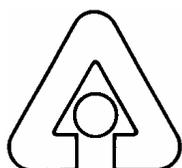


Chemical Technology
Division
Chemical Technology
Division
Chemical Technology
Division
Chemical Technology
Division
**Chemical Technology
Division**
**Chemical Technology
Division**
**Chemical Technology
Division**
Chemical Technology
Division
Chemical Technology
Division

Simulant Flowsheet Test with Modified Solvent for Cesium Removal Using Caustic-Side Solvent Extraction

by R. A. Leonard, S. B. Aase, H. A. Arafat,
C. Conner, J. R. Falkenberg,
M. C. Regalbuto, and G. F. Vandegriff



Argonne National Laboratory, Argonne, Illinois 60439
operated by The University of Chicago
for the United States Department of Energy under Contract W-31-109-Eng-38

Chemical Technology
Division
Chemical Technology
Division
Chemical Technology
Division
Chemical Technology
Division

Argonne National Laboratory, with facilities in the states of Illinois and Idaho, is owned by the United States Government and operated by The University of Chicago under the provisions of a contract with the Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor The University of Chicago, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or The University of Chicago.

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

ANL-02/22

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

**SIMULANT FLOWSHEET TEST WITH MODIFIED SOLVENT FOR CESIUM
REMOVAL USING CAUSTIC-SIDE SOLVENT EXTRACTION**

by

Ralph A. Leonard, Scott B. Aase, Hassan A. Arafat, Cliff Conner, John R. Falkenberg,
Monica C. Regalbuto, and George F. Vandegrift

Chemical Technology Division

April 22, 2002

CONTENTS

	<u>Page</u>
ABSTRACT	1
I. INTRODUCTION.....	1
II. EQUIPMENT AND MATERIALS	4
III. HYDRAULIC PERFORMANCE.....	8
IV. TEST PREPARATIONS.....	11
V. RESULTS.....	14
VI. DISCUSSION	18
VII. SUMMARY AND CONCLUSIONS.....	19
ACKNOWLEDGMENTS.....	20
APPENDIX A. ADDITIONAL INFORMATION ON HYDRAULIC PERFORMANCE.....	21
1. Single-Stage Operation.....	21
2. Four-Stage Operation	22
APPENDIX B. ADDITIONAL INFORMATION ON TEST PREPARATIONS	24
1. Contactor Block Temperature Measured by Two Different Methods.....	24
2. Change in Solvent Density	25
APPENDIX C. ADDITIONAL RESULTS	27
1. Measurements before the Test.....	27
2. Measurements and Observations during the Test.....	28
3. Measurements after the Test.....	34
4. Diluent Loss Rate	39
REFERENCES.....	41

FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	CSSX Flowsheet for 12-h Test (CS29).....	3
2.	Schematic of Operating Contactor Stage	5
3.	Cartridge Filter for SRS Simulant (DF) Feed	7
4.	Thermocouple Wires on Body of 2-cm Contactor	12
5.	Equipment Layout	13
6.	Changes in Decontamination Factor vs. Time for Test CS29	15
7.	Changes in Concentration Factor vs. Time for Test CS29.....	16
8.	Changes in Stripping Factor vs. Time for Test CS29.....	17
B-1.	Effect of Block Temperature on Temperature Difference between Two Methods.....	25
C-1.	Average Block and Effluent Temperatures during Test CS29	33
C-2.	Average Liquid Levels during Test CS29	34
C-3.	Cs Concentration Profile at End of Test CS29.....	39

TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Composition of Average SRS Simulant.....	6
A-1.	Hydraulic Performance of Single-Stage, 2-cm Contactor Using the Modified CSSX Solvent with Various Aqueous Phases.....	22
A-2.	Hydraulic Performance of Four-Stage, 2-cm Contactor Using the Modified CSSX Solvent with Various Aqueous Phases	23
B-1.	Contactor Block Temperature Measured by Two Different Methods.....	25
B-2.	Change in CSSX Solvent Density with Time in 2-cm Centrifugal Contactor	26
C-1.	D_{Cs} Values from Batch-Equilibrium Measurements before Test CS29	28

TABLES (continued)

<u>No.</u>	<u>Title</u>	<u>Page</u>
C-2.	Aqueous (DW) Raffinate for Test CS29	29
C-3.	Aqueous Strip (EW) Effluent for Test CS29	30
C-4.	Solvent Wash (FW) Effluent for Test CS29	31
C-5.	Organic (EP) Effluent for Test CS29	32
C-6.	Effluent Concentrations during Test CS29	35
C-7.	Overall Material Balance for Cs during Test CS29	36
C-8.	Cs Concentration in Equilibrated Stage Samples from Test CS29	37

SIMULANT FLOWSHEET TEST WITH MODIFIED SOLVENT FOR CESIUM REMOVAL USING CAUSTIC-SIDE SOLVENT EXTRACTION

by

Ralph A. Leonard, Scott B. Aase, Hassan A. Arafat, Cliff Conner, John R. Falkenberg,
Monica C. Regalbuto, and George F. Vandegrift

ABSTRACT

A modified solvent has been developed at Oak Ridge National laboratory (ORNL) for a caustic-side solvent extraction (CSSX) process that removes cesium (Cs) from Savannah River Site (SRS) tank waste. The modified solvent was evaluated using the same CSSX flowsheet, SRS simulant, and 33-stage minicontactor (2-cm centrifugal contactor) that had been used to test the previous CSSX solvent. As with the previous solvent, the key process goals were achieved: (1) the Cs was removed from the waste with decontamination factors greater than 40,000 and (2) the recovered Cs was concentrated by a factor of 15 in dilute nitric acid. Thus, the modified CSSX solvent can be used in place of the previous solvent while maintaining satisfactory hydraulic performance and still achieving process requirements at the bench scale.

I. INTRODUCTION

Savannah River Site (SRS) has 34 million gallons of high-level waste in 48 tanks that need to be decontaminated [LEVENSON-2000]. As a part of this process, cesium (Cs) will be removed from waste containing both supernatant liquid and dissolved salt cake, then vitrified for disposal. After the Cs is removed, the decontaminated solution will be immobilized in low-level grout.

To address the problem of removing Cs from alkaline solutions such as DOE tank wastes at Savannah River, South Carolina, and Hanford, Washington, a new extractant was developed at Oak Ridge National Laboratory (ORNL) that is very specific for Cs [BONNESEN-1998]. The new extractant is a calixarene-crown ether, calix[4]arene-bis(*tert*-octylbenzo-crown-6), designated BOBCalixC6. BOBCalixC6 is one component in a four-component solvent. The other three components are (1) a modifier, 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, also called Cs-7SB, which is an alkyl aryl polyether that keeps the extractant dissolved in the solvent and increases the ability to extract Cs in the extraction section;

(2) a suppressant, trioctylamine (TOA), which suppresses effects from anionic organic impurities so that the Cs can be back-extracted from the solvent in the strip section; and (3) a diluent, Isopar[®]L, which is a mixture of branched hydrocarbons. In earlier tests of the CSSX flowsheet to prove the concept [LEONARD-2000, -2001A] and to demonstrate multiday operation [LEONARD-2001B, -2002], the solvent composition was 0.01 M BOBCalixC6, 0.50 M Cs-7SB, and 0.001 M TOA in Isopar L. For the flowsheet test discussed in this report, a modified CSSX solvent was used. It is referred to hereafter as the “CSSX solvent.” Its composition is 0.007 M BOBCalixC6, 0.75 M Cs-7SB, and 0.003 M TOA in Isopar L [KLATT-2002]. With this change in composition, the CSSX solvent is no longer supersaturated with respect to BOBCalixC6. The modified solvent also has added resistance to third-phase formation at lower plant operating temperatures and to organic impurities that could limit back-extraction of the Cs from the solvent. The solvent density at 25°C is increased from 823 to 852 g/L. The Cs distribution ratios are changed only slightly.

The purpose of the test reported here was to demonstrate the CSSX process using the modified solvent. In this test, 30 L of SRS simulant was to be processed in 12.0 h as the modified solvent was recycled 9.8 times. As with the earlier solvent, the modified solvent was evaluated by seeing if it achieved both key CSSX process goals: (1) removing Cs from the waste with decontamination factors greater than 40,000 and (2) concentrating Cs by a factor of 15 in dilute nitric acid. The flowsheet for the 12-h test, given in Figure 1, shows the nominal flow rates for the test. Except for the solvent, this flowsheet is the same as that for the multiday test [LEONARD-2002]. In this test, designated “CS29,” 1.15 L of CSSX solvent was used to process 36.3 L of SRS simulant in 13.8 h as the solvent was recycled 11.2 times.

This work is part of the integrated research and development program supporting the SRS High-Level Waste Salt Processing Project (SPP). The research and development program is managed by the Pacific Northwest National Laboratory, Tanks Focus Area. This work was performed in collaboration with the Savannah River Technology Center (SRTC), ORNL, and the Idaho National Engineering and Environmental Laboratory (INEEL). At the time the work reported here was being performed, SRTC personnel were preparing for a CSSX flowsheet test with actual waste in the 2-cm centrifugal contactor using the modified solvent. Meanwhile, personnel at ORNL were working on solvent development and commercialization, and INEEL personnel were evaluating the hydraulics of the modified solvent in a larger (5.5-cm) single-stage contactor. The 12-h test at Argonne National Laboratory (ANL) is a key part of this solvent extraction effort, as it is the first demonstration of the operability of the full CSSX process with the modified solvent.

In the overall SPP work, the CSSX process was compared with two alternatives that also remove Cs from tank waste. These processes were (1) small-tank tetraphenylborate precipitation (STTP), where tetraphenylborate is used to precipitate out the Cs in small tanks, and (2) crystalline silicotitanate nonelutable ion exchange (CST), where crystalline silicotitanate is used to remove the Cs in packed beds [LEVENSON-2000]. In July 2001, the CSSX process was chosen as the Cs removal step designed for treatment of SRS tank waste at the Salt Waste Processing Facility (SWPF). For further information, see the Savannah River Site Salt Processing Alternatives Final Supplemental Environmental Impact Statement, DOE/EIS-0082-S2D, which was released to the public on July 20, 2001. The official selection of CSSX as the Record of Decision was in October 2001; see the Federal Register, Vol. 66, No. 201, pp. 52752–52756, October 17, 2001.

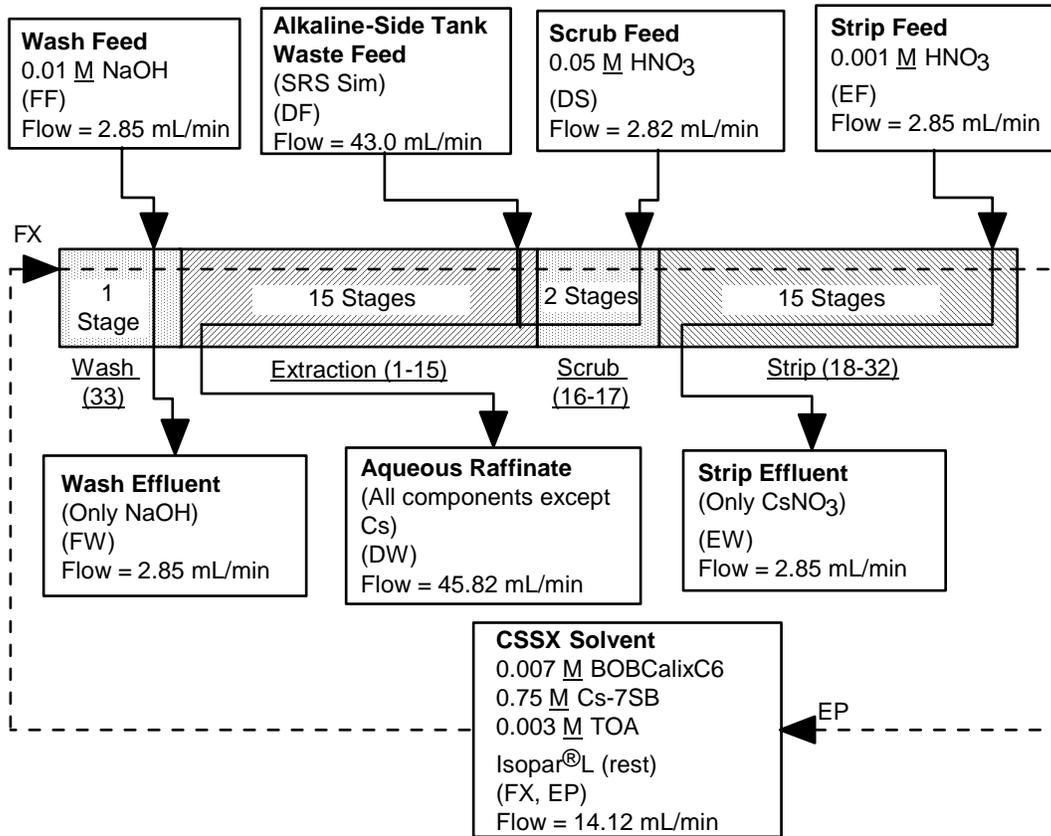


Fig. 1. CSSX Flowsheet for 12-h Test (CS29)

II. EQUIPMENT AND MATERIALS

This solvent extraction test was performed in a 33-stage, 2-cm annular centrifugal contactor located in an ANL glovebox. A schematic of an operating contactor stage is given in Figure 2. The contactor, which is manufactured in banks of four stages, was built at ANL (see ANL print number CMT-E1265, entitled "2-cm Contactor" and dated 1/6/94). These contactor stages were modified in FY2000 to improve stage efficiency to $88 \pm 4\%$ [LEONARD-2001A] and in FY2001 to improve hydraulics [LEONARD-2002]. Because the distribution ratio for Cs is very sensitive to temperature, increasing with decreasing temperature, the stages in the extraction section must be kept between 20 and 32°C. For purposes of plant design, the upper temperature limit in the extraction section has been set at 25°C, a conservative value that will make the CSSX process even more robust. If the stages in the extraction section get too hot, they will no longer be able to maintain the desired decontamination factor. If they get too cold, a second organic phase could form. A water-cooled chiller bar was used to control the temperature of the extraction section [LEONARD-2002]. The water, which was at 7.5°C, was recirculated from a cooling bath located outside the glovebox. The temperature inside the glovebox during the test was $23 \pm 1^\circ\text{C}$. Using the chiller bar, the block temperatures in the extraction section reached $28 \pm 2^\circ\text{C}$ during the test while the temperatures of aqueous raffinate (effluent) were $26 \pm 2^\circ\text{C}$. Since higher temperatures improve stripping, no chiller bar was attached to the strip section. The block temperatures there reached $41 \pm 2^\circ\text{C}$ during the test while the temperatures of the strip effluents were $31 \pm 2^\circ\text{C}$. No chiller bar was attached to either the scrub or wash sections, as the temperature in these two sections is not so important.

