Cesium Removal from Savannah River Site Radioactive Waste using the Caustic-Side Solvent Extraction (CSSX) Process

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Abstract: Researchers at the Savannah River National Laboratory successfully demonstrated the Caustic-Side Solvent Extraction (CSSX) process flow sheet using a 33-stage, 2-cm centrifugal contactor apparatus in two 24 h tests using actual high-level waste. The CSSX process for removal of cesium from alkaline solutions is the reference process for decontamination of high-level waste (HLW) at the Savannah River Site (SRS). The solvent consists of a calix[4]arene-crown-6 extractant, an alkyl-phenoxy alcohol modifier, and trioctylamine dissolved in an inert hydrocarbon matrix. Previously, we demonstrated the solvent extraction process with actual SRS HLW supernatant solution using a nonoptimized solvent formulation. Following that test, the solvent system was optimized to enhance extractant solubility in the diluent by increasing the modifier concentration. We now report results of two tests with the new and optimized solvent. The first test used a composite of supernatant solutions from two waste tanks, and the second test used a solution derived from dissolved salt cake. Test results showed that the CSSX process using the optimized solvent reduces ^{137}Cs in HLW supernatant solutions to concentrations below the waste acceptance criterion of 45 nCi/g for disposal as low-level waste (called "saltstone"). Waste decontamination factors as high as three million were achieved during testing. Test durations exceeded 24 h of uninterrupted operation and demonstrated hydraulic stability of the contactor array while operating with the optimized solvent. Carryover of organic solvent in aqueous streams (and aqueous in organic streams) was found

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to be less than 1%. The concentration factor (i.e., the ratio of the cesium concentration in the strip raffinate to the concentration in the waste) averaged approximately 13 during both tests, slightly below the process requirement of 15. Uncertainties in process flow-rate measurement and control prevented the test from achieving the target of 15.

INTRODUCTION

A solvent extraction process for removal of cesium from alkaline solutions has been developed utilizing a novel solvent invented at the Oak Ridge National Laboratory (1, 2). This solvent consists of a calix[4]arene-crown-6 extractant (BOBCalix) dissolved in an inert hydrocarbon matrix (Isopar® L). An alkyl-phenoxy alcohol modifier [1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butyl-phenoxy)-2-propanol, also known as Cs-7SB] added to the solvent enhances the extraction power of the calixarene and prevents the formation of a third phase. An additional additive, trioctylamine (TOA), improves stripping performance and mitigates the effects of any surfactants present in the feed stream. The solvent extraction process was successfully demonstrated with actual Savannah River Site (SRS) high-level waste supernatant solution during testing performed in 2001 (3). Subsequent to that test, the solvent system was optimized by decreasing the extractant concentration and increasing the modifier and suppressor concentrations (4). These changes corrected a potential problem with the original solvent formulation that thermodynamic analysis indicated was a metastable solution that could experience extractant precipitation during long-term use and storage. Also, radiolytic degradation of the TOA suppressor necessitated an increase in suppressor concentration. Therefore, the concentration of BOBCalix in the optimized solvent mixture was decreased from $0.01\,M$ in the initial formulation to $0.007\,M$. The Cs-7SB modifier concentration was increased from $0.50\,M$ in the initial formulation to $0.75\,M$. The TOA suppressor concentration was increased from $0.001\,M$ in the initial formulation to $0.003\,M$. Because of the change in solvent composition, the new test with supernatant waste was needed. In addition, a second test using a different waste composition was performed in an effort to expand our experience with the optimized solvent. The SRS tank farms store soluble high-level waste in two forms: supernatant solution and salt cake. Researchers postulate that the separation of the waste into two phases will create differences in composition between the two forms that may affect solvent extraction processing. The first test described here used supernatant solution from Tanks 37H and 44F. A second test intended to verify that the optimized solvent could also effectively decontaminate dissolved salt cake waste. SRS plans for waste dissolution in Tank 37H proved a timely source of dissolved salt cake for the CSSX demonstration. This paper summarizes the results of the two tests.

