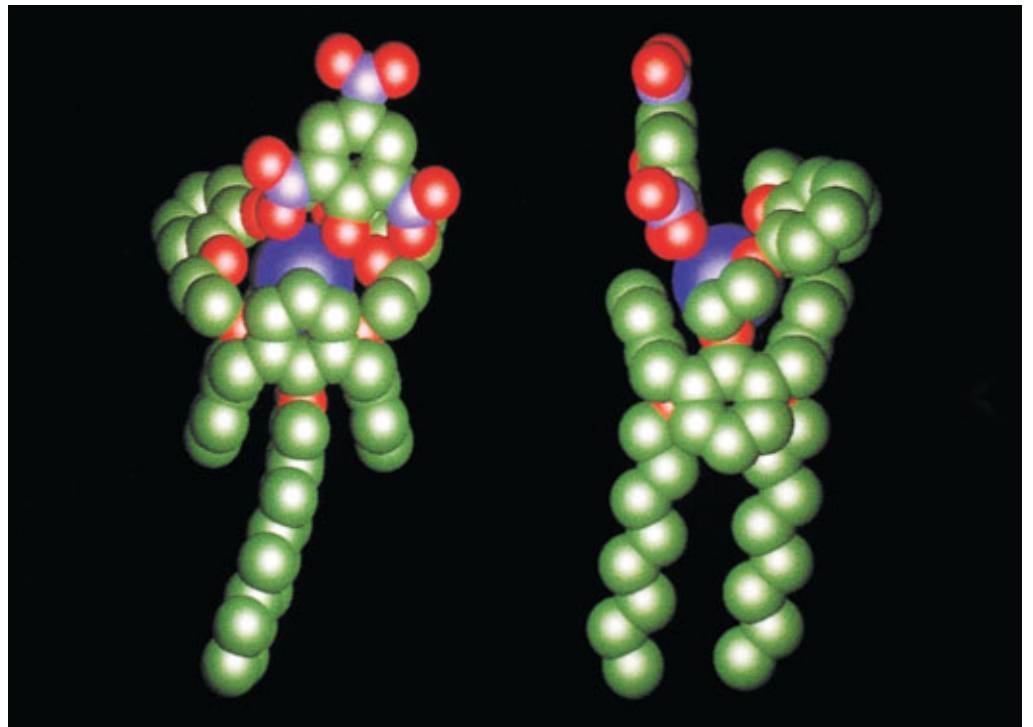


“CROWN MOLECULES” FOR SEPARATING CESIUM

After the minor actinides, the second category of radionuclides that must be isolated to optimize nuclear waste management concerns fission products, especially two cesium isotopes. If the cesium-135 isotope could be extracted, it could subsequently be transmuted or conditioned using a “tailor-made” process. Eliminating the 137 isotope from reprocessing and nuclear facility-dismantling waste would allow to dispose of most of this waste in near-surface facilities, and simply process the small remaining quantity containing long-lived elements. CEA research teams and their international partners have thought up “crown molecules” that could be used to pick out the cesium and meet these objectives.

Calixarene-crown compounds are highly selective, extremely resistant molecules that provide truly effective cesium traps. Shown here are front and side views of a di-octyloxy-calixarene-di-benzo-crown 6 molecule trapping a cesium atom (in dark violet).



CEA

Cesium, a highly mobile fission product

A small quantity of cesium (Cs) is produced in **fission** reactions occurring when uranium-235 is irradiated in a reactor (see box B, **Waste from the nuclear power cycle**). Its 137 **isotope** (^{137}Cs) is highly **radioactive** and has a **half-life** of thirty years. Its 135 isotope (^{135}Cs), on the other hand, is not very radioactive, but has a very long half-life (2.3 million years). It is an element that is potentially very mobile in the environment.

