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Nuclear Science and Technology Division

CAUSTIC-SIDE SOLVENT EXTRACTION SOLVENT-COMPOSITION RECOMMENDATION

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

The U.S. Department of Energy has selected caustic-side solvent extraction as the preferred cesium removal technology for the treatment of high-level waste stored at the Savannah River Site. Data for the solubility of the extractant, calix[4]arene-bis(*tert*-octyl benzo-crown-6), acquired and reported for the Salt Processing Program down-select decision, showed the original solvent composition to be supersaturated with respect to the extractant. Although solvent samples have been observed for approximately 1 year without any solids formation, work was completed to define a new solvent composition that was thermodynamically stable with respect to solids formation and to expand the operating temperature with respect to third-phase formation. Chemical and physical data as a function of solvent component concentrations were collected. The data included calix[4]arene-bis(*tert*-octyl benzo-crown-6) solubility; cesium distribution ratio under extraction, scrub, and strip conditions; flow sheet robustness; temperature range of third-phase formation; dispersion numbers for the solvent against waste simulant, scrub and strip acids, and sodium hydroxide wash solutions; solvent density; viscosity; and surface and interfacial tension. These data were mapped against a set of predefined performance criteria. The composition of 0.007 *M* calix[4]arene-bis(*tert*-octyl benzo-crown-6), 0.75 *M* 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, and 0.003 *M* tri-*n*-octylamine in the diluent Isopar® L provided the best match between the measured properties and the performance criteria. Therefore, it is recommended as the new baseline solvent composition.

1. BASIS FOR TASK AND SUMMARY RECOMMENDATION

The purpose of this report is to provide the experimental information that forms the basis for a recommended change in the baseline composition of the caustic-side solvent extraction (CSSX) solvent. The current baseline CSSX solvent composition is 0.010 *M* calix[4]arene-bis(*tert*-octyl benzo-crown-6), known as BOBCalixC6; 0.5 *M* 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, known as Cs-7SB modifier; and 0.001 *M* tri-*n*-octylamine (TOA) in the diluent Isopar® L.[1] Data for the solubility of BOBCalixC6 acquired and reported for the Salt Processing Program (SPP) alternative technology down-select decision showed that the above composition is supersaturated with respect to BOBCalixC6.[2] Although samples of the baseline solvent have been observed for approximately 1 year without any solids formation, the CSSX technical team recommended that a solvent-composition optimization task be undertaken to address the BOBCalixC6 solubility and other issues,[3] such as third-phase formation, as a function of the plant operating temperature.

To accomplish the task of recommending a new baseline solvent composition, the CSSX technical team and the Tanks Focus Area (TFA) and SPP management teams, in cooperation with the U.S. Department of Energy–Savannah River (DOE-SR), developed an experimental program designed to provide the required information. Part of this effort included the development of the solvent-composition selection criteria.[4]

The recommendation for the new solvent composition is a consensus opinion of the CSSX technical team. The recommended composition is as follows:

- 0.007 *M* BOBCalixC6,
- 0.75 *M* Cs-7SB modifier,
- 0.003 *M* TOA, and
- Isopar® L diluent.

Table 1 contains a summary of the bounding and goal selection criteria and the value of the experimental property for the respective criterion for the recommended solvent composition.

It should be noted that the criteria dealing with the change in the cesium distribution ratio D_{Cs} values as a function of solvent composition (i.e., solvent robustness) and the cost of solvent components did not enter into the decision process. These two criteria were intended to be used if the other criteria identified multiple acceptable compositions.

Table 1. Summary of selection criteria and associated properties

Criterion	Bounding condition	Goal condition	Value of property
BOBCalixC6 solubility	Thermodynamically stable	Thermodynamically stable	≥7.55 m*M* at 25°C
D_{Cs} values	Extraction D_{Cs}: >8 Scrub D_{Cs}: >0.6 Strip D_{Cs}: <0.16	Extraction D_{Cs}: >17.8 Scrub D_{Cs}: >1.6 Strip D_{Cs}: <0.15	Extraction D_{Cs} = 14.1 Scrub D_{Cs} = 1.3 Strip D_{Cs} = 0.10
Flow sheet robustness	1.0	3.0	>8.0
Third-phase formation	$15 \leq T \leq 35^{o}C$ at $[K^+] = 0.05$ *M*	$15 \leq T \leq 35^{o}C$ at $[K^+] = 0.05$ *M*	<10°C at $[K^+] = 0.05$ *M*
Dispersion number against simulant, scrub, and strip solutions	>4.0E–04	>4.0E–04	>5.0E–04
Dispersion number against NaOH wash solution	>4.0E–04	>4.0E–04	>4.5E–04 at 0.3 *M* NaOH
Solvent density	≤0.90 g/mL at 25°C	≤0.86 g/mL at 25°C	0.85 g/mL at 25.6°C

2. EXPERIMENTAL APPROACHES

2.1 SOLVENT TEST SAMPLES

A total of 13 test samples of solvent were prepared for this study. The compositions of these samples are given in Table 2. A sample of the baseline solvent was included for reference purposes. Single lots of modifier (Lot No. PVB B000894-48P) and BOBCalixC6 (Lot No. IBC 000714HMKC-0004) were used to prepare all of the test samples. Solvents containing 3 and 10 m*M* TOA were prepared by adding a measured amount of 0.2 *M* TOA in Isopar® L to the solvents originally prepared with 1 m*M* TOA. All solvents were washed twice with 0.1 *M* NaOH, twice with 0.05 *M* HNO_3, three times with deionized water, and allowed to stand overnight before being decanted into clean containers. Scrub (0.05 *M* HNO_3) and strip (0.001 *M* HNO_3) solutions were prepared by diluting commercially available stock solutions with deionized water. Sodium hydroxide solutions were prepared by diluting a commercially available standard solution. Savannah River Site (SRS) waste supernatant simulant was formulated according to the SRS procedure.[5] The nominal cesium concentration in all the simulant batches used in the testing was 0.00014 *M*. Aliquots of the solvent were transferred to the Nuclear Science and Technology Division (NSTD) at Oak Ridge National Laboratory (ORNL) for measurements of dispersion number, viscosity, density, surface tension, and interfacial tension. Other measurements, plus the initial solvent preparation, were carried out in the ORNL Chemical Sciences Division (CSD).

Table 2. Test sample compositions

Solvent identification	Test no.	BOBCalixC6 (m*M*)	Cs-7SB modifier (*M*)	TOA (m*M*)
Current baseline		10	0.50	1
B001107-3-1	1	10	0.65	1
B001107-3-2	2	8	0.65	1
B001107-3-3	3	10	0.75	1
B001107-3-4	4	8	0.75	1
B001107-3-5	5	6	0.75	1
B001107-3-6	6	8	0.85	1
B001107-3-7	7	6	0.85	1
B001107-3-8	8	8	1.00	1
B001107-3-9	9	6	1.00	1
B001107-3-2A	10	8	0.65	3
B001107-3-2B	11	8	0.65	10
B001107-3-4C	12	8	0.75	3
B001107-3-4D	13	8	0.75	10

2.2 EXPERIMENTAL PROCEDURES

2.2.1 BOBCalixC6 Solubility Studies

A series of solvents were prepared from five different pristine nonwashed solutions of Cs-7SB modifier in Isopar® L (0.5, 0.65, 0.75, 0.85, and 1.0 *M*) containing 1 m*M* TOA as follows. Three and one-half grams of BOBCalixC6 (Lot 000714 HMKC-0004) was dissolved in 50 mL of modifier solution in Isopar® L by applying sonication and heating to about 50°C, cooling to room temperature, and then seeding with about 2 mg of recrystallized BOBCalixC6. The samples were then shaken and divided into six samples of equal volume. Samples in duplicate were placed in a water bath at 15°C, an air box at 25°C, and an incubator at 35°C. Agitation was effected by shaking in the water bath and wheel rotation in the air box and incubator. The initial concentration of BOBCalixC6 in each sample was 59 m*M*. After a given time interval, the samples were allowed to settle for 30 to 60 min, whereupon an aliquot of the supernatant solution was withdrawn, filtered through No. 40 filter paper, diluted with chloroform, and submitted for high-performance liquid chromatography (HPLC) analysis. Samples archived from the solubility study initiated approximately 1 year ago[2] were also analyzed.

2.2.2 Extraction, Scrub, and Strip Protocol

Extraction, scrub, and strip (ESS) tests were performed on all of the samples listed in Table 2. The experiments were conducted following the protocol defined in Ref. 2, using organic:aqueous volume ratios (O:A) of 1:3 on extraction and 5:1 on scrubs and strips. An extra scrub step was added to the previous protocol[2] to more realistically approximate the flow sheet. It should be noted that the solvent weakly extracts sodium and potassium, and the second scrub step more completely removes these metals from the solvent prior to stripping. With only one scrub, the first strip step is expected to yield slightly higher values of D_{Cs} because the incomplete scrubbing of sodium and potassium implies that these metal nitrates will report to the aqueous phase of the first strip step, thereby increasing the aqueous-phase nitrate concentration. The data validating the modified ESS protocol are given in Table 3. The data confirm that addition of the second scrub improves stripping performance as expected. The D_{Cs} values are slightly dependent on the O:A ratios employed, with better performance occurring when the strip O:A ratio is lower. All stripping D_{Cs} values converge to the same value upon successive stripping. In the solvent-optimization tests, an increase in modifier concentration is expected to increase sodium and potassium extraction.[2] However, the consequent negative impact on stripping is expected to be essentially eliminated by the second scrub and thus appropriately rendered an insignificant factor in solvent selection.

