

Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation

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ANNUAL PROGRESS REPORT

U.S. Department of Energy

Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation

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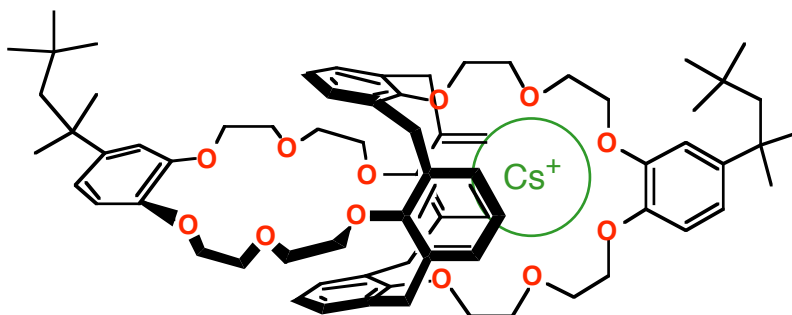
*Not supported under this project. Research at PNNL was sponsored by the Environmental Management Science Program of the Office of Science, U. S. Department of Energy, under contract no. DE-AC06-76RLO 1830 with Pacific Northwest National Laboratory, operated by Battelle Memorial Institute. Research at Texas Tech University was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-FG03-94ER14416 with Texas Tech University.

Research Objective

This project seeks a fundamental understanding and major improvement in cesium separation from high-level waste by cesium-selective calixcrown extractants. Systems of particular interest involve novel solvent-extraction systems containing specific members of the calix[4]arene-crown-6 family, alcohol solvating agents, and alkylamines. Questions being addressed pertain to cesium binding strength, extraction selectivity, cesium stripping, and extractant solubility. Enhanced properties in this regard will specifically benefit cleanup projects funded by the USDOE Office of Environmental Management to treat and dispose of high-level radioactive wastes currently stored in underground tanks at the Savannah River Site (SRS), the Hanford site, and the Idaho National Environmental and Engineering Laboratory.¹ The most direct beneficiary will be the SRS Salt Processing Project, which has recently identified the Caustic-Side Solvent Extraction (CSSX) process employing a calixcrown as its preferred technology for cesium removal from SRS high-level tank waste.² This technology owes its development in part to fundamental results obtained in this program.

Disposal of high-level waste is horrendously expensive, in large part because the actual radioactive matter in underground waste tanks at various USDOE sites has been diluted over 1000-fold by ordinary inorganic chemicals.¹⁻³ Vitrification of the waste to produce a borosilicate glass waste form is the preferred treatment of the high-level waste prior to geologic disposal.¹ However, to vitrify the entire mass of the high-level waste would be prohibitively expensive. Accordingly, technologies are needed to remove radionuclides such as ¹³⁷Cs from the waste so that the bulk of it may be diverted to cheaper low-level waste forms and cheaper storage. After a decade of technology development and demonstration beginning in the early 1990s, some technologies like CSSX are already on their way to implementation.⁴ Nevertheless, it is recognized that fundamental results will continue to add value toward improvements in existing technologies and advancement of alternative technologies.^{1a}

To address such needs, chemical research at Oak Ridge National Laboratory (ORNL) has focused on calixcrown extractants, molecules that possess crown ether functionalities supported on a calixarene framework. This hybrid molecule possesses a cavity that is highly complementary for the Cs⁺ ion vs. the Na⁺ ion,⁵ making it possible to cleanly separate cesium from wastes that contain 10,000- to 1,000,000-fold higher concentrations of sodium. X-ray structural investigations, both at ORNL and elsewhere,⁶ have shown that this unique cavity is bounded on two sides by opposing aromatic groups on the calixarene framework. This cleft closely complements the size and "soft" electronic characteristics of the guest Cs⁺ ion and is thought to provide for the high selectivity observed. The polyether loop provides additional coordination for cesium, again with size and conformational properties that complement the Cs⁺ ion. The overall coordination ability of



Calix[4]arene-bis(*t*-octylbenzo-crown-6)
"BOBCalixC6"
(As complexed with Cs⁺ ion)

the calixcrown is strongly influenced by substituents both on the polyether loop and on the aromatic groups of the calixarene framework.

