Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A SOLUTION, FOR CESIUM REMOVAL FROM HIGH-SALINITY ACIDIC OR ALKALINE LIQUID WASTE: THE CROWN CALIX[4]ARENES

Jean Francois Dozol[a]; Nicole Simon[a]; Veronique Lamare[a]; Helene Rouquette[a]; Serge Eymard[a]; Bernard Tournois[a]; Daniele De Marc[a]; Rose Marie Macias[a]
[a] DEA Cadarache, France

To cite this Article Dozol, Jean Francois , Simon, Nicole , Lamare, Veronique , Rouquette, Helene , Eymard, Serge , Tournois, Bernard , De Marc, Daniele and Macias, Rose Marie(1999) 'A SOLUTION, FOR CESIUM REMOVAL FROM HIGH-SALINITY ACIDIC OR ALKALINE LIQUID WASTE: THE CROWN CALIX[4]ARENES', Separation Science and Technology, 34: 6, 877 — 909
To link to this Article: DOI: 10.1080/01496399908951072
URL: http://dx.doi.org/10.1080/01496399908951072

SEPARATION SCIENCE AND TECHNOLOGY, 34(6&7), pp. 877–909, 1999

A SOLUTION FOR CESIUM REMOVAL FROM HIGH-SALINITY ACIDIC OR ALKALINE LIQUID WASTE: THE CROWN CALIX[4]ARENES

Jean Francois Dozol, Nicole Simon, Veronique Lamare, Helene Rouquette, Serge Eymard, Bernard Tournois, Daniele De Marc DCC/DESD/SEP, and Rose Marie Macias DIST/UDC
DEA Cadarache 13108, Saint Paul Lez Durance, France

ABSTRACT

The scientific literature abounds with articles on the extraction of cesium from liquid waste. From the 1940s, several classes of inorganic exchangers were used for cesium removal, such as zeolites, hexacyanoferrates, zirconium phosphate, ammonium phosphomolybdate, and, more recently, crystalline silicotitanate. Later, organic compounds like formophenolic resins, tetraphenylboron, or extractants such as dicarbollides or crown ethers were proposed. Generally, these compounds were only able to efficiently remove cesium under restrictive conditions (alkaline medium, low salinity, etc.) The performances of most of these compounds strongly decreased as the acidity (or salinity) of the liquid waste increased. Artifices had to be implemented to improve the performances of extractants. A restricted number of inorganic exchangers allowed the cesium removal, but often they could not be eluted or needed prohibitive volumes of saline eluent, leading to large volumes of secondary waste.

Calix[4]arenes monocrown or biscrown, blocked in 1,3 alternative cone conformation, display an exceptional efficiency for cesium extraction, even from very acid or alkaline media. Moreover, they possess an important selectivity for cesium over sodium that makes possible the extraction of cesium from media containing high sodium nitrate loadings. Another advantage, since the extraction of cesium is reversible, is that the stripping of cesium can be carried out in deionized water, a property which leads to very high concentration factors.

INTRODUCTION

Since the 1940s, many efforts have been devoted to the removal and recovery of cesium from nuclear liquid waste. Indeed, cesium possesses two long-lived isotopes, ^{135}Cs and ^{137}Cs. The removal of the latter, along with ^{90}Sr and actinides, enables the waste to be decategorized and to be directed to a subsurface repository, where these long-lived nuclides, present in low amounts in the waste, can be disposed of in geological formations after vitrification. In the framework of the French Actinex program, studies were launched for the recovery of minor actinides and long-lived fission products from spent fuel dissolution acidic solutions, in order to destroy them by transmutation or to encapsulate them in specific matrixes. Efforts have to be directed toward ^{135}Cs, which is one of the most harmful elements because of its long half-life and mobility in the repository. Liquid wastes that have to be treated are quite different:

- very acidic solutions arising from the PUREX process for the removal of ^{135}Cs;
- acidic or alkaline solutions generated by reprocessing operations or nuclear facility dismantling; moreover, they contain large amounts of inactive salts, particularly sodium nitrate and ^{137}Cs at trace levels.

In order to minimize the volume of waste, it is of outstanding importance to find a compound able to remove cesium, with high efficiency and selectivity, from acidic or alkaline, high-salinity media and then to release this cation, if possible, in deionized water.

CESIUM RECOVERY PROCESSSES

Inorganic exchangers were the first compounds studied for the treatment of radioactive liquid waste. Their preparation and properties have been summarized in two books (1,2).

In 1981, an extensive survey of the methods of medium-activity waste treatment was carried out under the auspices of the Commission of the European Communities

(CEC), taking into consideration several different techniques: chemical precipitation, ion exchange, adsorption, membrane process, electric process, and foam separation (3). A large part of this survey was devoted to cesium. Technical reports were also provided by the International Atomic Energy Agency (IAEA), and an international conference was organized in Vienna on this topic (4,5,6,7). Studies launched to restore the site of Hanford (USA) also produced several reports on different compounds able to recover cesium (8,9).

Ion Exchanger or Insolubilization Processes

Most of the studies for cesium removal were carried out, at first, with inorganic ion exchangers and, later, with organic ion exchangers and extractants. The main ion exchangers used for cesium removal are discussed in the paragraphs that follow.

Zeolites are only used for cesium recovery from neutral or alkaline media; moreover, one has to underline a sharp efficiency decrease as the concentration of competitive cations increases (10,11,12). They were used for the treatment of French UNGG or British Magnox spent fuel storage ponds and the recovery of cesium from the reactor building after the Three Mile Island accident (7,13).

The ion exchangers used are hexacyanoferrates, zirconium phosphate, ammonium molybdophosphate or tungstophosphate, and, more recently, crystalline silicotitanate. The advantages of these compounds are the simplicity of implementation and the radiation stability, which are very important for the removal of cesium and strontium from high-activity waste. Generally, cesium sorption on these ion exchangers is hardly reversible. Thus, the reuse of these exchangers requires large volumes of high-salinity eluent or the solidification of the exchanger into ceramics; in both cases, the concentration factor is low. These drawbacks and an insufficient mechanical stability make such compounds unsuitable for the recovery of cesium from high-activity liquid waste. Moreover, one has to point out that no satisfactory solution has been found for hexacyanoferrates, as these compounds cannot be directly "ceramized" or incorporated into classical embedding matrixes (7,11,14,15,16,17).

Formophenolic resins can only be used for treatment of low- or medium-activity waste and at high pH values; moreover, their elution needs large volumes of acid. A

resin obtained by condensation of formaldehyde and resorcinol was tested at the Savannah River site, where it displayed a satisfactory chemical and radiochemical stability and a high selectivity for cesium over sodium. Promising results were obtained for cesium removal from alkaline solutions in India with the same type of resin (18,19).

Because of hydrolysis in acidic medium, tetraphenylborate (TPB) is only used in alkaline or neutral medium. The treatment of high-level waste at Savannah River includes TPB precipitation of cesium and simultaneous sorption of actinides and strontium on sodium titanate, with the resulting slurry being concentrated using stainless filters. The major insoluble constituent of the cake that develops during filtration is TPB, which leads to a decrease of the filtration rate and, hence, of concentration factor. The TPB process has other drawbacks: TPB has to be destroyed before vitrification since the amount of organic compounds is too great. Moreover, one must remove benzene, which is generated during the TPB hydrolysis and then dissolves into the decontaminated salt solution and into the water used to wash the precipitate (20,21,22,23,24).

Solvent Extraction Processes

Since the end of the 1970s, considerable progress has been made for the recovery of cesium with the implementation of two classes of extractants: dicarbollides, first synthesized by Hawthorne and extensively studied by Czech scientists, and crown ethers discovered by Pedersen, who found them to have exceptional ability to complex alkaline cations (25,26).

Co(III)dicarbollide, a very lipophilic anion, behaves as a cation exchanger. Its efficiency strongly decreases as the acidity or the salinity of the solutions being treated increases. This extractant, studied in the Rez Nuclear Institute (formerly Czechoslovakia) and later at the Radium Institute (formerly USSR), diluted in nitrobenzene, allows cesium and strontium (by adding polyethylene glycol) to be extracted from fission product solutions. Cesium and strontium are back-extracted with concentrated nitric acid (higher than 5 *M*). With a batch of 300 kg of dicarbollide, prepared in former Czechoslovakia, industrial tests were conducted in the reprocessing

plant RT-1 in the Chelyabinsk region (Russia). About 2 MCi of cesium and strontium was recovered from high-activity waste. It is the only process for cesium and strontium recovery used on an industrial scale. It was pointed out in Chelyabinsk that cesium and strontium are recovered after denitration of the high-activity solutions (HNO_3, 0.5 *M*). However, the dicarbollide process has two major drawbacks: it must be diluted in harmful nitrobenzene or in fluorinated diluents (allowing cesium to be extracted from acidic medium), and the reextraction is only possible with very acidic solutions. Moreover, the dicarbollide solubility in water, which is relatively low, increases with acidity (about 2 m*M* in HNO_3) (27,28,29,30,31,32,33,34,35).

