Sample Results from the Next Generation Solvent Program Real Waste Extraction-Scrub-Strip Testing

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LIST OF REVISIONS		
Revision Number	**Summary of Changes**	**Date**
0	Initial Report	6-3-2013
1	Updated with new temperature correction factors from ORNL	8-6-2013
1	Added appendix detailing temperature correction	8-6-2013
1	Updated supporting text	8-6-2013

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) performed multiple Extraction-Scrub-Strip (ESS) testing using real waste solutions, and three Next Generation Solvent (NGS) variations, which included radiologically clean pure NGS, a blend of radiologically clean NGS and radiologically clean BOBCalixC6 (NGS-MCU), and a blend of radiologically clean NGS and radiologically contaminated BOBCalixC6 from the MCU Solvent system. The results from the tests indicate that both the NGS and the NGS-MCU blend exhibit adequate extraction, scrub and strip behavior.

LIST OF ABBREVIATIONS

AD	Analytical Development
ARP	Actinide Removal Project
ESS	extraction, scrub, strip
ISDP	Interim Salt Disposition Program
MCU	Modular Caustic-side Solvent Extraction Unit
NGS	Next Generation Solvent
ORNL	Oak Ridge National Laboratory
SHT	solvent hold tank
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAC	Waste Acceptance Criteria
%RSD	percent relative standard deviation

1.0 Introduction

This report details the results of the NGS and NGS-MCU tests (four in total) with real waste. The solvents used were three Next Generation Solvent (NGS) variations, which included radiologically clean pure NGS, a blend of radiologically clean NGS and radiologically clean BOBCalixC6 (NGS-MCU), and a blend of radiologically clean NGS and radiologically contaminated BOBCalixC6 from the MCU Solvent system.

This work was specified by Task Technical Request [1] and by Task Technical and Quality Assurance Plan (TTQAP).[2]

Details for the work are contained in controlled laboratory notebooks.[3]

2.0 Experimental Procedure

Six Tank 21H samples (i.e., dip sample bottles HTF-21-12-96, HTF-21-12-97, HTF-21-12-98, HTF-21-12-99, HTF-21-12-100, and HTF-21-12-101) arrived at SRNL on October 3, 2012. The samples were optically clear, with no visible solids present. Researchers measured the density of each of the solutions. With customer concurrence, the samples were combined and mixed. This material served as a qualification sample for Salt Batch 6,[4] and the remaining material was saved for use for the NGS program.

The bulk chemical composition of this material is reported in Table 1.

Table 1. Tank 21H Composition

Analyte	Result
density	1.304 g/mL
Free OH	1.90 M (10%)
NO_3^-	2.23 M (10%)
NO_2^-	0.474 M (10%)
Al	0.199 M (10%)
K	0.0118 M (10%)
^{137}Cs	1.28E+08 (5.00%) (dpm/mL)

The analytical uncertainty is typically <1% for density measurements.

2.1 ESS Test Conditions

For the ESS tests, material from the Tank 21H composite was used. For each test, the researchers used a nominal starting volume of 80 mL of aqueous feed and 20 mL of prepared solvent.[Σ] For the first test, the solvent was the pure NGS, of a composition listed in Table 2. For the second test, the solvent was a blended material "NGS-MCU". This blended material was created from the current MCU solvent formulation [Υ] and a

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[Σ] This set of volumes for the extraction step corresponds to a 4:1 A:O volume ratio. In the scrub and strip tests, the A;O volume ratio was 1:3.75.

[Υ] This batch of solvent was originally prepared with no extractant as S2-NOBOB-T-WI (see WSRC-NB-2005-00060). The extractant was added later (see WSRC-NB-2007-00054).

prepared solution that would create a blended material designed to mimic the MCU solvent during initial NGS operations (this preparation was of an initially non-radiologically contaminated material, or "non-rad").[5] For the third and fourth tests, the solvent was identical to the one used in the second test, except that the MCU solvent was actual samples from the MCU solvent hold tank (SHT). The used solvent was from the October 2012 quarterly samples [6] for the third test and for the fourth test the solvent was from the January 2013 quarterly samples.[7] The first two tests were run in parallel, at the same time. The last two tests were run individually.

