

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

**FY 2004 Annual Report, Environmental Management Science Program, Project #73803**

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

June 30, 2004

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***

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](mailto: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](mailto: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: [bonnesenpv@ornl.gov](mailto:bonnesenpv@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](mailto: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

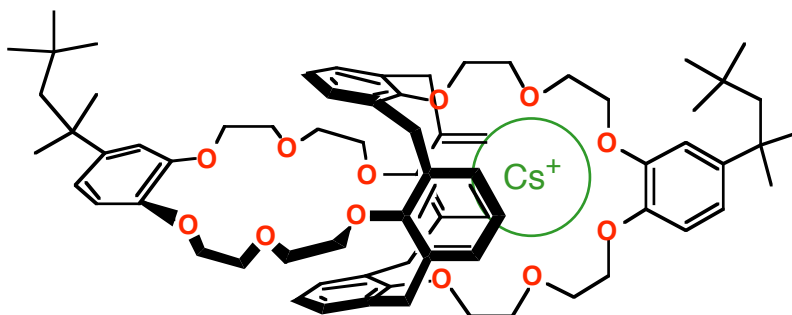
Program Officer: Gary K. Jacobs, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6119, P.O. Box 2008, Bldg. 4500S. Phone: (865) 574-7374. Fax: (865) 574-7287. E-mail: [jacobsbk@ornl.gov](mailto:jacobsbk@ornl.gov).

## 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.<sup>1</sup> 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.<sup>2</sup> 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.<sup>1-3</sup> Vitrification of the waste to produce a borosilicate glass waste form is the preferred treatment of the high-level waste prior to geologic disposal.<sup>1</sup> However, to vitrify the entire mass of the high-level waste would be prohibitively expensive. Accordingly, technologies are needed to remove radionuclides such as <sup>137</sup>Cs 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.<sup>4</sup> Nevertheless, it is recognized that fundamental results will continue to add value toward improvements in existing technologies and advancement of alternative technologies.<sup>1a</sup>

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<sup>+</sup> ion vs. the Na<sup>+</sup> ion,<sup>5</sup> 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,<sup>6</sup> 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<sup>+</sup> 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<sup>+</sup> ion)

conformational properties that complement the Cs<sup>+</sup> 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).<sup>7,8</sup> 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.<sup>9</sup> Having this stripping method allowed the cesium to be concentrated in a relatively pure aqueous stream and the extractant to be regenerated for recycle.<sup>10</sup> 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.<sup>11,12</sup>

Despite these successes, the CSSX process represents young technology that can benefit substantially from further fundamental inquiry, as well as further applied R&D.<sup>4b</sup> 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.

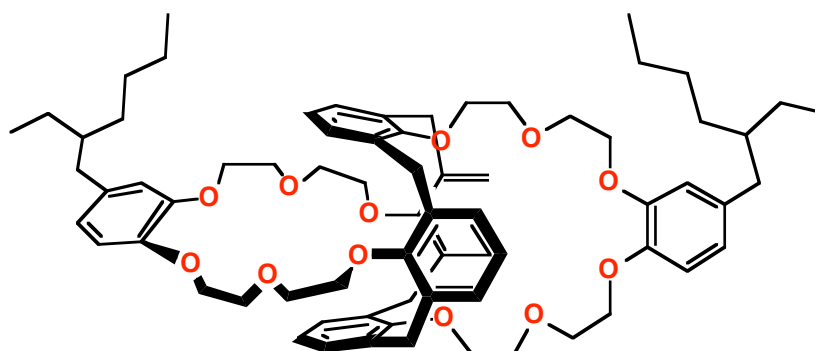
**Objectives in the past year.** Since the last annual report, it was intended to further concern ourselves with the synthesis and properties of our new alkylated analogs of BOBCalixC6, submit a manuscript for publication, and inform potential site users of this progress. We also desired to obtain further 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.<sup>13</sup> 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  $57 \pm 2$  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  $57 \pm 2$  mM of BOBCalixC6 prepared using sonication were not stable. From these super-saturated solutions, solid BOBCalixC6 precipitated to afford an equilibrium concentration of only  $6.7 \pm 0.2$  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.