EXPERIMENTAL

Waste Sample Origin and Preparation

SRS waste management personnel provided three 38 L samples of high-level waste. The first test of the optimized solvent used a composite waste sample of supernatant liquids from Tanks 37H and 44F. The composite sample contained approximately equal volumes from the two source tanks. The second test used waste taken from Tank 37H in April 2002, during salt cake dissolution operations. In both cases, the supernatant liquids were more concentrated than desired for the solvent extraction test and were diluted to approximately $6 M Na^+$ using $1.6 M NaOH$ solution. Use of sodium hydroxide for the dilution prevents precipitation of aluminum compounds by maintaining a high-hydroxide concentration. Portions of the diluted waste were analyzed by routine methods providing the compositions listed in Table 1.

Contactor Configuration

The process equipment consisted of a 33-stage, 2-cm annular centrifugal contactor apparatus used in previous actual waste demonstrations at the

Table 1. Composition of the diluted waste samples*

Component	Concentration (M)	
	Tank 37/44 Composite	Tank 37 Dissolved Salt Cake
Na^+	5.52	6.22
K^+	0.035	0.039
Cs^+	0.00017	0.00034
Free OH^-	4.1	3.7
NO_3^-	0.57	0.73
NO_2^-	0.41	0.88
AlO_2^-	0.18	0.54
SO_4^{2-}	0.044	<0.006
CO_3^{2-}	0.068	<0.02
PO_4^{3-}	0.006	0.02
F^-	<0.11	<0.012
Cl^-	0.15	0.009
Radionuclide	Activity (d/m/mL)	
^{137}Cs	1.6×10^9	3.2×10^9
Density	1.222 g/mL	1.240

*Table shows composition after dilution with 1.6 M NaOH.

Savannah River National Laboratory. Argonne National Laboratory personnel designed and fabricated the contactor stages. A previous report describes details of the apparatus configuration and process flow sheet (3). Figure 1 shows a process flow diagram specific to these tests, and Fig. 2 shows a picture of the apparatus.

The filtered waste was metered into the contactor apparatus with a Fluid Metering, Inc., pump. Glass aqueous-organic decanters received the exit streams from the contactors, disengaged the two phases, and allowed measurement of second-phase carryover. During tests, researchers monitored the test apparatus and measured process stream flow rates from timed collection volumes. Personnel collected samples by placing sample containers under the outlet points of the continuously flowing streams. Samples of the solvent feed stream were not taken during the test to avoid disrupting the hydraulic flow conditions.

Stage Efficiency

At the end of each test, researchers drained the contents of each stage into polypropylene bottles. Selected samples were transferred to glass separatory funnels, shaken at ambient temperature for 1 min, then allowed to separate for approximately 16 h. The final temperature was measured and portions of each phase were analyzed for ^{137}Cs using gamma ray spectroscopic techniques.
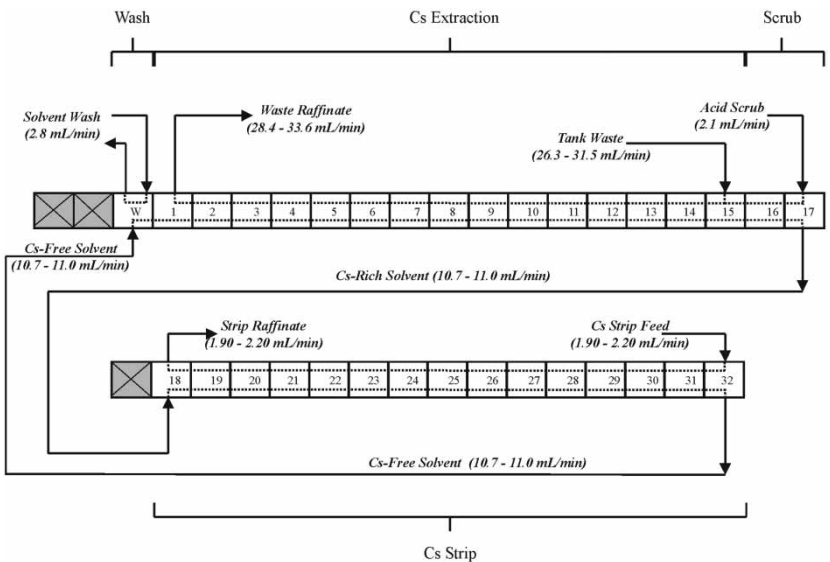