Table 3. Validation data for the modified ESS protocol

	Value of D_{Cs} by O:A ratios[a]			
	1:3 (E) 5:1 (SS)	1:5 (E) 3:1 (SS)	1:3 (E) 5:1 (SS)	1:5 (E) 3:1 (SS)
Extraction	17.6	17.1	16.6	17.3
Scrub no. 1	1.55	1.57	1.56	1.57
Scrub no. 2	NA	NA	1.56	1.57
Strip no. 1	0.137	0.130	0.120	0.116
Strip no. 2	0.080	0.075	0.078	0.071
Strip no. 3	0.064	0.064	0.062	0.062
Strip no. 4	0.052	0.054	0.052	0.054

[a] The letter "E" denotes O:A ratio for extraction; "SS" denotes O:A ratio for scrub and strip.

2.2.3 Third-Phase Determination

Third-phase formation experiments involved the ten solvents containing 1 m*M* of TOA and three different simulants: baseline simulant ($[\mathrm{Cs}^+]$ = 0.14 m*M*, $[\mathrm{K}^+]$ = 0.02 *M*); high-potassium simulant ($[\mathrm{Cs}^+]$ = 0.14 m*M*, $[\mathrm{K}^+]$ = 0.05 *M*); and high-potassium, high-cesium simulant ($[\mathrm{Cs}^+]$ = 0.44 m*M*, $[\mathrm{K}^+]$ = 0.05 *M*). These conditions encompass those that could be potentially encountered with real wastes.[1] After two repeated contacts with the simulants (O:A = 1:3) at 25°C, the solvent samples were cooled in a water bath and shaken periodically. The presence and/or absence of a third phase was determined by independent examination by two researchers.

2.2.4 Dispersion-Number Measurement

Dispersion numbers were determined under extraction, scrubbing, and stripping conditions in the presence of cesium. Prior to use, all new or previously used glassware and plastic vessels were washed by rinsing with tap water three times, rinsing with demineralized water three times, rinsing with ethanol two times, and rinsing with acetone two times. The equipment was allowed to air dry or was dried with a stream of dry nitrogen or argon before use. In all tests, phase volumes proportional to the flow rates of the solvent, scrub, and strip solutions in the CSSX baseline flow sheet were placed into a 100-mL graduated Pyrex® cylinder. The position of the interface was recorded. The cylinder was capped with a ground-glass stopper, and the solutions were agitated for 20 s. Agitation was suspended for 10 s and then resumed for an additional 20 s. At the end of the second agitation, a stopwatch was started and the time required for the interface to return to its original position was recorded. In these tests, the “original” position was assumed to be that within 1–2 mm of the interface prior to the agitation and when all indications of dispersed phases at the interface had disappeared. The total height of the dispersion within the cylinder was measured. Each determination was repeated three times. Dimensionless dispersion numbers were calculated according to the expression[6]

$$N_{Di} = \frac{1}{t_b}\sqrt{\frac{z}{g_c}} \quad , \tag{1}$$

where t_b is the break time in seconds, z is the dispersion band height in centimeters, and g_c is the gravitational force of 981 cm/s^2.

2.2.5 Density

The solvent densities were measured using procedures based on ASTM D891[7] and ASTM D1429,[8] using new 50-mL class A borosilicate glass volumetric flasks with ground-glass stoppers. Calibration of the volumetric flasks for density measurements was performed based on ASTM E542.[9] A Mettler AE260 analytical balance (S/N J19097) capable of measuring to 0.1 mg was used to weigh the flasks. National Institute of Standards and Technology (NIST)–based test weights were used to check the balance calibration. A thermometer accurate to 0.1°C (LaPine 398-12-53) was used to measure the temperature of the liquid in the flasks. The flasks were cleaned and dried before each use as described above, using tap water, deionized water, ethanol, and acetone, followed by drying with argon gas. Each flask was filled using a 10-mL transfer pipette to just below the line and then adjusted to the line with a small transfer pipette. The actual volume of each flask was calculated from the weight of the water contained.

2.2.6 Viscosity

The viscosities of each of the nine candidate solvents and the original solvent were measured at 20, 25, 30, 35, and 40°C using procedures adapted from ASTM D2196[10] and the Brookfield viscometer operating instructions.[11] The determinations were made using a Brookfield rotational viscometer, model LVTDV-II, serial number D15869, with a UL adapter. The water jacket on the UL adapter was heated and cooled by a VWR model 13270-615 circulation bath, with 190-Ws cooling, and operated at a coolant recirculation rate of ~2 L/min. It contained a 50/50 mixture of ethylene glycol and water, which was circulated by the water bath circulation pump. The thermometer used, the LaPine 398-12-53, was immersed in the water bath for the temperature measurement. (There is no room in the UL adapter for a thermometer.) The spindle speed was set to give a torque percent reading in the middle or upper portion of the scale. The UL adapter (a large-diameter spindle in a cylindrical container just slightly larger in diameter than the spindle) is used for measuring low-viscosity liquids (liquids with viscosities between 1 and 20 cP). The UL adapter with spindle holds 16 mL of sample for measurement.

Each test was begun by adding the test solvent to the UL adapter, installing it on the viscometer, starting the spindle rotation at 60 rpm, and then setting the temperature bath to 20°C. After the temperature had stabilized for several minutes, the viscosity of the sample was measured. The temperature bath was then adjusted to the next temperature and the system temperature allowed to stabilize before the next reading was taken.

2.2.7 Surface Tension and Interfacial Tension

The surface tensions of each of the nine candidate solvents, the original solvent, simulant, strip solution, and scrub solution were measured at ~25°C using a CSC Du Nouy tensiometer (serial number 013457) with a 6-cm-circumference ring. The experimental procedures were adapted from ASTM D971[12] and ASTM D1331.[13] The tensiometer was calibrated against known weights and its zero point adjusted according to the procedure of the manufacturer. Interfacial tension was determined by measuring the force necessary to detach a planar ring of platinum wire from the surface of the liquid of higher surface tension, that is, upward from the aqueous-organic interface. To calculate the interfacial tension, the force so measured was corrected by an empirically determined factor that depends upon the force applied, the densities of both organic and aqueous layers, and the dimensions of the ring. Measurements are made under rigidly standardized nonequilibrium conditions in which the measurement is completed within 60 s after formation of the interface. The surface tension of deionized water was measured to determine that the apparatus was functioning correctly. A value of 71–73 dyn/cm must be obtained; the literature value at 25°C is 72.0 dyn/cm.[14]

A Teflon™ sample container having a minimum diameter of 45 mm was used. The container was cleaned as described above (with tap water, deionized water, ethanol, and acetone) between each solvent/aqueous determination. The ring was then flamed in a blue gas flame, using spinning to obtain rapid, uniform heating. The ring should barely glow orange and should be heated for no more than 5 s.

Interfacial tension measurements were made by carefully placing a layer of the organic on the surface of the aqueous layer (the aqueous layer was placed in the container first and the ring submerged in this layer) until a depth of at least 10 mm was reached using a pipette. This procedure was used to ensure that minimum mixing occurred and that the organic did not touch the surface of the submerged ring. The organic-aqueous interface was allowed to age for 30 ± 1 s after the last of the organic had been layered onto the water. The platform was lowered and the value at rupture recorded. The measurement was timed so that, as nearly as possible, 30 s was required to draw the ring through the interface. The entire operation, from the time of pouring the organic onto the aqueous until the interface ruptured, was completed in about 60 ± 10 s. Each solvent was tested in duplicate, with the cup and the ring cleaned between the two readings.

The interfacial tension of the sample was calculated by means of the following equation:

$$\text{Interfacial tension, dyn/cm} = P \times \mathrm{F}\ , \tag{2}$$

where P is the scale reading when the film ruptures (in dynes per centimeter), and F is the factor converting the scale reading (in dynes per centimeter) to interfacial tension, as obtained from Eq. (3). The value of the diameter ratio, *R*/*r*, for the ring, as specified by the manufacturer, is 53.6. The value of F is obtained as follows:

$$F = 0.7250 + [0.01452P/C^2(D - d) + 0.04534 - 1.679/(R/r)]^{½} , \qquad (3)$$

where C is the circumference of the ring (5.992 cm); D is the density of the aqueous layer at 25°C, in grams per milliliter; d is the density of organic layer for interfacial testing at 25°C, in grams per milliliter; *R* is the radius of ring, in centimeters; and *r* is the radius of the wire of the ring, in centimeters.

