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

FY 2005 Annual Report, Environmental Management Science Program, Project #73803

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July 6, 2005

This research was sponsored by the Environmental Management Science Program of the Office of Science, U. S. Department of Energy, under a) contract no. DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC; and b) Grant DE-FG02-03ER6376 with Texas Tech University. Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE.

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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Statistics since start of renewal Oct. 1, 2004:
Number of undergraduate students: 1
Number of graduate students: 2
Number of postdocs: 1

EMSP Project:	#73803
Contract #:	DE-AC05-00OR22725 (ORNL, FWP No. ERKP601) DE-FG02-03ER6376 (TTU)
Project Duration:	Oct. 1, 2000 – Sept. 30, 2006
Program Officer:	Gary K. Jacobs, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, P.O. Box 2008, Bldg. 4500S. Phone: (865) 574-7374. Fax: (865) 574-7287. E-mail: jacobsgk@ornl.gov .

Summary

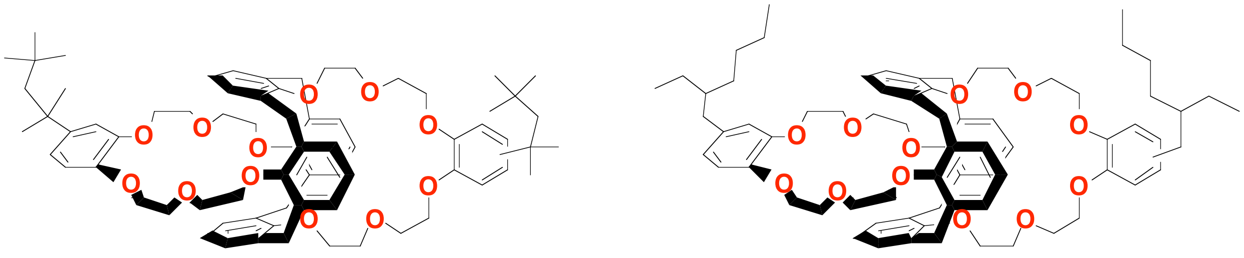
This project unites expertise at Oak Ridge National Laboratory (ORNL) and Texas Tech University (TTU, Prof. Richard A. Bartsch) to answer fundamental questions addressing the problem of cesium removal from high-level tank waste. Efforts focus on novel solvent-extraction systems containing calixcrown extractants designed for enhanced cesium binding and release. Exciting results are being obtained in three areas: (1) a new lipophilic cesium extractant with a high solubility in the solvent; (2) new proton-ionizable calixcrowns that both strongly extract cesium and "switch off" when protonated; and (3) an improved solvent system that may be stripped with more than 100-fold greater efficiency. Scientific questions primarily concern how to more effectively reverse extraction, focusing on the use of amino groups and proton-ionizable groups to enable pH-switching. Synthesis is being performed at ORNL (amino calixcrowns) and TTU (proton-ionizable calixcrowns). At ORNL, the extraction behavior is being surveyed to assess the effectiveness of candidate solvent systems, and systematic distribution measurements are under way to obtain a thermodynamic understanding of partitioning and complexation equilibria. Crystal structures obtained at ORNL are revealing the structural details of cesium binding. 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 U. S. Department of Energy (USDOE) sites.

Research Objectives

Purpose. The overall goal of this project, unchanged from the previous performance period (EMSP Project No. 73803), is to seek increased fundamental understanding and major improvement in cesium separation from high-level waste by the calix[4]arene-crown-6 family of cesium-selective extractants. Expected results are targeted toward needs in high-level-waste (HLW) remediation, primarily at the USDOE Savannah River Site (SRS) and Hanford Site. Results have in particular strongly benefited HLW cleanup at the SRS, where plans now call for implementation of the Caustic-Side Solvent Extraction (CSSX) process in the $1B SRS Salt Waste Processing Facility (SWPF) now being designed by private industry. The development of the CSSX process was made possible in part by results from this research, and its successful implementation will likely depend in part on basic knowledge gleaned from future efforts under this project. As discussed below, significant strides have been made on the specific objectives that had been set forth previously. Most notably, promising results have been obtained toward significantly improved extraction and stripping of cesium, and it is the primary purpose of the renewal proposal to bring such results to fruition. Specific objectives are proposed for synthesis of compounds of the types previously targeted (see below), characterization of their binding behavior toward cesium, and development of a thermodynamic understanding of cesium extraction behavior. The teaming to reach these objectives involves direct partnership of ORNL with TTU under joint EMSP funding.

Three basic thrusts are being pursued. First, it is a goal to develop a basic understanding of the thermodynamic processes of ion partitioning and complexation in systems containing selected calixcrowns, alcohol synergists, and alkylamines. These components are critical for strong, selective, and reversible extraction, though their function remains to be fully understood. 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 an amine as “suppressor.” Second, it is a goal to seek enhanced stripping by means of proton switches, that is, to use the large pH change from alkaline extraction conditions to weakly acidic stripping conditions to bring about dramatic decomplexation. Third, it is proposed to develop stronger, more selective cesium ligands based on the calix[4]arene frame. The second and third goals will be pursued at ORNL and TTU mainly by the synthesis of new calixcrown and other solvent components based on design considerations drawn from our previous work and from molecular modeling in collaboration with Benjamin P. Hay at PNNL. New compounds will be characterized by extraction surveys, systematic distribution equilibrium studies, NMR spectroscopy, and structural analysis by X-ray crystallography. In addition to understanding complexation-decomplexation equilibria, we will seek to improve extractant properties such as stability to decomposition and selectivity over competing ions. Finally, it will be the goal to transfer this basic knowledge to our collaborators, site users, private industry, and other applied researchers associated with high-level waste remediation.