Gerow studied the extraction of cesium and strontium from acidic, high-activity liquid waste with crown ethers. The chosen diluent was a mixture of TPB and kerosene compatible with the PUREX process used at the Savannah River Plant. The highest distribution coefficients (about 2) were achieved by using bis-(4,4′ (5′)-(l-hydroxyheptyl]benzo)-18-crown-6 (0.02 *M*) in the mixture of didodecylnaphthalene-sulfonic acid (0.076 *M* or 5%)–TBP (27%)–kerosene (68%) for cesium extraction from nitric solutions (3 *M*) (36,37).

Blasius chose DB21C7, among several other crown ethers, to remove cesium from two medium-activity wastes containing primarily sodium nitrate and nitric acid (MAW 1: HNO_3, 1 *M*; $NaNO_3$, 0.5 *M*; MAW 2: HNO_3, 0.8 *M*; $NaNO_3$, 3.4 *M*). Only DB21C7, used in high-dielectric-constant diluents such as nitromethane (D = 2.03) or nitrobenzene (D = 1.03), substantially extracts cesium. Even at higher concentrations (5×10^{-2} *M*), the distribution coefficients were too low for practical applications. One method for increasing cesium extraction is the addition of voluminous and polarizable anions such as molybdophosphate, TPB, or hexachloroantimonate. Some of these compounds are not useful; for example, TPB is hydrolyzed, while molybdophosphate leads to precipitation. The addition of hexachloroantimonate to DB 21 C7 diluted in nitrobenzene allows cesium to be quantitatively removed from MAW I (38,39).

To improve the cesium extraction, McDowell presented several strategies (40,41):

- using a high anion concentration in the aqueous phase;
- implementing modifiers such as nonylphenol or 2-ethylhexanol in order to

- increase the organic-phase polarity and improve the ion-solubilizing ability of the organic diluent;
- transforming the crown ethers into cation exchangers by adding lipophilic acid or by attaching an acid moiety to the crown ether.

Later, in another paper, McDowell predicted that the most powerful cesium extractant should be di-tert-butylbenzo-21C7 (42). This crown ether ($5 \times 10^{-2} M$) used with didodecylnaphthalenesulfonic acid, diluted in toluene, displays distribution coefficients higher than 100 when contacted with an aqueous phase, 0.1 *M* HNO_3. One has to point out that the distribution coefficients sharply decrease as the acidity increases (40–42).

Sachleben extensively studied the extraction of alkali cations using benzo- or tert-alkylbenzo-21C7 or –24C8. Addition of benzo substituents onto 24C8 enhances both the distribution coefficients and the selectivity for the larger cations; the tert-benzo-24C8 exhibits the highest distribution coefficients, but the selectivity is lower than that obtained with di-benzo-21C7 (43).

Dietz, for cesium extraction from very acidic solutions (4 *M* HNO_3), tested several crown ethers, the most efficient ($D_{Cs} = 4$) of which was the DtBB21C7 (0.1 *M*) diluted in methylpentanone, and, as for strontium, evidenced the role of the dissolved water in the diluent. In another publication, he reported the highest Cs/Na selectivity with 21C7 derivatives, but the most efficient extractant was 4,4′-(5′-di[(1-hydroxyethylhexyl)-benzo]-18C6 associated with TBP (0.2 *M*) which, when contacted with an acidic solution (4 *M* HNO_3), gave $D_{Cs} = 30$. Dietz concluded that these results are comparable to those reported for synergistic systems implementing a lipophilic organic anion (44,45).

In efforts devoted to the removal of cesium from evaporator acid concentrates with high sodium content ($NaNO_3$, 4 *M*; HNO_3, 1 *M*), cesium distribution coefficients were 0.3 with tert-butylbenzo-21-C7 or *n*-decylbenzo-21-C7 (0.25 *M*) diluted in the mixture decanol/hexylbenzene. These crown ethers made transfer of cesium possible, but the transport through supported liquid membranes was far from being complete. Dicarbollides tested under the same conditions displayed no cesium extraction (46,47,48).

BIBLIOGRAPHY ON CESIUM REMOVAL

All the compounds previously described enable cesium to be recovered. It is interesting to compare the number of publications dealing with these compounds for the extraction of cesium from nuclear liquid waste. For this survey, the databases consulted by computer were INIS and Chemical Abstracts, respectively, provided by IAEA and the American Chemical Society. The databases have been consulted since the beginning: 1967 for Chemical Abstracts and since 1970 for INIS.

For each compound, the same strategy was adopted:

i. According to the nature of the compound, the following terms were used for the research: absorption, decontamination, extraction, ion exchange, recovery, removal, and separation.

ii. References related to encapsulation, immobilization, incineration, solidification, and vitrification were discarded.

iii. In the case of compounds presenting different appellations or compounds presenting close properties, the research was as follows:
   - For hexacyanoferrate to ferrocyanide and ferricyanide.
   - For ammonium phosphomolybdate to molybdophosphate and ammonium phosphotungstate.
   - Phenolic resin to include formaldehyde, phenolformaldehyde, and resorcinol resins.
   - Search for zeolites was extended to the main cesium-specific media: chabazite, clinoptilolite, and mordenite.
   - Only nuclear technology and nuclear waste were taken into account for Chemical Abstracts.
   - Investigations were limited to waste treatment (E 5100), separation processes (B 1130), and chemical and physicochemical studies (B 1201) for INIS.
   - The double references were suppressed; only the remaining corpus identified the number of references per year.

Since 1967, the large number of publications (i.e., 919) demonstrates the importance of the problem and the difficulty in solving it. More than 50% of the publications deal with hexaferrocyanates (27.4%) and zeolites (24.5%). These compounds had already been extensively studied in 1967 and are still being studied 30 years later (Figures 1 and 2).

Other inorganic exchangers, phosphomolybdates and zirconium phosphates, show a different behavior: 4 or 5 publications per year since 1975 for the first one, a maximum for the latter in 1983, and then a decrease. Since 1992, new inorganic ion exchangers have been proposed; the increase in the number of publications attests to the fact that the silicotitanate results are promising (Figure 3).

Tetraphenylboron was mainly studied between 1981 and 1993; difficulties in using this compound can explain the decrease of publications since 1994. However, an impetus for the study of phenolic resins has been observed since 1994: 19 publications in three years (Figure 4).

Three classes of extractants were proposed for the removal of cesium: crown ethers, dicarbollides, and calixarenes. The crown ethers, discovered in 1967, were quickly applied to the cesium recovery from nuclear waste. One has to point out a strong increase of publications for these compounds in 1995 and 1996. Since their discovery, publications dealing with cesium extraction by crown ethers are abundant. Investigations on dicarbollides were mainly carried out by Czech and later by USSR scientists. Recently, interest in these compounds has extended to France, Japan, and the United States. At first, *p*-tert-alkylcalixarenes were studied by Izatt, and then functionalized calixarenes, obtained in the framework of an European project by adding functional groups, were used for the removal of cesium from radioactive liquid waste (Figure 5).

This research, although not exhaustive, highlights the importance of the work performed during the last 30 years and shows that compounds, already investigated in 1967 (like hexaferrocyanates or zeolites) continue to be studied. Except for some peculiar cases, these compounds do not seem to be able to solve the problems of cesium removal.

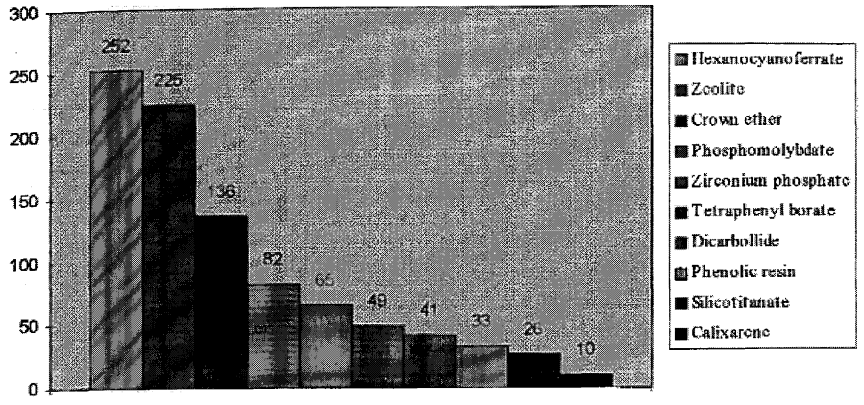

FIGURE 1. Number of publications between 1967 and 1996.

