

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

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Bruce A. Moyer, Eve Bazelaire, Peter V. Bonnesen, Jeffrey C. Bryan, Lætitia H. Delmau,
Nancy L. Engle, Maryna G. Gorbunova, Tamara J. Keever, Tatiana G. Levitskaia,
Richard A. Sachleben, and Bruce A. Tomkins
Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN
37830-6119

Richard A. Bartsch
Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061

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ANNUAL PROGRESS REPORT

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

Lead Principal Investigator: Bruce A. Moyer, Oak Ridge National Laboratory, Bldg. 4500S, MS 6119, P.O. Box 2008, Oak Ridge, TN 37831-6119. Phone: 865-574-6718. Fax: 865-574-4939. E-mail: moyerba@ornl.gov

co-Principal Investigator: Prof. Richard A. Bartsch, Dept. of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061. Phone: 806-742-3069. Fax: 806-742-1289. E-mail: richard.bartsch@ttu.edu

co-Principal Investigator: Peter V. Bonnesen, Oak Ridge National Laboratory, Bldg. 4500S, MS 6119, P.O. Box 2008, Oak Ridge, TN 37831-6119. Phone: 865-574-6715. Fax: 865-574-4939. E-mail: bonnesenv@ornl.gov

co-Principal Investigator: Lætitia H. Delmau, Oak Ridge National Laboratory, Bldg. 4500S, MS 6119, P.O. Box 2008, Oak Ridge, TN 37831-6119. Phone: 865-576-2093. Fax: 865-574-4939. E-mail: delmaulh@ornl.gov

Statistics since start of renewal Oct. 1, 2004 (does not include Texas Tech Univ.):

Number of undergraduate students: 1

Number of graduate students: 0

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

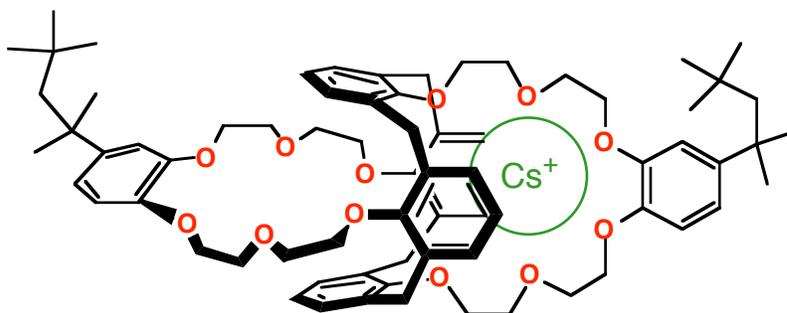
Program Officer: Gary K. Jacobs, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, P.O. Box 2008, Bldg. 4500S. Phone: (865) 574-7374. Fax: (865) 574-7287. E-mail: jacobsgk@ornl.gov.

Research Objectives

General project objectives. 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 less expensive 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



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

conformational properties that complement the Cs⁺ ion. The overall coordination ability of 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. Such extraction experiments are augmented with spectroscopic and other physical techniques as needed to address structural questions. 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.

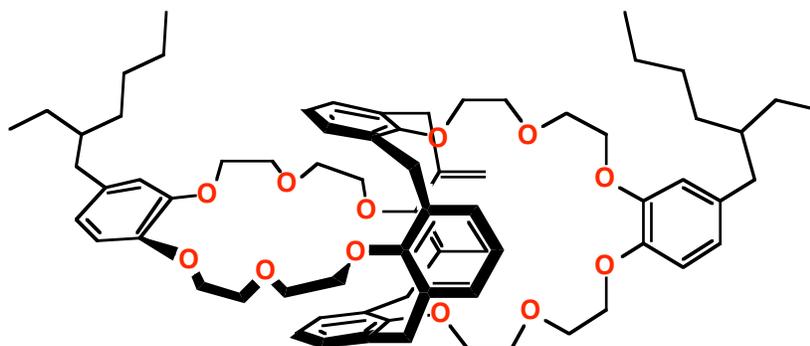
Objectives in the past year. Since the last annual report, it was intended to further concern ourselves with the synthesis and properties of our new alkylated analogs of BOBCalixC6, submit a manuscript for publication, and inform potential site users of this progress. We also desired to obtain further understanding of the pH-switching ability of amino-derivatized calixcrowns, including progressing in the preparation of alkylated analogs. In the renewal of this project, we formalized the participation of Prof. Bartsch at TTU as a co-Principal Investigator. His efforts in the past year have been directed toward initiating synthesis and characterization of new ionizable calixcrowns designed to have improved selectivity and pH-switched extraction-stripping ability.

