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Results of the Extraction-Scrub-Strip (ESS) Tests With Solvent Using IBC BOBCalix

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EXECUTIVE SUMMARY

Two Extraction, Scrub, and Strip (ESS) tests were performed on two BOBCalix solvent samples prepared using BOBCalix from IBC Advanced Technologies ("IBC"). The purpose of testing this sample is to confirm if the newly sourced BOBCalix displays the correct extraction and stripping behavior with cesium.

The first batch of BOBCalix solvent was prepared using IBC lot#220310KC-1. The second batch was prepared using IBC lot#220615KC-3A.

The ESS tests showed acceptable performance of the solvent for extraction, scrub, and strip operations. The extraction $D_{(Cs)}$ values for the tests were 12.9 and 13.6. This value is consistent with results from previous ESS tests using similar solvent formulations. Similarly, the strip cesium distribution ratios (0.0588/0.0342/0.0258 and 0.0575/0.0335/0.0262) 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) relies on BOBCalix solvent to selectively remove Cs from the salt waste solutions. Historically, this solvent relies on two of four components that are single-sourced. In order to broaden the supply base for the solvent components, IBC Advanced Technologies (IBC) has been selected as a vendor for the BOBCalix, which is the compound used to extract cesium from alkaline salt waste.

A sample of IBC-produced BOBCalix (lot#220310KC-1) was delivered to SRNL on 3/29/22. A portion of this material was used to prepare solvent of the same formulation used at SWPF. [*] This solvent was used in an ESS test to confirm the suitability of this material.

A second sample of IBC-produced BOBCalix (lot#220615KC-3A) was delivered to SRNL on 6/16/22. This material was used in the same fashion as the first lot.

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 the ESS tests, as well as the analytical purity results. This type of 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 Procedure

From each lot, a portion of the material was used to prepare 100 mL of the BOBCalix solvent formulation. The preparation proceeded via the typical procedure, but the researchers noted that despite extensive agitation, there remained a small quantity of very fine solids that remained undissolved. SRNL did not attempt to remove the solids. This is most easily noted by shining a flashlight through the solution, causing the light to scatter from the suspended solids and cause the solution to appear to glow. See Figure 1. From the HPLC sample preparation it appeared that the solids were soluble in dichloromethane, but not isopropanol.

It was deemed unlikely that these solids would hinder the solvent performance for the ESS test so the decision was made to continue with the test, without filtration in an attempt to remove the solids.

For the Extraction, Scrub, and Strip (ESS) test, Savannah River Mission Completion provided the salt simulant (RL-0002668) which was prepared by SWPF.[iv] SRNL added a de minimis volume of ^{137}Cs source to make the radioactivity in the parent solution ~1E+06 dpm/mL (a goal activity

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[*] 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.

to provide enough activity for easy radiocounting, but to provide minimal dose to personnel). See Table 1 for the composition as provided by the customer, as prepared. Please note the ^{137}Cs value is calculated and was not directly measured.

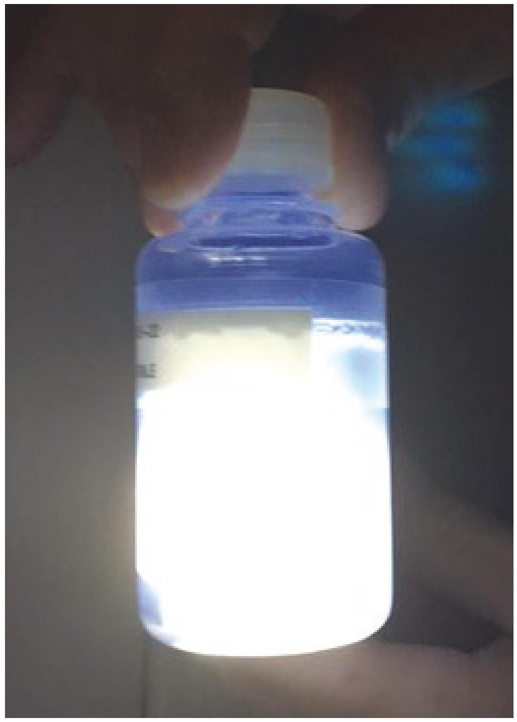

Figure 1. Fine Solids in the Prepared Solvent (with backlight)

The simulant was used as-prepared without analysis for confirmation, but it should be noted that SWPF personnel have measured previous batches of this simulant recipe. The values provided are from the preparation recipe. However, the typical analytical uncertainty for the cation and anions are 10%. The analytical uncertainty for the ^{137}Cs is 5%.

