**Development of the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) Process for Cesium Removal from High-Level Tank Waste–11346**

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## ABSTRACT

This paper describes the chemical performance of the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) process in its current state of development for removal of cesium from the alkaline high-level tank wastes at the Savannah River Site (SRS) in the US Department of Energy (USDOE) complex. Overall, motivation for seeking a major enhancement in performance for the currently deployed CSSX process stems from needs for accelerating the cleanup schedule and reducing the cost of salt-waste disposition. The primary target of the NG-CSSX development campaign in the past year has been to formulate a solvent system and to design a corresponding flowsheet capable of boosting the performance of the SRS Modular CSSX Unit (MCU) from a current minimum decontamination factor of 12 to ≥40,000. The chemical approach entails use of a more soluble calixarene-crown ether, called MaxCalix, allowing the attainment of much higher cesium distribution ratios ($D_{Cs}$) on extraction. Concurrently decreasing the Cs-7SB modifier concentration is anticipated to promote better hydraulics. A new stripping chemistry has been devised using a vitrification-friendly aqueous boric acid strip solution and a guanidine suppressor in the solvent, resulting in sharply decreased $D_{Cs}$ on stripping. Results are reported herein on solvent phase behavior and batch Cs distribution ratios for waste simulants and real waste together with a preliminary flowsheet applicable for implementation in the MCU. The new solvent will enable MCU to process a much wider range of salt feeds and thereby extend its service lifetime beyond its design life of three years. Other potential benefits of NG-CSSX include increased throughput of the SRS Salt Waste Processing Facility (SWPF), currently under construction, and an alternative modular near-tank application at Hanford.

## INTRODUCTION

### General R&D Goals for Next Generation Caustic-Side Solvent Extraction
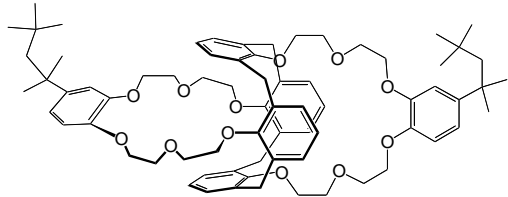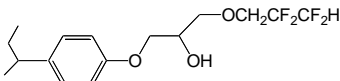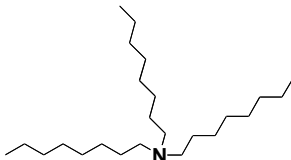
This paper describes the development and testing of the chemistry of the Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) process for removal of cesium from the high-level salt wastes stored in underground tanks in the US Department of Energy (USDOE) complex. Current results apply directly to processing salt waste at the Savannah River Site (SRS) but may also be extended by implication to Hanford wastes. Together, SRS and Hanford tank wastes represent the most costly and complex problem in the cleanup of the USDOE sites [1]. Salt waste constitutes the predominant volume fraction of tank waste (82% at Hanford and 88% at the SRS), and cesium-137 is the predominant radionuclide in the salt waste, making cesium-137 the major target for separation in the development and implementation of tank pretreatment technologies [2]. Solvent-extraction and ion-exchange technologies are being implemented for cesium separation respectively in the SRS Salt Waste Process Facility (SWPF) and Hanford Waste Treatment Plant (WTP), both under construction. The Caustic-Side Solvent Extraction (CSSX) process as designed and demonstrated previously [3–8] will be deployed in the SWPF [9], scheduled to be

commissioned in 2015. Pilot testing of the CSSX process for SWPF began with the start-up of the Modular CSSX Unit (MCU) at the SRS in April 2008 [10–13]. By December 2010, this first-of-a-kind facility has processed over 1.2 Mgal of feed while providing valuable lessons learned [12,13] and demonstrating sustained operation. While still providing data for SWPF, the MCU is now an operational part of the SRS Salt Waste Disposition Program. Its service life, however, is by design only approximately three years, since it was only intended to process a limited volume of low-curie feed ($\leq$1.1 Ci/gal). From a general point of view, motivation for seeking higher performance for the CSSX process stems essentially from near-term needs for tank space, long-term needs for accelerating the cleanup schedule, and overall cost savings in salt-waste disposition [1,2]. Specific opportunities for realizing such benefits include extension of the service life of the MCU, increasing the processing rate of the SWPF, and providing a backup technology for Hanford, possibly in the form of a near-tank modular unit similar to MCU [14]. The most urgent need is to extend the service life of MCU so that it can continue to process salt waste at least until SWPF comes on line, and accordingly, R&D efforts in the past year have focused on providing NG-CSSX technology that can meet this goal. In so doing, R&D also lays the groundwork for the potential applications at SWPF and Hanford.

**Description of the Current CSSX Technology**

As shown by the recent MCU experience, the CSSX process is robust and performs in some respects even better than expected [12,13], but there are clear improvements in the technology that could serve to advance the salt-processing goals described above. To explain the approach to effecting these improvements, the basic features of the CSSX solvent system currently in use at MCU and being implemented in SWPF will first be outlined. The CSSX solvent system is defined in Table I. The chemical function of each solvent component has been summarized in a recent review [3]. Briefly, BOBCalixC6 selectively binds $Cs^+$ ion vs virtually all competing ions. It is employed at or just under its solubility limit of 0.007 M, which limits the attainable cesium distribution ratio $D_{Cs}$ to approximately 14 at 25°C for the average SRS salt-waste composition [5]. The modifier Cs-7SB is required to boost the solubility of BOBCalixC6, prevent third-phase formation, and enhance the extraction strength. Its concentration was set at 0.75 M, both to raise the BOBCalixC6 solubility and to increase $D_{Cs}$ as far as possible without seriously compromising the hydraulic performance of the contactors [4]. Used at only 0.003 M, TOA suppresses impurity and ion-pair dissociation effects that would otherwise impair stripping performance [15]. In simplest terms, the solvent cycle functions by nitrate concentration swing. That is, the high nitrate concentration in the salt waste drives the extraction, forming the complex $[(BOBCalixC6)Cs^+]NO_3^-$ in the organic phase, and a low nitrate concentration in stripping allows the

Table I. Components of the CSSX Solvent [3].[a]

| Extractant | Modifier | Suppressor |
|---|---|---|
|  |  |  |
| BOBCalixC6 | Cs-7SB | TOA |
| Calix[4]arene-bis(*tert*-octylbenzocrown-6) | 1-(2,2,3,3-tetrafluoropropoxy),-3-[4-(*sec*-butyl)phenoxy]-2-propanol | Tri-*n*-octylamine |
| 0.007 M | 0.75 M | 0.003 M |

[a]The components are dissolved in Isopar® L diluent, an isoparafinic hydrocarbon.