Research Progress and Implications

Reporting Period. This report summarizes work performed during the first year following renewal of this 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. 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. A series of new calixcrowns functionalized with primary amine groups have been shown in proof-of-principle tests to undergo pH-switched extraction-stripping cycling. A simple 1:1:1 metal:ligand:nitrate organic-phase species was shown to form upon extraction, under which conditions the calixarene is in the neutral form. Such compounds illustrate that enhanced stripping may be possible by appending amino groups to the calixarene extractant, whereby protonation under mildly acidic conditions expels the cesium. Good progress has been made at TTU in the synthesis of a series of proton-ionizable calixcrowns as an alternative approach to pH-switched extraction and stripping. In this case, the extraction mechanism becomes that of ion exchange vs. ion-pair extraction, and stripping is effected by "turning off" the ion exchange by reprotonation of the calixcrown. Provided that the effective acidity of these compounds can be adjusted to the needed operating range, they could possibly offer advantages over the amino-substituted calixcrowns.

Synthesis and Evaluation of Alkylated Calix[4]arene-crown-6 ethers. As reported in last year's annual report, a substantial improvement in solubility was obtained with an analog of BOBCalixC6, the macrocycle currently employed in the CSSX process for extracting cesium. In

the new calixcrown, BEHBCalixC6 (see inset at right), the *tert*-octyl sidechains in BOBCalixC6 are replaced with 2-ethylhexyl side chains, with essentially no change in cesium extraction strength. The synthesis and initial evaluation of this new calixcrown, BEHBCalixC6, have been published.¹³ The paper describes the



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

solubility, cesium extraction, and potassium loading behavior of BEHBCalixC6 as compared with those of BOBCalixC6. Equilibrium concentrations of BEHBCalixC6 in Isopar L diluent modified with 0.5 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (Cs-7SB) over the course of 41 weeks of gentle agitation at 25 °C were unchanged from the initial concentration of 57 ± 2 mM. No evidence of precipitation or third-phase formation was observed. It should be noted that this solubility is not an upper limit, as the solution was not saturated. In contrast, solutions initially containing 57 ± 2 mM of BOBCalixC6 prepared using sonication were not stable. From these super-saturated solutions, solid BOBCalixC6 precipitated to afford an equilibrium concentration of only 6.7 ± 0.2 mM after 41 weeks. Solubility studies of

the calixcrowns in solvents equilibrated with aqueous phases containing metal ions (such as with sodium or potassium present) were also conducted. Third-phase tests under metal-loading conditions showed that BEHBCalixC6 resists third-phase formation as well as, or better than, BOBCalixC6. With increasing potassium loading from an alkaline sodium nitrate solution, both calixcrowns at 20 mM in modified Isopar L exhibited comparable onset of third-phase formation, gauging by the decreasing mass balance in cesium extraction from the same solutions. However, the BEHBCalixC6 solvent exhibited no visible indications of third-phase formation until the aqueous potassium concentration reached 0.75 M. In comparison, the BOBCalixC6 solvent suffered visible third-phase formation when the aqueous potassium nitrate concentration reached 0.25 M.