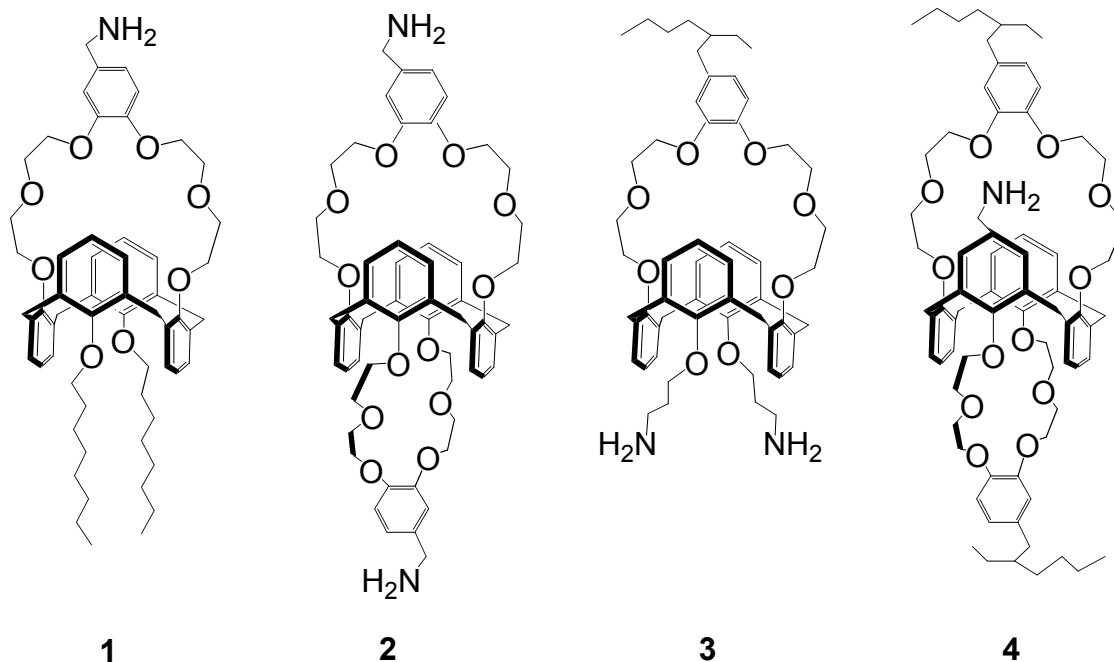
With regard to synthesis, the 2-ethylhexyl groups that improve the solubility also make the synthesis and purification of BEHBCalixC6 more difficult than that of BOBCalixC6. However, the difficulty in synthesis is derived from having two additional steps early in the overall synthetic pathway, namely 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.**

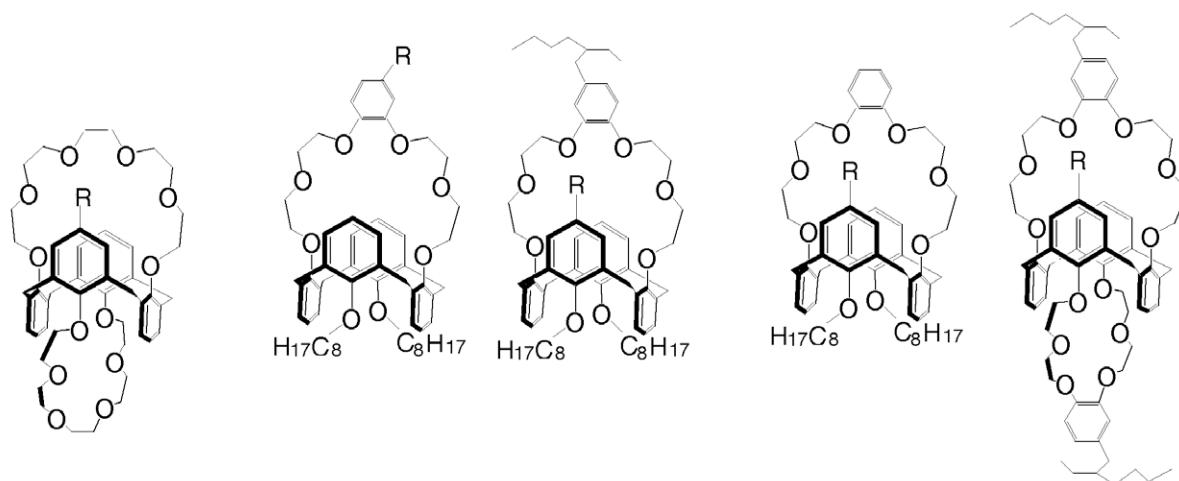
We previously reported that the incorporation of an amine functionality into cesium-selective calix[4]arene-crown-6 extractants could dramatically improve the efficiency of release of cesium from the calixcrown upon protonation, depending on the location of the amine.<sup>14</sup> Neutral calixcrowns extract Cs<sup>+</sup> 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.<sup>14</sup> 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.<sup>15</sup> 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  $\text{Cs}^+$  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  $\text{Cs}^+$  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  $\text{CsBNO}_3$ . 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.<sup>14,15</sup> NMR experiments will be conducted to investigate the binding of Cs<sup>+</sup> 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**

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.