BOBCalixC6 complex to release $CsNO_3$ to the aqueous strip phase. In the process, a 0.050 M $HNO_3$ scrub solution is employed to remove all extracted components other than $CsNO_3$ and to acidify the solvent phase. Major ions removed in scrubbing include $Na^+$, $K^+$, and various anions that can substitute for nitrate, such as nitrite, chloride, and hydroxide equivalents. Stripping is then accomplished with 0.001 M $HNO_3$. Solvent cleanup is achieved by washing with 0.01 M NaOH, designed to remove rogue anions (e.g., dibutylphosphate, *sec*-butylphenol, and surfactants like dodecylsulfonate) that can otherwise accumulate in the solvent and eventually interfere with stripping [15,16]. To achieve a concentration factor (CF) of 15, the SWPF will employ organic:aqueous (O:A) volumetric phase ratios of 1:3 (extraction, organic-to-feed), 5:1 (scrub), 5:1 (strip), and 5:1 (wash). MCU employs similar O:A ratios with a slightly smaller CF of 12.

**Proposed Next-Generation CSSX Technology**

Recent research efforts [17–19] have established an attractive approach to dramatically boost both extraction and stripping efficiency as well as to improve hydraulic efficiency. On the extraction side, efforts have sought to identify a more soluble calixarene-crown ether, allowing the attainment of much higher $D_{Cs}$ with increased calixarene concentration, which in turn means that a higher decontamination factor (DF) can be obtained in the same number of extraction stages, provided that stripping can also be improved. It also means that more challenging feed types, such as Hanford salt waste with high potassium content, can be processed, as the resulting lower $D_{Cs}$ values can be offset with higher calixarene concentration [18,19]. At the same time, a new stripping chemistry has been devised with vitrification-friendly boric acid that will sharply decrease $D_{Cs}$ on stripping. The strategy entails decoupling the stripping section from the nitrate-swing principle, as otherwise the increased calixarene concentration would simply increase the stripping $D_{Cs}$ by approximately the same factor as that on extraction, to no gain for overall process efficiency. To accomplish this, it was necessary to switch to an alkaline scrub so that not only will potassium be removed, but the nitrate in the solvent will also be replaced by hydroxide equivalents. The hydroxide equivalents can then react with boric acid in the strip solution to make inextractable cesium borate, effecting super-efficient stripping. A scrub with NaOH has the added benefit of better compatibility with the alkaline conditions of extraction, mainly in eliminating one possible source of particulate solids and its attendant difficulties (e.g., clogged coalescers [12,13,20] and crud formation) due to aqueous carryover into scrubbing and scrub solution mixing with waste feed in the first extraction stage; that is, aluminate precipitation upon neutralization of drops of waste feed is avoided. Increasing throughput entails a three-pronged strategy. First, increased $D_{Cs}$ values allow O:A ratios to be decreased on extraction, which at constant total throughput begets increased salt feed throughput. Further, the more soluble calixarene allows the modifier concentration to be decreased, thereby decreasing solvent density and viscosity, which in turn promotes better hydraulics. Finally, provided hydraulics and up- or down-stream operations are not adversely impacted, a higher salt feed concentration could be processed.

**Specific R&D Targets**

Improving the MCU performance to the point that its service life can be extended without restriction represents a remarkable challenge, yet the data obtained on NG-CSSX to date indicates that this should be technically achievable, possibly even with increased throughput. Basically, the challenge amounts to making a substantial change in the composition of the solvent, scrub solution, and strip solution and likely O:A ratios but yet retaining the current equipment configuration with at most minor modification. By design, MCU achieves a minimum DF of 12 [10], although it actually operates an order of magnitude better [12,13]. The R&D goal for NG-CSSX is to achieve DF $\geq$ 40,000, meeting Class A regulatory requirements for any salt feed type whether the process is adapted for use in modular near-tank units or in full-scale facilities. It should be noted that this goal is likely conservative. The Class A regulatory limit for Cs-137 is $5.93 \times 10^{-3}$ Ci/gal (see 10 CFR 61.55), implying that a much lower DF than 40,000 will allow all realistic SRS feeds to meet the Class A limit. The Saltstone Production Facility requires a DF

that is half of the R&D target (40,000) for radiation protection at the facility [21]. In addition to the enhanced DF, efforts also seek increased throughput as a desirable outcome of the R&D program. The maximum throughput of the MCU is nominally 8.5 gpm, though 6 gpm is the highest throughput employed as of 2010. A reasonable target is 12 gpm, which could result from a combination of improvements due to decreased O:A ratio, better hydraulics, contactor modification, and possibly increased feed sodium concentration. Results reported herein will focus on the composition and batch extraction performance of the NG-CSSX solvent, especially related to the MCU life extension. Further details on the development of this system together with its performance in contactors will be the topic of other reports. Some implications for treating Hanford waste are also included herein for comparison.

## EXPERIMENTAL SECTION

### Materials

Solvent components were obtained from commercial sources and judged to be of adequate purity for use as received. *N,N'*-Dicyclohexyl-*N''*-isotridecylguanidine, the active guanidine reagent in LIX® 79, was supplied by Cognis. Calix[4]arene-bis(*tert*-octylbenzocrown-6) (BOBCalixC6) was obtained from IBC Advanced Technologies. 1-(2,2,3,3-Tetrafluoropropoxy),-3-[4-(*sec*-butyl)phenoxy]-2-propanol (Cs-7SB modifier), calix[4]arene-bis[4-(2-ethylhexyl)benzocrown-6] (BEHBCalixC6), and 1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6 (MaxCalix) were obtained from Marshallton Research. Tri-*n*-octylamine (TOA) was obtained from Aldrich, and Isopar L was obtained from ExxonMobil. Solvents were prepared by weighing appropriate amounts of extractant, modifier, and suppressor (TOA or LIX 79 guanidine) into volumetric flasks and diluting with Isopar L to the mark.