Significant progress has been made toward such objectives in the previous funding period, yet fundamental questions still remain. Among the most important findings is a better understanding of the relationship between the structure of alkyl appendages on mono- and bisbenzo calix[4]arene-crown-6 extractants and solubility behavior, allowing us to prepare new calix-crowns that alleviate the limitations due to low solubility of the current CSSX extractant BOBCalixC6 (Fig. 1). The most promising candidates remain to be fully characterized with regard to solubility and extraction behavior. Second, progress has been made on the synthesis of new amino derivatives of the calix[4]arene-crown-6 platform for greatly enhanced stripping. Further synthesis efforts are needed, and the binding and extraction of cesium ion remains to be elucidated structurally and thermodynamically. Third, new proton-ionizable calix-crown-6 compounds generously provided by Prof. Bartsch under independent funding were tested and shown to exhibit promising properties for enhanced extraction and stripping. Further synthesis and extraction studies will be required to bring this family of compounds to fruition. Finally, thermochemical aspects of cesium extraction and stripping by BOBCalixC6 and related extractants remain to be understood.



Calix[4]arene-bis[*tert*-octylbenzocrown-6]
"BOBCalixC6"

Calix[4]arene-bis[(2-ethylhexyl)benzocrown-6]
"BEHBCalixC6"

Figure. 1. Alkyl-substituted calixcrowns. BEHBCalixC6 has substantially higher solubility than the current baseline CSSX extractant BOBCalixC6 (Engle, et al., 2004).

This project addresses the OBER long-term environmental-remediation goal "Develop science-based solutions for cleanup and long-term monitoring of Department of Energy (DOE) contaminated sites." It is clearly aimed toward development of a science-based solution to tank-waste cleanup. Further, the fundamental knowledge will provide a reference point for problem solving and technology improvement as major cleanup processes (e.g., CSSX) are implemented at USDOE sites.

Specific EM needs benefited by this research. The major need for this research stems from the fact that a young technology, the CSSX process (two patents), is about to be implemented at the SRS for removal of cesium from high-level salt waste stored there in underground tanks. Although tests of the process have demonstrated that it meets stringent site requirements, the process chemistry is not fully understood. As the CSSX process transitions from present conceptual design through plant commissioning, greater understanding would mean decreased risk of costly technology failure. This issue was recently magnified by the U. S. National Academy of Sciences ("Research Needs for High-Level Waste Stored in Tanks and Bins at U.S. Department of Energy Sites," National Academy Press, 2001):

> "A technological risk in HLW management is the risk that existing technologies will fail to accomplish goals and performance requirements set by environmental remediation policies or regulations. The EMSP can contribute to reducing technological risk by funding a basic research program focused on alternative processes and improved approaches to current baseline plans, …"

Risk reduction can be expected from the use of basic knowledge to anticipate and solve problems. Moreover, as unexpected technical problems are encountered in process implementation, a better foundation of directed fundamental knowledge increases the likelihood that such problems will be experienced as minor ones with relatively obvious solutions. The consequences of technology failure can be costly, an example being the shutdown of the in-tank precipitation (ITP) process at the SRS. As a further measure of risk reduction, an existing research team will be maintained as a resource of expertise during the CSSX maturation.

Technology improvements arising from further fundamental research may be expected to have significant impact in terms of cost reduction and reliability. Solvent-extraction methods were specifically supported in recommendations of the U.S. National Academy of Sciences (2001):

> "A long-term basic research effort is needed to complement the activities within the ESPIP [a former program within the EM] to identify sorbents and separation methods for cesium, strontium, technetium, and transuranic elements that are effective and operable in high-ionic-strength alkaline or acidic solutions and high radiation fields…Research in solvent extraction separation methods is needed to identify stable, selective, high-capacity extractants that also are inexpensive and commercially available. In addition, solvent extraction methods would be particularly valuable for use with acidic waste solutions for which sorbents are less effective."

Particular improvements in cesium extraction that could yield dividends include an increase in calixarene solubility, extraction-stripping efficiency, and selectivity. The current solvent system for CSSX is near the solubility limit of the calixarene extractant, BOBCalixC6. If an alternative extractant could be found with higher solubility and no sacrifice of other properties, a risk of process upset due to supersaturation and crystallization of the calixarene could be eliminated. In addition, more flexible process design would be enabled, facilitating potential applications at other sites, such as Hanford, where a major call for proposals for cesium-removal technologies was issued through CH2MHILL in 2004. At least one proposal from industry employed CSSX technology. Significant cost savings may also be anticipated from increased extraction-stripping efficiency resulting in reduced number of stages and corresponding footprint reduction. The key parameter is the ratio of the cesium distribution ratio on extraction (D_{Cs} = 14) to that on stripping (D_{Cs} = 0.05); this factor has been optimized at approximately 280. It is currently determined by the "nitrate concentration swing" used in the flowsheet to alternately extract (high nitrate concentration) and strip (low nitrate concentration). If stripping, for example, could be made to be dependent on some other variable such as pH, it could be possible to increase overall process efficiency, reducing footprint or increasing the concentration factor or both. In HLW treatment, plant cost is directly related to footprint. Another improvement that might be valuable would be to increase the Cs/K selectivity, as potassium is the chief competing cation and may be high in concentration at Hanford. In addition, increasing the extraction strength could mean cost savings via decrease in the expensive calixarene concentration.

