Performance Testing of the Next-Generation CSSX Solvent with Actual SRS Tank Waste

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Abstract: Efforts are underway to qualify the Next-Generation Solvent for the Caustic Side Solvent Extraction (CSSX) process. Researchers at multiple national laboratories have been involved in this effort. As part of the effort to qualify the solvent extraction system at the Savannah River Site (SRS), SRNL performed a number of tests at various scales. First, SRNL completed a series of batch equilibrium, or Extraction-Scrub-Strip (ESS), tests. These test used ~30 mL of Next-Generation Solvent and either actual SRS tank waste, or waste simulant solutions. The results from these cesium mass transfer tests were used to predict solvent behavior under a number of conditions.

At a larger scale, SRNL assembled 12 stages of 2-cm (diameter) centrifugal contactors. This rack of contactors is structurally similar to one tested in 2001 during the demonstration of the baseline CSSX process. Assembly and mechanical testing found no issues. SRNL performed a non-radiological test using 35 L of cesium-spiked caustic waste simulant and 39 L of actual tank waste. Test results are discussed; particularly those related the effectiveness of extraction.

Keywords: cesium, solvent extraction, high level waste, centrifugal contactor

INTRODUCTION

A solvent extraction system for removal of cesium from alkaline solutions was developed utilizing a novel solvent invented at the Oak Ridge National Laboratory (ORNL).[1] This solvent consists of a calix[4]arene-crown-6 extractant dissolved in an inert hydrocarbon matrix. A Modifier is added to the solvent to enhance the extraction power of the calixarene and to prevent the formation of a third phase. An additional additive is used to improve stripping performance and to mitigate the effects of any surfactants present in the feed stream.[2] The process that deploys this solvent system is known as Caustic Side Solvent Extraction (CSSX). The solvent system has been deployed at the Savannah River Site (SRS) in the Modular CSSX Unit (MCU) since 2008.

The MCU uses centrifugal contactors (with 10-in diameter rotors for extraction stages and with 5-in diameter rotors for scrub and strip stages) to provide mechanical mixing and phase separation between the solvent and alkaline waste solutions by way of two separations. The first separation extracts cesium from the waste solutions into the solvent system; the second separation strips the cesium from the solvent system while providing a nominal cesium concentration volumetric factor of 15. The decontaminated salt solution is sent to the SRS Saltstone Facility and the concentrated cesium stream is transferred to DWPF. From its radioactive start-up in April 2008 until the end of August 2011, MCU processed more than 2 million gallons of HLW solution for disposition.

Subsequent development efforts by ORNL have identified an improved solvent system that can raise the expected decontamination factor (DF) in MCU from ~200 to more than 40,000.[3] The improved DF is attributed to an increased distribution ratio for cesium (DCs) in extraction from ~15 to ~60 from an increased solubility of the calixarene in the solvent from 0.007 M to >0.050 M, and use of boric acid (H_3BO_3) stripping that yields D(Cs) values less than 0.01. The improved solvent system contains four components: 1) 0.050 M 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy) calix[4]arene-benzocrown-6, also known as MaxCalix, is the extractant; 2) 0.50 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, or Cs-7SB, is the Modifier; 3) 0.003 M *N,N'*-dicyclohexyl-N"-isotridecylguanidine, or DCiTDG, is the suppressor; and 4) C_{12}-isoparaffinic hydrocarbon, or Isopar® L, is the diluent. The modified solvent system is referred to as the Next Generation CSSX Solvent (NGCS).

EXPERIMENTAL

Solution Compositions and Analyses

Solvent Composition: A single 1-liter batch of solvent was prepared for the 2-cm contactor tests. The completed solvent contains 616.80 g of Isopar® L, 47.84 g of MaxCalix extractant, 169.18 g of Cs-7B Modifier, and 1.22 g of DCiTDG (guanidine). Each 2-cm contactor test used a fresh aliquot of solvent from this batch of solvent. ESS tests used solvent from different source batches but of the same nominal composition.

Non-Radioactive Simulant Composition: One batch of non-radioactive waste simulant was prepared for use during testing. The simulant chemically approximated the waste from Tank 49H (i.e., the current waste being processed in MCU) with the exception of minor metal and organic compounds. The purpose of the simulant was to provide non-radioactive feed for verifying proper hydraulic operation of the contactor test apparatus and for "spiking" known amounts of ^{137}Cs to verify decontamination and concentration factors. A 45-L batch of the simulant was prepared as a cesium-free solution. Once prepared and filtered, four liters of the simulant batch was separated and maintained cesium free. Cesium chloride was added to the remaining 41 liters of simulant solution and the resulting solution filtered. The final Cs concentration was ~83 mg/L, which is high enough to measure a DF in excess of 6500. Calculated concentrations of the primary components are listed in Table 1.

Table 1. Composition of Tank 49H Simulated Waste Solutions

Component	Concentration (M)		Component	Concentration (M)
Na^+	6.5		CO_3^{2-}	0.25
K^+	0.013		SO_4^{2-}	0.057
Cs^+	0.00085*		Cl^-	0.00085*
OH^-	2.65		PO_4^{3-}	0.0047
NO_3^-	2.29		$C_2O_4^{2-}$	0.0013
NO_2^-	0.65		SiO_3^{2-}	0.0046
AlO_2^-	0.19		$COOH^-$	0.021
* Omitted from 4 L of Cs-free simulant solution				

High Level Waste Composition: SRS tank farm personnel provided a 39-L sample of liquid radioactive waste from Tank 49H. The waste is from the period of MCU operation referred to as Macrobatch 3 (i.e., the third major operating campaign) and contains a mixture of material from several other waste tanks. The solution density was measured using a 2 mL volumetric density tube weighed on a balance sensitive to ±0.001 g. Samples of the Tank 49H composite were analyzed without any filtering or other alterations. These analyses (Table 2) confirm the general nature of the material.

