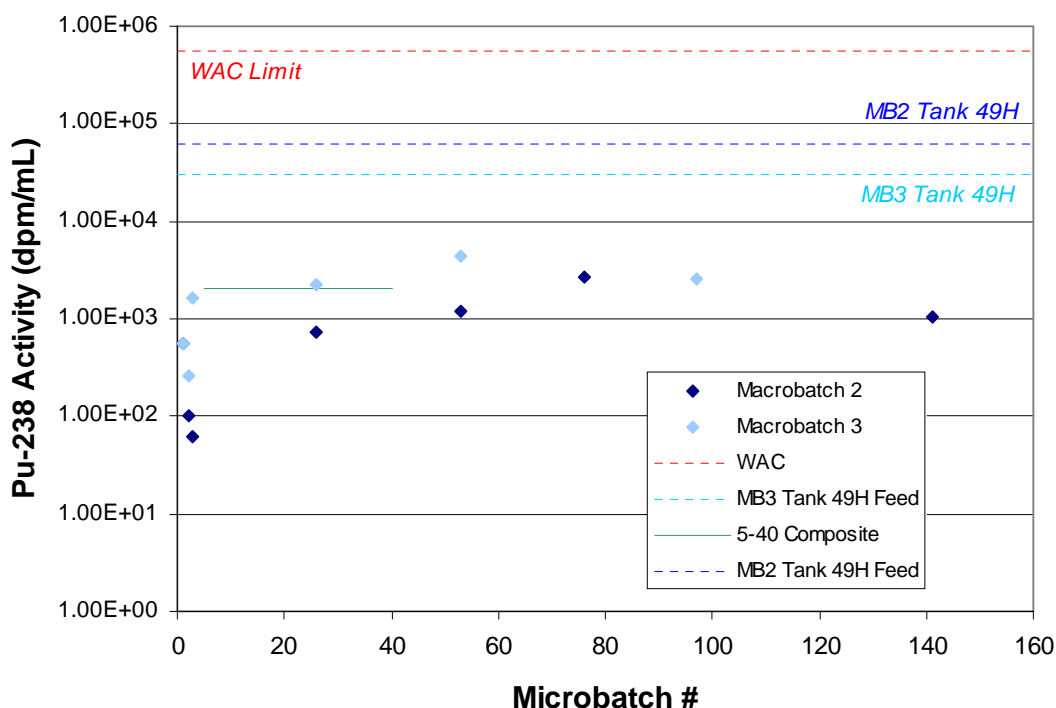| Microbatch	Sample ID	Sample Date	^{238}Pu (dpm/mL)	^{90}Sr (dpm/mL)	^{137}Cs (dpm/mL)
DSSHT					
composite 5-40	Footnote 1		2.02E+03 (5.00%)	2.70E+03 (6.87%)	1.30E+06 (5.00%)
26	MCU-10-500	10/6/2010	2.22E+03 (5.44%)	2.67E+03 (16.7%)	7.42E+05 (5.00%)
53	MCU-10-684	11/8/2010	4.34E+03 (4.57%)	3.24E+03 (13.5%)	6.04E+05 (5.00%)
97	MCU-11-33	1/9/2011	2.59E+03 (4.54%)	2.89E+03 (6.71%)	8.54E+05 (5.00%)
SEHT					
composite 5-39	Footnote 2		NA	NA	NA
40	MCU-10-600	10/30/2010	<2.31E+00	<7.56E+02	1.91E+09 (5.00%)
45	MCU-10-652	11/5/2010	9.25E+00 (20.5%)	<1.92E+03	2.10E+09 (5.00%)
49	MCU-10-698	11/9/2010	5.50E+02 (6.09%)	6.58E+03 (13.7%)	1.22E+05 (5.00%)
Feed Waste (Tank 49H)	██████████████		3.00E+04	3.57E+05	1.45E+08 (5.00%)

[1] The DSSHT composite was prepared from MCU-10-175, -179, -187, -195, -199, -209, -384, -392, -434, -476, -480, -488, -492, -548, -556, -560, -568, -575, -580, -588, and -596. This corresponds to a microbatch samples range of 5-40.

[2] The SEHT composite was prepared from MCU-10-163, -171, -183, -203, -213, -220, -221, -230, -235, -243, -255, -259, -267, -276, -280, -288, -296, -376, -380, -388, -400, -404, -408, -423, -424, -427, -428, -429, -430, -464, -472, -484, -496, -504, -512, -524, -532, -544, -552, -564, -572, -584, -592. This corresponds to a microbatch samples range of 5-39. The ^{238}Pu, ^{90}Sr, and ^{137}Cs sample results for this composite are not available as of this writing.