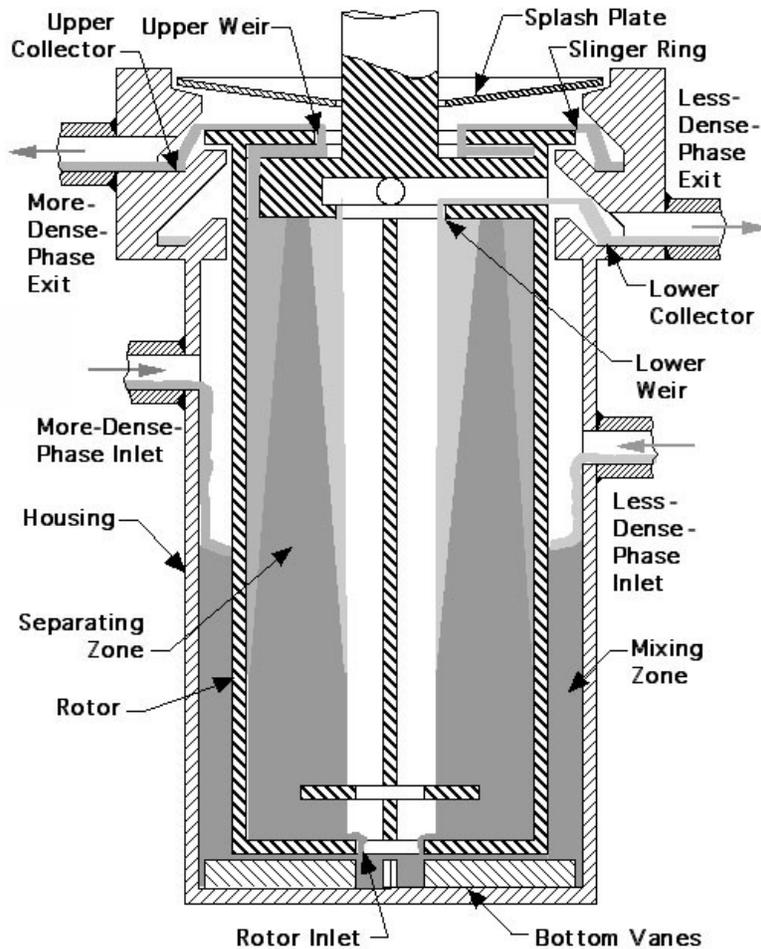


Fig. 2. Schematic of Operating Contactor Stage

For the 12-h CSSX flowsheet test, a highly alkaline simulant for tank supernate waste was prepared using a method supplied by SRS personnel [PETERSON-2000]. It has the composition given in Table 1 and is designated the "SRS simulant." Based on its composition, its estimated density is 1258 g/L at 22°C [WALKER-1998]. Its measured density was 1249.6 ± 1.4 g/L at 17.5°C. Assuming the effect of temperature on the density of the SRS simulant is the same as that for water, which is -0.21 g/L between 18 and 22°C, the density of the simulant would be 1248.7 g/L at 22°C. When the 30 L of SRS simulant were blended with the 8 L of leftover simulant from the multiday test [LEONARD-2002], the density of the blend was 1237.3 ± 0.9 g/L at 18.2°C. The continuing formation of solids in the leftover simulant apparently lowered the density of the filtered solution. When the density of the leftover simulant was measured a year earlier, just before the multiday test, it was 1250.8 ± 2.6 g/L at 22 ± 3 °C. The density of this simulant was not measured again. Before the 12-h test, the SRS simulant was spiked with 1.0 mCi/L of ^{137}Cs . Because of concerns about being able to measure a decontamination factor of 40,000, the ^{137}Cs spike was twice as concentrated as that used in the

multiday test. The scrub feed was 0.05 M HNO₃, the strip feed was 0.001 M HNO₃, and the solvent wash feed was 0.01 M NaOH. All four aqueous feeds were prepared at ANL.

Table 1. Composition of Average SRS Simulant

Component	Conc., mol/L	Component	Conc., mg/L
Na ⁺	5.6	Copper	1.44
K ⁺	0.015	Chromium	75
Cs ⁺	0.00014 ^a	Ruthenium	0.82
OH ⁻	2.06	Palladium	0.41
NO ₃ ⁻	2.03	Rhodium	0.21
NO ₂ ⁻	0.50	Iron	1.44
AlO ₂ ⁻	0.28	Zinc	8
CO ₃ ²⁻	0.15	Tin	2.4
SO ₄ ²⁻	0.14	Mercury	0.05
Cl ⁻	0.024	Lead	2.1
F ⁻	0.028	Silver	0.01
PO ₄ ³⁻	0.007	Tri-n-butyl phosphate (TBP)	0.5
C ₂ O ₄ ²⁻	0.008	Di-n-butyl phosphate (DBP)	25
SiO ₃ ²⁻	0.03	Mono-n-butyl phosphate (MBP)	25
MoO ₄ ²⁻	0.000078	n-Butanol	2
NH ₃	0.001	Formate	1500
		Tri-methylamine (TMA)	10

^a This is the total Cs concentration in the average SRS tank waste. It is the Cs concentration used here with the addition of ¹³⁷Cs at a tracer level of 1.0 mCi/L. The ¹³⁷Cs concentration in the average SRS tank waste is 22.6% of the total Cs concentration.

After the SRS simulant was prepared, it was filtered using a pleated cartridge filter made of polypropylene with a pore size of 0.45 μm. The cartridge filter, available from Cole-Parmer (Vernon Hills, Illinois; see catalog no. U-29830-10), is 10 in. (25.4 cm) long in a 304 stainless steel housing with a forged brass cap that is nickel plated. The filter has a throughput of 1 to 10 gpm (3.8 to 38 L/min), a filter area of 9.87 ft² (0.917 m²), and a maximum pressure of 250 psi (1.72 MPa). Because of the continuing formation of solid particles in the SRS simulant, it was filtered again just before being pumped to the contactor as the DF feed (see Fig. 1 for stage nomenclature). This cartridge filter was located inside the glovebox. The top of the filter can be seen in Figure 3, behind the two 4-L DF feed tanks.



Fig. 3. Cartridge Filter for SRS Simulant (DF) Feed

A “four-component simulant” was used for hydraulic testing of the 2-cm contactor, operator training and the shakedown test (CS28), and the startup of the 12-h CSSX flowsheet test (CS29). This simulant approximates the composition of the SRS simulant. It is prepared by dissolving 127.48 g of NaOH first, then 105.04 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 34.5 g of NaNO_2 , and 99.85 g of NaNO_3 in water for each liter of solution. As this simulant is prepared, NaOH reacts with $\text{Al}(\text{NO}_3)_3$ as follows:



Thus, the final ionic composition of the four-component simulant is 4.86 M Na^+ , 2.07 M OH^- , 2.01 M NO_3^- , 0.5 M NO_2^- , and 0.28 M AlO_2^- . It has an estimated density of 1226 g/L at 22°C [WALKER-1998]. Its measured density was 1215 ± 2 g/L at 22°C.

The CSSX solvent for test CS29 was prepared by Peter Bonnesen at ORNL and shipped to ANL. The solvent density for this batch, 190W, was 851.6 ± 1.7 g/L at 25°C when measured

at ORNL before shipping. It was 852.0 ± 1.1 g/L at 25°C when measured at ANL after receipt of the shipment. The earlier CSSX solvent for test CS28 was also prepared by Peter Bonnesen at ORNL and shipped to ANL. The solvent density for this batch, 150W, was 851.8 ± 1.7 g/L at 25°C when measured at ORNL before shipping. It was 840.6 ± 0.9 g/L at 25°C when measured at ANL after receipt of the shipment. When this solvent batch was examined closely, it was found to have stratified with a more-dense layer at the bottom of the solvent bottle. This layer was not a separate phase, but a more-dense region within the solvent. When the density was measured, the less-dense liquid above the more-dense region was taken as the density sample. Thus, the measured sample had a lower density than expected. When the solvent bottle was shaken, schlieren patterns could be seen as the more-dense liquid mixed with the rest of the solvent. After the initial mixing of the two regions, the schlieren patterns disappeared and did not reappear. The solvent density was re-measured and found to be 853.0 ± 1.0 g/L at 25°C . This is in reasonable agreement with the original density measurements at ORNL. Based on a discussion with Peter Bonnesen of ORNL, it is possible that such a solvent separation could occur if the solvent had been cooled down to or below 0°C . Shipping records showed that the 150W batch was shipped from ORNL by ground UPS on Friday, January 18, 2002, and arrived at ANL on Wednesday, January 23, 2002. The UPS truck was not heated. Weather records show that the solvent could have experienced temperatures as low as 12°F (-11°C). It is thought that these low temperatures, especially with some residual water in the solvent from the final solvent wash, allowed the partial separation of the solvent to occur. Mixing the partially separated solvent corrected the problem with no apparent harm to the solvent. The D_{Cs} values for the solvent, which had been 10.1 ± 1.1 for the less-dense region, increased to 12.8 ± 0.3 after mixing. This increase put D_{Cs} close to 14.1 ± 0.3 , the value measured at ORNL before batch 150W was shipped.

Recent work at ORNL has confirmed that CSSX solvent will stratify at low temperatures. When the two phases were warmed and remixed, solvent properties were restored [DELMAU-2002].

III. HYDRAULIC PERFORMANCE

The hydraulic performance of a 33-stage, 2-cm centrifugal contactor was improved in FY2000 so that stage efficiency was increased during multistage operation. This increase was needed to carry out a full test of the CSSX flowsheet [LEONARD-2001A]. The most important change was smoothing the flow between stages. This smooth flow occurs naturally in larger contactors with interstage flows greater than 50 to 100 mL/min [LEONARD-1999, -2001C].

This range of flow rates defines a transitional region between lower flow rates where liquid surface tension controls (releasing the liquid from the collector ring in discrete liquid slugs, which is called slug flow) and higher flow rates where liquid momentum controls (driving the liquid from the collector ring as a continuous stream). For smaller units with lower flow rates, the stage efficiency was increased from 60 to 90% by using a wire rope in each interstage line to smooth out the interstage flow and increase the liquid level in the annular mixing zone [LEONARD-2001A]. In subsequent testing of the CSSX flowsheet, a solvent wash stage was added so that there were 33 contactor stages.

The hydraulic performance of the 33-stage, 2-cm centrifugal contactor was further improved in FY2001 so that liquid levels in the interstage lines were reduced. If the levels get high enough, contactor flooding can occur. Flooding causes significant other-phase carryover and can shut down the contactor. These improvements were needed to ensure good contactor operation for the duration of a multiday test of the CSSX flowsheet. The improvements were obtained by (1) using a plastic insert to reduce the resistance to flow between the stages and (2) increasing the diameter of the upper rotor weir so that the maximum throughput for the extraction section is increased [LEONARD-2002]. As a general rule of thumb, a multistage contactor should be operated at no more than 50 to 67% of its maximum throughput for single-stage operation. When new contactors are built, the need for inserts can be eliminated by making the inlet lines tangential (or nearly tangential), rather than perpendicular, to the spinning rotor.

With these changes, the hydraulic performance of the 2-cm centrifugal contactor was very good for the CSSX flowsheet. However, it had to be checked with the modified solvent to be sure that nothing had changed. Of special concern was the higher density of the modified solvent. This could cause a problem when operating with aqueous phases having densities close to water, since the density of the two phases would be closer than before. When the densities are too close, the contactor rotor must be adjusted by reducing the diameter of the more-dense-phase (upper) weir so that it is closer to that of the less-dense-phase (lower) weir. However, the diameters of the upper weirs had just been enlarged to get better performance for the previous CSSX solvent. There was no easy way to make them smaller. If the diameter of the upper weir were too large, one would get significant (>1%) organic phase in the aqueous effluent.

When the hydraulic performance of the 2-cm centrifugal contactor was evaluated with the modified solvent and the various aqueous phases for the CSSX flowsheet, it was found to be very good. In the extraction section, the maximum throughput for single-stage operation was 105 ± 15 mL/min. When this maximum throughput was exceeded, a carryover of >1% aqueous phase in the organic effluent was observed. For four-stage operation, operation was okay at the

planned operating conditions for the extraction section. This section has the highest throughput, with 45.8 mL/min of aqueous phase and 14.12 mL/min of organic phase, for a total flow rate of 60 mL/min.

As the solvent wash section is only one stage, the evaluation of hydraulic performance was only for one-stage operation. This was done by operating at a total flow rate of 40 mL/min and an organic/aqueous (O/A) flow ratio of 5. Hydraulic performance was tested over the full range of flow conditions by making the unit pass through every O/A flow ratio as it approached a flow ratio of 5. This was done by starting in both initially aqueous- and organic-continuous modes, as described in Appendix A. No problems were observed during these approaches to steady-state operation. The flow rate used was much higher than the 16.97 mL/min required for the CSSX flowsheet.

