

## Applied and Fundamental Research: Their Mutual Stimulation in the Real World of Chemistry – Developing Calixbiscrowns for Nuclear Waste Treatment

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### Abstract

This commentary describes the development of calixbiscrowns for nuclear waste treatment. The development has been world wide with the involvement of scientists and governments.

In a stimulating 1990 article assessing the state of organic chemistry and where its future directions might lie, Seebach [1] stated that “The primary motivations that once induced chemists to undertake natural products syntheses no longer exist. Instead of target structures themselves, molecular function and activity now occupy centre stage.” He further noted that the inexorable evolution of chemistry reflected in such a perception had involved the blurring of distinctions between not only long-recognised subdivisions of chemistry but between chemistry and many other areas of Science. One expression of these changes has been the rise of supramolecular chemistry [2]. Supramolecular chemistry, based on the use of labile interactions to control the assembly of kinetically inert molecular species into functional superstructures, has been associated with a new vocabulary of terms such as host–guest chemistry, molecular and ionic recognition, supramolecular catalysis, self organization, self assembly and many others. Particularly important as the building blocks of supramolecular systems has been a variety of molecules with macrocyclic structures, the most important of these being the crown ethers [3], the cryptands [4], the spherands [5], the cyclophanes [6], the calixarenes [7] and the natural cyclodextrins [8]. We consider here an example from the field of calixarene chemistry illustrating the passage of the study of a “supermolecule” from synthesis to significant applications.

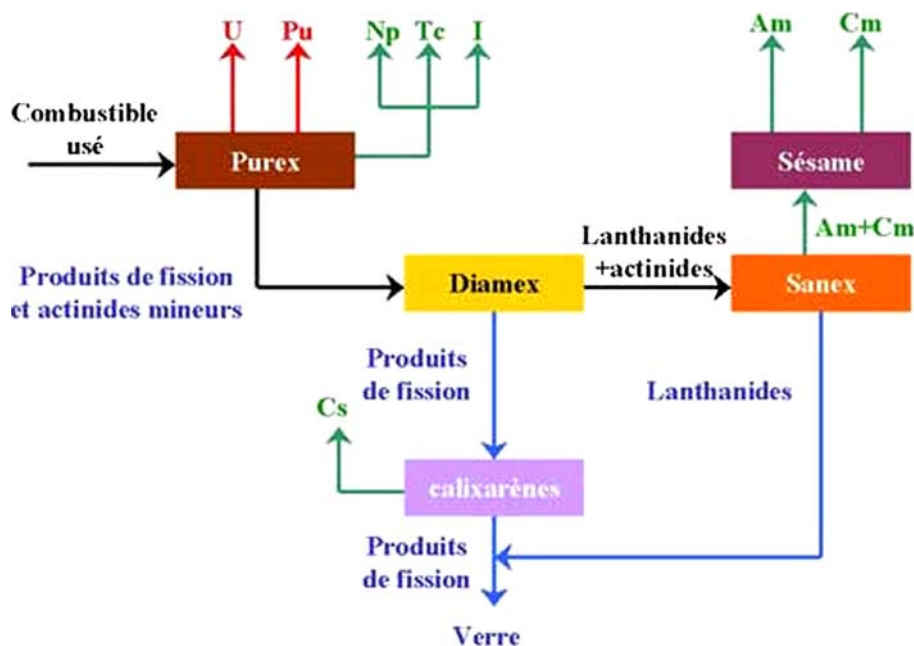
In the cases where a fundamental discovery finds a true industrial application, one or two decades of development are commonly required. From the field of supramolecular chemistry, a striking illustration of this is provided in the now established use of calixarenes, in particular calix[4]biscrowns, molecules which are in fact a hybrid of two types of macrocycle, in the treatment of

nuclear waste. Such waste treatment is of course of enormous significance for a future in which energy sources must become increasingly limited and must necessarily be used with great concern for both efficiency and safety.

Nuclear waste management schemes differ from country to country, but the practical approach adopted in most is to dispose of wastes in environmentally acceptable ways that minimise the volume of both low- and high-activity materials. To most effectively use the storage space available, chemists and engineers have been working on various methods to segregate wastes of differing activity with maximum efficiency. The idea is to reduce in particular the volume of high-activity wastes, which must be stored with the utmost security and to provide low-activity wastes, which can be consigned to cheaper above-ground storage facilities. To avoid storage, an attractive possibility is the isolation of a given radionuclide in a form sufficiently pure to allow its transmutation to a non-radioactive species. This is a possibility, which can be realised in the case of caesium ( $^{135}\text{Cs}$ ,  $^{137}\text{Cs}$ ) through the use of calixcrowns.