3. EXPERIMENTAL RESULTS

3.1 BOBCALIXC6 SOLUBILITY

The data on the BOBCalixC6 are a combination of information acquired from the experiments conducted in the latter portion of FY 2001 (see Experimental Section) and from the previous experiment reported in Ref. 2. This summary of the experimental results is necessary because of the long periods of time required for the BOBCalixC6 to achieve the solubility equilibrium condition. Table 4 summarizes the data obtained from the most recent solubility study.

Table 4. BOBCalixC6 solubility data from FY 2001 study[a]

	BOBCalixC6 (m*M*)								
	15°C			25°C			35°C		
Cs-7SB (*M*)	Initial	4 wks	8 wks	Initial	4 wks	8 wks	Initial	4 wks	8 wks
0.50	59	17.5	8.80	59	11.7	10.7	59	9.5	7.94
0.65	59	22.9	11.5	59	17.3	14.0	59	12.9	9.72
0.75	59	35.0	15.2	59	19.7	13.1	59	15.4	11.2
0.85	59	45.6	18.3	59	35.7	15.9	59	20.5	14.7
1.0	59	49.5	25.7	59	54.1	23.1	59	44.7	19.0

[a] Each value is the average of duplicate analyses.

The time trend analysis of the data shows that after 8 weeks, solubility equilibrium has not been achieved. Nevertheless, the data imply the supersaturation of the baseline solvent.

A conservative estimate of the lower bound of the BOBCalixC6 solubility at 25°C was obtained by reanalysis of samples from the solubility study that was initiated approximately 1 year ago.[2] These samples had been stored at temperature with intermittent agitation. Selected results are summarized in Fig. 1. As indicated in the legend, data are shown for both as-received and recrystallized BOBCalixC6 and for equilibrium approached from the direction of both dissolution and precipitation. In each case, no TOA or water is present in the solvent; that is, solid BOBCalixC6 is suspended in Cs-7SB at the indicated concentration in Isopar® L only. A tabulation of the data after 1 year, including systems containing TOA and water, is given in Table 5. Except for the single data point at 0.25 *M* Cs-7SB, which shows a deviation of ±26%, the average analytical deviation among duplicate samples is ±3.5%. The data show that TOA and water have little or no effect on BOBCalixC6 solubility.

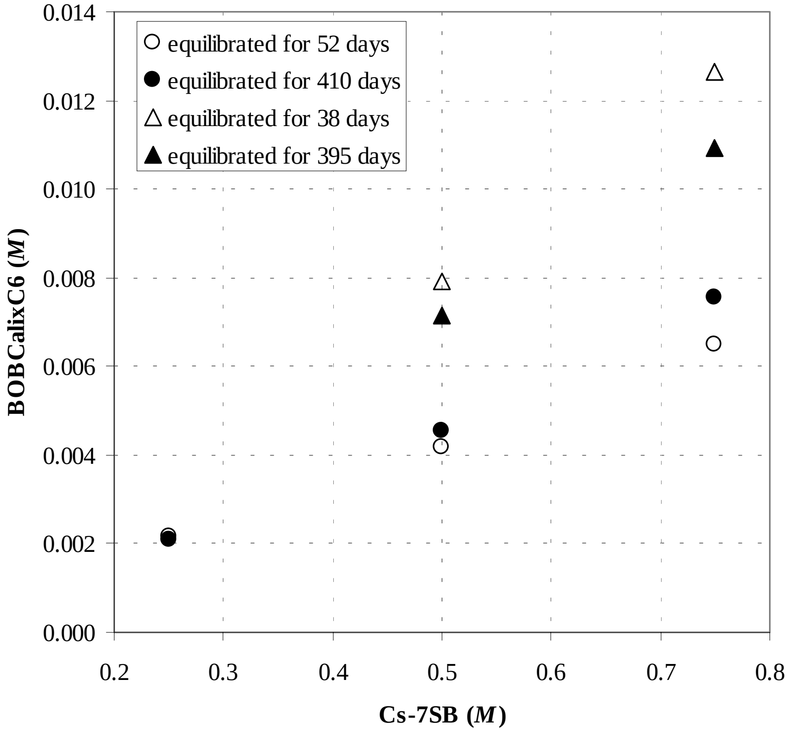

Fig. 1. Comparison of BOBCalixC6 solubility data. The circles correspond to solubility tests performed by dissolution with recrystallized calixarene; the triangles correspond to solubility tests performed by precipitation with calixarene used as-received.

Conservatively, the lower bound of the BOBCalixC6 thermodynamic solubility corresponds to the recrystallized BOBCalixC6 that has been dissolving over the course of the past 13 months. At 0.75 *M* Cs-7SB, the lower bound at 25°C is 7.55 m*M*. Although the solubility of BOBCalixC6 generally increases with increasing Cs-7SB concentration, a gap exists between the data for the recrystallized BOBCalixC6 that is dissolving and the as-received BOBCalixC6 that is precipitating.

Table 5. BOBCalixC6 solubility data from FY 2000 study[a]

Sample no.	Cs-7SB (*M*)	TOA (m*M*)	Solvent washed?	Dissolution method	BOBCalixC6 purification	BOBCalixC6 (m*M*)	BOBCalixC6 average (m*M*)
5-A	0.25	0	No	Dissolve	Recrystallized	2.62	
5-B	0.25	0	No	Dissolve	Recrystallized	1.55	2.08
6-A	0.50	0	No	Dissolve	Recrystallized	4.31	
6-B	0.50	0	No	Dissolve	Recrystallized	4.76	4.54
7-A	0.75	0	No	Dissolve	Recrystallized	6.98	
7-B	0.75	0	No	Dissolve	Recrystallized	8.12	7.55
8-A	0.50	1	No	Dissolve	Recrystallized	4.38	
8-B	0.50	1	No	Dissolve	Recrystallized	4.48	4.43
9-A	0.50	1	Yes	Dissolve	Recrystallized	4.26	
9-B	0.50	1	Yes	Dissolve	Recrystallized	4.64	4.45
10-A	0.50	1	No	Precipitate	Recrystallized	6.18	
10-B	0.50	1	No	Precipitate	Recrystallized	6.68	6.43
11-A	0.50	0	No	Precipitate	As received	7.26	
11-B	0.50	0	No	Precipitate	As received	7.05	7.15
12-A	0.75	0	No	Precipitate	As received	11.1	
12-B	0.75	0	No	Precipitate	As received	10.8	10.95
13-A	0.50	0	Yes	Precipitate	As received	5.11	
13-B	0.50	0	Yes	Precipitate	As received		

[a] HPLC analysis of samples held at 25°C for approximately 13 months.

From the data shown in Fig. 1, one may conclude that the true solubility of BOBCalixC6 in Isopar® L that contains only Cs-7SB at 25°C lies within this gap. Both sets of data show a very slow convergence over the course of the past year. The increases in solubility upon dissolution were 8.4 and 16.5% for 0.5 and 0.75 *M* Cs-7SB, respectively. The comparable decreases upon precipitation were 9.7 and 13.4% for 0.5 and 0.75 *M* Cs-7SB, respectively. At this time, it is impossible to determine conclusively whether the upper set differs from the lower set because of the purity of BOBCalixC6 or because of the direction from which equilibrium is being approached. However, we argue that the latter cause is more probable, because the high concentration of Cs-7SB likely negates any effects on solubility of minor impurities in the as-received BOBCalixC6. As discussed earlier,[2] these impurities apparently have an effect on the rate of dissolution of BOBCalixC6. Whereas recrystallized BOBCalixC6 can be dissolved very slowly (even with prolonged sonication and warming), the as-received material, nominally 97% pure, quickly dissolves to concentrations as high as 50 m*M*. For this reason, it has been impractical to experimentally approach equilibrium by precipitation of recrystallized BOBCalixC6. It is clear, then, that the lower bound of 7.55 m*M* BOBCalixC6 at 0.75 *M* Cs-7SB is a conservative estimate for the BOBCalixC6 solubility. Not only is the final plateau concentration of BOBCalixC6 likely to be higher, but the most realistic condition in a plant environment is for equilibrium to be approached by precipitation of the as-received material.

3.2 CESIUM DISTRIBUTION RESULTS

The cesium distribution data obtained with the ESS tests are summarized in Tables 6 and 7. The data in Table 6 are for the series of test samples containing 1 m*M* TOA, and the results in Table 7 are for the series of test samples containing varying amounts of TOA and modifier with fixed BOBCalixC6 concentration.

