Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

We put science to work.™

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Extraction,-Scrub, -Strip Test Results from the Interim Salt Disposition Program Macrobatch 10 Tank 21H Qualification Samples

T. B. Peters

June 2017

SRNL-STI-2017-00373, Revision 0

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2017-00373
Revision 0

Keywords: *MCU, NGS, ESS*

Retention: *Permanent*

Extraction, -Scrub, -Strip Test Results from the Interim Salt Disposition Program Macrobatch 10 Tank 21H Qualification Samples

T. B. Peters

June 2017

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

____

T. B. Peters, Advanced Characterization and Processing Date

TECHNICAL REVIEW:

____

C. A. Nash, Advanced Characterization and Processing, Reviewed per E7 2.60 Date

APPROVAL:

____

B. J. Wiedenman, Manager Date
Advanced Characterization and Processing

____

D. E. Dooley, Director Date
Chemical Processing Technologies

____

E. A. Brass, Manager Date
MCU & Salt/Sludge

EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) analyzed samples from Tank 21H in support of qualification of Macrobatch (Salt Batch) 10 for the Interim Salt Disposition Program (ISDP). The Salt Batch 10 characterization results were previously reported.[ii,iii]

An Extraction, -Scrub, -Strip (ESS) test was performed 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 Tank Farm Engineering to project a cesium decontamination factor (DF). This test used actual Tank 21H material, and a sample of the NGS Blend solvent currently being used at the Modular Caustic-Side Solvent Extraction Unit (MCU).

The ESS test showed acceptable performance with an extraction $D_{(Cs)}$ value of 110. This value is consistent with results from previous salt batch ESS tests using similar solvent formulations. This is better than the predicted value of 39.8 from a recently created $D_{(Cs)}$ model.[i]

TABLE OF CONTENTS

LIST OF TABLES vii
LIST OF ABBREVIATIONS viii
1.0 Introduction 1
2.0 Experimental Procedure 1
2.1 Quality Assurance 1
3.0 Results and Discussion 1
3.1.1 Strip Effluent and DSS Results 2
4.0 Conclusions 3
5.0 References 5

LIST OF TABLES

Table 1. Cesium Distribution Ratios ($D_{(Cs)}$) for the ESS Tests 2

Table 2. Strip Effluent and DSS ^{137}Cs Results 2

Table 3. Temperature Coefficients 4

LIST OF ABBREVIATIONS

$D_{(Cs)}$	Distribution Ratio for Cesium
DF	Decontamination Factor
DSS	Decontaminated Salt Solution
ESS	Extraction, Scrub, Strip
ISDP	Interim Salt Disposition Program
MCU	Modular Caustic Side Solvent Extraction Unit
NGS	Next Generation Solvent
SE	Strip Effluent
SRNL	Savannah River National Laboratory
TOA	Trioctylamine
TTQAP	Task Technical and Quality Assurance Plan

1.0 Introduction

This report provides distribution ratio for cesium ($D_{(Cs)}$) and cesium concentration in the SE and decontaminated salt solution (DSS) streams obtained from performance of an Extraction, Scrub, Strip (ESS) test using the Tank 21H qualification sample; this data will be used by Tank Farm Engineering to project a cesium decontamination factor (DF) for Interim Salt Disposition Program (ISDP) Macrobatch (Salt Batch) 10. Previous documents reported the chemical and radiological characterization required for qualification of the salt batch.[ii,iii] This work was specified in a Technical Task Request[iv] as Task 5 and in a Task Technical and Quality Assurance Plan (TTQAP).[v] This task is not required for salt batch qualification unless use of a different solvent is implemented at MCU; data/observations from this demonstration will be used for process knowledge. Details of the work are contained in controlled laboratory notebooks.[vi]

2.0 Experimental Procedure

For the ESS test, material from the Tank 21H composite (samples HTF-21-16-104, -105, and -106) was used. The test used the same general protocol as used in previous macrobatch salt waste testing and is formalized in a Savannah River National Laboratory (SRNL) manual.[vii] The test used a nominal starting volume of 80 mL of aqueous salt solution feed and 20 mL (4:1 aqueous:organic volume ratio) of freshly sampled (from Modular Caustic Side Solvent Extraction Unit (MCU)) Next Generation Solvent (NGS) blend. ♥ The scrub and strip solutions were 0.025 M NaOH and 0.01 M boric acid, respectively, and used an organic:aqueous volume ratio of 3.75:1.

