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Results of Cesium Mass Transfer Testing for Next Generation Solvent with Hanford Waste Simulant AP-101

T. B. Peters
A. L. Washington, II
S. D. Fink

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Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

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REVIEWS AND APPROVALS

AUTHORS:

T. B. Peters, Author, SRNL/SASP Date

A. L. Washington, II, Co-author, SRNL/SASP Date

TECHNICAL REVIEW:

C. A. Nash, Technical Reviewer, SRNL/ACP Date

APPROVAL:

S. D. Fink, SRNL/SASP, Manager Date

S. L. Marra, SRNL/E&CPT Research Programs, Manager Date

EXECUTIVE SUMMARY

SRNL has performed an Extraction, Scrub, Strip (ESS) test using the next generation solvent and AP-101 Hanford Waste simulant. The results indicate that the next generation solvent (MG solvent) has adequate extraction behavior even in the face of a massive excess of potassium. The stripping results indicate poorer behavior, but this may be due to inadequate method detection limits. SRNL recommends further testing using hot tank waste or spiked simulant to provide for better detection limits. Furthermore, strong consideration should be given to performing an actual waste, or spiked waste demonstration using the 2cm contactor bank.

LIST OF ABBREVIATIONS

ANL – Argonne National Laboratory
DSS – Decontaminated Salt Solution
DSSHT – Decontaminated Salt Solution Hold Tank
ESS – Extraction, Scrub, Strip
IC – Ion Chromatography
ICPES – Inductively Coupled Plasma Emission Spectroscopy
ICPMS – Inductively Coupled Plasma Mass Spectroscopy
MCU - Modular Caustic-Side Solvent Extraction Unit
NGS – Next Generation Solvent
ORNL – Oak Ridge National Laboratory
SE – Strip Effluent
SEHT – Strip Effluent Hold Tank
SRNL - Savannah River National Laboratory

1.0 Introduction

The Savannah River Site currently utilizes a solvent extraction technology to selectively remove cesium from tank waste at the Multi-Component Solvent Extraction unit (MCU). This solvent consists of four components: the extractant – BoBCalixC6,[a] a modifier – Cs-7B,[b] a suppressor – trioctylamine, and a diluent, Isopar L ™. This solvent has been used to successfully decontaminate over 2 million gallons of tank waste. However, recent work at Oak Ridge National Laboratory (ORNL), Argonne National Laboratory (ANL), and Savannah River National Laboratory (SRNL) has provided a basis to implement an improved solvent blend. This new solvent blend – referred to as Next Generation Solvent (NGS) – is similar to the current solvent, and also contains four components: the extractant – MAXCalix,[c] a modifier – Cs-7B,[d] a suppressor – LIX-79 ™ guanidine, and a diluent, Isopar L ™. Testing to date has shown that this "Next Generation" solvent promises to provide far superior cesium removal efficiencies, and furthermore, is theorized to perform adequately even in waste with high potassium[e] concentrations such that it could be used for processing Hanford wastes. SRNL has performed a cesium mass transfer test in to confirm this behavior, using a simulant designed to simulate Hanford AP-101 waste.

2.0 Experimental Procedure

A previously prepared batch of Hanford AP-101 waste was obtained and analyzed to confirm that the composition had not changed from its original values.[1] SRNL analyzed the waste using Inductively Coupled Plasma Emission Spectroscopy (ICPES), Ion Chromatography (IC) and Inductively Coupled Plasma Mass Spectroscopy (ICPMS). Table 1 provides the important analyte concentrations.

Table 1. Important Analytes for the AP-101 Simulant

Analyte	Concentration (mg/L)	Analyte	Concentration (mg/L)
Al	6,500	PO_4^{3-}	309
K	26,300	SO_4^{2-}	1180
Na	114,000	Rb	3.00
NO_2^-	32,000	Cs	5.66
NO_3^-	99,100		

The analytical uncertainty for each analyte is 10%, except for Cs and Rb, which is 20%.

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[a] BoBCalixC6 is short for Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
[b] Cs-7b is short for (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, CAS # 308362-88-1
[c] MAXCalix is short for 1,3-*alt*-25,27-Bis(3,7-dimethyloctyl-1-oxy) calix[4]arene-benzocrown-6
[d] LIX-79 ™ guanidine is short for N, N'-cyclohexyl, N''-isotridecyl
[e] Potassium interferes with the cesium removal and is strictly limited in the feed material to MCU.