The microbatch 49 SEHT sample results are noticeably different from previous samples in this Macrobatch. A check with MCU operations indicates there was no facility outage just before microbatch 49, or any unusual event. The pH of this sample was measured to be 5, so it is not a DSSHT sample accidentally labeled as a SEHT sample. A review of F/H Lab results from SEHT samples indicates that the temporally closest sample from the same day gave a ^{137}Cs result of 2.20E+09 dpm/mL and a pH measurement of 2.25. Therefore, it appears that the SRNL SEHT sample from microbatch 49 is compromised, and most likely consists of a small quantity of SEHT sample highly diluted with some flush water. We consider this sample compromised and recommend it not be taken as a genuine SEHT sample.

While we do not have many data points for this Macrobatch, what we do have shows a similar pattern to the comparable samples from Macrobatch 2 operations. Figure 1 shows all of the Macrobatch 3 DSSHT [238]Pu samples we have analyzed to date, overlaid against the comparable Macrobatch 2 samples. Figure 2 shows the same for [90]Sr. Figure 3 shows the similar ^{137}Cs data, but also includes the SEHT samples.

Figure 1. [238]Pu Data for Selected Macrobatch 2 and 3 DSSHT Samples

While the graph of the Pu data can show the overall trend, it is also important to consider the decontamination factors (DF). While rigorous determination of the DF requires
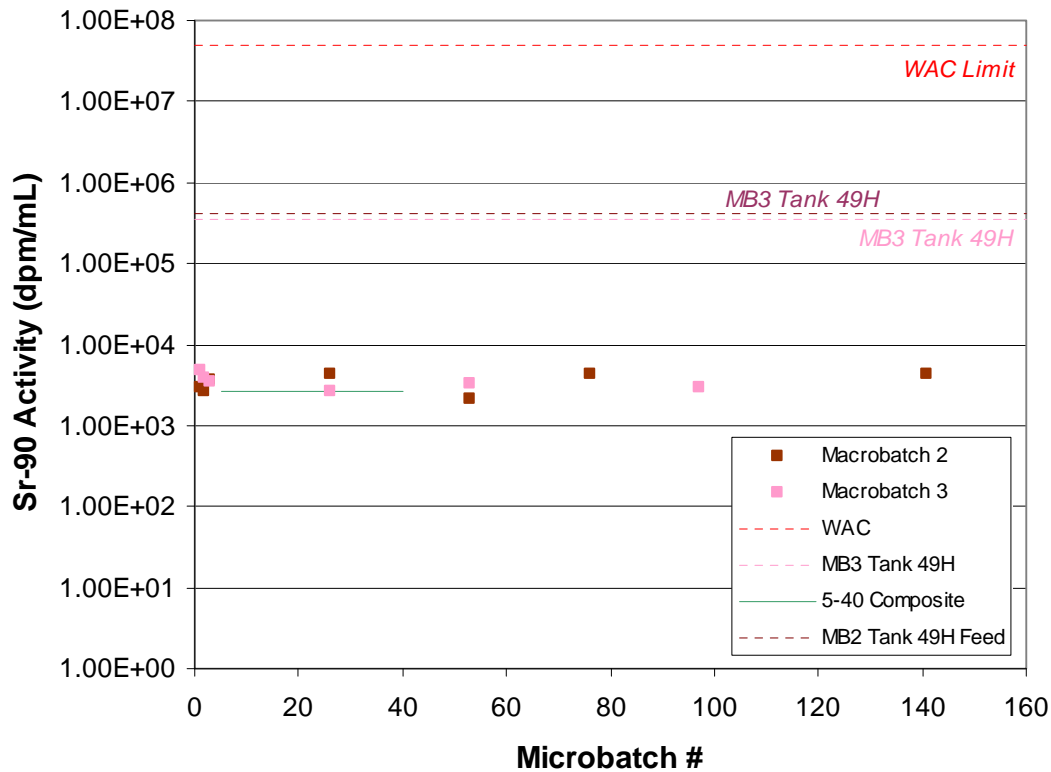
considerations of the flow rates as recorded in the facility, we present the data to give a general comparison between Macrobatch 2 and 3.

