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Consideration of Factors Affecting Strip Effluent pH and Sodium Content

T. B. Peters

July 2015

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EXECUTIVE SUMMARY

A number of factors were investigated to determine possible reasons for why the Strip Effluent (SE) can sometimes have higher than expected pH values and/or sodium content, both of which have prescribed limits. All of the factors likely have some impact on the pH values and Na content.

Cesium Loading Effects on SE pH

Higher cesium concentrations in the feed can affect the pH in the SE. However, the effect is small, and largely localized to the first 2 contacts. Therefore, this test set indicates that increases in the cesium in the feed (such as the 0.8 Ci/gal for Salt Batch 8), should not challenge the Defense Waste Processing Facility (DWPF) SE pH limit.

Effects of Altering the SE

The strip acid (0.01 M boric acid) is a weak acid. At the pH ranges typically noted in the SE, small changes in strip feeds can have a noticeable effect on the pH. In particular, Savannah River National Laboratory (SRNL) notes that the presence of nitrate anion in the SE appears to promote an acid-base reaction with the suppressor, which raises the pH in the SE. Future research may determine if it is possible to use this chemical mechanism to slow the rate of suppressor degradation.

Effects of Mixing Energy and Time

Mixing in the scrub contactors can entrain caustic scrub solution into the solvent. The entrained scrub solution can in turn react with strip acid in the strip contactors and affect the pH of the strip effluent. Attempts to duplicate the entrainment in the scrub contactors indicate that at least for the scrub steps, a contact time of 24 hours may not be long enough to consistently reach equilibrium for the distribution of cesium. However, even short contact times give cesium distributions that are acceptable. Attempts to imbue higher mixing energies led to either emulsions or poor phase separations which prevented further conclusions on pH or sodium from being discerned. F/H has also noted this effect in a few past SE samples.

Consideration of Sodium Content in the SE

A review of historical sodium concentrations in the SE shows that routine operations do not challenge the new DWPF limit of 265 mg/L. While SRNL recommends continuing to monitor sodium content in the SE, no special actions should be required to operate below the 265 mg/L limit.

LIST OF ABBREVIATIONS

DSS	decontaminated salt solution
DSSHT	Decontaminated Salt Solution Hold Tank
DWPF	Defense Waste Processing Facility
ESS	Extraction- scrub- strip (test)
ICPMS	inductively coupled plasma mass spectroscopy
MCU	Modular Caustic-Side Solvent Extraction Unit
RSD	Relative standard deviation
SE	Strip Effluent
SEHT	Strip Effluent Hold Tank
SRNL	Savannah River National Laboratory
TiDG	N,N',N''-tris (3,7-dimethyloctyl) guanidine
TTQAP	Task Technical and Quality Assurance Plan
WAC	Waste Acceptance Criteria

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1.0 Introduction

As part of routine operations, the Modular Caustic-Side Solvent Extraction Unit (MCU) is required to analyze monthly samples from the Decontaminated Salt Solution Hold Tank (DSSHT) and Strip Effluent Hold Tank (SEHT). The analyses include, among other things, pH and sodium content. The current Waste Acceptance Criteria (WAC) for DWPF¹ limits the pH of the effluent stream to between 2 and 11. While the recent Strip Effluent (SE) samples are well within that limit (pH < 9), the pH values are higher than the DWPF limits (pH of 6-8) in a previous DWPF WAC. The MCU customer has requested SRNL investigate the reasons for the higher than anticipated pH readings.

Furthermore, the recent WAC revision added a new requirement for the sodium content to be ≤ 265 mg/L. SRNL was tasked with investigating whether or not this new limit represents an operating difficulty to MCU.

This document is part of a customer request² to examine the history of the sodium content and pH of the SE, as well as estimate whether or not the future SE samples will challenge the pH and sodium limits. SRNL wrote a Task Technical and Quality Assurance Plan (TTQAP) to describe the work scope.³ Previous documents provide partial sets of results.^{4,5} This document summarizes previous and additional results.

2.0 Experimental Procedure

2.1 Effect of K and Cs Loading on the pH and Cs Distribution

As specified in the TTQAP, the first set of tests was intended to examine if increased amounts of cesium and potassium in the aqueous feed can affect the pH in the SE. If the calix binds a cesium or potassium cation, there must be an anion associated with the “loaded calix”. If the anion is a caustic anion, such as hydroxide or deprotonated Modifier, this could affect the SE pH, as the moderate acidity (~ pH of 6) of the strip acid is very sensitive to carryover of caustic species.