The hydraulic performance in the scrub and strip sections was evaluated by testing the strip section. The maximum throughput for single-stage operation was 72 ± 8 mL/min. When the maximum throughput was exceeded, a carryover of >1% aqueous phase in the organic effluent (>1% A in O) was observed. Four-stage operation was generally okay at the planned operating conditions of 2.85 mL/min of aqueous phase and 14.12 mL/min of organic phase, for a total flow rate of 16.97 mL/min. In one case, starting initially in the aqueous-continuous mode, >1% O in A was seen in the aqueous effluent from stage 1. To correct this situation, the rotor at stage 1 was turned off for two minutes while the aqueous and organic flows were continued. The organic phase backed up in the organic interstage line between stages 1 and 2. When the rotor was turned back on, the amount of organic phase in the aqueous effluent had become undetectable. Earlier, turning off the rotor for 0.5 and 1 min did not clear the organic phase in the aqueous effluent. In a second case, starting initially in the organic-continuous mode, >1% O in A was seen in the aqueous effluent from stage 1. To correct this situation, all pumps and rotors were turned off for 0.5 min. When everything was restarted, the amount of organic phase in the aqueous effluent had become undetectable. If 0.5 min had not worked, longer times (1, 2, or 5 min) would have been used. This rest time gives the dispersion in the mixing zone a chance to coalesce. Subsequent attempts to recreate >1% organic phase in the aqueous effluent were not successful.

While doing the 4-stage hydraulic performance tests under the strip-section conditions, a liquid level of 50 to 60% was observed in one of the interstage lines on the organic side, the line going from stage 1 to stage 2. Inspection of stage 2 showed that the insert for the organic inlet did not extend into the mixing zone. When the insert was adjusted so that it extended 0.8 mm into the mixing zone, the liquid level in the interstage line dropped to 10–20%. This adjustment

demonstrates how inserts reduce the flow resistance for the interstage liquid entering the mixing zone.

Further details on the hydraulic performance of the 2-cm contactor prior to the 12-h test are given in Appendix A.

IV. TEST PREPARATIONS

Preparations for the 12-h test (CS29) were similar to those used for the multiday test [LEONARD-2002]. Work was done on the contactor housings, rotor bodies, and feed tanks, and included training personnel and an operational readiness review. The contactor housings and the rotor bodies were cleaned before the test. As the motor/rotor assemblies were mounted, they were tested to be sure that rotor speed and direction of rotation were correct, the rotor runout was within specifications, and rotor rotation was not hindered by the contactor housing, the wire rope, or the insert. In the multiday test, digital thermometers were used to measure stage temperatures. They were attached to the center of the large stainless steel block that forms the top part of the contactor housing containing the collector rings and the upper mixing zone. In test CS29, they were replaced with thermocouples that can be seen in Figure 4. All of the thermocouples were connected to a single readout device that could be set manually to access any thermocouple. To simplify installation, the readout device was put in the glovebox.

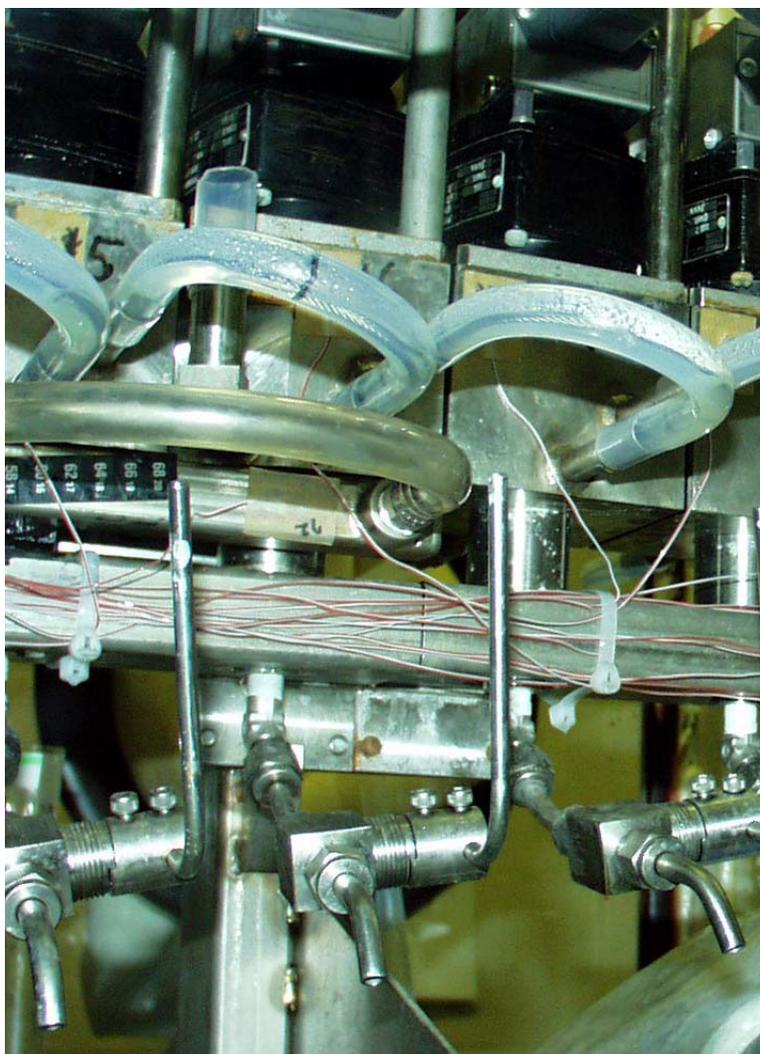


Fig. 4. Thermocouple Wires on Body of 2-cm Contactor

The DF feed tank was 50 L, which was much smaller than the 207-L drum used for the multiday test. The smaller tank was used because test CS29 only needed to run for 12 h. As shown in Figure 5, the tank was located in a limited access area outside the glovebox to minimize radiation exposure to personnel during the test. The hot DF feed was pumped to a 4-L pre-filter feed tank inside the glovebox. A second pump pushed the DF feed through the DF cartridge filter to the 4-L DF feed tank. A third pump transferred the DF feed to the contactor at stage 15 at the desired flow rate. During startup, a cold (nonradioactive) four-component simulant was used as the DF feed. It did not use the hot DF feed line into the glovebox. Instead, the cold simulant was bagged into the glovebox in 4-L bottles and was fed directly to stage 15 using only the third pump. Only one low-level waste (raffinate) drum was required. As shown in Figure 5, it was located in a limited access area outside the glovebox to minimize the number of bag-outs required during the test. All of the DW raffinate was pumped to this tank along with the FW

this training, general readiness for the 12-h test was evaluated, including final checks of the equipment, the hydraulic performance of the contactor, the log sheets developed to record pertinent data and observations, the startup and shutdown procedures, and process operations designed to minimize individual and collective radiation doses. The laboratory training was very important and could not be replaced with more classroom training. While the two-shift operation worked well, three-shift operation is recommended for longer multiday tests.

For test CS28, the CSSX flowsheet was run cold, that is, with no radioactive Cs. The apparent ^{137}Cs concentration was measured in the various effluent streams. The results showed that ^{137}Cs measurements could not be made at the low concentrations required to detect a decontamination factor of 40,000. This problem occurred because the contactor test prior to test CS28 was a flowsheet test using U, Pu, Np, and Tc. The residual contamination from these elements gave an alpha component in the liquid scintillation counting that precluded seeing ^{137}Cs at the low concentrations required. To get around this, the contactor was further cleaned with water until doing so no longer proved effective. This procedure was repeated with 1 M HNO_3 . It was repeated again with a mixture of 1 M HNO_3 and 0.05 M HF. Finally, a mixture of 1 M HNO_3 and 0.2 M HF was used only once, as the drain liquid showed some color, indicating that the stainless steel of the contactor had been attacked by the HF. In the end, gamma counting was used in place of liquid scintillation counting. By increasing the ^{137}Cs in the DF feed from 0.5 to 1 mCi/L, taking larger samples, and counting for long times, it was possible to detect ^{137}Cs at the low concentrations needed to measure a decontamination factor of 40,000.

Before test CS29 was started, our preparations were examined during an operational readiness review conducted by David Chamberlain of ANL on March 12, 2002. As a part of this review, the equipment and sample bottles were checked to see that they were properly labeled and corresponded with the procedure and log sheets. The safety review for the test and the radiation work permit were also reviewed along with the plans made to limit personnel radiation exposure.

Further details on test preparations prior to the 12-h test are given in Appendix B.

V. RESULTS

The CSSX process with the modified solvent was tested in a 33-stage, 2-cm centrifugal contactor using the flowsheet shown in Figure 1. This test was a nominal 12-h test that was carried out on March 19–20, 2002. The actual test time was 13.8 h (827 min). In the extraction

section, the solvent extracts Cs from the aqueous SRS simulant as the two phases flow countercurrent to each other. As the solvent flows from stage 1 to 15 (see Fig. 1), its Cs concentration increases; as the SRS simulant flows in the opposite direction, from stage 15 to 1, its Cs concentration decreases. The effectiveness of the extraction section is defined by the decontamination factor, which is the concentration of Cs in the aqueous SRS simulant (DF) entering stage 15 divided by that in the aqueous raffinate (DW) exiting stage 1. As shown in Figure 6, the average decontamination factor for the test CS29, $420,000 \pm 100,000$, exceeded the process goal of 40,000 by a factor of 10. In calculating the average, the first point at 5 min into the test ($1.4E+06$) was not included, as the process had not reached steady-state conditions. However, this point is shown in Figure 6.

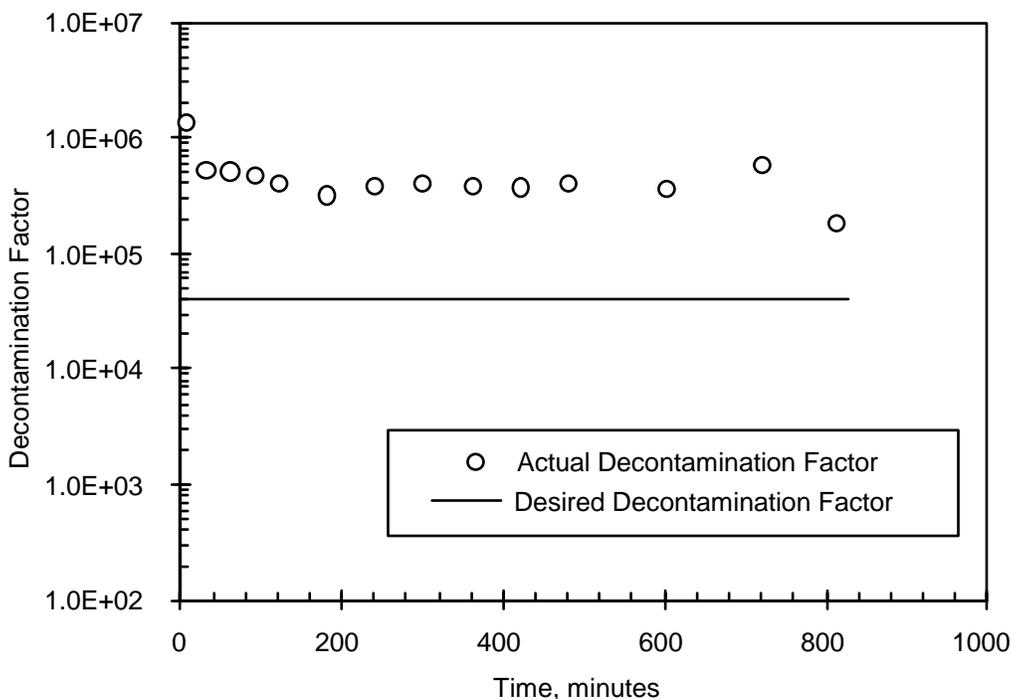


Fig. 6. Changes in Decontamination Factor vs. Time for Test CS29

The solvent leaving the extraction section at stage 15 is loaded with essentially all of the Cs that entered with the SRS simulant waste feed (DF). The solvent enters the scrub section, stages 16 and 17 in Figure 1, where weakly extracted impurities are removed along with any entrained aqueous phase. In addition, the entrained alkaline aqueous phase is neutralized and made slightly acidic. The scrubbed solvent then enters the strip section at stage 18. In the strip section, the Cs is recovered from the solvent and comes out in the aqueous strip effluent (EW). Since the flow of the aqueous strip feed (EF) is 1/15 of the aqueous waste feed (DF) flow, and since essentially all of the Cs entering in the DF feed goes out in the aqueous strip effluent (EW),

the Cs is concentrated by a factor of 15 in the EW effluent. This [EW]/[DF] ratio, called the concentration factor, is plotted in Figure 7 as a function of time for test CS29. The average value of the concentration factor is 15.5 ± 1.2 , which meets the second process goal. At 300 min into test CS29, the aqueous strip (EF) feed rate was determined to be high and was decreased by 7%. Before this change, the average concentration factor was 14.7 ± 0.3 ; afterwards, it was 16.5 ± 1.3 , an increase of 13%. These results show how the concentration factor depends on the waste (DF) and strip (EF) feed rates and is controlled by them. In calculating the average concentration factor, the first point at 5 min into the test (8.6) was not included, as the process had not reached steady-state conditions. However, this point is shown in Figure 7.