Targeted tank-waste simulant compositions are given in Table II according to preparative methods described in detail in earlier reports [16,17]. Constituent species are named in the table as the chemical forms added, not necessarily to be taken as the forms actually present after mixing. Appropriate amounts of reagent-grade chemicals were weighed into volumetric flasks in the order prescribed. Significant precipitate formed upon adding the NaOH, which is considered normal, and the mixture was stirred for several hours and then allowed to settle, normally for a few days before use. Actual component concentrations therefore may differ from the concentrations tabulated [16]. The SRS-15 simulant is designed to represent the average SRS tank-waste composition [22]. The SRS-45 simulant has the same composition, except that 0.030 M more $KNO_3$ has been added to represent the upper bound of 0.045 M for the potassium concentration. The Hanford simulant corresponds to Hanford tank 241-AP-108 normalized to 6 M sodium (simulant #6 in [17,23]). It represents the worst Hanford case in terms of highest potassium concentration and correspondingly lowest cesium distribution ratio, giving the most difficulty in achieving a high decontamination factor.

### Methods

Third-phase formation experiments involved three solvents, each containing 0.5 M Cs-7SB modifier and 0.003 M LIX 79 guanidine with various types of calixarenes: 0.050 M BEBHCalixC6, 0.050 M MaxCalix, and a mixture of 0.046 M MaxCalix and 0.004 M BOBCalixC6. Each of these solvents was separately contacted with three different waste simulants: SRS-15 (0.015 M $K^+$), SRS-45 (0.045 M $K^+$), and Hanford (0.174 M $K^+$). The test encompasses potassium loading conditions that the solvents may encounter during its use in the NG-CSSX process up to the worst case for SRS and Hanford. Solutions of the solvents were prepared and prewashed prior to use in the following manner: one contact sequentially with 0.010 M HCl, $H_2O$, then decreasing concentrations of NaOH (0.3 M, 0.1 M, 0.03 M, and 0.01 M), and then once or twice with $H_2O$ until the solution was pH neutral. The washed solvents and individual

Table II. Target Compositions of Aqueous Tank-Waste Simulants.

| Analyte or Species | SRS-15 mol/L | SRS-45 mol/L | Hanford mol/L |
|---|---|---|---|
| Principal constituents: | | | |
| Al as $(Al(OH)_4^-)$ | 0.280 | 0.280 | 0.570 |
| $Cl^-$ | $2.4 \times 10^{-2}$ | $2.4 \times 10^{-2}$ | $9.4 \times 10^{-2}$ |
| $CO_3^{2-}$ (TIC) | 0.150 | 0.150 | 0.367 |
| $Cs^+$ (Total) | $1.4 \times 10^{-4}$ | $1.4 \times 10^{-4}$ | $5.82 \times 10^{-5}$ |
| $K^+$ | 0.015 | 0.045 | 0.174 |
| $Na^+$ | 5.60 | 5.60 | 6.00 |
| $NO_2^-$ | 0.500 | 0.500 | 1.17 |
| $NO_3^-$ | 2.03 | 2.06 | 1.90 |
| $OH^-$ (Free) | 2.06 | 2.06 | 1.45 |
| $SO_4^{2-}$ | 0.140 | 0.140 | $3.22 \times 10^{-2}$ |
| Minor inorganic constituents: | | | |
| Ag(I) | $9.3 \times 10^{-8}$ | $9.3 \times 10^{-8}$ | |
| Bi(III) | | | $5.6 \times 10^{-5}$ |
| $Ca^{2+}$ | | | $3.8 \times 10^{-4}$ |
| $CrO_4^{2-}$ | $1.4 \times 10^{-3}$ | $1.4 \times 10^{-3}$ | $1.0 \times 10^{-2}$ |
| Cu(II) | $2.3 \times 10^{-5}$ | $2.3 \times 10^{-5}$ | |
| $F^-$ | $2.8 \times 10^{-2}$ | $2.8 \times 10^{-2}$ | $1.3 \times 10^{-2}$ |
| Fe(III) | $2.6 \times 10^{-5}$ | $2.6 \times 10^{-5}$ | $1.0 \times 10^{-4}$ |
| Hg(II) | $2.5 \times 10^{-7}$ | $2.5 \times 10^{-7}$ | $2.1 \times 10^{-9}$ |
| La(III) | | | $1.0 \times 10^{-5}$ |
| $MnO_4^-$ | | | $2.1 \times 10^{-5}$ |
| $MoO_4^{2-}$ | $7.0 \times 10^{-5}$ | $7.0 \times 10^{-5}$ | |
| Ni(II) | | | $3.3 \times 10^{-4}$ |
| $NH_3$ | $1.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | |
| Pb(II) | $1.0 \times 10^{-5}$ | $1.0 \times 10^{-5}$ | $9.7 \times 10^{-5}$ |
| Pd(II) | $3.8 \times 10^{-6}$ | $3.8 \times 10^{-6}$ | |
| $PO_4^{3-}$ | $7.0 \times 10^{-3}$ | $7.0 \times 10^{-3}$ | $1.3 \times 10^{-2}$ |
| Rh(III) | $2.0 \times 10^{-6}$ | $2.0 \times 10^{-6}$ | |
| Ru(III) | $8.1 \times 10^{-6}$ | $8.1 \times 10^{-6}$ | |
| Si(IV) | $3.0 \times 10^{-2}$ | $3.0 \times 10^{-2}$ | $2.3 \times 10^{-3}$ |
| Sn(II) | $2.0 \times 10^{-5}$ | $2.0 \times 10^{-5}$ | |
| $Sr^{2+}$ | | | $4.5 \times 10^{-6}$ |
| Zn(II) | $1.2 \times 10^{-4}$ | $1.2 \times 10^{-4}$ | |
| Zr(IV) | | | $2.4 \times 10^{-5}$ |
| Minor organic constituents: | | | |
| n-Butanol | $2.7 \times 10^{-5}$ | $2.7 \times 10^{-5}$ | |
| Tri-n-butylphosphate (TBP) | $1.9 \times 10^{-6}$ | $1.9 \times 10^{-6}$ | |
| Di-n-butylphosphate (DBP) | $1.2 \times 10^{-4}$ | $1.2 \times 10^{-4}$ | |
| Mono-n-butylphosphate (MBP) | $1.6 \times 10^{-4}$ | $1.6 \times 10^{-4}$ | |
| Formate $(HCO_2^-)$ | $3.3 \times 10^{-2}$ | $3.3 \times 10^{-2}$ | |
| Oxalate $(C_2O_4^{2-})$ | $8.0 \times 10^{-3}$ | $8.0 \times 10^{-3}$ | $1.0 \times 10^{-2}$ |
| Trimethylamine | $1.7 \times 10^{-4}$ | $1.7 \times 10^{-4}$ | |