### **References**

1. (a) "Research Needs for High-Level Waste Stored in Tanks and Bins at U.S. Department of Energy Sites," National Research Council, National Academy Press, 2001. (b) Nuclear Wastes: Technologies for Separations and Transmutation, National Research Council, National Academy Press, Washington, D.C., 1996; pp. 192, 193. (c) Bunker, B.; Virden, J.; Kuhn, B.; Quinn, R. In Encyclopedia of Energy Technology and the Environment; John Wiley & Sons, Inc., 1995, p 2023-2032.
2. Department of Energy Record of Decision: Savannah River Site Salt Processing



- Alternatives, Federal Register, Vol. 66, No. 201, pp. 52752–52756, October 17, 2001.
3. (a) TWINS Database, <http://twins.pnl.gov:8001/twins.htm>. (b) "Final Environmental Impact Statement: Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes", Report DOE/EIS-0113 (Vol. 2 of 5) Appendix A, U.S. Department of Energy, Dec., 1987.
  4. (a) Jones, R. T. "High Level Waste Salt Processing Project (SPP) Project No. W852 Caustic side Solvent Extraction Pilot Plant Project Authorization Package (U) (Critical Decision 1 (CD-1) Package)," Document No. WSRC-RP-2001-00924, Westinghouse Savannah River Company, Aiken, South Carolina, October 3, 2001. (b) Harmon, H.; Leugemors, R.; Schlahta, S.; Fink, S.; Thompson, M.; Walker, D. *Savannah River Site Salt Processing Project: FY 2002 Research and Development Program Plan*; PNNL-13707, Rev. 1; Pacific Northwest National Laboratory, Richland, WA, December 2001. (c) *Design, Construction, and Commissioning of a Salt Waste Processing Facility*, Request for Proposal No. DE-RP09-02SR22210, Amendment 002, U. S. Department of Energy, Savannah River Operations Office, Aiken, South Carolina, January 9, 2002.
  5. Dozol, J. F.; Simon, N.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; De Marc, D.; Macias, R. M. A solution for cesium removal from high-salinity acidic or alkaline liquid waste: The crown calix 4 arenes. *Sep. Sci. Technol.* **1999**, *34*, 877-909. Lamare, V.; Bressot, C.; Dozol, J. F.; Vicens, J.; Asfari, Z.; Ungaro, R.; Casnati, A. Selective extraction of cesium at tracer level concentration from a sodium nitrate solution with calix-crowns. Molecular modeling study of the Cs<sup>+</sup>/Na<sup>+</sup> selectivity. *Sep. Sci. Technol.* **1997**, *32*, 175-191. Hill, C.; Dozol, J. F.; Lamare, V.; Rouquette, H.; Eymard, S.; Tournois, B.; Vicens, J.; Asfari, Z.; Bressot, C.; Ungaro, R.; Casnati, A. Nuclear Waste Treatment by Means of Supported Liquid Membranes Containing Calix-Crown Compounds. *J. Incl. Phenom. Mol. Recogn. Chem.* **1994**, *19*, 399-408.
  6. (a) Thuery, P.; Nierlich, M.; Lamare, E.; Dozol, J. F.; Asfari, Z.; Vicens, J. Bis(crown ether) and azobenzocrown derivatives of calix 4 arene. A review of structural information from crystallographic and modelling studies. *J. Incl. Phenom. Macrocycl. Chem.* **2000**, *36*, 375-408. (b) Thuery, P.; Nierlich, M.; Bryan, J. C.; Lamare, V.; Dozol, J. F.; Asfari, Z.; Vicens, J. Crown ether conformations in 1,3-calix 4 arene bis(crown ethers): crystal structures of a caesium complex and solvent adducts and molecular dynamics simulations. *J. Chem. Soc.-Dalton Trans.* **1997**, 4191-4202.
  7. Moyer, B. A.; Alexandratos, S. D.; Chiarizia, R.; Dietz, M. L.; Hay, B. P.; Sachleben, R. A. "Design and Synthesis of the Next Generation of Crown Ethers for Waste Separations: An Inter-Laboratory Comprehensive Proposal," Final Report, Environmental Management Science Program Project 55087, Oak Ridge National Laboratory, Oak Ridge, TN, July 2000; posted on the WWW site of the USDOE Environmental Management Science Program.
  8. Haverlock, T. J.; Bonnesen, P. V.; Sachleben, R. A.; Moyer, B. A. Analysis of Equilibria in the Extraction of Cesium Nitrate by Calix[4]arene-bis(t-octylbenzo-crown-6) in 1,2-Dichloroethane. *J. Inclusion Phenom. Mol. Recognit. Chem.* **2000**, *36*, 21-37.
  9. Delmau, L. H.; Bonnesen, P. V.; Moyer, B. A. A Solution to Stripping Problems Caused by Organophilic Anion Impurities in Crown-Ether Based Solvent Extraction Systems: A Case Study of Cesium Removal from Radioactive Wastes. *Hydrometallurgy* **2004**, *72* (1,2), 9–19. Delmau, L. H.; Van Berkel, G. J.; Bonnesen, P. V.; Moyer, B. A. *Improved Performance of the Alkaline-Side CSEX Process for Cesium Extraction from Alkaline High-Level Waste Obtained by Characterization of the Effect of Surfactant Impurities*; ORNL/TM-1999/209;