Generic USDOE needs for cesium separation from HLW. Contamination by the mobile fission product ^{137}Cs ($t_{1/2}$ = 30 y) is one of the ubiquitous environmental problems in the USDOE complex. Produced in high yield from nuclear fission, this radionuclide is present in the majority of wastes and contaminated soils and groundwaters associated with reprocessing sites. Considering the decades of active cleanup by the USDOE ahead and the continued monitoring that will be required throughout the present century, it may be assumed that understanding the fundamental chemistry of cesium, efficient means to separate it from various media, and its environmental impact will effectively remain a generic USDOE research need for decades.

As regards high-level waste in particular, ^{137}Cs decay contributes a major fraction of the total radiation hazard, heat load, and 300-year environmental risk. In general, its separation is required for the safe and economical disposal of the bulk of the waste in low-activity waste (LAW) forms. Consequently, cesium separation from radioactive wastes has been recognized as a national research need, just as it has been of long-standing, broad international interest. In the United States, nuclear wastes from reprocessing activities since the Manhattan Project have been stored in tanks and bins. Alkaline tank wastes at the Savannah River (35 Mgal) and Hanford (54 Mgal) sites represent the greatest fraction of the stored HLW. So-called "salt waste," comprised of supernatant liquid and salt cake, is the largest fraction (roughly 85%) of the alkaline waste, and ^{137}Cs is the predominant radionuclide (ca. 98% at the SRS) in the salt fraction. At both the SRS and Hanford sites, a combination of economics, regulations, and agreements dictate that cesium must be removed and vitrified, a task that will not be complete till at least 2028. Toward meeting the technology needs for accomplishing this goal, planning within the Office of Environmental Management has consistently targeted cesium separations for R&D.

Benefits of improved cesium solvent extraction may be foreseen in the context of current thrusts within the USDOE Office of EM. Planning for cleanup at the SRS and Hanford is now centered around the EM Mission Acceleration Initiative, stressing alternative technologies, acceleration of cleanup, and reduced costs. At the SRS, cesium solvent extraction will be implemented not only at the SWPF, but also in modular units that can be deployed at a smaller scale. At Hanford, the Waste Treatment Plant (WTP) under construction will employ ion exchange for cesium removal. Cesium solvent extraction represents a potential backup technology for the Hanford WTP. With certain improvements in cesium solvent extraction (e.g., a more soluble calixarene extractant), it is likely based on available data from applied EM efforts that a competitive process flowsheet could be obtained. It should also be pointed out that possible application for cesium solvent extraction could be found at the Idaho National Laboratory (INL). Although the waste stored at this site is acidic, it is feasible to employ cesium solvent extraction under these conditions using calixarene-crown extractants, and research is in progress as INL is examining process options very similar to CSSX. We earlier showed that the approach being used at ORNL could with some modification be extended directly to the acidic INL wastes. Moreover, research in France has been successful in demonstrating cesium removal from reprocessing-type waste.

Approach. The use of calix-crown extractants possessing various types of functional groups that can act as "proton-switches", specifically, functional groups that can be deprotonated or protonated during the course of the pH shifts experienced during the extraction-strip cycle, are being investigated. Such pH-sensitive calix-crown derivatives may lead to dramatic improvements in overall binding-release efficiency. Three types of functional groups are being examined: weakly acidic (proton-ionizable) groups that will be anionic under alkaline extraction conditions and neutral under stripping conditions; weakly basic tertiary amine functional groups that will be neutral under alkaline extraction conditions and protonated under acidic (stripping) conditions; and more strongly basic guanidine functional groups that will be neutral under alkaline extraction conditions and essentially fully protonated even under neutral conditions.

For the proton-ionizable calix-crowns (see below), the mechanism of extraction under alkaline conditions is formally cation exchange. Under weakly acidic conditions, the cation exchange will be reversed, that is, "switched off." Proton-ionizable functional groups that have been investigated include methyl and trifluoromethyl sulfonamides; new ones being investigated include carboxylic acid, sulfonamides, and an -trifluoromethyl secondary alcohol. To provide greater solubility in hydrocarbon solvents, lipophilic groups will be incorporated into the ligands. In addition to lipophilic, proton-ionizable bis-crown calixes, an analogous family of lipophilic, proton-ionizable mono-crown calixes are being prepared.

When basic amine or guanidine functionalities are appended to neutral calixcrowns, the cesium is expected to be extracted as an ion pair under alkaline conditions, as the basic groups are neutral. In this case, the anion is nitrate, co-extracted for charge balance with the cesium. Under acidic conditions, the positive charge from the ammonium or guanidinium groups may, depending on their location relative to cesium, exert sufficient charge repulsion to force cesium out of the cavity. The guanidine-derivatized calix-crowns would function in a similar manner, but we anticipate that this more basic group will require far less acidity for protonation, and thus cesium release can be affected under neutral or even slightly alkaline conditions. The synthetic efforts will build largely on our previous work; however, the guanidine-derivatized compounds will be new. The syntheses of these would in many cases start with suitable non-alkylated (primary) amine-derivatized calix-crowns such as we are already synthesizing.