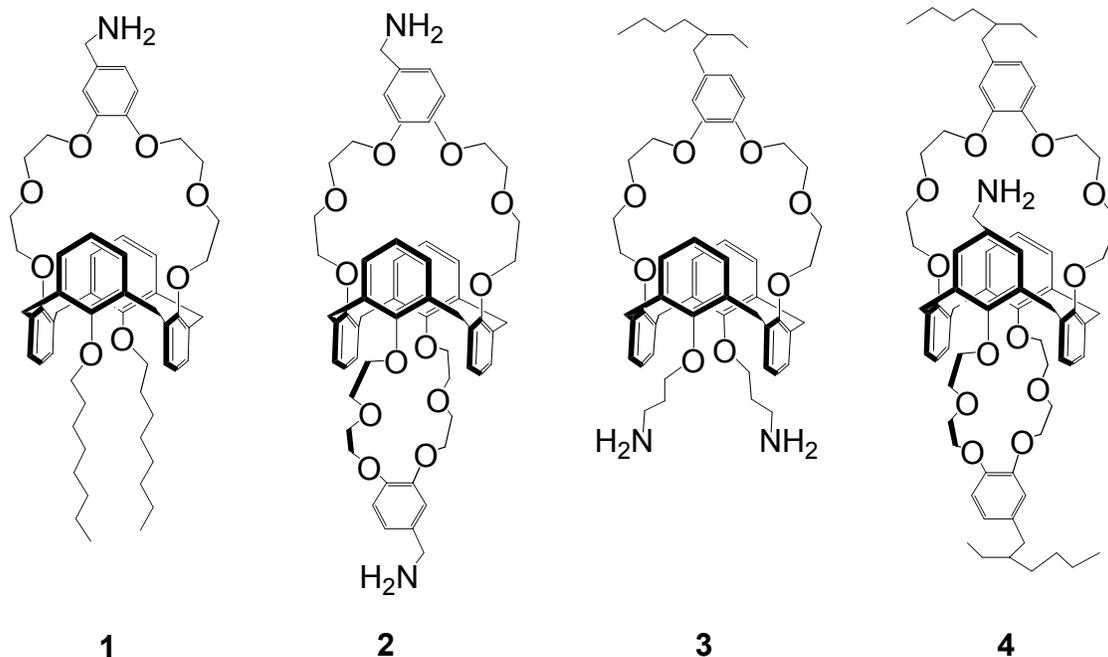
With regard to synthesis, the 2-ethylhexyl groups that improve the solubility also make the synthesis and purification of BEHBCalixC6 more difficult than that of BOBCalixC6. However, the difficulty in synthesis is derived from having two additional steps early in the overall synthetic pathway, namely three steps to prepare 4-(2-ethylhexyl)catechol as opposed to only one step to prepare 4-*tert*-octylcatechol. The remaining three steps from the alkylcatechol 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%). Particularly difficult is the last purification step that involves a challenging separation of side products by column chromatography. 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. The presence of so many stereoisomers for BEHBCalixC6 tends to cause broadening of the bands during chromatography, and it is currently difficult to purify the material in quantities exceeding 5 grams at a time.

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

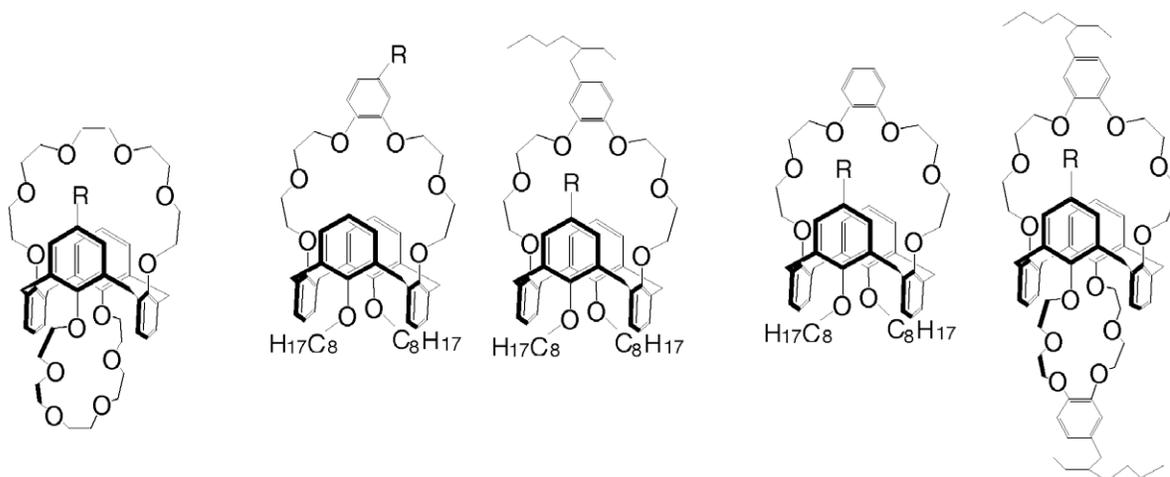
We previously reported that the incorporation of an amine functionality into cesium-selective calix[4]arene-crown-6 extractants could dramatically improve the efficiency of release of cesium from the calixcrown upon protonation, depending on the location of the amine.¹⁴ Neutral calixcrowns extract Cs⁺ by co-extraction of an aqueous-matrix anion, such as nitrate. When the organic phase is then contacted with an acidic aqueous phase, the amine functionalities become protonated, destabilizing cesium complexation. We hypothesize that the destabilization occurs via charge-charge repulsion. To probe the scientific question of the relationship between the strength of the destabilizing effect and the proximity of the amine groups to the cesium binding cavity, three classes of amine-derivatized calixcrowns were prepared, as shown in the Figure below.¹⁴ 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—was by far the most effective, as previously reported (see extraction results below). The synthesis of **4** has been successfully performed at the multigram scale.