Table 2. Composition of the Tank 49H Sample

Analyte	**Concentration**	**% Unc.**	**Analyte**	**Concentration**	**% Unc.**
Na^+	150,000 mg/L	10	Free OH	2.65 M	10
K^+	505 mg/L	10	NO_3^-	188,000 mg/L	10
Rb^+	0.476 mg/L	20	NO_2^-	4160 mg/L	10
Cs^+	2.09 mg/L	20	SO_4^{2-}	6490 mg/L	10
Al^{3+}	5110 mg/L	10	PO_4^{3-}	874 mg/L	10
Mass-235	0.183 μg/L	20	CO_3^{2-}	0.239 M	10
Mass-238	26.1 μg/L	20	F^-	<100 mg/L	10
^{137}Cs	1.44E+08 dpm/mL	5.00	Cl^-	373 mg/L	10
			oxalate	175 mg/L	10
^{90}Sr	3.57E+05 dpm/mL	9.41	formate	919 mg/L	10
			density	1.269 g/mL	10
^{238}Pu	6.76E+04 dpm/mL	5.64			
$^{239/40}Pu$	1.27E+04 dpm/mL	5.67			

Centrifugal Contactor Apparatus

The process flowsheet is shown in Figure 1. The process equipment used for these tests centered on 12 stages of 316 stainless-steel, 2-cm annular centrifugal contactors designed and fabricated by Argonne National Laboratory (ANL). The contactors were grouped into five extraction stages, two scrub stages, and five strip stages in a single-tiered configuration (Figure 2). Each rotor was fabricated to support total flow rates of approximately 60 mL/min.[4] Inter-stage lines were stainless steel to promote improved wetting and flow characteristics. The tubing for feed lines were made of polypropylene (for aqueous streams) or Teflon^{TM} (for solvent streams).