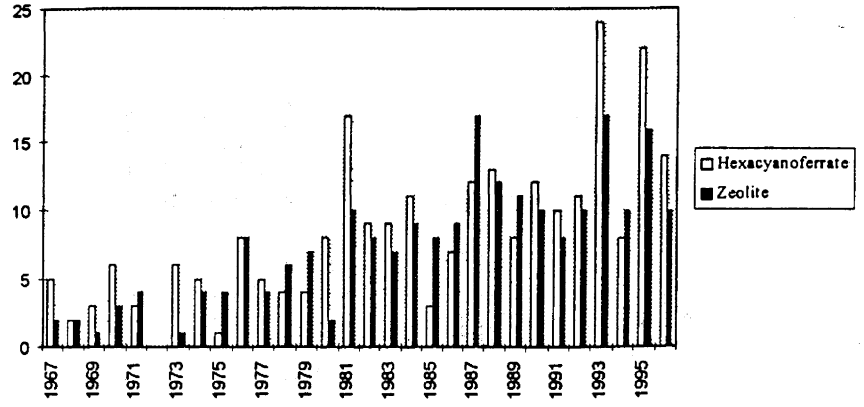

FIGURE 2. Number of publications dealing with hexacyanoferrate and zeolite.

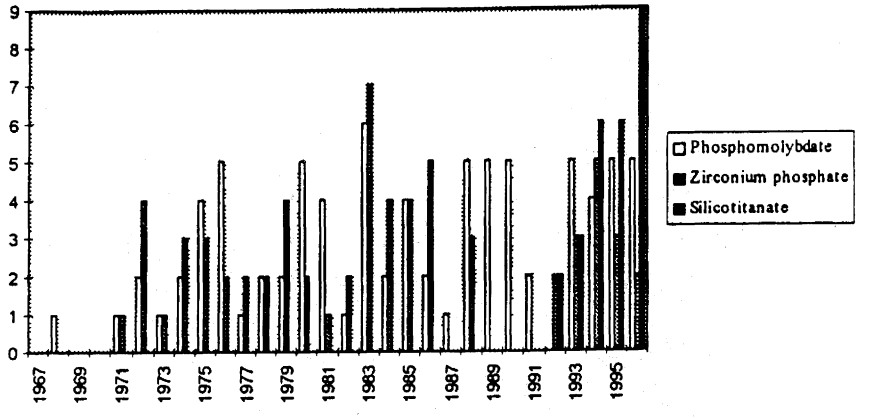

FIGURE 3. Number of publications dealing with phosphomolybdate, zirconium phosphate, and silicotitanate.

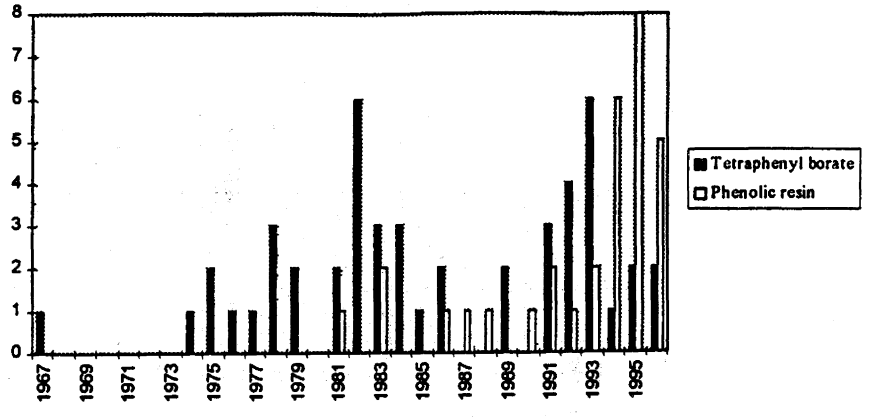

FIGURE 4. Number of publications dealing with tetraphenylborate and phenolic resin.

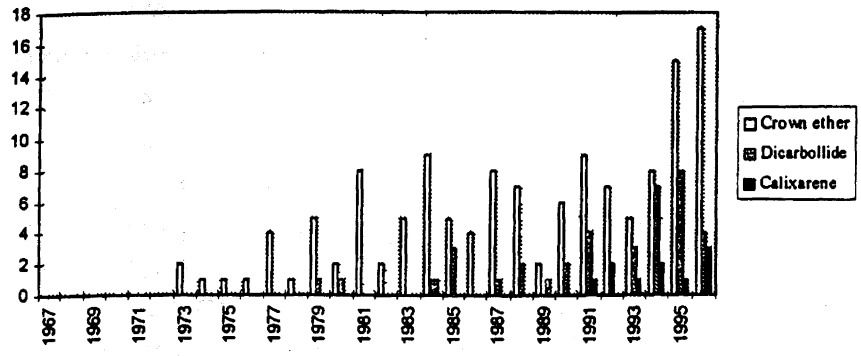

FIGURE 5. Number of publications dealing with crown ethers, dicarbollides, and calixarenes.

It is likely that very specific macrocyclic compounds, with the progress of the host-guest chemistry and the help of molecular modeling, will be tailored and substituted to become inorganic exchangers in the future,

CALIXARENES

The name "calixarenes" was proposed by Gutsche for the cyclic oligomers obtained by condensation of formaldehyde with *p*-alkyl phenols. The use of the word "calix," which means "vase" in Greek, was suggested by the shape of the tetramer which can adopt a beaker-like conformation (Figure 6). The suffix -arene indicates the presence of aryl groups in the molecule (49,50,51).

p-tert-Butyl calix[4]arenes are cyclic compounds constituted by four phenolic units linked by methylene groups, which present four conformations: cone, partial cone, 1,2 alternate, and 1,3 alternate (Figure 7).

First of all, well known *p*-tert-butyl calix[n]arenes were patented by Izatt for cesium transport through thick liquid membranes from an alkaline medium, using a mixture of diluents able to dissolve these compounds: methylene chloride, carbon tetrachloride, and dichloromethane (52,53,54).

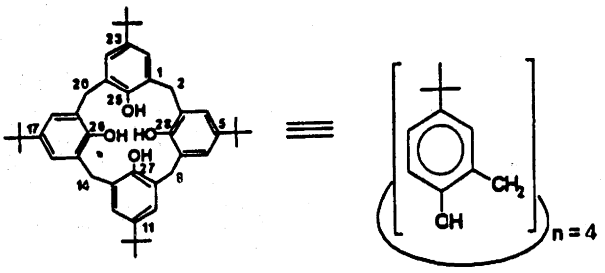

FIGURE 6. *p*-tert-Butyl calix[4]arenes.

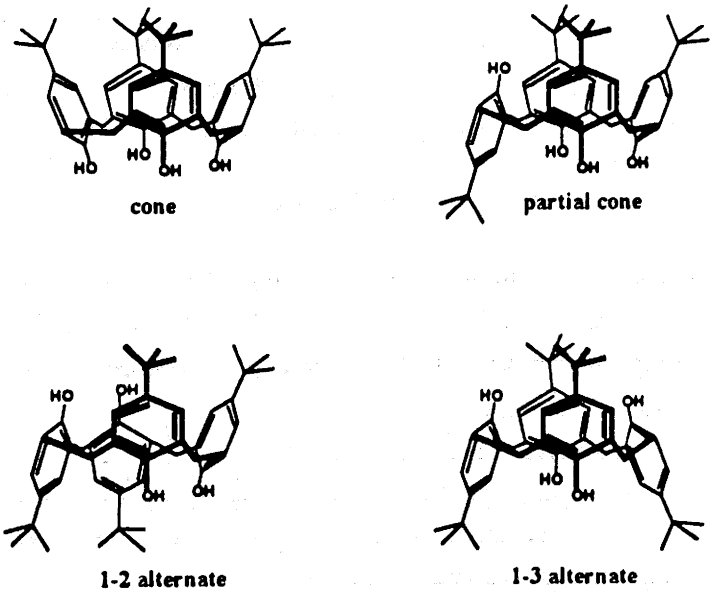

FIGURE 7. Conformations of *p*-tert-butyl calix[4]arene.

From 1990, an important project granted by the CEC gave a stimulus to the studies of functionalized calixarenes and particularly to dialkyl calix[4]arenes-crown prepared by Ungaro. Simultaneously, Vicens synthesized calix[4]arenes-biscrown (55,56,57).

Calix[4]arene-crown-*n* compounds consist of a calix[4]arene frame, maintained in the 1,3 alternate conformation by a polyethylene glycol bridge containing *n* oxygen atoms (Figure 8a). The two remaining phenolic units are either derived with alkyl chains (dialkyl-calix[4]arene-crown-*n*) or bridged with a second identical polyethylene glycol chain (calix[4]arene-biscrown-*n*). The crowns can include one or two benzene units (Figure 8b). The compounds of interest for cesium removal are in the 1,3 alternate conformation.