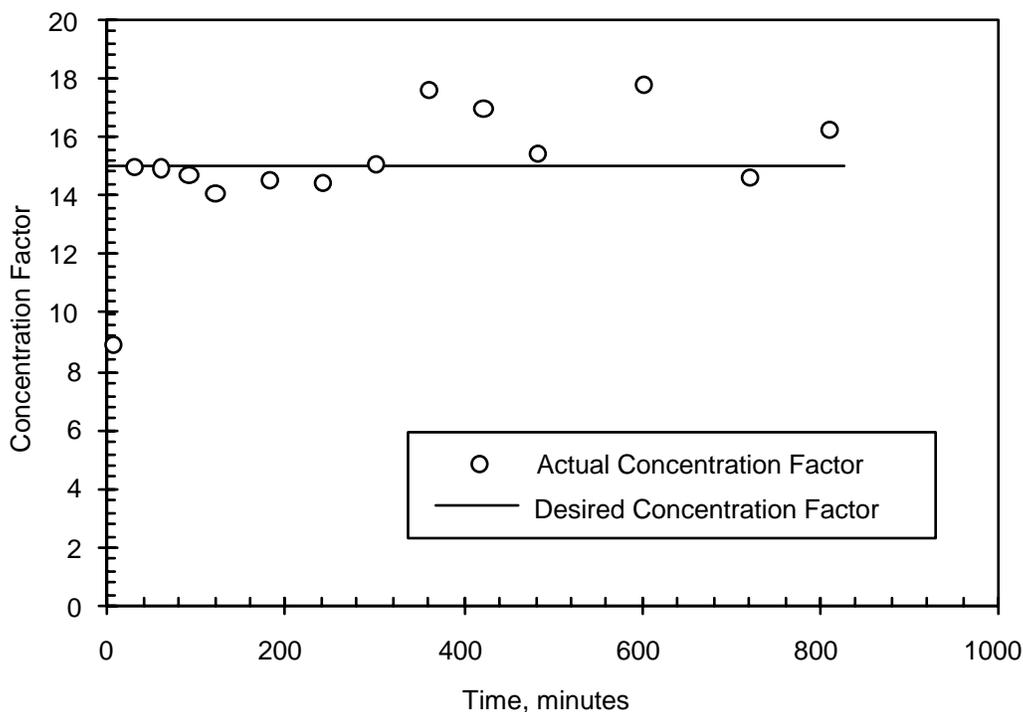


Fig. 7. Changes in Concentration Factor vs. Time for Test CS29

In the strip section, the solvent flows countercurrent to the aqueous strip solution of 0.001 M HNO_3 . This solution strips the Cs from the solvent. That is, as the solvent flows from stage 18 to 32, its Cs concentration decreases; as the aqueous strip solution flows in the opposite direction, from stage 32 to 18, its Cs concentration increases. The effectiveness of the strip section is defined by the stripping factor, which is the Cs concentration in the aqueous SRS simulant (DF) entering stage 15 divided by that in the organic effluent (EP) exiting stage 32. As shown in Figure 8, the average stripping factor for test CS29, $400,000 \pm 160,000$, exceeded the process goal of 40,000 by a factor of 10. The required stripping factor is the same as the decontamination factor so that the solvent can be recycled. The stripping factors at 480 and

600 min are not shown on the chart, as the EP concentrations were below the detection limit. However, the values for the average stripping factor were still high, >410,000 and >970,000, respectively.

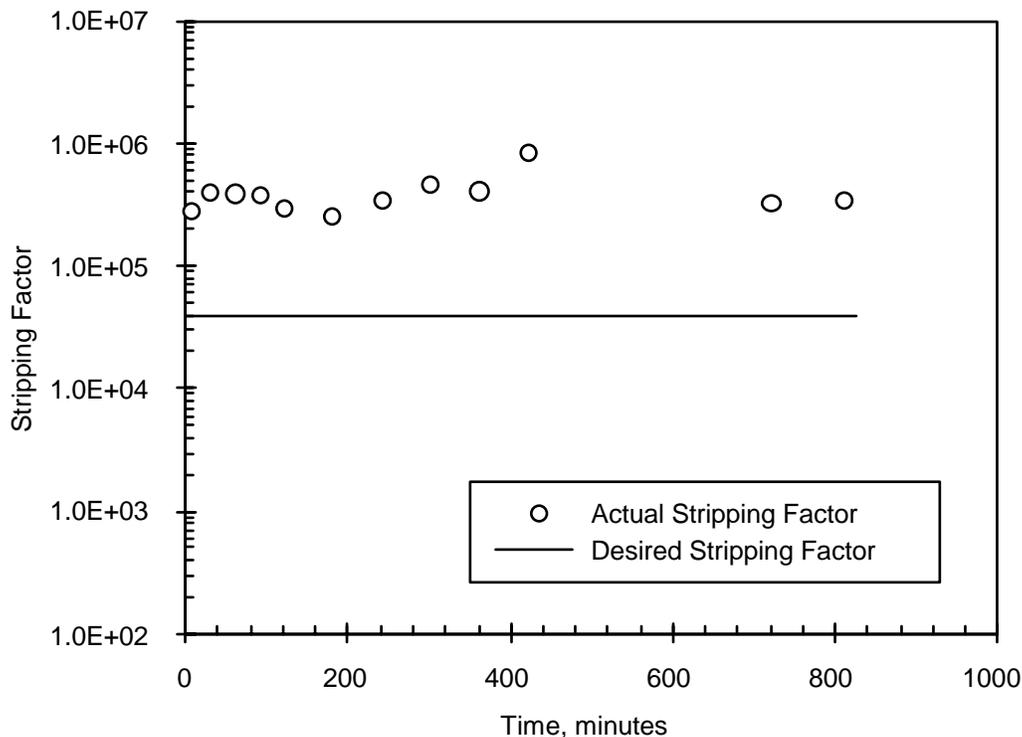


Fig. 8. Changes in Stripping Factor vs. Time for Test CS29

Thus, test CS29 met both process goals, that is, a decontamination factor >40,000 and a concentration factor of 15 were maintained while recycling the solvent 11 times over a test time of 13.8 h. No evidence of degradation in solvent performance was observed, based on the relatively constant values for the decontamination and stripping factors over the 13.8 h of the test. There was evidence of diluent evaporation, because solvent density at 25°C increased from 852.0 to 856.2 g/L over the 13.8 h of the test.

Additional results from the multiday test are given in Appendix C. This includes flow rates, temperatures, pH values, liquid levels in the interstage lines, Cs concentrations in the effluent streams, and Cs concentrations in both phases for each stage at the end of the test. The Cs concentration profile is compared with a computer model to determine stage efficiency. The calculations give an average stage efficiency of 85% for the extraction section and 92% for the strip section. These mass transfer efficiencies for multistage operation are similar to the 83 to 89% values seen during the multiday CSSX test [LEONARD-2002].

VI. DISCUSSION

A major concern at the start of hydraulic testing was that the diameter of the upper weirs of the rotors was too large for the higher solvent density. If this were the case, there would have been significant (>1%) organic phase in the aqueous effluent (>1% O in A). This was not seen at all for the single-stage tests. During some multistage tests, >1% O in A was occasionally seen. However, this behavior seemed to be path-dependent. It could be eliminated very simply by shutting down all of the rotors and pumps, letting the dispersions in each stage break, and restarting the contactor. Thus, it does not appear that the diameter of the upper weirs of the rotors was too large for the higher density of the modified solvent. During this hydraulic testing, it was shown again how important the inserts are in keeping the liquid level in the interstage lines low during multistage operation. If the inlet ports in future contactors are made tangential to the spinning rotor, it should be possible to eliminate the inserts.

The approach of the CSSX process to steady state can be followed by looking at the data for the concentration factor. The rate at which this factor approaches steady state is controlled by the rate at which the DF feed brings Cs into the contactor. The concentration factor was 8.9 at 5 min (0.08 h) into the test, 15.0 at 30 min (0.50 h), and 15.0 at 60 min (1.00 h). Thus, the CSSX process run in centrifugal contactors reaches steady state within 30 min (0.50 h).

Solids had been a problem in the multiday test [LEONARD-2002]. To avoid this, the DF feed was filtered again just before it was used. When the rotor in stage 15, the stage where any solids would enter, was inspected after the test, no white solids were seen on the inside wall of the rotor. Thus, with DF feed filtration immediately before processing, the solids problem seems to have been eliminated.

A simple density model was developed [LEONARD-2002] to predict the solvent density as a function of temperature and the concentrations of the extractant, modifier, suppressant, and diluent. The model assumes there is no interaction between solvent components that would affect their individual density contributions. In this model, BOBCalixC6 has a molecular weight of 1149.53 g/mol and a density of 1054 g/L at 25°C; Cs-7SB has a molecular weight of 338.35 g/mol and a density of 1173.5 g/L at 25°C; TOA has a molecular weight of 353.69 g/mol and a density of 809 g/L at 25°C; and Isopar L has a density of 759.7 g/L at 25°C. Finally, the effect of temperature on density for all components is -0.77 (g/L)/°C in the neighborhood of 25°C. With this model, the density of CSSX solvent at 25°C is calculated to be 851.5 ± 2.0 g/L. This agrees very well with the measurements made at ANL and ORNL. This model was used with the increase in solvent density to calculate the evaporative loss of diluent from the solvent.

Calculations were made to see if the diluent loss rate from the solvent was consistent with the estimated diluent vapor pressure. The diluent loss rate was calculated in two different ways: (1) making a material (volume) balance for the solvent and (2) using the change in solvent density with the final solvent volume. The vapor pressure for Isopar L was estimated from data supplied by the manufacturer to be 31 Pa at 20°C and 124 Pa at 40°C. The observed diluent losses could be explained for test CS29 by using these vapor pressures along with an estimate of the total gas flow through the 2-cm contactor. The results suggest that, if the gas (air) flow through the contactor can be reduced, the diluent loss rate would be decreased. See Appendix C for details.

VII. SUMMARY AND CONCLUSIONS

In preparation for the 12-h test, the hydraulic performance of the 2-cm contactor with the modified CSSX solvent was tested and found to be just as good as with the previous CSSX solvent. This good hydraulic performance was demonstrated for both single-stage and multistage operation.

During the training test, the contactor was found to have alpha contamination from the previous flowsheet test, which had used a lot of U, Pu, Am, and Np. There was enough alpha contamination to prevent measuring a Cs decontamination factor of 40,000 using liquid scintillation. Efforts to remove this material could not get the contamination down to a level at which liquid scintillation could be used. The contamination could get down to a level where gamma activity could be used if the amount of ^{137}Cs per unit volume were doubled, the sample volumes were increased, and the counting times were made longer. The concentration profile measured at the end of the test (see Fig. C-3 in Appendix C) shows that the Cs concentration changed more smoothly from stage to stage than was seen earlier in the multiday test [LEONARD-2002]. This is attributed to the additional cleaning that the contactor received.

Using the modified solvent, the CSSX process to remove Cs from SRS high-level waste was tested for 12 h in a 33-stage, 2-cm centrifugal contactor. This demonstration of the CSSX flowsheet used an average SRS simulant for the waste feed. The two key process goals were achieved and maintained: (1) the Cs was removed from the waste with decontamination factors greater than 40,000 and (2) the recovered Cs was concentrated by a factor of 15 in dilute nitric acid. In this test, 1.15 L of solvent was recycled a total of 11 times while processing 36 L of SRS simulant. The Cs had an average decontamination factor of 420,000 and an average concentration factor of 15.5. The average stage efficiency was 85% for the extraction section and

92% for the strip section, which were very close to the mass transfer efficiencies seen in earlier CSSX tests [LEONARD-2001A].

This 12-h test demonstrated that the modified solvent works just as well with the CSSX flowsheet as the previous solvent, maintaining satisfactory hydraulic performance and achieving process requirements at the bench scale.

ACKNOWLEDGMENTS

This work was supported by the Office of Environmental Management of the U.S. Department of Energy through (1) the Office of Project Completion and (2) the Tank Focus Area of the Office of Science and Technology under Contract W-31-109-Eng-38 with Argonne National Laboratory, managed by the University of Chicago.

The authors wish to acknowledge the help of Allen Bakel, Evan Freiberg, Kevin Quigley, Artem Guelis, Joe Hirsch, and Mark Sreniawski, all of the ANL Chemical Technology Division, in preparing for and carrying out the test. David Chamberlain of the ANL Chemical Technology Division conducted the operational readiness review. Peter Bonnesen of ORNL prepared the CSSX solvent used in this test.

APPENDIX A

ADDITIONAL INFORMATION ON HYDRAULIC PERFORMANCE

Further information on the hydraulic performance of the 2-cm contactor is given here for the extraction, strip, and solvent wash sections of the CSSX flowsheet. Conditions in the scrub and strip sections were nearly identical, so the scrub section was not tested, as it was assumed that the scrub section will have the same hydraulic performance as the strip section. The solvent wash section was omitted in the multistage (four-stage) tests, since it has only one stage. To allow for the establishment of steady-state conditions, the flows were maintained for at least three residence times before samples were taken. For these tests, rotors X1 through X4 were placed in contactor housing stages 13A through 16A. These four 2-cm contactor rotors have been modified in the same way as the 2-cm rotors in the glovebox. The rotor modifications are described in earlier reports [LEONARD-2001A, -2002].

In these hydraulic performance tests, contactor operation was defined as satisfactory if the other-phase carryover was <1% in both effluent streams. To test the full range of contactor operation, the contactor was started in the initially aqueous-continuous mode and then in the initially organic-continuous mode. In a normal startup, the contactor is first filled with aqueous (more-dense) phase. Because of this, the operation is initially aqueous-continuous. To start up as an initially organic-continuous operation, the flow of the aqueous phase must be turned off while the organic (less-dense) phase continues to flow and the rotors continue to spin. By operating in this way for 3 to 6 residence times, the aqueous phase is purged from the mixing zones, making the dispersion there organic-continuous. When the aqueous flow is restarted, this gives contactor startup from an initially organic-continuous condition. By starting in both the initially aqueous- and organic-continuous modes, the full range of possible flow conditions is created in each stage and any path-dependent problems will be brought to light. If only one phase can be the continuous phase at a specific flow condition, the results will be about the same, no matter which phase was the initial continuous phase. By testing in this way and finding that the final hydraulic performance is satisfactory no matter which phase was the initial continuous phase, one can conclude that the section should be resistant to poor hydraulic performance triggered by process upsets.

1. Single-Stage Operation

To evaluate the hydraulic performance of the modified CSSX solvent in the various sections of the process, two-phase, single-stage tests were carried out in a 2-cm contactor. In these tests, the flow rate of each phase was increased while maintaining a constant O/A flow

ratio. When hydraulic performance became unsatisfactory, the increases were stopped. At each flow rate, the hydraulic performance was evaluated by using aqueous-continuous and organic-continuous initial modes. The amount of organic in the aqueous effluent (O in A) and the amount of aqueous in the organic effluent (A in O) were measured and the appearance of each effluent was noted. Test results are given in Table A-1 for the conditions in the extraction (four-component simulant), strip (0.001 M HNO₃), and solvent wash (0.01 M NaOH) sections. They show that the modified solvent gives good hydraulic performance for single-stage operation over the range of conditions required for the CSSX flowsheet.