2.1 Quality Assurance

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

3.0 Results and Discussion

Table 1 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 NGS solvent were used (see Appendix).

The temperature in the Shielded Cells during the ESS test ranged from 25 ºC to 27 ºC with an average temperature of 26.3 ºC. As a comparison, the results from the previous macrobatch qualification ESS test (using the NGS Blend) are displayed.[x]

♥ The NGS-MCU blend was initially a 50/50 volume % blend of MCU solvent and a prepared mixture of compounds, that once mixed, gives a nominal composition as follows: 0.0035 M BOBCalixC6, 0.5M Cs-7SB Modifier, 0.0015 M trioctylamine (TOA), 0.003 M TiDG, 0.0465 M MaxCalix, and the balance Isopar ™ L. Since the material was created in 2013, the TOA and BOBCalixC6 have been depleting with no further trims of these two materials.

Table 1. Cesium Distribution Ratios ($D_{(Cs)}$) for the ESS Tests

Material	Extraction	Scrub#1	Scrub#2	Strip#1	Strip#2	Strip#3
SB 10 NGS Blend	110	12.1	13.1	0.00760	0.00263	0.00810
SB 9 NGS Blend	52.4	2.78	0.781	0.000266	0.000396	<0.0019

The current test shows the expected behaviors, with good overall performance. The extraction step $D_{(Cs)}$ is better than that for Salt Batch 9, and the strip steps $D_{(Cs)}$ are slightly poorer than the previous SB9 ESS test, although all the results are not atypical. The scrub results are higher than seen before but indicate retention of ^{137}Cs in the organic phase during scrubbing which is a desired effect [⊗] and is likely correlated with the high pH values in the used scrub solution (see Table 2). The high pH values in the scrub may be due to aqueous carryover from the exteraction step.

In past years when MCU was using an older solvent formulation, SRNL had an extraction stage $D_{(Cs)}$ predictor model which allowed SRNL to get an early indication of possible extraction problems. With the new solvent formulation this prediction was lacking. A new extraction stage $D_{(Cs)}$ predictor model has been created by SRNL,[i] and this model predicts an extraction $D_{(Cs)}$ value of 39.8.

3.1.1 Scrub Effluent, Strip Effluent and DSS Results

During, and at the end of the ESS test, the gamma activities and pH in the scrub effluent, SE and the DSS for a single extraction were measured (Table 2).

Table 2. Scrub Effluent, Strip Effluent and DSS ^{137}Cs Results

Sample	^{137}Cs (dpm/mL)	pH
Salt Batch 10 Feed	2.84E+08	14
DSS	1.18E+07	14
Scrub Effluent #1	1.40E+08	14
Scrub Effluent #2	1.09E+08	13
Strip Effluent #1	3.84E+09	8
Strip Effluent #2	2.35E+08	7
Strip Effluent #3	6.59E+06	7

[⊗] Any cesium that gets scrubbed out in the scrub stages proceeds forward into the extraction contactors where it will be extracted.

The 1-σ analytical uncertainty on the ^{137}Cs activity is 5%. The ^{137}Cs results are typical, given the high ^{137}Cs activity in the feed. The analytical uncertainty is ±1 pH unit for the pH measurement performed with colorimetric strips. The pH results from the test are typical.

4.0 Conclusions

Results of the ESS test are typical of the salt batch feeds and the solvent in use. There is no unexpected behavior and there are no anticipated issues for cesium removal.

Appendix. Temperature Correction Factors for the ESS Tests

The actual MCU facility uses active temperature control to keep the extraction and scrub steps at 23 °C, and the strip steps at 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:

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

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 BOBCalix-based solvent, and one set of coefficients for use in NGS type solvents with MaxCalix (NGS, cold blend, hot blend).