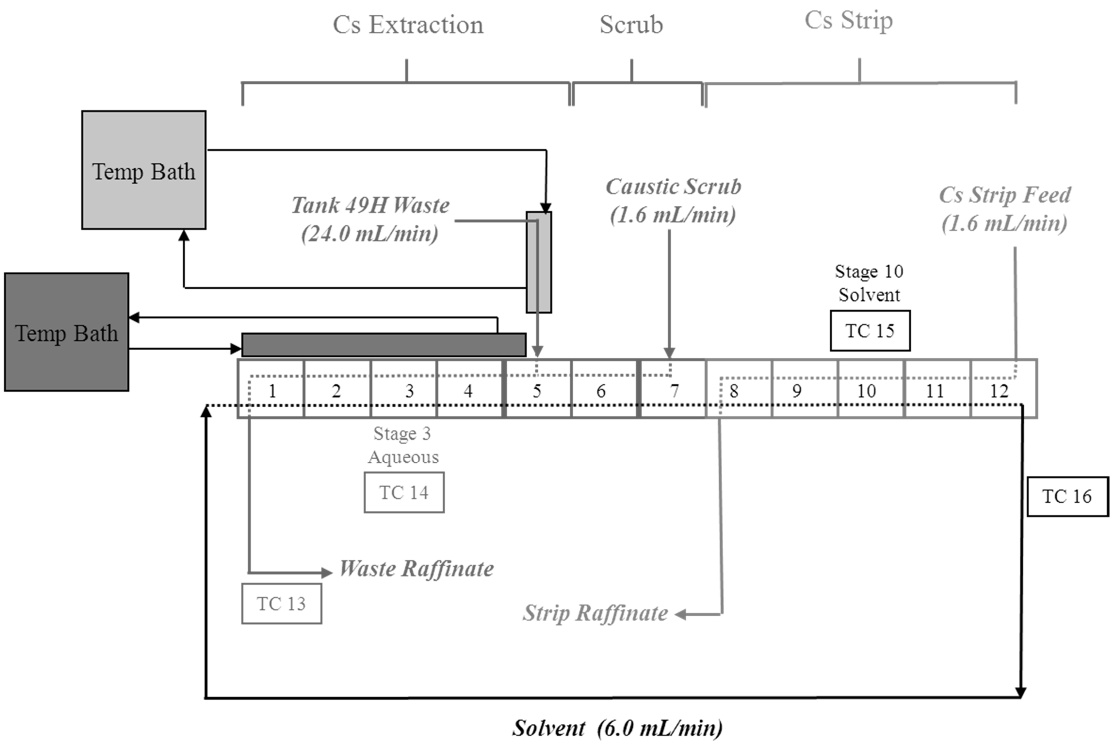

Figure 1. Process Flow Diagram

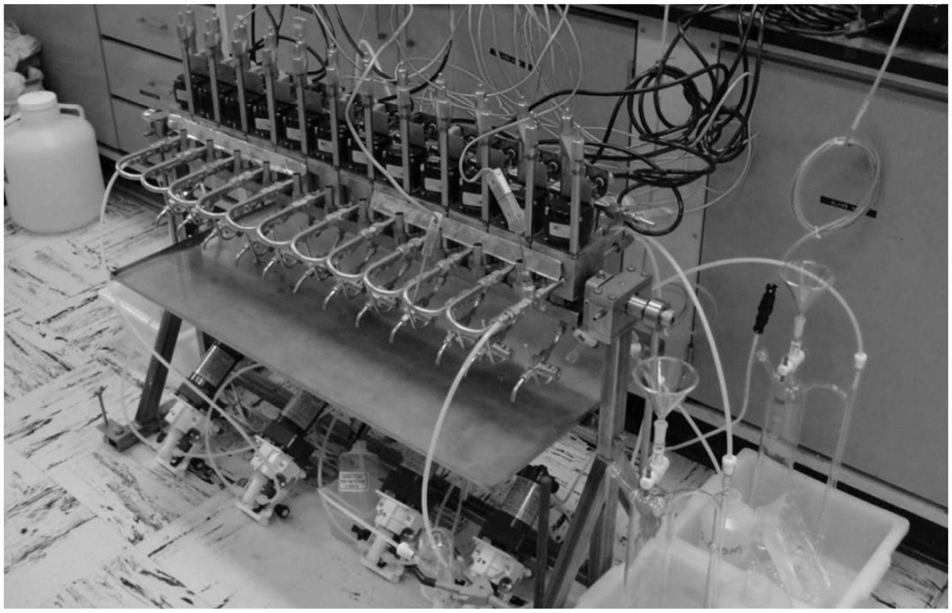

Figure 2. Contactor Apparatus for Waste Testing

To maintain the temperature of the extraction section at 23±3 °C, a section of ¾" square stainless steel tube was pressed against the bodies of the five extraction stages (Stage 1-5). The stainless steel tube had an inlet and outlet for flowing chilled water through the tube, entering at Stage 1 and exiting at Stage 5. Chilled water was supplied from a ThermoCube Model 400 solid-state cooling/heating unit. Due to elevated temperature in the Shielded Cells during the test period

(~30 °C), the Tank 49H solution (fed into Stage 5) was also cooled using a small glass heat exchanger. Chilled water for the feed-stream heat exchanger was supplied from a separate ThermoCube Model 400 cooling/heating unit.

The waste feed for the simulant tests was filtered prior to delivery of the simulant solution to the laboratory. The Tank 49H waste was filtered through an 8-micron Parker Balston cartridge filter as it was being added to the Waste Feed vessel. The exit streams from the contactors were equipped with aqueous-solvent decanters to disengage the liquid phases and observe second-phase carryover.

During the non-radioactive simulant test, a square stainless steel tube was used to control the temperature of the strip section at 33±3 °C instead of the feed temperature. However, in the radioactive test, the need to cool the extraction section took priority over control of the strip section temperature, and the cooling/heating unit dedicated for strip section temperature control was used to cool the Tank 49H feed solution. The temperatures of the strip stages were not controlled during the HLW test, but were still maintained at or near the desired range of 33±3 °C.

Type K (Omega Engineering) thermocouples were attached to the contactor bodies for all 12 stages to provide temperature monitoring. Additionally, Type K thermocouples were installed to monitor liquid temperatures in four locations: 1) aqueous stream exiting Stage 1, 2) aqueous stream flowing from Stage 3 to Stage 2, 3) organic stream flowing from Stage 10 to Stage 11, and 4) organic stream exiting Stage 12. Due to heat generated by the centrifugal contactor motors conducted into the contactor bodies, we determined that the four liquid temperatures were the more reliable process fluid values and these temperatures were used as the basis for control decisions.

Liquids were fed to the contactors using pumps manufactured by Fluid Metering, Inc. (FMI). All aqueous feed streams were fed from graduated glass feed vessels. Changes in vessel volumes over time were used as the primary method of flow rate monitoring. The flow rate of the solvent stream was measured using grab samples at the exit of Stage 12.

Test Methods

Extraction-Scrub-Strip Protocol: As a measure of the equilibrium distribution ratios for Cs [D(Cs)], SRNL performed several ESS tests, using the same or similar solvent and aqueous feed materials. The ESS test is a series of organic (solvent)-aqueous (Tank 49H solution) contacts. For these tests, the researchers used a nominal starting volume of 120 mL of Tank 49H waste (or 90 mL of waste simulant) aqueous feed and 40 mL of fresh, unused next-generation solvent (30 mL of solvent for waste simulant test).

There were typically one or two extraction steps, two scrub steps, and three strip steps. Between each step the phases were separated, a portion of each phase was removed for analysis, and one of the phases was placed back in the funnel and contacted with a new organic or aqueous phase. The two phases were shaken for two minutes and then allowed to contact for ~24 hours before proceeding to the next step. The Cs concentration for the non-radioactive ESS tests was determined using inductively coupled plasma mass spectroscopy (ICPMS). For radioactive tests, the ^{137}Cs concentration was measured using gamma spectroscopy.

Centrifugal Contactor Operations: Researchers operated the solvent extraction contactor apparatus in the following manner. To initiate an experiment, the contactor rotors were started and the scrub and strip stages were filled with scrub (0.025 M NaOH) and strip (0.01 M H_3BO_3)

solutions. With the scrub and strip feeds flowing, startup simulant flow was initiated into the extraction bank at Stage 5. The startup simulant was a Tank 49H simulant solution containing no cesium. After achieving steady aqueous flow through the extraction stages (Stages 1 to 5), the solvent feed to Stage 1 was initiated. When solvent was observed exiting the final strip stage (Stage 12) the aqueous feed was switched from the startup simulant solution to the test solution (containing cesium).

During each test, researchers monitored key process characteristics every 15-30 min. Liquid samples were taken by placing sample containers at the outlet points of the continuously-flowing streams. The three sample locations were: 1) decontaminated salt solution (DSS) exiting the DSS decanter at the aqueous outlet from Stage 1, 2) strip effluent (SE) exiting the SE decanter at aqueous outlet from Stage 8, and 3) solvent outlet from Stage 12 prior to the solvent decanter.