Design and synthesis will take into account the need for reasonable solubility of the target calixcrowns in nonpolar organic solvents. We have already learned a great deal regarding how the type and location of alkyl substituents on the calix-crown affect both solubility and cesium binding strength. Solubility of extractants and their complexes is a necessary criterion for successful application, where precipitates, third phases, gels, and "cruds" can have a devastating effect. Furthermore, it is desirable to operate in a regime where the solubilities of the components are not near their limits. The new ethylhexyl analog of BOBCalixC6, calix[4]arene-bis[4-(2-ethylhexyl)benzo-crown-6] (called BEHBCalixC6), represents a marked improvement in solubility, as the maximum solubility in modified alkane is more than 60 mM, at least seven times greater than that of BOBCalixC6 (Fig. 1). However, the synthesis of BEHBCalixC6 is currently more labor-intensive than that of BOBCalixC6, and proposed research will address synthesis optimization. As pointed out earlier, a more soluble calix-crown extractant decreases technology risk and increases flexibility in process design, increasing broadened applicability (e.g., Hanford waste).

Toward maximizing productivity in these thrust areas, a strong collaboration unites efforts at ORNL and TTU. This particular team will focus expertise and special facilities in organic synthesis (Bartsch at Texas Tech, Bonnesen at ORNL) and extraction chemistry (Moyer and Delmau at ORNL) in a holistic manner that will both create insights at the molecular level and create opportunities for application in USDOE HLW cleanup.

Research Progress and Implications

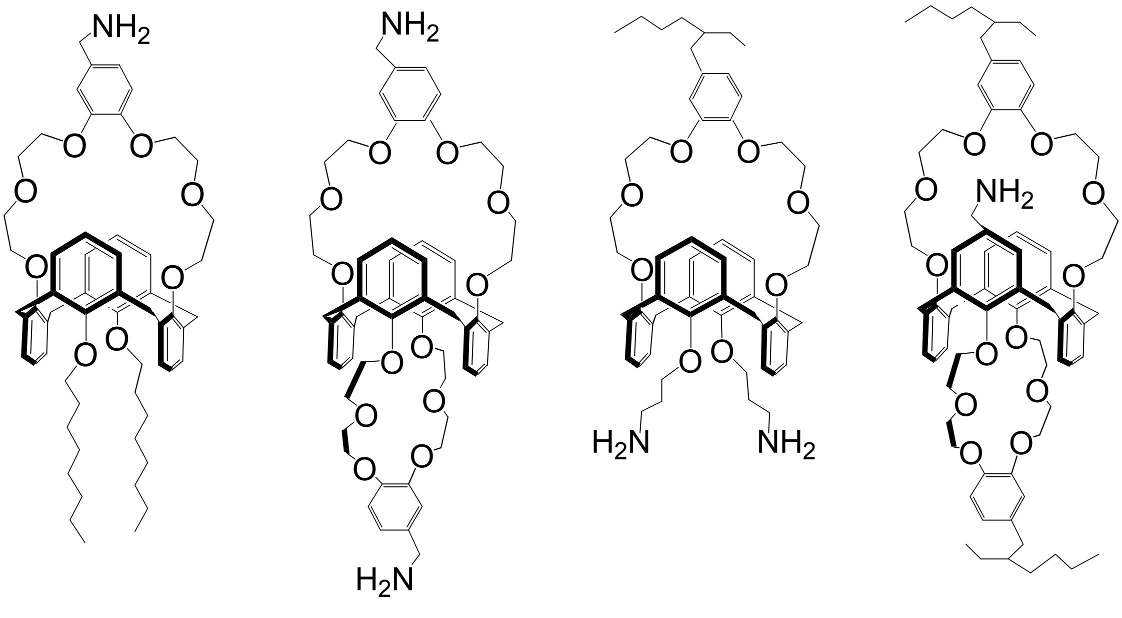
Reporting Period. This report summarizes work performed in FY 2004, the first year of the current three-year renewal period. Significant progress in this time has been obtained at ORNL on synthesis and evaluation of new alkylated calixcrowns that have enhanced solubility in modified alkane diluents. 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, 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. 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. Synthesis of proton-ionizable calix crowns at TTU has been highly productive, resulting in the preparation of 14 compounds in experimental quantities. Tests at ORNL have revealed striking extraction strength and pH-switching.

Synthesis and Evaluation of Alkylated Calix[4]arene-crown-6 ethers. As shown in a recent publication (Engle, et al, 2004) substantial improvement in solubility was obtained with an analog of BOBCalixC6 where the *tert*-octyl sidechains were replaced with 2-ethylhexyl sidechains (Fig. 1), with essentially no change in cesium extraction strength. This new calixcrown, BEHBCalixC6, retained a nominal equilibrium solubility of 57 ± 2 mM at 25 ºC in the Isopar L process diluent containing the CSSX solvent modifier Cs-7SB at 0.50 M over a period of 41 weeks. This solubility is not an upper limit, however, as the solution was not saturated. Comparatively, BOBCalixC6 achieved an equilibrium (saturation) solubility of only 6.7 ± 0.2 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 solvents containing these calixcrowns under potassium loading conditions revealed that BEHBCalixC6 was resistant to third-phase formation at potassium concentrations up to 0.75M, whereas equivalent solvent containing BOBCalixC6 showed third-phase formation when the potassium concentration was just 0.25 M. The synthesis of BEHBCalixC6 presently requires two additional steps in the synthesis relative to the synthesis of BOBCalixC6. However, these additional steps occur early in the synthetic pathway and pertain to the synthesis of the starting alkyl phenol (three steps to prepare 4-(2-ethylhexyl)-catechol as compared to 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 that had been previously prepared also demonstrated solubility behavior at least equal to BEHBCalixC6 (ca. 57 ± 2 mM), but again since the calixcrowns were not saturated, the maximum solubility is likely higher. Relative to the biscrowns above, the cesium distribution ratios for the monocrowns from a simple salt matrix run about 10% lower.