For these tests, a full Extraction- scrub- strip (ESS) regime was performed, using the Blended solvent[⊕] and one of two types of salt simulant spiked with either non-radioactive cesium or potassium. The salt simulant recipe was used in previous related work but varied from the previously used recipe in that there was no initially added potassium chloride.⁶ One test used a cesium nitrate spike of 50 mg/L and the second was spiked to 150 mg/L. The third test in this set had neither cesium nor potassium added and the fourth was spiked to 50 mg/L of potassium chloride. The major constituents of the solution composition are shown in Table 1.

[⊕] The blended solvent was originally created by mixing the BOBCalix solvent with a cocktail that generated a blended solvent that was nominally 0.5 M modifier, 46.5 mM MaxCalix, 3.5 mM BOBCalix, 1.5 mM trioctylamine, and 3 mM TiDG.

Table 1. Major Components of the Salt Simulant Component Simulant (M)

Component	Concentration (M)
Free NaOH	2.2
Nitrate	1.99
Nitrite	0.529
Al	0.29
Sulfate	0.138
Phosphate	0.0068
Total Na	5.28

Freshly prepared Blended solvent was used in all testing that required organic solvent. Table 2 shows the composition of the Blended solvent.

Table 2. Blended Solvent Composition Component Blended Solvent Content (M)

Component	Concentration (M)
MaxCalix	0.0465
BOBCalixC6	0.0035
Trioctylamine	0.0015
TiDG Guanidine	0.003
Modifier	0.50
Isopar™ L	Balance

For the ESS tests, the solvent was used as prepared. For other tests using this Blended solvent, it was pre-contacted with caustic to convert the guanidinium (N,N',N''-tris (3,7-dimethyloctyl) guanidine - TiDG) into the guanidine form.^o

The details of the ESS tests have been demonstrated previously and the current method and application are documented.⁷ For the present work, SRNL used one extraction, two scrub and three strip steps. The work followed an approved procedure.⁸ In each case there was a delay between each extraction, scrub, or strip step. Our extraction and strip steps used a delay as short as 6 hours, but the scrub steps required 24 hours to separate cleanly. Due to a perceived slow phase separation for the scrub steps, the decision was made to place all the ESS tests in a shaker oven that was temperature controlled to 23 °C. MCU runs extraction and scrub stages at 23 °C

^o As prepared, the solvent uses a guanidinium chloride salt (protonated guanidine with a chloride anion) which cleanly dissolves. Once this material contacts caustic, the guanidinium is deprotonated into the freebase neutral guanidine form.

and strip at 33 °C. Scrub (nominally 0.025 M NaOH) and strip (nominally 0.01 M boric acid) solutions were prepared as necessary, and spiked with additional species as needed.

Testing was performed by:

Step#1

- Contact Blended solvent with ^{137}Cs radiospiked scrub solution in the proper 3.75 O:A phase ratio.
- Use hand mixing as per the standard ESS protocol.
- After mixing, let the solutions separate over a 48 hour period (at room temperature), and sample each phase at 2, 4, 8, 24, and 48 hours to determine the ^{137}Cs content.
- Perform in duplicate.

This should determine the time required to reach phase separation when using hand mixing.

Step#2

- Contact Blended solvent with ^{137}Cs radiospiked scrub solution in the proper 3.75 O:A phase ratio.
- Use a tissue homogenizer to provide more powerful mixing.
- After mixing, let the solutions separate over a 48 hour period, and sample each phase at 2, 4, 8, 24, and 48 hours to determine the ^{137}Cs content.
- Perform in duplicate.

This should determine the time required to reach phase separation when using more powerful mixing energies.

Step#3

- Contact Blended solvent with ^{137}Cs radiospiked scrub solution in the proper 3.75 O:A phase ratio.
- Use a tissue homogenizer to provide more powerful mixing.
- After mixing, let the solutions separate for a period of time equal to the equilibrium time established in step #2.
- At 25, 50, 75 and 100% of the equilibrium time, remove a portion of the organic phase.
- This portion undergoes its own ESS-type contact with strip acid, in a 3.75 O:A phase ratio, using hand mixing.
- At 50 and 100% of the equilibrium time determined from step #1, measure the pH and sodium content of a sample of the aqueous phase.