Table 6. ESS results obtained with constant TOA concentration[a]

BOBCalixC6 (m*M*)	Cs-7SB (*M*)	Extr.	Scrub no. 1	Scrub no. 2	Strip no. 1	Strip no. 2	Strip no. 3	Strip no. 4
10	0.50	17.2	1.52	1.52	0.114	0.070	0.055	0.051
10	0.65	19.6	1.75	1.79	0.136	0.084	0.066	0.057
10	0.75	20.7	1.91	1.91	0.152	0.092	0.072	0.062
8	0.65	15.4	1.38	1.44	0.109	0.066	0.053	0.045
8	0.75	16.1	1.52	1.54	0.120	0.075	0.056	0.050
8	0.85	17.2	1.68	1.66	0.134	0.077	0.062	0.053
8	1.00	17.7	1.87	1.78	0.145	0.086	0.069	0.060
6	0.75	12.2	1.12	1.16	0.089	0.051	0.042	0.036
6	0.85	12.3	1.23	1.25	0.095	0.055	0.044	0.040
6	1.00	13.6	1.39	1.39	0.112	0.065	0.051	0.046

[a]Temperature = 25°C.

Interest in increasing the TOA concentration is twofold. First, as the TOA concentration increases, the CSSX process becomes more resistant to anionic impurities. Second, thermal[2] and radiolytic[15,16] stability test results showed that TOA is the solvent component most susceptible to decomposition. However, the concentration cannot be increased excessively, because the organic-phase concentration of nitrate in the scrub stage will increase by the protonation of TOA. This nitrate will be partially released in

Table 7. ESS results obtained with two selected solvents with variable TOA concentrations[a]

TOA (m*M*)	Extr.	Scrub no. 1	Scrub no. 2	Strip no. 1	Strip no. 2	Strip no. 3	Strip no. 4
			BOBCalixC6 = 8 m*M*, Cs-7SB = 0.65 *M*				
1	15.4	1.38	1.44	0.109	0.066	0.053	0.045
3	14.9	1.08	1.39	0.116	0.081	0.069	0.056
10	14.7	1.00	0.76	0.134	0.104	0.090	0.076
			BOBCalixC6 = 8 m*M*, Cs-7SB = 0.75 *M*				
1	16.4	1.54	1.55	0.121	0.073	0.059	0.052
3	15.5	1.26	1.49	0.124	0.083	0.075	0.059
10	15.2	1.20	0.70	0.137	0.101	0.091	0.078

[a] Temperature = 25°C.

the first strip stage, causing the value of D_{Cs} for the first strip stage to increase, which could ultimately limit the stripping effect. Assuming an O:A ratio of 5:1 in the strip section, the stripping effect becomes inhibited when the first strip D_{Cs} value becomes equal to or greater than 0.2. The data show that stripping will not be inhibited at TOA concentrations as high as 10 m*M*.

The results show that values of D_{Cs} for the two scrubs decrease as the concentration of TOA increases. This behavior is expected since the overall concentration of nitrate in the organic phase increases to ensure the electroneutrality of the protonated TOA. The D_{Cs} values for the first strip also increase. Again, this result is expected because the higher concentration of protonated TOA in the organic phase results in more nitrates being released in the first strip stage. As a result of this higher nitrate concentration in the first strip stage, more stages are required for the D_{Cs} value to converge to the limiting value. This limiting value should, in principle, be the same for all TOA concentrations.

Based on the cesium distribution ratio (D_{Cs}) data contained in Tables 6 and 7, all of the tested solvent compositions meet the D_{Cs} acceptance criterion.

The D_{Cs} values in Tables 6 and 7, when analyzed as log(D_{Cs}) vs log(BOBCalixC6 concentration) and log(D_{Cs}) vs log(Cs-7SB modifier concentration), are linear with slopes approximately equal to one. Using these relationships, a simple set of equations can be used to predict the D_{Cs} values as a function of the BOBCalixC6 and Cs-7SB modifier concentrations. The results of the prediction for BOBCalixC6 and modifier concentrations about the recommended solvent composition are given in Appendix A, Table A.1.

3.3 FLOW SHEET ROBUSTNESS

A series of Spreadsheet Algorithm for Stagewise Solvent Extraction (SASSE)[17] calculations were performed using the D_{Cs} values contained in Tables 6 and 7. The assumptions used in these calculations include the following: (1) the extraction and scrub D_{Cs} values are proportional to the concentration of free BOBCalixC6 in the organic phase; (2) the BOBCalixC6 is loaded with only one cesium ion; (3) the D_{Cs} value for the strip is proportional to the concentration of nitrate in the aqueous phase; (4) the total cesium concentration of the waste feed is 0.00014 *M*; (5) the temperature of the entire contactor cascade is 25°C; (6) the stage efficiency is 80%; (7) 0.1% other-phase carryover occurs between stages; (8) there are 15 extraction stages, 2 scrub stages, and 15 strip stages; (9) there are 20.1 gal/min of waste feed and 1.33 gal/min of strip feed; and (10) the O:A in the scrub section is 5.0.

The results of the calculations are given in Table 8. The robustness number (Rb) is defined as the ratio of the decontamination factor for a given set of flow sheet conditions to the process-required bounding decontamination factor of 40,000. The baseline flow sheet specifies a solvent flow rate of 6.6 gal/min.[1] The maximum robustness was obtained by varying the solvent flow rate, which is shown in the fourth column of Table 8.

All of the solvent compositions tested meet the bounding criterion for robustness at the baseline solvent flow rate; however, the two solvent compositions containing 10 m*M* TOA do not meet the “goal” (i.e., the target criterion) for robustness. When the solvent flow rate is adjusted to achieve the maximum robustness, all of the solvent compositions meet the goal for robustness.

It should be noted that the SASSE calculations are conservative since they assume a constant process temperature and a stage efficiency of 80%. In the actual process, the extraction section will be kept cooler than the strip section, thereby improving the process robustness. For example, if the extraction section were at 25°C, the scrub section at 29°C, and the strip section at 33°C, the robustness for the baseline solvent at a flow rate of 6.6 gal/min increases from 21.9 to 80.7. Thus, process robustness can be increased substantially by means of temperature control.

While a stage efficiency of 80% was assumed for the centrifugal contactor, the expected efficiency will be greater than 90%.[18,19] Assuming a 90% stage efficiency in the SASSE calculations at 25°C, the robustness for the baseline solvent at a flow rate of 6.6 gal/min would increase from 21.9 to 599. Thus, higher stage efficiency, which we can expect with the plant-scale contactors, will also increase process robustness.

Table 8. Calculated robustness for various CSSX solvent compositions

Solvent identification[a]	Rb at 6.6 gal/min waste feed	Rb_{max}	Optimum flow rate (Flow rate at Rb_{max}, gal/min)
Current baseline	21.9	25.3	6.1
B001107-3-1	11.9	26.4	5.3
B001107-3-2	25.0	25.3	6.7
B001107-3-3	6.6	23.6	4.9
B001107-3-4	19.3	20.7	6.2
B001107-3-5	8.8	24.3	8.5
B001107-3-6	15.7	21.2	5.8
B001107-3-7	9.1	17.8	8.0
B001107-3-8	7.3	15.4	5.4
B001107-3-9	14.3	15.6	7.0
B001107-3-2A	8.8	10.1	6.1
B001107-3-2B	1.1	3.0	5.3
B001107-3-4C	6.9	9.7	5.8
B001107-3-4D	1.0	3.2	5.1

[a] See Table 2 for the composition of the specified solvent.

3.4 THIRD-PHASE FORMATION

One of the major criteria the solvent must meet is the absence of third-phase formation for the expected maximum loading of the solvent at 15°C, which occurs at the high cesium and potassium concentrations. This requirement was determined in FY 2001 at the time the process temperature range was established.[1] The results of the third-phase evaluations for solvents containing 1 m*M* TOA are presented in Table 9. Results of these experiments indicate that the use of any solvent containing 10 m*M* BOBCalixC6 is not recommended at a Cs-7SB modifier concentration less than 0.75 *M*.

Table 9. Temperature range for third-phase appearance

		Temperature range (°C)		
BOBCalixC6 (m*M*)	Cs-7SB (*M*)	Full SRS simulant	High-potassium simulant	High-cesium and high-potassium simulant
10	0.50	15.0 – 16.5	17.5 – 20.0	17.5 – 20.0
10	0.65	12.0 – 13.0	15.0 – 16.5	15.0 – 16.5
10	0.75	10.0 – 11.0	12.0 – 13.0	12.0 – 13.0
8	0.65	10.0 – 11.0	12.0 – 13.0	12.0 – 13.0
8	0.75	8.5 – 9.0	10.0 – 11.0	10.0 – 11.0
8	0.85	7.5 – 8.0	8.5 – 9.0	8.5 – 9.0
8	1.0	6.5 – 7.0	6.5 – 7.0	6.5 – 7.0
6	0.75	6.5 – 7.0	8.0 – 8.5	8.5 – 9.0
6	0.85	5.0 – 6.5	7.0 – 7.5	7.0 – 7.5
6	1.00	F[a]	F[a]	F[a]

[a] The letter "F" indicates that the solvent did not exhibit a third phase at 5°C. However, because of the high concentration of modifier, the solvent viscosity had increased significantly at that temperature, making observation of a third phase difficult.