Previous EMSP results elucidated the underlying extraction equilibria in cesium nitrate extraction by the calixcrown used in the CSSX process, calix[4]arene-bis(*t*-octylbenzo-crown-6), designated here as BOBCalixC6 (see structure).^{7,8} This understanding led to key improvements in the development of the CSSX process under the EM Efficient Separations and Crosscutting Program, entailing a method to back-extract or “strip” cesium from the calixcrown subsequent to cesium extraction from waste.⁹ Having this stripping method allowed the cesium to be concentrated in a relatively pure aqueous stream and the extractant to be regenerated for recycle.¹⁰ Closing the cycle then made possible the design of a process flowsheet and successful demonstration through collaboration with Argonne National Laboratory and Savannah River Technology Center under funding from the Office of Project Completion and the Tanks Focus Area of the USDOE Office of Environmental Management.^{11,12}

Despite these successes, the CSSX process represents young technology that can benefit substantially from further fundamental inquiry, as well as further applied R&D.^{4b} First, reversibility of the process (stripping efficiency) still presents the greatest potential for improvement. Second, although the calixcrown extractants for cesium are two orders of magnitude stronger than the next best simple crown ether, a minor fraction of the extractant capacity is utilized. Third, potassium competes significantly with cesium for the calixcrown binding site, an important issue in dealing with Hanford wastes having potassium concentrations as high as 1 M. Fourth, the calixcrown solubility needs to be improved. And finally, the mechanism of extraction must be understood in detail to provide the base of knowledge from which further development of the technology can be rationally made.

Toward addressing these needs, synthesis and characterization of new solvent components are being performed at ORNL and through collaboration with Texas Tech University (TTU, Prof. R. A. Bartsch). Extraction behavior is being surveyed to assess the effectiveness of candidate solvent systems, and systematic distribution measurements are being modeled toward a thermodynamic understanding of controlling equilibria. Complexation phenomena are the focus of studies at Virginia Polytechnic Institute & State University (VPISU, Prof. H. W. Gibson). The overall objective is a significant advance in the predictability and efficiency of cesium extraction from high-level waste in support of potential implementation at USDOE sites.

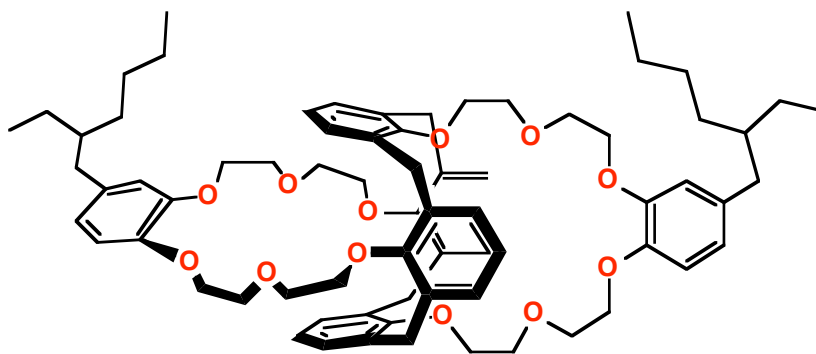
Research Progress and Implications

Reporting Period. This report summarizes work performed during the final year of a three-year project. Significant progress in this time has been obtained at ORNL on synthesis and evaluation of new alkylated calixcrowns that have enhanced solubility in modified alkane diluents.¹³ This result could lower technology risk in implementation of the CSSX process in that the process operates nearly at the solubility limit of the calixarene used in this process, BOBCalixC6. Higher solubility also opens up possible alternative process options at other USDOE tank-waste sites and possible applications in cesium concentration for analysis. In addition, four new calixcrowns functionalized with primary amine groups have been shown in proof-of-principle tests to undergo pH-switched extraction-stripping cycling.¹⁴ Such compounds illustrate that enhanced stripping may be possible by appending amino groups to the calixarene cesium extractant, whereby protonation under mildly acidic conditions expels the cesium.