Table 1. Composition of the SWPF Salt Simulant (RL-0002668) subsequently spiked with ^{137}Cs at SRNL

Analyte	Molarity (M)	Analyte	Molarity (M)
Na^{+}	5.56	AlO_2^{-}	0.208
K^{+}	0.0155	$C_2O_4^{2-}$	8.35E-03
Cs^{+} (cold)	4.24E-04	PO_4^{3-}	7.11E-03
Zn^{2+}	1.19E-04	MoO_4^{2-}	8.25E-05
Sr^{2+}	1.07E-04	NO_3^{-}	1.83
Cu^{2+}	2.16E-05	NO_2^{-}	0.503
Sn^{2+}	2.04E-05	Cl^{-}	2.45E-02
Free OH	2.35	SO_4^{2-}	0.140
CO_3^{2-}	0.150	F^{-}	2.84E-02
Density	1.238 g/mL	^{137}Cs	1.25E+06 dpm/mL

The ESS test used SRNL's protocol for analyzing macrobatch salt waste as formalized in an SRNL manual.[v] 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 freshly prepared IBC/BOBCalix. This solvent was used without further alteration or analysis. The density of this solvent was measured as 0.845 g/mL (first batch, 20.1 ˚C), and 0.848 g/mL (second batch , 20.1 ˚C) which is close to the nominal value of 0.851 g/mL.[vi] 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 by gammascan. Aqueous phases were also measured for pH by pH paper. Temperature control (see Appendix A) 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. A Design Check, at minimum, was performed as a technical review of this report. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60.[vii] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[viii] All work, analysis, and documentation were completed commensurate with the QA classification specified by the customer and performed according to the TTQAP.

3.0 Results and Discussion

Table 2 shows the results from the ESS tests, 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 a previous non-IBC test.

The temperature in the shaker oven during the ESS test ranged from 22.8 ºC to 23.1 ºC for the extraction and scrub steps and 32.3 to 33.0 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
Test – lot#220310KC-1	12.9	1.17	0.414	0.0588	0.0342	0.0258
Test – Lot#220615KC-3A	13.6	1.07	0.38	0.0575	0.0335	0.0262
Previous Test [ix]	13.2	1.28	1.40	0.0585	0.0338	0.0289

The test results show that the solvent meets performance criteria for the system. The measured strip distribution values are ~4-6× better than the maximum threshold values suggesting good stripping behavior. The scrub#2 D-values are slightly lower than typical, although this is not detrimental to the process. There was no evidence of increased or newly generated solids (not counting the previously noted very slight amount of fines from the solvent preparation), 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 17.0 for the submitted salt solution. [x] 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.[†] 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 (Tables 3 and 4).

[†] A range of salt solution compositions with similar sodium concentrations (6.25 to 6.5 M) were modeled. See Table B-1 in reference x 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 from Test Lot#220310KC-1

Sample	AQ ^{137}Cs (dpm/mL)	ORG ^{137}Cs (dpm/mL)	AQ pH
Feed Solutions	1.25E+06	0	14
Extraction	2.31E+05	2.97E+06	14
Scrub#1	2.21E+06	2.57E+06	12
Scrub#2	4.23E+06	1.73E+06	2.5
Strip#1	6.83E+06	4.01E+05	3.0
Strip#2	1.70E+06	5.81E+04	3.5
Strip#3	2.69E+05	6.93E+03	3.5

Table 4. Aqueous and Organic Phase ^{137}Cs Results from Test Lot#220615KC-3A

Sample	AQ ^{137}Cs (dpm/mL)	ORG ^{137}Cs (dpm/mL)	AQ pH
Feed Solutions	1.11E+06	0	14
Extraction	1.95E+05	2.64E+06	14
Scrub#1	2.07E+06	2.25E+06	12
Scrub#2	4.08E+06	1.54E+06	2.5
Strip#1	5.96E+06	3.57E+05	4.0
Strip#2	1.44E+06	5.20E+04	3.0
Strip#3	2.36E+05	6.46E+03	3.0

The feed solution ^{137}Cs is a calculated value. 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.

4.0 Conclusions

Results of the ESS tests for these qualification samples meet the performance expectations. There is no unexpected behavior and there are no anticipated issues for cesium removal. The solvents using IBC BOBCalix perform adequately against simulant. However, testing the solvent against a real waste sample (a salt batch sample is available at SRNL) could be useful in examining the step-wise strip behavior, and ensuring that the real waste sample would not perform differently than the simulant.

The small amount of fine solids present is something new and the ramifications for SWPF are unknown at this time. SRNL recommends examining methods to remove the solids from solution and to collect enough solids for analysis to identify them precisely.

Appendix A. 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	BOBCalix	Temperature Range
Extraction	-47.95	22.8 – 23.1
Scrub#1	-86.82	22.9 – 23.1
Scrub#2	-74.24	23.0 – 23.1
Strip#1	-79.36	32.3 – 33.0
Strip#2	-82.94	32.3 – 33.0
Strip#3	-82.49	32.6 - 33.0

5.0 References

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