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Extraction, Scrub, and Strip Test Results for the Solvent Transfer to Salt Waste Processing Facility

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) prepared approximately 240 gallons of Caustic-Side Solvent Extraction (CSSX) solvent for use at the Salt Waste Processing Facility (SWPF).

An Extraction, Scrub, and Strip (ESS) test was performed on a sample of the prepared solvent using a salt solution prepared by Parsons to determine cesium distribution ratios ($D_{(Cs)}$), and cesium concentration in the strip effluent (SE) and decontaminated salt solution (DSS) streams. This data will be used by Parsons to help qualify the solvent for use at the SWPF.

The ESS test showed acceptable performance of the solvent for extraction, scrub, and strip operations. The extraction $D_{(Cs)}$ measured 15.5, exceeding the required value of 8. This value is consistent with results from previous ESS tests using similar solvent formulations. Similarly, scrub and strip cesium distribution ratios fell within acceptable ranges.

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LIST OF ABBREVIATIONS

CSSX	Caustic-Side Solvent Extraction
$D_{(Cs)}$	Distribution Ratio for Cesium
DF	Decontamination Factor
DSS	Decontaminated Salt Solution
EDL	Engineering Design Laboratory
ESS	Extraction, Scrub, and Strip
MCU	Modular Caustic Side Solvent Extraction Unit
SE	Strip Effluent
SRNL	Savannah River National Laboratory
SWPF	Salt Waste Processing Facility
TOA	Trioctylamine
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

This report provides information on the preparation of CSSX solvent at the SRNL Engineering Development Laboratory (EDL) for use in the Salt Waste Processing Facility.

Also provided are the distribution ratio for cesium ($D_{(Cs)}$) and the cesium concentration in the SE and DSS streams obtained from performance of an Extraction, Scrub, Strip (ESS) test using the prepared solvent and a salt simulant provided by Parsons. This work was specified in a Technical Task Request[i] and in a Task Technical and Quality Assurance Plan (TTQAP).[ii] Details of the work are contained in controlled laboratory notebooks.[iii]

2.0 Experimental Procedures

2.1 Solvent Preparation

From Modular Caustic Side Solvent Extraction Unit (MCU) operations over the years, the Savannah River National Laboratory (SRNL) accumulated stocks of components used to prepare CSSX solvent. SRNL used these leftover stocks of material to prepare a ~240 gallon batch of material for use at SWPF, using the established procedure.[iv] This material served as the source of the solvent and was used without further alterations or preparations.

2.2 ESS Testing

For the ESS test, Parsons provided the salt simulant and the as-weighed composition (LABCS-SSFS-002aRW09).[v] SRNL added a de minimus volume of ^{137}Cs source to make the parent solution ~1E+06 dpm/mL (a goal activity to provide enough activity for easy radiocounting, while providing minimal dose to personnel). See Table 1 for the composition of this material. This is the same procedure used as in the previous Parsons solvent ESS test.[vi]

Table 1. Composition of the Parsons Salt Simulant (LABCS-SSFS-002aRW09)

Analyte	Molarity (M)	Analyte	Molarity (M)
Na^+	6.37	AlO_2^-	0.251
K^+	0.0150	$C_2O_4^{2-}$	7.99E-03
Cs^+ (cold)	4.10E-04	PO_4^{3-}	5.18E-03
Zn^{2+}	1.24E-04	MoO_4^{2-}	7.86E-05
Sr^{2+}	1.05E-04	NO_3^-	2.21
Cu^{2+}	2.66E-05	NO_2^-	0.600
Sn^{2+}	2.10E-05	Cl^-	2.94E-02
Free OH	2.55	SO_4^{2-}	0.168
CO_3^{2-}	0.180	F^-	3.36E-02
Density	1.266 g/mL (21.1 °C)	^{137}Cs (nominal)	1E+06 dpm/mL

The analytical uncertainty for the cation and anions are 10%. The analytical uncertainty for the ^{137}Cs is 5%.

The test used the standard protocol for analyzing macrobatch salt waste as formalized in a SRNL manual.[vii] The test used a nominal starting volume of 90 mL of salt simulant feed and 30 mL (3:1 aqueous-to-organic volume ratio) of freshly prepared CSSX solvent.[a] This solvent was prepared at EDL for use at the SWPF. It is identified as "BOBCalix Solvent" and was used without further alteration or analysis. The density of this solvent was measured as 0.850 g/mL @ 21.1 °C which is close to the nominal value of 0.852 g/mL.[viii] The scrub and strip solutions were 0.05 M nitric acid and 0.001 M nitric acid, respectively, and used an organic to aqueous volume ratio of 5:1.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60.[ix] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[x]

3.0 Results and Discussion

Table 2 shows the results from the ESS test, corrected to the normal process operating temperatures (i.e., 23 ºC for extraction and scrub and 33 ºC for strip). For these tests, the temperature correction factors for the CSSX solvent were used (see Appendix). For comparison, the acceptable range of values are provided.[xii]

The temperature in the shaker oven during the ESS test ranged from 25.2 ºC to 25.5 ºC for the extraction and scrub steps and 31.9 ºC for the strip steps.

Table 2. Cesium Distribution Ratios ($D_{(Cs)}$) for the ESS Tests

Material	Extraction	Scrub#1	Scrub#2	Strip#1	Strip#2	Strip#3
Acceptable Range	>8	>0.6, <2	>0.6, <2	<0.2	<0.16	<0.16
This Test	15.5	1.24	1.30	0.0445	0.0263	0.0212

The current test shows the expected behaviors, with good overall performance. The measured strip distribution values are up to ~8X better than the maximum threshold values suggesting excellent stripping behavior.