For this reason, the CEA has put a great deal of effort into studying ways to extract Cs from nitric acid solutions resulting from spent nuclear **fuel reprocessing**. This work, carried out at Cadarache, has several aims. The first is to extract ^{135}Cs , which could be done

either immediately before or after extracting the **minor actinides** (**Diamex** process, see *Long-lived radionuclides partitioned at will*), from acid solutions of **fission products**, either for subsequent **transmutation** (see chapter II) or conditioning in specific matrices (see *Tailor-made matrices for long-lived radionuclides*). The second is to eliminate ^{137}Cs from liquid waste coming from the decontamination of dismantled nuclear facilities, or waste to which sodium (NaOH) or potassium (KOH) hydroxides have been added to make **actinides** and all fission products except Cs insoluble. Once rid of this highly radioactive isotope, the residual liquid effluent will have a very low **activity** level and will thus be suitable for near-surface disposal. The small volume of ^{137}Cs extracted will be managed as high-level waste with the other long-lived elements.

Calixarenes, extremely effective cesium traps

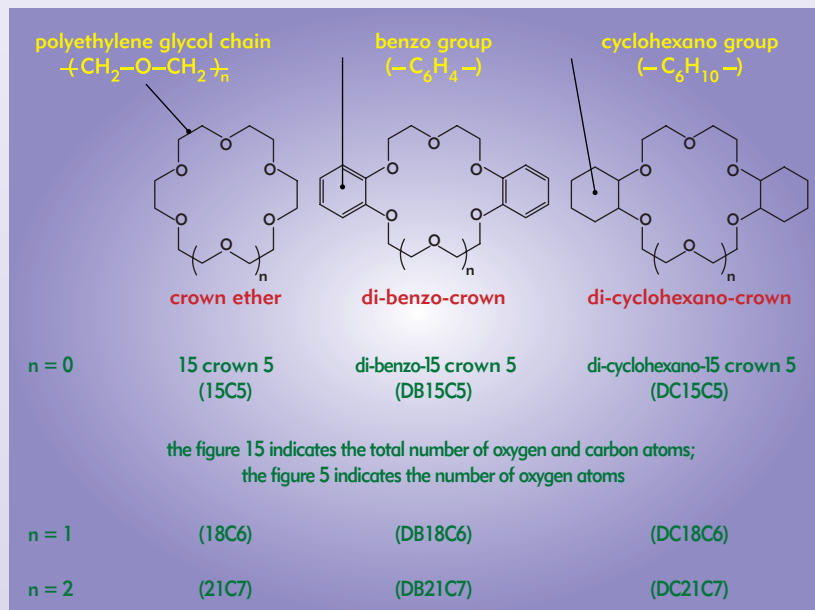
Specific molecules, known as calixarene-crown compounds, have been synthesized at the University of Parma in Italy (by Professor R. Ungaro’s team) and their properties studied at Cadarache for use in extracting cesium. The molecules must be highly selective and extremely resistant to trap the Cs from among countless different chemical species, in particular alkali metals (elements found in the first column of the periodic table), found in highly concentrated nitric acid solutions.

Studies have shown that certain calix[4]arene-crown compounds obtained by grafting one or two polyethylene glycol chains onto a calixarene structure (calixarene-*mono*-crown and *bis*-crown compounds) are highly effective

Crown ethers and calixarene-crown compounds

Crown ethers are macrocyclic compounds containing oxygen atoms O (cyclized polyethylene glycol chain) in their cyclic structure, and are able to accommodate ions with a positive electrical charge (cations) inside their cavity. Their discovery marked a milestone in the field of alkaline chemistry, for they are among the rare complexing agents of these elements. As crown ethers generally tend to dissolve in water, they can only be used in liquid-liquid extraction after reinforcing their hydrophobic property by adding benzo or cyclohexano groups. However, they do not have enough extractant power for them to remove the Cs from a very strong acid solution single-handedly.