Figure 1. Flow diagram for the 33-stage centrifugal contactor apparatus.
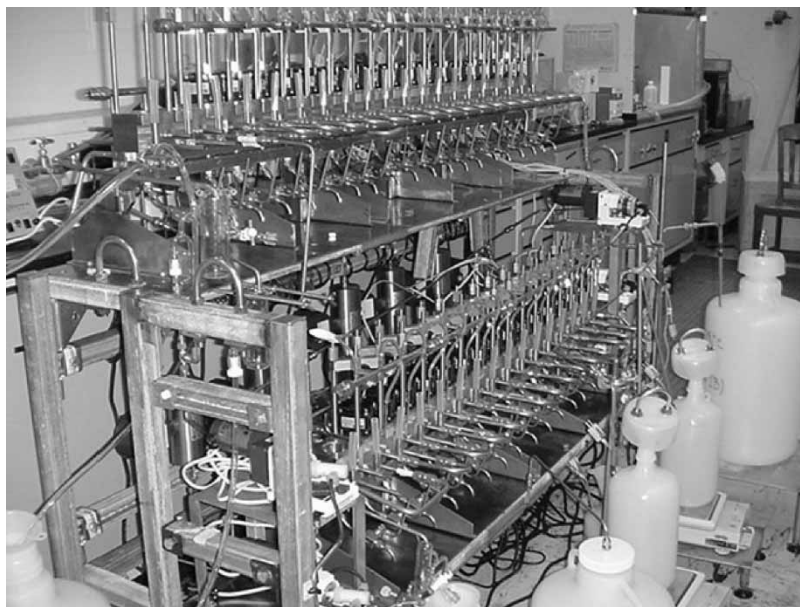
Figure 2. General contactor configuration.

Solvent Entrainment and Degradation

Researchers estimated the second-phase carryover from the volume of solvent that accumulated in the process decanters. High-performance liquid chromatography (HPLC) analysis of periodic samples of each stream provided concentrations of modifier and extractant. Due to the high Cs-137 activity in the strip raffinate samples, they were extracted with dichloromethane in the shielded facility, and the extract was removed for HPLC analysis. Fresh solvent was used for each test, and solvent degradation was measured on solvent samples taken at the start and end of each test. Modifier and extractant were measured by HPLC. Trioctylamine was measured by gas chromatography with mass spectral detection.

RESULTS AND DISCUSSION

Waste Composition

Evaporation of soluble high-level waste forms crystallized salt solids from the less-soluble components and supernatant liquid enriched in the more soluble components. When dissolved, the salt cake will produce solutions containing

less hydroxide, less cesium, and more nitrate than the supernatant solution (at equivalent sodium ion concentrations). The diluted Tank 37H/44F waste composition is typical of tank supernatant solutions. Free hydroxide (4.1 M) accounts for more than half of the total sodium concentration, and nitrate ion (0.57 M) is correspondingly low. The ^{137}Cs activity of the diluted sample $(1.6 \times 10^9 \, d/m/mL$ or $0.71 \, Ci/L)$ exceeds the average value $(0.37 \, Ci/L)$ expected in SRS soluble waste. The potassium ion (0.035 M) is also higher than average. The Tank 37H dissolved salt waste composition proved similar to supernatant solutions. After dilution, the Tank 37H waste contained 3.7 M free hydroxide and 0.73 M nitrate ion. Although the differences between the two wastes suggest more "salt cake" character in the second test, the differences are relatively minor. It is likely that the salt dissolution in Tank 37H had not proceeded significantly, and the sample obtained was largely supernatant liquid. However, the high concentrations of cesium and potassium in both waste samples makes decontamination more challenging than decontamination of average waste.