EXPERIMENTAL

Reagents

All the dialkyl calix[4]arene-crown compounds were synthesized and purified by Ungaro (University of Parma) in the framework of a project supported by the CEC. The calix[4]arene-biscrown 6 was synthesized and purified by Vicens and Asfari through a collaboration between the University of Strasbourg and the French Atomic Energy Commission (55,56). Each of these compounds was used without further purification in NPHE, synthesized by ERAS Labo. The inorganic salts used to prepare the synthetic solutions were analytical-grade products from Prolabo. The radioisotopes ^{22}Na and ^{137}Cs were provided by the Amersham Company.

Distribution Coefficient Measurements—Selectivity

Before distribution coefficient measurements, the organic solution was preequilibrated by contacting twice with an appropriate solution. Then the preequilibrated organic phase was mixed with an equal volume of fresh aqueous phase spiked with nuclides in sealed tubes for 1 h. Aliquots of each phase were analyzed by gamma spectrometry or by ion chromatography after centrifugation.

The selectivity of a cation M_1 toward another cation M_2 was measured by shaking the organic phase with an acidic aqueous solution (HNO_3 1 *M*) containing cations M_1 or

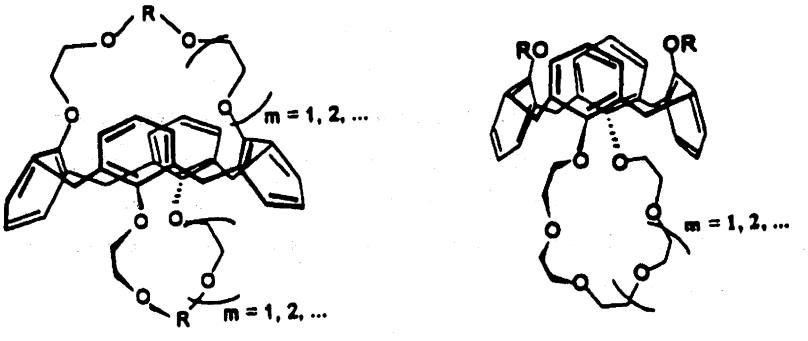

FIGURE 8a. Calix[4]arenes-crown-6.

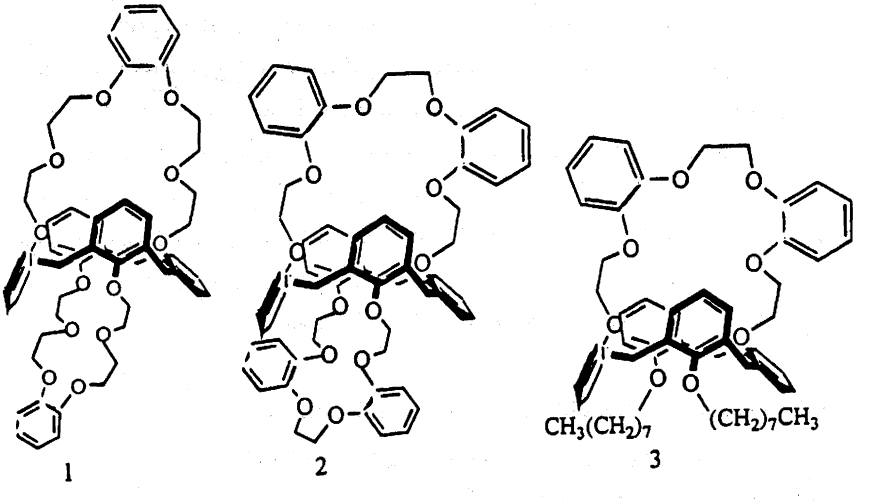

FIGURE 8b. 1: Calix[4]arene-bis-*o*-benzo-crown 6; 2: calix[4]arene-bis(dibenzo-crown 6); 3: calix[4]arene-dioctyl(dibenzo-crown 6).

M_2. The selectivity of the cation M_1 over M_2 is expressed as the ratio of distribution coefficients of the cations:

$$D_M = \frac{\sum[\overline{M}]}{\sum[\overline{M}]}, \quad (1)$$

$$\alpha = \frac{D_{M_2}}{D_{M_1}}, \quad (2)$$

where $\sum[\overline{M}]$ and $\sum[M]$ denote the total concentration of the metal species, respectively, in the organic phase and in the aqueous phase at equilibrium.

Supported Liquid Membranes

The thin flat sheet–supported liquid membrane (SLM) device, described by Stolwijk, was used (58). The volumes, equal of feed and stripping solutions, varied from 45 to 50 cm^3 and the areas of the membranes from 15 to 16 cm^2, depending on the glass devices manufactured by the Verre and Science Company (Figure 9). The support used was a Celgard 2500 membrane possessing the following characteristics: thickness, 25 μm; porosity, 45%; and average pore diameter, 0.04 μm. The SLM was prepared by soaking the Celgard membrane in the organic phase containing the calixarene diluted in NPHE. About 1.5-mg cm^{-2} of organic phase was incorporated in the membrane. The transport of these nuclides was followed by regular measurements of the radioactivity decrease in the feed solution and of the radioactivity increase in the stripping solution.

Nitrophenyl alkyl ethers (NPHE – hexyl; NPOE – octyl) were used because they lead to a stable membrane due to their very low solubility in water. Moreover, the basicity as well as the polarity of these nitrophenyl alkyl ethers improve cation extraction by a better solvation of nitrate anions.

The transport of ions through the SLM occurs because a chemical gradient is established between the feed solution and the stripping solution. The use of neutral carriers such as functionalized calixarenes leads to the coupled cotransport of cations and anions through the SLM. When evaporator concentrates or fission product solutions are used as the feed solution and deionized water as the stripping solution, the

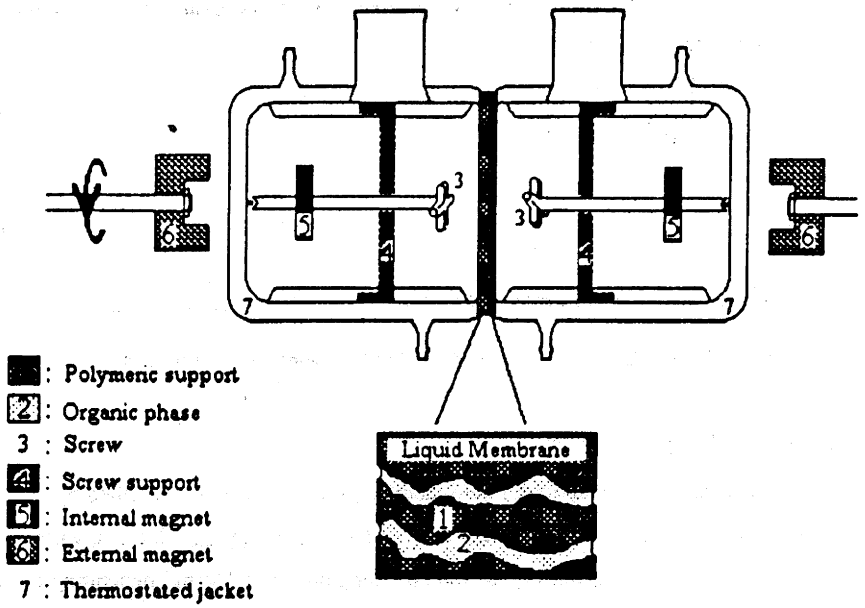

FIGURE 9. Supported liquid membrane setup.

concentration gradient of the nitrate anions will force the transport of cations M^+ against their own concentration gradient, thus leading to a concentration of these cations in stripping solution.

Daesi's Transport Model

The transport of M^+ from feed solution, spiked with radionuclides, was followed by regular measurement of the decrease of radioactivity in the feed solution or its increase in the stripping solution. This allows graphical determination of the constant permeabilities P_f and P_s (cm h^{-1}) of M, respectively, from feed and stripping solutions, by plotting the logarithm of the ratio C/C^o (or $1 - C'/C^o$) versus time, as described in the model proposed by Danesi (59):

$$Ln\left(\frac{C}{C_0}\right) = -\frac{\varepsilon S}{V} P_f t, \tag{3}$$

$$Ln\left(1-\frac{C'}{C_0}\right)=-\frac{\varepsilon S}{V}P_f t. \quad (4)$$

If $P_f > P_s$, it corresponds to an accumulation of cations in the membrane, due to an incomplete stripping.