Extraction under highly alkaline conditions, whereupon the calixarene is deprotonated, then begins the next cycle. Finally, increased understanding of solution complexation phenomena has been obtained in studies of pseudorotaxanes at VPISU.

Synthesis and Evaluation of Alkylated Calix[4]arene-crown-6 ethers. A substantial improvement in solubility was obtained with an analog of BOBCalixC6 where the *tert*-octyl sidechains were replaced with 2-ethylhexyl sidechains, with essentially no change in cesium extraction strength.¹³ This new calixcrown, BEHBCalixC6, retained a nominal equilibrium solubility of 54 ± 3 mM at 25 °C in the Isopar L process diluent containing the CSSX solvent modifier Cs-7SB at 0.50 M over a period of 16 weeks.

This solubility is not an upper limit, as the solution was not saturated. Comparatively, BOBCalixC6 achieved an equilibrium (saturation) solubility of only 8 mM after 41 weeks. These solubility studies involved only the free calixcrowns with no metal ions (such as cesium or potassium) present. (The solubility behavior of these



Calix[4]arene-bis(2-ethylhexylbenzo-crown-6)
"BEHBCalixC6"

calixcrowns under loading conditions will be examined.) The synthesis of BEHBCalixC6 does require two additional steps in the synthesis relative to the synthesis of BOBCalixC6. However, these additional steps occur early in the synthesis and pertain to the synthesis of the starting alkyl phenol (three steps to prepare 4-(2-ethylhexyl)-catechol and only one step to prepare 4-*tert*-octylcatechol.) The remaining three steps from the alkylphenol to the calixcrown are essentially the same for both compounds, and isolated yields of BEHBCalixC6 from the alkylcatechol are currently only slightly less (at about 30%) than isolated yields of BOBCalixC6 (at about 35–40%). The synthesis of BEHBCalixC6 is not yet optimized, particularly the last purification step involving column chromatography, and thus improvements in the yield may be possible. BEHBCalixC6 exists as a mixture of eight possible stereoisomers, arising from three sources of asymmetry: one from the position of the alkyl substituent on one benzocrown moiety relative to the alkyl substituent on the opposite benzocrown moiety (there is a mirror plane which includes one benzocrown unit in the plane and bisects the second), and one each from the 2-ethylhexyl groups. We believe that the additional isomers afforded by the chirality of the 2-ethylhexyl group is beneficial with regard to enhancing the overall solubility of BEHBCalixC6 in branched alkane diluents.

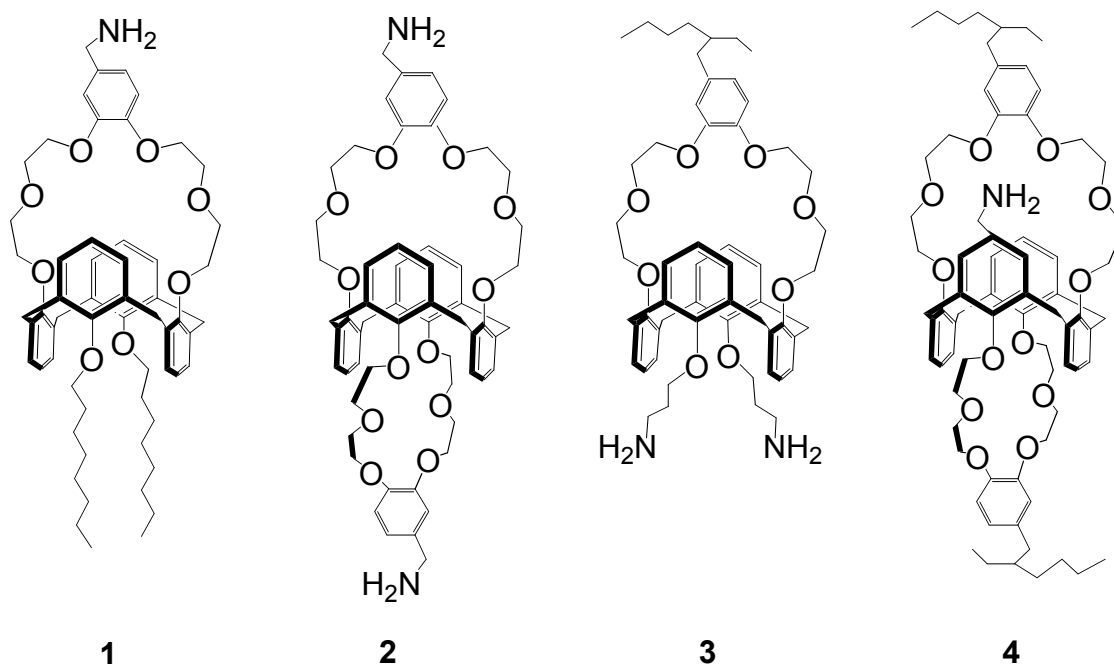
Two mono-crown calixes, ones that had been previously prepared, also demonstrated solubility behavior at least equal to BEHBCalixC6 (ca. 54 ± 2 mM), but again since the calixcrowns were not saturated, the maximum solubility is likely higher.¹³ Relative to the biscrowns above, the cesium distribution ratios for the monocrowns from a simple salt matrix run about 10% lower.