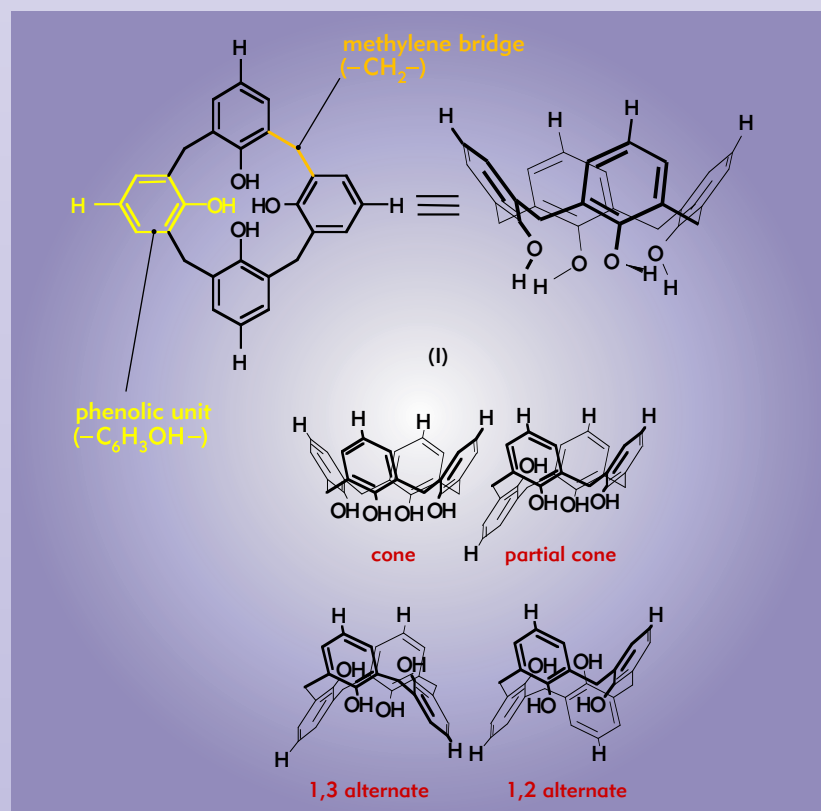
Calix[n]arenes are made up of n phenolic units linked by methylene bridges. The most common calixarenes are calix[4]arenes, calix[6]arenes, and calix[8]arenes, comprising 4, 6, and 8 phenolic units respectively. Owing to the mobility of the phenolic units around the bridging methylene group, calixarenes can assume different conformations in solution. Four have been identified for calix[4]arenes. Starting with the "cone" conformation, the "partial cone" conformation is obtained by reversing one of the phenolic units, while the "1,2 alternate" and "1,3 alter-



nate" conformations are obtained by reversing two adjacent or opposite phenolic units respectively.

Calixarene-*mono*-crown and *bis*-crown compounds are blocked in the 1,3 alternate conformation by binding the phenolic oxygen atoms in the calixarene cavity respectively with one or two polyethylene glycol chains $-(CHOH-CHOH)_n-$. To be effective, they must include six oxy-

gen atoms in the crown (crown 6) and be capable of the 1,3 alternate conformation. This property depends on the organizational structure of the crown, which varies according to the different substitutes that can be grafted. Initial experimental studies have shown that adding benzo groups would considerably improve Cs extraction from an acid aqueous phase, and enhance the selectivity⁽¹⁾ of the extraction process for Cs over Na. Extraction of Na and Cs at identical concentrations demonstrates the effectiveness and outstanding selectivity of calix[4]arenes-crown 6 for Cs over Na. As the selectivity level is more than 30,000 times greater for the most effective compounds, it is hard to determine the quantity of Na extracted. This high extractant power can be explained by the excellent match between the Cs cation and the calixarene crown comprising six oxygen atoms. The average distance between the Cs and the oxygen atoms is in the region of 3.1 angströms⁽²⁾, equivalent to that separating the Cs from the water molecules of its first hydration layer⁽³⁾. In addition, an interaction has been revealed between Cs and the delocalized electrons (π) of the benzenic units making up the calixarene cavity.