The flux of cesium is given by the relationship

$$J = PC. \quad (5)$$

When the cesium concentration in the organic phase reaches that of the carrier in the membrane or when the cesium concentration in the feed solution equals that of the carrier divided by the cesium distribution coefficient (measured when the feed and organic solutions are contacted), the carrier is saturated by cesium, and the flux of cations is independent of time:

$$J = E.D_0 / d_0, \quad (6)$$

where

C, C′ = concentration of the cation, respectively, in the feed or stripping solution at time t;

C = initial concentration of the cation in the feed solution;

ε = porosity of the SLM (%);

S = membrane surface area (cm^2);

V = volume of feed or stripping solution (mL);

t = time (h);

E = extractant concentration in the SLM;

D_0 = diffusion coefficient of cation-extractant complex; and

d_0 = product of membrane thickness by its porosity.

RESULTS

Selectivity—Stoichiometry

From Table 1, it can be observed that compounds with a polyethylene glycol chain containing six oxygen atoms are more efficient for cesium extraction and more selective toward cesium over sodium than those with five or seven oxygen atoms (60,61,62,63,64,65,66). *p*-tert-Butyl calixarenes with glycolic chains containing five

TABLE 1. EXTRACTION OF CESIUM AND SODIUM—Cs/Na SELECTIVITY

Aqueous feed solution: MNO_3, 5×10^{-4} *M*; HNO_3, 1 *M*
Organic solution: 10^{-2} *M* extracting agent in 1,2-nitrophenylhexyl ether

Compound	D_{Na}	D_{Cs}	α(Cs/Na)
Calix[4]arene-dimethoxy-crown 6	3×10^{-3}	4×10^{-2}	13
Calix[4]arene-hydroxyethoxy-crown 6	4×10^{-3}	4.2	>4200
Calix[4]arene-dipropoxy-crown 6	2×10^{-3}	19.5	>19,500
Calix[4]arene-diisopropoxy-crown 6	$<10^{-3}$	28.5	>28,500
Calix[4]arene-di-*n*-octyloxy-crown 6	$<10^{-3}$	33	>33,000
Calix[4]arene-di-*n*-octyloxy-dibenzo-crown 6	$<10^{-3}$	31	>31,000
Calix[4]arene-dimethoxy-crown 7	4×10^{-3}	7×10^{-3}	1.7
Calix[4]arene-biscrown 5	2×10^{-3}	0.4	400
Calix[4]arene-biscrown 6	1.3×10^{-2}	19.5	1,500
Calix[4]arene-biscrown 7	$<10^{-3}$	0.3	300
Calix[4]arene-bis-*p*-benzo-crown 6	$<10^{-3}$	2×10^{-2}	>20
Calix[4]arene-bis-*o*-benzo-crown 6	1.7×10^{-3}	32.5	19,000
Calix[4]arene-bis-dibenzo-crown 6	$<10^{-3}$	23	>23,000
Calix[4]arene-bis-naphthyl-crown 6	$<10^{-3}$	29.5	>29,000
Calix[4]arene-bis-diphenyl-crown 6	$<10^{-3}$	7×10^{-2}	>70
n-Decylbenzo-21-crown 7	1.2×10^{-3}	0.3	250
tert-Butylbenzo-21-crown 7	1.2×10^{-3}	0.3	250

oxygens are suitable for the extraction of potassium (67). The exceptional selectivity for cesium over sodium displayed by calixarenes crown (higher than that obtained with crown ethers, known for their ability to extract alkali ions) is only obtained when the calixcrowns adopt the 1,3 alternate conformation: Selectivities higher than 30,000 are reached for several calixarene crowns; as for the best fitted crown ethers for cesium extraction such as benzo-21-crown 7 compounds, selectivities do not exceed 300. This

very high selectivity can be explained by a good host-guest complementarity and preorganization and by an interaction between cesium and the π electrons of the benzene units of calixarenes. So, the conformationally mobile methoxy-calixarene-crown 6 displays a lower efficiency and selectivity than the calixarenes blocked in 1,3 alternative conformation (68,69,70,71).

Extraction of the different alkaline cations (except lithium) was studied by ion chromatography. As expected, the extraction efficiency increases with the size of the cation (Table 2). Calix[4]arene-bis-dibenzo-crown 6 extracts potassium, rubidium, and cesium with a lesser efficiency than calix[4]arene-bis-*o*-benzo-crown 6 and calix[4]arene-bis-naphthyl-crown 6, but extracts sodium much less than these two other calixarenes; thus, the apparent selectivity ([Na] = 1 *M*, [Cs] = 5×10^{-4} *M*) is higher for this one.

The selectivity of calixarenes was confirmed by the extraction of cesium from acidic solutions containing four moles of sodium nitrate (i.e., solutions simulating an evaporator concentrate). High distribution coefficients were obtained with the calixarenes-crown 6 in 1,3 alternative conformation and particularly with calix[4]arene-di-*n*-octyloxy(dibenzo-crown 6) and calix[4]arene-bis-(dibenzo-crown 6) (Table 3).

In spite of the two available complexation sites, calixarenes biscrown, like calixarenes monocrown, present the calixarene-cesium stoichiometry 1:1. This behavior can be explained by an electrostatic repelling of the second cation by the first one, already present in one of the two crowns.

The study of Sorel on the extraction of cesium nitrate, sodium nitrate, and nitric acid from aqueous solutions by the diisopropoxy-calixarene crown 6 led to a satisfactory description of the distribution of all compounds by taking into account the formation of the following cesium complexes: $(Calix)(CsNO_3)(H_2O)$ and $(Calix)_2(CsNO_3)(H_2O)_h$ when calixarene is contacted with neutral or alkaline solutions. With acidic solutions, $(Calix)_2(CsNO_3)$ and $(Calix)(HNO_3)_j(CsNO_3)$ complexes compete with (Calix) $(HNO_3)(H_2O)$h (72).

Extraction of Cesium from Acidic Medium

For all tested calixarenes, it can be noticed that cesium distribution coefficients increase as acidity increases. A maximum is reached for an acidity about 2 *M*; then

TABLE 2. EXTRACTION OF ALKALINE CATIONS—Cs/Na SELECTIVITY

Aqueous feed solution: MNO_3, 5×10^{-4} *M*; HNO_3, 1 *M* and $NaNO_3$, 1 *M*; HNO_3, 1 *M*
Organic solution: 10^{-2} *M* extracting agent in 1,2-nitrophenylhexyl ether

Compound	D_{Na} [Na] = 1 *M*	D_{Na}	D_K	D_{Rb}	D_{Cs}	α(Cs/Na)
Calix[4]arene-biscrown 6	10^{-3}	2.5×10^{-3}	0.2	3.2	20	2×10^4
Calix[4]arene-bis-o-benzo-crown 6	4×10^{-4}	1.9×10^{-3}	0.4	6.5	38	9.6×10^4
Calix[4]arene-bis-naphthyl-crown 6	3.4×10^{-4}	1.7×10^{-3}	0.4	6.5	>40	12×10^4
Calix[4]arene-bis-dibenzo-crown 6	1.4×10^{-4}		0.3	4.4	31	22×10^4

they decrease (Figure 10). These results can be predicted by modeling of extraction isotherms. For acidities lower than 2 *M*, $(Calix)(HNO_3)_j(CsNO_3)$ complexes are predominant and the thermodynamic activity of $CsNO_3$ increases with acidity; at higher acidities, $(Calix)(HNO_3)(H_2O)_h$ complexes become important and prevent the cesium extraction. However, the behavior of all the calixarenes is not identical; calixarene bis-crown displays the lowest distribution coefficients regardless of the acidity of the aqueous phase. The distribution coefficients of the two alkyl calixarenes monocrown, high in low-acidity medium, slowly increase until reaching the maximum. The calixarenes with benzo or naphtho groups are, by far, the more efficient extractants for cesium; around the maximum, distribution coefficients higher than 100 are reached. One of the most striking effects is the extremely high distribution coefficient value (between 200 and 300) for an acidity ranging between 2 and 4 *M* with the calixarenes including two benzene groups in the crown; this can be explained by a steric hindrance due to the aryl groups, preventing the extraction of nitric acid by the oxygen atoms of the crown. In very acidic medium, the evolution of the distribution coefficients is

TABLE 3. COMPETITIVE EXTRACTION OF CESIUM IN PRESENCE OF AN EXCESS OF SODIUM

Aqueous feed solution: HNO_3, 1 *M*; $NaNO_3$, 4 *M*; $CsNO_3$, 10^{-6} *M*
Organic solution: 10^{-2} *M* extractant in 1,2-nitrophenyl hexyl ether

Extractant	D_{Cs}	Extractant	D_{Cs}
Calix[4]arene-dimethoxy-crown 6	0.034	Calix[4]arene-biscrown 7	0.2
Calix[4]arene-hydroxyethoxy-crown 6	5.2	Calix[4]arene-bis-*p*-benzo-crown 6	<0.001
Calix[4]arene-dipropoxy-crown 6	12	Calix[4]arene-bis-*o*-benzo-crown 6	20
Calix[4]arene-diisopropoxy-crown 6	18	Calix[4]arene-bisnaphthyl-crown 6	8
Calix[4]arene-di-*n*-octyloxy-crown 6	25	Calix[4]arene-bisdiphenyl-crown 6	0.39
Calix[4]arene-di-*n*-oxtyloxy-dibenzo-C6	56	Calix[4]arene-bis-dibenzo-crown 6	54
Calix[4]arene-dimethoxy-crown 7	0.003	*n*-Decylbenzo-21-crown 7	0.12
Calix[4]arene-biscrown 5	0.03	tert-Butylbenzo-21 crown 7	0.12
Calix[4]arene-biscrown 6	10		

identical for all the calixarenes. It may be asserted that these results were obtained with NPHE as diluent; with the mixture NPHE (30%)–TPH (70%), the distribution coefficients continually increase in the range of 0–4 *M* HNO_3, whereas these calixarenes diluted in NPHE display maximum values for an acidity about 2 *M* HNO_3.