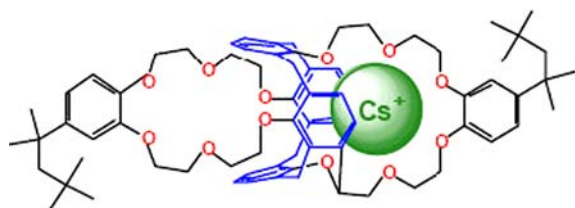
In a recent article entitled: “*Use of macrocycles in nuclear-waste cleanup: a real world application of a calixcrown in caesium separation technology*”, Moyer and coll [9] describe one of the United States’ Government projects [10], conducted in part at Oak Ridge National Laboratory, to develop reagents for caesium binding and extraction with regards to possible use in waste cleanup. The process developed, termed the Caustic-Side Solvent Extraction (CSSX) process for the separation of caesium, was specifically directed towards the treatment of accumulated high-level wastes stored in underground tanks at U.S. Department of Energy (USDOE) sites. They describe the overall technology itself, both in terms of the underlying chemistry and the engineering that makes the

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Scheme 1. French decontamination process PUREX [19].

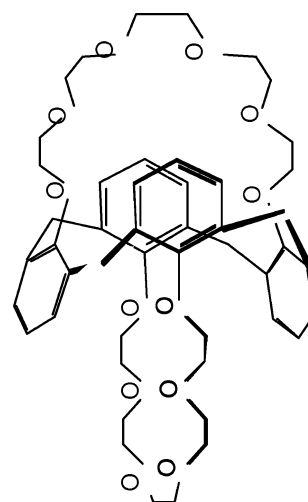
use of CSSX practical. This powerful technology, based on a macrocyclic cation receptor appropriately functionalised so as to be sufficiently lipophilic to function as extractants, came to maturation after 10 years research. World wide, governments are increasingly aware of the complexity of the energy supply problem for the future and their commitment to understanding all aspects of the use of nuclear energy has provided an enormous impetus to such work. The caesium-selective extractant used in the CSSX process is calix[4]arene-*bis*(*t*-octyl-benzo-crown-6) (**BOBcalixC6**) [11, 12]. In such a molecule, the calixarene serves as an inherently lipophilic, relatively rigid framework to which polyether rings of a size suitable for  $\text{Cs}^+$  binding can be attached. Since polyether chains tend to induce water-solubility, functionalisation with the octylbenzo groups is necessary to regain lipophilicity, though it has other subtle effects in enhancing Cs/Na selectivity, a factor, which is also influenced by interactions of the cation with the calixarene phenyl rings. Thus, the final molecular structure reflects the lessons drawn from a wide variety of fundamental studies of the factors influencing both the binding and extraction of metal ions by calixcrowns. The importance of such studies [13] was explicitly recognised by Moyer *et al.* as “lending a great confidence in CSSX from this perspective”.



BOBcalixC6.Cs<sup>+</sup> complex [12]

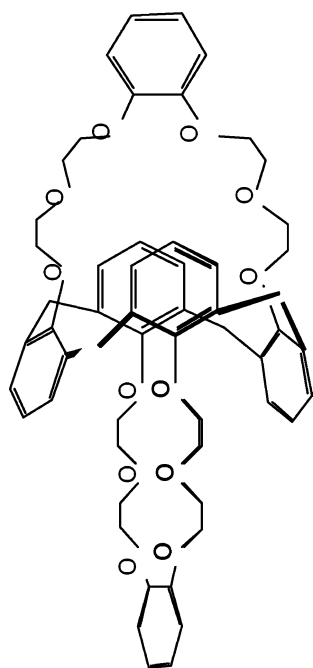
Scheme 2. BOBcalixC6.Cs<sup>+</sup> complex [12].

In France, under the «Loi Bataille», brought into force on the 30th of December 1991 by a vote of the French Parliament, the Commissariat à l’Energie Atomique (CEA) deposited, on the 6th of November 1992, a French Patent entitled: “*Calix[4]arènes-bis-couronnes, leur procédé de préparation et leur utilisation pour l’extraction sélective du césium et des actinides*” [14] which became applicable in the USA [15] on the 11th of October 1994. The French Patent (issued from the PhD work of Hill [16]) gave rise to an oral communication at *MacroAkron’94, 35th IUPAC International Symposium on Macromolecules* the same year, a review article [17] and a full paper 1 year later [18] in which Vicens, Dozol *and coll.* reported the synthesis of seven 1,3-calix[4]bis-crowns **BCs**<sup>7</sup> and their use as selective carriers of caesium through supported liquid membranes (SLM’s).



BC6

Scheme 3. BC6.



**BC6B**

Scheme 4. BC6B.

The application of the Danesi diffusional model allowed the transport isotherms of trace level  $^{137}\text{Cs}$  through SLMs (Supported Liquid Membranes) containing calix[4]biscrowns to be determined as a function of the ionic concentration of the aqueous feed solutions. Compounds **BC6** and **BC6B** appeared to be much more efficient than mixtures of crown ethers and acidic exchangers, especially in very acidic media.