While typical waste processed at MCU has a potassium concentration of <500 mg/L, and is restricted to have less than 0.05 M (1950 mg/L), the Hanford simulant contains over 26,000 mg/L. Furthermore, there are also detectable levels of rubidium present. While the effects of rubidium have not been extensively studied, it is known that Rb can interfere with Cs uptake.

Once the basic composition was confirmed, the researchers used this material without further alteration.

The extraction, scrub, strip (ESS) – or cesium mass transfer – test used the same general protocol as in the Macrobatch 4 qualification.[2] The only changes from this protocol were in the aqueous:organic volume ratios (Table 2).

Table 2. Aqueous:Organic Volume Ratios is Previous and Current ESS Tests

Previous ESS Test		Current ESS Test	
Step	Volume Ratio	Step	Volume Ratio
Extraction	3:1	Extraction	4:1
Srub	1:5	Scrub	1:3.75
Strip	1:5	Strip	1:3.75

3.0 Results

For the ESS test, the researchers used 120 mL of the AP-101 simulant, and 30 mL of freshly prepared NGS.

Table 3 shows the results from the ESS Test, corrected to the normal process operating temperatures (i.e., 23 ºC for extraction and 33 ºC for scrubbing and stripping).[3] As a comparison, the results from a previous ESS test that used a freshly prepared batch of NG solvent, 120 mL of actual Tank 49H material, and the same aqueous:organic volume ratios is also reported.

Table 3. Cesium Distribution Values for the ESS Test

Material	Extraction	Scrub #1	Scrub #2	Strip #1	Strip #2	Strip #3
Acceptable Range, current solvent	>8	>0.6, <2	>0.6, <2	<0.2	<0.16	<0.16
NGS vs. Tank 49H waste	88.1	5.01	3.00	0.00421	0.00469	0.00837
NGS vs. AP-101 simulant	8.67	6.56	2.74	0.00493	0.308	20.8

The ESS test using the tank waste utilized ^{137}Cs analysis with a 5.00% analytical uncertainty. The ESS test using the simulant used digestion and ICPMS, which has a nominal 20% analytical uncertainty. The ICPMS analytical uncertainty does not include the uncertainty added due to the digestion step, but the uncertainty from the digestion has not been quantified at this time. Thus, while comparing the results between the two ESS tests is appropriate, the uncertainty associated with the simulant test is at least four times as large as the hot test.

The distribution value for extraction is in line with pretest expectations from prior studies at ORNL on the impact of K and Cs concentrations on extraction efficiency. Scrub values are of the same magnitude as the Tank 49H test, but the stripping values for stages #2 and #3 are decidedly higher. We also measured the pH of each aqueous phase to check for excess phase carryover. We measured the pH values to be 14, 12.5, 8.0, 5.5, and 5.5 for scrub#1, #2, strip#1, #2, and #3, respectively. This indicates that there is enough aqueous carryover of high caustic to bias the scrub and first strip pH values high, even though the technicians are careful to avoid phase carryover. As the strip#1 values are very good, excess carryover of caustic or scrub solution is most likely not a factor. After analysis of the raw data, we consider it possible that the low initial amount of cesium (5.66 mg/L), combined with the better than expected Cs-removal performance is driving the Cs concentration low enough in the Strip #2 and #3 samples to be problematic. SRNL is considering using radio-spiked simulants in the future in order to avoid the detection limit issues.

Given the encouraging initial results with the ESS test, we propose that Argonne National Laboratory (ANL) and ORNL use this data to establish a set of operating parameters in order to perform a test using the 2cm contactor bank and a large volume of Hanford type simulant.

4.0 Conclusions

SRNL completed cesium mass transfer tests using the Next Generation Solvent and a simulated Hanford waste matching the composition of Tank AP-101. The measured extraction distribution value is 8.67 for the first extraction step. The results are encouraging enough such that SRNL recommends using ANL and ORNL to determine operating conditions to perform a test with the 2cm contactors in a hot test.

5.0 References

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