The results from these steps were intended to provide insights into how the time and energy of mixing can affect the strip pH through phase carryover.

The researchers prepared a salt simulant with a composition described in Table 1, with the addition of potassium nitrite to reach a potassium concentration of 650 mg/L. This salt solution was then contacted with freshly prepared Blended solvent, in order to convert any guanidinium in the solvent to the guanidine form. The freebase Blended solvent was then used without

further modification. Scrub solution (0.025 M NaOH) was prepared with a small ^{137}Cs spike, as a tracer.

Details of this work are kept in a SRNL electronic notebook.⁹

2.2 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. 2.¹⁰

3.0 Results and Discussion

3.1 Effect of K and Cs Loading on the pH

During each step of each ESS test, the pH of the aqueous scrub and strip solutions were measured by pH probe, these measurements are an indication if the high concentrations of Cs and K are bringing over caustic anions. The pH measurements on the aqueous phases have been tabulated (Table 3). The pH of the simulant aqueous feed and the decontaminated aqueous phases were not measured due to the high free hydroxide ($> 2\text{M}$) rendering the pH measurement meaningless.

Table 3. pH Results from Scrub and Strip Phases

Step	Test (mg/L Cs / mg/L K)			
	1 (50/0)	2 (150/0)	3 (0/0)	4 (0/50)
Scrub#1	12.51	12.45	12.53	12.49
Scrub#2	12.26	12.23	12.22	12.25
Strip#1	8.94	10.06	7.80	7.73
Strip#2	7.42	8.66	7.68	7.27
Strip#3	7.52	7.65	7.54	7.26

The analytical uncertainty is typically 0.1 pH units for the pH probe measurements.

While the pH of the SE at MCU is typically slightly above 8, a direct comparison is difficult here, as it is not possible to test the pH of the SE after each contactor.

Each test shows a decline in pH going from scrub#1 to scrub#2. This is likely due to a very small amount of caustic carryover from the extraction step into scrub#1. The scrub#1 results are the same for each test, and the scrub #2 results are also the same across each test.

Strip#1 shows the largest difference between tests, with the highest pH from the test with the most added cesium, and the second highest pH from the test with the second highest added

cesium. The test with only added potassium showed no significant differences from the control (third) experiment. Strip#2 also showed a test-dependent result with the same trends seen in Strip#1, but not to the same degree. Strip#3 showed no effective differences in the test results.

As an entire data set, this indicates that while there is some effect of increasing cesium loading, it tapers off the further along the strip cycle, and does not challenge the DWPF pH limits even with unreasonably high cesium added.

3.2 Effect of Cs Loading on the ESS Results

In addition to the pH data that was collected from the test outlined in section 3.1, for those tests that contained cesium in the aqueous phase, samples from each phase in each step were sent for analysis by inductively coupled plasma mass spectroscopy (ICPMS). Reported $D_{(Cs)}$ values for Cs were temperature corrected to 23 °C (extraction and scrub steps) or 33 °C (strip steps).¹¹ See Table 4.

Table 4. Cesium Distribution Ratios ($D_{(Cs)}$) for the ESS Tests

Material	Extraction	Scrub#1	Scrub#2	Strip#1	Strip#2	Strip#3
Test 1 (50 mg/L Cs)	56.8	3.29	1.21	0.00147	0.00751	3.57
Test 2 (150 mg/L Cs)	64.0	1.66	0.968	0.0250	0.00246	0.00672

The results of the ESS tests are largely as expected. The extraction, scrub and strip tests all give values roughly similar to those of other past ESS tests.[®] The one exception to this is strip#3 for test#1. The very high value is an indicator of introduction of cesium into the sample, likely through phase contamination (a small amount of AQ into the ORG). The absolute value of cesium in the organic phase in strip#3 was higher than in the strip#2 step, which is impossible unless cesium is introduced (contamination) at that stage. The differences between the tests for a specific step (for example, strip#1) are not likely to be attributable to experimental errors, but more likely to once again seeing the effect of the high mass loading of the cesium in the 150 mg/L test. Recall that it was strip #1 in the 150 mg/L tests that showed the highest pH value of all the tests. Higher pH values in the strip#1, caused by caustic ion carryover, likely suppress stripping, although the effect in these tests is not excessive.

It is gratifying to note that the far higher mass concentrations used in these tests (compared to real waste cesium concentrations) do not give any indication of saturating the ability of the solvent to remove extract cesium from the caustic salt. Given the very limited data set, it is not possible to know if the differences in the $D_{(Cs)}$ values between the two tests are related to the different amount of cesium in the aqueous feed.