simulants were placed at O:A = 1:4 in 50 mL polypropylene micro-tubes and then contacted by mounting on a rotating wheel using clips. The samples were contacted in a Fisher Scientific Low Temperature Incubator for a period of 30 minutes to allow for equilibration to the experimental temperature. The temperature was checked using a calibrated thermometer inside the incubator and was within ±0.2°C of the target value. After 30 minutes, the rotating wheel was stopped, and the phases were allowed to separate unassisted for 10 minutes at experimental temperature. The samples were observed visually by eye to determine the presence or absence of a third phase. In certain cases when a solvent appeared cloudy after settling, the sample would be centrifuged for 5 minutes at 3000 rpm in a Beckman Coulter™ Allegra 6R temperature-controlled centrifuge. If the solvents remained cloudy after centrifugation, a third phase was deemed to have formed. If no third phase formed, the temperature of the incubator was lowered by 1°C, and the solvents and simulants were then contacted again at the lowered temperature. The 1°C cooling steps were repeated until a third phase was visually observed in each sample. Two complete temperature cycles were performed. The uncertainty in the measurement in the third-phase onset temperatures is thus -0.2/+1.2°C.

Cesium distribution ratios with simulants were obtained in a manner similar to that described previously [17–19]. Phases were contacted in polypropylene micro-tubes mounted by clips on a disk rotated for 60 minutes for extractions and 45 minutes for scrubs and strips. Initial tests were performed under ambient conditions (22 ± 2°C). For temperature-dependence measurements, samples were equilibrated in a low-temperature incubator, constant-temperature air box, or a Lab-Line Imperial III Incubator operating at 15.0 ± 0.2°C, 25.0 ± 0.2°C, and 35 ± 1°C, respectively, as checked with a calibrated thermometer. After the contacting period, the tubes were centrifuged for 5 minutes at 3000 RPM at the experimental temperature. An appropriate aliquot of each phase was subsampled and counted using a Packard Cobra II Auto-Gamma counter. A spike of Cs-137 was added to the second and third aqueous strip solutions, owing to the low number of counts remaining after the each strip. To keep samples at the equilibration temperature for sampling, the samples were left in the temperature-controlled centrifuge and removed individually to be subsampled. The precision of $D_{Cs}$ values is ±5% (extraction and scrub), ±10% (first strip), and ±30% (second and third strips). Cesium distribution ratios ($D_{Cs}$) are given as the ratio of the background-corrected volumetric count rates of the radioisotope in each phase at equilibrium.

SRNL has performed a series of tests with real waste in order to corroborate the tests performed at ORNL. Three tests have been performed as of December 2010. All tests used the same general conditions, with the only variations being the composition of the organic and/or aqueous phases. There was no active temperature control, ambient temperatures being 22–27 ºC. Temperature corrections were applied based on data published on the CSSX solvent system with BOBCalixC6 [5]. The first test was a baseline, using the BOBCalixC6 solvent formulation (Table I) and an aqueous phase taken from Tank 49H, the current feed to the MCU. The second test used the new MaxCalix solvent formulation (see below) and the same Tank 49H aqueous phase as well as new scrub (0.025 M NaOH) and strip (0.1 M $H_3BO_3$) solutions. A third test used the new MaxCalix solvent formulation, Tank 49H waste that had been diluted with water to achieve a final density of 1.132 g/mL (i.e., the least dense waste allowable in the current MCU configuration), and 0.025 M NaOH scrub and 0.01 M $H_3BO_3$ strip solutions. (The SRNL tests started prior to final selection of the scrub and strip process conditions in the ORNL testing. Therefore, the second SRNL test with Tank 49H and the MaxCalix solvent used 0.1 M boric acid as the stripping solution, whereas the third test with more diluted Tank 49H waste used 0.01 M boric acid.) Only partial analyses from the third test are available currently. Due to the highly radioactive nature of the real waste, all the real-waste tests were performed in the SRNL High Activity Cells. The general procedure for the real-waste tests entailed shaking the solvent with aqueous phase in a 250 mL Teflon separatory funnel for 2 minutes, allowing the phases to separate unassisted for 24 h, and counting the $^{137}$Cs activity in each of the separated phases using an in-cell gamma counter. Cesium distribution ratios $D_{Cs}$ were calculated as above. For Extraction #1, 90 mL of aqueous phase and 30 mL of fresh solvent were contacted and separated as described above. The separatory funnel was cleaned with a few mL of Isopar L before further

use. The organic phase from Extraction #1 was placed back in the separatory funnel and contacted with an amount of scrub solution equal to one-fifth of the organic volume (Scrub #1). This general procedure was repeated once more with scrub solution (Scrub #2), followed by three contacts with strip solution (Strips #1–#3). Finally, the aqueous phase from the first extraction and fresh solvent were contacted at an O:A phase ratio of 1:3 and allowed to settle for 24 h (Extraction #2). Again, this was followed by phase separation and gamma counting of each phase.