Table A-1. Hydraulic Performance of Single-Stage, 2-cm Contactor Using the Modified CSSX Solvent with Various Aqueous Phases

Section	O/A Flow Ratio	Total Flow Rate, mL/min	Initial Continuous Phase	O in A Carryover, %	A in O Carryover, %	Appearance of A Phase ^a	Appearance of O Phase ^a
Strip	5	40	A	<0.5	<0.3	Clr	Hazy
"	5	40	O	<0.3	<0.3	V cldy	Hazy
"	5	40	A	<0.5	<0.3	V cldy	V cldy
"	5	40	O	0.5	0.3	Cldy	V cldy
"	5	63	A	<0.5	0.8	Cldy	V cldy
"	5	63	O	<0.5	0.8	Cldy	V cldy
"	5	80	A	0.5	3	Clr	V cldy
"	5	80	O	0.5	3	Clr	V cldy
Solvent Wash	5	40	A	<0.3	<0.3	V clr	Cldy
"	5	40	O	<0.5	<0.3	Hazy	Hazy
Extraction	0.33	90	A	<0.3	<0.3	Hazy	Crys clr
"	0.33	90	O	<0.3	<0.3	Hazy	Crys clr
"	0.33	120	A	<0.3	3	Cldy	Clr
"	0.33	120	O	<0.3	3	Cldy	Hazy

^a Appearance code: cldy = cloudy, clr = clear, crys = crystal, hazy = hazy, and v = very.

2. Four-Stage Operation

Tests were conducted in the 4-stage, 2-cm contactor to evaluate multistage hydraulic performance of the modified CSSX solvent in the various sections of the process. The organic phase entered the contactor at stage 1 and exited at stage 4. The aqueous phase entered the contactor at stage 4 and exited at stage 1. At each flow rate, the hydraulic performance was evaluated by using aqueous-continuous and organic-continuous initial modes. Test results are given in Table A-2 for the conditions in the extraction (four-component simulant) and strip

(0.001 M HNO₃) sections. They show that the modified solvent gives good hydraulic performance for multistage operation over the range of conditions required for the CSSX flowsheet.

Table A-2. Hydraulic Performance of Four-Stage, 2-cm Contactor Using the Modified CSSX Solvent with Various Aqueous Phases

Section	O/A Flow Ratio	Total Flow Rate, mL/min	Initial Cont. Phase	Aqueous Effluent: Appearance and O Carryover (O in A) ^a	Organic Effluent: Appearance and A Carryover (A in O) ^a	O-Side Interstage Line Backup	A-Side Interstage Line Backup	Corrective Action	Post Corrective Action Observations
Strip	5	16.95	A	App. = v cldy Carryover = 4%	App. = hazy Carryover = <0.3%	Line 1–2, 25% Line 2–3, 25% Line 3–4, 25%	Line 4–3, 10% Line 3–2, 10% Line 2–1, 10%	Switch the rotor in stage 1 for 30 s, then 60 s, then 2 min	O in A is 5% for 30 s, 6% for 60 s, <0.3% for 2 min
Strip	5	16.95	O	App. = v cldy Carryover = 1.1%	App. = hazy Carryover = <0.3%	Line 1–2, 25% Line 2–3, 25% Line 3–4, 25%	Line 4–3, 10% Line 3–2, 10% Line 2–1, 10%	Turn all rotors and pumps off simultaneously for 30 s	Detectable O in A disappeared
Strip	5	16.95	O	App. = v cldy Carryover = <0.3%	App. = hazy Carryover = <0.3%	Line 1–2, 25% Line 2–3, 25% Line 3–4, 25%	Line 4–3, 10% Line 3–2, 10% Line 2–1, 10%	None	No problem with O in A for this repeat test
Extr.	0.33	60	A	App. = cldy Carryover = <0.3%	App. = clr Carryover = <0.3%	Line 1–2, 70% Line 2–3, 25% Line 3–4, 25%	Line 4–3, 20% Line 3–2, 20% Line 2–1, 20%	None	Not applicable
Extr.	0.33	60	O	App. = cldy Carryover = <0.3%	App. = crys clr Carryover = <0.3%	Line 1–2, 50% Line 2–3, 25% Line 3–4, 25%	Line 4–3, 20% Line 3–2, 20% Line 2–1, 10%	None	Not applicable

^a Appearance code: cldy = cloudy, clr = clear, crys = crystal, hazy = hazy, and v = very.

APPENDIX B

ADDITIONAL INFORMATION ON TEST PREPARATIONS

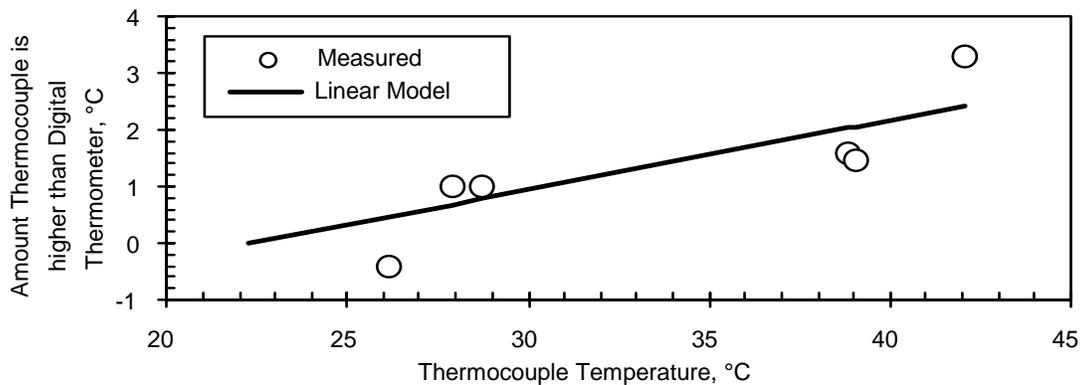
Further information on test preparations for the 12-h test of the CSSX flowsheet (CS29) is given here. The additional information covers (1) the block temperature measured by two different methods and (2) the change in solvent density with use. These measurements were made in conjunction with the training test (CS28) for the 12-h test.

1. Contactor Block Temperature Measured by Two Different Methods

In the multiday CSSX flowsheet test (CS27), the temperature of the selected contactor housing blocks was measured using a digital thermometer taped to the middle of the upper block [LEONARD-2002]. This block is 3 in. (76.2 mm) wide by 3 in. (76.2 mm) deep and 2-9/16 in. (65.1 mm) high. The digital thermometer is a handheld model with a 3.5-in. (88.9 mm) probe (Fisher model 15-078G) and an accuracy of $\pm 1^\circ\text{C}$ traceable to NIST standards. For test CS29, the block temperature was measured by thermocouples taped to the upper right or left corner of the block, as shown in Figure 4. The thermocouples have an accuracy of $\pm 0.5^\circ\text{C}$. To compare the two methods, the block temperatures of six contactor stages were measured by both methods during test CS28. The average temperatures, based on four readings over 3.5 h, are given in Table B-1. During this test, the glovebox temperature was $22.2 \pm 0.3^\circ\text{C}$. The data indicate that the difference between the two methods increases as the block temperature increases above room temperature. This difference between methods can be seen in Figure B-1. It is attributed to the larger size of the digital thermometer, which causes it to be influenced more by the glovebox temperature. A second reason for the difference between methods is that the thermocouple is mounted higher on the block, closer to the motor heating the block. The block temperature gives an indication of how much the contactor blocks are being heated by the motor and the amount of heat being removed by the chiller bar. The practical effect of this heating and cooling on the liquids flowing through the contactor is evaluated by measuring the effluent temperatures.

Table B-1. Contactor Block Temperature Measured by Two Different Methods

Average Thermocouple Readings (lowest first), °C	Average Digital Thermometer Readings, °C	Thermocouple Reading minus Digital Thermometer Reading, °C	Stage Number	Stage Location
26.1 ± 0.4	26.5 ± 0.3	-0.4 ± 0.6	8	Middle of extraction section
27.9 ± 0.3	27.0 ± 0.2	1.0 ± 0.2	15	DF feed stage
28.7 ± 0.7	27.7 ± 0.6	1.0 ± 0.6	1	DW raffinate stage
38.8 ± 0.3	37.2 ± 0.3	1.6 ± 0.2	18	EW effluent stage
39.0 ± 0.4	37.5 ± 0.4	1.5 ± 0.3	32	EP effluent stage
42.0 ± 0.3	38.7 ± 0.4	3.3 ± 0.3	25	Middle of strip section

**Fig. B-1. Effect of Block Temperature on Temperature Difference between Two Methods**

2. Change in Solvent Density

The solvent density increased with time during the multiday test of the CSSX flowsheet [LEONARD-2002]. This increase is attributed to evaporative loss of diluent (Isopar L) as the solvent was recycled through the 2-cm contactor. The smaller the solvent volume, the greater will be the effect of any diluent loss. We started with 1247 mL of solvent for test CS28. At the end of the test, there were 600 mL of solvent left in the EP/FX feed tank with some additional solvent in the contactor stages. The solvent density was measured at the start of test CS28 and 4 h later at the end of the test. The next day, the contactor was run another 3 h as part of a cleaning process to reduce alpha contamination. The density measurements, given in Table B-2, show that the density of the CSSX solvent slowly increased with time.

Table B-2. Change in CSSX Solvent Density with Time in 2-cm Centrifugal Contactor

Total Time Solvent Used, h	Solvent Density at 25°C, g/L	Notes
0	853 ±1	Fresh CSSX solvent at start of test CS28
4	863 ± 1	End of test CS28
7	871 ± 1	End of additional contactor operation

The amount of solvent lost by evaporation during test CS28 was determined by two methods. The first method used a material balance based on solvent volume. Of the 1247 mL of solvent that was present at the start of the test, 600 mL was left in the EP/FX tank; 464 mL was left in the contactor, based on the solvent flow rate (14.5 mL/min) and the time it took for the solvent to pass through the 33 stages (32 min); and 50 to 70 mL was in solvent samples (5 samples of 10 to 14 mL each). This leaves 113 to 133 mL of solvent that is not accounted for. This volume is assumed to be diluent that had evaporated. The second method used the change in solvent density in Table B-2 and the model for calculating solvent density given in LEONARD-2000. Based on the change in solvent density and an estimated 1064 mL of solvent left at the end of the test (600 mL of solvent were in the EP/FX tank and 464 mL of solvent were estimated to be in the contactor and associated lines), the diluent loss was calculated to be 116 mL. The two methods give the same diluent loss within the limits of experimental error. Based on the change in solvent density, the diluent loss rate was 0.48 mL/min.

APPENDIX C

ADDITIONAL RESULTS

Further results from the 12-h CSSX flowsheet test (CS29) are given here. These results include measurements made before and after the test, as well as measurements and observations made during the test. Finally, calculations were made to see if the change in solvent density could be explained by diluent evaporation from the solvent. These details supplement the test results given in the body of this report.

1. Measurements before the Test

Before the 12-h CSSX flowsheet test (CS29) was carried out, batch-equilibrium D_{Cs} values were measured using the solutions and the volume ratios specified for the tests. The D_{Cs} results, given in Table C-1, agree fairly well with estimated D_{Cs} values for the new CSSX solvent with only 0.001 M TOA (14.13 for the batch extraction; 1.32 and 1.35 for the two batch scrubs; and 0.104, 0.062, 0.049, and 0.043 for the four batch strips) [KLATT-2002]. As that report also shows, D_{Cs} in the extraction and scrub sections decreases as TOA increases to 0.003 M. In the strip section, D_{Cs} increases as TOA increases. The measured values in Table C-1 show the same trends. Using the values in Table C-1, the no-load D_{Cs} values in the extraction and scrub sections and the D_{Cs} value at low C_s concentrations in the strip section were calculated as given in LEONARD-2001D. The results are given in the footnotes to Table C-1. Tests 1–4 were performed at the same time in the batch strip tests. When the D_{Cs} value for test 4 was found to go up, test 5 was conducted. It showed that the D_{Cs} value was continuing to go down. Our experience is that the consecutive batch strip values go down until they become constant. Thus, it is likely that there was some problem with the fourth strip test. For this reason, it is recommended that D_{Cs} values for low C_s concentrations be based on the first three D_{Cs} values for the strip section.

Table C-1. D_{Cs} Values from Batch-Equilibrium Measurements before Test CS29

Section	Batch Test Number	O/A Volume Ratio	D _{Cs} at 25°C	Notes
Extraction	1	0.31	11.95	a
Extraction	2	0.31	11.59	
Scrub	1	5.0	1.029	b
Scrub	2	5.0	1.239	
Strip	1	5.0	0.106	c
Strip	2	5.0	0.083	
Strip	3	5.0	0.073	
Strip	4	5.0	0.091	
Strip	5	5.0	0.082	

^a Based on the extraction section data, the no load D_{Cs} value is 12.7 ± 0.2 .

^b Based on the scrub section data, the no load D_{Cs} value is 1.22 ± 0.15 .

^c Based on the first three D_{Cs} values for the strip section, the D_{Cs} value at low Cs concentrations in the strip section is 0.053 ± 0.010 ; for all five values, 0.065 ± 0.019 .

2. Measurements and Observations during the Test

During the flowsheet test CS29, effluent flow rates were measured by taking timed effluent samples. For flow rates above 10 mL/min, the collection time was 1 min; for lower flow rates, it was 5 min. In addition, the effluent appearance was checked, any other-phase carryover was noted, the effluent temperature was measured, and a sample of the liquid was taken for later determination of its Cs concentration. Using pH paper, the pH was measured for the aqueous effluent from the strip and solvent wash sections. The organic strip (EP) liquid effluent level in the EP/FX tank was noted. Time zero for the test was when hot (radioactive) DF feed was started. The test was continued until all of this SRS simulant was gone; the test ended at 827 min.

Measurements and observations for the DW effluent are summarized in Table C-2. The overall DW flow rate was 43.0 ± 1.2 mL/min, which was close to the target flow rate of 45.82 mL/min. The DW effluent was the coolest effluent, with an average temperature of $26.7 \pm 0.7^\circ\text{C}$. This was expected, since the temperature in the extraction section is lowered by the water-cooled chiller bar. Before the test, the DF and DS flow rates were found to be 42.5 mL/min (target 43.0 mL/min) and 2.86 mL/min (target 2.82 mL/min), respectively. During the test, the DS flow rate was found to be 2.92 ± 0.05 mL/min. Since the DF flow rate was not measured during the test, it was calculated from the DS and DW flow rates as 40.1 ± 1.2 mL/min.