A number of other new calixcrowns, both bis-crown ethers and mono-crown ethers, were prepared, and the solubility and cesium distribution behavior examined.¹³ Though none of these exhibited combined solubility or cesium extraction properties that make them replacement candidates for BOBCalixC6, nonetheless some interesting structure-function relationships were observed. With respect to alkyl group substitution on the benzo group of a benzo crown, *ortho*-substitutions with respect to the ether oxygens are highly detrimental to cesium binding strength,

and may, all things being equal, also be detrimental to alkane solubility. For mono-crown calixes, cesium binding strength was reduced when the alkyl substituents on the non-crown lower rim ether oxygens were branched (e.g., 2-ethylhexyl) rather than linear (e.g., *n*-octyl).

Synthesis and evaluation of calixarene-crowns with incorporated amine functionality.

We have hypothesized that the incorporation of amine functionality into the calix-crown could dramatically improve the efficiency of release of cesium from the calix-crown upon protonation. Neutral calix-crowns extract Cs^+ by co-extraction of an aqueous-matrix anion, such as nitrate. If the organic phase is then contacted with an acidic aqueous phase, the amine functionalities will become protonated, possibly destabilizing cesium complexation by charge-charge repulsion. The scientific question that is being investigated is the relationship between the proximity of the amine groups to the cesium binding cavity and the destabilizing effect on cesium binding. Toward probing this question, three classes of amine-derivatized calix-crowns have been prepared.¹⁴ The first has the amine attached to the phenyl group of the benzocrown unit (**1** and **2**); the second is particular to mono-crown calixes, in which the alkoxy group is a short alkyl chain with an amine terminus (**3**); and the last has the amine attached to one of the phenyl rings of the calixarene “upper rim” (**4**). Syntheses of primary amine-derivatized calix-crowns from all three classes have been completed, as shown in the figure below. Another question concerns the effect of substituents on the amine. It may be anticipated that alkyl substituents, for example, will have a strong effect on the calixarene solubility, pKa behavior of the amine, stability of the amine, and the destabilization of the binding site on protonation. Indeed, improved solubility must be sought, as the protonated form of **1–4** exhibited limited solubility in a survey of various diluents. Synthesis of alkylated analogs will be the focus of future work.



Of the amino-derivatized calixcrowns synthesized and evaluated, compound **4**—which can be considered a derivative of BEHBCalixC6, in which one aminomethyl moiety has been

attached to of the “upper rim” aryl groups of the calixarene—appears most promising (see extraction results below). The synthesis requires four additional steps relative to the synthesis of BEHBCalixC6; however, these steps all proceed in moderate to excellent yields. To date, about 1.2 grams have been prepared for evaluation.