To gauge the rate of phase separation, dispersion numbers were determined for dispersions of the NG-CSSX solvent with simulated waste at ambient temperature ($23 \pm 2°C$). Dispersion numbers are defined by the expression $N_{Di} = (z/a)^{1/2}/t_b$ [24], in which $z$ is the initial height of a dispersed column of solvent and aqueous solutions, $a$ is the acceleration applied to separate the dispersion, and $t_b$ is the time required for the dispersion band to collapse into its component phases. In the case of gravity settling, $a$ is replaced by the gravitational constant. In each test, 60 mL of simulant was placed into a graduated cylinder to which 20 mL of solvent was then added. The position of the interface was recorded as was the height of the liquid column. The cylinder was stoppered, agitated manually for 20 s, allowed to settle for 10 s, and agitated for a second time for 20 s. The time required for the interface to return to its original level was measured beginning at the end of the second period of agitation. All determinations were repeated a minimum of four times (giving a minimum of five measurements) for each simulant/solvent pair. All replicates were performed using the original aliquots of simulant and solvent.
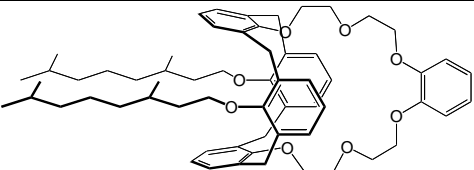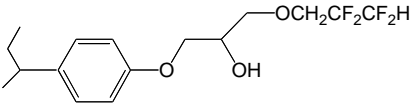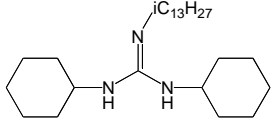
## RESULTS AND DISCUSSION

### Optimized NG-CSSX Solvent Composition

The components of the optimized NG-CSSX solvent are given in Table III. The solvent composition simultaneously accomplishes several objectives described above in identifying a highly soluble calixarene, raising the calixarene concentration to achieve a $D_{Cs}$ value on extraction well above that of BOBCalixC6 in the current CSSX solvent, lowering the modifier concentration to improve hydraulics, and switching to a guanidine type suppressor that works with boric acid strip solution [18,19].

MaxCalix was chosen as the preferred cesium extractant of two representative calix[4]arene-crown-6 compounds evaluated for NG-CSSX. The other alternative was BEHBCalixC6, calix[4]arene-bis[4-(2-

Table III. Optimized NG-CSSX Solvent Composition.

| Component | Concentration | Code | Chemical Name | Structure |
|---|---|---|---|---|
| Extractant | 0.050 M | MaxCalix | 1,3-*alt*-25,27-Bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6 |  |
| Modifier | 0.50 M | Cs-7SB | 1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol |  |
| Suppressor | 0.003 M | LIX® 79 | *N,N'*-Dicyclohexyl-*N''*-isotridecylguanidine |  |
| Diluent | | Isopar L | $C_{12}$-isoparaffinic hydrocarbon | |

ethylhexyl)benzocrown-6], an isomer of BOBCalixC6 in which the *tert*-octyl groups of BOBCalixC6 are replaced by 2-ethylhexyl groups [25]. Both BEHBCalixC6 and MaxCalix are soluble in NG-CSSX process solvent to at least 50 mM. Having cesium extraction power comparable to that of BOBCalixC6, BEHBCalixC6 had been earlier suggested as a more soluble replacement for BOBCalixC6 [17,19,25]. Further, BEHBCalixC6 had already been shown to perform well at 20 mM with 0.75 M Cs-7SB modifier in previous NG-CSSX development tests, all conducted at 25°C [17,19]. MaxCalix and BEHBCalixC6 are respectively representative of the mono- and bis-crown classes of calix[4]arene-crown-6 compounds possessing the 1,3-alt conformation (i.e., the phenolic groups of the calixarene ring alternate direction) [26,27]. Calixarenes having comparable structural elements in both classes exhibit comparable cesium extraction strength [28], and calixarenes in both classes have shown promise for cesium separations in nuclear applications [27]. The mono-crown calix[4]arenes tend to exhibit higher selectivity for cesium vs sodium and potassium, and benzocrown derivatives exhibit higher cesium selectivity vs sodium [28]. In particular, MaxCalix has recently been shown to be an attractive cesium extractant for combined removal of cesium and strontium from nitric acid solutions (FPEX process) [29]. On the basis of expected extraction performance, both BEHBCalixC6 and MaxCalix would therefore at first appear to be excellent replacement candidates for BOBCalixC6, perhaps with MaxCalix having a slight advantage on the basis of better selectivity. Toward a selection of a preferred calixarene, it was deemed most likely to find decisive differences in properties relating to phase behavior, especially susceptibility to third-phase formation, and interfacial properties that might be manifested in hydraulic performance. Third-phase formation represents one of the highest chemistry risks when approaching new solvent formulations, as it is both difficult to predict and intolerable in its effect on the chemical and hydraulic performance of a given flowsheet. From data reported below, third-phase formation alone was decisive.

**Third-Phase Formation Tests**

As shown in Table IV, MaxCalix and BEHBCalixC6 differ significantly in resistance to third-phase formation. When used in place of MaxCalix in the solvent composition given in Table III, BEHBCalixC6 forms a third phase at expected process temperatures. By contrast, the NG-CSSX solvent resists third-phase formation for average SRS simulant down to 6°C and, for the high-potassium simulant SRS-45, down to 12°C. Since 12°C is considered the desired upper temperature limit for third-phase formation [4,16], there are no third-phase issues for the NG-CSSX solvent defined in Table III for SRS application, and MaxCalix is therefore taken as the preferred calixarene.

Table IV. Temperatures of Third-Phase Formation (°C) for Representative Solvent Compositions and Simulant Compositions.[a]

| Waste Simulant | 50 mM MaxCalix (NG-CSSX solvent) | 46 mM MaxCalix 4 mM BOBCalixC6 (Blended solvent) | 50 mM BEHBCalixC6 |
|---|---|---|---|
| SRS-15 | 6 | 10 | 24 |
| SRS-45 | 12 | 13 | >25 |
| Hanford | 14 | 16 | >25 |

[a]All solvents contain 0.50 M Cs-7SB and 0.003 mM LIX 79 guanidine in Isopar L with the indicated calixarene added. The small concentration of TOA was neglected in the blended solvent composition. Temperatures correspond to the first visual observation of a third phase at the liquid-liquid interface in decreasing 1°C intervals for solvents equilibrated with the indicated aqueous waste simulant; uncertainty in third-phase onset temperature is -0.2/+1.2°C.