Table C-2. Aqueous (DW) Raffinate for Test CS29

Sample Number	Time, min	DW Flow Rate, mL/min	DW Temp, °C	DW Other-Phase Carryover, %	DW Appearance ^a
1	5	44.0	25.8	<0.5	Sl hazy, yel
2	30	44.0	26.0	<0.5	Sl hazy, yel
3	60	44.0	26.6	<0.5	Clr, yel
4	90	42.0	26.6	<0.5	Clr, yel
5	120	44.5	28.8	<0.5	Clr, yel
6	180	42.0	26.7	<0.5	Hazy, yel
7	240	42.5	26.8	<0.5	Clr, yel
8	300	43.0	26.6	<0.5	Clr, yel
9	360	43.0	26.5	<0.5	Clr, yel
10	420	40.0	–	<0.5	Clr, yel
11	480	44.0	–	<0.5	Clr, yel
12	600	44.0	26.3	<0.5	Clr, yel
13	720	43.0	26.7	<0.5	Clr, yel
14	810	42.0	26.8	<0.5	Sl hazy, yel

^a Appearance code: clr = clear, hazy = hazy, sl = slight, and yel = yellow.

Measurements and observations for the EW effluent are summarized in Table C-3. The overall EW flow rate was 2.86 ± 0.42 mL/min, which was very close to the target flow rate of 2.85 mL/min. The EW effluent had an average temperature of $30.2 \pm 0.8^\circ\text{C}$. The EW effluent was acidic throughout the test, with pH ranging from 3 to 5. Based on earlier tests of the pH paper, a pH of 3 corresponds to 0.003 M HNO₃ and a pH of 5, to 0.001 M HNO₃. Before the test, the EF flow rate was found to be 2.82 mL/min.

The EF flow rate could be measured and controlled fairly well manually using an electronic balance in conjunction with a FMI rotary piston pump. This technique, which is given in LEONARD-2001A, was also used for the other two cold feeds (DS and FF). During the first 300 min of test CS29, the EF flow rate was 3.13 ± 0.01 mL/min. During this same time, the EW flow rate was 2.84 ± 0.31 mL/min. This shows that flow rate variations are increased as the aqueous phase moves the 15 stages of the strip section. This is also seen as intermittent (slug) flow when the aqueous phase exits the strip section. Since slug flow in an effluent line will not affect stage efficiency, there are no wire ropes in the effluent lines. At 300 min into test CS29, the EF flow rate was lowered slightly so that it was closer to the target value. After 300 min, the EF flow rate was 2.90 ± 0.02 mL/min. During this same time, the EW flow rate was 2.85 ± 0.54 mL/min.

Table C-3. Aqueous Strip (EW) Effluent for Test CS29

Sample Number	Time, min	EW Flow Rate, mL/min	EW Temp, °C	EW Other-Phase Carryover, %	EW Appearance ^a	pH
1	10	2.65	28.7	<1.0	Hazy	4
2	35	2.55	28.6	<1.0	Clr	3.5
3	65	2.80	30.2	<1.0	Hazy, col	4
4	95	2.70	28.9	<1.0	Hazy, col	4
5	125	3.50	30.6	<1.0	Clr	4
6	185	2.90	30.7	<1.0	Clr, col	–
7	245	2.80	30.7	<1.0	Clr, col	4
8	305	3.40	30.8	<1.0	Clr, col	4
9	365	2.50	30.5	<1.0	Clr, col	4
10	425	3.10	30.8	<1.0	Clr, col	4
11	485	2.50	30.6	<1.0	Clr, col	4
12	605	2.20	30.4	<1.0	Clr, col	3
13	725	3.70	30.4	<1.0	Clr, col	3
14	815	2.78	30.8	<1.0	Crys Clr	3.5

^a Appearance code: clr = clear, col = colorless, crys = crystal, and hazy = hazy.

Measurements and observations for the FW effluent are summarized in Table C-4. The overall FW flow rate was 2.86 ± 0.13 mL/min, which was very close to the target flow rate of 2.85 mL/min. The FW effluent had an average temperature of 27.0 ± 0.4 °C and was alkaline throughout the test, with pH ranging from 9 to 12, based on measurements using pH paper. Before the test, the FF flow rate was found to be 2.86 mL/min. During the first 360 min of test CS29, the FF flow rate was 3.01 ± 0.07 mL/min. During this same time, the FW flow rate was 2.83 ± 0.16 mL/min. This shows that flow rate variations are increased only slightly, if at all, as the aqueous phase moves through the one stage of the solvent wash section. At 360 min into test CS29, the FF flow rate was lowered slightly so that it was closer to the target value. After 360 min, the FF flow rate was 2.92 ± 0.06 mL/min. During this same time, the FW flow rate was 2.90 ± 0.07 mL/min.

Table C-4. Solvent Wash (FW) Effluent for Test CS29

Sample Number	Time, min	FW Flow Rate, mL/min	FW Temp, °C	FW Other-Phase Carryover, %	FW Appearance ^a	pH
1	10	2.70	–	<1.0	Crys clr, sl yel	12
2	35	2.80	–	<1.0	Sl hazy, v lt yel	11
3	65	2.84	27.0	<1.0	Clr, col	10
4	95	2.60	27.7	<1.0	Clr, col	9
5	125	2.70	27.3	<1.0	Clr	8
6	185	3.00	26.7	<1.0	Clr, col	9
7	245	3.00	26.8	<1.0	Clr, col	9
8	305	3.00	26.4	<1.0	Clr, col	9
9	365	2.90	26.8	<1.0	Clr, col	9
10	425	–	–	<1.0	Hazy, col	–
11	485	2.90	–	<1.0	Hazy, col	10
12	605	2.80	27.2	<1.0	Sl cldy, col	9
13	725	2.90	–	<1.0	Clr, col	9
14	815	3.00	–	<1.0	Cldy	11

^a Appearance code: cldy = cloudy, clr = clear, col = colorless, crys = crystal, hazy = hazy, lt = light, sl = slight, v = very, and yel = yellow.

Measurements and observations for the EP effluent are summarized in Table C-5. The overall EP flow rate was 13.4 ± 2.2 mL/min, which is close to the target flow rate of 14.12 mL/min. Before the test, the FX flow rate was found to be 14.25 ± 0.25 mL/min. The EP effluent had an average temperature of 30.8 ± 0.4 °C. In one case, >1% A in O was seen in the EP effluent. On average, the amount of A in O was small, 0.3 ± 0.5 %. The liquid level in the effluent/feed (EP/FX) tank dropped slowly throughout the test. This is a result of taking solvent samples and losing diluent from the solvent by evaporation. In addition, the level also reflects variations in the liquid holdup in the contactor with time. At the start of the test, the fresh solvent had a density of 852.0 g/L. At the end of the 13.8-h (827-min) test, the solvent had a density of 856.2 g/L. This density increase is only 40% of that seen for the solvent in test CS28 (see Appendix B), which was shorter, only 4 h. The solvent used in test CS28 was from batch 150W; that for test CS29 was from batch 190W. As mentioned in Section II, batch 150W became stratified during shipment from ORNL to ANL, while batch 190W did not. This suggests that differences between these two batches allowed batch 150W to lose diluent by evaporation more rapidly. However, there is no reason to expect that this would be the case. The difficulty in measuring diluent loss and the difference in test conditions provide a more likely explanation for the apparent difference in loss rates between the two solvent batches.

Table C-5. Organic (EP) Effluent for Test CS29

Sample Number	Time, min	EP Flow Rate, mL/min	EP Temp, °C	EP Other-Phase Carryover, %	EP Appearance ^a	EP/FX Tank Level, mL
1	5	7.5	29.0	<0.005	Crys clr	590
2	30	12.5	30.6	0.3	Crys clr	585
3	60	15.5	31.2	0.03	Clr, col	550
4	90	18.0	31.4	0.08	Clr, col	550
5	120	9.0	31.3	0.006	–	550
6	180	14.0	30.9	<0.005	Clr, col	525
7	240	11.5	30.0	<0.005	Clr, col	500
8	300	15.0	30.7	1.8	Clr, col	500
9	360	11.0	30.4	0.005	Clr, col	500
10	420	14.0	–	0.2	Clr, col	500
11	480	13.0	–	0.03	Clr, col	470
12	600	12.5	30.9	0.3	Clr, col	475
13	720	14.5	–	0.03	Clr, col	500
14	810	13.5	31.0	0.8	Crys clr	430

^a Appearance code: clr = clear, col = colorless, and crys = crystal.

The amount of solvent lost by evaporation during test CS29 was determined by two methods. The first method used a material balance based on solvent volume. Of the 1150 mL of solvent estimated at the start of the test, 430 mL was left in the EP/FX tank; 482 mL was left in the contactor, based on the solvent flow rate (13.38 mL/min) and the time it took for the solvent to pass through the 33 stages (36 min); and 140 to 196 mL consisted of solvent samples (14 samples of 10 to 14 mL each). This leaves 42 to 98 mL of solvent that is not accounted for. This volume is assumed to be diluent that evaporated. The second method used the change in solvent density and the model for calculating solvent density given in LEONARD-2000. Based on the change in solvent density and an estimated 912 mL of solvent at the end of the test, the diluent loss was calculated to be 42 mL. Within the limits of experimental error, the two methods give the same diluent loss. Based on the change in solvent density, the diluent loss rate was 0.05 mL/min. This is only 10% of the diluent loss rate seen in test CS28. The higher diluent loss rate for test CS28 may indicate that (1) the contactor motors were running longer before startup, (2) the coolant flow to the chiller bar was not started until the cold DF feed was flowing into the extraction section, (3) the experimental error for this measurement is high, and, perhaps, (4) differences between the two solvent batches.

Other conditions measured during flowsheet test CS29 were the temperatures of selected contactor stages and the level of the liquid flowing through the interstage lines. The temperatures of the contactor stages were measured using thermocouples taped to the contactor block. The average temperature for each stage is given as a function of stage number in Figure C-1. All contactor temperatures were higher than the surrounding (glovebox) temperature of

22.9 ± 0.4°C. The stages cooled by the chiller bar, stages 1–15, had the lowest block temperatures, ranging from 27.4 to 30.3°C. The stages away from the chiller bar and with no external feeds, stages 20–30, had the highest block temperatures, ranging from 40.6 to 43.1°C. In every stage where a comparison is possible, the effluent stream temperature is between the contactor block temperature for that stage and the room (glovebox) temperature.

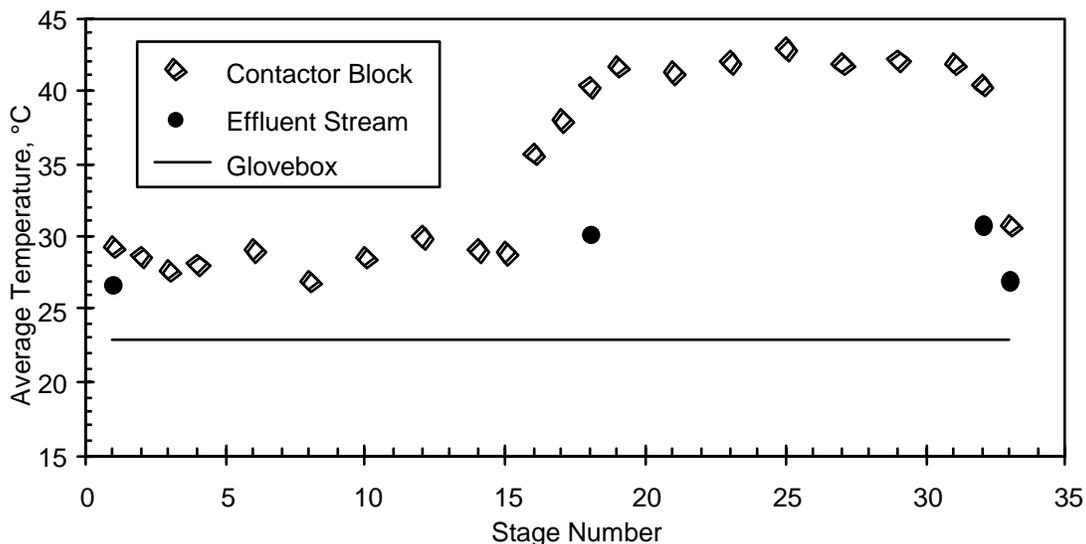


Fig. C-1. Average Block and Effluent Temperatures during Test CS29

The level of the liquid flowing through the interstage lines was estimated by the operators. The results, summarized in Figure C-2, give the average liquid level in each interstage line. The variability of the liquid level is ±15% or less for all but one stage. Most stages showed a variability of only ±5%. The liquid level in the organic interstage line going from stage 31 to 32 had a variability of ±30%. As discussed in LEONARD-2002, the few high liquid levels could probably be eliminated with a contactor that was built with inlet ports that were tangential to the mixing zone of each stage.

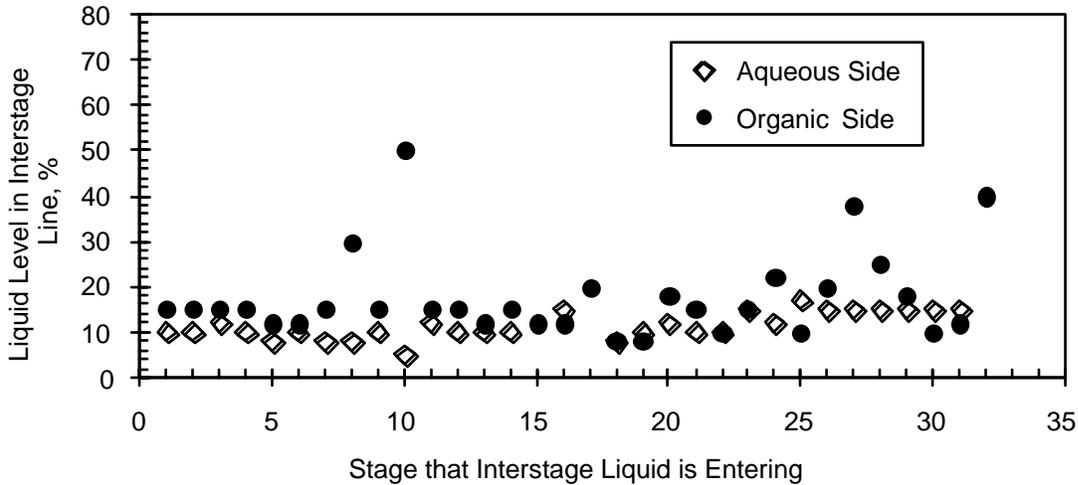


Fig. C-2. Average Liquid Levels during Test CS29

3. Measurements after the Test

After test CS29, the Cs concentration was measured for all available effluent samples. The results are listed in Table C-6 along with the DF concentration that is the basis value and the calculated decontamination, concentration, and stripping factors. Omitting the 5-min sample, the average Cs concentration is $3.6\text{E-}10 \pm 1.2\text{E-}10$ M for the DW raffinate, $2.17\text{E-}03 \pm 0.18\text{E-}03$ M for the EW effluent, $4.6\text{E-}10 \pm 2.6\text{E-}10$ M for the FW effluent, and $3.7\text{E-}10 \pm 1.0\text{E-}10$ M for the EP effluent. Several Cs concentrations were not available, as the samples were below the detection limit of the gamma counter for both counted samples. For these concentrations, “less than” values are reported.