At the end of each test, the motor rotation and feed pumps were stopped as quickly as possible to minimize disruption of the contents of each stage for the post-test stage samples. Stage samples were obtained by draining each stage into polypropylene bottles and pipetting a portion of the aqueous phase into a sample bottle.

Contactor Distribution Ratios and Stage Efficiency: At the end of each test, researchers drained the contents of each stage into polypropylene bottles. All stage samples were transferred to glass separatory funnels. For the non-radioactive test, extraction and scrub Stages 1-7 were placed in a shaker bath at 23 °C, shaken for several minutes, and then allowed to separate for approximately 24 hours; strip Stages 8-12 were placed in a shaker bath at 33 °C, shaken for several minutes, and then allowed to separate for approximately 24 hours. The final temperatures were measured and portions of each phase were analyzed for Cs. For the radioactive test, a similar protocol was followed except that all 12 stages were shaken at ambient temperature (which was 28.6 °C) and allowed to separate at ambient temperature. For non-radioactive solutions, ICPMS was used for analyses. For radioactive solutions, gamma spectroscopy was used to analyze the ^{137}Cs concentration.

Contactor Decontamination and Concentration Factors: During each test, researchers obtained samples of the three process streams (i.e., decontaminated salt solution, strip effluent, and stripped solvent) at intervals of 0.5-1.0 hours. Non-radioactive samples were analyzed for cesium by ICPMS and radioactive samples were analyzed by ^{137}Cs gamma counting techniques.

Contactor Minor Component Concentrations: Minor inorganic components in the aqueous and organic streams were measured by inductively coupled plasma emission spectroscopy (ICPES) and ICPMS for the non-radioactive test. Organic samples were first digested prior to analyses. Analyses were completed for the non-radioactive test every six hours on the decontaminated salt solution, strip effluent, and recycle solvent. Analyses of the minor inorganic components were also completed for the aqueous and organic samples taken from the stages at the end of the test.

RESULTS AND DISCUSSION

ESS Test Results

Table 3 shows the results from the Tank 49H waste and waste simulant ESS tests, corrected to the normal process operating temperatures (i.e., 23 ºC for extraction and 33 ºC for scrubbing and stripping). Although the temperature-correctections data have not yet been reported in the open literature, a similar behavior has been documented for the baseline solvent.[5] Table 3 also includes reference D(Cs) values for the MaxCalix solvent system.[3] The reference values serve as a point of comparison. However, when D(Cs) values do not meet the reference values, it does not necessarily indicate that a process upset has occurred, but should serve as motivation for increased scrutiny of the result and the conditions contributing to the result.

Table 3. Cesium Distribution Ratios for the ESS Tests using Tank 49H Real Waste or Simulant

Material	Extract #1	Extract #2	Scrub #1	Scrub #2	Strip #1	Strip #2	Strip #3
BOBCalix Solvent System (Baseline)							
Real Waste*	14.1	16.8	0.88	0.21	0.18	0.0082	0.020
MaxCalix Solvent System (Next Generation)							
Reference#	~60	~60	~2-4	~1-2.5	~0.33	~0.0007	~0.0003
Simulant#	81	59	3.6	1.1	0.0095	0.0024	0.34
Real Waste*	60	79	2.1	1.9	0.00026	<0.016	<0.84
Real Waste#	88	77	5.0	3.0	0.0042	0.0047	0.0094
* Extraction O/A =1:3; Strip O/A = 5:1 # Extraction O/A = 1:4; Strip O/A = 3.75:1							

For the ESS tests, the data for the simulant and Tank 49H waste tests show comparable results with the exception of Strip #3. In this case, the poorer detection limit of the analytical method used for the simulant test is the cause of the apparent poorer result.

Testing with Centrifugal Contactors

Prior to the test with HLW, one hydraulic performance verification test was conducted in a non-radioactive laboratory with Tank 49H simulated waste containing non-radioactive cesium. The objective of the tests was to verify that the system performed as designed. Approximately 34.5 L of Cs-containing simulated waste was processed through the system. The test was completed without interruptions, flow-rate issues, or significant second-phase carry-over.

Subsequently, the test with Tank 49H HLW was completed in the SRNL Shielded Cells Facility. The test fed radioactive feed for 26.75 h, and was completed without interruption or flow rate issues. Approximately 39 L of Tank 49H waste solution was decontaminated in the system. The feed rate set points and the observed feed rates for both tests are included in Table 4. The relative feed rates of the waste feed and strip solutions produced a Cs concentration factor of 14.7 for the simulant test and 16.3 for the Tank 49H HLW test.

Waste Decontamination: The objective for each test was to achieve a DF of 40,000 in an MCU-type configuration. Due to a reduced number of stages in the 2-cm contactor apparatus (five stages each for extraction and strip compared to seven stages of each for MCU), the target DF was 1944, assuming 90% stage efficiency for both extraction and stripping.

Due to analytical limits for detecting non-radioactive cesium, the maximum measurable DF for the extraction section was approximately 6.6E+03. Many of the hourly samples showed a DF greater than 6.6E+03 (with an average DF of >5.9E+03 (Figure 3). The data show a gradual decrease in DF from >6.6E+03 at 5 h to 3.9E+03 at 12 h with full recovery to >6.6E+03 at 13 h. The test log provides no indication for the gradual loss of DF or its recovery.