Table 2. Solvent Composition in Each Test (M)

Component	Test #1	Test #2	Test #3	Test #4
MaxCalix	0.0501	0.0465	0.0463	0.0464
BOBCalix	None added	0.0035	0.00350	0.00348
Cs-7SB Modifier	0.499	0.500	0.507	0.437
Trioctylamine	None added	0.0015	0.0015	0.000637
TiDG	0.00277	0.00325	0.00294	0.00305
Isopar L ®	balance	balance	balance	balance

All of the tests used the same general protocol as used in macrobatch qualification, although the scrub and strip solutions are different due to necessary changes in the solvent chemistry (scrub is 0.025 M NaOH, strip is 0.01 M boric acid).[8] Temperature corrections are provided from Oak Ridge National Laboratory (ORNL) documentation.[9]

2.2 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

Table 3 shows the results from the ESS Test, corrected to the normal process operating temperatures (i.e., 23 ºC for extraction and scrubbing and 33 ºC for stripping). See Appendix A for details. The overall changes in the D(Cs) compared to rev. 0 are a decline in extraction values for tests 3 and 4, and a large decline in all strip values for all tests.

Table 3. Cesium Distribution Values for the NGS ESS Tests

Test#	Material	Extraction	Scrub#1	Scrub#2	Strip#1	Strip#2	Strip#3
1	NGS	72.1	3.85	2.62	0.000735	0.000271	0.850
2	NGS-MCU (non-rad)	71.4	3.95	1.76	0.000806	0.000181	0.643
3	NGS-MCU (hot#1)	37.5	2.81	1.58	0.548	0.256	0.000589
4	NGS-MCU (hot#2)	47.2	2.53	1.53	0.000557	0.000139	0.00649

These first two tests – NGS and NGS-MCU (non-rad) gave virtually identical extraction and scrub and strip results, including anomalously high Strip#3 results (results in red text color). There was no reason to assume that Strip#3 was not viable, given the history of previous NGS ESS tests. Other than the strip#3 results, the results were within expectations. These two tests were run at the same time, while using different organic phases lead SRNL to believe that there was some sort of error introduced into the third strip step. While considering what errors were possible the researchers received the results for the third test (NGS-MCU (hot#1)). In this test, the Strip#1 and #2 results were anomalous compared to the first two tests (results in red text color).

In an attempt to confirm whether or not this behavior was endemic, a fourth ESS test was run. At the same time, a review of the pH measurements (using pH swipes) of each step in each test provided insight to the cause of the unusual results (Table 4).

Table 4. pH Values for the NGS ESS Test Strip Portions

Test #	Material	Strip#1	Strip#2	Strip#3
1	NGS	7	6	10
2	NGS-MCU (non-rad)	7	6	10
3	NGS-MCU (hot#1)	10	10	4
4	NGS-MCU (hot#2)	7	6	6
	Typical Range	7-9	7-6	5-6

The uncertainties on the pH measurements are typically 0.5 pH unit.

In past NGS ESS tests, the pH results for the Strip#1 samples are typically 7-9, and then drop to a pH of 5-6 by Strip#3 (the drop is due to the initial small amounts of high pH aqueous carryover). In the first two tests, the Strip#3 results showed both a high pH result (results in red text color), and a high distribution value, while the Strip#1 and #2 results showed normal behavior for both pH and distribution value. In the third test, the Strip#1 and #2 results showed high pH (results in red text color) and D values, while the Strip#3 result showed normal behavior for both. It appears that due to a human error, scrub solution (0.025 M NaOH) was used in place of strip acid (0.01 M boric acid) during those steps showing the unusual results.

The fourth ESS test was run with an extra level of oversight. In this test all the strip pH and D value results showed expected behavior. This data indicates that the wrong scrub and strip solutions were used during various parts of the testing.

This data demonstrates the ability of NGS and the NGS blend to successfully extract cesium from real SRS salt feed, and the non-radiologically contaminated prepared materials give virtually identical results. The decline in extraction values between the non-rad and hot blend solvents may be indicative of an interfering agent in the actual MCU solvent. Future SRNL work will examine the solvents for evidence of this, such as in degradation of the TiDG suppressor. Future work with Salt Batch 7 qualification will also examine multiple solvent configurations for evidence of poor behavior.

3.1 <u>ICPES results</u>

ICPES analyses of all 12 aqueous strip samples were performed (Table 5). In this table, shaded cells indicate steps that gave atypical results.