The data in Table IV further suggest that there are no third-phase issues in a solvent-blending strategy for transitioning MCU solvent inventory to the NG-CSSX process. Toward avoiding high disposal costs for the current MCU inventory, it would be desirable to simply add the NG-CSSX solvent components to the used MCU solvent inventory in appropriate quantities to give the target concentrations of 0.05 M total

calixarene, 0.5 M Cs-7SB, and 0.003 M guanidine suppressor. Assuming an approximate doubling of the MCU total solvent inventory on start-up of NG-CSSX, a prototype blended solvent composition was included in the third-phase formation test. It may be seen that an average aqueous feed composition would present no issues with regard to a 12°C lower limit for operating temperature, with only a slight compromise of 1°C higher for the high-potassium case SRS-45. MCU has a temperature control of 23 ± 3°C on extraction [13], and thus it may be concluded that a comfortable margin exists between operating temperature and onset of third-phase formation at worst case.

Third-phase formation data also bode well for a potential Hanford application. It may be seen in Table IV that the temperature of third-phase onset correlates with the potassium content of the feed in the order SRS-15 < SRS-45 < Hanford. More systematic experiments using a prototype CSSX solvent had previously revealed this correlation, relating it to potassium loading [16]. It is thus understandable how third-phase formation could be a potential risk for NG-CSSX, especially for a Hanford application, as the greater calixarene concentration in the solvent would lead to very high potassium loading. Whereas BEHBCalixC6 is comparable to BOBCalixC6 in susceptibility to third-phase formation under conditions relevant to current MCU operation [25], the higher potassium loading conditions have apparently proved overwhelming for BEHBCalixC6 (Table IV). On the other hand, MaxCalix performs well, suffering third-phase onset at 14°C in contact with Hanford simulant. This would not appear to be an issue if temperature control is employed or if the Cs-7SB modifier concentration is increased slightly. An implication of the third-phase formation data for further solvent development is that 0.5 M Cs-7SB appears to be the lowest practical concentration limit if MaxCalix is to be used at 0.050 M.

**Batch Extraction Performance Using SRS Waste Simulants and SRS Real Waste**

Batch testing of the NG-CSSX solvent confirmed the expectation [17–19] of high extraction strength and excellent stripping. Using SRS-15 and SRS-45 simulants, initial results of extract-scrub-strip (ESS) testing fashioned after previously described methodology [16–19] are given in Table V. In these experiments, NG-CSSX solvent was contacted in sequence with the indicated fresh aqueous phases. Phase ratios were set to deliver a concentration factor of 15. The 1:4 extraction phase ratio represents a useful incremental 6.7% potential increase in processing rate vs the current phase ratio of 1:3 used in CSSX. In agreement with earlier observations [16], we find $D_{Cs}$ to vary little with phase ratio, as cesium loading is small. Based on previous results [17–19], sodium hydroxide and boric acid were employed for the scrub and strip aqueous solutions, respectively. The NaOH concentration was an optimum set to maximize both removal of potassium and phase-disengagement rate. Although much higher boric acid concentrations are considered desirable for best hydraulics and lowest $D_{Cs}$ values in stripping, 10 mM boric acid is preferred to minimize impact on downstream vitrification operations at the

Table V. Extract-Scrub-Strip (ESS) Performance of the NG-CSSX Solvent Using SRS Waste Simulants.[a]

| Operation | Aqueous Phases | O:A Phase Ratio[b] | Cs distribution ratio ($D_{Cs}$) | |
|---|---|---|---|---|
| | | | SRS-15 simulant[c] | SRS-45 simulant[c] |
| Extract | SRS-15 or -45 simulants[c] | 1:4 | 60.7 | 51.1 |
| Scrub 1 | 0.025 M NaOH | 3.75:1 | 3.41 | 3.94 |
| Scrub 2 | " | 3.75:1 | 1.76 | 2.00 |
| Strip 1 | 0.010 M H$_3$BO$_3$ | 3.75:1 | 0.0022 | 0.0028 |
| Strip 2 | " | 3.75:1 | 0.0006 | 0.0006 |
| Strip 3 | " | 3.75:1 | 0.0004 | 0.0007 |

[a]The NG-CSSX solvent composition is shown in Table III. The experiment was performed at ambient conditions (22 ± 2°C). [b]These phase volume ratios allow the CSSX process to attain the same concentration factor of 15 obtained by the current process but also help to increase throughput. [c]The simulant compositions are given in Table II.

Defense Waste Processing Facility [30] and to reduce risk of emulsion formation. The effect of higher potassium concentration in the SRS-45 simulant may be noticed in the 16% drop in extraction $D_{Cs}$ relative to that obtained with SRS-15. This expected effect is ascribed to mild potassium loading.

A significant temperature dependence of cesium extraction, scrubbing, and stripping using the NG-CSSX solvent with SRS-15 simulant and preferred scrub and strip solutions may be seen in the data shown in Table VI. Characterized by decreasing $D_{Cs}$ values with increasing temperature, this result was expected from earlier experience with CSSX [5,16]. It may be seen that stripping remains effective over the entire tested range 15–35°C. On extraction, however, higher temperatures would compromise the ability of the solvent to achieve the target DF ≥ 40,000, necessitating temperature control in the extraction section. At lower temperatures, the effect is very advantageous for cesium extraction. However, potassium loading will simultaneously increase, placing a burden on the scrub section. As in current MCU operation, section-wise temperature control will therefore be necessary to achieve processing goals and will also be helpful in optimizing performance.

Table VI. Temperature Dependence of ESS Performance of NG-CSSX Solvent with SRS-15 Simulant.[a]

| Operation | Aqueous Phases | O:A Phase Ratio | $D_{Cs}$ 15.0 ± 0.2°C | $D_{Cs}$ 25.0 ± 0.2°C | $D_{Cs}$ 35 ± 1°C |
|---|---|---|---|---|---|
| Extract | SRS-15 | 1:4 | 127 | 51.1 | 11.0 |
| Scrub 1 | 0.025 M NaOH | 3.75:1 | 8.48 | 2.06 | 0.37 |
| Scrub 2 | " | 3.75:1 | 3.56 | 0.89 | 0.30 |
| Strip 1 | 0.010 M $H_3BO_3$ | 3.75:1 | 0.0052 | 0.0009 | 0.0005 |
| Strip 2 | " | 3.75:1 | 0.0007 | 0.0003 | 0.00003 |
| Strip 3 | " | 3.75:1 | 0.0005 | 0.0003 | 0.00008 |

[a]The NG-CSSX solvent composition is shown in Table III. The simulant composition is given in Table II.