3.5 SOLVENT DISPERSION NUMBERS

The results for the dispersion-number determinations are given in Table 10 and shown graphically in Fig. 2. The subset of the solvent test samples contained 1 m*M* TOA. The data for the baseline solvent are taken from earlier testing.[18] The results show that all nine compositions meet the dispersion number criterion for extraction, scrub, and strip conditions.

Dispersion-number determinations for a selected subset of the samples against 10 m*M* NaOH wash solutions are shown in Fig. 3. None of the solvent samples met the NaOH solvent-wash solution criterion. The 10 m*M* NaOH concentration was used during the FY 2001 flow sheet tests at Argonne National Laboratory,[20] which used simulant as the feed, and tests at Savannah River Technology Center,[21] which used real waste as the feed. During these tests, small amounts of emulsion formation were observed. Solvent samples B001107-3-4 and B001107-3-5 were determined to have the most-desirable

Table 10. Dispersion numbers for extraction, scrub, and stripping of CSSX solvents

Sample description[a]	Dispersion number Simulant/solvent	Scrub/solvent	Strip/solvent	Wash/solvent, 0.01 *N* NaOH (O:A = 5:1)
Original solvent[b]	0.00149	0.000964	0.00115	–
B001107-3-1	0.000750	0.001019	0.000909	–
B001107-3-2	0.000565	0.000700	0.000776	0.000221
B001107-3-3	0.001021	0.000522	0.000886	–
B001107-3-4	0.001025	0.000530	0.000941	0.000345
B001107-3-5	0.001181	0.000501	0.000876	0.000238
B001107-3-6	0.001051	0.000589	0.000751	0.000163
B001107-3-7	0.001252	0.000581	0.000846	0.000159
B001107-3-8	0.001201	0.000622	0.000541	–
B001107-3-9	0.001411	0.000408	0.000506	–

[a] See Table 2 for the composition of the specified solvent.
[b] Original solvent data were taken on the baseline virgin solvent.

characteristics when compared against all of the selection criteria. These two solvents were selected for dispersion-number determinations as a function of NaOH concentrations. The results of these tests are given in Table 11 and shown graphically in Fig. 4. When the NaOH concentration was 300 m*M*, these two solvent compositions met the dispersion-number criterion for solvent washing.

3.6 SOLVENT DENSITY

The results of the density determinations are presented in Table 12. As expected, solvent density is primarily dependent on the modifier concentration. The relationship between density and modifier concentration is shown in Fig. 5. All the solvent samples that were tested met the bounding criterion for density; however, the solvent samples with modifier concentrations equal to or greater than 0.85 *M* did not meet the goal for density.

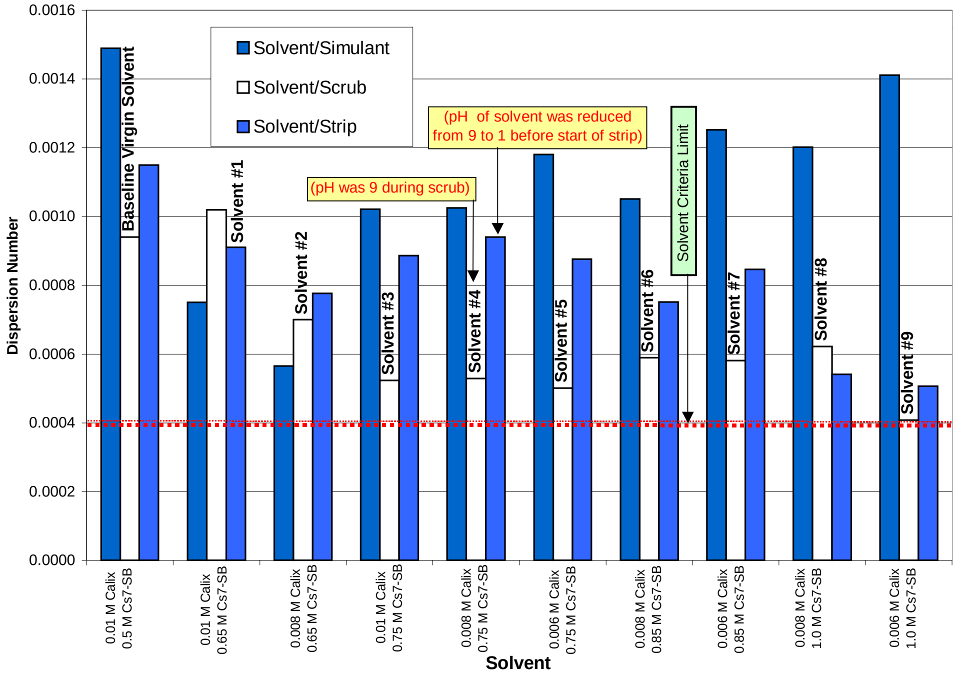

Fig. 2. CSSX solvent dispersion numbers for extraction, scrub, and strip conditions at baseline O:A ratios.

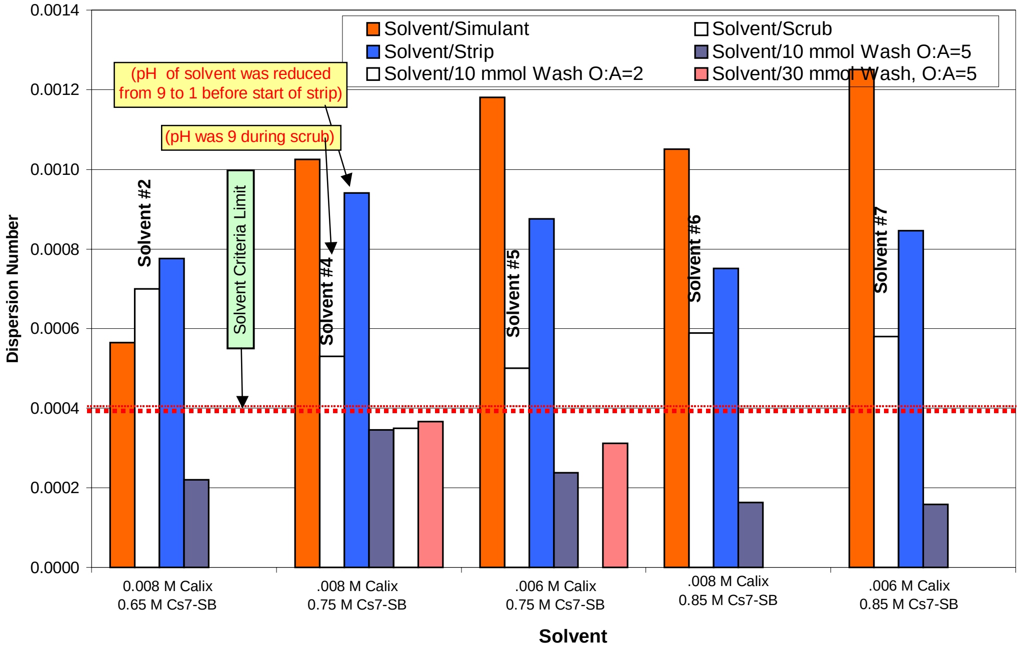

Fig. 3. CSSX solvent dispersion numbers for solvent wash with dilute NaOH.

Table 11. Dispersion numbers for washing of CSSX solvents B001107-3-4 and B001107-3-5

Solvent description[a]	Solvent/wash dispersion number 0.01 *M* NaOH wash	0.03 *M* NaOH wash	0.1 *M* NaOH wash	0.3 *M* NaOH wash
B001107-3-4	0.000345	0.000366	0.000368	0.000490
B001107-3-5	0.000238	0.000311	0.000241	0.000450

[a] See Table 2 for the composition of the specified solvent.

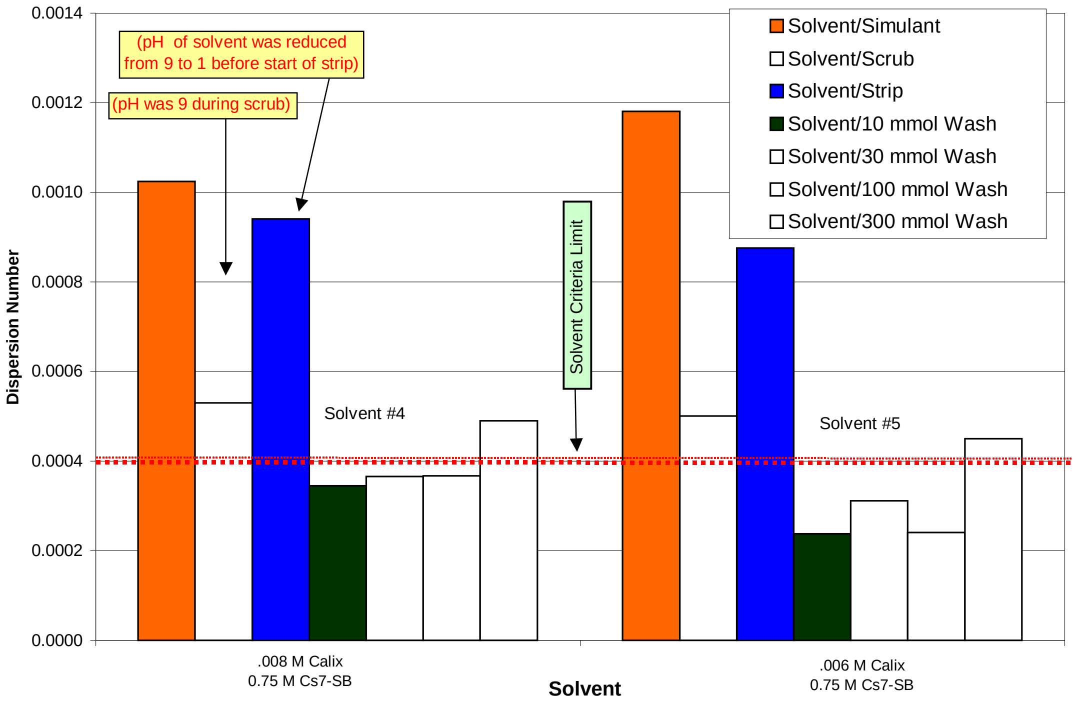

Fig. 4. CSSX solvent dispersion numbers for solvent wash conditions as a function of NaOH concentration.