Hydraulic Performance

The contactor apparatus processed 45 L of Tank 37H/44F supernatant waste during 24 h of operation in the first test, and 45 L of Tank 37H dissolved salt waste during 25.5 h in the second test. In both tests, the apparatus operated without interruption for the entire duration. Hydraulic performance was excellent with no observations of flooding in any of the stages and no unusual amounts of minor phase accumulation in the decanters. Table 2 shows the observed process stream flow rates. The second test contained two parts. The first part consisted of 16 h of operation of the test apparatus

Table 2. Process flow rates

	Tank 47H/44F waste		Tank 37H dis. salt	
Process stream	Duration (hrs into test)	Flow rate (mL/min)	Duration (hrs into test)	Flow rate (mL/min)
Waste raffinate	0–1.5	27.4 ± 0.7	0–16	32.3
	1.5–2.5	37.4 ± 1.2	16–25.5	36.8
	2.5–24	29.7 ± 0.9		
Solvent	0–24	1.5 ± 0.7	0–16	10.6
			16–25.5	8.3
Scrub	0–24	2.3 ± 0.5	0–25.5	2.3
Strip	0–15	2.01 ± 0.22	0–25.5	2.6
	15.1–24	2.15 ± 0.27		

at flow conditions (i.e., Organic/Aqueous phase ratio or O/A ratios) con-
sistent with previous test campaigns. The second part consisted of 9.5 h of
operations at a reduced solvent flow and, thus, reduced O/A ratios.

Waste Decontamination

The waste decontamination results in both tests demonstrate that the cesium-
removal capability of the optimized solvent greatly exceeds process require-
ments. Figure 3 shows plots of the waste decontamination factors (DFs) as
a function of elapsed time during the tests. The instantaneous DF values
display maxima in excess of 1 million and, with only one exception in the
second test, exceeded the required DF for the waste being processed. In the
second test, the average DF was 352,000 during the first 16 h of operation
and 28,600 during the final 9 h of reduced solvent flow operation. Decontami-
nation results for the first 16 h of the test greatly exceed the process target of
40,000. The DF value for the last 9 h does not exceed the target but, neverthe-
less, produced decontaminated waste that met the saltstone waste acceptance
criterion (WAC) for ^{137}Cs of <45 nCi/g. The acceptable DFs achieved at
the reduced O/A ratio in the latter part of the test indicate the robustness of
the process to changes in processing conditions. They also show that a
given contactor size can process waste faster (without exceeding the
contactor capacity) by decreasing the solvent flow rate and increasing the
waste feed rate, at the expense of lower (but acceptable) DFs.

Solvent Condition

The cesium concentration in the stripped solvent is a sensitive indicator of
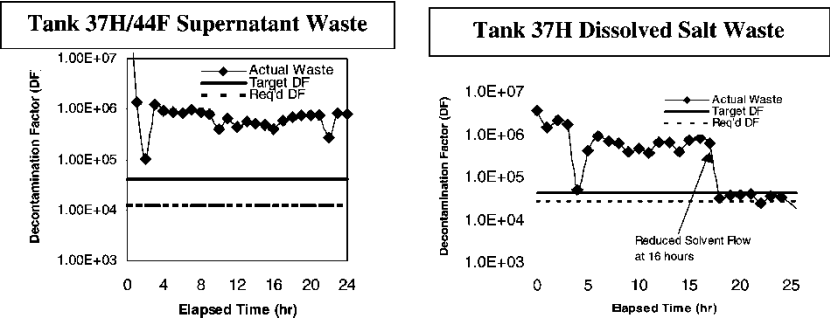overall system performance. Inadequate removal of cesium from the solvent

Figure 3.   Waste decontamination as a function of elapsed time.