[®] Most ESS tests measure radioactive Cs, which is in much lower mass concentration than these two tests.

3.3 Effects of Altering the SE

In addition to measuring the pH of the strip acid solutions after contact with the solvent, the unused stock solutions were measured for pH at 24 hours. See Table 5. No visual changes were observed, although this is expected given the types of material and the small scale.

Table 5. pH of Strip Solutions After Contact

Time	Test 1 (0.01 M H ₃ BO ₃)	Test 2 (0.02 M H ₃ BO ₃)	Test 3 (0.01 M H ₃ BO ₃ + 3mM NaNO ₃)	Test 4 (0.01 M H ₃ BO ₃ + 0.7mM NaHCO ₃)
2 hours	7.65	7.26	8.78	8.33
24 hours	8.57	8.09	8.93	8.52
24 hours - stock	6.98	6.54	6.51	7.40

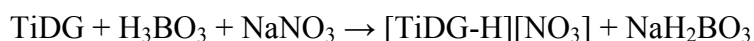
The analytical uncertainty is typically 0.1 pH units for the pH probe measurements.

From the pH measurements a number of effects can be discerned:

Effect of time – the pH of the strip solutions increased over time. The acid-base reaction is not immediate and varying the processing rates at MCU could result in variations in the pH of the SE.

Effect of boric acid concentration – Doubling the concentration of the boric acid resulted in a consistent lower pH than the 0.01 M boric acid strip. This is to be expected and could be utilized to effect small changes in the SE if desired.

Effect of nitrate – It is postulated that the boric acid alone does not promote an efficient acid-base reaction with the guanidine in the solvent. The sodium nitrate was added to the strip solution in the hopes that it would promote an acid-base reaction by providing an anion with sufficient solubility in the non-polar solvent:



Comparing the results from Tests #1 and #3, it appears that the added nitrate does have a moderate effect. Test #3 gave the highest pH value indicating the most extensive acid-base reaction. It may be possible to use this effect to our advantage. At this time, the TiDG suppressor in the solvent is degrading at rates higher than desirable. Ongoing work suggests that the freebase form of the TiDG is the form that is degrading, and not the protonated form. If the TiDG can be protonated in the SE, this could slow the degradation.

Effect of added buffer – The presence of a weak base such as bicarbonate should provide moderate stabilization from pH swings in the SE. While Test#4 showed the second lowest pH of all four tests (at 24 hours), it is difficult to say if the effect is significant.

3.4 Effects of Mixing on Carryover into the SE

Results from Initial Hand Mixing - Once the ^{137}Cs concentrations in each phase for each step were determined, these values were used to derive $D_{(\text{Cs})}$ values for at each point in time for this scrub step. The initial hand mixing tests were performed in duplicate. The resulting $D_{(\text{Cs})}$ values are reported in Table 6. Values in parentheses are the percent relative standard deviation (%RSD).

Table 6. $D_{(\text{Cs})}$ Results from the Hand Mixing Tests

Test	2 Hour	4 Hour	8 Hour	24 hour	48 Hour
hand mixing	2.13 (35%)	3.19 (21%)	3.42 (16%)	3.38 (25%)	4.25 (7.5%)

The hand mixing results indicate that the cesium transfer between phases is not complete at 24 hours. However, while the equilibrium has not been reached, the values are trending in the appropriate direction. Higher $D_{(\text{Cs})}$ values for the scrub steps indicate the ^{137}Cs preferring to remain in the solvent instead of partitioning into the scrub phase, which is a desired outcome. It is possible that the extraction and scrub steps also require longer than 24 hours to reach equilibrium, and this should be further investigated.

Results from Mixing with Tissue Homogenizer - After the hand mixing tests were performed; duplicate tests were performed using the tissue homogenizer. For this set, the tissue homogenizer was set to the next lowest setting (“2”) in order to avoid emulsifying the solutions. Other test parameters were the same as in the hand mixing tests. However, it was found that even with this low setting, the tissue homogenizer provided excessive mixing energy and as a result, an emulsion was formed that lasted over 72 hours. As a result, the initial attempts to use the tissue homogenizer failed.