- Oak Ridge National Laboratory, Oak Ridge, TN, October 1999. Bonnesen, P. V.; Delmau, L. H.; Haverlock, T. J.; Moyer, B. A. *Alkaline-Side Extraction of Cesium from Savannah River Tank Waste Using Calixarene-Crown Ether Extractant*; ORNL/TM-13704; Oak Ridge National Laboratory: Oak Ridge, TN, 1998.
10. Bonnesen, P. V.; Delmau, L. H.; Moyer, B. A.; Lumetta, G. J. Development of Effective Solvent Modifiers for the Solvent Extraction of Cesium from Alkaline High-Level Tank Waste. *Solvent Extr. Ion Exch.* **2003**, *21*(1), 141–17. Bonnesen, P. V.; Delmau, L. H.; Moyer, B. A.; Leonard, R. A. A Robust Alkaline-Side CSEX Solvent Suitable for Removing Cesium from Savannah River High Level Waste, *Solvent Extr. Ion Exch.* **2000**, *18*(6), 1079–1107.
  11. Leonard, R. A.; Aase, S. B.; Arafat, H. A.; Conner, C.; Chamberlain, D. B.; Falkenberg, J. R.; Regalbuto, M. C.; Vandegrift, G. F., Experimental verification of caustic-side solvent extraction for removal of cesium from tank waste. *Solvent Extr. Ion Exch.* **2003**, *21* (4), 505–526. Leonard, R. A., Aase, S. B., Arafat, H. A., Chamberlain, D. B., Conner, C., Regalbuto, M. C., Vandegrift, G. F., 2002. Multi-day Test of the Caustic-Side Solvent Extraction Flowsheet for Cesium Removal from a Simulated SRS Tank Waste, Report ANL-02/11, Argonne National Laboratory, Argonne, IL, Jan. 15, 2002.
  12. Norato, M. A.; Campbell, S. G.; Crowder, M. L.; Geeting, M. W.; Kessinger, G. F.; Pierce, R. A.; Walker, D. D. *High-Level Waste Demonstration of the Caustic-Side Solvent Extraction Process with Optimized Solvent in the 2-cm Centrifugal Contactor Apparatus Using Tank 37H/44F Supernate*; WSRC-TR-2002-00243, Rev. 0; Westinghouse Savannah River Company, Aiken, South Carolina, November 1, 2002. Norato, M. A.; Fink, S. D.; Fondeur, F. F.; Kessinger, G. F.; Pierce, R. A.; Walker D. D. *Demonstration of Caustic-Side Solvent Extraction with Optimized Solvent in the 2-cm Centrifugal Contactor Apparatus Using Dissolved Salt Cake from Tank 37H*; WSRC-TR-2002-00307; Westinghouse Savannah River Company, Aiken, South Carolina, September 3, 2002. Campbell, S. G.; Geeting, M. W.; Kennell, C. W.; Law, J. D.; Leonard, R. A.; Norato, M. A.; Pierce, R. A.; Todd, T. A.; Walker, D. D.; Wilmarth, W. R. *Demonstration of Caustic-Side Solvent Extraction with Savannah River Site-High-Level Waste*; WSRC-TR-2001-00223, Rev. 0; Westinghouse Savannah River Company, Aiken, SC, April 19, 2001.
  13. Engle, N. L.; P. V. Bonnesen, ; B. A. Tomkins, ; L. H. Delmau, ; Moyer, B. A. “Synthesis and Properties of Calix[4]arene-bis-[4-2-ethylhexyl]benzo-crown-6]: A Cesium Extractant with Improved Solubility,” (*Solvent Extr. Ion Exch.*, in press)
  14. Gorbunova, M. G.; Bonnesen, P. V.; Engle, N. L.; Bazelaire, E.; Delmau, L. H.; Moyer, B. A. New amino-functionalized 1,3-alternate calix[4]arene bis- and mono-(benzo-crown-6 ethers) for pH-switched cesium nitrate extraction. *Tetrahedron Lett.* **2003**, *44* (29), 5397–5401.
  15. Bazelaire, E.; Gorbunova, M. G.; Bonnesen, P. V.; Moyer, B. A., and Delmau, L. H. pH-switchable Cesium Nitrate Extraction with Calix[4]arene Mono- and Bis(benzocrown-6) Ethers Bearing Amino Functionalities, *Solvent Extr. Ion Exch.*, in press.