Table 2. ^{238}Pu Decontamination Factors for Selected Macrobatch 2 and 3 Samples

Microbatch Sample #	^{238}Pu DF Value	
	Macrobatch 2	**Macrobatch 3**
1	113	50.5
2	606	106
3	1010	17.1
26	83.6	12.5
53	52.8	6.41
76	23.4	no sample
97	no sample	10.7
141	60.0	no sample

A consideration of microbatch samples shows a decline in the Pu DFs. This may be due to the differences in the Pu concentration or the bulk chemical concentrations in the feed material.

A previous study investigated the concentration effects of the six most common anions in salt solutions (NO_3^-, OH^-, NO_2^-, $Al(OH)_4^-$, CO_3^{2-} and SO_4^{2-}).[5] The most appropriate predictive equation (7 day Pu DFs, equation 4) indicates that increasing NO_3^-, and SO_4^{2-} concentrations increase DF, while concentration increases in the other anions decrease the Pu DFs. Using the analyses of Macrobatch 2 and Macrobatch 3 as inputs to this predictive equation provides that Macrobatch 2 should have better Pu removal, by a factor of ~2. We are outside the range of several of the variables, such as nitrate concentration, time, scale of operations, and quantity of MST. Therefore, this result should be considered tentative, but we consider the relative comparison to be appropriate.

Figure 2. ^{90}Sr Data for Selected Macrobatch 2 and 3 DSSHT Samples

Table 3. ^{90}Sr Decontamination Factors for Selected Macrobatch 2 and 3 Samples

Microbatch Sample #	^{90}Sr DF Value	
	Macrobatch 2	**Macrobatch 3**
1	142	75.0
2	158	90.4
3	119	103
26	96.4	134
53	202	110
76	99.8	no sample
97	no sample	124
141	100	no sample

The ^{90}Sr values also show a slight decline between Macrobatch 2 and Macrobatch 3, but to a lesser extent compared to the plutonium DFs. The average Sr DF over the Macrobatch 2 samples is 137, while the average for the Macrobatch 3 samples is 106. If we examine the predicted DFs using the same study as we used with plutonium,[5] we predict a DF of 137 for Macrobatch 2 and 195 for Macrobatch 3. While this does not

match the trend in our data, at least we have no indication that bulk chemical properties are the cause of the slight strontium DF decline.

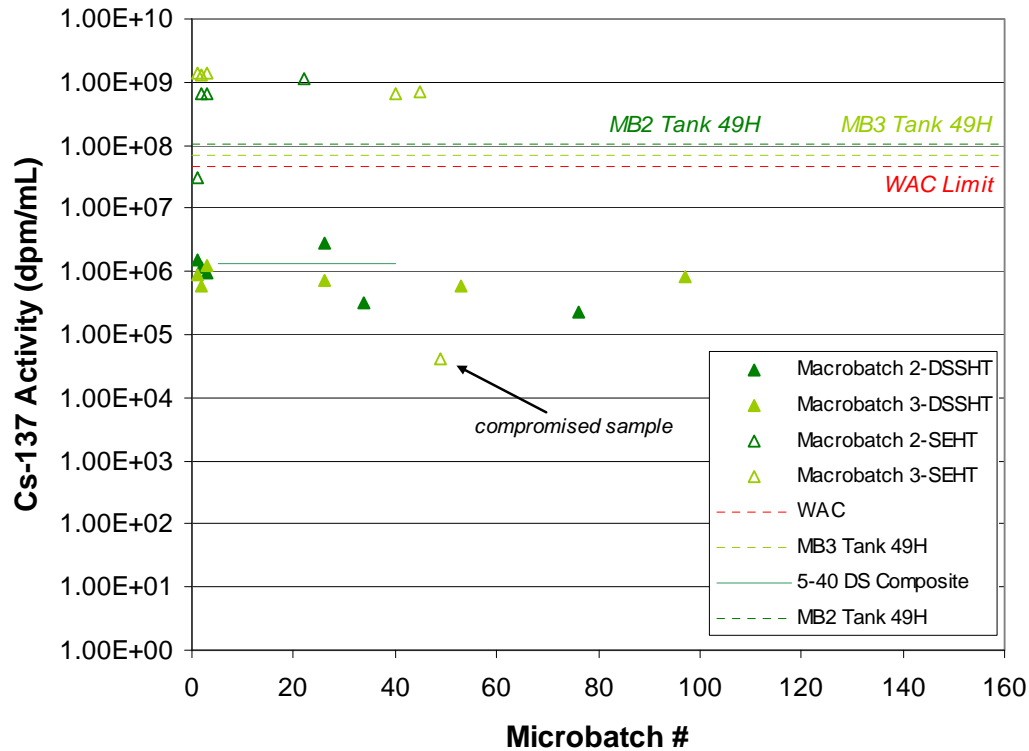**Figure 3. ^{137}Cs Data for Selected Macrobatch 2 and 3 Samples**