Table C-6. Effluent Concentrations during Test CS29

Sample	Time, min	Cs Conc. in Aqueous (DW) Raffinate, <u>M</u>	Cs Conc. in Aqueous Strip (EW) Effluent, <u>M</u>	Cs Conc. in Aqueous Wash (FW) Effluent, <u>M</u>	Cs Conc. in Organic Strip (EP) Effluent, <u>M</u>	Cs Conc. in Aqueous (DF) Feed, <u>M</u>	Decon. Factor, [DF]/[DW]	Conc. Factor, [EW]/[DF]	Stripping Factor, [DF]/[EP]
1	5	1.02E-10	1.25E-03	<1.58E-10	4.83E-10	1.40E-04	1,368,425	8.9	289,762
2	30	2.58E-10	2.10E-03	1.21E-10	3.49E-10	1.40E-04	541,777	15.0	401,336
3	60	2.68E-10	2.10E-03	1.04E-09	3.51E-10	1.40E-04	523,072	15.0	399,070
4	90	2.92E-10	2.07E-03	4.03E-10	3.56E-10	1.40E-04	478,794	14.8	392,789
5	120	3.45E-10	1.98E-03	3.21E-10	4.69E-10	1.40E-04	406,333	14.1	298,530
6	180	4.32E-10	2.04E-03	5.94E-10	5.50E-10	1.40E-04	323,826	14.6	254,476
7	240	3.62E-10	2.03E-03	2.80E-10	4.00E-10	1.40E-04	386,702	14.5	350,299
8	300	3.34E-10	2.11E-03	<1.58E-10	2.95E-10	1.40E-04	419,596	15.1	473,980
9	360	3.59E-10	2.47E-03	<1.58E-10	3.35E-10	1.40E-04	390,259	17.6	417,531
10	420	3.64E-10	2.38E-03	6.51E-10	1.61E-10	1.40E-04	384,598	17.0	869,286
11	480	3.45E-10	2.17E-03	4.91E-10	<3.4E-10	1.40E-04	406,333	15.5	>410,000
12	600	3.70E-10	2.50E-03	5.17E-10	<1.45E-10	1.40E-04	378,085	17.8	>970,000
13	720	2.36E-10	2.05E-03	8.98E-11	4.16E-10	1.40E-04	592,475	14.6	336,676
14	810	7.30E-10	2.28E-03	5.09E-10	4.06E-10	1.40E-04	191,691	16.3	344,888

An overall Cs material balance for test CS29 was calculated using the flow rates and Cs concentrations for the incoming and outgoing process streams. The results, summarized in Table C-7, show that 112.0% of the Cs was recovered. Since the key values for the Cs material balance had standard deviations of $\pm 10.2\%$ for the Cs concentration in DF, $\pm 8.0\%$ for the Cs concentration in EW, $\pm 3.1\%$ for the DF flow rate, and $\pm 4.4\%$ for the EW flow rate, the standard deviation for the material balance is $\pm 14.0\%$. Thus, within experimental error, there was 100% recovery of the Cs.

Table C-7. Overall Material Balance for Cs during Test CS29

Stream Identity	Stream In or Out	Average Stream Flow Rate, mL/min	Average Stream Cs Conc. , <u>M</u>	Cs Flow, millimoles/min
DF	In	40.08	1.40E-04	0.005610889
DS	In	2.92	0	0.000000000
EF	In	2.90	0	0.000000000
FF	In	2.92	0	0.000000000
FX	In	13.38	3.81E-10	0.000000005
Total Cs Flow In, mM/min:				0.005610894
DW	Out	43.0	3.61E-10	0.000000016
EW	Out	2.90	2.17E-03	0.006285767
EP	Out	13.38	3.81E-10	0.000000005
FW	Out	2.92	4.56E-10	0.000000001
Total Cs Flow Out, mM/min:				0.006285789
Amount of Cs recovered, %:				112.0

Shortly after test CS29 was completed, the aqueous and organic liquids in each stage were drained and collected in 60-mL polyethylene bottles. The stage samples were later equilibrated by shaking each collection bottle for 15–20 s. Immediately after equilibration, the sample temperature was measured. Then the two phases were separated and each phase was analyzed for its Cs concentration. These concentrations allow the apparent D_{Cs} value to be calculated for each stage. These concentrations, temperatures, and D_{Cs} values are given in Table C-8. Several Cs concentrations were not available (N/A), as the samples were below the detection limit of the gamma counter. Some of the concentrations and D_{Cs} values in the scrub, strip, and wash sections are higher than expected based on the values seen in Table C-1. This is attributed to one or more of the following: (1) residual high concentrations of Cs in the stage drain lines, (2) residual high concentrations of either acid or base in the drain lines, (3) the lower equilibration temperatures. To get an idea of how well the stage samples represent actual stage conditions (when available), the average Cs concentration for the each effluent stream is also listed.

Table C-8. Cs Concentration in Equilibrated Stage Samples from Test CS29

Stage Number	Cs Conc. (Aqueous) after Stage Sample Equilibrated, <u>M</u>	Cs Conc. (Organic) after Stage Sample Equilibrated, <u>M</u>	Equil. Temp., °C	D_{Cs}	Avg Cs Conc. in Aqueous Effluent Samples, <u>M</u>	Avg Cs Conc. in Organic Effluent Samples, <u>M</u>
1	N/A	1.16E-09	22.8	N/A	3.61E-10	
2	2.36E-10	3.50E-09	22.8	14.85		
3	5.81E-10	8.94E-09	22.8	15.39		
4	1.63E-09	2.83E-08	22.9	17.29		
5	3.55E-09	6.50E-08	23.1	18.32		
6	7.13E-09	1.31E-07	22.9	18.41		
7	3.01E-08	4.92E-07	23.0	16.36		
8	8.14E-08	1.33E-06	23.0	16.34		
9	1.62E-07	2.66E-06	23.4	16.42		
10	3.30E-07	6.10E-06	23.3	18.46		
11	8.75E-07	1.69E-05	23.4	19.29		
12	2.36E-06	4.30E-05	24.2	18.25		
13	5.73E-06	1.05E-04	23.5	18.34		
14	1.35E-05	2.19E-04	23.9	16.30		
15	4.13E-05	6.65E-04	24.0	16.10		
16	4.63E-04	7.98E-04	22.7	1.725		
17	4.59E-04	7.01E-04	22.7	1.528		
18	1.29E-03	4.77E-04	22.8	0.369	2.17E-03	
19	5.04E-04	1.32E-04	22.8	0.262		
20	1.55E-04	2.72E-05	22.7	0.175		
21	3.22E-05	5.29E-06	22.8	0.164		
22	6.46E-06	1.06E-06	22.8	0.165		
23	1.18E-06	2.39E-07	22.8	0.203		
24	4.24E-07	4.82E-08	23.1	0.114		
25	8.94E-08	1.31E-08	22.7	0.146		
26	2.47E-08	2.77E-09	22.5	0.112		
27	8.87E-09	1.09E-09	23.6	0.123		
28	3.35E-09	N/A	22.8	N/A		
29	1.82E-09	N/A	23.5	N/A		
30	2.07E-09	3.30E-10	23.5	0.159		
31	2.88E-09	3.15E-10	23.1	0.109		
32	8.32E-10	N/A	23.8	N/A		3.81E-10
33	N/A	8.44E-10	24.3	N/A	4.56E-10	

The concentrations of Cs in both phases of each stage at the end of test CS29 can be calculated using the SASSE model [LEONARD-1994]. The procedure for doing this for the CSSX process at a given temperature is given in LEONARD-2001D. The effect of temperature on the D_{Cs} values for the CSSX solvent was added by using information from BONNESEN-

2000. The enthalpy (H) for this Cs extraction reaction is obtained from the slope of each curve in Figure 5 of BONNESEN-2000. It is 42.8 kJ/mol for the extraction section, 61.8 kJ/mol for the scrub section, and 62.5 kJ/mol for the strip section. This means that, going from 20 to 30°C, D_{Cs} will drop by 1.79× in the extraction section, 2.31× in the scrub section, and 2.33× in the strip section. The equation for D_{Cs} that gives D_1 at T_1 knowing D_0 at T_0 is

$$D_1 = D_0 * \exp[(H/R) * \{(1/T_1) - (1/T_0)\}], \quad (C-1)$$

where T is the absolute temperature in K, H is as given above in kJ/mol, and R is 0.0083144 kJ/(mol·K). Using the temperature data above, the liquids flowing through the stages were estimated to be 26.7°C in stages 1–13, 25.3°C in stage 14, 23.9°C in stage 15, 27.0°C in stages 16–17, 30.2°C in stage 18, 31.2°C in stage 19, 33.2°C in stages 20–30, 31.5°C in stage 31, and 30.8°C in stage 32. Stage 33 was omitted from the model. In the SASSE calculations, the effect of diluent loss is included by increasing the no-load D_{Cs} values for the extraction and scrub sections and the D_{Cs} value at low concentrations in the strip section (see Table C-1) by 5.1%. Using the SASSE model with solvent recycle and the stage-to-stage concentration profile for Cs given in Table C-8, the best fit of the model to the data was found to be for a stage efficiency of 85% in the extraction section and 92% in the strip section. As can be seen in Figure C-3, the model is in reasonable agreement with the measured Cs concentrations. In the multiday test CS27 described in LEONARD-2002, the measured Cs concentrations at the end of the extraction section (stages 1–6) flatten out, while the model indicated the Cs concentration should continue to fall for several more stages. For test CS29, the model matched the measured Cs concentrations down to the end (stage 1). This is attributed to the extra care taken to get the unit clean. There is a similar good match for the strip section from stages 18 to 27. For stages 28 to 32, the measured Cs concentrations level out. Cleaning was less rigorous for the strip section, with only water being used. The 1 M HNO_3 cleaning solutions were not used, as they would then have to be completely removed to avoid compromising the operation of the strip section. The measured Cs concentrations for many strip stages seemed too high for the multiday test [LEONARD-2002]. This was attributed to contamination of the strip-stage drain lines during the process upset late in the test. For test CS29, where there was no process upset and the unit was well cleaned, the measured Cs concentrations follow the model until stage 28. Further cleaning would not have been especially useful, as the Cs concentrations were approaching and in some cases falling below the detection limit of the gamma counter.

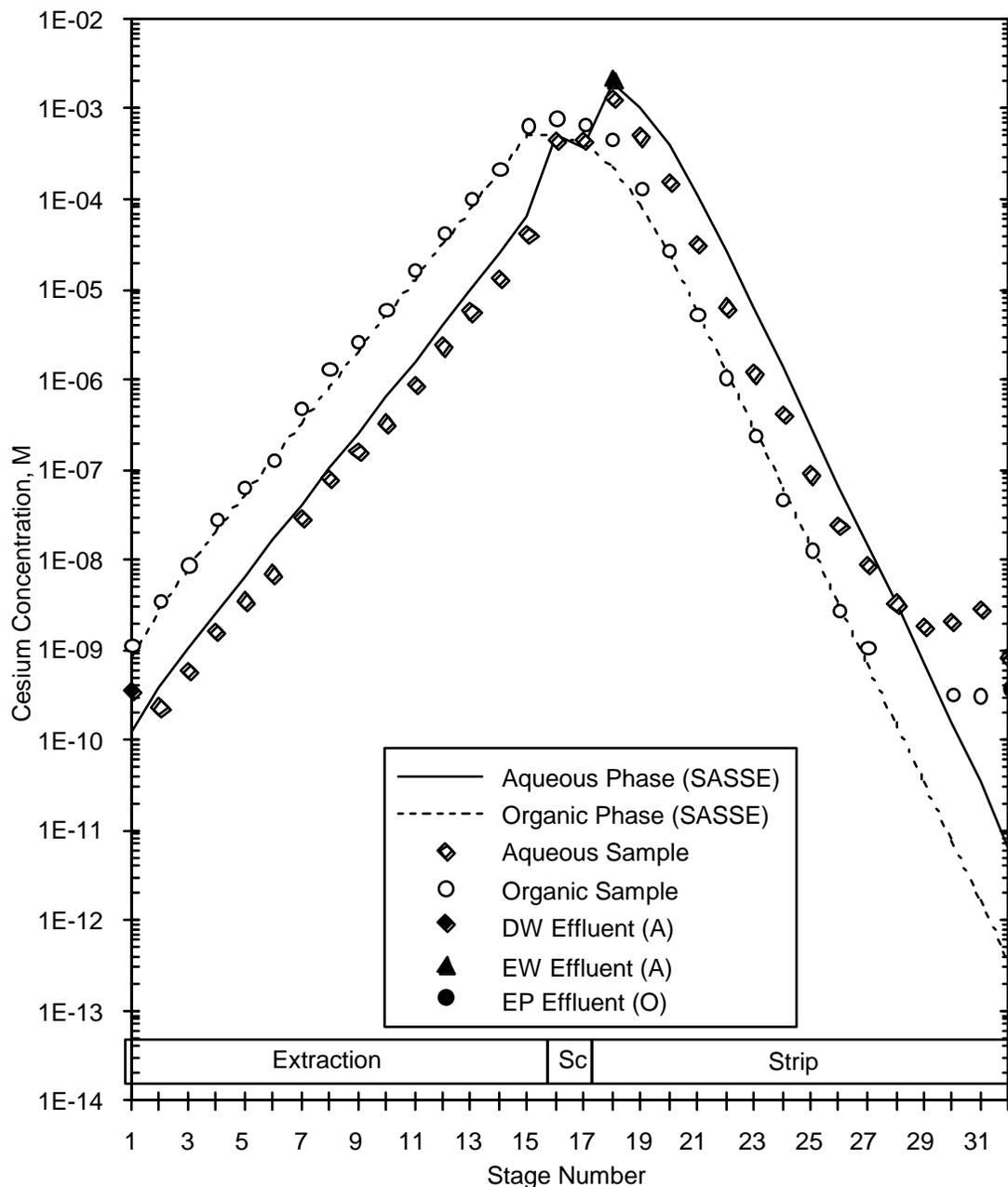


Fig. C-3. Cs Concentration Profile at End of Test CS29

4. Diluent Loss Rate

Calculations were made to see if the diluent loss rate from the solvent is consistent with the estimated diluent vapor pressure. The diluent loss rate was 0.48 mL/min for test CS28 (see Section 2 in Appendix B) and 0.05 mL/min for test CS29 (see Section 3 in this appendix). Based on the discussion in this appendix, the diluent rate for test CS29 is probably a more typical value for the CSSX process in the 2-cm contactor. The vapor pressure for Isopar L was estimated by