A second attempt was performed with a single test. In this case, the tissue homogenizer was set to its lowest setting. This time, the solution was mixed without an emulsion forming. The samples from each phase were removed at 2, 4, 8, 24, and 48 hours as in the hand mixing test, and sent for ^{137}Cs analysis. The analytical results were tabulated and used to calculate the resulting $D_{(\text{Cs})}$ values, which are reported in Table 7. Values in parentheses are the analytical uncertainty.

Table 7. $D_{(Cs)}$ Results from the Homogenizer Mixing Tests

Test	2 Hour	4 Hour	8 Hour	24 hour	48 Hour
homogenizer	1.68 (5.0%)	1.73 (5.0%)	2.20 (5.0%)	5.95 (5.0%)	5.37 (5.0%)

The results were somewhat surprising in that they indicate that while equilibrium appears to be reached by 24 hours, values from 2 to 8 hours were poorer, compared to the hand mixing tests. Superior mixing should in principle lead to shorter times to reach equilibrium.

Due to the inconsistencies in the $D_{(Cs)}$ results between the two sets of tests (Tables 6 and 7), and the difficulties in finding a suitable mixing regime, SRNL considers that due to the lack of centrifugal separation, (recall that the tissue homogenizer provides excellent mixing, but no separation, unlike a centrifugal contactor) we cannot be successful at implementing this test scope with the equipment on hand.

3.5 Consideration of Sodium Content in the SE

The original intent of the work scope was to investigate sodium carryover from the mixing studies. As those tests did not have a successful outcome, it is necessary to at least discuss historical sodium data.

Sodium is present in almost every SEHT sample sent to SRNL. This is the case for the previous (BOBCalix) and current solvent operations. For example, Salt Batches 2-6 were run with the BOBCalix solvent, while Salt Batch 7 was run with the current solvent formulation (see Table 8). Values in parentheses are the RSD.

Table 8. Average of Sodium Concentration in the SEHT Routine Samples for Salt Batches 2-7

Salt Batch	Sodium Concentration (mg/L)
2	88.5 (55%)
3	19.5 (38%)
4	47.3 (56%)
5	61.7 (34%)
6	55.6 (32%)
7	34.8 (17%)

SRNL believes that it is not the extractant taking up sodium into the solvent (and back out into the strip) that is the cause for the sodium in the SEHT samples. In principle, only potassium and cesium should be extracted into the solvent due to the action of the extractant.¹² If the extractant is a major cause for sodium uptake, then the sodium uptake and release should be proportional to the increase in the extractant concentration from the old solvent to the current formulation, which is not supported by routine sample results of the SEHT. It is much more likely that the sodium is due to a combination of mechanical carryover and an ORNL proposed mechanism involving solvent uptake of sodium via ion-pairing with deprotonated modifier.¹² While the current data set cannot distinguish between the two possible mechanisms, it should be possible to design an experiment to do so, if there is future work scope.

SRNL reviewed all sodium data for the SEHT samples for salt batches 2-7 (no ICPEs samples for salt batch 1 were performed). The only time the sodium concentration in the SEHT exceeded the new sodium limit of 265 mg/L was during the small period of time in salt batch 7 processing that MCU experienced the unique hydraulic issues which resulted in salt feed and/or decontaminated salt solution (DSS) to enter the SEHT and grossly raise the sodium concentration.¹³

Given the historical precedent, SRNL considers it unlikely that the DWPF sodium limit of 265 mg/L could be challenged under routine operating conditions.

4.0 Conclusions and Path Forward

Cesium Loading Effects on SE pH

Salt Batch 7 was found to have a total cesium concentration ($^{137}\text{Cs} + ^{135}\text{Cs} + ^{133}\text{Cs}$) of 2.56 mg/L. Salt Batch 8 was found to have a total cesium concentration ($^{137}\text{Cs} + ^{135}\text{Cs} + ^{133}\text{Cs}$) of 9.83 mg/L. This is still an order of magnitude less than the test with the highest cesium concentration (150 mg/L), which itself gave a single strip pH value (10.06) below the DWPF limit of 11. Therefore, this test set indicates that even if we go to 0.8 Ci/gallon feed, we should not challenge the DWPF pH limit.

Effect of Cs Loading on the ESS Results

These tests confirm that high mass loadings of cesium do not negatively impact the performance of the Blended solvent.

Effects of Altering the SE

At the pH ranges typically noted in the SE, small changes in strip feeds can have a noticeable effect on the pH.