Decontamination factors greater than 20 were obtained in the treatment of synthetic acidic radioactive wastes. Permeability coefficient measurements were conducted for repetitive transport experiments in order to qualify the SLMs' stability with time. Very good results (stable for more than 50 d) and high decontamination yields were observed with **BC6** and **BC6B**. For example, **BC6** and **BC6B** allowed selective removal of  $^{137}\text{Cs}$  from sodium containing solutions. A  $\text{Cs}^+/\text{Na}^+$  selectivity (needed in the French process in highly acidic conditions) of  $\sim 20,000$  was observed. Less than 100 mg of the  $\sim 100$  g of sodium (initially present in the feed solution) was transported in 24 h by **BC6B**, whereas more than 95% of trace level  $^{137}\text{Cs}$  was concentrated in the stripping solution. On the basis of the syntheses of selected receptors adapted to the technology and the evaluation of thermodynamic parameters for complexation and extraction, a module termed CALIXARENES was developed for incorporation into the French PUREX decontamination process (see Scheme 1 [19]). This established a model of broad utility to all members of the nuclear waste management community.

Both of the decontamination schemes described above can be seen as specific applications of some of the fundamental concepts of supramolecular chemistry and can in this sense be traced back to the seminal work of

Pedersen in 1967 [3a], ultimately recognised in the award of the 1987 Nobel Prize, on the macrocycles known as "crown ethers". Pedersen's work, performed in an industrial environment with particular applications in mind, was developed, refined and extended in academic laboratories, most notably those of his co-recipients of the Nobel Prize, to provide a vast number of new molecules, which in turn have found various applications in addition to nuclear waste treatment. The application in waste treatment, however, provides an outstanding example of the efficacy that is possible in collaborations between industry and research institutions both within and outside universities, the handling of high-level radioactive materials for testing being, of course, something that cannot take place within public universities. The assertion by Moyer [9] that "*this article is intended to serve as an example of how macrocyclic chemistry can be adapted for an industrial purpose use to meet the demanding requirements of real-world-systems*" is an affirmation of the value of such collaborations.

A congruent view is found in the words of Daustray and Saas in a popular scientific article [20] published in the Encyclopedia Universalis 2005 entitled: "*Stockage des déchets radioactifs*". The authors mention the 'real-world exploitation' and the active work devoted to the decontamination process in several countries. «*En particulier, pour l'extraction des produits de fission, l'effort porte actuellement sur l'utilisation des macrocycles, par exemple du type éther couronnes ou calixarènes; ces molécules cages peuvent être des extractants très spécifiques avec de forts taux de récupération; certaines d'entre elles pourront donc s'appliquer à l'extraction du césium, du strontium, voire des lanthanides et des actinides. Le coût élevé actuel de ces extractants conduit à les utiliser en association avec des technologies d'extraction fondées sur l'utilisation de systèmes membranaires (membranes liquides, membranes greffées, etc.). Les recherches sont très actives aux Etats-Unis, au Japon et en Europe*».

The communication of Vicens, Dozol *and coll.* [18] sparked continuing research devoted to the task of finding ever more efficient and discriminating systems for waste treatment. This has ranged from fundamental studies such as the use of XAFS and computational simulations to better characterise the nature of caesium-bis(crown)calixarene complexes in solution [21] to practical efforts to modify the properties of known extractants by introducing charge-carrying substituents to the molecules [22]. A continuing series of international conferences has always involved extended discussions of the applications of new calixarenes in selective complexation and extraction processes. Very recently, interest has become focussed on "nanomaterials" for use in caesium recovery. For example, novel mesoporous organosilicas containing size-selective micropores from covalently bound calixcrowns have been synthesized. Experiments on the extraction of caesium ions from water in the presence of high concentrations of sodium ions by the insoluble calixcrown-containing mesoporous organosilicas showed good uptake and high

caesium selectivity by these novel materials. Simple filtration removes the material containing the extracted caesium ions [23]. Further, Bu *et al.* [24] have reported the synthesis from calixbiscrowns of calixdendrimers considered to be potentially caesium selective complexants and absorbents.

In conclusion, it is worth reiterating that what might be regarded very much as an applied research problem (although there is a gap, often called “the death valley”, between fundamental and applied research), the treatment of nuclear wastes, has been a major stimulus for a wide range of fundamental research activities, some of which have in turn found significant applications and others of which have been important in reorienting a conceptual understanding of molecular science and which thus can be seen as having long-term influences. A wide range of analytical sensors have been based on calixarenes and have present application, while various functionalised calixarenes have been shown to have properties possibly exploitable in the “molecular machines” of the future [25]. The involvement of governments and their national research institutes, motivated by concerns for broad social imperatives in which science and technology play fundamental roles, has been crucial in the flowering of this field.

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