3.7 SOLVENT VISCOSITY

The results of the solvent viscosity measurements are shown in Fig. 6, and Fig. 7 shows the shear stress as a function of temperature. The data are presented in tabular form in Table 13.

Table 12. Solvent density determinations

Solvent identification[a]	Mass of solvent (g)	Density[b] (g/cm^3)	Calix (*M*)	Modifier (*M*)	Corrected volume (mL)	Mass of water (g)	Sp gr	50-mL vol. flask
Baseline[c]		0.810						
B001107-3-1	41.9085	0.8395	0.010	0.65	49.9202	49.7819	0.99723	1
B001107-3-2	41.9230	0.8395	0.008	0.65	49.9362	49.7979	0.99723	2
B001107-3-3	42.5920	0.8531	0.010	0.75	49.9242	49.7859	0.99723	3
B001107-3-4	42.5149	0.8525	0.008	0.75	49.8703	49.7322	0.99723	5
B001107-3-5	42.4714	0.8516	0.006	0.75	49.8703	49.7322	0.99723	5
B001107-3-6	43.0887	0.8644	0.008	0.85	49.8480	49.7099	0.99723	6
B001107-3-7	43.1036	0.8632	0.006	0.85	49.9362	49.7979	0.99723	2
B001107-3-8	44.0269	0.8819	0.008	1.00	49.9242	49.7859	0.99723	3
B001107-3-9	44.6565	0.8951	0.006	1.00	49.8925	49.7543	0.99723	4

[a] See Table 2 for the composition of the specified solvent.
[b] Temperature = 25.6°C.
[c] Measured previously on baseline virgin solvent.

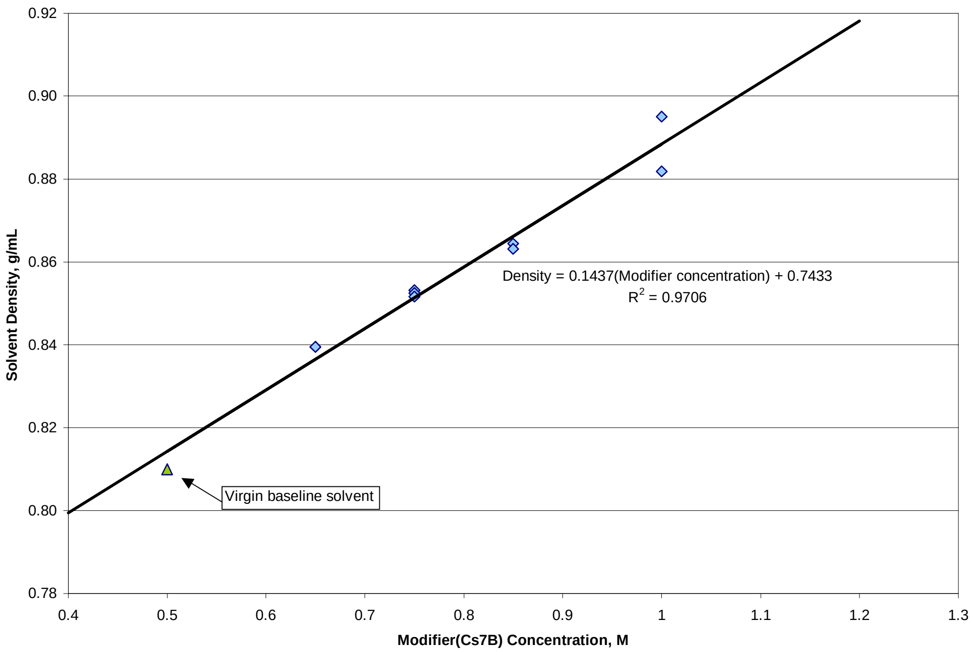

Fig. 5. CSSX solvent density as a function of Cs-7SB modifier concentration for 25.6°C.

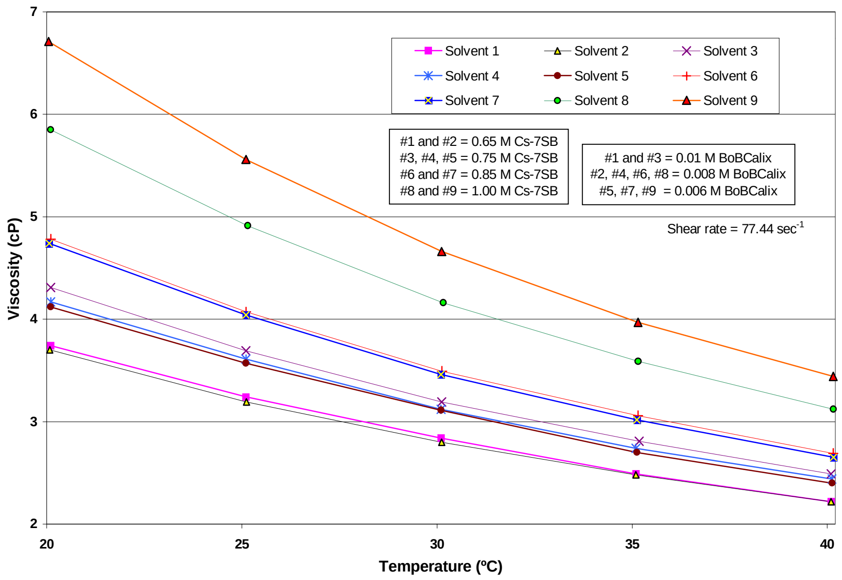

Fig. 6. Solvent viscosity as a function of temperature. The numbers in the legend are the test numbers from Table 2.

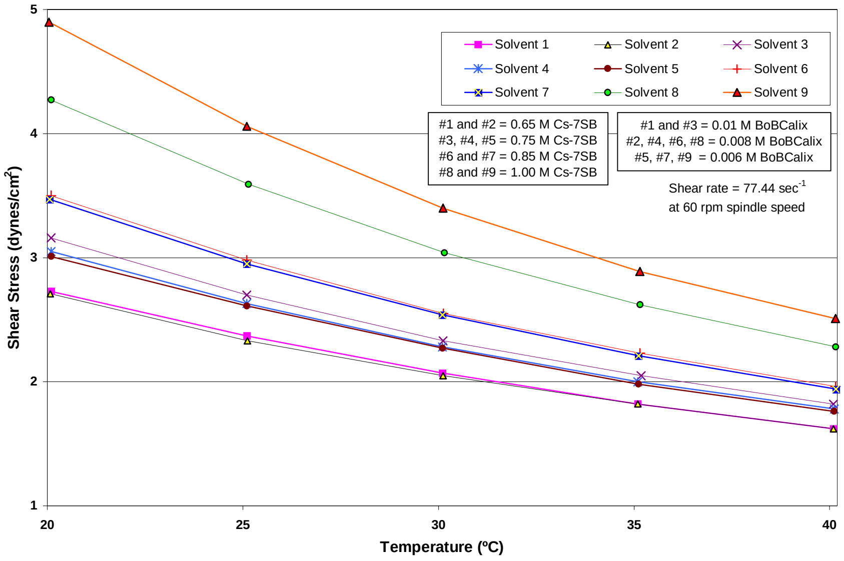

Fig. 7. Solvent shear stress as a function of temperature. The solvent numbers in the legend are the test numbers from Table 2.

The solvents with the lowest concentrations of the Cs-7SB modifier have the lowest viscosity. The BOBCalixC6 concentration has only a minor effect on the viscosity decrease, because its concentration decreases at a given Cs-7SB concentration. The viscosity of all solvent samples decreases with increasing temperature, as expected for this type of liquid.