Table 4. Feed Rate Set Points and Observed Flow Rates for 2-cm Contactor Tests

Process Feed	Set Point	Simulant Avg. Flow	Tank 49H HLW Avg. Flow
Waste Feed	24.0 mL/min	23.5 mL/min	24.5 mL/min
Solvent	6.0 mL/min	6.1 mL/min	6.1 mL/min
Strip	1.6 mL/min	1.6 mL/min	1.5 mL/min
Scrub	1.6 mL/min	1.6 mL/min	1.6 mL/min

The data were used with D(Cs) values reported later to calculate stage efficiencies using the SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) modeling program developed at ANL.[6] The calculations showed that the contactor stage efficiencies ranged from 89% to 91%.

Data for the Tank 49H waste test show strong performance relative to the target DF values throughout the entire test. With the exception of one sample at 24 h (likely due to sample contamination), all of the measured DF values ranged between 3.80E+04 and 1.08E+05 with an average DF of ~6.78E+04 (Figure 3). Calculations determined that the contactor stage efficiencies ranged from 94% to 96%.

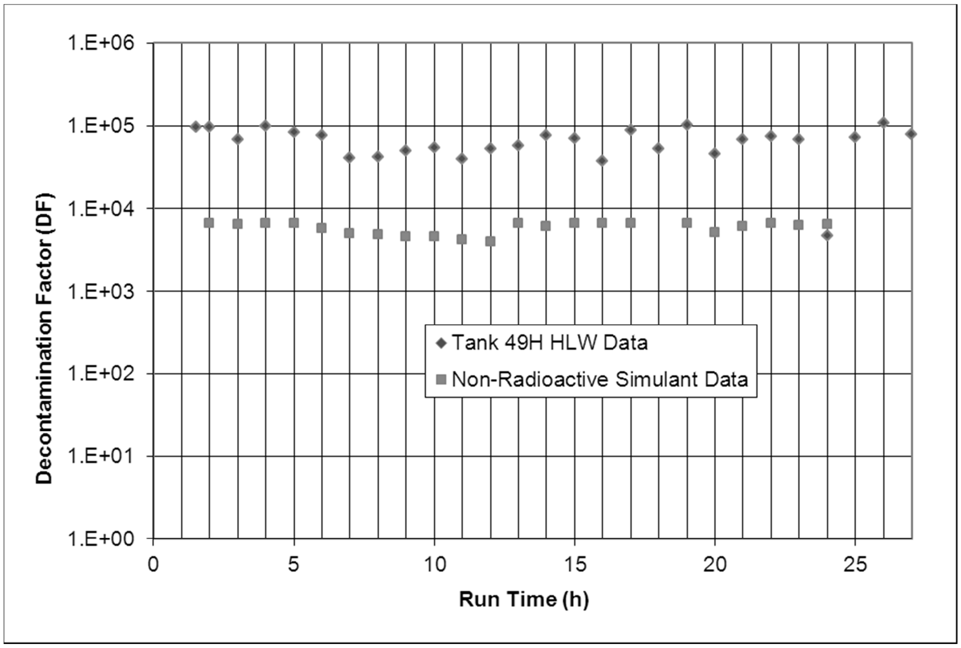

Figure 3. Decontamination Factors for Both Centrifugal Contactor Tests

Stage Temperatures: The non-radioactive test was conducted in a laboratory with an ambient temperature of 21 °C, compared to 30 °C for the HLW test. The temperatures in the extraction and strip stages were actively controlled. Consequently, the temperatures were maintained within acceptable ranges, which were 23±3 °C for extraction and 33±3 °C for strip. The aqueous flow out of Stage 1 (extraction) was controlled between 19.8 and 21.2 °C with an average of 20.6 °C.

The aqueous flow from Stage 3 to Stage 2 (extraction) was controlled between 21.0 and 22.1 °C with an average of 21.6 °C. The organic flow from Stage 10 to Stage 11 (strip) was maintained between 27.9 and 30.7 °C with an average of 29.4 °C. The organic flow out of Stage 12 (strip) ranged from 28.2 to 31.2 °C with an average of 30.0 °C. The Stage 6 (scrub) and Stage 7 (scrub) block temperatures operated at averages of 31.5 and 34.4 °C, respectively.

For the Tank 49H HLW test, some fluctuation of temperatures occurred throughout the test as a result of temperature changes in the shielded cells and inadvertent feed-line chiller shut downs between 6.0 h and 14.5 h after waste feeding began. The aqueous flow out of Stage 1 (extraction) was controlled between 22.2 and 24.1 °C for the first six hours, reached 24.7 °C between 6.0 and 14.5 h, and was controlled between 22.1 and 22.9 °C for the final 12 hours. Similarly, the aqueous flow from Stage 3 to Stage 2 (extraction) was controlled between 22.8 and 24.3 °C for the first six hours, reached 26.9 °C between 6.0 and 14.5 h, and was controlled between 22.5 and 23.7 °C for the final 12 hours. Although no direct measurements of the liquid from Stage 5 to Stage 4 were measured, due to the closer proximity to the waste solution feed location (Stage 5), the temperature in Stage 5 was probably higher than the temperatures measured between Stages 3 and 2. The organic flow from Stage 10 to Stage 11 (strip) was maintained between 34.5 and 37.5 °C with an average of 35.9 °C. The organic flow out of Stage 12 (strip) ranged from 34.7 to 37.4 °C with an average of 35.8 °C.