Table 4. ^{137}Cs Decontamination Factors for Selected Macrobatch 2 and 3 Samples

Microbatch Sample #	^{137}Cs DF Value	
	Macrobatch 2	Macrobatch 3
1	68.2	168
2	92.1	248
3	114	117
26	37.0	195
53	334	240
76	451	170

While there is a great deal of variation between the microbatch samples within their own macrobatch, as well as between macrobatches, the averages of all samples within a macrobatch is the same (Macrobatch 2 DF average = 183 vs. 179 for Macrobatch 3).

The ICPES results for the DSSHT samples are listed in Table 5, and the ICPES results for the SEHT samples are listed in Table 6. The "source material" column is the analyzed concentration of the analyte in Tank 49H. Note that material from Tank 49H

Table 5. ICPES Results for the DSSHT Samples

Analyte	DSSHT Sample Results (mg/L)				Source Material (mg/L)
	Microbatch 26	Microbatch 53	Microbatch 97	Composite 5-40	
Ag	<2.14	<2.14	<2.14	<2.14	<2.14
Al	3950	4310	4240	3720	5290
B	61.3	72	65.4	58.7	82.6
Ba	1.34	3.19	1.45	<1.18	<0.59
Be	<0.11	<0.11	<0.11	<0.11	<0.7
Ca	1.59	1.41	0.665	1.35	2.27
Cd	<0.84	<0.84	<0.84	<0.84	1.17
Ce	<6.6	<6.6	<6.6	<6.6	<6.6
Cr	53.7	59.2	58.3	50.6	71.6
Cu	<1.42	<1.42	<1.42	<1.42	1.68
Fe	1.4	1.49	1.25	2.49	12.2
Gd	<1.36	<1.36	<1.36	<1.36	<2.12
K	370	426	451	318	480
La	<1.08	<1.08	<1.08	<1	<1
Li	17.1	18.9	17.6	15	25.6
Mg	<0.25	<0.25	<0.25	<0.25	<0.25
Mn	<0.2	<0.2	<0.2	<0.2	0.88
Mo	6.28	6.36	6.56	6.62	8.47
Na	118000	126000	123000	111000	157000
Ni	<2.35	<2.35	<2.35	<9.3	<2.35
P	204	227	223	192	272
Pb	<7.31	<7.31	<7.31	<7.31	<7.31
S	1840	2030	2020	1790	2410
Sb	<6.88	<6.88	<6.88	<6.88	<10.4
Si	201	246	163	176	168
Sn	<4.29	<4.29	<4.29	<68.8	<4.29
Sr	<0.08	<0.08	<0.08	<0.08	<0.08
Ti	3.4	0.65	4.92	3.81	<0.17
U	<44.5	<44.5	<44.5	<44.5	<44.5
V	<0.52	<0.52	<0.52	<0.52	<0.52
Zn	8.54	9.12	8.26	8.78	6.5
Zr	<0.47	<0.47	<0.47	<0.89	<0.89

The analytical uncertainty for the ICPES samples is 10%.

Table 6. ICPES Results for the SEHT Samples

Analyte	SEHT Sample Results (mg/L)			
	Microbatch 40	Microbatch 45	Microbatch 49	Composite 5-39
Ag	<0.545	<0.541	<0.541	<0.856
Al	<2.76	<2.74	<2.74	<3.77
B	<0.516	<0.512	<0.512	<1.5
Ba	0.138	0.108	<0.038	<0.472
Be	<0.0322	<0.0320	<0.0320	<0.044
Ca	2.31	0.876	1.38	1.72
Cd	<0.103	<0.102	<0.102	<0.336
Ce	<1.93	<1.92	<1.92	<2.64
Cr	<0.308	<0.306	<0.306	<0.556
Cu	<0.142	<0.413	<0.413	<0.568
Fe	54.8	0.416	6.81	0.2
Gd	<0.416	<0.396	<0.396	<0.544
K	<5.86	<5.82	<5.82	<14
La	<0.293	<0.291	<0.291	<0.4
Li	<0.756	<2.20	<2.20	<0.692
Mg	0.797	0.281	0.205	0.524
Mn	0.396	<0.0582	0.105	<0.08
Mo	<1.25	<1.24	<1.24	<1.71
Na	18.2	30.0	2.55	20.1
Ni	<2.72	<2.71	<2.71	<3.72
P	<9.87	<9.81	<9.81	<13.5
Pb	<22.0	<21.8	<21.8	<2.92
S	<22.0	<21.8	<21.8	<30
Sb	<2.02	<2.00	<2.00	<2.75
Si	15.1	14.1	23.0	1.92
Sn	<1.26	<1.25	<1.25	<27.5
Sr	<0.0234	<0.0233	<0.0233	<0.032
Ti	<0.217	<0.215	<0.215	<0.296
U	<13.0	<12.9	<12.9	<17.8
V	<0.152	<0.151	<0.151	<0.208
Zn	2.05	1.14	0.722	6.47
Zr	<0.138	<0.137	<0.137	<0.356