Table 13. Solvent viscosity determinations[a]

Solvent[b]	Temperature (°C)	Torque (%)	Viscosity (cP)[c]	Shear stress (dyn/cm^2)
B001107-3-1	20.00	37.3	3.74	2.73
	25.00	32.3	3.24	2.37
	30.00	28.2	2.84	2.07
	35.00	24.9	2.49	1.82
	40.00	22.2	2.22	1.62
B001107-3-2	19.98	36.9	3.70	2.71
	25.02	31.9	3.19	2.33
	30.02	28.0	2.80	2.05
	35.00	24.8	2.48	1.82
	40.00	22.2	2.22	1.62
B001107-3-3	20.00	43.2	4.31	3.16
	25.00	36.9	3.69	2.70
	30.02	31.9	3.19	2.33
	35.08	28.0	2.81	2.05
	40.00	24.8	2.49	1.82
B001107-3-4	20.00	41.8	4.17	3.05
	25.00	36.0	3.61	2.63
	30.00	31.2	3.12	2.28
	35.00	27.4	2.74	2.00
	40.02	24.4	2.44	1.78
B001107-3-5	20.00	41.3	4.12	3.01
	25.00	35.7	3.57	2.61
	30.00	31.0	3.11	2.27
	35.02	27.1	2.70	1.98
	40.02	24.0	2.40	1.76
B001107-3-6	20.00	47.8	4.78	3.50
	25.00	40.7	4.07	2.98
	30.03	34.9	3.49	2.55
	35.05	30.5	3.06	2.23
	40.05	26.8	2.69	1.96
B001107-3-7	19.96	47.3	4.74	3.47
	25.00	40.3	4.04	2.95
	30.00	34.6	3.46	2.54
	35.02	30.2	3.02	2.21
	40.06	26.6	2.65	1.94
B001107-3-8	20.00	58.5	5.85	4.27
	25.05	49.0	4.91	3.59
	30.06	41.6	4.16	3.04
	35.06	35.8	3.59	2.62
	40.06	31.3	3.12	2.28
B001107-3-9	19.95	67.1	6.71	4.90
	25.00	55.4	5.56	4.06
	30.02	46.5	4.66	3.40
	35.05	39.7	3.97	2.89
	40.05	34.3	3.44	2.51

[a] Brookfield LVTDV-II (serial number D15869) UL adapter with heating jacket.
[b] See Table 2 for the composition of the specified solvent.
[c] SD = ±0.1 centipoise (cP).

3.8 SOLVENT INTERFACIAL TENSION

The results of the measurements are given in Tables 14–17 and are shown graphically in Figs. 8 and 9. The tables contain the data for the four series of tests. Figure 8 shows the surface tension of the solvents and also contains the surface tensions of the simulant, scrub solution, and strip solutions. Figure 9 shows the interfacial tension of the solvents versus simulant, scrub, and strip solutions. The results reveal nothing unusual, and the individual solvents behave similarly with the three aqueous solutions tested.

Table 14. Surface tension determinations

Solvent identification[a]	Density, D (g/cm^3)	Indicated surface tension (dyn/cm)		Instrument reading, average (P)	Correction factor from formula	Actual surface tension (dyn/cm)
		Trial 1	Trial 2			
B001107-3-1	0.8395	26.9	26.8	26.9	0.8896	23.9
B001107-3-2	0.8395	26.8	26.8	26.8	0.8895	23.8
B001107-3-3	0.8531	26.8	26.7	26.8	0.8888	23.8
B001107-3-4	0.8525	26.8	26.9	26.9	0.8890	23.9
B001107-3-5	0.8516	27.0	27.1	27.1	0.8893	24.1
B001107-3-6	0.8644	27.0	26.9	27.0	0.8886	23.9
B001107-3-7	0.8632	26.9	27.0	27.0	0.8886	23.9
B001107-3-8	0.8819	27.0	27.1	27.1	0.8879	24.0
B001107-3-9	0.8951	27.1	27.0	27.1	0.8874	24.0
Strip	0.9974	41.0	40.0	40.5	0.8999	36.4
Scrub	0.9984	48.3	48.1	48.2	0.9085	43.8
Simulant	1.2536	64.6	64.8	64.7	0.9122	59.0

[a] See Table 2 for the composition of the specified solvent.

Table 15. Interfacial tension versus simulant

Solvent identification[a]	Density (g/cm^3)	Indicated interfacial tension (dyn/cm)		Instrument reading, average (P)	Correction factor from formula	Actual interfacial tension (dyn/cm)
		Trial 1	Trial 2			
B001107-3-1	0.8395	20.5	20.8	20.7	0.9103	18.8
B001107-3-2	0.8395	20.8	20.7	20.8	0.9106	18.9
B001107-3-3	0.8531	20.9	20.8	20.9	0.9127	19.0
B001107-3-4	0.8525	20.7	20.5	20.6	0.9119	18.8
B001107-3-5	0.8516	20.7	20.6	20.7	0.9119	18.8
B001107-3-6	0.8644	20.3	20.4	20.4	0.9129	18.6
B001107-3-7	0.8632	20.2	20.4	20.3	0.9126	18.5
B001107-3-8	0.8819	20.5	20.5	20.5	0.9160	18.8
B001107-3-9	0.8951	20.1	20.3	20.2	0.9172	18.5

[a] See Table 2 for the composition of the specified solvent.

Table 16. Interfacial tension versus scrub solution

Solvent identification[a]	Density (g/cm^3)	Indicated interfacial tension (dyn/cm)		Instrument reading, average (P)	Correction factor from formula	Actual interfacial tension (dyn/cm)
		Trial 1	Trial 2			
B001107-3-1	0.8395	18.6	17.5	18.1	0.9703	17.5
B001107-3-2	0.8395	16.8	16.9	16.9	0.9640	16.2
B001107-3-3	0.8531	16.5	16.6	16.6	0.9706	16.1
B001107-3-4	0.8525	16.7	16.5	16.6	0.9704	16.1
B001107-3-5	0.8516	16.6	16.5	16.6	0.9696	16.0
B001107-3-6	0.8644	16.4	16.3	16.4	0.9772	16.0
B001107-3-7	0.8632	16.1	16.1	16.1	0.9748	15.7
B001107-3-8	0.8819	16.0	16.0	16.0	0.9892	15.8
B001107-3-9	0.8951	16.0	15.8	15.9	1.0016	15.9

[a] See Table 2 for the composition of the specified solvent.

Table 17. Interfacial tension versus strip solution

Solvent identification[a]	Density (g/cm^3)	Indicated interfacial tension (dyn/cm)		Instrument reading, average (P)	Correction factor from formula	Actual interfacial tension (dyn/cm)
		Trial 1	Trial 2			
B001107-3-1	0.8395	16.0	16.0	16.0	0.9599	15.4
B001107-3-2	0.8395	16.0	15.9	16.0	0.9596	15.3
B001107-3-3	0.8531	15.2	15.8	15.5	0.9651	15.0
B001107-3-4	0.8525	16.0	15.8	15.9	0.9670	15.4
B001107-3-5	0.8516	15.2	15.7	15.5	0.9639	14.9
B001107-3-6	0.8644	15.7	15.6	15.7	0.9736	15.2
B001107-3-7	0.8632	15.7	15.6	15.7	0.9727	15.2
B001107-3-8	0.8819	15.6	15.8	15.7	0.9880	15.5
B001107-3-9	0.8951	16.0	15.5	15.8	1.0015	15.8

[a] See Table 2 for the composition of the specified solvent.

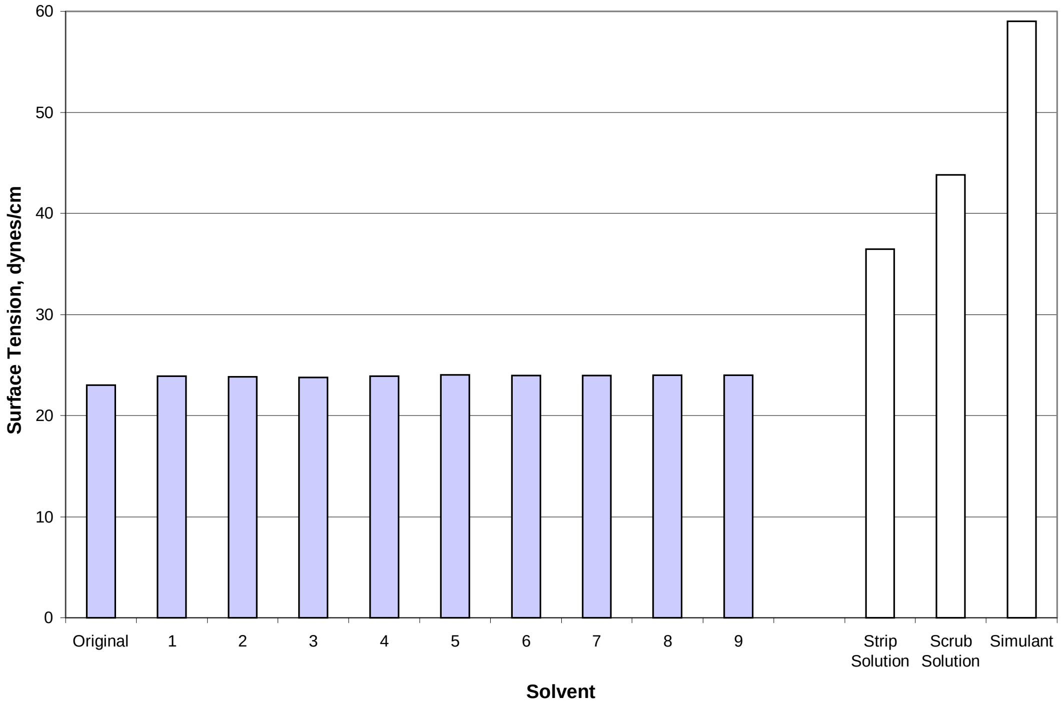

Fig. 8. Solvent and process solution surface tension. The numbers on the abscissa are the test numbers from Table 2.