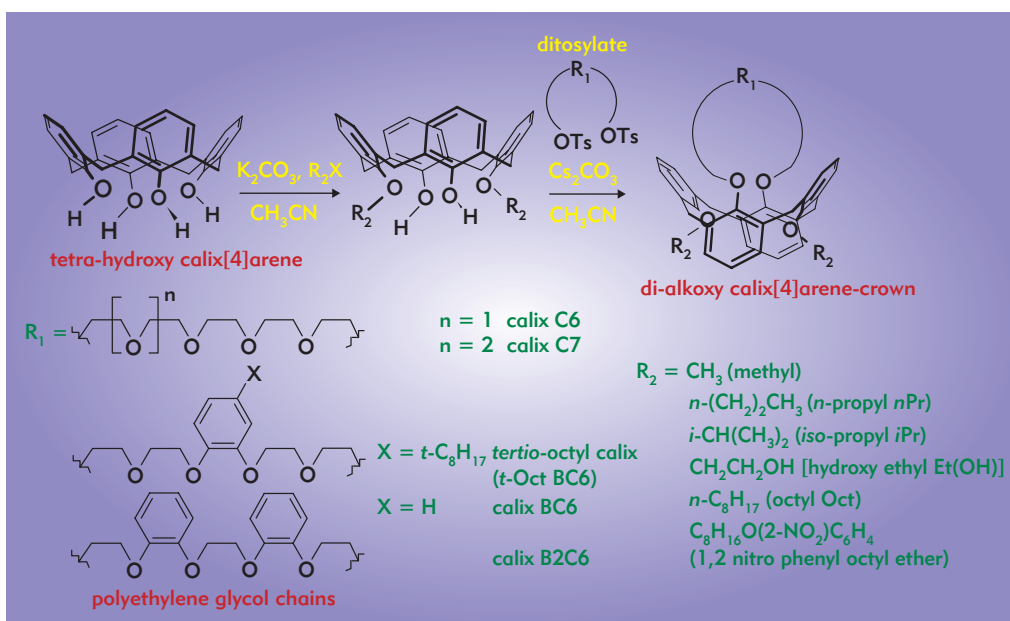


(1) Ratio of the distribution coefficients of the two cations involved.

(2) $1 \text{ \AA} = 10^{-10} \text{ m}$.

(3) Hydration occurs in successive concentric layers, with each layer interacting through hydrogen bonds with those preceding and following it.

Figure 1. Different steps in the synthesis of a di-alkoxy-calixarene-crown compound, and the structures and names of the different di-alkoxy calixarene-crown compounds formed depending on the polyethylene glycol chains added. Di-alkoxy calix[4]arene-crown compounds are synthesized from tetra-hydroxy calix[4]arene. The first step involves replacing two hydrogen atoms by two R_2 carbonated groups (alkylation) in the presence of potassium carbonate (K_2CO_3) in acetonitrile (CH_3CN). During the second step, two phenolic oxygen atoms are bound by ditosylate ($OTs-R_1-OTs$) in the presence of cesium carbonate (Cs_2CO_3) in acetonitrile.



and selective agents for use in separating out all Cs isotopes, found as traces, or even in presence of a very large quantity of sodium Na (4 to 6 mol/L), whatever the medium studied (box). It is difficult to separate Cs and Na because these two alkali ions have very similar chemical properties. A satisfactory degree of selectivity is also observed with respect to the other alkali metals. This is the case for potassium K and, to a lesser degree, rubidium Rb, a fission product whose chemical properties are even closer to those of Cs.

The use of different calixarenes (figure 1) for competitive extraction of Cs in the presence of large quantities of Na is more significant, as it provides an indirect estimation of the performance of the calixarenes in terms of selectivity. As the concentration ratio of the two **cations** is 4×10^6 , only extremely selective extractants are capable of extracting the much rarer cation. Crown ethers (box), tested under the same conditions, presented insufficient distribution coefficients⁽¹⁾ that were far below those of calixarene-crown compounds. The absence of acid does not affect the calixarene selectivity order observed in an acid medium. However, in the 2–12 pH range, distribution coefficients

decrease. This is because the presence of nitric acid intensifies the extraction capability of calixarenes by forming mixed **complexes** between calixarene, Cs, and nitric acid.

Cs extraction curves plotted from a nitric medium (figure 2) show that extraction of this cation increases with the acidity of the medium up to an optimum level reached when Cs extraction enters into competition with acid extraction. Furthermore, the presence of catechol groups $\text{-(C}_6\text{H}_2(\text{OH})_2\text{-)}$ on the crown augments the extraction capabilities of calixarenes, and the maximum extraction level shifts towards higher acidity levels. This phenomenon can be explained by reduced extraction of nitric acid, the approach of the crown oxygen atoms being more difficult.