Extraction from Neutral or Alkaline Media

In the range of pH 2 to 12, for high–sodium nitrate media, salinity being almost invariable, distribution coefficients are constant. One must emphasize that the absence of mixed complexes $HNO_3/CsNO_3$ leads to lower distribution coefficients than those obtained in acidic medium. In spite of a high Cs/Na selectivity, distribution

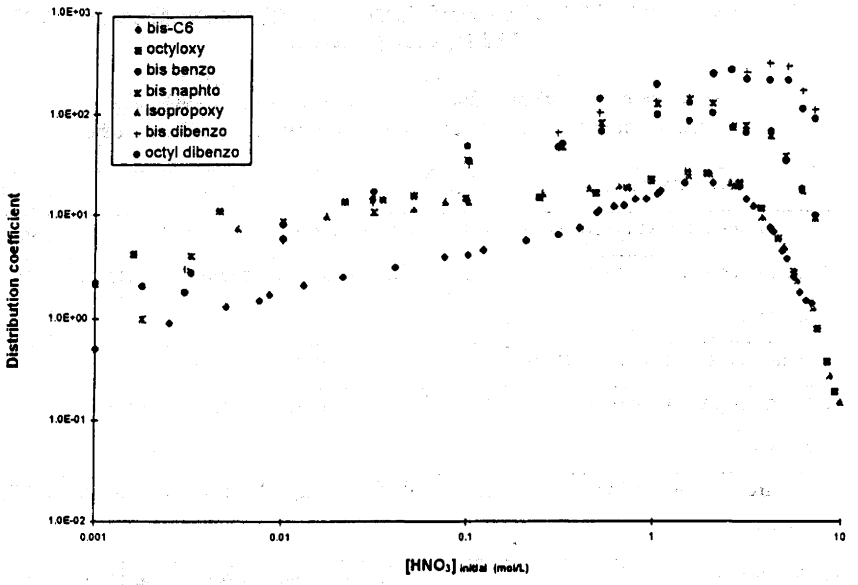

FIGURE 10. Distribution coefficients of cesium as a function of nitric acid concentration.

coefficients slightly decrease as the sodium nitrate concentration of the aqueous phase increases. Calixarenes bearing two benzene units, and particularly bis(dibenzo-crown), are the most efficient for cesium extraction and less sensitive to the salinity (Table 4).

Cation Transport

As distribution coefficients increase with the acidity or salinity of aqueous phases, stripping in deionized water is possible. Transport experiments were carried out with the different calixarenes from high-salinity acidic medium to water (Table 5). Calixarenes presenting the highest cesium distribution coefficients display the highest selectivity and, particularly, the most lipophilic with polyethylene bridges including benzene or naphthalene units: calix[4]-di-*n*-octyloxydibenzo-C 6 and calix[4]-bis-dibenzo-C 6, and, to a lesser extent, calix[4]-bis-dibenzo-C 6, calix[4]-bis-benzo-C 6, and calix[4]-bis-naphthyl-C 6.

TABLE 4. DISTRIBUTION COEFFICIENTS OF CESIUM FROM SODIUM NITRATE SOLUTIONS

Feed solution: $NaNO_3$, 1–4 *M*; $CsNO_3$, 10^{-6} *M*
Organic solution: 10^{-2} *M* extracting agent in 1,2-nitrophenyl hexyl ether

$NaNO_3$	1 *M*	2 *M*	3 *M*	4 *M*
Calix[4]arene-diisopropoxy-crown 6	-	11.5	6.6	-
Calix[4]arene-di-*n*-oxtyloxy-crown 6	12.5	9.7	8.2	6
Calix[4]arene-di-*n*-octyloxydibenzo-crown 6	37	20	18.5	15
Calix[4]arene-biscrown 6	16	11.5	9	6
Calix[4]arene-bis-*o*-benzo-crown 6	27	15	13	11
Calix[4]arene-bisnaphthyl-crown 6	30	19	14	11
Calix[4]arene-bis-dibenzo-crown 6	-	26	21	16

At the end of the transport, the relations (3) or (4) are no longer valid due to a parasitic cotransport of nitric acid; the linearity of relations (3) and (4) as a function of time can be recovered as long as nitric acid is removed from the stripping solution.

One has to underline that the use of very lipophilic calixarenes (all the tested calixarenes except the calix[4]biscrown), diluted in NPHE, leads to very stable supported liquid membranes, working several weeks (73).

In Danesi's model, the permeability P is related to the distribution coefficient D by the relation

$$P = \frac{D}{\frac{Dd_a}{D_a} + \frac{d_o}{D_o}}, \tag{7}$$

where

D_a denotes the diffusion coefficient of the cation in the aqueous phase, and

d_a is the thickness of Nernst aqueous layer.

When the stirring rates of the feed and stripping solutions are high, d_a decreases and approaches zero; then the permeability is proportional to the distribution

TABLE 5. ^{137}Cs TRANSPORT EXPERIMENTS THROUGH FLAT SHEET–SUPPORTED LIQUID MEMBRANES

Permeability determination after 6 h of permeation

Aqueous feed solution: $NaNO_3$ (4 *M*); HNO_3, 1*M*; aqueous stripping solution: deionized water; organic solution, 10^{-2} *M* carrier in NPHE

Compound	P_{Cs}(cm · h^{-1})	Compound	P_{Cs}(cm · h^{-1})
Calix[4]-hydroxyethoxy-crown 6	0.4	Calix[4]-biscrown 7	4×10^{-2}
Calix[4]-dipropoxy-crown 6	1.6	Calix[4]-bis-*p*-benzo-crown 6	3×10^{-3}
Calix[4]-diisopropoxy-crown 6	1.3	Calix[4]-bis-o-benzo-crown 6	2.8
Calix[4]-di-*n*-octyloxy-crown 6	1.9	Calix[4]-bis-naphthyl-crown 6	2.7
Calix[4]-di-*n*-octyloxydibenzo-crown 6	4.3	Calix[4]-bis-diphenyl-crown 6	0.1
Calix[4]-biscrown 5	9×10^{-2}	Calix[4]-bis-dibenzo-crown 6	4.3
Calix[4]-biscrown 6	1.3	*n*-Decylbenzo-21-crown 7	9×10^{-2}

coefficient:

$$P = \frac{D_o}{d_o} D. \quad (8)$$

In brief, the flux of cations is governed by the two following relations:

at high cesium concentrations (C > E/D),

$$J = E.D_o/d_o; \quad (6)$$

while at lower cesium concentrations,

$$J = P.C = D.C.D_o/d_o. \quad (9)$$

From the permeability, the diffusion coefficients, D_o, of the cation/carrier complexes can be determined (Table 6).

TABLE 6. DIFFUSION COEFFICIENTS OF CALIXARENES

Extractant	Diffusion coefficient ($cm^2\ h^{-1}$)
Calix[4]-diisopropoxy-crown 6	10.5×10^{-4}
Calix[4]-dioctyloxy-crown 6	9.2×10^{-4}
Calix[4]-biscrown 6	6.6×10^{-4}
Calix[4]-bis-benzo-crown 6	8.2×10^{-4}
Calix[4]-bis-naphtho-crown 6	6.2×10^{-4}

The exceptional selectivity of calixarenes monocrown or biscrown for cesium over sodium was confirmed by Haverlock on alkaline solution simulating Hanford tank supernatant waste. On the same alkaline solutions, calixarenes gave distribution coefficients 200 times higher than bis(tert-butylbenzo)-21-C 7 (74).

Tests on Fission Product Solution

The calix[4]-diisopropoxy-crown 6 and the calix[4]-biscrown 6 were tested on a high-activity liquid waste obtained by dissolution of a MOX fuel (burnup, 34,650 MWJ/t_U) and after extraction of uranium and plutonium by TBP (PUREX process).