Based on the data, it can be concluded that the temperature changes had a significant impact on the extraction stage temperatures, but that the impact on the strip stages was not detectable. Regardless of the magnitude of the temperature changes, the waste decontamination data exhibited no measurable change in overall DF as a function of temperature. The overall impact of temperature may be muted by suspected inefficient operation of the scrub section (discussed later).

Stage Data for Non-Radioactive Simulant Test: Cesium distribution ratios [D(Cs)] were measured for 11 of the 12 stages (Stage 7 was compromised during sample handling). Distribution ratios listed in Table 5 were measured on stage samples at 23 °C (Stages 1-6) and 33 °C (Stages 8-12) following the test. There was no need to perform a temperature correction of the D(Cs) values.[5]

In the initial analyses, problems were detected in the data for the organic in Stages 1-3 and 10-12. The samples were re-analyzed to yield the data in Table 5. In retrospect, the organic sample from Stage 4 should have also been analyzed as the D(Cs) value for Stage 4 appears to be in error. The distribution ratios in Stages 1-3 and 5 are in the acceptable range (Table 3) based on the ESS tests. The expected range for extraction D(Cs) values is 57-88, for scrub D(Cs) values is ~1.0-5.0, and for strip D(Cs) values is 0.002-0.016. The D(Cs) for scrub in Stage 6 is also in the expected range. The strip data for Stages 8-12 are higher than expected. The loss of the Stage 7 sample makes it difficult to determine if there were any issues associated with the scrub section that caused problems in stripping. As will be discussed later, a possible issue with scrubbing was noted during the test with actual Tank 49H waste.

Table 5. Equilibrium Distribution Ratios for Non-Radioactive Simulant Test

Section	Stage	Organic ^{133}Cs (μg/L)	Aqueous ^{133}Cs (μg/L)	Test Temp (°C)	D(Cs)
Extraction	1	1.30E+03	2.40E+01	23	54
Extraction	2	1.33E+03	1.78E+01	23	75
Extraction	3	2.26E+03	3.16E+01	23	72
Extraction	4	6.47E+04	2.33E+02	23	278
Extraction	5	2.69E+05	3.25E+03	23	83
Scrub	6	4.06E+05	2.19E+05	23	1.9
Scrub	7	Sample compromised			
Strip	8	1.62E+05	1.14E+06	33	0.14
Strip	9	7.28E+04	6.13E+05	33	0.12
Strip	10	7.71E+03	2.74E+05	33	0.028
Strip	11	1.14E+03	1.00E+05	33	0.011
Strip	12	1.71E+02	1.28E+04	33	0.013
Uncertainty of ^{133}Cs measurements is 20%					

Stage Data for the Tank 49H HLW Test: The quantity of cesium in the experiment allowed for measurement of distribution ratios in each stage at the end of the test. At the end of the test, a sample of the aqueous stream from each stage was submitted for ^{137}Cs analysis. Next, the remaining aqueous and organic for each stage were equilibrated and sampled. Due to equilibration at ambient temperature (28.6 °C), the D(Cs) values calculated from the analyses were corrected for temperature (23 °C for Stages 1-7 and 33 °C for Stages 8-12).[5] The activity levels for each stage, the calculated D(Cs) values, and the temperature-corrected D(Cs) values are listed in Table 6. The activity levels for equilibrium samples and aqueous samples pulled at shut down are plotted in Figure 4. When non-radioactive simulant data in Table 5 are plotted, the chart looks similar to Figure 4.

Table 6. Equilibrium Distribution Ratios for Tank 49H HLW Test

Section	**Stage**	**Organic ^{137}Cs, Equilibrium (dpm/mL)**	**Aqueous ^{137}Cs, Equilibrium (dpm/mL)**	**Aqueous ^{137}Cs, Shut Down (dpm/mL)**	**Test Temp (°C)**	**D(Cs)**	**D(Cs), Temp Corrected**
Extraction	1	< 3.47E+03	1.49E+05	1.96E+03	28.6	> 42.9	> 57.8
Extraction	2	< 4.10E+03	2.76E+05	6.85E+03	28.6	> 67.3	> 90.6
Extraction	3	6.93E+04	4.05E+06	7.79E+04	28.6	58.4	78.7
Extraction	4	5.75E+05	3.91E+07	8.39E+05	28.6	68.0	91.5
Extraction	5	7.02E+06	3.77E+08	1.17E+07	28.6	53.7	72.3
Scrub	6	5.10E+06	5.63E+08	2.16E+08	28.6	110	161
Scrub	7	6.83E+07	5.48E+08	2.32E+08	28.6	8.02	10.8
Strip	8	6.84E+08	1.18E+08	3.89E+08	28.6	0.17	0.14
Strip	9	1.36E+08	8.45E+06	6.26E+07	28.6	0.062	0.047
Strip	10	7.62E+06	4.28E+05	9.21E+06	28.6	0.056	0.048
Strip	11	2.19E+06	1.02E+05	1.61E+05	28.6	0.047	0.040
Strip	12	1.06E+06	6.57E+03	3.40E+05	28.6	0.006	0.005