SRNL performed tests with actual (radioactive) waste to validate the findings of simulant tests at ORNL [31]. The first test was a CSSX baseline test using the original BOBCalixC6 solvent formulation (Table I) and the corresponding 0.050 M $HNO_3$ scrub and 0.001 M $HNO_3$ strip solutions. The extraction $D_{Cs}$ value was found to be 14.1 with sequential scrub $D_{Cs}$ values of 0.88 and 0.21 and sequential strip $D_{Cs}$ values of 0.018, 0.0082, and 0.02, respectfully. Table VII contains the data from the second SRNL experiment with Tank 49H waste, this time using the NG-CSSX solvent. The measured extraction values of 61.8 and 81.6

Table VII. Extract-Scrub-Strip Performance of the NG-CSSX Solvent with Real Waste [31].

| Operation | Aqueous Phases | O:A Phase Ratio[b] | Cs distribution ratio ($D_{Cs}$) Uncorrected[c] | Corrected[c] |
|---|---|---|---|---|
| Extract 1 | SRS Tank 49H[a] | 1:3 | 54.2 | 61.8 |
| Extract 2 | SRS Tank 49H[a] | 1:3 | 67.1 | 81.6 |
| Scrub 1 | 0.025 M NaOH | 5:1 | 1.83 | 2.32 |
| Scrub 2 | " | 5:1 | 1.62 | 2.20 |
| Strip 1 | 0.1 M $H_3BO_3$ | 5:1 | 0.00045 | 0.00020 |
| Strip 2 | " | 5:1 | <0.027 | <0.011 |
| Strip 3 | " | 5:1 | <0.011 | <0.44 |

[a]The waste sample is a composite with a sodium concentration of ca. 6.8 M and a ^{137}Cs activity of $1.50 \times 10^8$ dpm/mL. [b]These are the phase volume ratios currently used in the CSSX process to attain a concentration factor of 15; in the NG-CSSX tests with simulant shown in Tables IV and V, the O:A were adjusted consistent with a flowsheet design improvement to increase throughput while still meeting the DF = 40,000 target (see below). [c]Correction to 25°C due to ambient conditions in the test. Strips #2 and #3 could not be quantified because of lack of remaining activity, and only upper limits can be provided.

for Extractions #1 and #2, respectively, are in good agreement with extraction values from the ORNL simulant tests using SRS-15 simulant. The scrub and strip behavior is quite similar to ORNL results, with the notable exception that the cesium values in Strips #2 and #3 fell below detection limits. A third SRNL test using more dilute waste gave moderately lower extraction values (e.g., near 40) for the first stage. This value is still quite favorable, possibly due to the lower free hydroxide concentration, a trend seen previously for the BOBCalixC6 performance [16]. Scrubbing and stripping values also appear good in the third test. The results from the third test involving the MaxCalix solvent and diluted real waste are incomplete at this time and will be fully reported at a later date.

**Preliminary Flowsheet Design**

Flowsheet design calculations performed using the SASSE spreadsheet [32] and extraction data given in Table V show that the NG-CSSX solvent and associated aqueous solutions can be "dropped into" the MCU equipment configuration, raising the minimum DF to ≥40,000 with likely increased waste feed processing rate. The magnitude of the increase in throughput, however, cannot be accurately forecasted pending planned contactor testing in FY 2011. As discussed above, the source of anticipated throughput gain arises both from lower O:A on extraction and from improved hydraulic properties of the NG-CSSX solvent, including lower viscosity and density and shorter batch phase-separation times. Correlations indicate that 12 gpm is potentially attainable, and this is the target shown in Figure 1. The attainment of 12 gpm relies on the normal expectation of increasing stage efficiency with increasing throughput. Although this expectation is sound, it must be confirmed in full-scale testing. Thus, a final flowsheet must await further testing in the coming year.
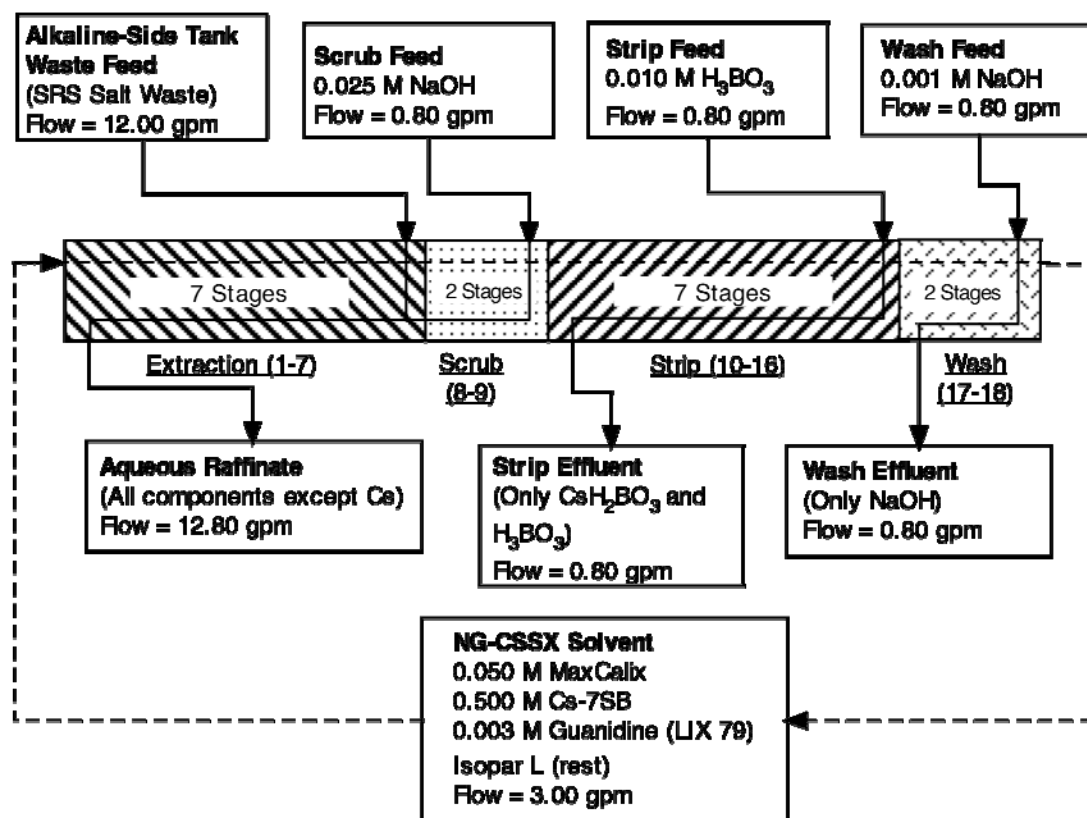


Figure 1. Using simulant test data shown in Table V, the above flowsheet was calculated.