The cesium extraction was carried out on the acidic PUREX raffinate (4 *M* HNO_3). The distribution coefficients obtained by contacting calixarenes-crown 6 (0.1 *M* diluted in NPHE) with the high-activity solution were higher than 50. Because of the high cesium concentration (4.15×10^{-3} *M* for a ^{137}Cs activity of 17.9 Ci L^{-1}), the calixarene concentration was increased ten times. Only rubidium was sensibly extracted with cesium. These trends were confirmed by SLM transport, where experiments allowed a selective transport of cesium and rubidium. The discrepancy between permeabilities obtained on simulated and real waste was about 10%. No other element except rubidium (i.e., Fe, Ru, Mo, Zr, Sb, Ce, Nd, Eu, Am, Cm) present in the feed solution was transported at a higher level than 1–2% (75).

Tests on Real Evaporator Concentrate

The major inactive components of the real acidic evaporator concentrate arising from reprocessing operations (1.05 *M* HNO_3) were sodium (2.62 *M*), magnesium (0.62 *M*), potassium (0.117 *M*), and cesium at trace level. The cesium distribution coefficient, determined by contacting the concentrate with the calix[4]arene-di-*n*-octyloxy-crown 6 diluted in NPHE (5×10^{-2} *M*), was higher than 14. Transport through supported liquid membranes confirmed the efficiency and the selectivity of the calixarene. Cesium was quantitatively transported, with a part of the residual plutonium (40%), from the concentrate to deionized water. No other element (Na, Mg, Al, K, Ca, Fe, and Zn) was transferred through the SLM (76).

CONCLUSIONS

Since the 1940s, many efforts have been devoted to cesium extraction. At first, inorganic ion exchangers such as zirconium phosphates, ammonium molybdophosphates, hexacyanoferrates, and zeolites were used; then organic resins and tetraphenylborate were introduced. In spite of studies conducted for decades, these compounds are only being used to solve specific problems.

At the end of the 1960s, implementation of solvent extraction with dicarbollides and crown ethers brought an important advance for cesium extraction, particularly in the former USSR with dicarbollides. Unfortunately, since the efficiency of the dicarbollide anion decreases as acidity increases, the extraction of cesium needs to be preceded by a denitration step. As far as crown ethers, high distribution coefficients can be obtained only if a lipophilic anion or additives like TBP are used. Furthermore, the selectivity for cesium over sodium is not sufficient to enable cesium to be extracted from high-sodium-content medium.

Calix[4]arenes-crown 6, in 1,3 alternative conformation, display higher efficiencies than the other well known extractants, dicarbollides or crown ethers, to remove cesium from high-acidity medium. They possess an exceptional selectivity for cesium over sodium that allows cesium to be quantitatively removed from media containing four or more moles of sodium per liter.

Studies carried out on several calixarenes crown compounds show that the presence of aryl groups on the crown strongly enhances the efficiency and the selectivity of these compounds. Today, molecular modeling helps us to conceive better-performing compounds (77,78,79).

The use of these calixarenes, which can be synthesized in large quantities, should provide a solution for cesium removal from acidic media (0.5–7 *M*) and from alkaline or neutral liquid waste, even in the presence of large amounts of sodium salts.

ACKNOWLEDGMENT

This work was partly financially supported by the Commission of the European Communities in the framework of the research program on Management and Storage of Radioactive Waste (Contract No. F12W-CT90-0062) and by COGEMA.

REFERENCES

1. C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier Publishing Co., Amsterdam, London, New York, 1964.
2. A. Clearfield, *Inorganic Ion Exchange Materials*, CRC Press, Boca Raton, Florida, 1982.
3. K. W. Carley-Macauly et al., *Radioactive Waste: Advanced Management Methods for Medium Active Liquid Waste*, Harwood Academic Publishers, Brussels, Luxembourg, 1981.
4. Feasibility of Separation and Utilization of Cesium and Strontium from High Level Liquid Waste, IAEA Technical Reports Series No. 356, Vienna, 1993.
5. Advances in Technologies for the Treatment of Low and Intermediate Level Radioactive Liquid Wastes, IAEA Technical Reports Series No. 370, Vienna, 1994.
6. Minimization of Radioactive Waste from Nuclear Power Plants and the Back End of the Nuclear Fuel Cycle, IAEA Technical Reports Series, No. 377, Vienna, 1995.

7. Inorganic Ion Exchangers and Adsorbents for Chemical Processing in the Nuclear Fuel Cycle, IAEA Technical Committee Meeting, Vienna, 1984.
8. G. N. Brown, L. A. Bray, C. D. Carlson, K. J. Carson, J. R. DesChane, R. J. Elovich, F. V. Hoopes, D. E. Kurath, L. L. Nenninger, and P. K. Tanaka, Comparison of Organic and Inorganic Ion Exchangers for Removal of Cesium and Strontium from Simulated and Actual Hanford 241-AW-101 DSSF Tank Waste, PNNL-11120, 1996.
9. S. F. Marsh, Z. V. Svitra, and S. M. Powen, Distribution of 15 Elements on 58 Absorbers from Simulated Hanford Double Shell Slurry Feed (DSSF), LA-12863, 1994.
10. D. Bradbury, D. Broadbent, G. A. Fitchett, T. J. Martin, and D. Reed, Solvent Extraction and Ion Exchange in the Nuclear Fuel Cycle, Logdmail-Mills, published by Society of Chemical Industry.
11. J. F. Dozol, S. Eymard, R. Gambade, and G. LaRosa, Application d'Exchangeurs Mineraux à la Decontamination d'Effluents Radioactifs FA et MA, EUR 10675 FR, 1986.
12. J. S. Buckingham, "Laboratory Evaluation of Zeolite Material for Removing Radioactive Cesium from Alkaline Waste Solutions," presented at the 2nd International Conference on Zeolites, Worchester, Massachusetts, 1970.
13. K. J. Hofsletter and C. G. Hilz, Sep. Sci. Technol. *18,* 1747 (1983).
14. S. Komarneni and R. Roy, Nature *229* (Oct. 21, 1982).
15. V. N. Reddy, J. Satyanarayana, G. S. Murty, and A. Dash, J. Radioanal. Nucl. Chem. *183,* 371 (1994).
16. M. Faubel and S. A. Ali, Radiochim. Acta *40,* 49 (1986).
17. G. J. Lumetta, M. J. Wagner, and C. D. Carlson, Solvent Extr. Ion Exch. *14,* 35 (1996).
18. L. A. Bray et al., Cesium Recovery Using Savannah River Laboratory Resorcinol Formaldehyde Ion Exchange Resins, PNL-7273, 1990.
19. S. K. Samantha et al., "Removal of Radiocesium from Alkaline Waste," presented at the National Symposium on Management of Radioactive and Toxic Wastes, Kalpakkan, India, 1993.

20. D. J. Wood and J. D. Low, Sep. Sci. Technol. *32*. 241 (1997).
21. R. A. Peterson, C. A. Nash, and D. J. McCabe, "Influence of Particulates on Crossflow Filter Performance with Tetraphenylborate Precipitate," presented at the AIChE Meeting, Gatlinburg, Tennessee, 1995.
22. R. E. Eibling, "Processing of Tetraphenylborate Precipitates in the Savannah River Site Defense Waste Processing Facility," presented at the American Chemical Society Meeting, Washington, D.C., 1990.
23. D. M. Ferrara, N. E. Bibler, and B. C. Ha, "Decomposition of Tetraphenyl Borate Precipitates Used to Isolate Cs-137 from Savannah River Site High-Level Waste," presented at Waste Management 93, Tucson, 1993.
24. D. T. Hobbs and D. D. Walker, "Chemical Pretreatment of Savannah River Site Nuclear Waste," presented at the American Chemical Society Meeting, Washington, D.C., 1992.
25. M. Hawthorne and T. Andrews, Chem. Commun. 443–444 (1965).
26. C. J. Pedersen, J. Am. Chem. Soc. *89*, 7017 (1967).
27. J. Rais, P. Selucky, and M. Kyrs, J. Inorg, Nucl. Chem. *38*, 1376 (1976); P. Selucky, J. Rais, M. Kyrs, and L. Kadlecova, J. Radioanal. Nucl. Chem. *148*, 227 (1991).
28. P. Selucky, J. Rais, M. Kyrs, and L. Kadlecova, J. Radioanal. Nucl. Chem. *148*, 227 (1991).
29. J. Rais, J. Plesek, P. Selucky, M. Kyrs, and L. Kadlecova, J. Radioanal. Nucl. Chem. *148*, 227 (1991).
30. M. Kyrs, S. Hermanek, J. Rais, and J. Plesek, The Method of Extraction Isolation of Cesium Cations from Their Aqueous Solutions, Czechoslovakian Patent 156933 (1974).
31. V. A. Babain, A. Y. Shadrin, L. N. Lazarev, and R. N. Kiseleva, Radiokhimya *35*(2), 81 (1993).
32. M. A. Afonin, V. V. Korolev, V. N. Romanovskii, V. V. Romanovskii, and V. M. Sedov, "Improvements in Partitioning Process of Liquid Highly Radioactive Waste by Using Cobalt Dicarbollyde Extraction," presented at Spectrum 90, Knoxville, Tennessee, 1990.