Increasing the concentration of the boric acid to 20 mM provided a noticeable drop in pH. It stands to reason that decreasing the boric acid concentration will result in higher pH values in the SE. Addition of sodium nitrate was not expected to have a direct effect on the pH. However, the results indicate that sodium nitrate promoted an acid-base reaction between the guanidine in the solvent and the boric acid, raising the pH of the SE. Addition of a small amount of sodium bicarbonate did not appear to have a strong effect on pH of the SE.

SRNL recommends further studies on the effect of deliberately adding nitrate salts to the SE, in order to protonate the TiDG.

Effects of Mixing Energy and Time

Results from the hand-mixing tests indicate that at least for the scrub steps, a contact time of 24 hours may not be long enough to consistently reach equilibrium for the distribution of cesium. However, even short contact times give cesium distributions that are acceptable for the scrub steps. It is possible that the extraction and scrub steps also require longer than 24 hours to reach equilibrium, and this should be further investigated.

Attempts to imbue higher mixing energies led to either emulsions or poor phase separations. SRNL feels that the lack of centrifugal separation (which is present in the centrifugal contactors) makes it impossible to study mixing effects. If future experiments are planned, consideration should be given to the use of small contactors.

Consideration of Sodium Content in the SE

A review of historical sodium concentrations in the SE shows that routine operations do not challenge the new DWPF limit of 265 mg/L. The sodium in the SEHT samples is likely due to mechanical carryover which is not likely to change at MCU.

5.0 References

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- ¹ X-DS-G-00008, Rev. 14, “Waste Acceptance Criteria for Sludge, ARP, and MCU Process Transfers to 512-S and DWPF”.
- ² Q. Nguyen, “Determine Causes for the Increase in Strip pH and Maximum Bounding Sodium Value in the SEHT”, X-TTR-H-00036, February 5, 2014.
- ³ T. B. Peters, A. L. Washington, II, “Task Technical and Quality Assurance Plan for pH and Sodium Impacts at DWPF”, SRNL-RP-2014-00166, May, 2014.
- ⁴ T. B. Peters, “Results from ESS Testing as Part of TTQAP SRNL-RP-2014-00166”, SRNL-L3100-2014-00112, June 2, 2014.
- ⁵ T. B. Peters, S. D. Fink, “Consideration of the Strip Effluent (SE) pH and Sodium Content”, SRNL-L3100-2014-00028, February 20, 2014.
- ⁶ D. T. Herman, M. R. Duignan, M. R. Williams, T. B. Peters, M. R. Poirier, F. F. Fondeur, “Mass Transfer and Hydraulic Testing of the V-05 and V-10 Contactors with the Next Generation Solvent”, SRNL-STI-2013-00413, July 2013.
- ⁷ Wilmarth, W. R., Healy, D. P., Wheeler, D. J., Mills, J. T., Dukes, V. H., and DiPrete, D. P., “Caustic-Side Solvent Extraction Batch Distribution Measurements for SRS High Level Waste Samples and Dissolved Saltcake”, WSRC-TR-2002-00336, Rev. 1, December 5, 2002.
- ⁸ D. D. Walker, “Extraction, Scrub, and Strip Testing of Solvent Extraction Systems,” SRNL Manual L29 ITS-205, September 2013.
- ⁹ T. B. Peters, “Effects of pH and Sodium on MCU”, ELN A4571-00084-14.
- ¹⁰ Savannah River National Laboratory, “Technical Report Design Check Guidelines”, WSRC-IM-2002-00011, Rev. 2.
- ¹¹ T. B. Peters, A. L. Washington II, “Sample Results from the Interim Salt Disposition Program Macrobath 8 Tank 21H Qualification Samples” SRNL-STI-2014-00561, rev.1, January 2015.
- ¹² B. A. Moyer, S. D. Alexandratos, P. V. Bonnesen, G. M. Brown, J. E. Caton Jr., L. H. Delmau, C. R. Duchemin, T. J. Haverlock, T. G. Levitskaia, M. P. Maskarinec, F. V. Sloop Jr., C. L. Stine, “Caustic-Side Solvent Extraction Chemical and Physical Properties Progress in FY2000 and FY2001”, ORNL/TM-2001/285, February 2002.
- ¹³ T. B. Peters, A. L. Washington II, L. N. Oji, C. J. Coleman, M. R. Poirier, “Sample Results from MCU Solids Outage”, SRNL-STI-2014-00336, September 2014.