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Extraction, Scrub, and Strip Test Results for the Salt Waste Processing Facility Sample Tank 202

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EXECUTIVE SUMMARY

An Extraction, Scrub, and Strip (ESS) test was performed on a sample from Tank-202. The purpose of testing this sample is to determine if the solvent is displaying the correct extraction and stripping behavior with cesium.

The ESS test showed acceptable performance of the solvent for extraction, scrub, and strip operations. The extraction $D_{(Cs)}$ measured 14.2, exceeding the required value of 8. This value is consistent with results from previous ESS tests using similar solvent formulations. Similarly, the 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
ESS	Extraction, Scrub, Strip
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

The Salt Waste Processing Facility (SWPF) has expressed some concern on the recent solvent performance, with reduced throughput and a slight reduction in perceived strip behavior. Parsons sent a sample from a solvent hold tank to the Savannah River National Laboratory (SRNL) in order to confirm that the solvent was demonstrating acceptable cesium removal behavior. The SWPF Tank-202 sample was delivered to SRNL on July 26 and used as-received. As-received the solution was pale yellow in color, but otherwise transparent, with no visible solids or second phases.

This report provides the distribution ratio for cesium ($D_{(Cs)}$) and the cesium concentration in the Strip Effluent (SE) and Decontaminated Salt Solution (DSS) streams obtained from performance of an Extraction, Scrub, Strip (ESS) test using Caustic Side Solvent Extraction (CSSX) solvent (sampled from Tank 202) and salt simulant provided by Parsons. This type of work was specified in a Technical Task Request[1] and in a Task Technical and Quality Assurance Plan (TTQAP).[2] Details of the work are contained in controlled laboratory notebooks.[3]

Figure 1. Sample Tank-202 As Received.

2.0 Experimental Procedure

For the Extraction, Scrub, and Strip (ESS) test, Parsons provided the salt simulant (LABCS-SSFS-002aRW09) which was prepared by Parsons.[4] SRNL added a de minimis volume of ^{137}Cs source to make the radioactivity in the parent solution ~1E+03 dpm/mL (a goal activity to provide enough activity for easy radio-counting, but to provide minimal dose to personnel). The simulant dose was lower than initially expected due to a dilution error in the spike, but adequate activity was still present. See Table 1 for the composition as provided by the customer, as prepared.

Table 1. Composition of the Parsons Salt Simulant (LABCS-SSFS-002a_LS_CR_C28_020) subsequently spiked with Cs-137 at SRNL.

Analyte	Molarity (M)	Analyte	Molarity (M)
Na^{+}	6.29	AlO_2^{-}	0.245
K^{+}	0.0150	$C_2O_4^{2-}$	7.97E-03
Cs^{+} (cold)	4.28E-04	PO_4^{3-}	7.03E-03
Zn^{2+}	1.18E-04	MoO_4^{2-}	8.37E-05
Sr^{2+}	9.95E-05	NO_3^{-}	2.21
Cu^{2+}	2.56E-05	NO_2^{-}	0.600
Sn^{2+}	1.95E-05	Cl^{-}	2.94E-02
Free OH	2.46	SO_4^{2-}	0.164
CO_3^{2-}	0.180	F^{-}	3.37E-02
Density	1.2734 g/mL	^{137}Cs	1.19E+03 dpm/mL

The simulant was prepared but not analyzed, with the exception of the ^{137}Cs. However, the typical analytical uncertainty for the cation and anions are 10%. The analytical uncertainty for the ^{137}Cs is 5%.

The test used SRNL's protocol for analyzing macrobatch salt waste as formalized in a SRNL manual.[5] 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 the Tank-202 sample.[i] This solvent was used without further alteration or analysis. The density of this solvent was measured as 0.8393 g/mL @ 21.6 ˚C which is close to the nominal value of 0.8225 g/mL.[6] 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. There was one extraction stage, two scrub stages, and three strip stages. Each phase in each stage was measured for ^{137}Cs activity. Aqueous phases were also measured for pH. Temperature control was provided by a shaker oven with active temperature control and measurement.

2.1 Quality Assurance

The customer requested QA classification for this work is Production Support. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60.[7] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[8] All work, analysis, and documentation were completed commensurate with the QA classification specified by the customer.

[i] The CSSX solvent has a nominal 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.

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,[vi] as well as results from the previous test.

The temperature in the shaker oven during the ESS test ranged from 23.4 ºC to 24.6 ºC for the extraction and scrub steps and 32.7 to 33.5 ºC for the strip steps. The temperature controller/probe combination had an uncertainty of ±1.7 ºC.

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	14.2	1.42	0.16	0.0469	0.0285	0.0085
Previous Test [9]	13.2	1.28	1.40	0.0585	0.0338	0.0289

The current test shows the solvent meets performance criteria for the system. The measured strip distribution values are ~4-19X better than the maximum threshold values suggesting good stripping behavior. The scrub#2 value is lower than typical, although this is not detrimental to the process. The low value may be due to the elevated pH in this step (see Table 3) which may be due to a small amount of carryover from the previous step. There was no evidence of solids, or poor phase separation 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 17.6 for the submitted salt solution.[10] 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.[ii] 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).

[ii] A range of salt solution compositions with similar sodium concentrations (6.25 to 6.5 M) were modeled. See Table B-1 in reference ix for the compositions. The predicted $D_{(Cs)}$ values for these solutions ranged from 1.72 to 21.4.

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

Sample	AQ ^{137}Cs (dpm/mL)	ORG ^{137}Cs (dpm/mL)	AQ pH
Feed Solutions	1.19E+03	1.41E+05	14
Extraction	8.59E+03	1.19E+05	14
Scrub#1	8.18E+04	9.58E+04	14
Scrub#2	2.95E+05	4.08E+04	5
Strip#1	1.64E+05	7.85E+03	3
Strip#2	2.32E+04	6.68E+02	3
Strip#3	4.75E+03	4.17E+01	3

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. The pH values for the salt simulant and extraction stages were not measured but known to be 14 due to the free hydroxide of > 1.0M.

The reader will note an increase in the cesium in the post-extraction aqueous sample. This is counter-intuitive given that the solvent should be removing the cesium from the aqueous phase. However, this is the expected result given that the solvent arrived from the plant with a much higher cesium loading than the aqueous phase.

4.0 Conclusions

Results of the ESS test for this qualification sample meets the performance expectations. There is no unexpected behavior and there are no anticipated issues for cesium removal. The solvent from SWPF seems to perform adequately against simulant. However, testing the solvent against a real waste sample (a salt batch sample is available at SRNL) could be useful is examining the step-wise strip behavior, and ensuring that the real waste sample would not perform differently than the simulant.

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 range measured during the test.

Table 4. Temperature Coefficients

Step	BOBCalixC6 [6]	Temperature Range
Extraction	-47.95	24.1-23.4
Scrub#1	-86.82	23.4-24.6
Scrub#2	-74.24	24.6-24.5
Strip#1	-79.36	33.5-32.8
Strip#2	-82.94	32.8-32.9
Strip#3	-82.49	32.9-32.7

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