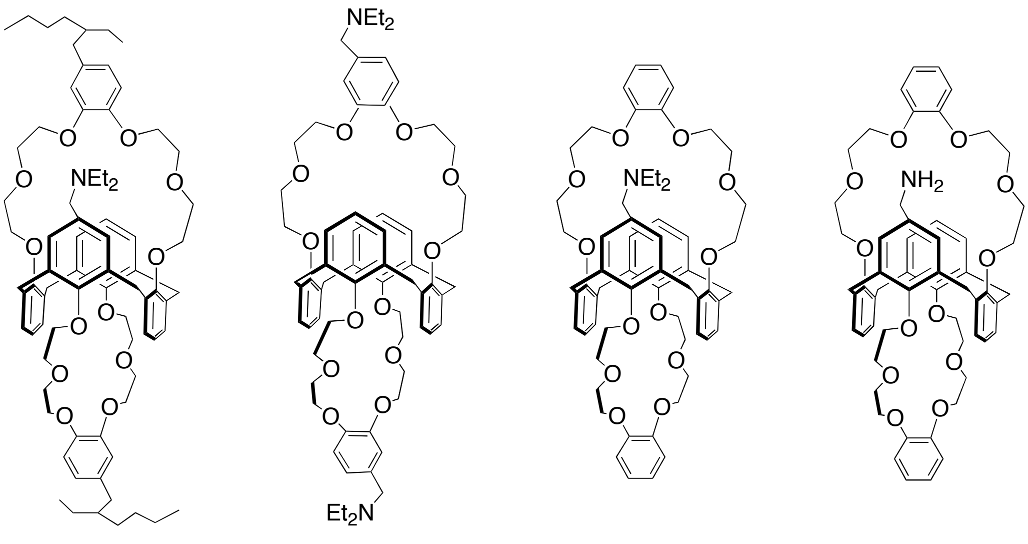
Synthesis and evaluation of calixarene-crowns with incorporated amine functionality. Previously, we hypothesized that the incorporation of amine functionality into the calix-crown could dramatically improve the efficiency of release of cesium from the calix-crown upon protonation. Neutral calix-crowns 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 were prepared and evaluated (Gorbunova, et al., 2003; Bazelaire, et al., 2004). As shown in Fig. 2, the first had the amine attached to the phenyl group of the benzocrown unit (**1** and **2**); the second was particular to mono-crown calixes, in which the alkoxy group is a short alkyl chain with an amine terminus (**3**); and the last had the amine attached to one of the phenyl rings of the calixarene "upper rim" (**4**). These four compounds were successfully prepared and evaluated. Of these, compound **4**—which can be considered a derivative of BEHBCalixC6, in which one aminomethyl moiety has been attached to one of the "upper rim" aryl groups of the calixarene—appeared to be the 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.

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, pK_a behavior of the amine, stability of the amine, and cesium binding. Indeed, improved solubility must be sought, as the protonated form of compounds **1**–**4** exhibited limited solubility in a survey of various diluents. In addition, it is expected that primary amines will have poor stability, especially in the presence of nitrite, which can under acidic conditions convert the amine group to a nitrosoamine. Toward gaining improved solubility and stability, we have embarked on the synthesis of alkylated analogs of compounds **2** and **4**. Compound **5** (Fig. 3) is the diethylamino



1 **2** **3** **4**

Figure 2. Amino-derivatized calixcrowns that have been synthesized and evaluated (Gorbunova, et al., 2003; Bazelaire, et al., 2004).



5 **6** **7** **8**

Figure 3. Alkyl-amino-derivatized calixcrowns (**5**-**7**) and an amino-calixcrown suitable for structure analysis (**8**).

analog of compound **4**, and compound **6** is the diethylamino analog of compound **2**. Compound **5** was prepared by reduction of the amide group –C(=O)NEt$_2$. The planned synthesis of compound **6** will be first attempted by simply alkylating amino-derivative **2.** Compound **7** without the "greasy" 2-ethylhexyl groups was prepared as an analog of **5** that would be amenable to X-Ray crystallographic studies. The structure of **7** has been determined and is shown below (Fig. 4). Crystallization trials resulted in crystals of **7** as the hydrochloride salt. The corresponding X-ray structure showed that the $(Et)_2NH^+$ group does not interact with the oxygen atoms in the crown ether. Instead, it forms a strong hydrogen bond to the chloride counterion, with observed N···Cl and H···Cl intermolecular distances of respectively 2.957 and 1.783 Å, and an N–H–Cl angle of 169.7°. As a result, the $(Et)_2NH^+$ group points away from the crown ether ring. Of interest is to determine whether the free amine (as in compound **8**) would also point away from the cavity, or if the N–Hs would point toward the cavity due to H-bonding interactions with the crown ether oxygens.