## 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>.

Research sponsored by the Environmental Management Science Program, Offices of Science and Environmental Management, U. S. Department of Energy, under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

#### 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.

Bazelaire, E.; Gorbunova, M. G.; Bonnesen, P. V.; Moyer, B. A., and Delmau, L. H. pH-switchable Cesium Nitrate Extraction with Calix[4]arene Mono- and Bis(benzocrown-6) Ethers Bearing Amino Functionalities, *Solvent Extr. Ion Exch.*, in press.

Engle, N. L.; Bonnesen, P. V.; Tomkins, B. A.; Haverlock, T. J.; Moyer, B. A. Synthesis and Properties of Calix[4]arene-Bis[4-(2-Ethylhexyl)Benzo-Crown-6], A Cesium Extractant with Improved Solubility. *Solvent Extr. Ion Exch.*, in press.

Huang, F.; Guzei, I. A.; Jones, J. W.; Gibson, H. W. Improvement of Complexation of a Bisparaquat by Formation of a Pseudocryptand-Based [3]Pseudorotaxane. *Angew. Chem., Int. Ed.*, submitted.

Jones, J. W.; Berg, M. A. G.; Huang, F.; Wang, H.; Habernicht, B. F.; Gibson, H. W. Solvent Effects and Host-Guest Complexation in Low Dielectric Constant Media for Systems Involving Charged Species. *Acc. Chem. Res.*, to be submitted.

Jones, J. W.; Huang, F.; Gibson, H. W. Iminium Ion Formation from the Condensation of Acetone and Secondary Ammonium Salts. *Tetrahedron*, to be submitted.

Jones, J. W.; Huang, F.; Gibson, H. W. Activity Coefficients and Ionic Strength Effects on Host-Guest Complexation in Low Dielectric Constant Solvents. *J. Am. Chem. Soc.*, submitted Sept. 2, 2003.

Gibson, H. W.; Yamaguchi, N.; Jones, J. W. Supramolecular pseudorotaxane polymers from complementary pairs of homoditopic molecules. *J. Am. Chem. Soc.* **2003**, *125* (12), 3522-3533.

Gorbunova, M. G.; Bonnesen, P. V.; Engle, N. L.; Bazelaire, E.; Delmau, L. H.; Moyer, B. A. New amino-functionalized 1,3-alternate calix[4]arene bis- and mono-(benzo-crown-6 ethers) for pH-switched cesium nitrate extraction. *Tetrahedron Lett.* **2003**, 44 (29), 5397-5401.

Huang, F. H.; Jones, J. W.; Slebodnick, C.; Gibson, H. W. Ion pairing in fast-exchange host-guest systems: Concentration dependence of apparent association constants for complexes of neutral hosts and divalent guest salts with monovalent counterions. *J. Am. Chem. Soc.* **2003**, 125 (47), 14458-14464.

Huang, F. H.; Zakharov, L. N.; Rheingold, A. L.; Jones, J. W.; Gibson, H. W. Water assisted formation of a pseudorotaxane and its dimer based on a supramolecular cryptand. *Chem. Commun.* **2003**, (17), 2122-2123.

Jones, J. W.; Bryant, W. S.; Bosman, A. W.; Janssen, R. A. J.; Meijer, E. W.; Gibson, H. W. Crowned dendrimers: pH-responsive pseudorotaxane formation. *J. Org. Chem.* **2003**, 68 (6), 2385-2389.

Jones, J. W.; Gibson, H. W. Ion pairing and host-guest complexation in low dielectric constant solvents. *J. Am. Chem. Soc.* **2003**, 125 (23), 7001-7004.

Sachleben, R. A.; Bryan, J. C.; Engle, N. L.; Haverlock, T. J.; Hay, B. P.; Urvoas, A.; Moyer, B. A. Rational Design of Cesium-Selective Ionophores: Dihydrocalix[4]arene Crown-6 Ethers, *European J. Org. Chem.* **2003**, 4862-4869. Joint sponsorship with the Office of Basic Energy Sciences.