assuming that the vapor pressure is proportional to the evaporation rate. The evaporation rate for Isopar L is given as 3 relative to 100 for n-butyl acetate on the 2001 Exxon Mobil Chemical data sheet for Isopar L. The vapor pressure for n-butyl acetate at 20°C is given as 1040 Pa (7.8 torr) on the 2000 solvent physical properties sheet from Honeywell Burdick & Jackson, Muskegon, Michigan. Using this information, the vapor pressure for Isopar L at 20°C is estimated to be 31 Pa. From a correlation in REID-1958, it appears that the vapor pressure of hydrocarbons such as Isopar L will double for every 10°C rise in temperature. Thus, at 40°C, the temperature of the contactor stage blocks in the strip section (see Table C-1), the vapor pressure for Isopar L is estimated to be 124 Pa. These vapor-pressure calculations neglect the effect of the other solvent components on the vapor pressure of Isopar L. For comparison with the estimated vapor pressure for Isopar L, an apparent vapor pressure can be calculated from the diluent loss rate for test CS29 (0.05 mL/min) if the amount of gas (air) passing through the contactor is known. Based on the purge gas flow alone, which is 1.4 L/min, the apparent vapor pressure for Isopar L is 362 Pa. Based on past experience (that is, the exit tubes for the less-dense phase in the rotor body can pump a considerable amount of gas out of the contactor), one author (Leonard) estimated that the gas pumped out with the EP effluent could be 2.3 L/min. When this is combined with the purge gas flow, the apparent vapor pressure for Isopar L is 137 Pa. If there is a small amount of additional gas flow out the three aqueous effluent ports (DW, EW, and FW) where the rotor does not pump gas as efficiently (0.4 L/min), the apparent vapor pressure for Isopar L is 124 Pa. This last scenario, which matches the estimated vapor pressure for Isopar L at 40°C, indicates that, with the higher temperatures in the contactor and reasonable estimates of gas (air) flow through the contactor, the observed diluent losses could be explained for test CS29.

If this simple model to explain the rate of diluent loss is correct, then diluent loss can be reduced by limiting the flow of gas (air) through the contactor. One way to do this would be to extend the effluent lines far enough below the surface of the tank liquid to keep any gas from being pumped out. This was not done during the CSSX flowsheet tests to allow effluent samples to be taken. The lines all stopped above the liquid surface of the effluent tanks. If all lines for exiting liquids are below the liquid surface in the effluent tanks, the gas flow through the contactor should be limited to the flow of the purge gas. Based on the diluent-loss model, this would have reduced the rate of diluent loss from the 2-cm contactor by a factor of three. Note that, while the effluent lines are sealed by the liquid in the effluent tanks, the effluent tanks themselves must not be sealed. If they are sealed, the entering liquid pressurizes the gas in the tank. When the pressure is high enough, liquid will be prevented from flowing out of the contactor and the contactor will become inoperable until the tank is vented.

REFERENCES

BONNESEN-1998

P. V. Bonnesen, L. H. Delmau, T. J. Haverlock, and B. A. Moyer, *Alkaline-Side Extraction of Cesium from Savannah River Tank Waste using a Calixarene-Crown Ether Structure*, Oak Ridge National Laboratory Report ORNL/TM-13704 (1998).

BONNESEN-2000

P. V. Bonnesen, L. H. Delmau, B. A. Moyer, and R. A. Leonard, "A Robust Alkaline-Side CSEX Solvent Suitable for Removing Cesium from Savannah River High Level Waste," *Sol. Extr. Ion Exch.* 18(6), 1079-1107 (2000)

DELMAU-2002

L. H. Delmau and F. V. Sloop, Jr., Oak Ridge National Laboratory, unpublished data (2002).

KLATT-2002

L. N. Klatt, J. F. Birdwell, P. V. Bonnesen, L. H. Delmau, L. J. Foote, D. D. Lee, R. A. Leonard, T. G. Levitskaia, M. P. Maskarinec, and B. A. Moyer, *Caustic-Side Solvent Extraction Solvent-Composition Recommendations*, Oak Ridge National Laboratory Report ORNL/TM-2001/258 (January 2002).

LEONARD-1994

R. A. Leonard and M. C. Regalbuto, "A Spreadsheet Algorithm for Stagewise Solvent Extraction," *Sol. Extr. Ion Exch.* 12(5), 909-930 (1994).

LEONARD-1999

R. A. Leonard, C. Conner, M. W. Liberatore, J. Sedlet, S. B. Aase, and G. F. Vandegrift, *Evaluation of an Alkaline-Side Solvent Extraction Process for Cesium Removal from SRS Tank Waste Using Laboratory-Scale Centrifugal Contactors*, Argonne National Laboratory Report ANL-99/14 (1999).

LEONARD-2000

R. A. Leonard, S. B. Aase, H. A. Arafat, C. Conner, J. R. Falkenberg, and G. F. Vandegrift, *Proof-of-Concept Flowsheet Tests for Caustic-Side Solvent Extraction of Cesium from Tank Waste*, Argonne National Laboratory Report ANL-00/30 (2000).

LEONARD-2001A

R. A. Leonard, S. B. Aase, H. A. Arafat, C. Conner, J. R. Falkenberg, and G. F. Vandegrift, *Development of an Improved 2-cm Centrifugal Contactor for Cesium Removal from High-Level Waste*, Argonne National Laboratory Report ANL-01/23 (2001).

LEONARD-2001B

R. A. Leonard, S. B. Aase, H. A. Arafat, D. B. Chamberlain, C. Conner, M. C. Regalbuto, and G. F. Vandegrift, *Interim Report on a Multi-Day Test of the Caustic-Side Solvent Extraction Flowsheet for Cesium Removal from a Simulated SRS Tank Waste*, Argonne National Laboratory Report ANL-01/10 (2001).

LEONARD-2001C

R. A. Leonard, M. C. Regalbuto, S. B. Aase, H. A. Arafat, and J. R. Falkenberg, *Hydraulic Performance of a 5-cm CINC Contactor for Caustic-Side Solvent Extraction*, Argonne National Laboratory Letter Report ANL/CMT/CSSX-2001/06 (2001). This report is being prepared for issue as Argonne National Laboratory Report ANL-02/18 (2001).

LEONARD-2001D

R. A. Leonard, *Caustic-Side Solvent Extraction for Optimized Solvent*, Argonne National Laboratory Letter Report ANL/CMT/CSSX-2001/07 (2001). This report is being prepared for issue as Argonne National Laboratory Report ANL-02/19 (2001).

LEONARD-2002

R. A. Leonard, S. B. Aase, H. A. Arafat, D. B. Chamberlain, C. Conner, J. R. Falkenberg, M. C. Regalbuto, and G. F. Vandegrift, *Multi-Day Test of the Caustic-Side Solvent Extraction Flowsheet for Cesium Removal from a Simulated SRS Tank Waste*, Argonne National Laboratory Report ANL-02/11 (2002).

LEVENSON-2000

M. Levenson, et al., *Alternatives for High-Level Waste Salt Processing at the Savannah River Site*, National Research Council, National Academy Press, Washington, DC (2000).

PETERSON-2000

R. A. Peterson, *Preparation of Simulated Waste Solutions for Solvent Extraction Testing*, Westinghouse Savannah River Co. Report WSRC-RP-2000-361 (May 1, 2000).

REID-1958

R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids: Their Estimation and Correlation*, McGraw-Hill, New York (1958).

WALKER-1998

D. D. Walker and G. K. Georgeton, *Viscosity and Density of Simulated Salt Solutions*, Westinghouse Savannah River Company Report WSRC-RP-89-1088 (October 19, 1989).

Distribution List for ANL-02/22

Internal (Printed and Electronic Copies):

S. B. Aase	E. Freiberg	M. C. Regalbutto (5)
H. A. Arafat	A. V. Guelis	M. J. Steindler
A. J. Bakel	J. E. Helt	G. F. Vandegrift
D. B. Chamberlain	R. A. Leonard (5)	S. K. Zussman
Y. I. Chang	D. Lewis (2)	
M. L. Dietz	K. L. Nash	

Internal (Electronic Copy Only):

TIS Files
D. L. Bowers
R. J. Finch
E. C. Gay
C. J. Mertz
J. Sedlet

External (Printed and Electronic Copies):

Chemical Technology Division Review Committee Members:

H. U. Anderson, University of Missouri-Rolla, Rolla, MO
R. A. Greenkorn, Purdue University, West Lafayette, IN
C. L. Hussey, University of Mississippi, University, MS
M. V. Koch, University of Washington, Seattle, WA
V. P. Roan, Jr., University of Florida, Gainesville, FL
J. R. Selman, Illinois Institute of Technology, Chicago, IL
J. S. Tulenko, University of Florida, Gainesville, FL
J. F. Birdwell, Oak Ridge National Laboratory, Oak Ridge, TN
P. V. Bonnesen, Oak Ridge National Laboratory, Oak Ridge, TN
S. G. Campbell, Westinghouse Savannah River Company, Aiken, SC
J. T. Carter, Westinghouse Savannah River Company, Savannah River Technology Center, Aiken, SC
C. Conner, BWX Technologies, Inc., Lynchburg, VA
L. H. Delmau, Oak Ridge National Laboratory, Oak Ridge, TN
H. D. Harmon, Westinghouse Savannah River Company, Aiken, SC
R. T. Jubin, Oak Ridge National Laboratory, Oak Ridge, TN
J. D. Law, Idaho National Engineering and Environmental Laboratory, Research Center, Idaho Falls, ID
R. Leugemors, Pacific Northwest National Laboratory, Richland, WA
G. J. Lumetta, Battelle, Pacific Northwest National Laboratory, Richland, WA
B. A. Moyer, Oak Ridge National Laboratory, Oak Ridge, TN
M. Norato, Westinghouse Savannah River Company, Aiken, SC

R. A. Pierce, Westinghouse Savannah River Company, Aiken, SC
P. C. Suggs, DOE-SR, Aiken, SC
M. C. Thompson, Westinghouse Savannah River Company, Savannah River Technology Center,
Aiken, SC
T. A. Todd, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID
D. D. Walker, Westinghouse Savannah River Company, Aiken, SC

External (Printed Copy Only):

Tanks Focus Area Technical Team, c/o B. J. Williams, Pacific Northwest National Laboratory,
Richland, WA
Tanks Focus Area Field Lead, c/o T. P. Pietrok, DOE, Richland Operations Office,
Richland, WA
Tanks Focus Area Headquarters Program Manager, c/o K. D. Gerdes, DOE-EM,
Germantown, MD

External (Electronic Copy Only):

ANL-E-Library
ANL-W-Library
DOE-OSTI
W. D. Clark, DOE-SR, Aiken, SC
S. M. Dinehart, Los Alamos National Laboratory, Los Alamos, NM
R. E. Edwards, Westinghouse Savannah River Company, Aiken, SC
S. D. Fink, Westinghouse Savannah River Company, Aiken, SC
L. N. Klatt, Oak Ridge National Laboratory, Oak Ridge, TN
D. E. Kurath, Battelle, Pacific Northwest National Laboratory, Richland, WA
K. T. Lang, USDOE, Washington, DC
J. W. McCullough, USDOE, Aiken, SC
C. P. McGinnis, Oak Ridge National Laboratory, Oak Ridge, TN
M. Miles, Oak Ridge National Laboratory, Oak Ridge, TN
A. L. Olson, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID
M. J. Palmer, Los Alamos National Laboratory, Los Alamos, NM
L. M. Papouchado, Westinghouse Savannah River Company, Aiken, SC
R. A. Peterson, Bechtel-Washington Process Technology, Richland, WA
B. M. Rapko, Battelle, Pacific Northwest National Laboratory, Richland, WA
R. D. Rogers, University of Alabama, Tuscaloosa, AL
K. J. Rueter, Bechtel-Washington Process Technology, Richland, WA
P. Rutland, Bechtel-Washington Process Technology, Richland, WA
S. N. Schlahta, Battelle, Pacific Northwest National Laboratory, Richland, WA
J. L. Swanson, Richland, WA
W. L. Tamosaitis, Westinghouse Savannah River Company, Aiken, SC
L. L. Tavlarides, Syracuse University, Syracuse, NY
D. W. Tedder, Georgia Institute of Technology, Atlanta, GA
V. Van Brunt, University of South Carolina, Columbia, SC

J. F. Walker, Oak Ridge National Laboratory, Oak Ridge, TN
J. S. Watson, Oak Ridge National Laboratory, Oak Ridge, TN
R. M. Wham, Oak Ridge National Laboratory, Oak Ridge, TN
V. Wheeler, Oak Ridge National Laboratory, Oak Ridge, TN
W. R. Wilmarth, Westinghouse Savannah River Company, Aiken, SC