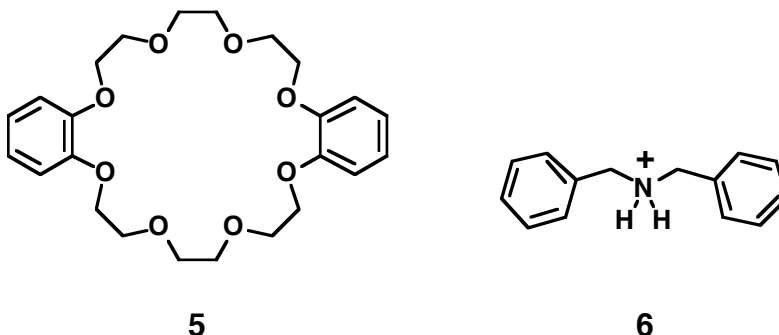
Extraction results demonstrated proof-of-principle for pH-switched extraction and release.¹⁴ The new calix[4]arene monocrowns **1** and **3** and calix[4]arene biscrowns **2** and **4** were compared to BOBCalixC6 and bis-(*n*-octyloxy)-calix[4]arene benzo crown-6 (containing no amino groups) as controls. The organic phase in each case consisted of a calixcrown at 2.5 mM in nitrobenzene, a diluent chosen for its high polarity, which promotes solubility of the calixcrowns and their complexes (precipitation problems under acidic conditions were encountered in surveys with other diluents) and which discourages ion-pairing. The absence or weakening of ion-pairing was expected to maximize the repulsive effect of the protonated amino group on binding of the Cs cation. In the case of control compounds BOBCalixC6 and bis-(*n*-octyloxy)-calix[4]arene benzo crown-6, 2.5 mM of tri-*n*-octylamine (TOA) was also added to the organic phase to serve as a control for the presence of an amine group.

Extractions were carried out from alkaline (1 M NaNO₃, 0.05 M NaOH, 10⁻⁴ M CsNO₃) and acidic (0.95 M NaNO₃, 0.05 M HNO₃, 10⁻⁴ M CsNO₃) aqueous solutions containing ¹³⁷CsNO₃ radiotracer (0.58 mCi/mL). A back-extraction (stripping) of the organic phase previously contacted with the alkaline aqueous phase was carried out using an acidic aqueous phase (0.95 M NaNO₃, 0.05 M HNO₃) containing no cesium or tracer. These aqueous conditions were selected so that the driving force for cesium nitrate extraction, as controlled by the aqueous nitrate concentration, was approximately constant in all cases. Hence, differences in extraction behavior on pH swing would be only due to the pH effect. In each case, equal phase volumes were equilibrated by gentle agitation in capped vials for 90 min at 25°C. The cesium distribution ratio D_{Cs} is defined as $[Cs]_{org}/[Cs]_{aq}$.

Results demonstrate large decreases in cesium extraction strength, as much as two orders of magnitude, upon acidification of the aqueous phase. Under alkaline conditions, except for the bis-amino-propoxy calix[4]crown **3**, the presence of the amino group does not change D_{Cs} significantly. On extraction from acidic solution, the controls BOBCalixC6 and bis-(*n*-octyloxy)-calix[4]arene benzo crown-6 exhibit decreased extraction (ca. 2–3-fold), an effect that may be taken as inhibition of cesium nitrate extraction by a common-ion effect due to nitric acid extraction. This inhibition is expected in all cases based on Le Chatelier’s principle and supports the extraction of cesium nitrate as dissociated ion pairs. Extraction under the acidic conditions decreases significantly for the all amino substituted compounds, and most significantly (two orders of magnitude) for the aminomethyl calix[4]arene biscrown **4**. Stripping under acidic conditions gives approximately the same value of the cesium distribution ratio D_{Cs} as extraction under nitric acid conditions, confirming that back-extraction is enhanced. Combination of high extraction ability under basic conditions and high stripping efficiency under acidic conditions make compound **4** an attractive extractant candidate among the amino substituted calix[4]arene crowns synthesized thus far.