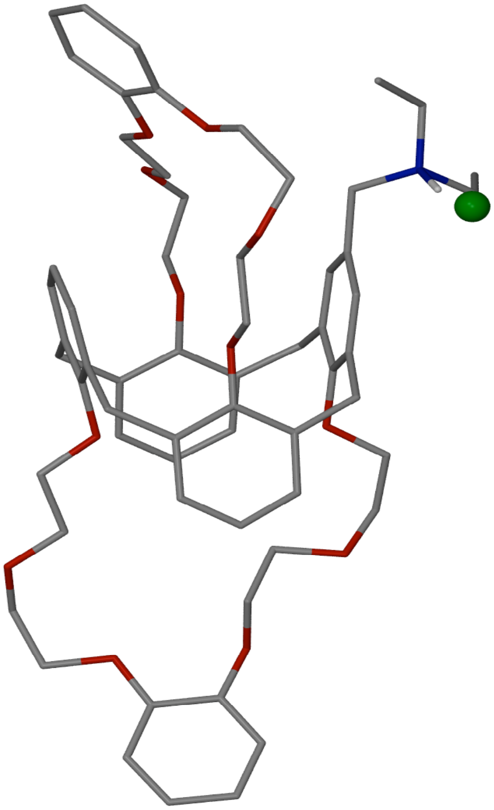


Figure 4. X-Ray crystal structure of 7.

In a recent publication (Bazelaire, et al., 2004), extraction results demonstrated proof of principle for pH-switched extraction and release. 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, and extractions were carried out from alkaline and acidic nitrate aqueous solutions containing $^{137}CsNO_3$ radiotracer. Results demonstrated up to a hundred-fold decrease in cesium extraction strength upon acidification of the aqueous phase.

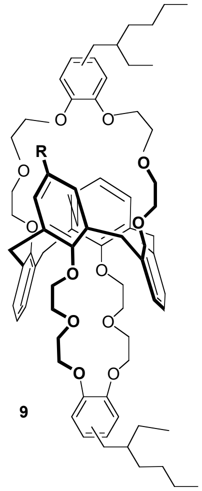
Under alkaline conditions, except for the bis-amino-propoxy calix[4]crown **3**, the presence of the amino group does not change D_{Cs} significantly. Extraction under the acidic conditions decreases significantly relative to the non-aminated control compounds for all amino-substituted compounds, and most significantly for aminomethyl calixcrown **4**. Stripping under acidic conditions gives approximately the same value of 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.

Experiments involving the radiotracer ^{137}Cs were conducted to determine the extraction stoichiometry of the complexed form of **4**. The data confirmed a 1:1 binding of cesium by **4** and the non-aminated control BEHBCalixC6 at low concentrations of cesium. Results at higher concentrations of cesium revealed that further loading of BEHBCalixC6 can be achieved to give a calix:cesium ratio of 1:2, in agreement with the number of crown rings available to complex cesium. In contrast, the stoichiometry between **4** and cesium remained unchanged, suggesting that one of the two crown cavities of this molecule is unsuitable for binding cesium, evidence that the nonfunctionalized crown ring contains the cesium.

Using conditions determined in the solvent extraction experiments, the ^{1}H, ^{13}C, and ^{133}Cs NMR spectra of **4** and BEHBCalixC6 were compared. Key protons were identified in the free ligand **4** and its 1:1 complex with cesium, showing that the largest chemical shift occurs in the nonfunctionalized side of the molecule. We interpret this result to indicate that the nonfunctionalized crown contains the cesium, in agreement with the results from the extraction experiments. The implication is thus that positioning the methylamino group on one of the phenyl groups on the calixarene "belt" destabilizes cesium binding, although the amino group itself is ordinarily capable of acting as an electron-pair donor.

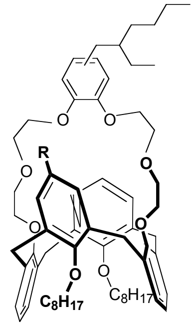
Synthesis and evaluation of proton-ionizable calixcrowns. Incorporating a proton-ionizable group into a macrocyclic ligand has a very important effect upon the efficiency with which a metal ion can be extracted into an organic medium. For practical metal ion extraction processes, the aqueous anions are chloride, nitrate, or sulfate. Transfer of such hydrophilic anions from the aqueous phase into an organic phase to provide an electroneutral extraction complex with a macrocycle-complexed metal ion is energetically unfavorable, which markedly diminishes the extraction efficiency. With a proton-ionizable group in the ligand, ionization provides the requisite anion for formation of an electroneutral extraction complex without transfer of an aqueous phase anion.