SRNL has an extraction stage $D_{(Cs)}$ predictor model which allows SWPF to get an early indication of possible extraction problems. This model predicts an extraction $D_{(Cs)}$ value of 17.9

[a] The CSSX solvent has a composition as follows: 0.007 M BOBCalixC6 [calix[4]arene-bis(*tert*-octylbenzo-crown-6)], 0.75M Cs-7SB Modifier [1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol], 0.003 M trioctylamine (TOA), and the balance Isopar ™ L. This formulation should not be confused with other, more recent iterations used at MCU.

for the submitted salt solution.[xi] The model predicts a wide range of distribution values (i.e., shows a high variance) at the composition range covered by this salt solution and tends to provide a positive bias.[Δ] Hence, the larger predicted distribution value does not pose a concern about the current measured result.

3.1.1 Aqueous and Organic Phase Results

At the end of the ESS test, the gamma activities of each phase, and the pH of the aqueous phases were measured (Table 3).

Table 3. Aqueous and Organic Phase ^{137}Cs Results

Sample	AQ ^{137}Cs (dpm/mL)	ORG ^{137}Cs (dpm/mL)	AQ pH
Salt Simulant Feed	1.47E+06	0	14
Extraction	2.42E+05	3.26E+06	14
Scrub#1	3.02E+06	2.79E+06	5.0
Scrub#2	2.23E+06	2.30E+06	2.0
Strip#1	9.37E+06	4.66E+05	3.0
Strip#2	2.09E+06	6.18E+04	3.0
Strip#3	2.80E+06	6.68E+03	3.0

The 1-σ analytical uncertainty on the ^{137}Cs activity is 5%. The analytical uncertainty is ±1 pH unit for the pH measurement performed with colorimetric strips. The pH results from the test are similar to values from prior testing.

4.0 Conclusions

Results of the ESS test for this prepared solvent sample meet the performance expectations. There is no unexpected behavior and there are no anticipated issues for cesium removal.

[Δ] A range of salt solution compositions with similar sodium concentrations (6.25 to 6.5 M) were modeled. See Table B-1 in reference xi for the compositions. The predicted $D_{(Cs)}$ values for these solutions ranged from 1.72 to 21.4. This wide distribution is heavily dependant on the potassium concentrations input to the model.

Appendix. Temperature Correction Factors for the ESS Tests

The SWPF facility uses active temperature control to keep the extraction and scrub steps at 23 °C, and the strip steps at 33 °C. The temperature during the ESS tests varied slightly over the course of the experiment within the control bands of the system used. 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:

correction factor = EXP((**COEF**/0.0083144)*((1/**TEMP**)-(1/(**STEP**)))) (Eqn. 1)

where "COEF" is the particular temperature coefficient (i.e., apparent enthalpy change) 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.

Table 4 lists the temperature coefficients for each step in an ESS test, as well as the actual temperature measured during the test.

Table 4. Temperature Coefficients

Step	BOBCalixC6 [xii]	Temperature
Extraction	-47.95	25.5
Scrub#1	-86.82	25.2
Scrub#2	-74.24	25.5
Strip#1	-79.36	31.9
Strip#2	-82.94	31.9
Strip#3	-82.49	31.9

5.0 References

[i] C. Conner, "SWPF Solvent Preparation, Qualification, Packaging and Delivery Tasks A and B", X-TTR-J-00001, Rev. 0, May 30, 2017.

[ii] T. B. Peters, "Task Technical and Quality Assurance Plan for Salt Waste Processing (SWPF) Solvent Qualification", SRNL-RP-2017-00296, June 2017.

[iii] T. B. Peters, "Parsons Solvent Work", ELN, A4571-00084-33.

[iv] "Next Generation Solvent Preparation", Manual L29 Procedure ITS-0173, Rev. 3, January 20, 2016.

[v] PTC-LAB-036, *Simulant Preparation Log Book*

[vi] T. B. Peters, "Extraction, Scrub, and Strip Test Results for the Salt Waste Processing Facility Caustic Side Solvent Extraction Solvent Sample" SRNL-STI-2017-00431, Rev. 0, August 2017.

[vii] "Extraction, Scrub, and Strip Testing of Solvent Extraction Systems", Procedure L29 Procedure ITS-0205, Rev. 0, September 2013.

[viii] L. H. Delmau, J.F. Birdwell, P. V. Bonnesen, L. J. Foote, T. J. Haverlock, L. N. Klatt, D. D. Lee, R. A. Leonard, T. G. Levitslaia, M. P. Maskarinec, B. A. Moyer, F. V. Sloop Jr., B. A. Tomkins, "Caustic-Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent", ORNL/TM-2002/190, October 2002.

[ix] "Technical Reviews", Manual E7, 2.60, Rev. 17, August 25, 2016.

[x] "Technical Report Design Checklist", August 2004, WSRC-IM-2002-00011, Rev. 2.

[xi] K. Adu-Wusu, D. D. Walker, T. B. Edwards, "Waste and Solvent Composition Limits for Modular Caustic-Side Solvent Extraction Unit (MCU)", WSRC-TR-2005-00258, May 26, 2005.

[xii] L. H. Delmau, J. F. Birdwell Jr., P. V. Bonnesen, L. J. Foote, T. J. Haverlocke, L. N. Klatt, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, B. A. Moyer, F. V. Sloop Jr., B. A. Tomkins, "Caustic-Side Solvent Extraction: Chemical and Physical Properties of the Optimized Solvent", ORNL/TM-2002/190, October 2002.