33. V. M. Esimantovskii, B. Y. Galkin, E. G. Dzekun, L. N. Lazarev, R. I. Lyubtsev, V. N. Romanovskii, and D. N. Shiskin, "Technological Tests on HAW Partitioning with the Use of Chlorinated Cobalt Dicarbollyde (CHCODIC): Management of Secondary Waste," presented at the Waste Management Meeting, Tucson, Arizona, 1992.
34. R. L. Miler, A. B. Pinkerton, P. K. Hurlburt, and K. D. Abney, Solvent Extr. Ion Exch. *13*, 813 (1995).
35. S. Hermanek, Rez Nuclear Research Institute, Czech Republic, unpublished results (1997).
36. I. H. Gerow, J. E. Smith, and M. W. Davis, Sep. Sci. Technol. *16* (5), 519 (1981).
37. I. H. Gerow and M. W. Davis, Sep. Sci. Technol. *14*, 395 (1979).
38. E. Blasius and K. H. Nilles, Radiochim. Acta. *35*(3), 173 (1984).
39. E. Blasius and K. H. Nilles, Radiochim. Acta. *36*(4), 207 (1984).
40. W. J. McDowell, Sep. Sci. Technol. *23*(12&13), 1251 (1988).
41. W. J. McDowell, B. A. Moyer, G. N. Case, and F. I. Case, Solvent Extr. Ion Exch. *4*(2), 217 (1986).
42. W. J. McDowell, G. N. Case, J. A. McDonough, and R. A. Bartsch, Anal. Chem. *64*, 3013 (1992).
43. R. A. Sacheleben, Y. Deng, and B. A. Moyer, Sep. Sci. Technol. *32*(1–4), 275 (1997).
44. M. L. Dietz, E. P. Horwitz, S. Rhoads, R. A. Bartsch, and J. Krzykewski, Solvent Extr. Ion Exch. *14*(1), 1 (1996).
45. M. L. Dietz, E. P. Horwitz, M. P. Jensen, S. Rhoads, R. A. Bartsch, A. Palka, J. Krzykewski, and J. Nam, Solvent Extr. Ion Exch. *14*(3), 357 (1996).
46. J. F. Dozol, S. Eymard, R. Gambade, G. LaRosa, and J. Casas, Decontamination des Concentrats d'Evaporateur en Cesium, Strontium et Transuraniens, EUR 13887 FR (1992).
47. J. F. Dozol, J. Casas, and A. Sastre, Sep. Sci. Technol. *30*(3), 435 (1995).

48. F. Teixidor et al., New Trends in the Separation of ^{137}Cs, ^{90}Sr, and Transplutonides, CEC Final Report, to be published.
49. C. D. Gutsche, *Calixarenes,* The Royal Society of Chemistry, Cambridge, England (1989).
50. *Calixarenes, A Versatile Class of Macrocyclic Compounds* (J. Vicens and V. Böhmer, Eds.), Kluwer, Dordrecht (1991).
51. V. Böhmer, Agnew. Chem. Int. Ed. Engl. *34, 713 (1995).*
52. R. M. Izatt, J. D. Lamb, R. T. Hawkins, P. R. Brown, S. R. Izatt, and J. J. Christensen, J. Am. Chem. Soc. *105*, 1782 (1983).
53. S. R. Izatt, R. T. Hawkins, J. J. Christensen, and R. M. Izatt, J. Am. Chem. Soc. *107*, 63 (1985).
54. R. M. Izatt, J. J. Christensen, and R. T. Hawkins, U.S. Patent 4,477,377, Oct. 16, 1984.
55. J. F. Dozol, V. Böhmer, A. McKervey, F. Lopez Calahorra, D. Reinhoudt, M. J. Schwing, R. Ungaro, and G. Wipff, New Macrocyclic Extractants for Radioactive Waste Treatment: Ionizable Crown Ethers and Functionalized Calixarenes, EUR 17615 EN (1995).
56. R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J. F. Dozol, C. Hill, and H. Rouquette, Agnew. Chem. Int. Ed. Engl. *33* (14), 1506 (1994).
57. Z. Asfari, C. Bressot, J. Vicens, C. Hill, J. F. Dozol, H. Rouquette, S. Eymard, V. Lamare, and B. Tournois, Anal. Chem. *67*, 3133 (1995).
58. T. B. Stolwijk, E. J. R. Sudhölter, and D. N. Reinhoudt, J. Am. Chem. Soc.*109*, 7042 (1987).
59. P. Danesi, Sep. Sci. Technol. *19* (11&12), 857 (1984–1985).
60. C. Hill, Ph.D. Thesis, Strasbourg University (1994).
61. R. Ungaro, J. F. Dozol, F. Arnaud, M. J. Schwing, G. Wipff, and D. N. Reinhoudt, "A New Calixcrown Extractant Selective for Caesium: Synthesis, Complexation, Extraction, Transport and Molecular Modeling," paper presented at the 4th Conference of the European Commission on the Management and Disposal of Radioactive Waste, Luxembourg (1996).

62. C. Hill, J. F. Dozol, V. Lamare, H. Rouquette, S. Eymard, B. Tournois, J. Vicens, Z. Asfari, C. Bressot, R. Ungaro, and A. Casnati, J. Incl. Phenom. *19*, 399 (1994).
63. R. Ungaro, A. Arduini, A. Casnati, A. Pochini, and F. Ugozzoli, IUPAC Pure Appl. Chem. *68*(6), 1213 (1996).
64. C. Bocchi, H. Careri, A. Casnati, and G. Mori, Anal. Chem. *67*, 4234 (1995).
65. J. F. Dozol, Z. Asfari, C. Hill, and J. Vicens, Bis-crown Calix[4]arenes, Method for Preparing Same and Use Thereof for Selectively Recovering Cesium and Actinides, International Patent WO 94/12502 (1994).
66. J. F. Dozol, H. Rouquette, R. Ungaro, and A. Casnati, Calix[4]arenes, Method for Preparing Same and Use Thereof for Selective Extraction of Cesium and Actinides, International Patent WO 94/24138 (1994).
67. W. F. Nijenhuis, E. G. Buitenhuis, F. de Jong, E. J. R. Sudholter, and D. N. Reinhoudt, J. Am. Chem. Soc. *113*, 7963 (1991).
68. A. Ikeda and S. Shinkai, Tetrahedron Lett. *33*, 48, 7385 (1992).
69. A. Ikeda, H. Tsuzuki, and S. Shinkai, Tetrahedron Lett. *35*, 45, 8417 (1994).
70. K. Araki, H. Shimizu, and S. Shinkai, Chem. Lett. 205 (1993).
71. F. Ugozzoli, O. Ori, A. Casnati, A. Pochini, R. Ungaro, and D. N. Reinhoudt, Supramolec. Chem. *5*, 179 (1995).
72. C. Sorel, Ph.D. Thesis, Paris VI University (1996).
73. C. Hill, J. F. Dozol, H. Rouquette, S. Eymard, and B. Tournois, J. Membrane Sci. *114*, 73 (1996).
74. T. J. Haverlock, P. V. Bonnesen, R. A. Sachleben, and B. A. Moyer, Radiochim. Acta. *76*, 1–2 (1997).
75. J. F. Dozol, N. Simon, H. Rouquette, S. Eymard, B. Tournois, V. Lamare, M. Lecomte, M. Masson, and C. Viallesoubranne, paper presented at Global 95, Versailles, France (1995).
76. J. F. Dozol, N. Simon, H. Rouquette, S. Eymard, B. Tournois, V. Lamare, M. Lecomte, M. Masson, and C. Viallesoubranne, presented at the 4th N.E.A. Partitioning and Transmutation International Information Exchange Meeting, Mito, Japan (1996).

77. V. Lamare, C Bressot, J. F. Dozol, J. Vicens, Z. Asfari, R. Ungaro, and A. Casnati, Sep. Sci. Technol. *32*(1–4), 175 (1997).

78. V. Lamare, J. F. Dozol, Z. Asfari, J. Vicens, F. Arnaud-Neu, S. Fuangfwasdi, P. Thuery, and M. Nierlich, paper presented at the 9th Int. Cong. Quantum Chem., Atlanta, June 9–14 (1997).

79. Z. Asfari, C. Naumann, J. Vicens, M. Nierlich, P. Thuery, C. Bossot, V. Lamare, and J. F. Dozol, New J. Chem. *20*, 1183 (1996).