The extraction behavior of calixcrown **4** has been examined in some detail during the past year.¹⁵ Among the results, a proof-of-principle extraction-scrub-strip cycle was successfully demonstrated. In the experiment, calixcrown **4** exhibited good cesium extraction strength and high selectivity for cesium over potassium and sodium. Most important, its extraction-stripping cycling efficiency, as measured by the ratio of distribution ratios ($D_{\text{ext}}/D_{\text{strip}}$) was 5.6 times greater than that obtained currently with the baseline CSSX solvent slated for use at the SRS for

High Level Waste treatment. An analysis of the stoichiometry of extraction of Cs^+ ion by **4** was carried out by a series of systematic distribution experiments followed by graphical data treatment (slope analysis). It was found that the extraction of Cs^+ by **4** in dodecane modified with 0.5 M Cs-7SB is consistent with the formation of the simple 1:1:1 metal:ligand:nitrate organic-phase species CsBNO_3 . In future work, it is desired to examine the effective equilibria occurring under acidic conditions so as to quantitatively assess the effect of protonation on cesium binding.



Synthesis and evaluation of proton-ionizable calixcrowns. In collaboration with Prof. Bartsch at TTU, we plan to examine proton-ionizable calixcrowns such as shown below, where R is a proton-ionizable group [e.g., $-\text{C}(\text{O})\text{NHSO}_2\text{CH}_3$, $-\text{C}(\text{O})\text{NHSO}_2\text{CF}_3$, or $-\text{CH}(\text{OH})\text{CF}_3$] as an alternative approach to pH-switchable cesium extraction and stripping. As detailed in the annual



report submitted independently by Prof. Bartsch, good progress on the synthesis of a series of candidate compounds has been made. These compounds have a single ionizable proton and one or two benzocrown-6 rings. For lipophilicity and solubility in modified alkane diluents, the benzo groups are being substituted with 2-ethylhexyl groups. Samples of such compounds will be tested in the coming year as they become available from TTU.

Planned Activities

Priority in the coming year will be accorded to the synthesis and characterization of pH-switchable calixcrowns. Amino-substituted calixcrowns will be synthesized in which the amino group bears alkyl substituents, both for lipophilicity and stability. 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 is needed, as the protonated forms of **1–4** exhibited limited solubility in a survey of various diluents.^{14,15} NMR experiments will be conducted to investigate the binding of Cs⁺ ion, particularly with regard to the question of which of two available crown rings in bis-crown calixes actually hosts the cation. Extraction measurements on proton-ionizable calixcrowns received from TTU will be carried out. 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. Personnel at the SRS have expressed interest in testing BEHBCalixC6, and future collaboration is anticipated.

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>.

Acknowledgments

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PUBLICATION LIST

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

ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM
PROJECT NO. 73803

FY 2001–2006 (Renewal period)

REPRINTS AVAILABLE ON REQUEST

Dr. Bruce A. Moyer, *Chemical Separations Group*, Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Bldg. 4500S, MS-6119, Oak Ridge, TN 37831-6119, U.S.A. Ph.: 865-574-6718. FAX: 865-574-4939. E-mail: moyerba@ornl.gov. WWW home page: <http://www.ornl.gov/sci/casd/csg/csgbro.htm> .

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Publications

Alexandratos, S. D.; Stine, C. L.; Sachleben, R. A.; Moyer, B. A. Immobilization of Lithium-Selective 14-Crown-4 on Crosslinked Polymer Supports. *Eur. Polym. J.*, submitted.

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