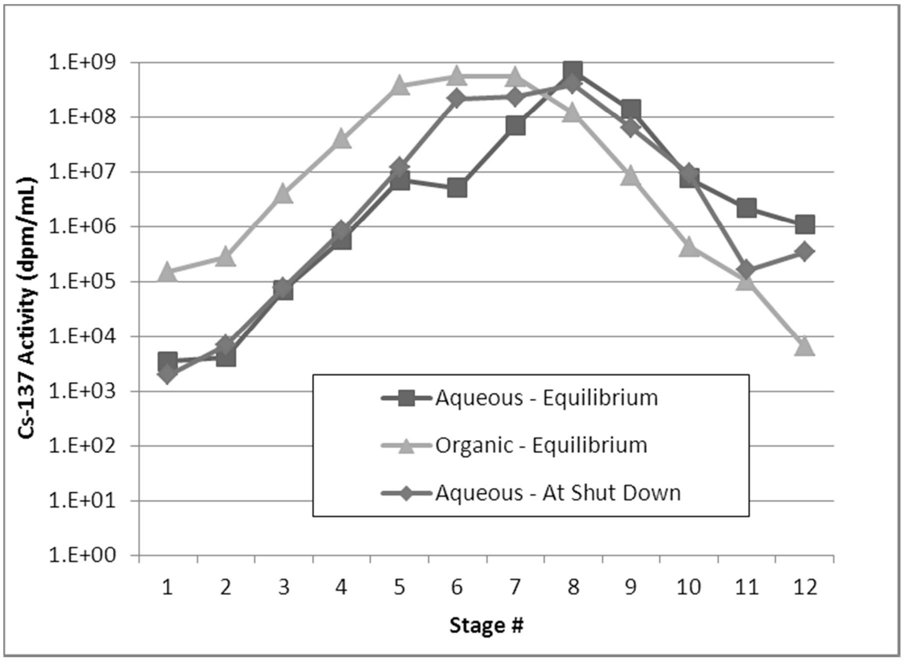

Figure 4. Stage Sample Data for the Tank 49H HLW Test

The similarity of both the equilibrium and shut-down aqueous data, particularly for Stages 1-5, 7-10, and 12 lend confidence to the data-collection techniques. It also indicates that the stages have achieved equilibrium in the contactors. The data also suggest that problems were encountered during the collection of Stage 6 equilibrium and the Stage 11 shut-down aqueous samples. The problem associated with Stage 6 is also reflected in the data in Table 6

The shapes of the aqueous and organic curves in Figure 4 have the expected shape relative to each other and provide a comparison to the data presented for the non-radioactive simulant test (Table 5). The D(Cs) values for the extraction section (Stages 1-5) are in the acceptable range and in general agreement with the ESS test data (Table 3).

In contrast, the D(Cs) values for the scrub and strip sections are not in the expected ranges. ESS values for scrub are 3.5-5.0 for the first scrub stage (Stage 6) and 1.0-3.0 for the second scrub stage (Stage 7). The calculated D(Cs) scrub values for the Tank 49H test were 161 for Stage 6 and 10.8 for Stage 7. A comparison of the equilibrium and shut-down data for Stage 6 aqueous samples (Figure 4) indicate a problem with either the analytical data or method used to produce the equilibrium sample.

However, two successive high values in scrub also suggest potential inefficient operation of the scrub section. If inefficient scrubbing occurred, the result would be less-than-optimal stripping results as inefficient scrubbing impacts the pH of the strip section. The data for the strip stages, especially the first strip stage, are not in the expected ranges. Data from the ESS tests determined D(Cs) values for strip of 0.004-0.010 for the first strip stage (Stage 8) and ~0.002-0.009 for subsequent strip stages (Stage 9-12). In the Tank 49H test, the D(Cs) value in Stage 8 started high (0.14) and gradually decreased from stage to stage until reaching a low value of 0.005 in Stage 12. Only the value for Stage 12 was in the expected range. However, these D(Cs) results show the robustness of the process as the overall process exceeded the target DF values even with the scrub and strip sections not performing as predicted in the ESS tests.

The SASSE modeling program was used to assess the impact of using the reference scrub and strip values (Table 3) instead of the measured values of Table 6. An average extraction D(Cs) value of 78.2 was used to reflect the average extraction D(Cs) data from the Tank 49H waste test. With reference scrub and strip, the ^{137}Cs activity in the DSS is reduced from <3.47E+03 dpm/mL (for Stage 1 of the Tank 49H waste test) to a calculated value of 1.43E+03 dpm/mL. Because the Stage 1 aqueous data in Table 6 is a "less-than" value, it is possible that the change in scrub and strip has no measureable impact. At best, this incremental improvement in decontamination reflects only a small fraction of the initial ^{137}Cs in the Tank 49H waste feed (1.44E+08 dpm/mL).

The equilibrium data were used to calculate stage efficiencies for the Tank 49H waste test using the SASSE modeling program. These calculations determined that average extraction and strip stage efficiencies were ~95%. For the minimum DF value of 3.80E+04, the calculated stage efficiencies were ~94%. This result further affirms that the solutions in the stages were at or near equilibrium.

<u>Distribution of Inorganic Components</u>: During the non-radioactive simulant test, the quantities of inorganic components were measured every six hours for the DSS, SE, and solvent streams using ICPES. The data are provided in Table 7 for those components that produced a measurable response. Of particular interest are those components that are chemically-similar to Cs, such as sodium (Na) and potassium (K). The data show that both Na and K were at measurable concentrations in the strip effluent but below the detection limit in the solvent. The presence of K and Na in strip samples is an indicator of incomplete scrubbing. Although the detection limits for Na and K in the solvent are fairly high, the data indicates that Na and K that are either entrained in or bound to the solvent are removed by the strip solution.

Sulfur (S), probably as sulfate, had measurable quantities consistently in the solvent. Furthermore, there are no measurable concentrations of S in the strip effluent. This suggests that sulfate reacts with the solvent and is not readily removed by the 0.01 M H_3BO_3. The concentration of sulfur in the solvent may not have reached a steady value during the test.