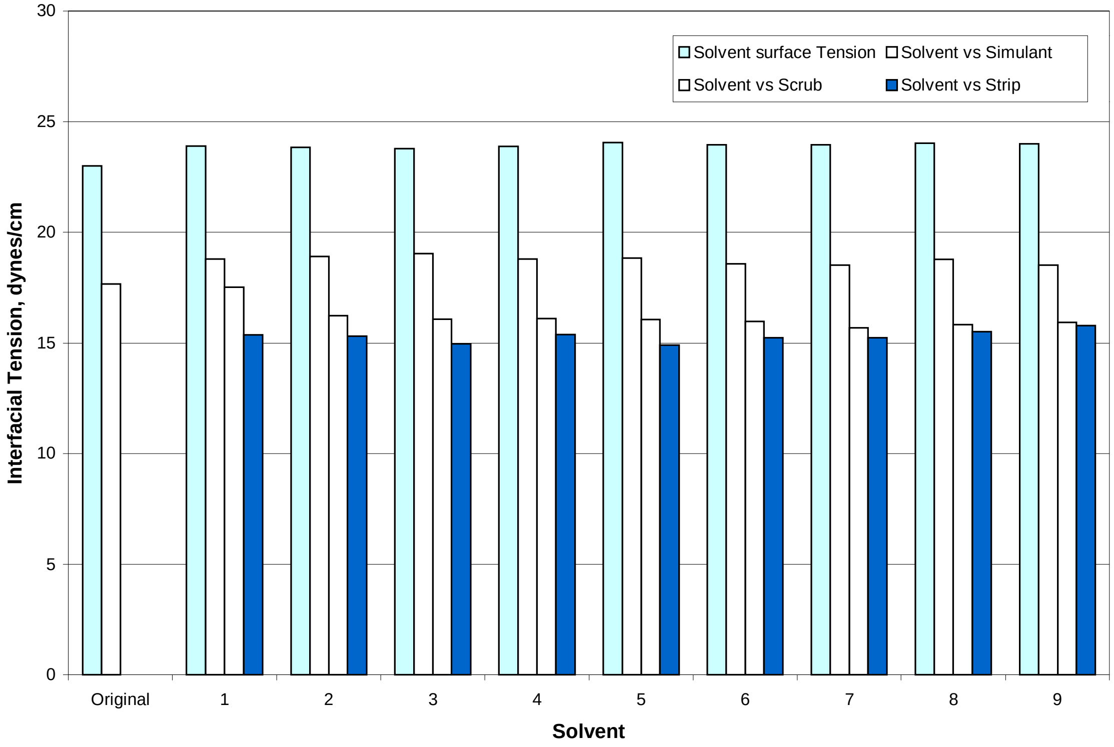

Fig. 9. Solvent interfacial tension in extraction, scrub, and strip contacts. The numbers on the abscissa are the test numbers from Table 2.

4. SOLVENT COMPOSITION RECOMMENDATION PROCESS

The process used by the CSSX team to arrive at the solvent-composition recommendation involved several actions. First, the experimental data described in this report were distributed to the team members. Second, two conference calls were held. During the first call, the methods of data acquisition and the significance of the data relative to the selection criteria were discussed.[4] The action item from this discussion was for each participant to make a recommendation concerning the solvent composition and forward this information to all of the participants. A compilation of the individual recommendations was distributed prior to the second conference call. The second call focused on the individual recommendations. Between the two calls, a technical presentation was given during the weekly TFA program status review.[22] The recommended composition was a consensus opinion of the CSSX technical team.

The rationale used by the CSSX team in arriving at the recommended solvent composition is described in Ref. 4.

The primary criterion involved the selection of a composition that is thermodynamically stable with respect to the solubility of BOBCalixC6. The fact that BOBCalixC6 has a solubility limit of 7.55 m*M* suggests that the concentration should be less than 7.5 m*M* to accommodate variations in solvent preparation without exceeding this limit. The solubility data also indicate that the thermodynamic solubility value for BOBCalixC6 is linked to the Cs-7SB modifier concentration. For example, if the BOBCalxC6 concentration is 7 m*M*, the Cs-7SB modifier concentration should be approximately 100 times higher. The data on third-phase formation also suggest the need for a solvent composition with a BOBCalixC6 concentration of 8 m*M* or less and a Cs-7SB modifier concentration of at least 0.65 *M*. The density criterion suggests compositions with the Cs-7SB modifier concentration equal to or less than 0.85 *M*. Contactor throughput and phase separation are dependent on the density difference of the two phases; that is, for a given contactor size, throughput is higher and the phase separation performance generally improves as the density difference increases.

Although all of the candidate compositions met the bounding criterion for the D_{Cs} values, only the current baseline composition meets the goal. Thus, a composition with D_{Cs} values close to the goal is preferred because it would provide the ability to process waste blends that have properties that are modestly different from those of the waste simulant composition. The flow sheet robustness calculations suggest a BOBCalixC6 concentration between 6 and 8 m*M* and a modifier concentration between 0.65 and 0.85 *M*.

The combination of BOBCalixC6 solubility, D_{Cs} values, and high flow sheet robustness, as well as the desire to have a low density, establishes the basis for the 7 m*M* BOBCalixC6 and 0.75 *M* Cs-7SB modifier concentration recommendation.

The 3 m*M* TOA concentration recommendation is based on three considerations. First, the flow sheet robustness calculations indicate that 10 m*M* TOA will require the use of an optimized solvent flow rate to achieve process performance above the bounding condition. Second, since TOA is the solvent component most susceptible to thermal and radiolytic decomposition, selecting a TOA concentration higher than the 1 m*M* baseline value will provide the CSSX process more resistance to the variations in anionic impurity content that are certain to be encountered with the different waste blends. Third, a TOA concentration greater than 1 m*M* will also provide greater flexibility in solvent preparation and process control.

The solvent dispersion numbers for all the solvent compositions tested against the waste simulant, scrub, and strip solutions met the selection criterion and consequently did not provide a means to differentiate between different solvent compositions. However, comparison of solvent dispersion numbers against the 0.01 *M* NaOH solvent wash solution indicates the need to reevaluate the NaOH concentration used for solvent washing.

Although the viscosity, surface tension, and interfacial tension were not explicitly identified in any of the selection criteria, these physical properties can impact the dispersion number. Therefore, experimental determination of these properties was included in the study to verify that no unexpected behavior occurred. The experimental results did not reveal any such behavior.

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Appendix A

PREDICTED D_{Cs} VALUES USING THE log VERSUS log RELATIONSHIPS BETWEEN D_{Cs} VALUES AND BOBCALIXC6 AND Cs-7SB MODIFIER CONCENTRATIONS

Table A.1. Predicted D_{Cs} values

	Cs-7SB modifier		
Process step	0.70 *M*	0.75 *M*	0.80 *M*
BOBCalixC6 = 6.5 m*M*			
Extraction	12.76	13.08	13.40
Scrub no. 1	1.16	1.22	1.28
Scrub no. 2	1.21	1.26	1.31
Strip no. 1	0.91	0.096	0.101
Strip no. 2	0.054	0.057	0.059
Strip no. 3	0.043	0.045	0.047
Strip no. 4	0.037	0.039	0.041
BOBCalixC6 = 7.0 m*M*			
Extraction	13.77	14.13	14.48
Scrub no. 1	1.26	1.32	1.38
Scrub no. 2	1.30	1.35	1.40
Strip no. 1	0.099	0.104	0.109
Strip no. 2	0.059	0.062	0.065
Strip no. 3	0.047	0.049	0.051
Strip no. 4	0.040	0.043	0.045
BOBCalixC6 = 7.5 m*M*			
Extraction	14.78	15.18	15.56
Scrub no. 1	1.35	1.42	1.49
Scrub no. 2	1.39	1.45	1.50
Strip no. 1	0.106	0.112	0.117
Strip no. 2	0.060	0.070	0.070
Strip no. 3	0.051	0.053	0.055
Strip no. 4	0.044	0.046	0.048

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