The analytical uncertainty for the ICPES samples is 10%.

undergoes a ~20 vol % dilution from ARP and MCU.[Υ] 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, Li, Na, P, and S) gives an average dilution factor of ~30%. This would suggest additional dilution is happening at ARP or MCU, possibly from high scrub acid flow, or rainwater addition from the sumps.

The DSSHT samples give the expected results – a dilution compared to the source material in the analytes. This is most easily see in those elements that should remain unaffected by the ARP and MCU chemistry – Al, B, Cr, S (from sulfate), P (from phosphate), etc. The notable exception to this is the silicon values which are higher than the feed material. The microbatch samples from the previous report[2] also show a trend of high silicon values. These higher silicon values may be due to slow dissolution of the solids observed during prior replacement of the pump in the SSRT.[6] It is unlikely that the higher than expected silicon is from sample handling or preparation.

The titanium results in the DSSHT samples are notable. In each case, 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. Testing in progress at SRNL has shown that Ti leaching from MST increases at higher free hydroxide concentration in the waste solution; this is suspected as a leading contributor to the Ti component in the MCU samples. The work on this subject is not complete and will be reported at a later date.

The SEHT samples follow the general trends observed for the previous sample results.[2] For example, the sodium levels in all of the SEHT samples to date show the same approximate concentration. This is a good indication that the bulk chemistry has not changed, and also suggests that the aqueous carryover from the feed material into the solvent, and then back to the SE is not varying too greatly. However, there are some results that merit further review. First, the silicon values in the samples in this report are notably elevated compared to SEHT results from the previous report. Second, the iron values in the SEHT samples from this report are showing a large variance. If the sodium levels indicate no large changes in carryover, then we are at a loss to explain the variations in the iron levels.

[Υ] Each 3600 gallon batch of material is mixed with 210 gallons of MST slurry, and is then combined with 1 volume of scrub acid for each 7.5 volumes of salt solution (this is double the nominal rate of scrub acid). This dilutes each 3600 gallons to 4318 gallons, or ~20 vol % increase in volume.

4.0 Conclusions

The results from the current microbatch samples do not show a trend established by previous samples in this macrobatch. Furthermore, the trends from this macrobatch are similar to that from comparable samples in Macrobatch 2. However, the plutonium and strontium DFs in this set of samples are less than comparable samples in Macrobatch 2. SRNL is looking into possible reasons for this disparity.

From a bulk chemical point of view, the ICPES results do not vary considerably between previous results and this Macrobatch. However, there are initial indications that the overall system dilution may be somewhat greater than theoretical (~30% vs. ~20%). ARP and MCU should check the aqueous inputs into their systems to make sure we are not out of specifications in such things as flush water (ARP) or scrub acid rate (MCU).

Finally, the titanium results 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.

5.0 References

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

[2] Peters, T. B., Fink, S. D., "Results from Macrobatch 3, Microbatches 1-3 Sample Analyses" SRNL-STI-2010-00575, September 2010.

[3] S. E. Campbell, "Blend Evaluation for Tank 49H Feed for ISDP Salt Batch 3", X-ESR-H-00209, March 16, 2010.

[4] T. B. Peters, S. D. Fink, "Results from ISDP3 Tank 49H Confirmatory Samples", SRNL-STI-2010-00234, April 2010.

[5] M. J. Barnes, T. B. Edwards, D. T. Hobbs, K. M. Marshall, "Strontium and Actinide Removal Testing with Monosodium Titanate and Other Sorbents", WSRC-TR-2001-00436, Rev.0, October 29, 2001.

[6] T. B. Peters, S. D. Fink, "Sample Results from Solids Isolated from the SSFT", SRNL-STI-2011-00022, March 2011.

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