Calixarene-crown compounds, whose synthesizing processes and applications are patented, can be used to extract Cs directly from fission product solutions remaining from the **Purex** process. The separation process is under development, and tests are being

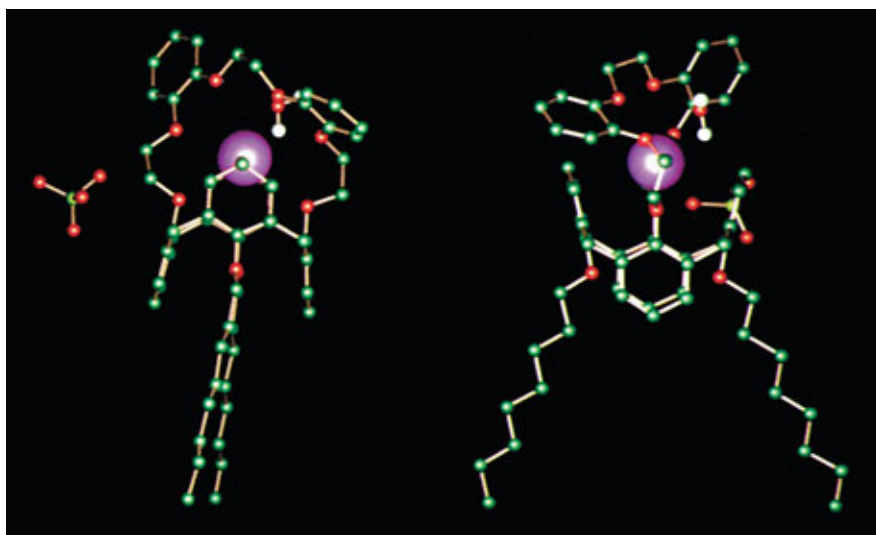
carried out on real radioactive solutions in the **Atalante** facility, in cooperation with the Radiochemistry and Process Department at CEA/Valrhô-Marcoule. After learning of the results obtained, Bruce Moyer's team at the Oak Ridge National Laboratory in Tennessee has adopted the calixarene-*bis*-crown compounds and is developing a process to extract Cs from basic solutions (6 mol/L of K and Na salts) for use in processing large quantities of liquid waste generated on certain USDOE (United States Department of Energy) sites, particularly in Hanford (Washington) and Savannah River (South Carolina).

Fruitful cooperation

The Waste Studies Department at Cadarache is studying functionalized calixarenes either in direct cooperation with the University of Strasbourg, or within the context of European projects. Since 1990, the European Commission has funded projects coordinated by CEA, associating it with ten or so Euro-

(1) Ratio of the extracted quantity to the quantity remaining in the solution.

● ● ● ● ●
Crystalline structure by X-ray diffraction (front and side views) of the di-octyloxy calix[4]arene-crown 6 complex with the potassium perchlorate ($K^+ ClO_4^-$) hydrated complex.