in the stripping section will eventually lead to poor extraction section performance. Inadequate stripping occurred during both tests but was corrected by adjustments of the solvent and aqueous flow rates. Figure 4 shows the cesium concentration in the solvent exiting the strip section of the apparatus. In the Tank 37H/44F supernatant waste test, the cesium activity in the solvent increased gradually for the first 15h. At 15.1 h, researchers increased the strip feed rate, resulting in a slow decline in the cesium activity. By the end of the test at 24 h, the solvent had fully recovered. In the Tank 37H dissolved salt test, cesium activity increased during the initial 8 h. At 8 h, researchers decreased the solvent flow rate, thereby increasing the efficiency of the strip section. [137]Cesium activity in the solvent decreased and returned to levels similar to the start of the test. The high ^{137}Cs value at 24 h does not correspond to any process upsets or changes in flow rates and may have been due to sample contamination. The concentration of the major solvent components did not change significantly during the approximately 10 turnovers experienced in each test. The modifier, extractant, and suppressor concentrations at the beginning and end of each test agreed with each other and with the theoretical solvent composition within the error ($\pm 10\%$) of the HPLC measurements. These results indicate that selective partitioning of solvent components to the waste or strip raffinate was not significant.
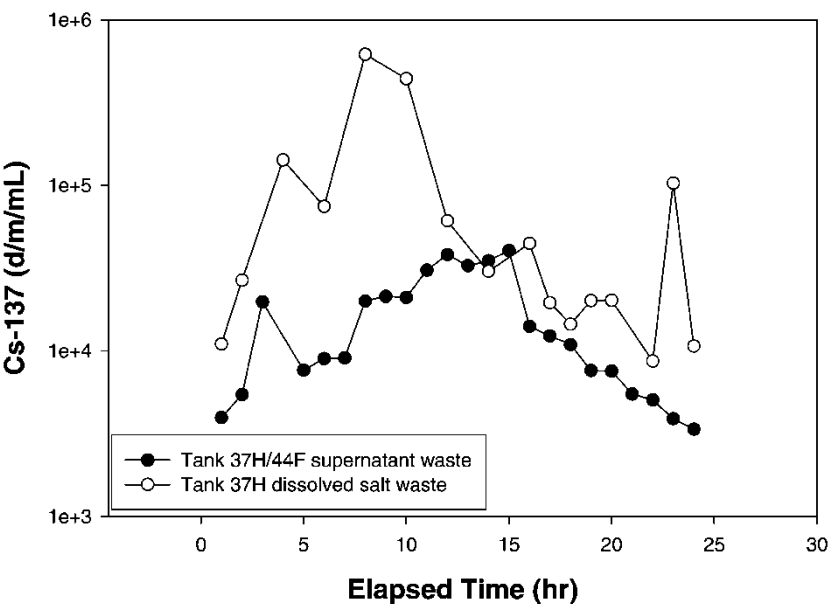

Figure 4. Cesium concentration in the solvent as a function of elapsed time.

Concentration Factors

The concentration factor (CF) is defined by the following equation:

$$CF = \frac{(^{137}Cs \text{ concentration in strip raffinate})}{(^{137}Cs \text{ concentration in waste feed})} \tag{1}$$

The CF values measured for the actual waste demonstration indicate steady state was achieved within the first 2 to 5 h of each test. Figure 5 shows plots of the CF values as a function of time during the tests. CF values averaged approximately 13 during the first test and during the first 16 h of the second test. Following the change in flow rates at 16 h into the second test, the CF value increased to 16. The average value of 13 throughout most of the test was slightly lower than the target value of 15. The low observed value suggests a bias in one of the flow rate measurements or possibly a systematic error in counting the feed or strip solution cesium activity.