**Dispersion-Number Tests**

Results from dispersion-number tests shown in Table VIII indicate that the NG-CSSX solvent should have good hydraulic performance in centrifugal contactors. A semi-quantitative indicator of hydraulic performance, the dispersion number is a dimensionless parameter determined from break times of batch liquid-liquid dispersions [24]. In general, dispersion numbers in the ranges $4–8 \times 10^{-4}$ and $8–16 \times 10^{-4}$ correspond respectively to "good" and "very good" hydraulic performance in centrifugal contactors. It may be therefore seen from Table VIII that no hydraulic issues are indicated. Actual hydraulic testing of NG-CSSX process solutions in centrifugal contactors is under way and will be reported elsewhere.

Table VIII. Dispersion Numbers for NG-CSSX Solvent (50 mM MaxCalix)

| | Phase Ratio (O:A) | Dispersion No. $N_{Di}$ |
|---|---|---|
| Extraction with SRS-15 | 1:4 | $9.95 \times 10^{-4}$ |
| Scrub with 25 mM NaOH | 3.75:1 | $6.78 \times 10^{-4}$ |
| Strip with 10 mM Boric Acid | 3.75:1 | $7.36 \times 10^{-4}$ |
| Wash with 10 mM NaOH | 5:1 | $6.61 \times 10^{-4}$ |

**Implications for Potential Application at SWPF and Hanford**

Although minimal data are currently available specifically applicable to a potential use of NG-CSSX in SWPF or Hanford applications, it is reasonable to anticipate a successful and straightforward development. The original development of the CSSX process using BOBCalixC6 focused on achieving a DF of ≥40,000 with a concentration factor of 15 in the removal of cesium from SRS tank wastes [16–19], and this is in fact the implementation of CSSX currently adopted for SWPF to begin processing in 2015 [9]. With 16 stages of extraction, the SWPF can easily meet the target DF with BOBCalixC6 at only 7 mM. Thus, the potential benefit of implementing NG-CSSX in the SWPF lies in faster processing rate rather than a higher DF. Two options could be pursued to this effect, either a limited implementation with NG-CSSX solvent only, keeping the acidic CSSX scrub and strip, or a full implementation of NG-CSSX solvent with alkaline scrub and boric acid strip. Both options would aim for a lower O:A ratio on extraction, which has the potential in itself to increase throughput by 5–20%. The required MaxCalix concentration could be as low as 10 mM in the former option or as high as 50 mM in the latter. The optimal concentration for SWPF will depend on the scrub and strip solutions selected, O:A ratio desired, modifier concentration used, and contactor hardware performance. The throughput enhancement could conceivably allow completion of the overall processing mission 2–3 years earlier at substantial savings.

As suggested previously [18,19], a modular Hanford application of NG-CSSX similar to MCU is feasible based on batch results and preliminary flowsheet calculations. The challenge of high potassium levels in the Hanford waste lies in the depressed $D_{Cs}$ values owing to potassium loading. Using the CSSX solvent (7 mM BOBCalixC6) with the Hanford simulant (Table II), a $D_{Cs}$ value of 3.40 was earlier obtained. Whereas this value is still high enough for successful process design, a modular unit would not be feasible [18,19]. With NG-CSSX, this restriction is lifted. Using the NG-CSSX solvent composition shown in Table III, a $D_{Cs}$ value of 25.1 was obtained for Hanford simulant. This extraction power should allow a modular flowsheet design giving a DF of 40,000 [18,19], higher than required [23]. Table IV shows that the NG-CSSX solvent resists third-phase formation adequately with a high-potassium Hanford simulant but may still require limited temperature control as used in the MCU. Obviously, there is considerable freedom in the design of a NG-CSSX process at Hanford, since the flowsheet would not have to accommodate an existing equipment configuration. For example, contactor design could be improved to yield higher throughput than is possible with MCU, and more extraction stages and fewer stripping stages

could be employed than used in MCU. Development efforts are planned to address these questions toward adapting NG-CSSX for an efficient Hanford application.

**CONCLUSIONS**

Two major conclusions are possible at this time:

- A minimum cesium decontamination factor of 40,000 is expected using the NG-CSSX solvent to treat SRS tank wastes in the MCU equipment configuration, even under the bounding conditions of waste potassium concentration. This DF will thus ensure that the Saltstone curie limit will not be exceeded by MCU, thereby extending its service life.
- Increased throughput in the MCU is likely attainable with this solvent. Although full-scale contactor hydraulic data have not yet been obtained, batch dispersion numbers indicate adequate hydraulic performance of the NG-CSSX solvent, and a reduction in extraction O:A ratios is feasible.

Work under way entails full-scale hydraulic and mass-transfer efficiency testing of contactors, including tests with coalescers, which will enable the final flowsheet design. A countercurrent test is planned with waste simulants and real waste in multistage mini-contactors to demonstrate the chemistry and expected countercurrent performance. Chemistry efforts will proceed to reduce risk by determining the distribution of minor components in the flowsheet, further examining solvent loss mechanisms, and devising an optimal wash stage.

Overall, the NG-CSSX process represents the culmination of nearly two decades of chemical and engineering R&D. Recent improvements have been transformational in potential impact by allowing cesium removal by solvent extraction in modular units that can be located near underground storage tanks. Ultimately, this development adds to the technological tools available to DOE in accelerating its cleanup schedule and reducing overall costs of its cleanup mission.

**ACKNOWLEDGMENT**

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