To increase the efficiency for solvent extraction of cesium by calix[4]arene-6 ligands, a series of calix[4]arene-biscrown-6 ligands (**9**) and three series of calix[4]arene-monocrown-6 ligands (**10**–**12**) have been designed, prepared, and characterized at TTU (Fig. 5) and forwarded



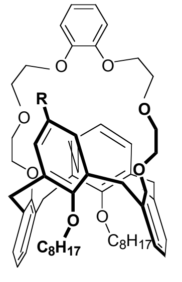
9

R = CO_2H, $C(O)NHSO_2CH_3$, $C(O)NHSO_2CF_3$



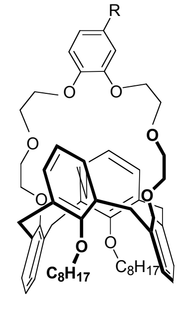
10

R = CO_2H, $C(O)NHSO_2CH_3$, $C(O)NHSO_2CF_3$, $C(O)NHSO_2Ph$, $C(O)NHSO_2C_6H_4$-4-NO_2, $CH(CF_3)OH$, H



11

R = $C(O)NHSO_2CH_3$, $C(O)NHSO_2CF_3$



12

R = $C(O)NHSO_2CH_3$, $C(O)NHSO_2CF_3$

Figure 5. Proton-ionizable calix-crowns synthesized and characterized.

to ORNL for evaluation. In all cases, multi-step synthetic pathways were required to realize the desired products. Ligands **9**–**12** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and combustion analysis.

The lipophilic calix[4]arene-biscrown-6 extractant series **9** has the same general structure as non-ionizable BOBCalixC6 with the exception that the lipophilic groups are 2-ethylhexyl instead of *t*-octyl and the presence over the face of one crown ring of a proton-ionizable group. In addition to a carboxylic acid group, the ionizable groups include two *N*-(X)sulfonyl carboxamide groups in which the acidity of the function is "tuned" by varying the electron-withdrawing ability of X. The change from X = CH_3 to CF_3 is expected to increase the ligand's acidity by about three pK_a units.

Since calix[4]arene-biscrown-6 extractants have two crown units, there is a possibility that in addition to the complexation of cesium ion by one crown unit, the second crown unit could complex cesium, thereby escaping the switching mechanism. Additionally, the possibility of sodium or potassium ion binding by the second crown unit could reduce the cesium extraction selectivity. To eliminate these unwanted effects, the lipophilic calix[4]arene-monocrown-6 series **10** was prepared. To allow the effect of varying the proton-ionizable group's acidity to be assessed, ligands with six different acidic functions located over the crown cavity were synthesized. These include a carboxylic acid group, four *N*-(X)sulfonyl carboxamide groups in which the acidity can be "tuned" by variation of X, and a very weakly acidic fluorinated alcohol group. For comparison of the proton-ionizable ligands with an analogous non-ionizable extractant, **10** with R = H was also prepared.

For evaluation of the influence of proton-ionizable group positioning relative to the crown cavity, extractant series **11** and **12** were realized. In **11**, the proton-ionizable group is located directly over the crown cavity. In **12**, the proton-ionizable points away from the crown cavity. For extractant series **11** and **12**, the proton-ionizable groups are of the *N*-(X)sulfonyl carboxamide variety with X = CH_3 and CF_3 to provide for a substantial acidity variation. For this comparison, the 2-ethylhexyl groups were not needed, as the *n*-octyl chains confer sufficient solubility.

Survey-type extraction experiments revealed that the proton-ionizable families **9** and **10** are not only strong extractants for cesium under alkaline conditions, but they also possess a striking switching-off effect under acidic conditions. Preliminary solubility tests were carried out in toluene and chlorinated diluents. It was determined that only the calixarenes substituted with 2-ethylhexyl groups (whether the calixarene is mono- or biscrown) were soluble in these diluents, in agreement with expectations. Extraction experiments were therefore conducted with these two families (**9** and **10**). Tests involved measuring the cesium distribution ratios (D_{Cs} values) for each calixarene at different pH values under constant aqueous nitrate conditions. The pH was maintained using buffer solutions prepared using borax, phosphate, or acetate salts. The entire family of monocrowns **10** was soluble in toluene, in which the switching effect was more pronounced. It may be seen in Fig. 6 that D_{Cs} swings as much as six orders of magnitude between alkaline and acidic conditions. Under alkaline conditions, the value of D_{Cs} increases to an expected plateau (except for R = $CHCF_3OH$, whose presumed plateau occurs at unreachable alkalinity), where the ionizable protons are presumed to be quantitatively exchanged for sodium ions. At the plateau, the effective extraction reaction is thus expected to be an exchange of sodium for more strongly favored cesium, a pH-independent process. A constant plateau value of approximately 200 is reached for all N-sulfonylcarboxamide compounds. It may be seen that the pH effect is governed by the nature of the ionizable group. Among the Nsulfonylcarboxamides tested, the strength of extraction at a given pH value below the range of plateau values follows the following order: X = trifluormethyl > *p*-nitrophenyl > methyl ~ phenyl. With decreasing pH, the curves exhibited lower slopes and even signs of leveling off. It is presumed that, in principle at least, the extraction reaction effectively becomes ion-pair extraction of cesium nitrate by the non-ionized calix-crown at sufficiently low pH. As only a few biscrowns were soluble in toluene, chloroform was chosen as a medium to compare the properties of the two families. Results for the monocrowns in chloroform were similar to the results in toluene, though the magnitude of change in D_{Cs} values with pH swing was not as large. Biscrowns exhibited even less change in D_{Cs}, as the curves tend to level off at a higher value of D_{Cs} in the low-pH region, undoubtedly owing to the fact that the second crown ring is capable of extracting cesium nitrate unencumbered by the presence of the ionizable group. We make the important conclusion that the pH-switching effect is enhanced by a blocking effect of the ionizable group upon cesium binding. That is, the neutral ionizable group must make cesium binding unfavorable by steric or hydrogen-bonding interactions.