Table 3 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 Eqn. 1 of the applicable reference in Table 3.

Table 3. Temperature Coefficients

Step	MCU(BOBCalix) [xi]	NGS [xii]
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

5.0 References

[i] T. Hang, E. P. Shine, "Decontamination Factor Prediction for Cesium Extraction Tests", SRNL-L3200-2015-00084, August 26, 2015.

[ii] T. B. Peters, "Results of Initial Analyses of the Salt (Macro) Batch 10 Tank 21H Qualification Samples", SRNL-STI-2017-00013, Rev. 0, January 2017.

[iii] T. B. Peters, C. J. Bannochie "Results from the Interim Salt Disposition Program Macrobatch 10 Tank 21H Qualification Samples", SRNL-STI-2017-00055, Rev. 0, February 2017.

[iv] A. Samadi-Dezfouli, "Salt Batch Qualification for Feed to the Interim Salt Disposition Project (ISDP)", X-TTR-H-00068, Rev. 0, October 2016.

[v] T. B. Peters, D. H. Jones, "Task Technical and Quality Assurance Plan for Qualification of Salt Batches for Feed to ISDP", SRNL-RP-2015-00704, Rev. 1, November 2016.

[vi] T. B. Peters, "Salt Batch 10 Qualification", ELN, A4571-00084-27.

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

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

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

[x] T. B. Peters, "Extraction-Scrub-Strip Test Results from the Interim Salt Disposition Program Macrobatch 9 Tank 21H Qualification Samples", SRNL-STI-2016-00078, Rev. 0, February 2016.

[xi] 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.

[xii] N. J. Williams, B. A. Moyer, "Temperature Dependence of the Next Generation Caustic Side Solvent Extraction (NG-CSSX) Process Solvent", ORNL-LTR-NGCSSX-012, August, 2011.

Distribution:

timothy.brown@srnl.doe.gov
michael.cercy@srnl.doe.gov
alex.cozzi@srnl.doe.gov
david.crowley@srnl.doe.gov
David.Dooley@srnl.doe.gov
a.fellinger@srnl.doe.gov
samuel.fink@srnl.doe.gov
erich.hansen@srnl.doe.gov
connie.herman@srnl.doe.gov
david.herman@srnl.doe.gov
Elizabeth.Hoffman@srnl.doe.gov
Kevin.Kostelnik@srs.gov
Kevin.Fox@srnl.doe.gov
john.mayer@srnl.doe.gov
daniel.mccabe@srnl.doe.gov
thelesia.oliver@srnl.doe.gov
frank.pennebaker@srnl.doe.gov
William.Ramsey@SRNL.DOE.gov
luke.reid@srnl.doe.gov
geoffrey.smoland@srnl.doe.gov
michael.stone@srnl.doe.gov
Boyd.Wiedenman@srnl.doe.gov
bill.wilmarth@srnl.doe.gov
earl.brass@srs.gov
Kevin.Brotherton@srs.gov
Richard.Edwards@srs.gov
Phoebe.Fogelman@srs.gov
Annah.Garrison@srs.gov
brent.gifford@srs.gov
Thomas.Huff@srs.gov
Vijay.Jain@srs.gov
Jeremiah.Ledbetter@srs.gov
Kristen.Marra@srs.gov
ryan.mcnew@srs.gov
Christina.Santos@srs.gov
john.schwenker@srs.gov
Amanda.Shafer@srs.gov
hasmukh.shah@srs.gov
jeffrey.crenshaw@srs.gov
james.folk@srs.gov
roberto.gonzalez@srs.gov
patrick.jackson@srs.gov
tony.polk@srs.gov
jean.ridley@srs.gov
patricia.suggs@srs.gov
timothy.baughman@srs.gov
earl.brass@srs.gov
Richard.Edwards@srs.gov
Thomas.Huff@srs.gov
ryan.mcnew@srs.gov
n-rao.pasala@srs.gov
john.schwenker@srs.gov
Christie.sudduth@srs.gov
arthur.wiggins@srs.gov
Records Administration (EDWS)