Homogeneous Complexation Chemistry of Crown Ethers. The impetus for the effort at VPISU has been possible utilization of organic ligand inclusion in the BOBCalixC6 macrocyclic framework, in order to enhance stripping via displacement of Cs⁺. Ionic species have played a dominant role in supramolecular chemistry dating back to Pedersen’s seminal discovery of the alkali metal-templated formation of crown ethers.¹⁵ Ionic components can act as hosts (H) or guests (G), but the latter role is more common, as exemplified by binding of Cs⁺ ion by

BOBCalixC6. Because of the charged nature of the Cs^+ guest, and in an effort to elucidate a better understanding on the influence of ionic strength effects in the CSSX process, we have previously applied the limiting Debye-Hückel equation to a model system, that of formation of complexes fashioned from dibenzo-24-crown-8 (**5**) and various salts of the dibenzylammonium cation (**6**).¹⁶ Called pseudorotaxanes, the complexes (**5**·**6**) feature threading of the di-substituted ammonium cation through the crown ether ring via hydrogen bonding. The early equilibrium treatment was flawed in that it assumed complete dissociation of the ion-paired ligand. We have since modified our model on the basis of ion-pairing, as described below.¹⁶



Piqued by our inability to reproduce association constants⁵ commonly reported in the literature, we undertook studies using well-defined host (**5**) and guest (**6**) solutions, using various salts of **6** ($6X^-$). ^1H NMR spectroscopy revealed that a) the apparent binding constant $K_{a,\text{exp}}$ uncorrected for ion-pairing or activity varies with host concentration, anion concentration, and anion, b) the chemical shifts associated with the complex are invariant with concentration and anion, and c) the chemical shifts of the salts themselves are concentration dependent. These results led us to conclude that the complex is not ion-paired and that a distinct equilibrium exists for the secondary ammonium salts. To explain these conclusions, we considered dissociation of the $6X^-$ ion pair as an explicit preequilibrium step in the complexation process, and it was possible to show that the observed behavior indeed obeys the derived equilibrium relationship for the series of anions PF_6^- , BF_4^- , $p\text{-MeC}_4\text{H}_6\text{SO}_3^-$ (tosylate), and CF_3COO^- . The model was successfully extended to include systems in which the complex itself ion-pairs and to include activity effects. We are vigorously examining our data according to this new treatment and will report results at a future date. Crucial to this examination will be the use of available pulsed field gradient spin-echo diffusion measurements, which will enable us to correlate diffusion rates of both the cation and anion in such complexes, as well as to detect the influence of salt aggregation.

Planned Activities

Further investment will be directed toward cesium extractants with improved solubility in alkane diluents. A manuscript covering the synthesis and properties of our new alkylated analogs to BOBCalixC6 will be submitted to an appropriate journal. Improved synthetic routes will be investigated toward lowering preparative costs. We will keep contacts at the Hanford and Savannah River sites informed of progress in connection with improving and extending the applicability of the CSSX process. Personnel at the SRS have expressed interest in testing

BEHBCalixC6, and future collaboration is anticipated.

New pH-switched calixarene extractants for more efficient extraction-stripping cycles will be investigated. For the amino-derivatized calix-crowns, continuing efforts will involve optimization of the synthetic pathways to promising compounds, and preparation of alkylated analogs (alkylation of the amine group with alkyl groups of various sizes) will be pursued. A collaboration with Prof. Bartsch at TTU will be fostered toward synthesis and characterization of new ionizable calix-crowns. Such compounds may exhibit higher selectivity, and their proton-ionizable property is expected to facilitate a pH-switched extraction-stripping cycle.

In general, equilibrium measurements of complexation and extraction will aim to elucidate thermodynamic processes of ion partitioning and complexation in systems containing selected crown ethers, calix-crowns, alcohol synergists, and alkylamines. Studies at VPISU will continue to examine pseudorotaxane systems as model complexes for elucidating effects of ion-pairing, activity, and anion structure. Basic questions to resolve include the role of ion-pairing and dissociation, the solvation of the anion by the alcohol, the possible proton-ionizable nature of the alcohols, and the role of amine solvent components. Theoretical results from the studies of B. P. Hay at PNNL will be assessed to identify synthetically attractive calix-crown extractants having predicted enhanced selectivity and extraction strength for Cs^+ vs. K^+ . Finally, it will be the goal to transfer this basic knowledge to collaborators, site users, private industry, and applied researchers associated with high-level waste remediation.

Information Access

A publication list is provided as an attachment to this report. See also the www home page of the ORNL Chemical Separations Group: <http://www.ornl.gov/csg>.

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