Table 5. ICPES Results from Strip Samples

Test	Solvent	Step	B (mg/L)	Na (mg/L)
1	NGS	strip#1	102	10.4
1	NGS	strip#2	108	6.03
1	NGS	strip#3	8.39	586
2	NGS-MCU (non-rad)	strip#1	95.7	11.7
2	NGS-MCU (non-rad)	strip#2	126	3.77
2	NGS-MCU (non-rad)	strip#3	9.31	591
3	NGS-MCU (hot#1)	strip#1	<0.199	599
3	NGS-MCU (hot#1)	strip#2	<0.199	605
3	NGS-MCU (hot#1)	strip#3	112	23.2
4	NGS-MCU (hot#2)	strip#1	102	33.6
4	NGS-MCU (hot#2)	strip#2	113	4.55
4	NGS-MCU (hot#2)	strip#3	119	41

The ICPES analytical uncertainty is 10%.

If during a test, scrub and strip solutions were accidently swapped, this becomes apparent in the ICPES results. The scrub solution is a 0.025 M NaOH solution (Na = 575 mg/L), while the strip solution is 0.01 M H_3BO_3 (B = 108 mg/L). The shaded cells all show precisely the pattern of results that would indicate scrub and strip solutions were accidently swapped – a high sodium (~575 mg/L) and low boron result (<10 mg/L).

The last test (NGS-MCU (hot#2)) has no such pattern, which corroborates the acceptable results in all strip tests.

4.0 Conclusions

- A demonstration of cesium extraction, scrubbing and stripping cesium mass transfer intended to partially mimic the MCU operations after addition of the NGS cocktail, yielded behavior within acceptable norms. The NGS-MCU solvent should behave similar to the NGS solvent. The values indicate the cesium removal should be superior to the current MCU solvent, and are comparable to previous tests using NGS.

- For the purposes of using modeling that only uses the cesium distribution values as inputs, SRNL proposes the following logic to distill the results of the four tests. For the extraction step, the results from all 4 tests will be averaged. For each scrub step, the results from all 4 tests will be averaged. For the strip #1, #2 steps, the averages of tests #1, 2, and 4 will be used, omitting the flier results in test#3. For the strip #3

step, the value from test#4 will be used, omitting the flier result in tests #1, 2 and omitting the result in test#3 (strip#3 step is really functioning as a strip#1 in that test). Given this logic, SRNL derives the following composite distribution values for systems using either pure NGS or NGS-MCU solvent.

- Extraction, 57.1
- Scrub 1, 3.28
- Scrub 2, 1.87
- Strip 1, 0.000699
- Strip 2, 0.000197
- Strip 3 0.00649

Appendix A Temperature Correction Factors

The actual MCU facility uses active temperature control to keep the extraction and scrub steps to 23 °C, and the strip steps to 33 °C. However, the ESS tests do not have active temperature control. During each step of an ESS test, the calculated distribution values must be corrected for temperature. The general formula for temperature correction is as follows:

$$\text{correction factor} = \text{EXP}((\mathbf{COEF}/0.0083144)*((1/\mathbf{TEMP})-(1/(\mathbf{STEP}))))$$

where "COEF" is the particular temperature coefficient for the step in question, the "TEMP" is the ambient temperature, in Kelvin, and "STEP" is 296.15 for extraction and scrub and 306.15 for strip steps.   There is one set of coefficients for the MCU solvent, and one set of coefficients for use in NGS type solvents with MaxCalix (NGS, cold blend, hot blend). In revision 0 of this report, a different set of NGS coefficients were used.

Table 6 lists the temperature coefficients for each step in an ESS test. The coefficients for the NGS solvent are derived from the van't Hoff formalism in equation 1 of the applicable reference.[9]

Table 6. Temperature Coefficients

Step	MCU [10]	NGS [9]
Extraction	-47.95	-90.12
Scrub#1	-86.82	-115.5
Scrub#2	-74.24	-91.40
Strip#1	-79.36	-80.18
Strip#2	-82.94	-143.4
Strip#3	-82.49	-65.63

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[2] T. B. Peters and S. D. Fink, "Task Technical and Quality Assurance Plan for Cesium Mass Transfer Test With Next Generation Solvent (NGS) and Miscellaneous White Papers", SRNL-RP-2012-00842, Rev. 0, December 2012.

[3] T. B. Peters, "Next Generation Solvent", SRNL-NB-2013-00032, May 14, 2013.

[4] T. B. Peters and S. D. Fink, "Sample Results from the Interim Salt Disposition Program Macrobatch 6 Tank 21H Qualification Samples," SRNL-STI-2012-00707, Rev. 0, December 2012

[5] E. T. Ketusky, "Recommended Quantities of Solvent Constituents for Next Generation Solvent (NGS)", SRR-SPT-2012-0039, November 7, 2012.

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