Bonnesen, P. V.; Delmau, L. H.; Haverlock, T. J.; Levitskaia, T. G.; Sachleben, R. A.; F. V. Sloop, Jr.; Moyer, B. A. *Science to Applications: Development of the Caustic-Side Solvent Extraction Process for Cesium Removal from Savannah River Waste*, Proc. 9th Biennial Internat. Conf. Nuclear and Hazardous Waste Management (Spectrum 2002), Reno, Nevada, Aug. 4-8, 2002.

Bryan, J. C.; Engle, N. L.; Sachleben, R. A., Syntheses and structures of dihydrocalix 4 arenes bearing O-benzonitrile and O-acetyl substituents. *J. Chem. Crystallogr.* **2002**, 32 (1-2), 33-38.

Gibson, H. W.; Yamaguchi, N.; Hamilton, L.; Jones, J. W. Cooperative self-assembly of dendrimers via pseudorotaxane formation from a homotritopic guest molecule and complementary monotopic host dendrons. *J. Am. Chem. Soc.* **2002**, 124 (17), 4653-4665.

Jones, J. W.; Zakharov, L. N.; Rheingold, A. L.; Gibson, H. W. Cooperative host/guest interactions via counterion assisted chelation: Pseudorotaxanes from supramolecular cryptands. *J. Am. Chem. Soc.* **2002**, 124 (45), 13378-13379.

Bryan, J. C.; Sachleben, R. A. Crystal structure of 26,28-bis(2-propenyloxy)calix[4]arene, C<sub>34</sub>H<sub>32</sub>O<sub>4</sub>. *Z. Krist.-New Cryst. Struct.* **2001**, 216 (4), 623-625.

Bryan, J. C.; Sachleben, R. A.; Urvoas, A. 5,17-Di-*tert*-butyl-25,27-dihydroxycalix[4]arene. *Acta Crystallogr. Sect. E.-Struct. Rep. Online* **2001**, 57, O781-O782.

Ji, H.-F.; Dabestani, R. T.; Brown, G. M.; Sachleben, R. A. A New Highly Selective Calix[4]Crown-6 Fluorescent Cesium Probe. *Chem. Commun.* **2000**, 833-834.

### Miscellaneous Reports and Summaries

Moyer, B. A.; Bazelaire, E.; Bonnesen, P. V.; Bryan, J. C.; Delmau, L. H.; Engle, N. L.; Gorbunova, M. G.; Keever, T. J.; Levitskaia, T. G.; Sachleben, R. A.; Tomkins, B. A.; Bartsch, R. A.; Talanov, V. S.; Gibson, H. W.; Jones, J. W.; Hay, B. P. *Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation*; Environmental Management Science Program FY 2003 Annual Report; Oak Ridge National Laboratory: Oak Ridge, TN, September, 2003; available on the World Wide Web site of the USDOE Office of Environmental Management, URL <http://emsp.em.doe.gov/>.

Moyer, B. A.; Bonnesen, P. V.; Bryan, J. C.; Engle, N. L.; Keever, T. J.; Levitskaia, T. G.; Sachleben, R. A.; Bartsch, R. A.; Talanov, V. S.; Gibson, H. W.; Jones, J. W.; Hay, B. P. *Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation*; Environmental Management Science Program FY 2002 Annual Report; Oak Ridge National Laboratory: Oak Ridge, TN, Aug., 2002; posted on the EMSP web site <http://emsp.em.doe.gov/> .

Moyer, B. A.; Bonnesen, P. V.; Bryan, J. C.; Engle, N. L.; Levitskaia, T. G.; Sachleben, R. A.; Bartsch, R. A.; Talanov, V. S.; Gibson, H. W.; Jones, J. W. *Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation*; Environmental Management Science Program FY 2001 Annual Report; Oak Ridge National Laboratory: Oak Ridge, TN, Aug., 2001; posted on the EMSP web site <http://emsp.em.doe.gov/> .

## Presentations

Delmau, L. H.; Bazelaire, E.; Bonnesen, P. V.; Gorbunova, M. G.; Moyer, B. A. Functionalization of Calix[4]arene-crown-6 with Amino Groups: Toward Improvement of Cesium Stripping. Thirteenth Symposium on Separation Science & Technology for Energy Applications, Gatlinburg, TN, October 27–30, 2003.

Gorbunova, M. G.; Engle, N. L.; Bazelaire, E.; Tomkins, B. A.; Haverlock, T. J.; Delmau, L. H.; Bonnesen, P. V.; Moyer, B. A. Synthesis of New Calixcrown Extractants for Cesium Separation from High-Level Waste. Thirteenth Symposium on Separation Science & Technology for Energy Applications, Gatlinburg, TN, October 27–30, 2003.