Table 7. Distribution of Inorganic Components (in mg/L) with Time – Simulant Test

ELEMENT	Sample	Start	0.5 h	6 h	12 h	18 h	24 h
Cs	DSS	<0.012	<0.0125	0.0147	0.0211	n/a	0.0130
	SE	0.19	252	978	976	1090	1120
	ORG	n/a	0.00374	0.00344	0.00905	0.00696	0.0069
K	DSS	491	484	483	477	n/a	476
	SE	9.78	19.9	23.3	24.5	24.1	29.8
	ORG	n/a	< 31.7	< 33.4	< 31.3	< 32.3	< 33.4
Na	DSS	140000	139000	134000	142000	n/a	138000
	SE	15.8	71.3	180	164	150	161
	ORG	n/a	< 11.0	<11.5	< 10.8	18.5	<11.5
S	DSS	1740	1750	1730	1720	n/a	1680
	SE	< 0.735	< 0.735	< 0.735	< 0.735	< 1.47	< 1.47
	ORG	n/a	13.4	19.3	27.1	36.7	42.1

n/a = no sample collected or sample compromised
Cs measurement uncertainty = 20%
Measurement uncertainty for all other analytes = 10%

Stage data were also collected for elements other than Cs. ICPES data for the aqueous and organic fractions of each stage after equilibration are provided in Table 8. The data for the extraction section shows that the concentrations of components are largely unchanged in the bank except for the concentration of Cs, which was reduced from 83.1 mg/L to 0.0316 mg/L in three extraction stages. The concentration of Cs for the final two extraction stages is relatively constant, possibly due to the presence of Cs in the solvent being fed to the extraction section in Stage 1. The presence of Cs in the solvent may be attributable to inefficient scrubbing discussed above. Inefficient scrubbing would negatively affect the strip section, thus leading to Cs being retained in the solvent recycled to Stage 1.

The stage data show comparable behavior for Cs, K, and Na in the strip section. For all three elements, the concentrations in the aqueous phase are highest in Stage 8 and decrease with each successive stage. The same is true for Cs in the organic phase, while the concentrations of K and Na are below the method detection limits. Conversely, S exhibits relatively constant concentrations across the strip section, both in the aqueous and organic phases. This is further indication that perhaps sulfate has attached to the solvent and is not removed by either the scrub or the strip solutions.

Table 8. Distribution of Inorganic Components (in mg/L) in the Contactor Stages at the End of the Test – Simulant Test

AQUEOUS							
Stage	1	2	3	4	5	Feed	
ELEMENT	Extraction						
Cs	0.0240	0.0178	0.0316	0.233	3.250	83.1	
K	457	559	568	534	568	512	
Na	136000	140000	135000	129000	139000	151000	
S	1660	1640	1620	1570	1670	1910	
Stage	6	7	8	9	10	11	12
ELEMENT	Scrub		Strip				
Cs	219	n/a	1140	613	274	100	12.8
K	1040	n/a	27.8	4.93	< 2.43	< 2.43	< 2.43
Na	1930	n/a	227	132	58.5	24.5	9.21
S	6.3	n/a	0.79	0.94	< 0.735	< 0.735	< 0.735
ORGANIC							
Stage	1	2	3	4	5		
ELEMENT	Extraction						
Cs	0.0454	0.042	0.0466	0.078	0.324		
K	289	346	325	305	325		
Na	69.3	63.4	62.8	43.6	72.9		
S	39.2	42.4	39.4	38.3	41.1		
Stage	6	7	8	9	10	11	12
ELEMENT	Scrub		Strip				
Cs	0.489	n/a	0.196	0.0878	0.0454	0.0337	0.0469
K	< 35.8	n/a	<38.5	< 36.3	< 33.1	< 36.9	< 38.3
Na	< 12.3	n/a	< 13.3	< 12.5	< 11.4	< 12.8	< 13.2
S	41.7	n/a	37.9	38.8	42	43.6	41.6
n/a = sample compromised							

CONCLUSIONS

The CSSX process flowsheet for the decontamination of HLW with a MaxCalix-based solvent system was demonstrated in a 12-stage, 2-cm diameter contactor apparatus. Simulated and actual Tank 49H wastes were processed in two tests. The simulant-waste test lasted 24 h with 20 solvent turnovers; the Tank 49H waste test lasted 27 h with 25 solvent turnovers. The test with the Tank 49H waste sample yielded an average DF for five extraction, two scrub, and five strip stages of 6.78E+04 at a nominal stage efficiency of 95%. A test with simulated waste produced an average DF of >5.9E+03 at a nominal stage efficiency of 90%. The Tank 49H test also confirmed that minor components present in the Tank 49H waste but absent from the simulant did not impact the process DFs. The relative feed rates of the waste feed and strip solutions produced a Cs concentration factor of 14.7 for the simulant test and 16.3 for the Tank 49H HLW test.

The 2-cm contactor apparatus operated without any hydraulic issues in both the non-radioactive simulant and the Tank 49H HLW tests. No flow disruptions were encountered and pumping rates remained stable throughout both tests. The ability to operate without issue may be in part the result of operating at ~53% of its expected throughput capacity.

Cesium distribution ratios measured by ESS tests for extraction were in good agreement with those measured for the 2-cm contactor tests. D(Cs) values from the ESS tests for scrub agreed with the non-radioactive simulant test, but there was lesser agreement for the Tank 49H HLW test. It is speculated that poor scrubbing produced less favorable D(Cs) values for strip, which were considerably higher than those measured by the ESS test. Regardless of the D(Cs) values for scrub and strip, the process exhibited its robustness by producing excellent DF values in spite of non-optimal scrub and strip performance.

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