Second-Phase Carryover

Second-phase carryover is defined as an unwanted liquid phase exiting in a primary product stream (e.g., the organic solvent exiting in the aqueous waste raffinate stream). Excessive second-phase carryover is indicative of poor hydraulic performance and can lead to large losses of solvent. In our apparatus, the majority of the second phase carryover accumulated in the decanters. However, losses occur from the decanters due to entrained droplets and solubility in the aqueous stream. Researchers estimated the second-phase carryover from the volume of solvent (or aqueous solution) that accumulated in the process decanters and from analysis of the aqueous phases for solvent components. Table 3 lists the results of these measurements.

Both actual waste tests achieved the process objective of <1 vol% second-phase carryover in all streams. There was no visible second-phase
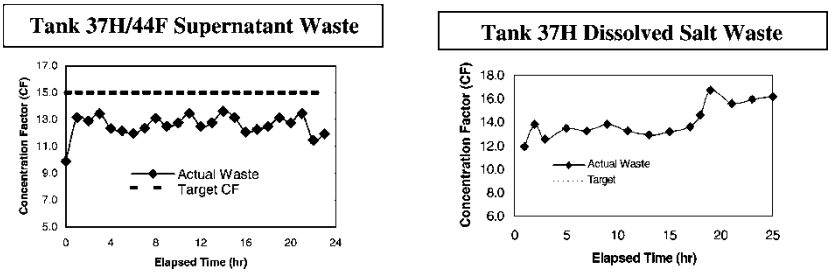

Figure 5. Concentration factors during the two tests.

Table 3. Combined minor phase carryover results

Decanter	Stream	Decanter (vol %)	Entrainment[a] (vol %)	Total (vol %)
Test 1: Tank 37H/44F supernatant waste				
D-1	Waste raffinate	<0.007	0.019	≤0.026
D-2	Solvent	<0.02	—	<0.02
D-3	Strip raffinate	0.20	0.016	0.22
D-4	Wash raffinate	0.15	0.012	0.16
Test 2: Tank 37H dissolved salt waste				
D-1	Waste raffinate	<0.006	0.017	≤0.023
D-2	Solvent	<0.02	—	<0.02
D-3	Strip raffinate	0.07	0.051	0.12
D-4	Wash raffinate	0.16	0.012	0.17

[a]As determined by HPLC analysis of the aqueous phase.

accumulation in either the waste raffinate or the stripped solvent decanters. In the strip raffinate decanter and wash receipt decanter, the second-phase carryovers were estimated at ≤0.20% and ≤0.15%, respectively. These low values for second-phase carryover are another indication of the excellent hydraulic performance observed during the demonstration.

The observed values greatly exceed the partition coefficients previously measured for solvent components in simulated waste (2), suggesting that the compounds are present due to entrainment rather than solubility. The measured partition coefficients suggest that modifier concentrations due to solubility should be less than 5 mg/L.