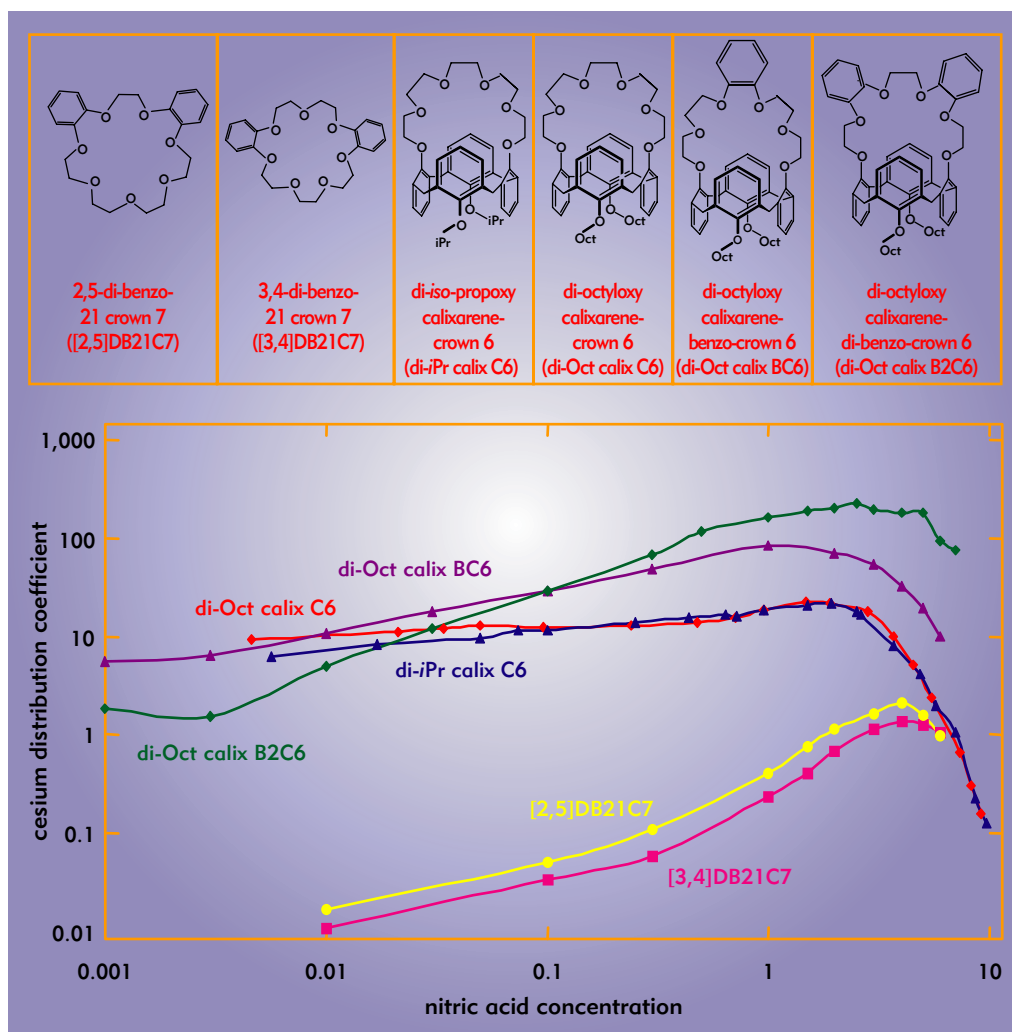


Figure 2. Comparison of the Cs extraction capability of different crown ethers and calix[4]arene-crown 6.

pean, mostly university, institutes. In this way, CEA works with all the different European teams specializing in calixarene synthesis. Another fundamental aspect is covered, with studies relating to X-ray diffraction, nuclear magnetic resonance (NMR), etc., and work involving molecular modeling and quantum-mechanics calculations. In addition, a contract has been signed with the Ukrainian Science Institute to develop a process for synthesizing calixarene-crown compounds on a large scale.

These European projects have enabled CEA to propose the synthesis of, and test many other calixarenes. CMPO (octyl phenyl di-iso butyl carbamoyl methyl phosphine oxide), developed in the United States in the 1980s, is the most effective extractant for actinides with different valences found in saline waste. Grafting CMPO functions onto a calixarene structure, a process performed by Professor V. Böhmer at the University of Mainz in Germany, yields a more powerful extractant. The chemist obtains comparable distribution coefficients with calixarene-CMPO and CMPO used at concentrations more than 250 times higher, and, more importantly, enhanced selectivity, which means that minor actinides can

be separated from all fission products, except for light lanthanides (especially lanthanum La, and cerium Ce). Calixarenes with six or eight phenolic units and di-ethyl-amide functions are used to extract strontium Sr, a highly radioactive fission product. Their performance far surpasses that of the best crown ethers (18C6) used to date in extracting Sr from strong acid media, and offer excellent chemical and radiochemical stability. These studies are conducted at the Physical-Chemistry Department at CEA/Saclay.

Molecules with a future

Calixarenes are clearly driving the spectacular, fast progress made in developing specific extractants for many cations. Less than ten years after their strong affinity for Cs came to light, calixarenes are now implemented in a straightforward process that might prove applicable to high-level radioactive solutions from the Purex process. The progress made is largely due to cooperation with various European teams (who far outstrip their American and Asian competitors), who are skilled in an extremely wide range of specialist fields (organic synthesis, molecular modeling, NMR, X-ray diffraction,

extraction, complexation, etc.). Even greater inroads are expected in coming years, when current results have been explained by computer-aided chemistry.

In addition, tests performed at Marcoule in October 2001 show that the Cs extraction efficiency of calixarene-crown compounds is in excess of 99%, making them the ideal molecules for use in nuclear waste management.

Jean-François Dozol
Nuclear Energy Division
CEA/Cadarache

and **Véronique Lamare**
Nuclear Energy Division
CEA/Saclay