Moyer, B. A.; Bonnesen, P. V.; Delmau, L. H.; Keever, T. J.; Sloop, F. V., Jr. Binding, Transport, and Separation of Radionuclides (Research Accomplishments Applicable to Decontamination, Radionuclide Decontamination Science & Technology Workshop, Los Alamos, NM, Sept. 16-17, 2003.

Gibson, H. W.; Ge, Z. X.; Huang, F. H.; Jones, J. W.; Wang, H.; Farcas, U., Mechanically interlocked macromolecular systems via pseudorotaxane self-assembly. American Chemical Society National Meeting, New York, NY, September 7-11, 2003.

Gorbunova, M. G., Bonnesen, P. V.; Engle, N. L.; Bazelaire, E.; Delmau, L. H.; Moyer, B. A. "New Amino-functionalized 1,3-alternate Calix[4]arene bis- and mono-(benzo-crown-6-ethers)," American Chemical Society National Meeting, New York, NY, September 7-11, 2003.

Bonnesen, P. V., Engle, N. L.; Gorbunova, M. G.; Haverlock, T. J.; Tomkins, B. A.; Bazelaire, E.; Delmau, L. H.; Moyer, B. A. "Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation," American Chemical Society National Meeting, New York, NY, September 7-11, 2003 (Invited).

Bonnesen, P. V.; Gorbunova, M. G.; Engle, N. L.; Bazelaire, E.; Tomkins, B. A.; Haverlock, T. J.; Delmau, L. H.; Moyer, B. A. "New Calix-Crown Extractants for Cesium Separation from High-Level Waste," 7<sup>th</sup> International Conference on Calixarenes (Calix2003), University of British Columbia, Vancouver, BC, Canada, August 13-16, 2003.

Huang, F. H.; Zakharov, L. N.; Rheingold, A. L.; Gibson, H. W.; Jones, J. W., Formation of a complex dimer assisted by water. 225<sup>th</sup> American Chemical Society National Meeting, New Orleans, LA, March 23-27, 2003.

Huang, F. H.; Zakharov, L. N.; Rheingold, A. L.; Gibson, H. W.; Jones, J. W., Cryptands: Powerful hosts for paraquat derivatives. 225<sup>th</sup> American Chemical Society National Meeting, New Orleans, LA, March 23-27, 2003.

Jones, J. W.; Huang, F. H.; Gibson, H. W.; Zakharov, L. N.; Rheingold, A. L., Cooperative host/guest interactions via counterion assisted chelation: Pseudorotaxanes from supramolecular cryptands. 225<sup>th</sup> American Chemical Society National Meeting, New Orleans, LA, March 23-27, 2003.

Gibson, H. W.; Ge, Z. X.; Jones, J. W.; Farcas, A., Self-assembly with macromolecular building blocks. 225<sup>th</sup> American Chemical Society National Meeting, New Orleans, LA, March 23-27, 2003.

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, K. Kavallieratos, T. G. Levitskaia, and F. V. Sloop, Jr., "Fundamental Principles and Applications of Host-Guest Chemistry in Liquid-Liquid Separation Systems," Technical University of Dresden, Dresden, Germany, Nov. 11, 2002 (Invited).

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, K. Kavallieratos, T. G. Levitskaia, and F. V. Sloop, Jr., "Fundamental Principles and Applications of Host-Guest Chemistry in Liquid-Liquid Separation Systems," DEHEMA Symposium "Supramolecular Strategies for Selective Solvent Extraction Processes," Frankfurt am Main, Germany, Nov. 8, 2002 (Invited).

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, K. Kavallieratos, T. G. Levitskaia, and F. V. Sloop, Jr., "Strategies for Accommodating the Anion in the Extraction of Alkali Metal Salts and an Application in Nuclear Waste Cleanup," Royal Society of Chemistry Symposium "Co-ordination Chemistry in Action," Univ. of Edinburgh, Edinburgh, Scotland, United Kingdom, Nov. 6, 2002 (Invited).

P. V. Bonnesen, L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, R. A. Sachleben, and B. A. Moyer, "Development of the Caustic-Side Solvent Extraction Process for Cesium Removal from Savannah River Waste," Spectrum 2002, Reno, Nevada, August 4-8, 2002.

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, K. Kavallieratos, T. G. Levitskaia, and F. V. Sloop, Jr., "Recognition, Binding, and Separation of Ions by Novel Ion Receptors: From Principles to Applications," Chemical Sciences Division Seminar, Oak Ridge National Laboratory, July 23, 2002 (Invited).

P. V. Bonnesen, N. L. Engle, T. J. Haverlock, M. P. Maskarinec, B. A. Moyer, "Recent Progress Towards Synthesizing Calix[4]arene Crown Ethers with Improved Alkane Solubility for Waste Treatment Applications," XXVII International Symposium on Macrocyclic Chemistry, Park City, UT, June 23-27, 2002.