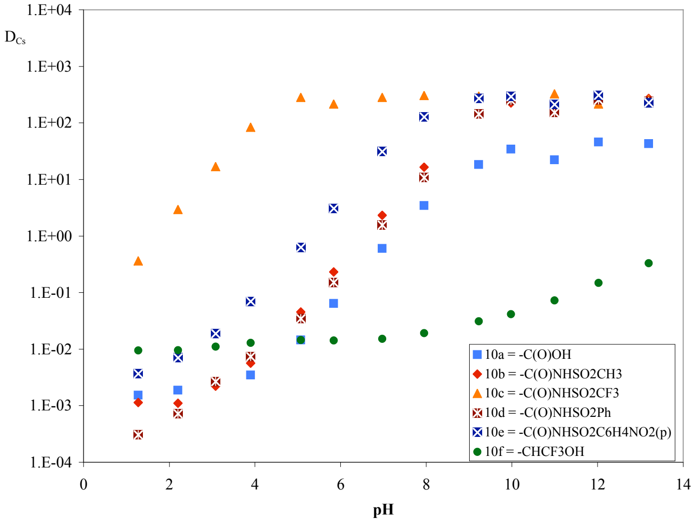


Figure 6. Cesium extraction as a function of pH from constant aqueous nitrate solutions by proton-ionizable calix[4]arene monocrown-6 compounds in toluene.

Investigation of novel approaches to cesium release (stripping). In that the neutral calix[4]arene-crown-6 compounds are proven cesium extractants that have moved into the realm of industrial processes, it remains of interest to examine chemical mechanisms by which extraction may be more efficiently reversed. This becomes a question of varying the aqueous electrolytes under stripping conditions, assuming that the extraction conditions are normally fixed by a particular waste matrix. The role of the tri-*n*-octylamine (TOA) or alternative compound as a suppressor of impurity effects also becomes a variable. One question of interest arises in whether acidic conditions are necessary to effect stripping. Tests were therefore carried out to test the feasibility of a complete extraction-scrub-strip (ESS) cycle under caustic conditions. The baseline CSSX process involves acidic scrub and strip stages, using nitric acid at low concentrations. The new caustic scrub and strip conditions aimed at obtaining similar D_{Cs} values as those obtained with nitric acid. Based on former modeling studies, the scrub D_{Cs} value could be maintained around 1.3 by using 0.5 M sodium hydroxide. The tests were run, and this value was actually validated. Regarding stripping, it was demonstrated that the use of sodium hydroxide at low concentration yielded cesium distribution ratios too high to achieve a useful solvent regeneration, as D_{Cs} increased with each stripping contact. A successful alternative was to use 1 mM cesium hydroxide. The cesium distribution ratios decreased at first to remain constant after the 3rd strip at 0.06. However, the use of cesium hydroxide did not address the potential problem of organophilic impurities present in the system. This issue can be solved using the same concept as that of TOA under acidic conditions, that is, using a weak base that can be protonated at a given pH. In this case, it was proposed that an alkylguanidine would function in the same way as TOA but in a higher pH range. The trialkylguanidine present in the commercial extractant Lix 79 can be protonated at pH values under 11.5. In this case, stripping was conducted using sodium bicarbonate at 10 mM. Very promising results were obtained with D_{Cs} values as low at 0.002 (an improvement of a factor of 30 vs acidic stripping) for the third strip. Studies are on-going to isolate the guanidine and to use other stripping solutions.

Planned Activities

Primary emphasis in the remainder of the current three-year funding period will be placed on understanding and developing the chemistry of pH-switchable calix-crowns, particularly the proton-ionizable families introduced by TTU. Collaboration with Prof. Bartsch at TTU will be fostered toward synthesis and characterization of new ionizable calix-crowns. Questions include controlling the acidity of the ionizable group, particularly to weaken it so that it "switches on" only at the elevated alkalinity of typical waste matrices. Solubility and chemical stability will be examined as a function of ionizable group and alkyl substituents toward use in an aliphatic solvent system. Further efforts will be devoted to elucidating the structure of the free ligands and their complexes with cesium and other alkali metals. Extraction studies will aim at a definitive model of speciation and equilibria over the entire range of pH. For the amino-derivatized calix-crowns, continuing efforts will involve further optimization of the synthetic pathways to promising compounds, and preparation of alkylated analogs (alkylation of the amine group with alkyls groups of various sizes) will continue.

Further investment will be directed toward cesium extractants with improved solubility in alkane diluents. These efforts will primarily focus on improving the synthetic method for BEHBCalixC6 toward lowering preparative cost, as this compound exhibits substantial improvement in solubility already, with essentially no effect on extraction and likely no effects on chemical stability. 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 continue to express interest in testing BEHBCalixC6, and future collaboration is anticipated.

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. 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, the role of amine (or guanidine) solvent components, and novel approaches to stripping. Theoretical results from the studies of B. P. Hay at PNNL will be monitored 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

See also the www home page of the ORNL Chemical Separations Group: http://www.ornl.gov/csg.

Acknowledgments

This research was sponsored by the Environmental Management Science Program of the Office of Science, U. S. Department of Energy, under a) contract no. DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC; and b) Grant DE-FG02-03ER6376 with Texas Tech University. Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE. Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE.

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