Stage Data

Researchers estimated the stage efficiencies by comparing the cesium concentration data from the stage samples taken at the end of each test. The observed stage data were compared to calculated concentrations obtained from the Spreadsheet Algorithm for Stagewise Solvent Extraction (SASSE) (5). SASSE-calculated cesium concentrations for each stage at 5% efficiency increments were compared to the measured stage concentrations. The comparison is based on the slope of the lines through the predicted and measured values and not on the overlap of the predicted values with the measured data points. The slopes match well with extraction and strip stage efficiencies of 80–90%. Figure 6 shows the SASSE results and contains the waste raffinate, strip effluent, and stripped solvent cesium concentrations from the end of the test, plotted against the stage from which the streams exit the contactor apparatus.
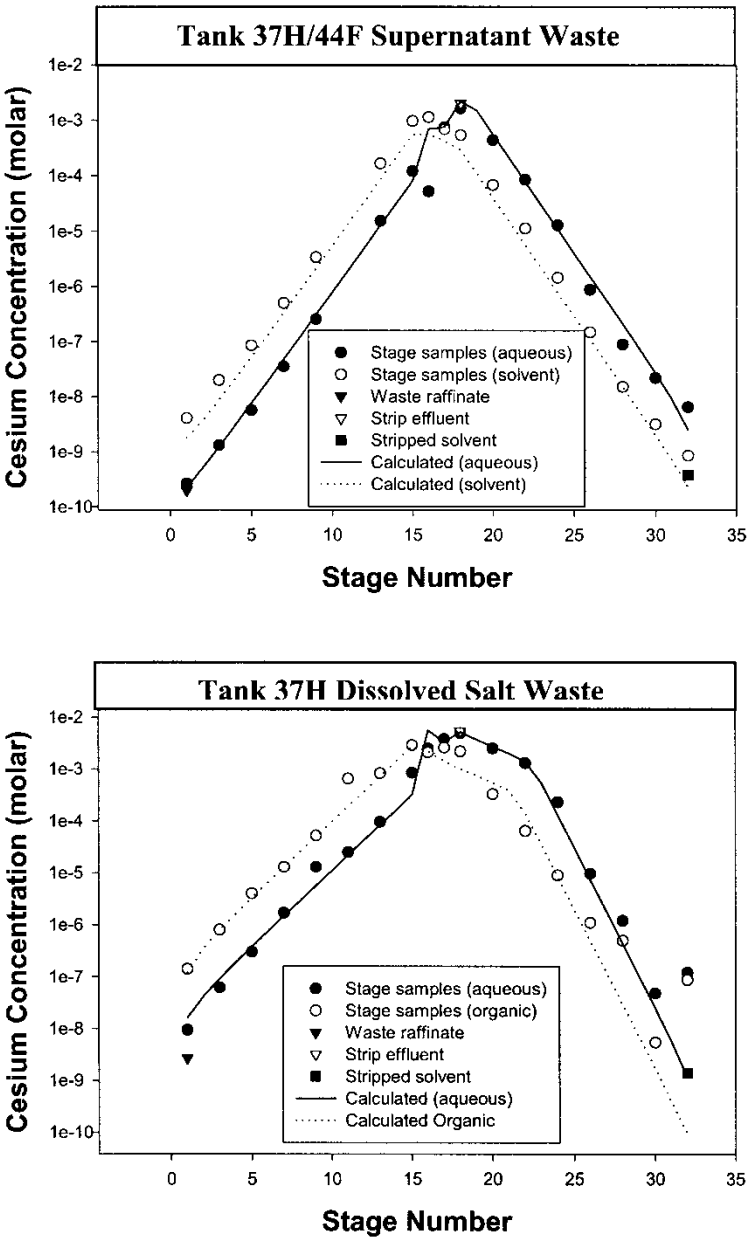
Figure 6. Comparison of stage sample data and SASSE calculated concentrations.

Table 4.   Temperature ranges for contactor sections

Contactor section	Target (°C)	Temperature range (°C)	
		Tank 37H/44F	Tank 37H Dis. Salt
Extraction	>20 and <25	21–26	21–26
Scrub	>20	30–37	32–37
Strip	>20	33–40	35–42

Stage Temperatures

Thermocouples attached to the outside of contactor stages in each section of the test apparatus measured temperatures during the test campaign. The temperatures in each section remained fairly stable within the ranges shown in Table 4. It should be noted that the wash stage temperature is included in the extraction section temperature range. Typically, temperatures for stages where process streams enter the contactors are significantly higher or lower than other stages in that section. For example, Stage 1 typically measured 25°C to 26°C compared to 21°C to 24°C for other extraction stages. In this case, the higher temperature of Stage 1 is caused by injection of warm solvent that recently exited the much-warmer strip section.

CONCLUSIONS

Researchers demonstrated the CSSX process flow sheet for the decontamination of Tank 37H/44F composite high-level waste supernatant solution and Tank 37H dissolved salt cake waste using an optimized solvent mixture in a 33-stage, 2-cm centrifugal contactor. Two tests with actual waste solution show the optimized solvent composition exhibits excellent hydraulic performance and meets process requirements for waste decontamination, solvent carryover and stability, and stage efficiency.

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