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, R. A. Sachleben, and F. V. Sloop, Jr., "Industrial-Scale Macrocyclic Chemistry: CSSX Process for Cesium Removal from Nuclear Waste Using a Calixcrown," XXVII International Symposium on Macrocyclic Chemistry, Park City, UT, June 23-27, 2002 (Invited).

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, Nancy L. Engle, T. J. Haverlock, K. Kavallieratos, T. G. Levitskaia, R. A. Sachleben, and F. V. Sloop, Jr., "Fundamentals of Ion Recognition in Liquid-Liquid Systems and Their Applications to Nuclear-Waste Cleanup," Dept. of Chemistry Seminar, Univ. of Illinois at Urbana-Champaign, Urbana, IL, May 2, 2002 (Invited).

Ge, Z. X.; Jones, J. W.; Gibson, H. W. Non-covalent block copolymers by self-assembly: New polypseudorotaxanes. 223<sup>rd</sup> American Chemical Society National Meeting, Orlando, FL, Apr. 7-11, 2002.

B. A. Moyer and G. J. Lumetta, "Solvent Extraction Technologies for Mission Acceleration Initiative: NaOH Removal & Tc, Tc Removal," Mission Acceleration Initiative Technology Demonstration Workshop, Pacific Northwest National Laboratory, Richland, WA, Apr. 2-3, 2002 (Invited).

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, Nancy L. Engle, T. J. Haverlock, T. G. Levitskaia, R. A. Sachleben, and F. V. Sloop, Jr., "Ion-Recognition Approaches to the Treatment of Alkaline High-Level Waste by Liquid-Liquid Extraction," Dept. of Chemistry Seminar, Univ. of California, Berkeley, CA, Feb. 1, 2002 (Invited).

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, R. A. Sachleben, and F. V. Sloop, Jr., "The CSSX Process for Cesium Separation from HLW: Resurrection in the Valley of Death," EMSP High-Level Waste Workshop, Richland Washington, Nov. 7-9, 2001 (Invited).

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, L.N. Klatt, T. G. Levitskaia, R. A. Sachleben, F. V. Sloop, Jr., and R. D. Spence, "Caustic-Side Solvent Extraction Solvent Chemistry," Overview of basic research and applied development for posting on the Savannah River Site Salt Processing web site, Oct. 2001.

T. G. Levitskaia, V. S. Talanov, R. A. Bartsch, and B. A. Moyer, "New Strategy for Selective Cesium Solvent Extraction: Combination of Ion Recognition and Ion Exchange in a Single Calix[4]arene-Biscrown-6 Host," Twelfth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, Oct. 15-18, 2001.

B. A. Moyer, P. V. Bonnesen, G. M. Brown, J. C. Bryan, L. H. Delmau, T. J. Haverlock, T. G. Levitskaia, and F. J. Sloop, "Liquid-Liquid Extraction Approaches to the Treatment of Alkaline High-Level Waste," ACS National Meeting, Chicago, IL, Aug. 26-30, 2001 (Invited keynote lecture).

B. A. Moyer, P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, K. Kavallieratos, T. G. Levitskaia, R. A. Sachleben, and F. V. Sloop, Jr., "Fundamental Challenges in Taking Calix-crowns from Host-Guest Principles Through Full-Scale Plant Design for Decontaminating Nuclear Waste," Gordon Research Conference on Inorganic Chemistry, Newport, RI, July 15-20, 2001 (Invited).

B. A. Moyer, "Caustic-Side Solvent Extraction: Solvent Chemistry," Crown Ethers Workshop, Aiken, SC, Aug. 6,7, 2001.

B. A. Moyer, "Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation," Tanks Focus Area Mid-Year Review, Mar. 14, 2001.

Gibson, H. W.; Bosman, A. W.; Bryant, W. S.; Jones, J. W.; Janssen, R. A. J.; Meijer, E. W., Cooperative complexation of dendritic hosts. 221<sup>st</sup> Meeting of the American Chemical Society, San Diego, CA, Apr. 1-5, 2001.

P. V. Bonnesen, J. C. Bryan, L. H. Delmau, T. J. Haverlock, R. A. Sachleben, and B. A. Moyer, "From the Laboratory to the Tank Farm: Fundamental and Applied Issues in the Use of Calixarene-Crown Ethers in the Cleanup of U.S. DOE Nuclear Wastes," Symposium on Supramolecular Chemistry in Biology, Medicine, and the Environment, 52nd Southeast-56th Southwest Combined ACS Regional Meeting, New Orleans, LA, Dec. 8, 2000.